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JPPS-682; No. of Pages 17
ARTICLE IN PRESS

Progress in Polymer Science xxx (2011) xxx–xxx

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Food packaging based on polymer nanomaterials

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ARTICLE INFO

Article history:
Received 23 September 2010
Received in revised form 25 February 2011
Accepted 25 February 2011
Available online xxx

Keywords:
Polymer
Nanomaterials
Nanocomposites
Nanotechnology
Properties
Structure
Morphology
Food
Packaging
Environment
Health
Regulation issues
Application
Improved packaging
Active packaging
Smart packaging
Intelligent packaging
Eco-sustainability

ABSTRACT

Since its starting in the 19th century, modern food packaging has made great advances as results of global trends and consumer preferences. These advances are oriented to obtain improved food quality and safety. Moreover, with the move toward globalization, food packaging requires also longer shelf life, along with the monitoring of safety and quality based upon international standards. Nanotechnology can address all these requirements and extend and implement the principal packaging functions – containment, protection and preservation, marketing and communications. Applications of polymer nanotechnology in fact can provide new food packaging materials with improved mechanical, barrier and antimicrobial properties, together with nano-sensors for tracing and monitoring the condition of food during transport and storage.

The latest innovations in food packaging, using *improved, active and smart nanotechnology* will be analyzed. It will be also discuss the limits to the development of the new polymer nanomaterials that have the potential to completely transform the food packaging industry.

Contents

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doi:10.1016/j.progpolymsci.2011.02.003

Please cite this article in press as: Silvestre C, et al. Food packaging based on polymer nanomaterials. Prog Polym Sci (2011), doi:10.1016/j.progpolymsci.2011.02.003

1. Introduction

Polymer nanotechnology is a broad interdisciplinary area of research, development and industrial activity that involves the design, manufacture, processing and application of polymer materials filled with particles and/or devices that have one or more dimensions of the order of 100 nanometers (nm) or less [1–4]. The extraordinary potential of this novel technology to provide enabling routes for development of high-performance materials has attracted the attention of researchers, from physics, chemistry, biology to engineering.

Over the last decades, the use of polymers as food packaging materials has increased enormously due to their advantages over other traditional materials [5,6]. In the polymer global market that has increased from some 5 million tonnes in the 1950s to nearly 100 million tonnes today, the 42% is covered by packaging (Fig. 1), with the packaging industry itself worth about 2% of Gross National Product in developed countries (Applied Market Information Ltd., 2007). Polymer packaging provides many properties including strength and stiffness, barrier to oxygen and moisture, resistance to food component attack and flexibility.

Novel and efficient polymer materials for food packaging based on nanotechnology can provide innovative solutions to increase the performance of the polymers further adding safety, economical and environmental advantages, such as reduction to zero of any critical interaction with food matrices and with human health, reduction of the energy-inputs for production, transport and storage, increase of biodegradability and barrier protection to gases and light, reduction of volume of waste material to be disposed of in landfills, contribution to decrease CO_2 emissions [7–16].

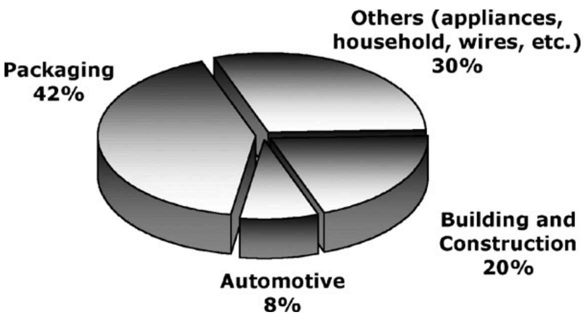

Fig. 1. Polymer global market.

Although the large amount of researches being undertaken in industry and academia, polymer nanotechnology for food packaging is still in a development stage. The envisaged direction is to look at the complete life cycle of the packaging (raw material selection, production, analysis of interaction with food, use and disposal) integrating and balancing cost, performance, health and environmental considerations (Fig. 2). Successful technical development of polymer nanomaterials for food packaging (PNFP) has to overcome barriers in safety, technology, regulation, standardisation, trained workforce and technology transfer in order that commercial products can benefit from the global market potential and requires therefore a high degree of multidisciplinary. Moreover, because of its enormous growth application potential, the emerging technology of PNFP will be a major provider of new employment opportunities, based upon growing international commercial success combined with ecological advantages.

This paper provides an overview of the latest innovations in food packaging based on polymer nanomaterials. It begins with a brief history of food packaging, an introductive description of the properties of the polymer and their use in the food packaging. The article then describes the current state of research and development regarding polymer nanotechnologies within the food packaging section. Finally, the article discusses the barriers to the development of the new nano-sized components focusing on the balance between benefits and hazards on health and environment, the current regulatory framework, the public engagement, the consumer perception and the future perspectives.

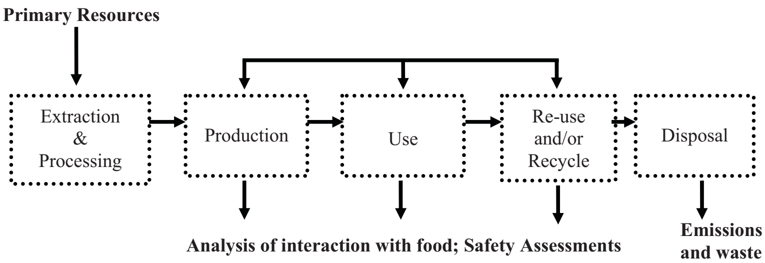

Fig. 2. Complete life cycle of the packaging.

2. State of art

Polymer nanotechnology is actually developed mainly to improve barrier performance pertaining to gases such as oxygen and carbon dioxide. It is proved also to enhance the barrier performance to ultraviolet rays, as well as to add strength, stiffness, dimensional stability, and heat resistance. Once perfected, sure from a safety point of view and produced at a competitive ratio cost/performances, the new PNFP will be very attractive for extensive applications. The use of polymer nanotechnology can in fact extend and implement all the principal functions of the package (containment, protection and preservation, marketing and communication) [10,12–22]. This is the reason why many of the world's largest food packaging companies are actively exploring the potential of polymer nanotechnology in order to obtain new food packaging materials with improved mechanical, barrier and antimicrobial properties and also able to trace and monitor the condition of food during transport and storage.

In particular the following main applications for polymer nanomaterials for food packaging will be discussed:

- "Improved" PNFP – the presence of nanoparticles in the polymer matrix materials improves the packaging properties of the polymer-flexibility, gas barrier properties, temperature/moisture stability;
- "Active" PNFP – the presence of nanoparticles allows packages to interact with food and the environment and play a dynamic role in food preservation;
- "Intelligent" PNFP – the presence of nanodevices in the polymer matrix can monitor the condition of packaged food or the environment surrounding the food and can also act as a guard against fraudulent imitation.

2.1. "Improved" PNFP

The possibility to improve the performances of polymers for food packaging by adding nanoparticles has led to the development of a variety of polymer nanomaterials [23–29]. Polymers incorporating clay nanoparticles are among the first polymer nanomaterials to emerge on the market as improved materials for food packaging. Clay nanoparticles (Fig. 3) have a nanolayer structure with the layers separated by interlayer galleries [2,4,29]. In order to take advantage of the addition of clay, a homogeneous dispersion of the clay in the polymer matrix must be obtained. It was reported that entropic and enthalpic factors determine the morphological arrangement of the clay nanoparticles in the polymer matrix [30–32]. Dispersion of clay in a polymer requires sufficiently favourable enthalpic factors that are achieved when polymer clay interactions are favourable. For most polar polymers, the use of alkyl-ammonium surfactants is adequate to offer sufficient excess enthalpy and promote formation of homogeneous nanocomposites. According to Kornmann et al. [33,34] the driving force for the initial resin diffusion into the galleries is the high surface energy of the clay that attract the polar resin molecules.

Four morphological arrangements can be achieved: non-intercalated nanocomposites, intercalated nanocomposites, exfoliated nanocomposites and flocculated nanocomposites (Fig. 4). The appearance of these morphologies is dependent on the strength of interfacial interactions between the matrix and the filler. As reported by Sinha Ray and Okamoto [4], in intercalated nanocomposites the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay/polymer ratio. Intercalated nanocomposites are normally interlayered by a few molec-

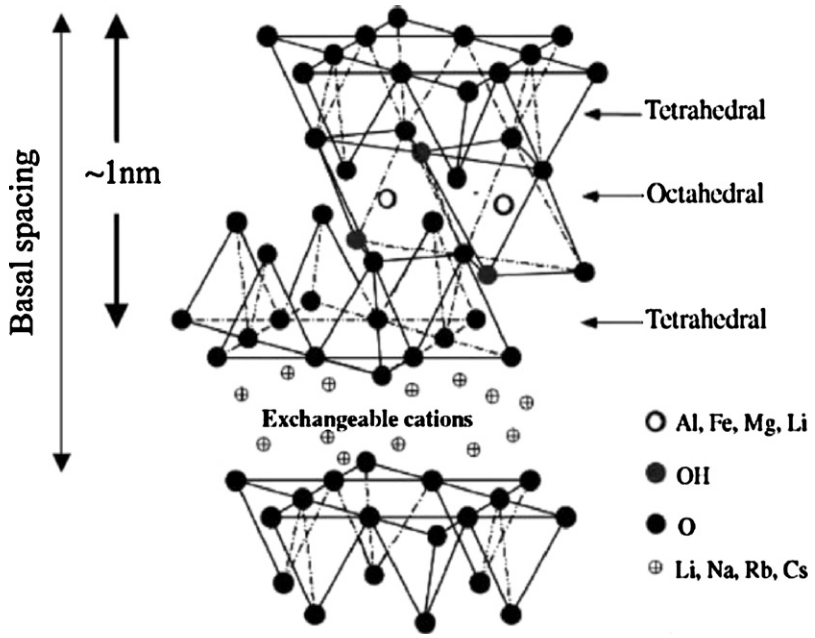

Fig. 3. The structure of 2:1 layered silicates.

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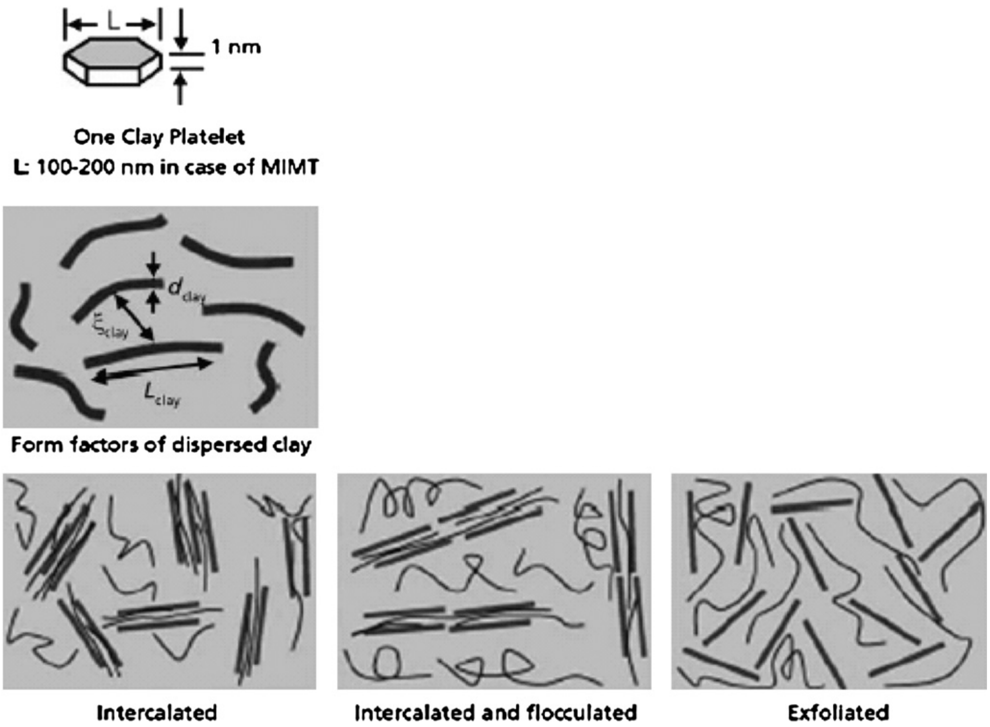

Fig. 4. Schematic illustration of different types of thermodynamically achievable polymer/layered silicate nanocomposites.
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ular chains of the polymer. In some cases silicate layers are flocculated due to hydroxylated edge–edge interaction of the silicate layers. The exfoliated nanocomposites consist of individual nm-tick layers suspended in a polymer matrix and are a result of extensive penetration of the polymer in the silicate layers with the spacing between layers expanded up to 10 nm or more. Vaia et al. [35] proposed an expanded and more complete classification scheme where the intercalated and exfoliated structure are listed into ordered or disordered structures, depending on the change of spacing and orientation of nanoparticles. An intermediate morphology between intercalation and exfoliation, called partial exfoliation, can also be present. In the case of ordered exfoliation, the ordered and parallel arrangement of nano-layers is preserved and a homogeneous morphology is observed. In the case of disordered exfoliation individual nanolayers are randomly distributed in the matrix.

The overall morphology of the clay nanocomposites is still more complex, as changes in the structure and morphology of the matrix can also occur due to the presence of the filler. Consequently characterization of structures is essential to establish relationships among preparation, processing and properties. WAXD and TEM are the techniques most used in order to establish the polymer-layer structure composite morphologies. Through WAXD it is possible to monitor the position, shape and intensity of the based reflections from the silicate layers and therefore to identify the nanocomposites structures. In the exfoliated nanocomposites, the extensive layer separation results in the disappearance of any diffraction peak from the layers. Conversely for intercalated nanocomposites the increase of the distance between layers provides a peak at lower angles. TEM analysis is complementary to WAXD and can give insights in the spatial distribution of the layers. Also Atomic Force Microscopy (AFM) has been used to obtain more details on the morphology. Exfoliation is the ultimate goal of most researchers in because this morphology is expected to lead to dramatic improvements of the properties with a reduced loading of fillers than traditional composites. Many researchers have claimed to have obtained clay nanocomposites with exfoliated structures based on X-ray and TEM results. Several examples of X-ray diffraction patterns of epoxy–clay nanocomposites formed from different organoclays are shown in Fig. 5. All the patterns are characterized by the absence of the 0 0 l diffraction peak, providing strong evidences that the clay nanolayers are exfoliated.

Polymer nanocomposites can be prepared by solution, (in situ) polymerization and melt processing. Detailed information on the preparation methods and structure analysis of polymer–clay nanocomposites can be found in Refs. [1–4,29].

Several different polymers and clay fillers can be used for obtaining clay–polymer nanomaterials. The polymers most used are polyamide, nylon, polyolefins, polystyrene, ethylene–vinylacetate copolymer, epoxy resins polyurethane, polyimides and polyethylene terephthalate. The nanoclay generally used is the montmorillonite (MMT), a hydrated alumina-silicate layered clay consisting of an edge-shared octahedral sheet of aluminum hydroxide between two silica tetrahedral layers [30].

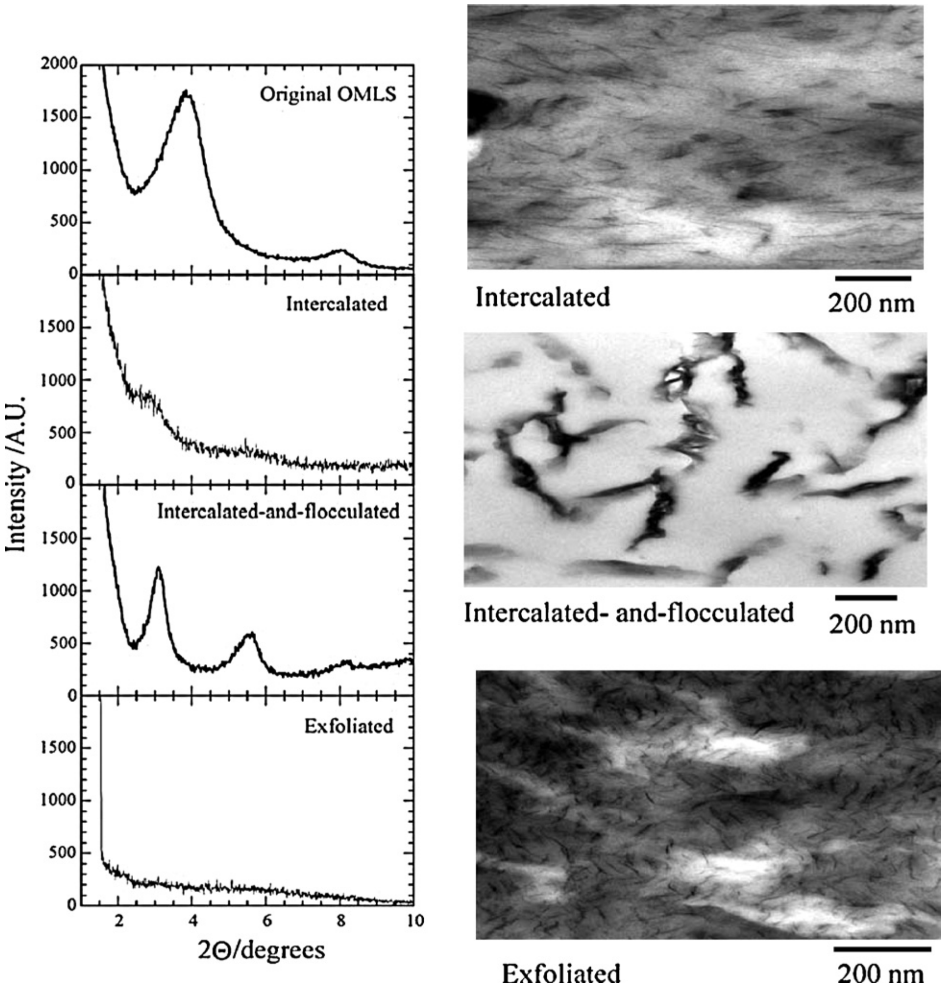

Fig. 5. WAXS and TEM images from different structure in nanocomposites.
Reproduced with permission from Elsevier Ltd. [4].

MMT is relatively cheap and widely available natural clay derived from volcanic ash/rocks. This type of clay is characterized by a moderate negative surface charge compensated by exchangeable cations (typically Na^+ and Ca^{2+}). The homogeneous dispersion in organic polymers of MMT as well as of the most clays is not easy due to the hydrophilicity of its surface [4,28,29,35–39]. Several methods have been used in order to obtain a homogeneous distribution of clay in the matrix and the exfoliation of the clay, modifying the clay, the polymer and/or adding compatibilizer agents. Modified montmorillonite has been obtained by substituting inorganic cations of MMT with organic ammonium ions [39–44].

When well dispersed in the matrix the clay limits the permeation of gases, and provides substantial improvements mainly in the gas barrier properties. These improvements have led to the development of nanoclay–polymer nanomaterials for potential use in a variety of food-packaging applications, such as processed meats, cheese, confectionery, cereals, boil-in-the-bag foods, as well as in extrusion-coating applications for fruit juices and dairy products, or co-extrusion processes for the manufacture of bottles for beer and carbonated drinks. Many studies have reported the effectiveness of nanoclays in decreasing oxygen and water vapour permeabilities of several polymers [39–49]. The most widely known theories to explain the improved barrier properties of polymer–clay nanocomposites are based on a theory developed by Nielsen [45], which focuses on a tortuous path around the clay plates, forcing the gas permeant to travel a longer path to diffuse through the film (Fig. 6). According to the theory the increase in path length is a function of the high aspect ratio of the clay filler and the volume % of the filler in the composite. In order to take into consideration several deviations from Nielsen's theory of the experimental results, Beall [46,47] proposed a new model focused on the polymer–clay interface and on the influence of the clay on the free volume on the region around the clay layer as the governing factor, in addition to the tortuous path.

The main advantage of using nanoclays is therefore a marked increase in the barrier of the polymer material to gas and water. In many commercial applications it is claimed that clay particles can cut permeability as

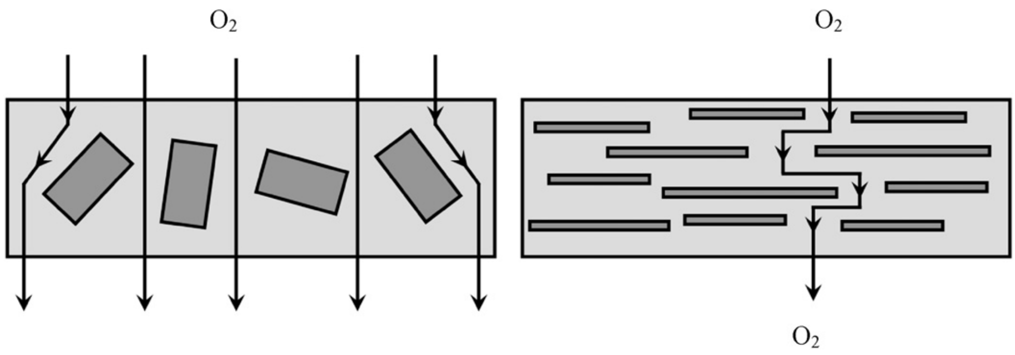

Fig. 6. Tortuous path around the clay platelet.

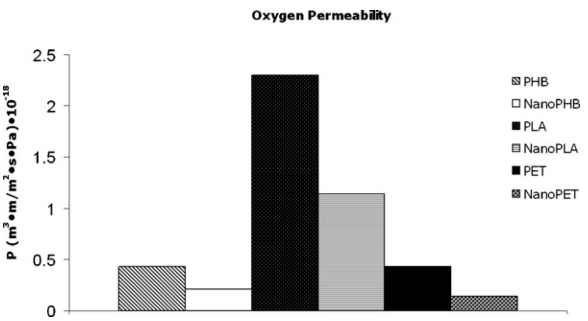

Fig. 7. Oxygen permeability for different polymer/clay nanocomposites. Reproduced from Sage Productions [50,51].

much as 75% (Fig. 7) [50,51]. Very recently, at research level, a new methodology is reported for preparation of a transparent clay–polymer material with an oxygen barrier that seems to cut permeability at almost 100%. Thin films of sodium montmorillonite clay and branched polyethylenimine were deposited on various substrates using layer-by-layer assembly [52]. For polyethylene terephthalate it was obtained oxygen transmission rate below the detection limit of commercial instrumentation (<0.005 cc/(m^2 day atm)). This is the lowest permeability ever reported for a polymer–clay composite and it is believed to be due to a brick wall nanostructure created by the alternate adsorption of polymeric layers and highly oriented, exfoliated clay platelets (Fig. 8).

Clays have been also reported to improve mechanical properties, thermal stability and resistance to fire of several polymers, for polyethylene, polypropylene, Nylon 6, poly(e-caprolactone), polyethylene terephthalate, etc. [48,49,53–57] (Table 1). The increased thermal stability has been attributed to a slower diffusion of volatile decomposition products within the nanocomposites containing the clay particles.

Table 1
Properties of nanocomposites.

Property	Microcomposite	Nanocomposite
Young modulus	↑	↑
Toughness	↓↓↓	↓
Barrier properties	↓	↑↑↑
Temperature resistance	↑	↑↑
Transparency	↓↓↓	↓
Cost	↓	↑
Common loading	20–50%	2–5%

Due to the improvements in the performances the incorporation of nanoclays into packaging offers the following additional advantages:

- Reduction in raw materials, due to the improved stiffness and savings in the cost of transportation, storage and recycling due to the lighter packaging.
- Elimination of expensive secondary processes, such as laminations for barrier packaging or mechanical surface finishing and easier recycling due to the less complex structures nanocomposites may have.
- Reduction in machine cycle time and temperature, by the modification of the physical and thermal properties of polymers.

Also carbon nanotubes, silicon oxide and Ag oxide nanocoating, used for their antibacterial activity, see next section, as well as several other nanoparticles have been found to improve, together with other properties, barrier and mechanical properties. Deep attention is focused on carbon nanotubes (CNTs), both one-atom thick single-wall nanotube and several concentric nanotubes that present extraordinarily high elastic modulus and tensile

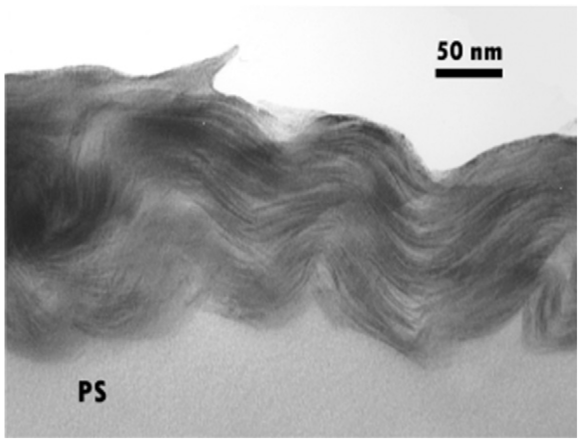

Fig. 8. TEM cross-sectional image of a 40-bilayer film with clay and pH 10 PEI.
Reproduced with permission from the American Chemical Society [52].

strength (1 TPa and 200 GPa, respectively). The addition of CNTs to several polymers such as PVOH, polypropylene, polyamide and PLA causes an improvement of the tensile strength, modulus, toughness [58–62] and an improved water vapour transmission rate (up to 200% for example PLA). Some studies are also reported on the addition of silica nanoparticles ($n\mathrm{SiO_2}$), these studies claim that the addition improves mechanical and/or barrier properties of matrices based on polypropylene [24].

2.2. "Active" PNFP

Active packaging [11] is designed to deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food. At the moment active PNFP have been mainly developed for antimicrobial packaging applications, see next section. Other main promising applications comprise oxygen scavengers, ethylene removers and carbon dioxide absorbers/emitters.

Metal nanoparticles, metal oxide nanomaterials and carbon nanotubes are the most used nanoparticles to develop antimicrobial active PNFP. These particles function on direct contact, but they can also migrate slowly and react preferentially with organics present in the food.

Silver, gold and zinc nanoparticles are the most studied metal nanoparticles with antimicrobial function, with silver nanoparticles already found in several commercial applications. Silver, that has high temperature stability and low volatility, at the nanoscale is known to be an effective anti-fungal, anti-microbial and is claimed to be effective against 150 different bacteria [63,64].

Several mechanisms have been proposed for the antimicrobial property of silver nanoparticles (Ag-NP): adhesion to the cell surface, degrading lipopolysaccharides and forming "pits" in the membranes [65]; penetration inside bacterial cell, damaging bacteria DNA [66], and releasing antimicrobial Ag^+ ions [67] which bind to electron donor groups in molecules containing sulphur, oxygen or nitrogen. Silver nanocomposites have been obtained by several researchers and their antimicrobial effectiveness has been reported. Higher efficiency of silver nanocomposites against silver microcomposites is reported by Damm et al. [68] that compared the efficacy of polyamide 6/silver-nano- and microcomposites against *Escherichia coli* (Table 2). The same authors in another study reported the long persistence of the anti-bacterial activity of the silver nanocomposites [69].

Silver nanoparticles are also used in conjunction with zeolites minerals and gold nanoparticles. In these cases interesting and promising synergic effect against of some microorganisms are observed. The use of the combination siver/zeolite and silver/gold produces a greater anti-bacterial effect than silver alone, although no commercial application has been found at the moment [70]. Also zinc nanocrystals have been recently used as an anti-microbial, anti-biotic and anti-fungal agent when incorporated plastic matrix [71].

Titanium dioxide (TiO_2), zinc oxide (ZnO), silicon oxide (SiO_2) and magnesium oxide (MgO) are the most studied oxide nanoparticles for their ability to be UV blockers and photo-catalytic disinfecting agents [72]. These particles have been used in sun creams for many years and as white colorants for paper, paints, plastics and printing inks. They are white in appearance but they are no longer visible in sun creams when their particle sizes are reduced below 100 nm. The use of TiO_2 as a photo-catalytic disinfecting material for surface coatings [73] is under study in packaging. The TiO_2 photo-catalysis, which promotes peroxidation of the polyunsaturated phospholipids and fatty acid of microbial cell membranes [73], can be used to inactivate several food-related pathogenic bacteria [74–76]. TiO_2 powder-coated packaging films were developed and found active against *E. coli* contamination on food surfaces [75], faecal coliforms in water [76]. The visible light absorbance and the photocatalytic bacterial inactivation under UV irradiation of TiO_2 [77–81] is improved by metal doping.

Table 2
Concentration of *E. coli* in the LB-suspension after 24 h contact with the polymer specimens at ambient temperature.

Sample	Concentration of bacteria in the suspension after 24 h CFU ml^{-1} [a]
Control	$2.1 \pm 0.2 \times 10^6$
Neat PA	6 $4.1 \pm 0.8 \times 10^6$
0.025 wt.% nanosilver in PA6	$3.5 \pm 0.4 \times 10^5$
0.06 wt.% nanosilver in PA6	0
0.19 wt.% nanosilver in PA6	0
0.37 wt.% nanosilver in PA6	0
0.63 wt.% nanosilver in PA6	0
1.5 wt.% nanosilver in PA6	0
0.64 wt.% microsilver in PA6	$1.2 \pm 0.1 \times 10^6$
1.1 wt.% microsilver in PA6	$6.3 \pm 0.6 \times 10^5$
1.9 wt.% microsilver in PA6	$3.8 \pm 0.4 \times 10^5$

Reproduced with permission from Elsevier Ltd. [68,69].
[a] The initial concentration of bacteria was $1.8 \pm 0.2 \times 106$ CFU ml^{-1}.

More recently the antimicrobial properties of nano-ZnO and MgO have been discovered. Compared to nanosilver, the nanoparticles of ZnO and MgO are expected to provide a more affordable and safe food packaging solutions in the future. Nanomaterials containing nano-ZnO-based light catalyst, claimed to sterilize in indoor lighting have been recently introduced. It as reported that ZnO exhibits antibacterial activity that increases with decreasing particle size [82]. This activity does not require the presence of UV light (unlike TiO_2), but it is stimulated by visible light [83]. The exact mechanism of action is still unknown. ZnO nanoparticles have been incorporated in a number of different polymers including polypropylene [84], where absorbing UV light, without re-emitting as heat, improves also the stability of polymer composites.

Carbon nanotubes could be used not only for improving the properties of polymer matrix, but also for their antibacterial properties. Direct contact with aggregates of CNTs was demonstrated to be fatal for *E. coli*, possibly because the long and thin CNTs puncture the microbial cells, causing irreversible damages [85]. The application of CNT at the moment is stopped as, several studies suggest that CNTs are cytotoxic to human cells, at least when in contact to skin [86] (see next section for health concerns).

Active packaging by nanotechnology can also contribute to decrease the deterioration of many foods either directly or indirectly oxidation with the incorporation of nano O_2 scavengers [87]. Direct oxidation reactions result in browning of fruits and rancidity of vegetable oils, to name a few examples. Food deterioration by indirect action of O_2 includes food spoilage by aerobic microorganisms. The presence of O_2 in a package can trigger or accelerate oxidative reactions that result in food deterioration and facilitate the growth of aerobic microbes and moulds. Both direct and indirect oxidative reactions result in adverse qualities such as off-odours, off-flavours, undesirable colour changes, and reduced nutritional quality. O_2. Oxygen scavengers remove O_2 (residual and/or entering), thereby retarding oxidative reactions. Several nanoparticles, including TiO_2 nanoparticles were used to produce oxygen scavenger films [87].

Some nanoparticles based on silver, that have anti microbial activity, are able also to absorb and decompose ethylene [88]. Ethylene is a natural plant hormone produced by ripening produce. Removing ethylene from a package environment helps extend the shelf life of fresh produce like fruits and vegetables.

2.3. "Intelligent/smart" PNFP

Intelligent food contact materials are mainly intended to monitor the condition of packaged food or the environment surrounding the food [89–91]. This technology can inform with a visible indicator the supplier or consumer that foodstuffs are still fresh, or whether the packaging has been breached, kept at the appropriate temperatures throughout the supply chain, or has spoiled. Key factors in their extensive application are cost, robustness, and compatibility with different packaging materials. First developments were based on devices which were incorporated with the product in a conventional package with the aim to monitor the package integrity and the time–temperature history of the product and the effective expiration date). The food expiration date is estimated by industries by considering distribution and storage conditions (especially temperature) to which the food product is predicted to be exposed. However, it is well known that such conditions are not always the real ones, and foods are frequently exposed to temperature abuse; this is especially worrying for products which require a cold chain. Time temperature indicators (TTI's), that began appearing on some food products in the late 20th century, allow suppliers to confirm that the foods have been kept at the appropriate temperatures [92]. They fall into two categories: one relies on the migration of a dye through a porous material, which is temperature and time dependent, the other makes use of a chemical reaction (initiated when the label is applied to the packaging) which results in a colour change. These indicators allow consumers to feel confident about what they are purchasing and manufacturers to trace their foods along the supply line: Moreover, by checking food as it moves through the supply chain, companies can identify and address areas of weakness.

Moreover, micropores and sealing defects in packaging systems can lead food products to an unexpected high exposure to oxygen, which can result in undesirable changes. Nanoparticles can be applied as reactive particles in packaging materials to inform about the state of the package. The so-called nanosensors are able to respond to environmental changes (e.g., temperature or humidity in storage rooms, levels of oxygen exposure), degradation products or microbial contamination [93].

When integrated into food packaging, nanosensors can detect certain chemical compounds, pathogens, and toxins in food, being then useful to eliminate the need for inaccurate expiration dates, providing real-time status of food freshness [94].

The recent developments for smart PNFP include oxygen indicators, freshness indicators and pathogen sensors. Oxygen allows aerobic microorganism to grow during food storage. There has been an increasing interest to develop non-toxic and irreversible oxygen sensors to assure oxygen absence in oxygen free food packaging systems, such as packaging under vacuum or nitrogen.

Lee et al. [94] developed an UV-activated colorimetric oxygen indicator, which uses nanoparticles of TiO_2 to photosensitize the reduction of methylene blue (MB) by triethanolamine in a polymer encapsulation medium, using UVA light. Upon UV irradiation, the sensor bleaches and remains colourless, until it is exposed by oxygen, when its original blue colour is restored. The rate of colour recovery is proportional to the level of oxygen exposure.

Mills and Hazafy [95] used nanocrystalline SnO_2 as a photosensitizer in a colorimetric O_2 indicator with the colour of the film varying depending on the O_2 exposure. Also pH indicators based on organically modified silicate nanoparticles have been recently introduced [96].

The freshness indicators monitor the quality of the packed food by reacting to changes that take place in the fresh food product as a result of the microbiological growth. As reported by Smolander in her review [97] on freshness indicators for food packaging, a crucial prerequisite in the successful development of freshness indicators is knowledge about the quality-indicating metabolites. The freshness sensor has to be able to react to the presence of these metabolites with the required sensitivity. The indication of freshness is based on a colour change of the indicator tag due to the presence of the microbial metabolites produced during spoilage. It is to be noted that the formation of the different metabolites depends on the nature of the packed products spoilage flora and type of packaging. The embedded sensors in a packaging film must be able to detect food-spoilage organisms and trigger a colour change to alert the consumer that the shelf life is ending/ended. A list of the freshness indicators reacting to the presence of quality indicating metabolites is also reported [97].

Several types of gas sensors have been developed, which can be used for quantification and/or identification of microorganisms based on their gas emissions. Metal oxide gas sensor is one of the most popular types of sensors because of their high sensitivity and stability [98].

Sensors based on conducting nanoparticles embedded into an insulating polymer matrix to detect and identify food borne pathogens by producing a specific response pattern for each microorganism are under investigation [99–101]. At the moment three kinds of bacteria (*Bacillus cereus*, *Vibrio parahemolyticus* and *Salmonella* spp.) could be identified from the response pattern produced by such sensors.

Further developments in the field include the so-called "Electronic Tongue" technology that is made up of sensor arrays to signal condition of the food. The device consists of an array of nanosensors extremely sensitive to gases released by spoiling microorganisms, producing a colour change which indicates whether the food is deteriorated [101]. DNA-based biochips are also under development which will be able to detect the presence of harmful bacteria in meat or fish, or fungi affecting fruit.

Other advances in the field at an early stage of research include devices that will provide a basis for intelligent preservative-packaging technology that will release a preservative if food begins to spoil.

3. Current industrial applications

Nanotechnology has been applied by packaging industry since some years. According to recent reports by iRAP Inc. and BBC Research, summarized by Plastemart the total nano-enabled food and beverage packaging market in the year 2008 was US$ 4.13 bln and forecasted to grow to US$ 7.3 bln by 2014. Active technology represents the largest share of the market and will continue to do so in 2014, with US$ 4.35 bln in sales, and the intelligent segment will grow to US$ 2.47 bln in sales.

In food products, bakery and meat products have attracted the most nano-packaging applications, and in beverages, carbonated drinks and bottled water dominate; however, only a few of these systems have been developed and are being applied now. Among the regions, Asia/Pacific, in particular Japan, is the market leader in active nano-enabled packaging, with 45% of the current market, valued at US$ 1.86 bln in 2008 and projected to grow to US$ 3.43 bln by 2014 with an annual increase of 13%. In the United States, Japan, and Australia, improved and active packaging is already being successfully applied to extend shelf-life while maintaining nutritional quality and ensuring microbiological safety.

In Europe the industrial application are coming slowly. The main reasons for this are legislative restrictions and a lack of knowledge about acceptability to European consumers, as well as the efficacy of such systems and the economic and environmental impact such systems may have.

However, to date, with the exception of some materials such as nanoclays, the costs of manufacturing and using such nanoparticles are too great, compared to the advantages achieved in the final commercial pack. Consequently, most packaging incorporating nanoparticles is currently receiving attention at the research stage rather than in commercial applications. This great opportunity for advancement will continue to be overlooked by the commercial packaging industry until the cost of manufacture becomes more affordable.

Although the great performances of PNFPs, the industrial applications are relatively slowly setting, with few large corporations (Honeywell, Mitsubishi Gas and Chemical, Bayer, Triton Systems and Nanocor) currently acting as pioneers. In general it appears to be a reluctance to embrace this new technology due to cost and variability in the quality of some of the products and drawbacks in the production of PNFP. Pre-polymerization and post polymerization methods for preparing nanocomposites have several problems. Pre-polymerization production can disrupt the polymerization process, which is often critical and requires much developmental time and expense to achieve good yields and controllability, and post polymerization often requires time to achieve a good dispersion of the nanoparticles in the composite, in the case of improved PNFP based on clay nanoparticles.

The processing conditions optimization becomes a crucial point in the production and it can be expensive and favours low cost-competitive initiative. It is a complicated process to go from plastic pellets to a blown bottle. It requires heating and blowing that form to the shape of the bottle with expensive, very high-speed equipment, designed for the specific material. To use different material with different properties (mainly flow characteristics and crystallization/solidification rate) it is necessary equipment conversion that accepts new material through recalibration. This is certainly a big investment for converters to make.

Currently, clay particles at the nanoscale are the most common commercial application of nanoparticles and account for nearly 70% of the market volume. The industrial applications of nanoclay in multilayer film packaging include beer bottles, carbonated drinks and thermoformed containers. Nanoclays embedded in plastic bottles and nylon food films stiffen packaging and reduce gas permeability keeping oxygen-sensitive foods fresher and extend shelf life. Bayer polymers has created a low cost nanoclay composite interior coating for paperboard cartons to keep juice fresher. PET beer bottles utilizing nanoclays produced by Nanocor® are distributed by ColorMatrix. The storage time of beer in normal PET bottles is about 11 weeks and it increases to about 30 weeks, when a nanoclay barrier is used.

Example of commercial application of nanoparticles other than clay to produce improved PNFP is by the SIG Chromoplasts P that applies a silicon oxide coating layer by plasma deposition of less than 100 nm inside PET bottles. According to the company, it increases the shelf life for 12oz carbonated soft drink bottles almost threefold to more than 25 weeks. The system has also been used on beer bottles. Thin coatings (20–150 nm) can also be applied to the outer surfaces of bottles.

Active and intelligent packaging are the areas where nanotechnology is expected to have a large impact. In the case of active PNFP, few products, mainly based on the use of silver nanoparticles, as antimicrobials in food packaging have already emerged: FresherLonger™ storage containers contain silver nanoparticles in a polypropylene base material for inhibition of growth of microorganisms (NSTI 2006). Silver nanoparticles have has been also incorporated into plastic food containers by several companies such as Sharper Image® and BlueMoonGoods in the US, Quan Zhou Hu Zeng Nano Technology in China, and A-DO Global in South Korea. These companies claim that the particles provide anti-bacterial and anti-microbial properties that keep food safer, fresher, healthier and tastier.

Silver zeolites (with trade name Zeomic Sinanen Zeomic Co. Ltd.) are one of the commercial nanoparticles used in active PNFP packaging film: this material has FDA (Food and Drug Administration) approval for food contact use. Silver

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zeolites from Agion Technologies have approval for use by EFSA (European Food Safety Authority) for food packaging.

Nanocomposites such as Nanocor's Imperm or Honeyell's Aegis OX with oxygen radical scavenging ability give plastic bottle 6-month of shelf life when filled with beer. Interesting is this last application where nanocomposite film incorporating active O_2 scavengers and passive nanocomposite clay for barrier control as an example of application of both improved and active nanotechnology.

In the case of smart PNFP, time/temperature indicators (TTI's) are currently having the higher share. Several applications are proposed, but most of them have limitations in that they require multiple components (dyes, reactants, and porous layers), which can affect accuracy under some circumstances. Timestrip plc (www.timestrip.com) has developed disposable labels that measure elapsed time from minutes up to over a year in different environment (freezer, refrigerator, at normal ambient temperature and even at higher temperatures). These labels are based on porous nanomembranes through which a food grade liquid diffuses in a consistent and repeatable way.

At research level biosensors that use fluorescent dye particles attached to bacteria antibodies are very interesting. If bacteria are present in the food being tested, the nano-sized dye particles become visible. No need to send out to the lab and wait days for culturing results with these two examples of instantaneous sensors. For example, sensors have been developed that detect *Staphylococcus* enterotoxin B, *E. coli*, *Salmonella* spp., and *Listeria monocytogenes* [101]. This kind of nanosensors can also detect allergen proteins to prevent adverse reactions to foods such as peanuts, tree nuts, and gluten. The freshness indicators nanosensors to detect pathogens, spoilage, chemical contaminants, or product tampering, or to track ingredients or products through the processing chain [102] present several advantages: rapid and high-throughput detection, simplicity and cost effectiveness, reduced power requirements and easier recycling; and finally not necessity of exogenous molecules or labels. New solutions with positive indications for the future are nanosensors for tracking, tracing and brand protection. Few smart PNPF are already applied to tag products: California's Oxonica makes Nanobarcodes from nano-particles that contain silver and gold stripes varying in width, length and amount, such that billions of combinations can be created to tag individual products. The barcodes applications could be forthcoming in tracing food batches.

Intelligent PNFP can have also application in defence and security applications. Developing small sensors to detect food-borne pathogens will not just extend the reach of industrial agriculture and large-scale food processing. It can be also a national security priority. With present technologies, testing for microbial food-contamination takes 2–7 days and the sensors that have been developed to date are too big to be transported easily.

4. Concerns on environment and health safety

The foreseeable extensive use of nanotechnologies by food packaging industry, as well as by any other sector using nanotechnology is stirring up environment and health safety concerns.

4.1. Environmental impact

The widespread use of nanoparticles has as an inevitable consequence an increase in emissions to the environment, through air, groundwater and soil. In the case of release to the environment, the special properties of nanoparticles can result in undesired effects in the environment. Moreover, besides having direct toxic properties, nanomaterials due to their specific form, surface or charge may also interact with chemicals in an undesired way or bind nutrients. And this it is true also for nanoparticles used in food packaging.

Nanomaterials can enter the environment in the course of their lifecycle. How long they survive there, and in which form, i.e. how long they persist, is still matter of investigation. Boxall et al. [103] estimated environmental nanoparticles concentrations that might be expected in air, soil and water to be in the ng/l to μg/l range. Comparison with available toxicity data for lethal and sublethal effects these concentrations were significantly lower than those likely to cause biological effects, indicating a low level of risk. It is important to recognize, however, that as new particles and applications are developed, and as more information becomes available on fate and behaviour, routes of uptake and entry into the atmosphere, these predictions may change. Moreover, the nanomaterials once entered in the environment have the potential to accumulate in the environmental organisms. In accordance with the exposure routes resulting from production, processing and use, the fate of the starting products of nanoscale substances and their transformation products must be followed (life-cycle analyses, exposure scenarios) and measured in the target compartments. Several steps must be followed: identification of the nanoparticles that are persistent and accumulate in the environment through suitable measurement methods for the identification in water, soil and sediment; analysis of the behaviour of the nanomaterials after use, during disposal, land filling, incineration or reutilization; testing of ecotoxicity during the entire life. A crucial factor for the determination of a risk of exposure to nanomaterials is the stability of these nanoparticles; in particular it should therefore be examined how stable and long-lived these forms are, whether and under which conditions undergo modifications, upon entry into the environment.

In terms of the development of possible fate scenarios of the nanoparticles in the environment, knowledge is gradually becoming available. Recently some papers [104–107] stressed that the behaviour of nanoparticles in the environment depend not only on the physical and chemical character of the nanomaterial and their concentration, but also on the characteristics of the receiving environment. Given their small size nanoparticles can be widely distributed by air, where the research findings on the behaviour and impact of natural ultrafine dust or ultrafine dust formed during incineration can be partially applied.

In soil, because of their large, active surfaces, nanoparticles can bind and mobilise pollutants like heavy metals or organic substances and therefore pose a threat to ground water. Depending on receiving environment, nanomaterials, if not degraded or dissolved, will tend to aggregate and eventually settle onto the substrate.

Generally industrial products and wastes tend to end up in waterways which ultimately discharge to the sea. Upon release to water, dispersed nanomaterials are expected to behave according to the phenomena described in colloid science [101–110]. The estimation of concentrations, the surface properties of the nanomaterials and the aqueous phase physical–chemical properties are very important factors to determine how these nanomaterials might interact with organic matter and potentially be adsorbed.

In this review only the studies of the fate scenarios of nanoparticles used in food packaging (TiO_2 and silver nanoparticles and carbon nanotubes) are reported.

For these nanoparticles predictive modelling work was published [104,111]. Recently for nano-TiO_2 particles this modelling analysis was validated by experimental work: the nano-TiO_2 particles were traced in a small stream and their concentrations was found lying within the range of the modelling prediction [112,113]. Modelling approach was also used [114,115] to predict sedimentation of carbonaceous nanoparticles and their effect on pollutant mobility in groundwater. Three independent studies attempted to predict the impacts to the environment of widespread use of nanosilver. Two of them estimate that sewage treatment plants could likely handle the amount of silver introduced into the septic waste stream from certain products containing nanosilver. Sewage treatment plants can handle between 10 and 100 times the amount of nanosilver currently released or estimated to be released in the near future [111,116,117]. All three studies rely on assumptions whose validity should be revaluated as more data are obtained.

Few reports are dealing with the impact of few nanoparticles on aquatic organisms. Impacts to fish have been reviewed by Handy et al. [115] who found evidence of toxicity, whereas Zhang et al. [118] found accumulation of cadmium in the viscera and gills of fish facilitated by the presence of titanium dioxide nanoparticles [119] made comparative toxicity studies of early life stages of zebrafish and revealed a higher toxicity associated with zinc oxide in both bulk and nanoparticles form. Nano zinc oxide delayed hatching rates and survival and led to tissue ulceration in surviving hatchlings. One study of quails exposed to silver nanoparticles through drinking water showed that silver nanoparticles at the highest concentration tested (25 mg/kg) affected gastrointestinal microflora, with a significant increase in the proportion of lactic acid bacteria [120].

There is little published work to document the uptake or interaction of nanoparticles with plants, although Morelli and Scarano [121] describes the formation of nanocrystals of cadmium on phytoplankton. It was found that there was a near linear relationship between toxicity and the release of silver ions from the particles, which accumulated in the phytoplankton [122]. It has been suggested that plant tissues may act as a scaffold for aggregation of metallic nanoparticles in situ [115] and that lipophilic nanoparticles such as carbon nanotubes may be taken up by microbial communities and by root systems and may consequently accumulate in plant tissues [123].

In conclusion the knowledge of the behaviour and effects of nanoparticles in the environment and living organism is increasing almost exponentially, caused by a massive interest of the scientific community and increased funding. However, the field is by far from mature. Current predictions suggest that environmental concentrations are likely to be considerably lower than those found to cause biological effects in the laboratory and the likelihood for significant ecotoxicological damage appears to be low. The contribution of the nanoparticles used in food packaging to the total of the environmental concentration seems to be sure negligible.

Moreover, the presence of nanoparticles in the environment could be also beneficial. Several studies are now starting to appear on the use on nnanotechnology for transformation and detoxification of pollutants in the environment. The methods called nanoremediation in situ entails the application of reactive nanomaterials to enable both chemical reduction and catalysis to mitigate the pollutants of concern, with no groundwater pumped out for above-ground treatment, and no soil transported to other places for treatment and disposal [124]. It is claimed that nanoremediation could have the potential to reduce the overall costs of cleaning up large-scale contaminated sites, reduce cleanup time, eliminate the need for treatment and disposal of contaminated dredged soil, and reduce some contaminant concentrations to near zero, and it can be done in situ. Of course also in this case in order to prevent any potential adverse environmental impacts, proper evaluation, including full-scale ecosystem-wide studies, of these nanoparticles needs to be addressed before this technique is used on a mass scale.

Other interesting aspect of the impact of nanoparticles on the environment is the use of nanoparticles as 'nano-additives' for two opposite purposes: degradation and stabilization of polymers under different environmental conditions and durability under various environmental conditions. A recent paper reviews the status of worldwide research for this innovative application of nanoparticles that could be greatly exploited in the next future [125].

4.2. Impact on human health

Three different ways of entrance penetration of nanoparticles in the organism are possible: inhalation, entrance trough skin penetration and ingestion.

Growing scientific evidences report that free nanoparticles can cross cellular barriers and that exposure to some of these nanoparticles may lead to oxidative damage and inflammatory reactions [12,126–137].

In the case of nanomaterials for food packaging many people fear risk of indirect exposure due to potential migration of nanoparticles from packaging.

For food packaging nanomaterials, the inhalation and the entrance trough skin penetration is almost exclusively related to workers in the nanomaterials producing factories. For these workers personal protection is recommended with the use of gloves, glasses, masks with high efficiency particular filters.

For the final consumers of food packaged with nanomaterials the first concern is to verify the extend of migration of nanoparticles from the package into the food and then if this migration happens, the effect of the ingestion of these nanoparticles inside the body from the mouth to the final gastrointestinal tract. There is a crucial need to understand how these particles will act when they get into the body, how and if the nanoparticles are absorbed by the different organs, how they body metabolize them and how and in which way the body eliminate them.

Few studies are present in literature on the migration of nanoparticles from the package to the food [12,138,139]. Two studies analyzed the migration of clay from PET bottles and films of potato-starch and potato starch polyester blends. In both cases insignificant detectable migration of nanoclay is observed. Another study reports the migration of silver nanoparticles from food containers made of polypropylene nanosilver composites. Also in this case level of silver migration lower than the limit of quantification is detected.

Although these cases seem to give some reassurance about safety, the number of tests on migration is too limited and further investigation need to be performed before using these materials.

The presence of nanoparticles embedded in packaging film can have also positive influence on the migration from food packaging into food of chemicals that may produce potential adverse health effects. de Abreu [140] addressed the migration of caprolactam, 5-chloro-2-(2,4-dichlorophenoxy)phenol (triclosan) and trans,trans-1,4-diphenyl-1,3-butadiene (DPBD) from polyamide and polyamide-nanoclays to different types of food simulants. The presence of polymer nanoparticles was found to slow down the rate of migration of those substances from the matrix polymer into the food up to six times.

Little is known about what happens if these nanomaterials get into the body. The risk assessment of nanomaterials after ingestion has been studied only for few of the nanoparticles used in food packaging. Some results on TiO_2 [141–146], Ag nanoparticles [147] and carbon [148–153] nanoparticles/nanotubes show that nanoparticles can enter circulation from the gastro-intestinal tract. These processes are likely to depend on the physical–chemical properties of the nanoparticles, such as size, and on the physiological state of the organs of entry. The translocation fractions seem to be rather low; however, this is subject of current intense research. After the nanoparticles have reached the blood circulation, the liver and the spleen are the two major organs for distribution. Circulation time increases drastically when the nanoparticles are hydrophilic and their surface is positively charged. For certain nanoparticles all organs may be at risk as, for all organs investigated so far, either the chemical component of the nanoparticles or the nanoparticles themselves could be detected, indicating nanoparticle distribution to these organs. These organs include the brain and testis/the reproductive system. Distribution to the foetus *in utero* has also been observed. As the knowledge of the long-term behaviour of nanoparticles is very limited, a conservative estimate must assume that insoluble nanoparticles may accumulate in secondary target organs during chronic exposure with consequences not yet studied. There is a specific concern considering the possible migration of nanoparticles into the brain and unborn foetus. Research in both of these areas has to be conducted in order to either confirm or reject the hypothesis of nanoparticles association with various brain diseases. The effect of other particles used in food packaging on the health is under investigation, like ZnO nanoparticles [154] and fullerenes [155].

5. Regulation issues

As developments in nanotechnology continue to emerge, its applicability to the food industry is sure to increase. The success of these advancements will be strictly dependent on exploration of regulatory issues. A wide variety of government agencies has taken interest in nanotechnology. The latest reports of the U.S. Food and Drug Administration (FDA) of the European Food Safety Authority (EFSA) are here reviewed. The Food and Drug Administration (FDA) issued in July 2007 its Nanotechnology Task Force Report. Anticipating the potential for rapid commercialization in the field, the FDA report recommended consideration of agency guidance that would clarify what information industry needs to provide FDA about nanoproducts, and also when the use of nanoscale materials may change the regulatory status of products. In order to assist manufacturers to ensure product safety, the FDA is in the process of developing a guidance document for nanotechnology, which will become available before the end of 2010.

More information is available at http://www.nano.gov. Additional information may also be found at the National Cancer Institute website http://nano.cancer.gov.

In term of regulation issues on the assessment of the risks of nanotechnology, the European Food Safety Authority EFSA seems to be head: in fact on February 2009 it has concluded its assessment of the potential risks of nanotechnologies for food and feed, providing a scientific opinion on potential risks arising from nanoscience and nanotechnologies on food and feed safety [156]. In view of the multidisciplinary nature of this subject, the task was assigned to the European Food Safety Authority (EFSA) Scientific Committee. It is claimed that nanotechnologies offer a variety of possibilities for application in the food and feed area, in production/processing technology, to improve food contact materials, to monitor food quality and freshness, improved traceability and product security, modification of taste, texture, sensation, consistency and fat content, and for enhanced nutrient absorption. Food packaging makes up the largest share of current and short-term predicted markets. The EFSA concluded its assessment of the potential risks of nanotechnologies, stating that a cautious, case-by-case approach is needed as many uncertainties remain over its safe use. In particular current uncertainties for risk assessment and the possible applications in the food and feed area arise due to presently limited information on several aspects. Specific uncertainties apply to the difficulty to characterize, detect and measure nanoparticles in food/feed and the limited information available in relation

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to aspects of toxicokinetics and toxicology. There is limited knowledge of current usage levels and (likely) exposure from possible applications and products in the food and feed area. The risk assessment paradigm (hazard identification, hazard characterization, exposure assessment and risk characterization) is considered applicable for nanoparticles. However, risk assessment of nanoparticles in the food and feed area should consider the specific properties of the nanoparticles in addition to those common to the equivalent non-nanoforms. It is most likely that different types of nanoparticles vary as to their toxicological properties. The available data on oral exposure to specific nanoparticles and any consequent toxicity are extremely limited; the majority of the available information on toxicity of nanoparticles is from in vitro studies or in vivo studies using other routes of exposure.

A working document is currently being discussed by the European Commission and Member States; it may become a proposal for rules on substances and materials that are tricky and not dealt with elsewhere in the legislation. Until such legislation is completed and adopted, nano-materials will continue to be dealt with by a combination of general EU food law and more specific controls on particular materials.

The main EU regulatory framework related to use of food contact materials is still the Regulation (EC) 1935/2004. It states that any material intended for food contact must be suitably and inactive to avoid that the substances are transferred to products, in such quantities to harm human health or to bring about an unacceptable change in food composition or properties. This rule is for any material that may transfer its constituents into food with unbearable results and it affects also the migration of “nanocomponents” from packaging. The Regulation also applies to the use of: “active packaging” and “intelligent packaging”, it recognizes that they are not inert by design, and, therefore, addresses the main requirements for their use. So any nano-sized ingredient intended to be released would have to be evaluated as a direct food additive. The general approach is that the material ingredients, additives and more are included in positive lists of admitted ingredients. Restrictions on these substances take the form of limits of their migration into foodstuffs or limits on the composition of the materials. These rules are relevant also for nanomaterials but the safe maximum migration limits that have been determined for macro-components cannot be applied to their nano-equivalents, due to possible differences in their physic, chemical or biological properties. EU regulation describes also test procedures. It has to be already determined if the current test procedures are valid also with respect to the possible transfer of nanoparticles from materials into foods. A working document is currently being discussed by the European Commission and Member States; it may become a proposal for rules on substances and materials that are tricky and not dealt with elsewhere in the legislation. Until such legislation is completed and adopted, nano-materials will continue to be dealt with by a combination of general EU food law and more specific controls on particular materials. The current EU legislation clearly places the responsibility of products safety on the manufacturers’ shoulders; they have to carry out an adequate risk assessment based on data for migration, toxicity and intake. Also the U.S. Food and Drug Administration (FDA) currently does not specifically require nanoparticles to be proved safe but does require manufacturers to provide tests showing that the food goods employing are not harmful. Industry must bear the burden of demonstrating the safety of the material under its intended conditions of use.

6. Consumer perception

People’s emotions play an important role in people’s perception on new technologies nanotechnology, and values determine people’s reactions to information on nanotechnology. From the latest surveys it results that in Europe and USA there are different consumer perceptions for food nanotechnology [157–159].

Recent report shows that in Europe public awareness of nanotechnology is gradually emerging and that European consumers whilst are positive about the opportunities of nanothechnology in several application, they are sceptical of the use of nanoparticles in food. Different is the situation and the consumer perception in USA, 80% of the participants in a recent survey on nanotechnology had heard very little or nothing at all about nanotechnology, but they expect many advantages of nanotechnology for safer and better food. However, the 2006 National Science Foundation-funded survey in the USA of public perceptions of nanotechnology products found that US consumers are willing to use specific products containing nanoparticles even if there are health and safety risks when the potential benefits are high.

These surveys demonstrate that there is an urgent need for informed public debate on nanotechnology and food. Nanotechnology can be applied in all aspects of the food chain, both for improving food safety and quality control, and as novel food ingredients or additives, even to have positive effect on the environment which may lead to unforeseen health risks. There are also some concerns about implementation guidelines and risk assessment methods. The general public lacks awareness of nanotechnology in general, and applications of nanotechnology in food in particular. This must be addressed in public dialogue initiatives in the short term.

7. Conclusions

Application of polymer nanotechnology can provide new packaging materials with improved performances and market analysis predicts billion dollar markets for food materials produced with nanotechnology within five years. Undoubtedly these innovative packaging solutions based on nanotechnology to be of complete success must also fulfil requirements on food safety (controlling microbial growth, delaying oxidation, and improving tamper visibility), product quality (managing volatile flavours and aromas), convenience, and sustainability. There are currently several dozen food and beverage products with nanotechnology on the market and under investigations according to their producer or experts. However, without a public debate on nanotechnology in food, then acceptance of the products by the consumers, implementation of guidelines and risk assessment methods for the environment and health, it is difficult to determine how many of these products can found suitable application.

For an extensive use of nanotechnology in food packaging there are also a number of important issues to consider. The most important ones are the safety concerns due to possible migration of nanoparticles from the packaging material into food, and their eventual toxicological effects. There is limited scientific data about migration of most types of nanoparticles, but it is reasonable to assume that migration may occur: hence the need to reduce to zero this migration and to have accurate information on the effects of nanoparticles to human health following chronic exposure is imperative. It is necessary for the producers not only to assure product quality ensuring regulatory compliance but also to involve the consumer providing clear information in regard to benefits/possible risks balance.

Finally it must be reported that biodegradable bioplastics, usually made from plant-based materials, that are generally not included in this review, have become a big research focus for nanotechnology (in 2008, global output of biodegradable plastics reached around 300,000 tonnes) and need therefore full consideration as green food packaging [160–162]. Leading players include Natureworks – with a potential PLA capacity of 140,000 tonnes/y – cited as the world's largest biodegradable plastics producer, BASF, Cereplast, Novamont and Metabolix [162]. However, their barrier and mechanical properties are still inferior to fossil fuel derived polymers, which currently limits their use for some applications, and so further research will be required to improve this. However, certain biopolymers have the added functionality of being antimicrobial, thus bionanocomposites can become even more attractive as the added value is multiplied. Several papers are available on this subject and the interested reader can be found the most recent ones in the reference list [160–162].

Acknowledgements

The authors acknowledge support from the European Community's Seventh Framework Programme [FP7/2007–2013] under Grant Agreement No. 218331 NaPolyNet and Cost Action FA0904.

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