

Nanotechnology in Plastic Food-Contact Materials

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ABSTRACT: A review is presented concerning the application of nanotechnology in the polymer food-packaging sector. Emphasis is placed on the benefits of polymer nanocomposite materials in terms of their improved mechanical and processability properties but also in terms of more packaging-oriented attributes, such as enhanced barrier properties. In addition, nanotechnology is expected to introduce some novel and beneficial characteristics to plastic packaging materials. These characteristics include the

induction of antimicrobial properties, oxygen scavenging, enzyme immobilization, and sensing of food conditions. Besides these novel properties, the need to explore the potential health impact of nanoparticles is also discussed, with a focus on the possibility of nanocomponent migration into the packaged foodstuff. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3720–3739, 2011

Key words: nanocomposites; nanotechnology; plastics

INTRODUCTION

The term *nanotechnology* refers to a multidisciplinary field of applied science and technology that aims to control matter in the nanometer-scale range. One nanometer (nm) is one billionth, or 10^{-9} , of a meter. On a nanometer scale, that is, from 100 nm down to the size of atoms, the properties of materials can be very different from those on a larger scale. The interest in nanoscale materials stems from the fact that new properties are acquired at this length scale and, equally important, that these properties change with their size or shape.¹ The broadness in the scope of nanotechnology makes it hard to be defined, as it may mean different things when approached from a scientific, legal, environmental, regulatory, or even ethical point of view. A practical definition implies that nanotechnology is the design, characterization, production, and application of structures, devices, and systems by controlled manipulation of size and shape at the nanometer scale (atomic, molecular, and macromolecular scale) that produces structures, devices, and systems with at least one novel/superior characteristic or property.²

Even if the term *nanotechnology* has been introduced rather recently in scientific research, the development of its central concepts happened over a longer period of time. The seed of the concept was

initially planted by the physicist Richard Feynman at an American Physical Society meeting back in 1959 with his talk entitled “There’s Plenty of Room at the Bottom.”³ The first definition of the term *nanotechnology* was given later by Norio Taniguchi of the Tokyo Science University in 1974, as follows: “Nanotechnology mainly consists of the processing, of separation, consolidation, and deformation of materials by one atom or one molecule.”⁴ Since then, nanotechnology has opened up new avenues of research and development in a number of science and technology fields, including medicine, cosmetics, agriculture, food technology, and material science. The unusual physicochemical properties of the nanoscale are attributable to the small size of the nanoparticles (surface area and size distribution), the chemical composition (purity, crystallinity, electronic properties, etc.), the surface structure (surface reactivity, surface groups, inorganic or organic coatings, etc.), and their solubility, shape, and aggregation. By some estimates, nanotechnology promises to far exceed the impact of the Industrial Revolution and is projected to become a US\$1 trillion market by 2015.⁵ Polymer technology could not be excluded from this nanorevolution.

Polymeric materials have traditionally been filled with natural or synthetic compounds to ameliorate their properties or simply to reduce cost. Polymer composites are widely used in applications such as transportation, construction, electronics, and consumer products. The properties of particle-reinforced polymer composites are strongly influenced by the dimensions and microstructure of the dispersed phase. Filler materials are in the form of particles,

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fibers, or plate-shaped particles. However, although conventionally filled or reinforced plastics are widely used in various everyday fields, it is often reported that the addition of these fillers leads to practical problems in the resulting composite materials, such as weight increases, brittleness, and opacity.⁶ Quite often, most of these reinforced materials present poor interactions at the interface of both components, as macroscopic reinforcing components usually contain defects. However, these defects become less important as the particle size of the reinforcing component decreases.³

Polymer nanocomposites, on the other hand, are a new class of materials that overcomes these problems and, at the same time, has the potential to introduce novel properties to the final material. These two-phase systems consist of a polymeric matrix and dispersed inorganic particles of nanometer scale; that is, at least one dimension of these particles is in the nanometer range.⁷ Depending on how many dimensions are in the nanometer range, one can distinguish isodimensional nanoparticles when the three dimensions are on the order of nanometers, nanotubes, or whiskers when two dimensions are on the nanometer scale, and finally, layered crystals or clays present in the form of sheets of one to a few nanometers thick and hundreds to thousands of nanometers in extent. A uniform dispersion of nanoparticles leads to a very large matrix–filler interfacial area, which results in unique properties in the final material. Nanocomposites display enhanced mechanical, thermal, flame-retardant, and barrier properties, which assist in the achievement of high-level performances across various applications.^{6–8} Fillers with a high ratio of the largest to the smallest dimension [i.e., aspect ratio (α)] are particularly interesting because of their high specific surface area, which provides better reinforcing effects.^{3,6} The unique properties of the nanocomposite polymeric materials are not typically shared by their more conventional microscopic counterparts. It is, therefore, clear that these unique properties can be attributed to their nanometer-sized features and the extraordinarily high surface area of the dispersed nanocomponents.³

In recent years, nanotechnology has become a wide-ranging, multibillion-dollar global industry. The global nanotechnology market is widely expected to reach US\$1 trillion by 2015 and to occupy approximately 2 million workers.^{5,9} Polymer nanocomposites account for a large part of this market, the demand for such materials is expected to grow further because of the declining prices of nanomaterials and composites, production levels are expected to increase, and technical issues concerning the dispersion of the nanocomponents in the polymer matrix are due to be surpassed. A large number of reports, reviews, patent applications, and com-

pany products have indicated that applications of nanotechnology have also started to make an impact on different aspects of the food industry and associated industries, such as plastic food packaging.³

When one focuses on nanocomposite food-contact polymers, there seems to be an overall increase of interest for such materials. Nanotechnology is already one of the most powerful forces for innovation in food packaging, as the advantages of nanocomposite plastics are numerous, and the possibilities for application in the packaging industry are endless. In addition to conventional benefits, such as the upgrade in mechanical properties and the reduction of weight, nanocomponents are known to enhance the barrier properties of polymers;⁷ this renders these materials even more attractive in the plastic packaging industry. In the same time, nanocomponents can introduce new capabilities that will literally transform food packaging in the near future. Such innovations include the detection of pathogens, antimicrobial properties, and many more smart and/or active packaging features that will benefit food safety and quality.

POLYMER–CLAY NANOCOMPOSITES

Although several nanoparticles can serve as possible additives to enhance polymer performance, the packaging industry has mainly focused its attention during the past decade on layered inorganic solids, such as clays and silicates. As a result, polymer–clay nanocomposites were the first nanocomposites to be developed and introduced to the market as enhanced materials for the food-packaging sector. Currently, clay particles at the nanoscale are the most common commercial application of nanoparticles in food packaging and account for nearly 70% of the market volume (the market for food packaging containing nanomaterials has been predicted to be \$20 billion by 2020).¹⁰ The mineral clay component most often used in such polymer nanocomposites is montmorillonite (MMT), which is a relatively cheap clay, abundant in nature, and derived from volcanic ash and rocks. Nanoclay has a natural layered structure, where the layers or platelets have submicrometer dimensions, except for their thickness, which is only about 1 nm. When dispersed in a polymer matrix, these platelets force gases to follow a tortuous path through the material; this greatly slows their transmission. The nanolayer structure of clays thus increases the path of diffusion that penetrating molecules of gases or other substances must take; this provides substantial improvements in the barrier properties of the end nanocomposite products.^{7,11,12}

The significant improvement in the properties and the relatively simple processability, coupled with the

TABLE I
PA Nanocomposite Products and Producers

Product	Region	Producer	Matrix
Durethan	Europe	Lanxess	PA6
NycoNano	United States	Nycoa	PA6
Aegis	United States	Honeywell	PA6
Nanoblend	Europe	PolyOne	PA6
Nanomide	Asia	NanoPolymer	PA6
Ecobesta	Asia	Ube Industrie	PA6
Systemer	Asia	Showa Denko	PA6 copolymer
Imperm	All	Nanacor	MXD6

LANXESS was spun off from Bayer in early 2005.

availability and low cost of silicates, has led to the development of nanoclay-polymer composites for potential use in a variety of food-packaging applications, such as processed meats, cheeses, cereals, boil-in-the-bag foods, extrusion-coating applications for fruit juices and dairy products, and coextrusion processes for the manufacturing of bottles for beer and carbonated drinks. The polymers that are most often used for clay-polymer nanocomposites are polyamides (PAs), polyolefins, polystyrene (PS), ethylene vinyl acetate (EVA) copolymer, some epoxy resins, polyurethane, polyimides, and poly(ethylene terephthalate) (PET).³ There are currently eight nanocomposite barrier products available (Table I). Seven are based on polyamide 6 (PA6), and one is a specialized PA known as MXD6.¹³

Fundamentals

Polymer-layered silicate nanocomposites consist of inorganic nanolayers of clay filler and organic polymers. Although the incorporation of such clay minerals in polymer matrices has been known for almost 50 years,⁶ the systematic study of such nanocomposite materials gained momentum in the 1990s. Two major works led to the revival of interest in these materials: first, the synthesis of PA6-MMT nanocomposites by the Toyota research group, which highlighted the fact that very small amounts of layered silicate loadings resulted in remarkable improvements in the thermal and mechanical properties,^{8,14} and second, the observation by Giannelis et al.¹⁵ that the melt-mixing of polymers with layered silicates without the use of organic solvents is a versatile and environmentally friendly approach for synthesizing polymer nanocomposites.

The most commonly used layered silicates for the preparation of polymer nanocomposites belong to the same general type of 2:1 layered phyllosilicates or smectites. The crystal structure of such silicates resembles a stack of layers. These layers consist of two coordinated tetrahedral silicon atoms, fused to an edge-shared octahedral sheet of either aluminum

or magnesium hydroxide (Fig. 1).^{8,14} The layer thickness is approximately 1 nm, and the lateral dimensions may vary from 30 nm to several micrometers or even larger, depending on the layered silicate, the source of the clay, and the method of preparation (e.g., clays prepared by milling typically have lateral platelet dimensions of approximately 0.1–1.0 μm).⁶ This geometry leads to a high ratio of the largest to the smallest dimension (α), with values exceeding 1000. The formation of the layer into stacks is separated by a regular van der Waals gap, which is called the *interlayer* or *gallery*. The interlayer dimension is determined by the crystal structure of the silicate. As an example, for dehydrated Na MMT, this dimension is approximately 1 nm.¹⁶

MMT, hectorite, and saponite are the most commonly used layered silicates in polymer nanocomposite materials.¹⁴ However, these layered silicates are not the only type of clay that can be incorporated into polymer matrices. In addition to layered silicates, some studies have recently focused on the use of sepiolite to produce polymer nanocomposites. Sepiolite is a hydrated magnesium silicate (part of the phyllosilicate family) that forms a nanocomponent with a needlelike structure, showing an alternation of blocks and channels that grow up in the fiber direction. It has a structure similar to the 2:1 layered structure of smectites, formed by two tetrahedral silica sheets enclosing a central sheet of octahedral magnesium, with the exception that the layers lack continuous octahedral sheets. The discontinuous nature of the octahedral sheet facilitates the formation of rectangular channels, which contain some exchangeable calcium and magnesium cations and zeolitic water. These nanotunnels account, in large part, for the high specific surface area and excellent sorption properties of sepiolite. Besides that, sepiolite has good mechanical

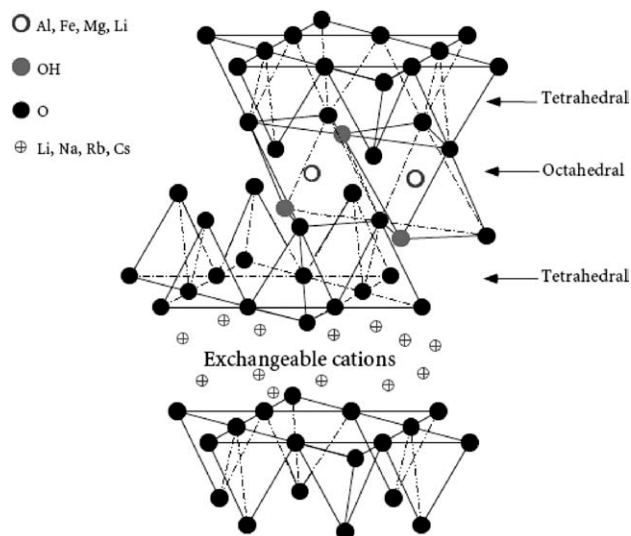


Figure 1 Structure of the 2:1 phyllosilicates.

and thermal properties; these make it an ideal reinforcing agent of polymeric materials.^{17–19}

Formation and structure

The successful formation of a polymer–clay nanocomposite relies on two key characteristics of the reinforcement component. The first characteristic is the ability to modify the surface chemistry of the silicates through ion-exchange reactions with organic and inorganic cations to produce a polymer-compatible nanocomponent. The second characteristic is the ability of the silicate particles to disperse into individual entities (layers or needles). These two characteristics are, of course, connected to each other because the degree of dispersion of a layered silicate in a particular polymer matrix depends on the interlayer cation modification.¹⁴

The homogeneous dispersion of most clays in organic polymers is not easy because of the hydrophilicity of the clay surface. As a result, in their virgin state, layered silicates are only miscible with hydrophilic polymers, such as poly(ethylene oxide) and poly(vinyl alcohol).⁶ In incompatible polymer–clay systems, which typically correspond to more conventionally filled polymers, poor interaction between the organic and the inorganic components results in poor mechanical and thermal properties. To render the clays miscible with the polymer matrix, one must exchange the alkali counterions in the interlayer with a cationic–organic surfactant. For this, alkyl ammonium ions are mostly used, although sulfonium and phosphonium ions are also possible alternatives.²⁰ These cations lower the energy of the silicate surface and improve the wetting characteristics with the polymer matrix. Moreover, the long organic chains of such species result in an increase of the gallery height and facilitate the diffusion of the polymeric chains between the layers, a process that may eventually result in their complete separation.^{6,14}

At present, four principal strategies have been considered to produce polymer-layered silicate nanocomposites: (1) *in situ* template synthesis, (2) intercalation of the polymer or prepolymer from solution, (3) *in situ* intercalative polymerization, and (4) melt intercalation.²¹

- *In situ* template synthesis: This technique involves the direct synthesis of clay particles within the polymer matrix by the hydrothermal treatment of a gel containing the polymer and the silicate building blocks. This technique has been widely used for the synthesis of double-layer, hydroxide-based nanocomposites but is far less developed for layered silicates. It is based on self-assembly forces, where the polymer aids the nucleation and growth of the inorganic host crys-

tals and gets trapped within the layers as they grow.²⁰ The major disadvantage of *in situ* template synthesis is the involvement of the high temperatures that are a prerequisite for the synthesis of clay minerals, but it also leads to the decomposition of the polymeric chains.⁶

- Intercalation of the polymer or prepolymer from solution: This process refers to a multistage process in which the silicates are initially dispersed and swollen in a solvent. In a second stage, the polymer is also added to the solution and adsorbed onto the clay platelets. Finally the evaporation step follows, which leads to the reassembly of the clay layers to sandwich the polymer chains in the absence of the solvent. The disadvantage of this technique relies on the fact that large quantities of solvents are difficult to handle in an industrial environment.^{6,8}
- *In situ* intercalative polymerization: In this technique, the layered silicate is swollen within the liquid monomer (or within a monomer solution), and the polymerization occurs between the swollen sheets.²¹ Polymer formation can be initiated by heat or radiation, the diffusion of a suitable initiator, or an organic initiator or catalyst fixed through cationic exchange inside the interlayer before the swelling step by the monomer.⁶
- Melt intercalation: This alternative strategy consists of the blending of organically modified clay with the polymer by the heating of the mixture above the polymer softening point. The latter technique presents some great advantages over the aforementioned techniques. In particular, its compatibility with conventional processes, such as extrusion or injection molding, renders melt blending the simplest and most economically favorable method for industrial applications. In addition, the absence of solvents minimizes environmental consequences and also eliminates the competing host–solvent and polymer–solvent interactions, which in many cases, limit clay dispersion. These advantages have rendered melt intercalation the almost standard approach for the synthesis of polymer–clay nanocomposites.⁸

Besides this traditional class of polymer–filler composites, two types of nanocomposites can be thermodynamically obtained, depending on the strength of interfacial interactions between the polymer matrix and layered silicate (Fig. 2): (1) intercalated nanocomposites, where the insertion of polymer chains into the layered silicate structure occurs in a crystallographically regular manner and with a repeat distance of a few nanometers, regardless of the polymer-to-layered-silicate ratio, and (2) exfoliated or delaminated nanocomposites, where the

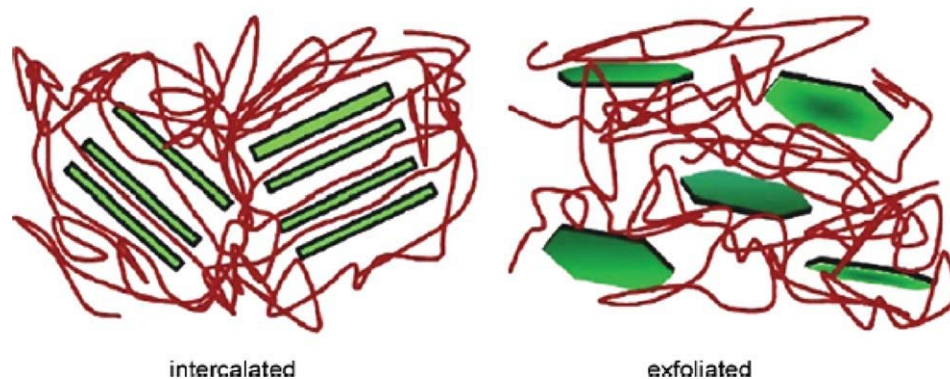


Figure 2 Schematic illustration of the intercalated and exfoliated polymer-layered silicate nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

individual silicate layers are separated in the polymer matrix by average distances that totally depend on the clay loading.¹⁴

The exfoliation or delamination configuration is of particular interest because it maximizes the polymer-clay interactions and makes the entire surface of layers available for the polymer. Just a small weight percentage of clay, properly distributed throughout the polymer matrix, creates a significantly higher surface area for polymer-filler interfacial interactions than conventional composites.²⁰ This should lead to the most significant changes in the mechanical and physical properties. The coupling between the tremendous surface area of the clay and the polymer matrix facilitates stress transfer to the reinforcement phase and allows for mechanical property improvements.²² In general, it is well established that the ultimate properties of reinforcing composite elements are reached as they become smaller because of the increased interface area. However, the smaller the reinforcing elements are, the larger their internal surface is, and hence, their tendency to agglomerate rather than to disperse homogeneously in a matrix increases.⁶

PROPERTIES OF POLYMER-CLAY NANOCOMPOSITES

Plastic is probably the most common form of food packaging used today because of its unique benefits, which are unmatched by other packaging materials, such as paper and glass. The processing of polymers can result in a variety of forms and appearances; these make it an especially useful material for food-packaging applications and provide, at the same time, good mechanical properties, flexibility, reduced weight, and attractive end-product appearance. With the use of nanocomponents, plastic packaging can be made even lighter and stronger and can exhibit a better thermal performance.

Mechanical properties

Layered silicate nanocomponents have been proven to enhance, to a great extent, the properties of the polymers in which they are dispersed. Among those properties, impressively large increases in the tensile modulus and flexural modulus of nanocomposites at really low filler contents have drawn a lot of attention. The mechanism that explains the reinforcing action of layered silicates is based on the contact surface between the matrix and the reinforcement. Rigid fillers are naturally resistant to straining because of their high moduli. Therefore, when a relatively softer matrix is reinforced with such fillers, the polymer, particularly that adjacent to the filler particles, becomes highly restrained mechanically. This enables a significant portion of an applied load to be carried by the filler, with the assumption, of course, that the bonding between the two phases is adequate.⁶

However, on the basis of experimental evidence, some authors have argued that the dramatic improvement in the modulus for such extremely low clay concentrations cannot be attributed simply to the introduction of the higher modulus inorganic filler layers. A proposed theoretical approach assumes a layer of affected polymer on the filler surface. This stiff interfacial zone presents a much higher modulus than the bulk equivalent polymer. Obviously, for such high- α fillers, as in the case of layered silicates, the surface area exposed to the polymer is huge, and therefore, the significant increase in the modulus due to the stiff interface is not surprising, even for very low filler contents.²³ As discussed later in the barrier properties section, this stiff interfacial zone is also found to play a crucial role in reducing the diffusion of migrants through polymer nanocomposites.

In general, the addition of an organically modified layered silicate in a polymer matrix results in significant improvements in the Young's modulus and the tensile strength compared to that of the neat polymer material, whereas the elongation at break is

reduced. Pavlidou and Papaspyrides⁶ tabulated an extensive database of published data regarding the effect of clay nanocomponents on the reinforcement of various polymers. As many polymer–clay nanocomposite studies have reported, the tensile properties, such as Young's modulus, are primarily a function of the clay content.²⁴ It must be noted, however, that the general observation of such correlations has indicated a constant large rate of increase in the modulus up to a certain weight fraction of nanoclay (typically, 10 wt %), whereas above this threshold, a plateau is observed. This change corresponds to a passage from totally exfoliated structures to partially exfoliated–partially intercalated structures when the clay content exceeds a certain value, as indicated by X-ray diffraction and transmission electron microscopy analysis results.⁶ In addition, this trend highlights the effect of the aforementioned stiff interfacial zone and is in total accordance with this theoretical approach. It is believed that above a certain limit of clay dispersion, the additional silicate layers are incorporated into polymer regions that are already affected (and stiffened) by other silicate layers, and thus, it is expected that the enhancement of the modulus will become much less dramatic.²³

Besides the content percentage of layered clay, other parameters are also known to affect the mechanical properties of polymer–layered clay nanocomposites. These parameters include the organic modification of the clay, the presence of a compatibilizer (e.g., maleic anhydride in the case of polyolefins²⁵ or EVA²⁶), the nanocomposite production method, the molecular weight of the polymer chains, and also the average length of the clay layers because the latter determines their α and, hence, their surface area.^{6,14}

Thermal properties

In addition to improved mechanical properties, the incorporation of clay into the polymer matrix is generally found to enhance the thermal stability by acting as an enhanced insulator and also as a barrier of mass transport for the volatile products generated during decomposition. In addition, the nanoclay may assist in the formation of char after the thermal decomposition of the polymer. The thermal stability of polymeric materials is generally studied by thermogravimetric analysis. With this technique, one can monitor the weight loss due to the formation of volatile products after degradation at high temperature as a function of temperature (and/or time). When heating occurs under an inert gas flow, a nonoxidative degradation occurs, whereas the use of air or oxygen (O_2) allows oxidative degradation of the samples.^{27,28}

In most of the reported cases, nanoclay led to an increased decomposition temperature of the nanocomposite in comparison with the pristine matrix,

acting as a heat insulator. In oxidative conditions, the organoclay acted as a shield to the polymer against the action of oxygen, dramatically increasing the thermal stability.²⁹ However, many experimental studies have shown contradictory results, especially in the case of the thermal degradation of PA6-based nanocomposites, a material that is already used in packaging applications. It was mentioned that PA6 nanocomposites have a somewhat lower stability than neat nylon 6, an observation that was attributed to the degradation effect of the quaternary alkyl ammonium treatment on MMT. Another explanation may be found in the presence of water in the nanoparticles. It was mentioned³⁰ that although PA6 did not degrade at the processing temperature, there was a significant decrease in the molecular weight in PA6 nanocomposites under the same conditions. It is believed that the degradation might depend on water in the nanocomposites, which may cause hydrolytic cleavage of the polymeric chains. In general, despite the improvement of thermal stability that numerous studies have indicated, decreases in the thermal stability of polymers upon nanocomposite formation have also been reported, and various mechanisms have been put forward to explain the results. It may be possible that nanosilicates have two opposing functions in the thermal stability of nanocomposites: a barrier effect, which should improve the thermal stability, and a catalytic effect on the degradation of the polymer matrix, which should decrease the thermal stability.⁶

Nanoclays are also known to affect the thermal aging of polymers. Kiliaris et al.³¹ addressed the long-term viability of a melt-compounded PA6–clay nanocomposite by performing accelerated aging tests at 120 and 150°C for up to 35 days. It was shown that nanoclay assisted the stabilization of the polyamidic matrix in high temperatures when compared to the pristine matrix. This effect was attributed to the stabilization effect of the transition metals present in the clay as impurities.

An increase of the heat distortion temperature of polymers upon nanoclay dispersion has also been observed; this makes such materials even more attractive from an application or industrial point of view. The heat-distortion temperature or heat-deflection temperature (HDT) is the temperature at which a polymer sample deforms under a specified load. Thus, it is an index of the heat resistance of a polymeric material due to an applied load and can be measured by the procedure given in ASTM D 648. In general, improvements in HDT have been reported in polymer nanocomposites, a fact becoming more important as the quality of clay dispersions improves from intercalated to exfoliated forms.³² Especially in the case of PA6–clay nanocomposites, the significant improvement in HDT has been attributed to the

presence of strong hydrogen bonds between the polymer matrix and the clay surface.³³ The extent of HDT improvement in PA6-layered clay nanocomposites has varied, with reported values from 20°C³⁴ to 90°C.³⁵ It must be noted, however, that as in the case of tensile modulus, this HDT enhancement reaches a plateau above a certain weight fraction of the clay.⁶

Optical and rheological properties

Polymer-layered clay nanocomposites exhibit, in general, excellent optical clarity, a property that is very crucial for the aesthetics of the end product to be used in packaging applications. Conventional microsized particles used as reinforcing agents, for instance, scatter light and reduce the light transmittance and optical clarity. On the other hand, layered silicate platelets, albeit their micrometer lateral size, are just 1 nm thick. Thus, when single layers are dispersed in a polymer matrix, the resulting nanocomposite is optically clear in the visible region, whereas there is a loss of intensity in the UV region.¹⁴ The clarity of the end products also relies on the close values of the refractive indices between the MMT and most polymers. MMT has a refractive index of 1.505,³⁶ whereas, for example, the relevant value for PAs is 1.53 and for polypropylene (PP) is 1.46.³⁷ It must be noted, however, that in higher weight fractions of clay, the nanocomponents decrease the haze of blown films. Beatrice et al.,³⁸ for instance, reported that nanoclay influenced mostly the haze of the films, decreasing this property from 21.6% for pure PA6 to 11.0% for a 3 wt % nanoclay content. The level of transmittance, however, was not affected.

The rheological properties of a nanocomposite polymeric material are also critical properties for the evaluation of material processability in the melt state. In the case of polymer-layered silicate nanocomposites, this knowledge is desirable for two reasons. First, the melt processing behavior is crucial in unit operations, such as injection molding. Second, because the rheological properties of particle-filled materials are sensitive to the structure, particle size, shape, and surface characteristics of the dispersed nanoclay, the rheological properties potentially offer a means for assessing the state of dispersion in nanocomposites directly in the melt.⁶ It is generally expected that when polymer-clay nanocomposites are formed, the viscosity at low shear rates increases with filler concentration. On the other hand, at high shear rates, shear thinning behavior is usually observed. This may be attributed to the alignment of silicate layers toward the direction of flow at high shear rates.³⁹ Many authors have verified the shear thinning behavior at high shear rates for a PA6 nanocomposites containing clay in comparison with the pristine matrix. Xu et al.⁴⁰ indicated this behav-

ior in PA6 containing 1 wt % MMT, whereas Kiliaris et al.⁴⁰ observed a slight depression of rheology in PA6 nanocomposites in a broad range of clay contents up to 7.5 wt % and attributed it to the clay retardation effect on the entanglement mobility of polymer chains and the modification of the entanglement network when it was sheared. In any case, it is of great interest to note that the absolute value of the melt viscosity of the nanocomposite was significantly lower than that of neat nylon 6 or the other composites, which implied good melt processability over a wide range of processing conditions.⁶

BARRIER PROPERTIES

The aforementioned improvements in the thermomechanical properties of polymers due to the presence of nanoreinforcement indicate that food-packaging polymer nanocomposites are more capable of withstanding the stress of thermal food processing, transportation, and storage, and they offer the possibility of reducing material usage and/or weight for such applications. However, the most important asset of such materials that has stimulated the interest of their use as food-packaging materials is their improved barrier properties.

Conventional polymers that have been traditionally used in packaging applications include polyethylene, PP, PS, poly(vinyl chloride) (PVC), PET, and PA. The choice of a material for a given application relies on many factors, such as the type of foodstuff that needs to be protected, the nature of the substances that need to remain within the package (CO₂, aromas, flavoring compounds) or outside of it (oxygen, humidity, etc.), the cost of material, the shelf life of the foodstuff, the processability of the material, the appearance of the end product, and the overall thermomechanical properties requirement. In any case, a limiting property of polymeric materials in food packaging is their inherent permeability to gases and vapors, including oxygen, carbon dioxide, water, and organic vapors. For this reason, alternative solutions are very often followed that include the use of multilayered films composed from a hydrophilic polymer and a hydrophobic polymer or even nonpolymeric materials, such as aluminum.⁴¹ It is obvious that such solutions are costly, not only in terms of packaging production but also from the perspective of material recycling.⁴²⁻⁴⁴

On the other hand, polymer nanocomposites offer a promising alternative for plastic food-packaging applications with respect to the barrier properties improvement. In the case of layered silicate nanoreinforcements, the impermeable clay layers force a tortuous path for a migrant that diffuses through the nanocomposite. As a result, the permeability through nanocomposite polymer films can be

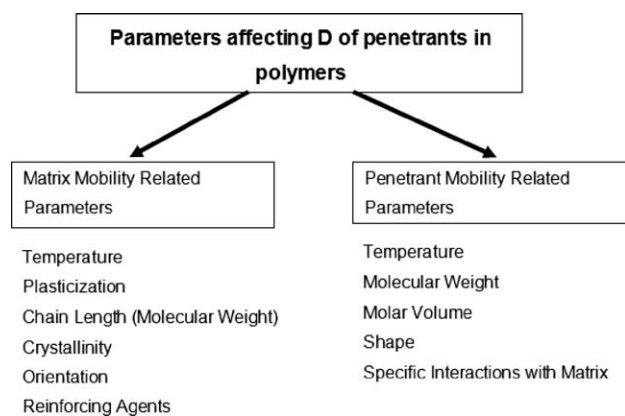


Figure 3 Parameters affecting the diffusion of penetrant through the polymers.

reduced significantly, even with small loadings of exfoliated nanoclays. The relevant research on polymer–clay nanocomposites concerns mostly oxygen, carbon dioxide, and nitrogen barrier films for the packaging of food and carbonated drinks.

General considerations of mass transport through the polymers

Penetrant transport in polymers is a complex process that can be affected more or less by many parameters and is generally controlled by diffusion. It can be defined as the property of this material to be penetrated and crossed by molecules, being controlled by the rigidity of the matrix and also by the mobility of the penetrant molecule. In general, the parameters that affect diffusion in polymers can be categorized as those that affect the polymer matrix mobility, such as temperature, chain length,⁴⁵ plasticization,^{46,47} crystallinity, orientation, and the presence of a reinforcing agent,⁴⁸ and those that affect the mobility of the penetrant molecule, such as the molecular weight,⁴⁹ molar volume,⁴⁷ shape of the penetrants,⁵⁰ or even specific interactions, such as hydrogen bonding between the matrix and the penetrant.⁴⁶ A schematic representation of this categorization is given in Figure 3.

The transport mechanism is very different for a gas or a vapor in comparison with the transport of a liquid or a solid penetrant. It is described by a solution–diffusion mechanism. In a general way, the transport phenomena can be into five successive stages,⁵¹ with the polymer film considered a homogeneous and nonporous material:

- Diffusion through the limit layer of the side corresponding to the higher partial pressure (upstream side).
- Absorption of the gas (by chemical affinity or solubility) by the polymer.

- Diffusion of the gas inside the membrane polymer.
- Desorption of the gas at the side of lower partial pressure.
- Diffusion through the limit layer of the downstream side.

Generally, the formation of a limit layer of gas staying on each side of the polymeric film may be neglected, as the resistances associated with these steps are not important relatively to the other steps. The process can then be described as follows: condensation and solution of the penetrant at one surface of the film, followed by diffusion in the form of a liquid through the material under the influence of a concentration gradient, and finally evaporation at the other surface to the gaseous state.⁴⁸ The permeability coefficient (K) is, by definition, the product of the solubility coefficient (S) and the diffusion coefficient (D):

$$K = DS \quad (1)$$

Flaconnèche et al.⁵² provided an extensive review on the available experimental methods for the measurement of the permeability, diffusion, and sorption of gases and vapors in polymeric materials.

Diffusion is the process by which a molecule (organic liquid, vapors, gases, solid, etc.) is transferred in the polymeric matrix due to random molecular motions. So, it is a kinetic term that reflects the penetrant mobility in the polymer phase as affected by the matrix resistance to the transport. The diffusion of heavier penetrants (liquids or solids) in polymers is substantially slower than that of gases and vapors. Dole et al.⁴⁹ provided a correlation of D values for various polymers versus the molecular weight of the penetrant (Fig. 4). It was indicated through this correlation that the diffusion of low-molecular-weight substances (i.e., gases and vapors) is primarily controlled by their own mobility rather than the global mobility of the matrix–penetrant system that controls the mass transport of liquids or solids. By observing Figure 4, one can see, for instance, that a comparison between the rigid dry PET and the rubbery low-density polyethylene (LDPE) shows a small difference in the D values when the molecular weight of the penetrant is low. On the contrary, this difference becomes more significant in higher penetrant molecular weights, with slower diffusion rates in PET by more than 1 million times for penetrant molecular weights exceeding 100 g/mol.

Solubility, on the other hand, has a thermodynamic origin, and it depends primarily on the polymer–penetrant interactions and on the gas condensability in lower molecular weight substances. In the case of gases, for low pressures and an ideal gas, Henry's law describes the phenomenon:

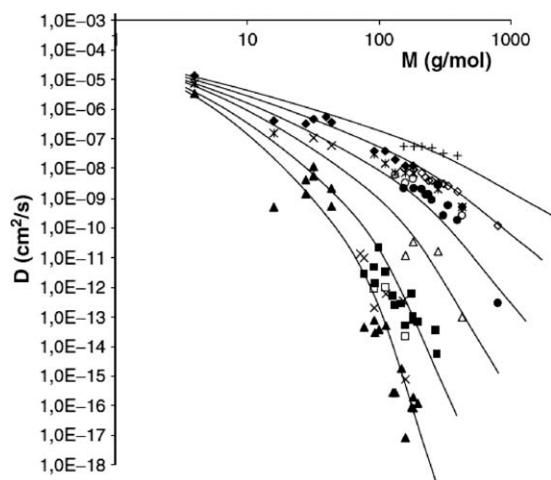


Figure 4 Variation of D with the molecular weight (logarithm scale) of surrogates at 40°C in (□) polyvinylidene chloride (PVDC), (△) PA (at 60% relative humidity), (×) PS, (*) HDPE, (◆) LDPE, (○) plasticized PVC, (▲) PET (dry conditions), (■) PET (in contact with ethanol), (◇) PP in contact with glyceryl tripelargonate, (●) PP, and (+) PP at 70°C. Reproduced by Dole et al.⁴⁹

$$C = k_D P \quad (2)$$

where C is the concentration, P is the pressure of the gas, and k_D is the proportionality constant of Henry's law. The constant k_D is, in fact, S of the gas in the polymer and is independent of the concentration at a given temperature. In practice, for the permeation of simple gases of low molecular weight in rubbery polymers (i.e., at temperatures above their glass-transition temperature) and under relatively moderate pressures, the departures from Henry's law for the sorption are negligible. However, in the most general case, S for a given penetrant-polymer system is a function of the temperature and the pressure or the concentration of the penetrant.⁴⁸

Role of the reinforcing agents

Before one discusses the effect on nanoparticles on the barrier properties of polymers, it is important to take into account some general considerations regarding the role of conventional reinforcing agents or fillers in these properties. The diffusion and transport phenomena in filled polymers depend on three parameters, namely, the nature of the fillers, the degree of adhesion, and their compatibility with the polymer matrix. If the used filler is compatible with the polymer matrix, it will take up the free volume within the amorphous regions of the polymer matrix and create a tortuous path for the permeating molecules. The extent of the tortuous path is dependent on the volume fraction of the filler and the shape and orientation of the particles. On the other hand, when the filler is incompatible with the polymer,

voids tend to occur at the interface of the two components, which lead to an increase in the free volume of the system and, consequently, to an increase in the permeability. The effect of incompatibility on the barrier properties can be evaluated by a comparison of the permeation data to the predictions of Maxwell's law for the composite system. This law [eq. (3)], developed for systems composed of a permeable matrix in which are dispersed spherical impermeable spheres of micrometric size, defines the relative permeability (P) as a function of the volume fraction of the dispersed phase (ϕ):⁵¹

$$\frac{P_{\text{composite}}}{P_{\text{matrix}}} = \frac{2(1 - \phi)}{2 + \phi} \quad (3)$$

As Maxwell's law considers a perfect interface between the components, any deviations toward higher permeation rates can be readily attributed to the presence of voids in the interface.⁵³

Besides the tortuous effect that retards mass transfer through composite materials, fillers are also known to directly affect the morphological properties of the matrix, altering its rigidity. As a result, reinforcing agents may also have an indirect effect on the barrier properties by inducing crystallization formation or even the reduction of the glass-transition temperature. Of course, all of these effects are maximized in the case of nanoreinforcing materials.

Mechanism of barrier property improvement: The tortuous path

Generally, polymer-layered silicate nanocomposites are characterized by very strong enhancements of their barrier properties. The mass transport mechanism of gasses permeating a nanolayered reinforced polymer is similar to that in a semicrystalline polymer, in which transport only takes place in the amorphous phase rather than in the impermeable crystalline phase. In most theoretical approaches, the nanocomposite is considered to consist of a permeable phase (polymer matrix) in which nonpermeable nanolayers are dispersed. There are three main factors that influence the permeability of a nanocomposite: the volume fraction of the nanolayers, their orientation relative to the diffusion direction, and their α .⁷

The reduced permeability of nanocomposites is due to the decrease of both factors affecting the permeation, namely, solubility and diffusion. With the presence of nanoparticles, a decrease of the solubility is expected in the nanocomposite because of the reduced polymer matrix volume and a decrease in diffusion due to a more tortuous path for the diffusing molecules. The reduction of D is much higher than that of S , as the volume fraction of nanolayers

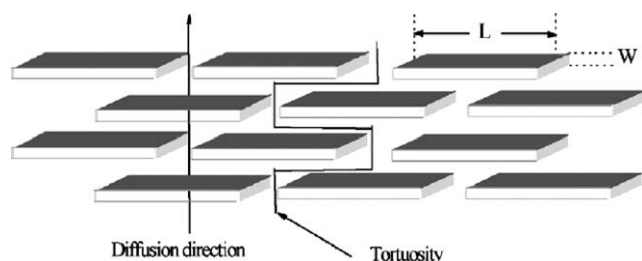


Figure 5 Tortuous diffusion path in an exfoliated polymer-clay nanocomposite when used as a gas barrier.

is very low, and, thus, the reduction of the matrix volume is very small. The major factor, however, is the tortuosity, which is connected directly to the shape and degree of dispersion of the nanolayers and affects the diffusion process. The degree of dispersion of the nanocomponents is determined by the degree of delamination of the clay. The fully delaminated (exfoliated) nanocomposite presents much higher values for the tortuosity factor (τ) and α in comparison with the partially delaminated (intercalated) nanocomposite, and it is much more effective for use in barrier membranes for gases.⁷

Nielsen⁵⁴ proposed a simple model to describe the permeability in filled polymer systems based on a preceding work of Michaels and Parker,⁵⁵ regarding mass transport in two-phase systems. According to this model (Fig. 5), the nanoparticles are homogeneously dispersed in the matrix and have a length L and thickness W , whereas their orientation is perpendicular to the direction of penetrant diffusion. In this case, S of the penetrant in the nanocomposite is given by

$$S = S_0(1 - \phi) \tag{4}$$

where S_0 is the solubility coefficient of the pristine matrix and ϕ is the volume fraction of the dispersed nanolayers. D , on the other hand, is retarded because of the forced tortuous path that the penetrant has to follow. As a result, D is given by

$$D = \frac{D_0}{\tau} \tag{5}$$

where D_0 is the diffusivity of the penetrant in the neat matrix. This factor is dependent on α and the shape and orientation of the nanolayers, defined as⁶

$$\tau = \frac{l'}{l} = 1 + \frac{L}{2W}\phi \tag{6}$$

where l' is the distance that a solute must travel to diffuse through the membrane when nanolayers are present (the tortuous path) and l is the thickness of the composite film. By combining eqs. (1), (4), and (5), one derives the following expression for K of the composite:

$$\frac{K}{K_0} = \frac{1 - \phi}{\tau} \tag{7}$$

where K_0 is the permeability coefficient of the unfilled polymer. By combining eqs. (6) and (7) and taking into account the fact that α is equal to L/W , one finds that the following equation stands correct:

$$\frac{K}{K_0} = \frac{1 - \phi}{1 + \frac{\alpha}{2}\phi} \tag{8}$$

This equation shows that the permeability of the nanocomposite decreases with the increase of ϕ and α . In practice however, the limit for its validity is for approximate ϕ values lower than 8–10% because the particles have a tendency to aggregate in higher filler contents.^{7,13}

Although Nielsen's model is frequently used to describe the permeability through polymer-clay nanocomposites, it must be mentioned that it was developed to describe mass transfer through conventional composites. As a result, discrepancies between the experimental data and the theoretical predictions of eqs. (4)–(8) may be attributed either to inadequacies of the model or to incomplete orientation of the particles within the nanocomposite film plane, as the key assumption of the Nielsen model is that the sheets are placed in an arrangement such that the direction of diffusion is normal to the direction of the sheets. Clearly, this arrangement results in the highest tortuosity, and any deviation from it would, in fact, lead to false estimations of the barrier properties.⁶ In addition, this model is based on the assumption that the presence of nanoparticles does not affect the diffusivity of the polymer matrix (D_0). However, experimental observations have demonstrated that the mobility of the polymer matrix, which is intimately connected to the mass transport properties, is lowered by clay incorporation.

More recently, Adame and Beall⁵⁶ introduced the idea of the constrained polymer region, which affects the permeation in polymer-clay systems. The proposed model focuses on the polymer-clay interface as the governing factor in addition to the tortuous path. It defines four regions in the polymer-clay system rather than two: (1) the impermeable clay, (2) a surface-modifier phase, (3) the constrained polymer region that exists 50–100 nm from the surface of the clay, and (4) the unconstrained polymer region, which corresponds to the pristine matrix (Fig. 6). Gas permeability is still considered to follow a tortuous path. The surface modifier region is assumed to be small enough (1–2 nm) that it has little effect on the gas permeability of the composite. The constrained region, on the other hand, is assumed to have a gas D that is different than the bulk polymer. The polymer in this region is considered to have a

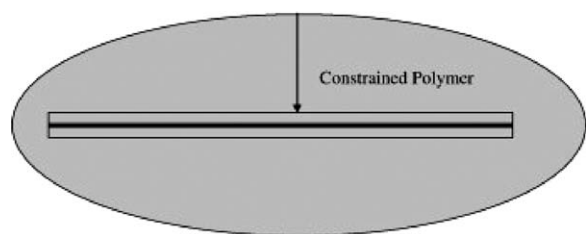


Figure 6 Schematic of the constrained polymer model showing the clay plate as the black line in the center of an ellipse, the small rectangle as the surface modifier phase, and the remainder of the ellipse as the constrained polymer region.

lower free volume and, therefore, a lower D than the unfilled polymer matrix. This model provides a correction factor (C_F) that can be applied to the Nielsen model to take into account the constrained polymer region, formulated as

$$C_F = V_{bp} + \left(\frac{V_{cp}}{R_D} \right) \quad (9)$$

where V_{bp} is the volume fraction of the bulk unconstrained polymer, V_{cp} is the volume fraction of constrained polymer, and R_D is the ratio of the diffusion coefficients of the constrained region (D_c) and unconstrained region (D_o).

In addition to the layer geometry, other impermeable filler geometries have been also considered by other theoretical approaches, such as hexagonal flakes and disks, which have led to different values of α . An extensive review of such models was given by Choudalakis and Gotsis.⁷ The most interesting approach found in the literature is probably the model of Cussler et al.,⁵⁷ given by

$$\frac{K}{K_o} = \left(1 + \frac{a^2 \phi^2}{1 - \phi} \right) \quad (10)$$

Equation (10) predicts a rapid reduction of the relative permeability at small values of ϕ , in contrast with the model of Nielsen, which needs either a high volume fraction or high α for the same reduction. As a result, it seems to better describe the effect of nanoclays that improve the barrier properties even when dispersed in low quantities. Picard et al.⁵⁸ provided a comparison between experimental permeability data in PA6–MMT nanocomposites and published theoretical models, proving that Cussler's model prediction offers the best accuracy for describing the experimental results.

The presence of nanoparticles in a polymer matrix may also affect the structural characteristics of the polymer. The induction of crystallinity is possible by means of heterogeneous crystal formation. This process includes two stages, namely, nucleation and

crystal growth. However, although it is well established that nanometer-sized clay platelets are effective nucleating agents, different effects have been reported on the linear growth rate and the overall crystallization rate, depending on the type of polymer.^{6,39}

In any case, crystals are also impermeable to diffusion and contribute to the tortuous path. In fact, it is known at least for the case of PAs,⁵⁹ that because of the crystals, the amorphous chains in the interface of crystalline regions have a different density than the bulk amorphous phase, a concept that is relevant to the aforementioned constrained polymer region induced by clay dispersion. Sabard et al.⁶⁰ highlighted another mechanism that contributes to the enhancement of barrier properties in polymer–clay nanocomposites. In their work, ethanol sorption experiments were conducted in 0.5 and 1 wt % clay PA6 nanocomposites, acquired through different formation methods, which resulted in different crystalline morphologies of the matrices. The barrier properties of the nanocomposites containing a high percentage of γ crystals were found to be improved in comparison with samples that were primarily crystallized in the α form (even if the overall degree of crystallinity remained the same). This was attributed to the formation of thicker γ -crystal lamellae associated with the presence of nanoclay in PA6.

Permeability in the polymer nanocomposites

The study of barrier properties in polymer nanocomposites with layered silicates is a topic that has been extensively studied the past decade. There are numerous examples in the literature showing the extent of the improvements in various polymer–clay systems.

Exfoliated clay modified PET is one nanocomposite case commonly investigated in both academic and industrial laboratories for barrier applications. *In situ* polymerized PET–exfoliated clay composites were noted to show a reduction in oxygen permeability to one half of the control polymer with only 1 wt % clay.⁶¹ PET–exfoliated clay composites also prepared via *in situ* polymerization with a clay-supported catalyst exhibited an impressive reduction in oxygen permeability to as low as one-tenth of the relevant permeation in pristine PET with 1–5 wt % clay.⁶² The moisture vapor transmission, however, did not show any significant change. On the other hand, Ke and Yongping⁶³ tested the oxygen permeability of intercalated PET nanocomposites. It was found that a small amount of clay effectively reduced the permeability of the PET film. When the content of organically modified montmorillonite reached 3 wt % the permeation of oxygen was reduced to half that of the pure PET film.

Many studies have been dedicated to the barrier properties of PA–nanoclay composite films. Such

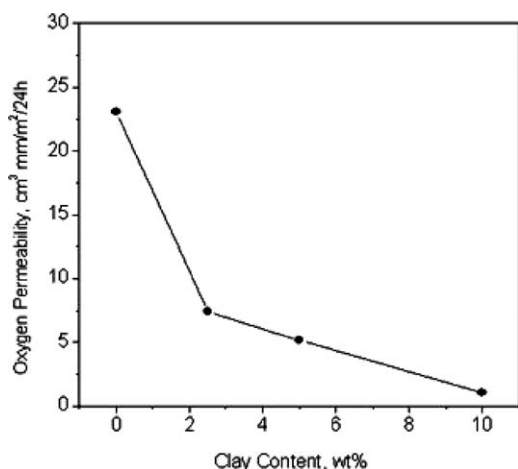


Figure 7 Oxygen permeability as a function of the clay concentration for the PA6 and PA6–clay (Cloisite 30B) nanocomposites. Reproduced by Swain et al.⁶⁴

materials have already been introduced to the market as packaging materials (Table I) and are currently used either as films or as barrier layers in multilayered PET bottles for beer and carbonated drinks. The nanoclay content of commercial PA nanocomposites varies from 2 to 8%. Above this range, exfoliation becomes increasingly difficult, and its effect on polymer rheology creates processing problems during package conversion. Nanocomposite PA commercial products fall into two general categories: regular and high load. Regular products have nanoclay loadings in the 2–4% range and high loads of 5–8%. As a rule of thumb, regular-load products improve the barrier properties by two times for oxygen and water vapor transmission, whereas high-load products extend the improvement to at least four times.¹³

Focusing on the permeability of gases through PA–clay nanocomposites, Swain and Isayev⁶⁴ assessed the oxygen permeability in PA6 including 2.5, 5, and 10 wt % MMT (Cloisite 30B). The authors reported a significant reduction in the oxygen permeability from 23.05 cm³ mm/m²/24 h in the pristine polymer to 1.01 cm³ mm/m²/24 h for the nanocomposite with 10% clay content (Fig. 7). Pereira et al.⁶⁵ also reported an even more impressive reduction in the oxygen permeability by 1000 times compared to the control sample in a PA6 nanocomposite including 5.5 wt % MMT (Cloisite 30B). The same type of modified MMT was used in low quantities (2 phr) to form exfoliated PA6 nanocomposites by Tsai et al.⁶⁶ The barrier properties of such films in terms of CO₂ permeation measurements was found to be enhanced by seven times.

The effect of nanoclay on the control of liquid water sorption in PAs is also significant. PAs are hygroscopic polymers because of the presence of amide groups, which tend to absorb water. This

water absorption effect leads to a substantial limitation of their applications, as their properties are reduced because of plasticization.^{59,67} However, the incorporation of clay nanoparticles can reduce water absorption and, at the same time, enhance the mechanical properties of PAs. A compilation of published data is given in Table II, correlating the equilibrium liquid water content and D of water in PAs. It is shown, for instance, that in the case of polyamide 6,6 (PA6,6) with increasing clay content, the water absorption at saturation decreased rapidly from 7.6% for PA6,6 to 5.2% for the nanocomposite containing 5 wt % clay.

However, the enhancement of barrier properties due to nanoclay dispersion should not be taken for granted. Alexandre et al.⁶⁸ reported that despite the tortuosity effect, the toluene permeability of polyamide 12 (PA12)–clay nanocomposites increased with the clay fraction. This odd result was attributed to the matrix–clay interface. In the case of toluene permeation, the strong permeant–matrix interactions and the PA12–clay interface balanced the tortuosity effect, as it was suggested that toluene molecules could get through the filled polymer film by going through the polymer and also by diffusing along a preferential path, lined with the clay–matrix interfacial zones. On the other hand, in the same study,

TABLE II
Liquid Water D and Equilibrium Water Content for Various PA–MMT Nanocomposites

Nanocomposite	Reinforcement content (%)	D (10 ⁻⁸ cm ² /s)	M_{∞} (%)	Reference
PA 6 (40°C)	0	2.3	9.6	11
	2	1.9	8.3	
	4	1.6	8.8	
	6	1.4	8.9	
	8	1.3	9.6	
PA 6 (50°C)	0	3.8	9.4	11
	2	3.8	8.4	
	4	3.3	8.7	
	6	3.0	8.7	
	8	2.9	9.3	
PA 6 (60°C)	0	7.9	9.0	11
	2	5.4	8.2	
	4	6.5	8.4	
	6	5.2	8.6	
	8	5.3	9.0	
PA 6 (100°C)	0	—	6.0	32
	3	—	4.1	
	5	—	3.5	
PA6,6 (100°C)	0	3.6	7.6	107
	3	2.5	5.6	
	5	2.4	5.2	
	10	2.3	4.7	
Polyamide 10,12 (25°C)	0	—	3.1	108
	1	—	2.5	
	3	—	2.1	
	5	—	1.7	

M_{∞} , equilibrium water content.

nitrogen and water permeation was found to be reduced to one-half in PA12 with 4 wt % MMT (Cloisite 30B). Similarly, Ogasawara et al.⁶⁹ reported improved helium gas barrier properties in epoxy–MMT nanocomposites compared to the pure resin. Dispersing MMT particles in the epoxy decreased D . For example, D of the nanocomposite with 6 wt % clay was approximately one-tenth that of the base polymer. On the other hand, the solubility increased with MMT dispersion, and permeability remained almost constant because of the balance of diffusivity and solubility.

In summary, although a decrease of diffusivity is a well-established result in polymer nanocomposite materials, some contradictory results have been reported concerning the saturation uptake values of various solvents or gases. Increases of the saturation uptake level may be attributed to clustering phenomena. It is worth noticing, however, that in nanocomposites, the coexistence of phases with different permeabilities can cause complex transport phenomena. On the one hand, the organophilic clay gives rise to superficial adsorption and to specific interactions with the solvents. In turn, the polymer phase can be considered, in most cases, as a two-phase crystalline–amorphous system or a nanoclay–amorphous phase system, with the crystalline and the nanoclay regions being generally impermeable to penetrant molecules. However, theoretical approaches that take into account a third, constrained amorphous region in the polymer have been proven to better describe the transport phenomena. The presence of the silicate layers may be expected to cause a decrease in permeability because of the more tortuous path for the diffusing molecules that must bypass impenetrable platelets. At the same time, however, the influence of changes in the matrix crystallinity and chain mobility induced by the presence of the filler should always be taken into consideration.

NANOTECHNOLOGY ENHANCEMENTS IN FOOD PACKAGING

In addition to reinforcing nanoparticles, which have as a main role in improving the mechanical and barrier properties of packaging materials, there are several other types of nanostructures responsible for other functions, providing active and intelligent properties to the packaging system. Before highlighting the nanotechnology contribution to intelligent and smart food packaging, it would be useful to define these terms. According to European regulations 1935/2004/EC and 450/2009/EC, *active materials and articles* are defined as “materials and articles that are intended to extend the shelf life or to maintain or improve the condition of packaged food.” They are designed to deliberately incorporate com-

ponents that would release or absorb substances into or from the packaged food or the environment surrounding the food. On the other hand, *intelligent materials and articles* are defined as “materials and articles which monitor the condition of packaged food or the environment surrounding the food.”⁷⁰

Active packaging technologies include antimicrobial activity, oxygen scavenging, enzyme immobilization, and so on. Intelligent packaging in some way senses certain properties enclosed by the food or the environment in which it is kept and is able to inform the manufacturer, retailer, and consumer of the state of these properties. Examples of such applications include time–temperature indicators, gas leakage indicators, ripeness indicators, toxin indicators, biosensors, and radio frequency identification (RFID).^{70,71} Some materials may even have multiple applications that possibly overlap, such as some immobilized enzymes that can act as antimicrobial components, oxygen scavengers, and/or biosensors.⁷²

Antimicrobial properties

The incorporation of antimicrobial compounds into food-packaging materials has been a topic of interest for many years. Materials with antimicrobial activity could help control the growth of pathogenic and spoilage microorganisms and lead to the extension of a product’s shelf life. An antimicrobial nanocomposite film could be an overall solution to foodstuff packaging because of its acceptable structural integrity and barrier properties, which are attributed to the nanocomposite matrix, and also the antimicrobial properties that might be introduced by natural antimicrobial agents impregnated within.⁷³ Materials in the nanoscale range have a higher surface-to-volume ratio when compared with their microscale counterparts. This allows nanomaterials to be able to attach more copies of biological molecules; this confers greater efficiency in terms of antimicrobial effectiveness. Nanoscale materials have been investigated for antimicrobial activity so that they can be used as growth inhibitors, killing agents, or antibiotic carriers.⁷³ The most common nanocomposites used as antimicrobial films for food packaging are based on silver, which is well known for its strong toxicity to a wide range of microorganisms and which has a high temperature stability and low volatility.⁷⁴

Silver nanocomposites have been produced by several researchers, and their antimicrobial effects are usually reported. Rai et al.⁷⁵ provided a comprehensive review on the antimicrobial mechanisms and applications of silver. Damm et al.⁷⁶ reported that PA6 filled with 2 wt % Ag NPs was effective against *Escherichia coli*, even after it was immersed in water for 100 days. The same group⁷⁷ also compared the efficiency of PA6–silver nanocomposites and

microcomposites and reported that nanocomposites with a low silver content presented an increased efficiency against *E. coli* versus microcomposites with a much higher silver content. Besides PAs, many other polymers, for example, polyurethane, polyethylene, poly(ethylene oxide), silicone rubber, and methacrylate copolymers, have been filled or coated with elemental silver nanoparticles. In all cases, good activity against different kinds of bacteria was found.⁷⁷ It has been demonstrated that doping titania (TiO₂) with silver greatly improved photocatalytic bacterial inactivation. This combination was used by Cheng et al.,⁷⁸ who reported good antibacterial properties from TiO₂-Ag⁺ particles in a nanocomposite with PVC.

Titanium dioxide on its own has been used in coated packaging films and has been shown to considerably reduce *E. coli* contamination of food surfaces.⁷⁹ However, its use is abated by the fact that it requires UV light to act as a disinfecting material. On the other hand, zinc oxide exhibits antibacterial activity that increases with decreasing particle size.⁸⁰ This activity is stimulated by visible light. Zinc oxide nanoparticles have been incorporated into a number of different polymers, including PP.⁸¹ Huang et al.⁸² reported the antimicrobial efficacy of MgO nanocrystals. By comparing MgO and TiO₂, the authors showed that even in the absence of irradiation, MgO is a good antimicrobial agent with possible commercial applications. Other nanoparticles, such as carbon nanotubes and nisin, are also known to have antimicrobial properties.⁷²

Chitosan is a biopolymer derived from chitin (a polysaccharide constituent of crustacean shells). It has seen much interest in recent years as a material for the encapsulation of nutraceuticals and in packaging applications. In addition to its utility as a packaging material, it also exhibits antimicrobial properties.⁸³ This has led a number of groups to investigate its incorporation into different composite materials, which could have applications in health care and food packaging, in combination with clays, which could then be used in polymer composites. Wang et al.⁸⁴ prepared a chitosan-rectorite nanocomposite. It was shown that increases in the chitosan amount and the interlayer distance of the layered silicates in the nanocomposites lead to a stronger antibacterial effect.

Oxygen scavenging and enzyme immobilization

Oxygen is often responsible for the deterioration of many fresh foods by either acting directly or indirectly. Direct oxidation reactions, for example, result in the browning of fruits and the rancidity of vegetable oils. Food deterioration by the indirect action of O₂ includes food spoilage by aerobic microorganisms. The incorporation of O₂ scavengers into food packaging

can maintain very low O₂ levels, which is useful for several applications.⁷² A very interesting case is the photocatalytic activity of nanocrystalline titania under UV radiation. Oxygen scavenger films were successfully developed by Xiao et al.,⁸⁵ by the addition of titania nanoparticles to different polymers. The authors suggested their use for packaging a wide variety of oxygen-sensitive products. However, as in the case of its antimicrobial mechanism, TiO₂ acts by a photocatalytic mechanism, and its major drawback, also in this case, is the requirement of UV A light.⁸⁶

Enzymes are widely used by the food industry for many types of processes. Immobilized enzymes act as bioactive materials and promise to provide innovative solutions to the food sector through breaking down undesired elements within a food product or by catalyzing the production of useful substances beneficial for the health of the consumer.⁸⁷ As an example, the incorporation in the package of enzymes such as lactase or cholesterol reductase could increase the value of the food product and answer the needs of consumers with enzyme-related health problems.⁷² Enzymes, however, are very sensitive, and thus, key challenges in such applications include the management and maintenance of appropriate processing conditions. The advantages of nanotechnology-based systems on such applications relates to the larger surface area, which is made possible by surface modifications at the nanoscale.⁸⁸ Several techniques can be used to produce films for enzyme immobilization. Rudra et al.⁸⁹ used a layer by layer assembly technique to obtain a polypeptide multilayer antimicrobial nanofilm constituted by negatively charged layers of poly(L-glutamic acid) and positively charged layers of egg white lysozyme, a chicken enzyme widely employed as a food preservative. The nanofilms were effective in inhibiting the growth of *Micrococcus luteus*. In addition, the authors demonstrated simple control of the releasing rate of lysozyme by adjusting the amount of film layers.

On the other hand, electrospinning has also been proved to be a simple and quick technique for producing nanofibers from a wide range of materials on which the entrapment of bioactive molecules is feasible. The technique uses a strong electric field to eject a jet of a viscous polymer solution from a capillary. The jet solidifies via solvent evaporation or cooling and results in a fiber-based structure. The large specific surface area and the fine porous structure of electrospun nanofibers make them an excellent enzyme support, greatly increasing the catalyzing ability of immobilized enzymes, as proven by many authors.^{90,91}

Sensors in packaging

The use of sensor technologies for packaging aims to provide a visible indicator to the supplier or

consumer that a packaged product is still fresh or whether the packaging has been spoiled. The food expiration date is currently estimated by consideration of the distribution and storage conditions, such as temperature, to which the food product is predicted to be exposed. However, quite commonly, such conditions are not always the real ones, and foods are frequently exposed to temperature abuse. Moreover, micropores or sealing defects in packaging systems can lead food products to have an unexpectedly high exposure to oxygen, which can result in undesirable changes. When integrated into food packaging, nanosensors can detect certain chemical compounds, pathogens, and toxins in food and are then useful in eliminating the need for inaccurate expiration dates and providing real-time status of food.⁷² The interest in nanotechnology applications on this field is focused on the evolution of nanosensors to detect contamination, product tampering, spoilage, and pathogens.⁹²

On the basis of applied studies of the surface properties of materials, several types of gas sensors have been developed that translate chemical interactions between particles on the surfaces into a response signal. Metal oxide gas sensors are one of the most popular type of sensors because of their high sensitivity and stability.⁷² Oxygen sensors are a quite common example with respect to nanotechnology applications in intelligent packaging systems. During food storage, there is always a chance of aerobic microbe growth in the presence of oxygen. The ability to detect oxygen within packages of fresh foodstuffs at an early stage could alert the consumer that the packaging has been compromised, even if there are no visual indications to suggest this. Such systems for the purpose of food packaging usually rely on changes in the color of dyes in the presence of oxygen. Advances using nanoparticles are expected to produce sensitive systems that respond quickly to the presence of oxygen by producing strong color changes. For example, researchers at the University of Strathclyde⁹² produced a hydroxyethyl cellulose polymer film oxygen sensor containing titanium dioxide nanoparticles and the blue dye indigo tetrasulfonate. After incorporation in the packaging, the sensor is exposed to UV light, and the dye is photobleached (a reaction catalyzed by titanium dioxide) and remains so until it is exposed to atmospheric oxygen levels, when it rapidly returns to a deep blue color in less than 3 min. Recently, nanocrystalline SnO₂ has been used as an O₂ indicator by the combination of glycerol with a redox dye and hydroxyethyl cellulose as an encapsulating polymer. This system is photoactivated through exposure to UV B light and remains bleached until it is exposed to O₂, whereupon it turns blue.⁹³

Carbon dioxide sensors are another possibility for the use of nanoparticles in polymer packaging sys-

tems. Von Bültzingslöwen et al.⁹⁴ described the development of a CO₂ sensor based on the indicator 1-hydroxypyrene-3,6,8-trisulfonate immobilized in a hydrophobic organically modified silica matrix. The sensor was proven stable over a period of at least 7 months, and its output was in excellent agreement with standard reference methods for carbon dioxide analysis. Michel et al.⁹⁵ reported the preparation of nanostructured GdCoO₃ powders that had a typical morphology of nanostructured laminae. The authors showed that GdCoO₃ could be considered a suitable carbon dioxide gas sensor material because it has a low response time to CO₂ detection and is able to detect quite low changes in the concentration of this gas in a given atmosphere.

Packaging could also benefit from the presence of materials that would indicate that the barrier properties have been reduced through heat, mechanical stress, or leakage. In some cases, this can be achieved with oxygen-sensing technologies, which indirectly indicate a break in the packaging. New research using a variety of different nanomaterials may offer solutions that directly indicate the quality of the packaging material. For example, photonic crystals have been shown to change color depending on structure, a property that could be exploited for strain sensors. Other alternatives include diacetylenes, which change color in response to mechanical stress and temperature changes, a phenomenon that could be stabilized and enhanced through the nanostructuring of the polymers, for example, by enclosing a nanoporous silica support or nanocrystals of urethane-substituted polydiacetylenes. Time-temperature indicators allow suppliers to confirm that processed foods requiring refrigeration have been kept at the appropriate temperatures throughout the supply chain. However, such structures have limitations, as they require multiple components (dyes, reactants, porous layers), which can affect accuracy under some circumstances.⁹² As a result, a single-component system would be an improvement that could be introduced through nanotechnology in the near future. Another sector in which nanotechnology could certainly play a key role is RFID tags. Researchers at the Georgia Institute of Technology⁹⁶ are experimenting with integrating nanocomponents in ultrathin polymer substrates for RFID chips containing biosensors that can detect food-borne pathogens or sense the temperature or moisture of a product.

HEALTH SAFETY ASPECTS

So far, the attention of this work has focused on the improved and novel properties that nanoparticles can introduce to plastic materials used for food packaging. However, concerns have been raised regarding the effect of nanoparticles on biological

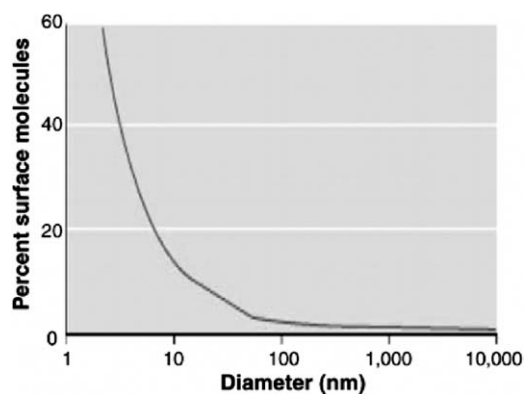


Figure 8 Particle size (diameter) versus the number of surface molecules (expressed as a percentage of the molecules in the particle).

systems and the possible impact of such materials on human health. From an ethical point of view, the need to comprehensively explore the possible toxicological effects of nanoparticles is mandatory, especially in the case of food-related applications.

The unusual properties of nanoparticles are primarily based on their nanoscale size and their extreme surface area. As the size of a particle decreases toward the nanoscale, many properties start to change in comparison with the same material in its macroscale. For example, the color and the melting temperature of gold are very different in the nanoscale than in conventional gold.⁹⁷ Unfortunately, it seems that the toxic effects of otherwise inert materials are also very different in the nanoscale; as the surface area of particles increases, a greater proportion of their atoms or molecules start to be displayed on the surface rather than the interior of the material. Figure 8 shows the inverse relationship between the particle size and the number of molecules present on the particle surface. The increase in surface area determines the potential number of reactive groups on the particle surface.⁵ The change in the physicochemical and structural properties of engineered nanoparticles with a decrease in size could be responsible for a number of material interactions that could lead to toxicological effects. Nel et al.⁵ described many mechanisms through which nanoparticles react fatally with cells. The chain generation of reactive oxygen species and the resulting oxidative stress is the best developed paradigm to explain this toxic effect. At this point, there have not been many studies that have focused on the toxicology of nanomaterials; much of the published research has been related to inhalation exposure of engineered nanoparticles. The potential effects of nanoparticles through the gastrointestinal route are largely unknown. The application of nanotechnology in food has, therefore, led to concerns that the ingestion of nanosized ingredients and additives through

food and drinks may pose certain hazards to consumer health. Such concerns have arisen from a growing body of scientific evidence, which indicates that free engineered nanoparticles can cross cellular barriers and that exposure can be harmful to cells.³

In the literature, there are some examples of the effects of nanoparticles on complex organisms. For instance, Lee et al.⁹⁸ conducted a rigorous study of silver nanoparticle toxicity *in vivo*, using nanoparticles 5–46 nm in diameter. The diffusion and accumulation of such particles in live zebrafish embryos were monitored; this indicated the evolution of abnormalities in the embryos due to nanosilver presence. A similar study from Bai et al.⁹⁹ indicated the fatal effect of ZnO nanoparticles with a 30-nm size, again in zebrafish embryos. It was shown that in high concentrations (50 and 100 mg/L in water), ZnO nanoparticles killed the embryos, whereas at lower concentrations, abnormalities in their evolution were once again observed. On the other hand, a study from Sayes et al.¹⁰⁰ concluded that nanocrystalline TiO₂ was cytotoxic to a cell culture only at concentrations higher than 100 mg/mL, and furthermore, the extent to which nanoscale titania affected cellular behavior was not dependent on the particles surface area. In an *in vitro* study on human epithelial cell cultures with SiO₂ nanoparticles, Chen and von Mikecz¹⁰¹ showed that particles smaller than 70 nm could enter cell nuclei and inhibit the DNA replication and transcription, whereas larger particles (>200 nm) did not alter the nuclear structure and function. In a more recent study, Trouiller et al.¹⁰² highlighted the differences between the inert conventional TiO₂ and its nanocounterpart by conducting *in vivo* experiments. TiO₂ nanoparticles were issued to rats through drinking water, and it was demonstrated that nano-TiO₂ may have caused respiratory tract cancer. However, the mechanism of carcinogenesis was not revealed.

It is quite obvious from the aforementioned examples that the application of nanotechnology in the food sector results in concerns regarding the possible ingestion of nanosized ingredients, which could pose certain hazards to consumer health. The main likely route of nanoscale particle entry to the gut is through consumption of food and drinks. Chaudhry et al.³ and Bouwmeester et al.¹⁰³ described in detail the mechanisms by which nanoparticles enter the human body. In short and focusing on the gastrointestinal tract, it was noticed that the uptake of nanoparticles depends on diffusion and accessibility through mucus, initial contact with the gut epithelium, and various uptake and translocation processes. There seems to be a tendency of smaller particles to diffuse faster through the mucus layer than larger particles, but the diffusion rate also depends on the charge of the particle. In general, the mucus

layer can thus be considered the first barrier that particles have to pass before entering the body, whereas the gastrointestinal epithelium represents the second barrier.

Nanotechnology is currently used in many food-related sectors, including the agricultural production phase, food processing, food additives, and of course, packaging. In general, the currently known and projected applications of nanotechnology for the food sector fall into the following main categories:³

- Food ingredients that have been processed or formulated to form nanostructures.
- Nanosized, nanoencapsulated, or engineered nanoparticle additives that have been used in food.
- Nanomaterials that are incorporated to develop improved, active, or intelligent food packaging.
- Nanotechnology-based devices and materials used, for example, for nanofiltration, water treatment, and nanosensors for food safety and traceability.

With regard to food-packaging safety, it becomes clear from a number of reports that there is currently no nanospecific regulation in the European Union.¹⁰³ However, general regulatory controls in the European Union that govern the composition, properties, and use of food-contact materials are based on the regulation (EC) 1935/2004. According to this regulation, any material or article intended to come in contact directly or indirectly with food must be sufficiently inert to preclude substances from being transferred to the food in quantities large enough to endanger human health or to bring about an unacceptable change in the composition of the food or a deterioration in its organoleptic properties.³ The regulation is broad enough to include the possible migration of nanocomponents from plastic composite materials into packaged food. However, it only precludes the use of substances if they are transferred in quantities large enough to endanger human health. In the case of nanoparticles, there are two factors that remain unanswered and require a more specific regulation. First, the potential risk from nanoparticles has to be defined better in terms of the transfer rate and the properties of the substances in the nanoscale. Second, the large quantity is more or less irrelevant in the case of nanoparticles, as mass alone is not a good metric. The total surface area seems a more critical parameter with respect to nanotoxicity and should be also considered.

In any cases, the main risk of consumer exposure to nanoparticles from the aspect of food packaging is likely to take place through the potential and unmeant migration of nanoparticles from the packaging material to food and drinks. In the case of

deliberate nanoparticle release (e.g., smart antimicrobial packaging), the nanoparticle should be treated as a food additive rather than a packaging component and be controlled from another perspective.

For the unintended migration of nanoparticles, data for such polymer–nanoparticle systems are scarce, even though a number of plastic packaging materials containing nanomaterials are already commercially available. Avella et al.¹⁰⁴ measured the migration of minerals (Fe, Mg, Si) from a 4 wt % silicate (MMT)–biodegradable starch nanocomposite to packaged vegetables. The polymer composite was formed into bags in which the vegetables were packaged and remained in contact for 10 days at 40°C. From the analysis of the mineral concentration in the vegetables, it was shown that there was only an insignificant trend in the concentration increase of Fe and Mg, whereas a higher Si content was observed in the vegetables, attributed to the presence of nanoclay in the films. This study, however, provided only a small piece of information for a biodegradable material and not for the more rigid plastic nanocomposites, which are more likely to be used in food and drink containers, such as PAs or PET.

In another study, Simon et al.¹⁰⁵ provided mathematical estimations for D and the overall migration of nanoparticles with a 5-nm radius from conventional polymer materials, such as polyolefins, PS, and PET, to foodstuff. The estimated D values for all of the polymers were quite low; for example, at 25°C, the estimated D for LDPE was 6.6×10^{-15} cm²/s, whereas for the same polymer at 25°C, the experimental D of CO₂ was 3.7×10^{-7} cm²/s, and the D of a common additive such as Uvitex OB at 40°C was 3.2×10^{-10} cm²/s.⁴⁹ The overall migration quantity of the nanoparticles after 1 year was also predicted to be very low. The prediction results indicated that the migration of nanoparticles from packaging to food will be detected mainly in the case of very small particles with the radius of approximately 1 nm from polymer matrices that have a relatively low dynamic viscosity and that do not interact with the nanocomponents. These conditions could be met, for example, in the case of nanocomposites of silver with polyolefins, but for bigger nanocomponents that are bound in polymer matrices with relatively high dynamic viscosities (e.g., MMT in PAs), the migration is not predicted to be detectable.

Finally, it must be noted that the European Food Safety Authority (EFSA) was recently required to give a scientific opinion¹⁰⁶ regarding the use of titanium nitride (TiN) nanoparticles in PET bottles. According to the petitioner, nano-TiN is intended to be used as an additive to PET bottles up to 20 mg/kg, whereas the produced bottles will come in contact with liquid foodstuff for typical hot-fill/pasteurization or long-time storage at room temperature

applications. Experiments showed that nano-TiN formed agglomerates (20 nm in diameter) in PET, and migration tests into food simulants showed that no nano-TiN could be detected at levels exceeding 5 µg/L after a contact of 2 h at 70°C followed by 10 days at 40°C. Therefore, in the absence of detectable migration, the petition was approved by EFSA, and no further toxicological data were required for the use of nano-TiN in PET bottles up to 20 mg/kg.

CONCLUSIONS

Polymer nanocomposites are a new class of materials that have the potential to introduce novel properties and features to the food-packaging industry. During the last 2 decades, polymer-layered silicate nanocomposites have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvement in material properties when compared with the pristine polymer or conventional microcomposites and macrocomposites. These nanocomposite materials have improved mechanical properties, and when used in packaging applications, they are able to withstand the stress of thermal food processing, transportation, and storage, and they give the possibility of reducing material usage and/or weight. On the other hand, the final packaging material can be still attractive to consumers, as clarity, processability, and recyclability are not affected.

However, the major advantage of nanocomposites that renders them attractive for food-packaging applications is the fact that nanoparticles improve the barrier properties of polymers. This is attributed mostly to the lengthening of the diffusion path of the permeating gas molecules because of the increase of the tortuosity, which leads to a higher shelf life of the packaged foodstuff. PA-nanoclay composites are already available commercially for such applications, either in the form of films or as barriers in PET multilayer bottles.

Moreover, several nanoparticles may provide active or intelligent properties to food-packaging materials. These benefits include antimicrobial properties, oxygen scavenging ability, enzyme immobilization, and indication of the degree of exposure to some degradation-related factor. As a result, nanocomposites do not only passively protect the food against the diffusion of gases but also incorporate novel properties to the packaging material, upgrading its added value and actually enhancing the stability of packaged foods or indicating their quality to consumers.

However, there are many safety concerns about nanomaterials as their size may allow them to penetrate into cells. A material possesses significantly different properties in the nanoform than in its bulk form; this renders our current knowledge of the tox-

icity of materials inappropriate to be projected onto those properties in the nanoscale. Toxicological studies have already highlighted the fatal effect of nanoparticles on cells and organisms. So far, scientific data have indicated that there is a limited possibility for the migration of nanoparticles from the composite packaging material to foodstuffs. However, much more has to be done not only with regard to the quantity of nanoparticles but also to how their surface area affects their toxicity.

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