ObservatoryNANO

Nanotechnologies for food packaging

Reporting the science and technology research trends

Douglas K. R. Robinson and Mark J. Morrison

Table of Contents

Reference this report as:

Robinson D. K. R. And Morrison M. J. (2010)
Nanotechnologies for food packaging: Reporting the science and technology research trends:
Report for the ObservatoryNANO.
August 2010. www.observatorynano.eu

Contact:
douglas.robinson@nano.org.uk

Section 3: Nanotechnology in Food Packaging and Distribution

Keywords: packaging, nanoclay, nanofiber, nanocomposites, bionanocomposite, exfoliated, biopolymer, smart packaging, active packaging, sensor, RFID, self-healing, supply chain.

3.1 Definition

Food packaging and distribution for the purpose of this report is defined as materials used to package fresh and processed foods (barrier packaging), materials that interact with food or packaging internal environment (food contact materials and active packaging), mechanisms of indicating the quality of the food in a package (intelligent packaging) and the procedures and systems in place to monitor supply chains and authenticate items (RFID tags and other tagging technologies).

3.2 Short Description

Historically, packaging has been developed to protect food from heat, light, moisture, oxygen, microorganisms, insects and dirt. Food preservation, augmenting the longevity of food, has also been a key requirement. In the past few decades we have seen an increase in the required functionalities of prolonging the shelf life of foods by **controlling** microbial, enzymatic and biochemical reactions of the internal environment of food packaging via a number of strategies such as oxygen removal, controlled release of salts, carbon dioxide etc.

Other drivers alongside food protection/preservation include containment and waste reduction, convenience packaging, traceability and tamper indication. These requirements for broader functionality have provided the stimulus for a number of fields of material development:

- Advanced food contact materials (FCMs) incorporating nanomaterials to improve packaging properties such as temperature and moisture stability, flexibility, barrier properties etc.
- Active packaging (internal environment control including interacting with food contained within)
- Smart packaging (including functionalities such as trace & track and indication of authenticity)
- Biodegradable packaging materials

Nanotechnologies offer promising innovations for these broad functional requirements. In particular, nanocomposites promise enormous potential in the near-term for a number of these, and we are seeing the first products on the market. Examples of products include Imperm® for CO_2 release reduction (Nanocor® Inc), Aegis® OX a barrier nylon resin for oxygen scavenging (Honeywell) and Durethan® KU2-2601 (Bayer AG) for enhanced barrier properties. Examples of biopolymer based nanocomposites include NanoBioTer® and Degradal® (in development)[1] which incorporate nanoscale additives for controlled or accelerated compostability and biodegradability.

3.3 State of R&D

Food can be packaged using a number of different materials, the most prominent of which are: plastics, paper and cardboard, metal, and glass, and the packaging industry itself is valued at approximately 2% of Gross National Product in developed countries[2]. Plastics are virtually ubiquitous in packaging, as single material films and containers, in combination with other plastics, or as coatings for other materials (such as paper card and metals). The global consumption of plastics has increased from some 5 million tonnes in the 1950s to nearly 100 million tonnes today[3]. Of this amount, approximately 44% is used for a relatively short period and then discarded. Plastics used for packaging purposes make up a significant portion of this, and food packaging materials in turn account for approximately 50% (by weight) of total packaging sales[4].

A number of broad drivers in the packaging sector are shaping innovation in product and process development.

These drivers include decreasing material and energy usage, reducing packaging weight (termed light-weighting), increase food safety and quality (through improved performance in a variety of environmental conditions plus additional functionality), and recyclability or biodegradability (food packaging accounts for some two-thirds of total packaging waste).

These broad **packaging drivers** are linked to **broader food sector drivers**, which include the interest in decreased food wastage (by improving shelf-life and giving visual indicators as to food's freshness), and an increasing demand for convenience food.

In conjunction with an effective packaging system, improvements in identification of items and stock control can support the effective delivery of food from production to the consumer and can assist in maintaining appropriate conditions throughout the food prodcution and distribution chain (through monitoring or interacting with the food). Such support systems include RFID tags for logging the movement of stock at all stages of the supply chain, smart packaging which can give indications of various factors effecting the food quality (e.g. moisture, microbial activity, ethylene, tempterature profile[5], etc.) and other tags to provide covert or overt identification and authentication.

Nanocomposite materials offer improved functionality over traditional composites and polymers in terms of barrier properties, strength, elasticity and optical clarity. Nanocomposites can be functionalised to include other characteristics, for example, antimicrobial properties, visual indicators of food freshness, means of identification and authentication, and approaches to augment the ease of tracking.

Another, growing, demand is linked with the drive towards sustainability. Most polymer composite materials are based on fossil fuel derivatives, but research into biopolymers (sourced from wood and crop waste) is offering biodegradable alternatives. The inherent drawbacks of pure biopolymers (dependent on type include drawbacks such as poor barrier properties and poor mechanical properties) can be mitigated by the inclusion of nanotechnology to form nano-enabled biocomposites (bionanocomposites). Most nanocomposite materials employed, or being developed for use, in the food packaging industry contain nanoclay particulates, however other composites containing nanoparticles, nanotubes or nanofibres of metals, metal oxides, biopolymers[6],[7],[8] and other carbon-based materials are also being developed (outlined in more detail later in the report).[9]

.

3.3.1 Barrier Packaging

Many fresh and processed foods are packaged in an inert or low oxygen atmosphere (by purging air with nitrogen or carbon dioxide); a procedure known as modified atmosphere packaging (MAP) that can increase shelf-life four-fold, by inhibiting microbial growth and consequently food spoilage. In most circumstances the packaging material used is polymer-based, however, these have limitations. While materials such as glass and metals are completely impermeable to gases, in contrast plastics are semi-permeable; which can affect food and drink quality undesirably over relatively short periods of time (e.g. carbon dioxide escape from carbonated drinks, oxygen ingress to packaged foods resulting in faster decay, and ethylene spread between fruits resulting in faster ripening).

Plastics, however, can be made more impermeable to gases through the addition of coatings (e.g. deposition of a thin film of alumina) or through the inclusion of nanoparticulates within the polymer matrix. Nanoparticulates have a relatively large surface area than larger fillers, which favours the filler-matrix interactions and the performance of the composite.[10] Not only do nanoparticles have advantages because of this improved filler-matrix interaction, acting as nanoreinforcements, they also act as small, physical barriers to the progress of gas molecules across the polymer, and if present in sufficient numbers effectively reduce gas transport to negligible levels. They do this by complicating the path of gas as it transports through the material. Such "tortuous" paths provide a significant advantage to polymer based packaging.[11] However, to achieve this level of barrier quality requires excellent dispersion of the nanoparticulate throughout the polymer matrix. This dispersion is affected by three different chemistries: the polymer itself, the nanoscale filler, and the inter-facial materials (compatibilisers) used to help disperse the nanoscale filler evenly through the polymer. Nanomaterials added to polymers can have other properties too, such as enzyme immobilisation, antimicrobial activity, etc. These will be described in brief later in the report.

3.3.1.1 Nanoclays

Polymer–clay nanocomposites were developed at the end of 1980s,[12] and first put on the market by Toyota. In the following decade, researchers began exploring the potential of these nanocomposites for applications in food packaging with a steady growth in research activity since then.[13] Nanocomposites are mixtures of nanomaterial fillers with polymers (fossiel fueld derived or bio-based). Such nanomaterials can take the form of flakes (as with clays)[14] as fibres[15] or whiskers or nanoparticles.[16] We first will describe polymer-clay nanocomposites - the most active area of nanomaterial based food packaging with a number of products on the market.

Clays consist of multiple layers of complex metallic ores (with the major constituents being aluminium and magnesium silicates). There are a number of different types, however those of particular interest to the packaging industry are smectite, kaolonite, montmorillonite, and hectorite. Structurally they are aggregates of stacked, ultrafine layered particles (or tactoids). Each layer (or platelet) within the tactoid is of the order of 1 nm thick and a few hundreds of nm in the other two dimensions. The ratio of the platelet length to its thickness is known as its *aspect ratio*. Clays, due to their relative abundance and low cost, have been used historically as materials for building, and containers for foodstuffs. However, a **greater understanding of the nanoscale features of clays, and the ability to disperse the ultrafine layers within other materials** has led to increased interest in their application in composite materials; to provide properties to lightweight polymers that would usually only be found in heavier or more expensive materials (such as glass or metals).

The key requirement for the generation of nanoclay composites is separation of the ultrafine layers, a process known as exfoliation. Depending on the degree of separation, the resultant composite is known as phase separated or immiscible (no exfoliation of clay platelets); intercalated (partial separation of clay platelets with polymer found between them, however some association between layers remains) and exfoliated (platelets are dispersed throughout the polymer matrix). Figure 1 illustrates this process. Immiscible composites are microcomposites (or conventional composites), which may have improved mechanical properties, but provide limited improvement in the barrier properties (note the limited "tortuous path"? since in this case the microcomposite create agglomerates, the path is less tortuous than the others (see complicated path for the exfoliated example in the schematic below). In contrast to immiscible composites, intercalated[17] and exfoliated[18 19] composites are nanocomposites which exhibit properties described below. Generally speaking, the higher the degree of exfoliation, the greater the improvement in barrier and mechanical properties.

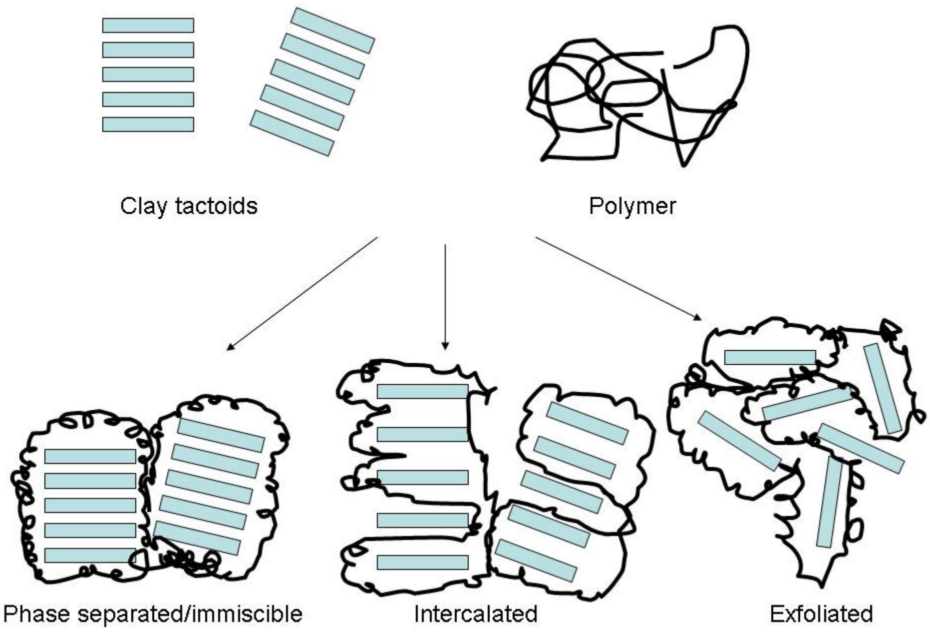

Figure 1 Creation of polymer clay composites. Without clay platelet separation a microcomposite is produced (phase separated/immiscible). Separation of the clay platelets leads to an intercalated nanocomposite, and full separation to an exfoliated nanocomposite. (Adapted from Rhim and Ng, 2007[20]).

The chemistries of the clay and polymer play a critical role in determining the degree of exfoliation. The nanoclay is usually treated with an organic compound (such as quaternary ammonium salts) which has a dual purpose. First it separates the platelets (up to two to three fold), and second it can act as a 'compatibiliser', by interacting with the non-polar regions of the polymer and favouring their intercalation between clay platelets. Both actions facilitate exfoliation, by promoting polymer entry to the space between platelets. Such clays are known as organo-clays (Cloisite®, manufactured by Southern Clay Products Inc, is an example of an organically modified montmorillonite[1]).

[1] Southern Clay Products Inc http://www.nanoclay.com/

Many different types of polymer have been used, including polypropylene, polyethylene, polyacrylamide, polycarbonate, polystyrene, and polyimide[21,22], and as will be discussed below, several natural biopolymers. However, it is polyamide-based nanoclay composites that have seen the greatest development with many now successfully commercialised (e.g. Durethan[2], Imperm[3], and Aegis[4]). Quaternary ammonium salts with different alkyl groups can be used for different polymers to assist in exfoliation, however in the case of highly organophilic polymers (such as polyethylene) additional compatabilisers such as polar monomers are added, to help stabilise the polymer platelet interaction.

Nanoclay polymer composites can be produced by a number of different methods:

- solution intercalation – the organo-clay is first swollen with solvent (e.g. water or an organic solvent) before mixing with polymer. The polymer diffuses between the nanoclay layers, displacing the solvent;
- in situ intercalative polymerisation – the organo-clay is swollen within a solution of monomer; so that polymerisation occurs between the clay layers;
- melt intercalation – (used for thermoplastic polymers) the organo-clay and polymer are mixed at a temperature above the softening point of the polymer.

Polymer clay mixes are also subjected to mechanical stress to help shear inter-platelet forces and allow the polymer to diffuse between layers. Of the above techniques, melt intercalation is favoured, as it is compatible with current industrial processes and reduces the requirement of solvent (and consequent waste). Other considerations for the production of polymer nanocomposites are the aspect ratio of the platelets (the higher this is the more difficult to exfoliate), the viscosity of the mix (higher amounts of nanoclay can improve exfoliation by increasing viscosity, but above a certain level this can lead to agglomeration and poorer composite properties)[23], and both the nature of the extruder (the device used to mix components and produce the final composite) and duration of the mixing process within it.

The degree of exfoliation and the aspect ratio of nanoplatelets within the polymer matrix correlate with altered properties of the nanocomposite compared with the pure polymer. These include:

- gas barrier properties – the nanoclay platelets act as physical barriers to the passage of gas, thus gas molecules must take a longer route through the polymer (the so-called 'tortuous path'), resulting in lower gas transmission.[242526272829] The greater the degree of exfoliation, the greater the gas barrier properties.
- liquid barrier properties – the nanoclay platelets reduce moisture ingress to the polymer, which leads to polymer swelling, and can reduce the polymer's mechanical and gas barrier properties.[3031]
- mechanical properties – the interaction between platelets and the polymer leads to increased tensile strength and elasticity. In addition, the glass transition temperature and thermal properties can be affected by the inclusion of nanoclays (e.g. improved fire resistance). These properties are dependent not only on the degree of exfoliation and concentration of nanoclay, but also the chemistries of the individual components.

Despite these benefits to the pure polymer, the addition of nanoclay in general does not significantly affect the optical clarity. In the case of some thermoset polymers, the nanoclay platelets can aid polymerisation.

While many nanocomposites are employed as free-standing packaging (such as bottles and films), they can also be applied as coatings to other materials, such as paperboard and metals. These can be for barrier purposes, or to impart greater strength. In some cases a coating can provide superhydrophobicity[32] (a property that can be exploited to minimise the amount of foodstuff retained by, or rather stuck to, the packaging).

---

[2] Bayer http://www.research.bayer.com/edition_15/15_polyamides.pdfx
[3] Nanocor http://www.nanocor.com/Cases/case_imperm.asp
[4] Honeywell http://www51.honeywell.com/sm/aegis/applications.html

There are a number of different technologies that can be used to coat other materials with nanocomposites including dip-coating, spin-coating, electrospinning, and ultrasonic spraying[21,33,34]. By using different materials in a layer-by layer assembly procedure, multiple layers can be built up, each with a variety of functionalities (e.g. gas barrier, moisture barrier, or a 'smart' property- see below).

3.3.1.2 Other materials used for nanocomposites

A number of other nanomaterials can be added on their own, or in addition to nanoclays, to polymers to provide additional barrier or functional properties for food packaging purposes. These include metal and metal oxide nanoparticles, nanofibres[35] and nanotubes[36].
Silica **nanoparticles** can be inserted into certain polymer matrices (such as polypropylene or starch) to improve mechanical or barrier properties of composites [37] [38] [39] [40]and biodegradable films. [41] Starch **nanocrystals** (platelets of a thickness of ranging between 6-9nm) have been found to improve the mechanical properties of films and inhibit there elongation.[42] [43] Other nanoparticle fillers have been explored also, for example, DuPont are marketing a titanium dioxide nanoparticulate (Light Stabilizer 210) to block UV light and provide a longer shelf-life for food (this is currently before the US regulatory authorities for use in non-contact food packaging materials); and Rohm and Haas are marketing acrylic nanoparticles (Paraloid BPM-500) to increase the strength of polylactic acid, a biodegradable polymer. Another form type of nanoparticle which is garnering a lot of interest is chitosan. In the form of **whiskers** (500nm long and 50nm in diameter) improve mechanical and barrier properties (especially water resistance).[44] [45] [46] They have also been incorporated into hydroxypropyl methylcellulose (HPMC) films and have been shown to improve mechanical and barrier properties.[47]

Nanofibres of cellulose have attracted a lot of attention due to the availability of cellulose meaning a potentially low cost, both financially and environmentally, nanocomposite..[48] [49] .[50] [51] [52] Recently a number of researchers have produced nanocomposites of a pea starch matrix with cellulose whiskers as filler (the whiskers themselves being produced from pea shell fibers) which not only had improved barrier and mechanical properties, it also displayed high transparency properties.[53] Although of less R&D activitiy than the nanocomposites filler mentioned previously, carbon nanotubes (single and multiwalled) have and are being investigated for potential food packaging nanocomposites with matrices of poly(ethylene-2,6-naphta-lene), [54] PVOH,[55] polypropylene[56] [57] and polyamide[58].

3.3.2 Antimicrobial and Antimycotic Packaging

In addition to acting as a passive barrier, packaging can contribute to the control of microbial growth in foodstuffs, [59] which can lead to spoiling or in the case of pathogenic microorganisms, disease and illness.

Most activities to combat this have centred around nanocoatings or nanocomposites using nanoparticulates of silver and zinc oxide, however there is also research into the antimicrobial effects of natural biological compounds[60] [61]. Nanomaterials are being actively researched for specific functions such as microbial growth inhibition,[62] as carriers of antibiotics[63] and as killing agents[64] [65] [66] [67] [68].

Silver nanoparticles have been incorporated into a wide variety of consumer goods including clothing, electrical goods, kitchenware, and wound dressings[69]. Nanoparticulate silver releases ions more efficiently than in the bulk form, and it is the silver ions that have a bactericidal by inhibiting a wide variety of biological processes within the bacteria[70]. As the levels of silver ions liberated are relatively low, and therefore potentially having relatively low toxic effects in humans, it is likely that nanoparticulate silver will be included in further composite materials. However, there is some concern over the effects of large amounts of silver ions being discharged into the environment and accumulating in ecosystems, as silver ions are known to be toxic to aquatic life.

Zinc oxide exhibits antibacterial activity that increases with decreasing particle size[71]. This activity does not require the presence of UV light (unlike titanium which is dioxide photocatalytic disinfecting material for surface coatings)[72 73]but is stimulated by visible light[74]. The exact mechanism(s) of action is still unknown. Zinc oxide nanoparticles have been incorporated in a number of different polymers including polypropylene[75]. In addition zinc oxide effectively absorbs UV light, without re-emitting as heat, and therefore improves the stability of polymer composites.

Titanium dioxide coated packaging film has been shown to considerably reduce E. coli contamination of food surfaces[76] and has also been shown to disinfect water from fecal coliform.[77] Combining Titanium Dioxide with Silver has been shown to improve the disinfection process though improving photocatalyis.[78]

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 nutriceuticals (see report 'Food Processing and Functional Food'). In addition, to its utility as a packaging material, it also exhibits antimicrobial properties[79]. This has led a number of groups to investigate its incorporation into different composite materials which could have applications in healthcare and food packaging, including using it as a 'green' reagent to reduce and stabilise silver ions[80], in combination with clays such as rectorite which could then be used in polymer composites[81,82].

3.3.3 Bio-based and biodegradable packaging

For many plastics recycling is made difficult as a result of the different components involved, which means that the item cannot be processed in a single step, but needs to be dismantled and component plastics separated. One way to avoid this, but to still achieve sustainability, is to use biodegradable polymers from renewable sources. These are generally proteins or carbohydrates and can be derived from animal or plant origin. Lipid films can be created also, but these tend to be used to directly coat and protect foodstuffs (and are described in the report 'Food Processing and Functional Food'). When biopolymers (such as cellulose) are mixed with nanoclay particles, the resultant nanocomposites exhibit improved barrier properties compared with the pure polymer, and after their useful life can be composted and returned to the soil[3]. Other nanomaterials can be used including metal oxide nanoparticles, and carbon nanofibres and nanotubes.

In addition to melt extrusion, many biopolymers such as cellulose, collagen and zein (derived from corn) have been synthesised as nanofibres using electrospinning equipment. In some cases these have superior properties to the traditionally cast polymer, including increased heat resistance[83,84], and in addition, mats of such nanofibres possess a highly nanoporous structure and can be used as support matrixes for additional functionality.

Other biopolymers that have been combined with nanoclays include chitosan, starch, casein, whey, and gelatine[3]. The potential applications vary from stand alone barrier films to coatings on other polymers and paper based packaging, to direct coating of foodstuffs.

Such biodegradable nanocomposites could be of great use in other agrifood application areas, such as the plastics used in agriculture (polytunnels, wrapping for feed, wrapping for hay, etc) that are either disposed of into landfill or burned by farmers (estimated to be on the order of 6.5 million tonnes[3] per annum). Instead of incineration, they could be composted and returned to the soil.

The main considerations when using natural polymers, are that they often have poor mechanical strength, and are permeable to water. As with other nanocomposites, significant research still needs to be undertaken to determine how properties can be best enhanced for specific applications through the use of different nanoparticulates such as nanowhiskers[85 86] and nanofibres[8788], plasticisers (some biopolymers, such as starch, are not thermoplastic) and melt conditions. The addition of biobased nanomaterials as reinforcements in biopolymers have also been shown to improve moisture barrier properties of films, [899091] leading to fully biobased nanocomposites.

As well as using nanomaterials for reinforcing biopolymers novel nanostructures can be used to add extra functionalities such as antimicrobial activities, biocatalyst properties using enzymes[92], quality indicators and sensors. These will be descrivbed in the following section.

3.3.4 Active and Smart Packaging

Smart packaging responds to its environment either to regulate an external effect or to produce a visual readout of a change. It includes materials that can regulate the internal environment of packaged foodstuffs to maintain food quality (e.g. through the release or absorption of substances), sensors that provide an indication of the storage history of the product and whether it is still fresh, and materials which can repair minor damage (self-heal)[93,94]. A recent report shows that the current active packaging segment is dominated by oxygen scavengers, moisture absorbers and barrier packing product, accounting for 80% of the market. With bakery and meat products having attracted most nano-enabled packaging technology to date. [95]

3.3.4.1 Regulating the internal packaging environment

The most rudimentary form of regulation is the control of the temperature of the foodstuff. Manufacturers of chilled or fresh foods want to ensure that their produce reaches the consumer in good condition, however there are inevitable breaks in the cold chain, for example due to transfer between different transport systems. If these occur in high ambient temperatures, food quality can quickly deteriorate. Ideally, it would be useful to have a protective material, which is cheap, recyclable or re-usable and does not add significantly to package weight or volume. Traditional insulating materials (such as polystyrene) are bulky and inappropriate for this use, as they would add significantly to transport costs. In contrast, nanostructured foams, which are considerably thinner than conventional materials for the same thermal properties, could be an alternative, if available at low enough cost (at present these are used more for building insulation). An alternative system based on low cost materials, has been developed by researchers in New Zealand. This system based on nanoporous calcium silicate is loaded with a phase change material (such as paraffin wax) that can mitigate the effects of an increase in external temperature over a short period of time (five hours), while having similar dimensions to bubble wrap[96].

Self-heating or cooling systems are an attractive option for consumers. Essentially the chemistry is simple. Exothermic reactions are used for self-heating (e.g. mixing water and calcium oxide) while evaporation of a refrigerant (e.g. water or carbon dioxide) is used for self-cooling. There are several examples of self-heating systems on the market, and at least one for self-cooling. It is unclear whether nanomaterials would offer significant improvements to self-heating efficiencies, however they may provide increased efficiencies for self-cooling, and there is at least one patent, based on fullerenes, for this purpose[97]. In the longer-term, completely different platforms such as combination thin-film photovoltaic and thermoelectric systems could be used (to harness solar power to drive the cooling effect of thermoelectric materials, in much the same way as solid-state coolers).

Gas scavenging or absorbing systems are also of interest for food packaging. There are several on the market using conventional technologies, such as the AGELESS system from Mistubishi Gas Chemical Co. which contains iron salts and vitamin C, and absorbs oxygen within a sealed package[5]. Research using nanostructured materials may offer enhancements by: increasing the surface area of the active component (through nanoparticles, or loading of a nanoporous material such as silica, with active material). For example, preliminary work with polymer nanocomposites containing titanium dioxide, shows that these exhibit similar oxygen scavenging properties, in the presence of UV, as conventional iron and polymer based materials[98].

[5] Mistubishi Gas Chemical Co. http://www.mgc.co.jp/eng/products/abc/ageless/index.html

Other research themes have looked at the active release of compounds, to help maintain food quality. Mostly these are based on conventional technologies to release preserving compounds such as carbon dioxide or ethanol, however the last few years has seen the development of systems based on nanomaterials. Research patented from SouthWestern Research Institute provides a means for the release of antimicrobial agents (such as chlorine dioxide) inside packaging to inhibit microbial growth. This uses nanoscale capsules which release chlorine dioxide upon exposure to moisture[99] or nanoparticles of materials such as titanium dioxide to photo-catalyse the production of such gases from inert reactants[100]. This research is now developed by the Microactive Corporation.

3.3.4.2 Enzyme immobilization systems

Enzymes are widely used by the food industry for many types of processes. Immobilised enzymes act as bioactive materials, in this case they catalyse a reaction, and are promising to provide innovative solutions to the food sector through breaking down undesired elements within a food product or catalyzing the production of useful substances beneficial for the health of the consumer. [101] [102] [103] [104]

Enzymes are very sensitive, and thus key challenges in their application include managing and maintaining appropriate processing conditions. In addition, to maximize the life time of such immobilized enzymes, they must not come into contact with compounds which will affect their activity in a negative way (pH is a particularly relevant)[105] [106] [107]

For food packaging, enzymes such as cholesterol reductase have been used and we observe increased activity in R&D for packaging applications[108] [109] [110] The advantages of nanotechnology based systems relate to the larger surface area made possible by topographic surface modifications at the nanoscale.[111]

3.3.4.3 Self-healing composites

Self-healing polymers have been the subject of intense research for over 20 years. These systems respond to stresses, fractures, tears, and punctures by mobilising polymers or monomers to repair existing bonds, or create new ones. In some case this requires input of energy (light or heat) in others it is driven solely by chemical reactions within the endogenous system, including self-catalysis by polymer components. For example, ionomers, which are polymers that contain polar and ionic side-groups, have shown the ability to re-close small punctures. One that is marketed as a self-healing polymer is based on poly(ethyleneco-methacrylic acid) (EMAA), React-A-Seal®. Although the precise mechanism is unknown, it is theorised that polymer chain movement as a result of elastic recovery, provides the kinetic energy to bring side-chains in contact and for re-establishing links with other side-chains.

Other research, particularly for thermoset polymers, has included catalysts and monomers (encapsulated by emulsions or fibres), which are released upon stress of the polymer matrix, and react to form new polymer. At the moment, this active area of research is focused on microparticles and fibres. Whether nanotechnology could offer increased efficiency, e.g. through nano-emulsions, or new application areas is unknown. Although such systems have been primarily developed for use in higher value added fields, such as structural composites for automotive and aeronautic components, this technology could have applications in food packaging.

Recent research has investigated the use of nanoparticles as the medium for repair of cracks within thermoplastic polymers. In contrast to other self-healing systems which rely on the re-formation of polymer bonds, this involves nanoparticle migration within a composite material to the site of damage, driven thermodynamically by repulsive interactions between the polymer matrix and the nanoparticle filler (the same constraints which make it difficult to evenly distribute nanoscale fillers throughout polymers in the first instance)[112,113].

3.3.4.4 Sensor technologies in packaging

Sensor technologies for packaging should provide a visible indicator to 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 use are cost, robustness, and compatibility with different packaging materials. Nanosensors to detect contamination, product tampering, for spoilage and pathogen detection are been actively developed with some already commercially available. [114]

Oxygen sensors

During food storage, aerobic microbes may proliferate if given access to oxygen. The ability to detect the presence of oxygen within packages of, for example, fresh meat, at an early stage could alert the (aware) 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 rely on changes in the colour of dyes in the presence or absence of oxygen. A key challenge is to develop such sensors/indicators which are non-toxic and irreversible[115] (if there is oxygen present (even briefly) in the lifetime of a packaged food, it is important to maintain the record and not have the indicator return to signalling "safe" when oxygen is removed).

One commercialised, microtechnology product is 'Ageless Eye'[6] which is pink in the absence of oxygen and blue in its presence. Advances using nanoparticles are expected to produce more sensitive systems that respond faster and produce stronger colour changes. For example, researchers at the University of Strathclyde have produced a hydroxyethyl cellulose polymer film oxygen sensor, containing titanium dioxide nanoparticles and the blue dye, indigo-tetrasulphonate. Following incorporation in the packaging, the sensor is exposed to UV light, the dye is photobleached (a reaction catalysed by the titanium dioxide) [116] and remains so until exposed to atmospheric oxygen levels, when it rapidly (within three minutes) returns to a deep blue colour (even in the dark)[117]. Recently nanocrystalline SnO2 has been used as an O2 indicator combining glycerol with a redox dye and hydroxyethyl cellulose. This system is photoactivated through exposure to UVB light and remains bleached until exposed to O2, whereupon it turns blue. [118]

Stress and temperature sensors

While there is much research in the area of self-healing polymers, as described above, it is unlikely in the near future to be used in food-packaging. Packaging would therefore benefit from the presence of materials which would indicate that barrier properties have been compromised, through heat or mechanical stress. In some cases this can be achieved using oxygen sensor technologies, which indirectly indicate a break in the packaging.

New research using a variety of different nanomaterials may offer colour-assisted solutions. For example, photonic crystals have been shown to change colour dependent on structure, a property which can be exploited for strain sensors. Such structures have been successfully synthesised in flexible polymer composites by researchers at Southampton and Darmstadt Universities[119]. Other alternatives include diacetylenes, which have been shown to change colour in response to mechanical stress or temperature changes, a phenomenon which can be stabilised and enhanced through the nanostructuring of the polymers, for example by enclosing in a nanoporous silica support[120] or as nanocrystals of urethane-substituted polydiacetylenes[121].

[6] Mistubishi Gas Chemical Co. http://www.mgc.co.jp/eng/products/abc/ageless/eye.html

Time temperature indicators (TTI's) allow suppliers to confirm that processed foods requiring refrigeration have been kept at the appropriate temperatures throughout the supply chain. 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, the rate of which is temperature dependent. These have limitations in that they require multiple components (dyes, reactants, porous layers), which can affect accuracy under some circumstances, and so a single component system would be an improvement. Timestrip plc has developed a colloidal gold based system (iStrip)[122] which is red in colour at temperatures above freezing. Freezing leads to the irreversible agglomeration of the gold nanoparticles resulting in a clear solution, a useful indicator to detect the accidental freezing of chilled goods.

Biosensors

A great many platforms are being developed for the detection of biomolecules and microbes that are based on nanotechnology (see report on 'Agricultural Production'), however most of these are incorporated within devices, and require the extraction of a sample to determine the presence of the target molecule. When considering such systems for food packaging, these are focused on detecting microbial growth. The challenge for such systems is that they must be capable of being integrated within the packaging, provide an easily distinguished response (most likely a colour change), and be cheap to manufacture. It is most likely that the presence of microbial contamination will be detected indirectly by measuring changes in gas composition within the package as a result of microbial growth, using gas sensor technologies described above.

Alternatively, systems based on caged biomolecules (e.g. fullerenes, liposomes, or nanoporous silica) that are linked to a colourimetric dye, could be developed for this purpose, as they provide stability for the detector molecule, could be incorporated in a permeable membrane within the main package, and do not require additional factors (e.g. pre-processing, power). One example of this comes from research at Tufts University where the potential of nanostructured silk as a platform for biosensors has been shown. The silk fibrils can be shaped into 'lenses' and modified with various biomolecules, which when bound to targets (such as microbial proteins) alter the shape of the silk lens resulting in a colour change. As the silk is biodegradable and edible, such sensors could be incorporated within packaging[123,124].

Biosensors such as conducting polymers can also be used by detecting the gases released during microbe metabolism.. [125] [126] [127] [128] The sensors are formed through inserting concucting nanoparticles into an insulating matrix, where the change in resistance correlates to the amount of gas released. Such sensors have been developed for detecting food borne pathogens through quantification of bacterial cultures. [129] At the beginning of the last decade, such sensors coupled with a neural network was demonstrated to provide a means of evaluating chicken freshness. [130]

3.3.4.4 RFID tags and tracking

Radio Frequency Identification (RFID) tags have been in use for a number of years now, but manly utilised for high value items such as clothing and electronics. They typically consist of two modules, one responsible for processing and information storage, the second (an antenna) responsible for transmitting and receiving information. A second device, the reader, is used to obtain information from the tag, and depending on the radio frequency used, this can be at distance of several tens of metres. RFID tags for the packaging industry are passive, they have no associated power source, and gain energy to transmit information from the incoming radio waves from the reader.

Their value is that multiple items can be monitored at every stage in the supply chain without the need for line of sight; therefore potentially increasing the speed and efficiency of distribution. This is a critical factor in modern supply chains where large amounts of raw materials may be coming from different global regions to be processed in one site, then distributed to consumers (in many different global regions). It is widely envisioned that RFID tags are expected to replace barcodes[131].

RFID tags at present are largely based on silicon semiconductor technologies, however recent research could change this, allowing cheaper and easier production on a number of different materials. Printable electronics (using conducting polymers, such as pentacene and oligothiophene, and metallic inks, including copper, silver and gold nanoparticles) are being developed by a number of institutes and companies around the globe[131,132]. While at present most are based on desktop ink-jet printing, other forms more suited to high production levels (as already used in the printing industry) could be developed. In addition to printed systems, some research groups are exploring the use of carbon nanotubes as antenna[133,134]. However, this technology is not as highly developed as conductive inks based on metal nanoparticles. Interestingly, there is some research into combining RFID tags with chemical sensing functions. One group has produced a prototype for ethylene sensing (for fruit ripeness)[135], while another has demonstrated the potential of this technology by constructing a moisture sensor[136]. While these are both microelectronic systems, the potential for nanotechnology to enhance such systems is clear.

Many different systems are being developed including nanoscale bar-codes, quantum dots, and magnetic nanoparticles, however whether these are likely to be used widely within food packaging is unclear, and will be dependent on cost per unit and ease of use. It is more likely that RFID tags will serve a dual purpose of tracking and authenticating items. For a full description of anti-counterfeit and authentication technologies please see the security sector report 'Anti-counterfeiting, Authentication, and Positioning').

3.4 Additional Demand for Research

The underlying drivers in all packaging areas are reducing costs, while increasing sustainability and functionality. Polymer nanocomposites represent an exciting field with applications in a number of different areas. However, there is still much to be learned regarding the parameters which affect the final structure and properties of the composite, and how to regulate these through processing conditions and chemistries of the polymer, nano-filler and additional materials such as plasticisers and compatibilisers. The drive towards greener and sustainable manufacturing means that biopolymers will be increasingly used. These have the advantage that in theory recycling is no longer necessary (and with that the difficulties that arise separating the mix of polymers usually present in one package)- such biopolymer nanocomposites can be composted - however if bionanocomposites are to become a major element in food packaging, composting and waste management is an issue to be dealt with (and should be considered in advance). Currently, biopolymer barrier and mechanical properties are still inferior to fossil fuel derived polymers, which currently limits their use for some applications, however recent work on bionanocomposites and bio-based nanofibres show great promise and the potential to compete with fossil-fuel based composites w.r.t. mechanical and barrier properties. In addition, a number of bionanocomposites have additional functionalities, such as antimicrobial characteristics which make the nascent technology of bionanocomposite a very attractive option.

Active packaging is an area where nanotechnology is expected to have a large impact. RFID tags, temperature and gas sensors based on nanomaterials are in development and in some cases these have already been commercialised. Self-healing composites are unlikely to appear in food packaging materials in the foreseeable future due to the large cost, and the fact that such materials would need to be approved for food contact use or GRAS (generally accepted as safe). Biosensor technologies will need considerable development before they are robust enough to be included in food packaging material.

3.5 Applications and Perspectives

A number of companies already use polymer nanocomposite materials in their products (such as Miller and Hite). Compostable nanocomposites are also beginning to appear on the market, for example Innovia films has developed and patented a compostable nanoparticle coated packaging for foodstuffs with effective gas barrier properties, which uses nanoparticles of starch and a matrix of synthetic polymers[137]; the acrylic nanoparticle, Paraloid BPM-500, used by Rohm and Haas in its biopolymer, polylactic acid (PLA), allows wider applications of PLA. Other examples are NanoBioTer® from Nanobiomatters. In addition the following nanoclay-polyner nanocomposite[138] barrier products have been reported to be commercially available[139]: (NycoNano™ (NYCOA, USA), Nanoblend™ (PolyOne, USA), Nanomide™ (Nanopolymer Composites Corporation, Taiwan), Systemer (Showa Denko, Japan), Ecobesta® (Ube Industries Ltd., Japan).

Other barrier properties are important. Companies such as Nanograde GmbH market polymer composites containing nanoparticles of silver and calcium phosphate that demonstrate microbicidal activity. Other companies reported to include nanoparticles in food container products include Sharper Image®, US; A-DO Global, China; BlueMoonGoods, US; Everin, UK; JR Nanotech Plc., UK). [140] UV absorbers such as nanoparticulate zinc oxide, are likely to be used in materials other than polymer composites. According to John Parkes, director of quality at Rockware Glass, in *'15 or 20 years' time, all clear glass could be produced with a generic UV-blocking agent.'*[141]

Scavenging systems are also likely to benefit from nanotechnology. Multisorb Technologies Inc has patented technology using oxidisable sub-micron particles for use as oxygen scavengers in packaging[142].

With regards to printable electronics and RFID tags there are several companies developing and marketing these technologies. Companies such as Cima NanoTech and Novacentrix manufacture copper and silver nanoparticle based inks. These can be formulated in aqueous or organic suspensions and printed onto a variety of substrates. Other active players include Du Pont, HP, Samsung, and Hitachi.

There are, however, a number of non-technical issues to consider. These include regulatory and safety issues for materials used in food contact environments, and ethical issues arising from the use of RFID tags to track products, which in turn could contribute to tracking or storing information on consumers[143].

3.6 Current Situation within the EU

Several EU projects have been funded to look at packaging. For example, the SustainPack project (funded under FP6) looked at a number of drivers and market pulls for the fibre-based packaging industry, in particular sustainability and the impact that nanotechnology could have[144]; the GoodFood project (funded under FP6) looked at sensor technologies for food safety and quality assurance at different stages of the food production and supply chain[145]; Natural Antimicrobials for Innovative Safe Packaging (NAFISPACK) is an FP7 funded project that will look at antimicrobials in packaging and the risk of their migration into food[146].

As far as sustainability is concerned there is a long way to go. A study published by UK-based market analysts Applied Market Information (AMI) in early 2008, claims that the market for bioplastics remains small, this is compounded by the fact that there appears to be inadequate facilities for recycling or composting. According to AMI, "Less than one per cent of global polymers are currently classified as compostable bioplastics according to the European EN 13432 standard."[147]

- **BIOSURF** explores amino-functionalised norbornene polymers in order to be further implemented as biocide antimicrobial and anti-deposit surfaces also used in food packaging. All surfaces in contact with food would then be free of potentially hazardous microorganisms.

- Multifunctional nanomaterials for intelligent food packaging applications form a principle subject of a project titled **NANOPACK**.
- **FRESHFILM** develops an innovative recycling food packaging material for meat mainly and also for vegetables, salads and pasta, with oxygen scavenger properties to enable a slowing of the oxidization process within the food being stored by creating an oxygen poor atmosphere and effectively acting as an anti-oxidant.
- **FLEXSMELL** aims to realize a hybrid (organic-inorganic) very low-cost, ultra low-power olfaction system based on bio-receptor and implemented on a flexible substrate for wireless applications.
- The main objective of **BADANA** project is to design a process which enables to extract high-quality natural fibre from banana plant waste and to exploit the fibres properties in making polymer composites. These sustainable moulded composite products will be used in the automotive, packaging, and consumer goods industries.
- The project **SAFETECHNOPACK** aims to improve the research capacity in chemical contamination from the food contact materials, and to make a new food packaging materials using nanotechnology and active antimicrobial packaging technologies.
- The main objective of **NAFISPACK** project is to develop novel packaging technologies that will detect and avoid or reduce the growth of pathogens and spoilage microorganism responsible for product lost in perishable food products of interest.

References

[1] www.nanobiomatters.com

[2] Robertson G.L. (2006) Food Packaging: Principles and Practice, Second Edition (2006). Gordon L. Robertson

[3] Zhao R. X., Torley, P. & Halley, P. J. (2008) Emerging biodegradable materials: starch- and protein-based bio-nanocomposites. Journal of Materials Science, 43, 3058-3071

[4] Marsh K. & Bugusu B. (2007) Food Packaging—Roles, Materials, and Environmental Issues. Journal of Food Science, 72, R39-R55.

[5] Such temperature indicators are of great interest in food manufacturing and packaging firms, especially in the frozen food industry, where temperature shifts effect the shelf life dramatically. Therefore a way of profiling the temperature changes of the packaged food would allow for more effective judgement of the quality of the food within the package. A first order vision that we have seen in industry meetings includes an adaptable best before date linked with such indicators. Other approaches that are being investigated have a symbol or traffic light system which allows rapid quality assessment along the food supply chain.

[6] Kriegel C., Arrechi A., Kit K., McClements D. J. and Weiss J. (2008) Fabrication, functionalization, and application of electrospun biopolymer nanofibers. Critical Reviews in Food Science and Nutrition, 48:775–797

[7] Torres-Giner S., Ocio M. J. and Lagaron J. M. (2008) Development of Active Antimicrobial Fiber-Based Chitosan Polysaccharide Nanostructures using Electrospinning. Engineering in Life Sciences Volume 8 Issue 3, Pages 303 - 314

[8] Matthews J. A., Wnek G. E., Simpson D. G. And Bowlin G. L. (2002) Electrospinning of Collagen Nanofibers. Biomacromolecules, 3, 232-238

[9] An additional point is that virtually all polymers used in food packaging are thermoplastic, rather than thermoset. As such they can be melted after use and re-moulded into another product. Issues arise, however, when different polymers are included in one product, requiring mechanical separation before re-use - an opportunity for innovative R&D?

[10] de Azeredo H.M.C. (2009) Nanocomposites for food packaging applications. Food Research International 42 (2009) 1240–1253

[11] Rhim J. W. & Ng P. K. W. (2007) Natural biopolymer-based nanocomposite films for packaging applications. Critical Reviews in Food Science and Nutrition, 47, 411-433

[12] Collister J. (2002) Commercialisation of polymer nanocomposites. In R. Krishnamoorti & R. A. Vaia (Eds.), Polymer nanocomposites: Synthesis, characterisation and modelling. Washington: American Chemical Society.

[13] Ray S., Easteal A., Quek S. Y. & Chen, X. D. (2006). The potential use of polymer–clay nanocomposites in food packaging. International Journal of Food Engineering, 2(4).

[14] Alexandre, M., & Dubois, P. (2000) Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Materials Science and Engineering, 28, 1–63.

[15] Torres-Giner S., Ocio M. J. and Lagaron J. M. (2008) Development of Active Antimicrobial Fiber-Based Chitosan Polysaccharide Nanostructures using Electrospinning. Engineering in Life Sciences Volume 8 Issue 3, Pages 303 - 314

[16] Wu C. L., Zhang M. Q., Rong M. Z. & Friedrick K. (2002) Tensile performance improvement of low nanoparticles filled-polypropylene composites. Composites Science and Technology, 62, 1327–1340

[17] Ludueña L. N., Alvarez V. A., & Vasquez A. (2007) Processing and microstructure of PCL/clay nanocomposites. Materials Science and Engineering: A, 121–129

[18] Adame D. & Beall G. W. (2009) Direct measurement of the constrained polymer region in polyamide/clay nanocomposites and the implications for gas diffusion. Applied Clay Science, 42, 545–552.

[19] Alexandre B., Langevin D., Médéric P., Aubry T., Couderc H., Nguyen Q. T.(2009) Water barrier properties of polyamide 12/montmorillonite nanocomposite membranes: structure and volume fraction effects. Journal of Membrane Science, 328(1–2), 186–204.

[20] Rhim J. W. & Ng P. K. W. (2007) Natural biopolymer-based nanocomposite films for packaging applications. Critical Reviews in Food Science and Nutrition, 47, 411-433

[21] Paul, D.R. & Robeson L.M. (2008) Polymer nanotechnology: Nanocomposites. Polymer, 49, 3187-3204.

[22] De Abreu D. A. P., Losada P. P., Angulo I. & Cruz J. M. (2007) Development of new polyolefin films with nanoclays for application in food packaging. European Polymer Journal, 43, 2229-2243

[23] Sun L., Boo W-J., Clearfield A., Sue H-J. & Pham H.Q. (2008) Barrier properties of model epoxy nanocomposites. Journal of Membrane Science, 318, 129–136

[24] Mangiacapra P., Gorrasi G., Sorrentino A., & Vittoria V. (2006). Biodegradable nanocomposites obtained by ball milling of pectin and montmorillonites. Carbohydrate Polymers, 64, 516–523

[25] Lotti C., Isaac C. S., Branciforti M. C., Alves R. M. V., Liberman S., & Bretas R. E. S. (2008). Rheological, mechanical and transport properties of blown films of high density polyethylene nanocomposites. European Polymer Journal, 44, 1346–1357

[26] Koh H. C., Park J. S., Jeong M. A., Hwang H. Y., Hong Y. T., Ha S. Y.. (2008) Preparation and gas permeation properties of biodegradable polymer/layered silicate nanocomposite membranes. Desalination, 233, 201–209

[27] Cava D., Giménez E., Gavara R., & Lagaron J. M. (2006) Comparative performance and barrier properties of biodegradable thermoplastics and nanobiocomposites versus PET for food packaging applications. Journal of Plastic Film and Sheeting, 22, 265–274

[28] Cabedo L., Giménez E., Lagaron J. M., Gavara R. & Saura J. J. (2004). Development of EVOH–kaolinite nanocomposites. Polymer, 45(15), 5233–5238

[29] Bharadwaj R. K., Mehrabi A. R., Hamilton C., Trujillo C., Murga, M. Fan R., Chavira A. (2002) Structure-property relationships in cross-linked polyester-clay nanocomposites. Polymer, 43(13), 3699–3705

[30] Jawahar P. & Balasubramanian M. (2006). Preparation and properties of polyester-based nanocomposite gel coat system. Journal of Nanomaterials, 4

[31] Bharadwaj R. K. (2001) Modeling the barrier properties of polymer-layered silicate nanocomposites. Macromolecules, 34, 9189–9192

[32] Jaber J. A. & Schlenoff J. B. (2006) Recent developments in the properties and applications of polyelectrolyte multilayers. Current Opinion in Colloid & Interface Science, 11, 324-329

[33] Jang W. S., Rawson I. & Grunlan J. C. (2008) Layer-by-layer assembly of thin film oxygen barrier. Thin Solid Films, 516, 4819-4825

[34] Ultrasonic Spray technology, Sono-Tek Corp, http://www.sono-tek.com/nanotechnology/SubCategory/1

[35] Torres-Giner S., Ocio M. J. and Lagaron J. M. (2008) Development of Active Antimicrobial Fiber-Based Chitosan Polysaccharide Nanostructures using Electrospinning. Engineering in Life Sciences Volume 8 Issue 3, Pages 303 - 314

[36] Liu Y-L,Chen W-H. and Chang Y. (2009) Preparation and properties of chitosan/carbon nanotube nanocomposites using poly(styrene sulfonic acid)-modified CNTs. Carbohydrate Polymers Volume 76, Issue 2, 17 March 2009, Pages 232-238

[37] Xiong H. G., Tang S. W., Tang H. L. and Zou P. (2008) The structure and properties of a starch-based biodegradable film. Carbohydrate Polymers, 71, 263–268

[38] Vladimiriov V., Betchev C., Vassiliou A., Papageorgiou G. & Bikiaris D. (2006) Dynamic mechanical and morphological studies of isotactic polypropylene/fumed silica nanocomposites with enhanced gas barrier properties. Composites Science and Technology, 66, 2935–2944

[39] Wu C. L., Zhang M. Q., Rong M. Z. & Friedrick K. (2002) Tensile performance improvement of low nanoparticles filled-polypropylene composites. Composites Science and Technology, 62, 1327–1340

[40] Jia X., Li Y., Cheng Q., Zhang S. & Zhang B. (2007) Preparation and properties of poly(vinyl alcohol)/silica nanocomposites derived from copolymerization of vinyl silica nanoparticles and vinyl acetate. European Polymer Journal, 43, 1123–1131

[41] Tang S., Zou P., Xiong H., & Tang H. (2008) Effect of nano-SiO2 on the performance of starch/polyvinyl alcohol blend films. Carbohydrate Polymers, 72, 521–526

[42] Kristo E. & Biliaderis C. G. (2007) Physical properites of starch nanocrystal-reinforced pullulan films. Carbohydrate Polymers, 68, 146–158

[43] Chen Y., Cao X., Chang P. R. & Huneault M. A. (2008) Comparative study on the films of poly(vinyl alcohol)/pea starch nanocrystals and poly(vinyl alcohol)/native pea starch. Carbohydrate Polymers, 73, 8–17

[44] Lu Y., Weng L. & Zhang L. (2004) Morphology and properties of soy protein isolate thermoplastics reinforced with chitin whiskers. Biomacromolecules, 5, 1046–1051

[45] Sriupayo J., Supaphol P., Blackwell J. & Rujiravanit R. (2005) Preparation and characterization of a-chitin whisker-reinforced chitosan nanocomposite films with or without heat treatment. Carbohydrate Polymers, 62, 130–136

[46] López-León T., Carvalho E. L. S., Seijo B., Ortega-Vinuesa J. L. & Bastos-González D. (2005) Physicochemical characterization of chitosan nanoparticles: electrokinetic and stability behavior. Journal of Colloid Interface Science, 283, 344–351

[47] De Moura M. R., Aouada F. A., Avena-Bustillos R. J., McHugh T. H., Krochta J. M. & Mattoso L. H. C. (2009) Improved barrier and mechanical properties of novel hydroxypropyl methylcellulose edible films with chitosan/tripolyphosphate nanoparticlses. Journal of Food Engineering, 92, 448–453

[48] Podsiadlo P., Choi S. Y., Shim B., Lee J., Cuddihy M. & Kotov N. A. (2005) Molecularly engineered nanocomposites: layer-by-layer assembly of cellulose nanocrystals. Biomacromolecules, 6, 2914–2918.

[49] Helbert W., Cavaillé C. Y. & Dufresne A. (1996) Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part I: processing and mechanical behaviour. Polymer Composites, 17(4), 604–611

[50] Azizi Samir M. A. S., Alloin F. & Dufresne A. (2005) Review of recent research into cellulosic whiskers, their properties and their application in nanocomposites field. Biomacromolecules, 6, 612–626

[51] Hubbe M. A., Rojas O. J., Lucia L. A. & Sain M. (2008) Cellulosic nanocomposites: a review. Bioresources, 3(3), 929–980

[52] Dubief D., Samain, E. & Dufresne A. (1999) Polysaccharide microcrystals reinforced amorphous poly(b-hydroxyoctanoate) nanocomposite materials. Macromolecules, 32(18), 5765–5771

[53] Chen Y., Liu C., Chang P. R., Cao X. & Anderson D. P. (2009). Bionanocomposites based on pea starch and cellulose nanowhiskers hydrolyzed from pea hull fibre: effect of hydrolysis time. Carbohydrate Polymers, 76(4), 607–615

[54] Kim J. Y., Han S. & Hong S. (2008) Effect of modified carbon nanotube on the properties of aromatic polyester nanocomposites. Polymer, 49, 3335–3345

[55] Bin Y., Mine M., Koganemaru A., Jiang X. & Matsuo M. (2006) Morphology and mechanical and electrical properties of oriented PVA–VGCF and PVA–MWNT composites. Polymer, 47, 1308–1317

[56] Prashantha K., Soulestin J., Lacrampe M. F., Krawczak P., Dupin G. & Claes M. (2010) Masterbatch-based multi-walled carbon nanotube filled polypropylene nanocomposites: assessment of rheological and mechanical properties. Composites Science and Technology 2010

[57] López Manchado M. A., Valentini L., Biagotti J., & Kenny J. M. (2005) Thermal and mechanical properties of single-walled carbon nanotubes-polypropylene composites prepared by melt processing. Carbon, 43, 1499–1505

[58] Zeng H., Gao C., Wang Y., Watts P. C. P., Kong H., Cui, X. (2006) In situ polymerization approach to multiwalled carbon nanotubes-reinforced nylon 1010 composites: mechanical properties and crystallization behavior. Polymer, 47, 113–122

[59] Rhim J. W. & Ng P. K. W. (2007) Natural biopolymer-based nanocomposite films for packaging applications. Critical Reviews in Food Science and Nutrition, 47(4), 411–433

[60] Cha D. S. & Chinnan M. S. (2004) Biopolymer-based antimicrobial packaging: A review. Critical Reviews in Food Science and Nutrition, 44, 223-237.

[61] Luo P. G. & Stutzenberger F. J. (2008) Nanotechnology in the detection and control of microorganisms. In A. I. Laskin, S. Sariaslani, & G. M. Gadd (Eds.). Advances in Applied Microbiology (Vol. 63, pp. 145–181). London: Elsevier.

[62] Cioffi N., Torsi L., Ditaranto N., Tantillo G., Ghibelli L., Sabbatini L. (2005) Copper nanoparticle/polymer composites with antifungal and bacteriostatic properties. Chemistry of Materials, 17, 5255–5262

[63] Gu H. W., Ho P. L., Tong E., Wang L. & Xu B. (2003) Presenting vancomycin on nanoparticles to enhance antimicrobial activities. Nano Letters, 3, 1261–1263

[64] Huang L., Li D. Q., Lin Y. J., Wei M., Evans D. G. & Duan X. (2005) Controllable preparation of nano-MgO and investigation of its bactericidal properties. Journal of Inorganic Biochemistry, 99, 986–993

[65] Stoimenov P., Klinger R. L., Marchin G. L. & Klabunde K. J. (2002) Metal oxide nanoparticles as bactericidal agents. Langmuir, 18, 6679–6686

[66] Qi L. F., Xu Z. R., Jiang X., Hu C. & Zou X. (2004) Preparation and antibacterial activity of chitosan nanoparticles. Carbohydrate Research, 339, 2693–2700

[67] Lin Y. J., Li D. Q., Wang G., Huang L. & Duan X. (2005) Preparation and bactericidal property of MgO nanoparticles on c-Al2O3. Journal of Materials Science: Materials in Medicine, 16, 53–56

[68] Kumar R. & Münstedt H. (2005) Silver ion release from antimicrobial polyamide/ silver composites. Biomaterials, 26, 2081–2088

[69] see the Project on Emerging Nanotechnology, Consumer Product Inventory http://www.nanotechproject.org/inventories/consumer/

[70] Sondi I. & Salopek-Sondi B. (2004) Silver nanoparticles as antimicrobial agent: a case study on E-coli as a model for Gram-negative bacteria. Journal of Colloid and Interface Science, 275, 177-182

[71] Yammamoto O. (2001) Influence of particle size on the antibacterial activity of zinc oxide. International Journal of Inorganic Materials, 3, 643-646

[72] Robertson, J. M. C., Robertson, P. K. J., & Lawton, L. A. (2005) A comparison of the effectiveness of TiO2 photocatalysis and UVA photolysis for the destruction of three pathogenic micro-organisms. Journal of Photochemistry and Photobiology A: Chemistry, 175(1), 51-56.

[73] Kim, B., Kim, D., Cho, D., & Cho, S. (2003) Bactericidal effect of TiO2 photocatalyst on selected food-borne pathogenic bacteria. Chemosphere, 52(1), 277–281

[74] Jones N., Ray B., Ranjit K.T. and Manna A.C. (2008) Antibacterial activity of ZnO nanoparticle suspensions on a broad spectrum of microorganisms. FEMS Microbiology Letters, 279, 71-76

[75] Chandramouleeswaran S., Mhaske S. T., Kathe A. A., Varadarajan P. V., Prasad V. and Vigneshwaran N. (2007) Functional behaviour of polypropylene/ZnO-soluble starch nanocomposites. Nanotechnology, 18, 8

[76] Chawengkijwanich C. & Hayata Y. (2008) Development of TiO2 powder-coated food packaging film and its ability to inactivate Escherichia coli in vitro and in actual tests. International Journal of Food Microbiology, 123(3), 288–292

[77] Gelover S., Gómez L. A., Reyes K. & Leal M. T. (2006) A practical demonstration ofwater disinfection using TiO2 films and sunlight. Water Research, 40, 3274–3280

[78] Page K., Palgrave R. G., Parkin I. P., Wilson M., Savin S. L. P. & Chadwick, A. V. (2007) Titania and silver–titania composite films on glass-potent antimicrobial coatings. Journal of Materials Chemistry, 17(1), 95–104

[79] Qi L. F., Xu Z. R., Jiang X., Hu C. & Zou X. (2004) Preparation and antibacterial activity of chitosan nanoparticles. Carbohydrate Research, 339, 2693–2700

[80] Sanpui P., Murugadoss A., Prasad P. V. D., Ghosh S. S. and Chatteopadhyay A. (2008) The antibacterial properties of a novel chitosan-Ag-nanoparticle composite. International Journal of Food Microbiology, 124, 142-146

[81] Wang X. Y., Du Y. M., Yang H. H., Wang X. H., Shi X. W. and Hu Y. (2006b) Preparation, characterization and antimicrobial activity of chitosan/layered silicate nanocomposites. Polymer, 47, 6738-6744

[82] Wang X. Y., Du Y. M., Luo J. W., Lin B. F. and Kennedy J. F. (2007c) Chitosan/organic rectorite nanocomposite films: Structure, characteristic and drug delivery behaviour. Carbohydrate Polymers, 69, 41-49

[83] Huang Z. M., ZHANG, Y. Z., KOTAKI, M. & RAMAKRISHNA, S. (2003) A review on polymer nanofibers by electrospinning and their applications in nanocomposites. Composites Science and Technology, 63, 2223-2253.

[84] Torres-Giner S., Ocio M. J. and Lagaron J. M. (2008) Development of Active Antimicrobial Fiber-Based Chitosan Polysaccharide Nanostructures using Electrospinning. Engineering in Life Sciences Volume 8 Issue 3, Pages 303 - 314

[85] Lima M. M. D. & Borsali R. (2004) Rodlike cellulose microcrystals: structure, properties, and applications. Macromolecular Rapid Communications, 25(7), 771–787

[86] Anglès M. N. & Dufresne A. (2001) Plasticized starch/tunicin whiskers nanocomposite materials. 2. Mechanical behavior. Macromolecules, 34, 2921–2931

[87] Alexandre M. & Dubois P. (2000) Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Materials Science and Engineering, 28, 1–63

[88] Alemdar A. & Sain M. (2008) Biocomposites from wheat straw nanofibers: morphology, thermal and mechanical properties. Composites Science and Technology, 68, 557–565

[89] Sanchez-Garcia M. D., Gimenez E. & Lagaron J. M. (2008) Morphology and barrier properties of solvent cast composites of thermoplastic biopolymers and purified cellulose fibers. Carbohydrate Polymers, 71, 235–244

[90] Paralikar S. A., Simonsen J. & Lombardi J. (2008) Poly(vinyl alcohol)/cellulose nanocrystal barrier membranes. Journal of Membrane Science, 320(1–2), 248–258

[91] Svagan, A. J., Hedenqvist, M. S., & Berglund, L. (2009). Reduced water vapour sorption in cellulose nanocomposites with starch matrix. Composites Science and Technology, 69(3–4), 500–506.

[92] Avelina Fernandez, Sergio Torres-Giner, Jose Maria Lagaron (2009) Novel route to stabilization of bioactive antioxidants by encapsulation in electrospun fibers of zein prolamine. Food Hydrocolloids 23 (2009) 1427–1432

[93] Yam K. L., Takhistov P. T. and Miltz J. (2005) Intelligent packaging: Concepts and applications. Journal of Food Science, 70, R1-R10

[94] Brody A. L., Bugusu B., Han J. H., Sand C. K. and McHugh T. H. (2008) Innovative food packaging solutions. Journal of Food Science, 73, R107-R116

[95] iRAP Inc (2009) Nano-Enabled Packaging for the Food and Beverage Industry – A Global Technology, Industry and Market Analysis, iRAP Inc

[96] Johnston J. H., Grindrod J. E., Dodds M. and Schimischek K. (2007) Composite nano-structured calcium silicate phase change materials for thermal buffering in food packaging. 3rd International Conference on Advanced Materials and Nanotechnology. Wellington, NEW ZEALAND, Elsevier Science Bv.

[97] World patent number 0073718: Self-cooling beverage and food container using fullerene nanotubes

[98] Mills A., Doyle G., Peiro A. M. and Durrant J. (2006) Demonstration of a novel, flexible, photocatalytic oxygen-scavenging polymer film. Journal of Photochemistry and Photobiology a-Chemistry, 177, 328-331

[99] US patent number 5922776: Sustained release, transparent biocidal compositions

[100] US patent number 7273567: Energy-activated compositions for controlled sustained release of a gas

[101] Kandimalla V. B., Tripathi V. S. & Ju H. (2006) Immobilization of biomolecules in sol–gels: biological and analytical applications. Critical Reviews in Analytical Chemistry, 36(2), 73–106

[102] Lopez-Rubio A., Gavara R., & Lagaron J. M. (2006). Bioactive packaging: turning foods into healthier foods through biomaterials. Trends in Food Science & Technology, 17, 567–575

[103] Sergio Torres-Giner, María José Ocio, José María Lagaron (2009) Novel antimicrobial ultrathin structures of zein/chitosan blends obtained by electrospinning Carbohydrate Polymers 77 (2009) 261–266

[104] Christina Kriegel, Alessandra Arrechi, Kevin Kit, D. J. McClements & Jochen Weiss (2008) Fabrication, Functionalization, and Application of Electrospun Biopolymer Nanofibers. Critical Reviews in Food Science and Nutrition,48:8,775 — 797

[105] Avelina Fernandez, Sergio Torres-Giner, Jose Maria Lagaron (2009) Novel route to stabilization of bioactive antioxidants by encapsulation in electrospun fibers of zein prolamine. Food Hydrocolloids 23 (2009) 1427–1432

[106] Kandimalla V. B., Tripathi V. S. & Ju H. (2006) Immobilization of biomolecules in sol–gels: biological and analytical applications. Critical Reviews in Analytical Chemistry, 36(2), 73–106

[107] Lopez-Rubio A., Gavara R., & Lagaron J. M. (2006). Bioactive packaging: turning foods into healthier foods through biomaterials. Trends in Food Science & Technology, 17, 567–575

[108] Appendini P. & Hotchkiss J. H. (1997) Immobilisation of lysozyme on food contact polymers as potential antimicrobial films. Packaging Technology and Science, 10, 271–279

[109] Soares N. F. F. & Hotchkiss J. H. (1998) Naringinase immobilization in packaging films for reducing naringin concentration in grapefruit juice. Journal of Food Science, 63, 61–65

[110] Fernández A., Cava D., Ocio M. J. & Lagaron J. M. (2008) Perspectives for biocatalysts in food packaging. Trends in Food Science & Technology, 19(4), 198–206

[111] Fernández A., Cava D., Ocio M. J. & Lagaron J. M. (2008) Perspectives for biocatalysts in food packaging. Trends in Food Science & Technology, 19(4), 198–206

[112] Wu D. Y., Meure S. and Solomon D. (2008) Self-healing polymeric materials: A review of recent developments. Progress in Polymer Science, 33, 479-522

[113] Crosby A. J. & Lee J. Y. (2007) Polymer nanocomposites: The "nano" effect on mechanical properties. Polymer Reviews, 47, 217-229

[114] Nachay K. (2007) Analyzing nanotechnology. Food Technology, 61(1), 34–36

[115] Gutiérrez-Tauste D., Domènech X., Casañ-Pastor N. & Ayllón J. A. (2007) Characterization of methylene blue/TiO2 hybrid thin films prepared by the liquid phase deposition (LPD) method: application for fabrication of light-activated colorimetric oxygen indicators. Journal of Photochemistry and Photobiology A: Chemistry, 187, 45–52

[116] Lee S. K., Sheridan M., & Mills A. (2005) Novel UV-activated colorimetric oxygen indicator. Chemistry of Materials, 17(10), 2744–2751

[117] Mills A., Tommons C., Bailey R. T., Tedford M. C. and Crilly P. J. (2008) UV-activated luminescence/colourimetric O-2 indicator. International Journal of Photoenergy, 6

[118] Mills A. & Hazafy D. (2009) Nanocrystalline SnO2-based, UVB-activated, colourimetric oxygen indicator. Sensor and Actuators B: Chemical, 136(2), 344–349

[119] Pursiainen O.L.J., Baumberg J.J., Ryan K., Bauer J., Winkler H., Viel B. and Ruhl T. (2005) Compact strain-sensitive flexible photonic crystals for sensors. Applied Physics Letters, 87, 101902

[120] Lu Y. F., Yang Y., Sellinger A., Lu M. C., Huang J. M., Fan H. Y., Haddad R., Lopez G., Burns A. R., Sasaki D. Y., Shellnutt J. and Brinker C. J. (2001) Self-assembly of mesoscopically ordered chromatic polydiacetylene/silica nanocomposites. Nature, 410, 913-917

[121] Wang X., Yang K., Ye H., Wang Y. P., Lee J. S. and Sandman D. J. (2006a) Methods for the preparation of micro- and nanocrystals of urethane-substituted polydiacetylenes. Journal of Macromolecular Science Part a-Pure and Applied Chemistry, 43, 1937-1943

[122] World patent number 2007148321: Irreversible Coolness Detector. Marketed as iStrip, http://www.timestrip.com/

[123] Lawrence B. D., Cronin-Golomb M., Georgakoudi I., Kaplan D. L. and Omenetto F. G. (2008) Bioactive silk protein biomaterial systems for optical devices. Biomacromolecules, 9, 1214-1220

[124] Edible sensors may indicate bacterial contamination, Food Technology Daily, 13.08.08

[125] Rajesh Takashima W. & Kaneto K. (2004) Amperometric phenol biosensor based on covalent immobilization of tyrosinase onto an electrochemically prepared novel copolymer poly(N-3-aminopropyl pyrrole-copolymer) film. Sensors and Actuators B, 102, 271–277

[126] Retama R. J. (2005) Synthesis and characterization of semiconducting polypyrrole/polyacrylamide microparticles with GOx for biosensor applications. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 239–244

[127] Ahuja T., Mir I. A., Kumar D. & Rajesh (2007) Biomolecular immobilization on conducting polymers for biosensing applications. Biomaterials, 28, 791–805

[128] Ahuja T., Mir I. A., Kumar D. & Rajesh (2007) Biomolecular immobilization on conducting polymers for biosensing applications. Biomaterials, 28, 791–805

[129] Arshak K., Adley C., Moore E., Cunniffe C., Campion M., & Harris J. (2007) Characterisation of polymer nanocomposite sensors for quantification of bacterial cultures. Sensors and Actuators B, 126, 226–231

[130] Galdikas A., Mironas A., Senuliene V., Šetkus A. & Zelenin D. (2000) Response time based output of metal oxide gas sensors applied to evaluation of meat freshness with neural signal analysis. Sensors and Actuators B, 69, 258–265.

[131] Subramanian V., Frechet J. M. J., Chang P. C., Huang D. C., Lee J. B., Molesa S. E., Murphy A. R. and Redinger D. R. (2005) Progress toward development of all-printed RFID tags: Materials, processes, and devices. Proceedings of the Ieee, 93, 1330-1338

[132] Tentzeris M. M. (2008) Novel paper-based inkjet-printed antennas and wireless sensor modules. IEEE International Conference on Microwaves, Communications, Antennas and Electronic Systems. Tel-Aviv, ISRAEL, IEEE

[133] Loh K. J., Lynch J. P. and Kotov N. A. (2007) Passive wireless sensing using SWNT-based multifunctional thin film patches. 13th International Symposium on Applied Electromagnetics and Mechanics. E Lansing, MI, Ios Press.

[134] Demoustier S., Minoux E., Le Baillif M., Charles M. and Ziai A. (2008) Review of two microwave applications of carbon nanotubes: nano-antennas and nano-switches. Comptes Rendus Physique, 9, 53-66

[135] Jedermann R., Behrens C., Westphal D. & Lamg W. (2006) Applying autonomous sensor systems in logistics - Combining sensor networks, RFIDs and software agents. Sensors and Actuators a-Physical, 132, 370-375

[136] Potyrailo R. A., Mouquin H. and Morros W. G. (2008) Position-independent chemical quantitation with passive 13.56-MHz radio frequency identification (RFID) sensors. Talanta, 75, 624-628

[137] World patent number 0240579: Coated films and coating compositions

[138] Kathleen A. Carrado and Peter Komadel (2009) Acid Activation of Bentonites and Polymer–Clay Nanocomposites ELEMENTS, VOL. 5, PP. 111–116

[139] Greiner R. (2009) Current and projected applications of nanotechnology in the food sector. *Nutrire:* rev. Soc. Bras. Alim. Nutr. = J. Brazilian Soc. Food Nutr., São Paulo, SP, v. 34, n. 1, p. 243-260

[140] Greiner R. (2009) Current and projected applications of nanotechnology in the food sector. *Nutrire:* rev. Soc. Bras. Alim. Nutr. = J. Brazilian Soc. Food Nutr., São Paulo, SP, v. 34, n. 1, p. 243-260

[141] The smart money is on intelligent design, Food Manufacture, 01.02.07

[142] US patent number 2007020456: Dry-coated oxygen-scavenging particles and methods of making them

[143] Assuring the safety of nanomaterials in food packaging: the regulatory process and key issues, Michael R. Taylor, Project on Emerging Nanotechnologies, 12th July 2008. http://www.nanotechproject.org/publications/archive/nano_food_packaging/

[144] http://www.sustainpack.com/index.php

[145] http://www.goodfood-project.org/

[146] Active packaging under the spotlight, Food Production Daily, 30.10.08

[147] Process may offer biodegradablity in petrochemical plastics, Food Production Daily, 04.08.08.