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Current and Projected Applications of Nanomaterials in the Food Sector

Ralf Greiner, Kathleen Oehlke and Rickey Yada

Pour faciliter la lecture, les parties essentielles en ce qui concerne la coenzyme Q10 NOVA ©SOL (hydrophile et micellaire) et la société Aquanova sont colorées en vert: page 4

Summary

The potential application and use (e.g. packaging, delivery of bioactives / nutrients) of engineered nanomaterials (ENMs) in food has shown great potential benefit and improvement over existing technologies. However, many of the applications are still in the research and developmental stage and would require rigorous food safety testing and ultimately consumer acceptance. Presently, the regulation and monitoring of nanomaterials in food regardless of global jurisdiction is a highly debated issue. In this respect, size is only one parameter (most proposed regulations have defined a nanoparticle as having a length scale of 1-100 nm) that should be considered. Properties such as chemical composition, unique physico-chemical properties of the ENMs, their interaction within the food matrix and with other food components as well as their potential uptake and absorptivity in the gastrointestinal tract need also to be considered. Such latter properties will all need to be examined in order to perform rigorous risk-benefit assessment. Within the European Union, which has taken an active role in regulating ENMs, nano/size-specific provisions have been implemented into several food-related Directives and Regulations. However, difficulties in the specific definition of ENMs and the lack of standardised methods for their detection and characterisation in complex matrices such as food, as well as their potential absorption, render the effective implementation of the legal requirements presently difficult.

Introduction

In the last decade, a variety of ENMs also suitable to be used in the food sector have been developed and investigated (Tarver 2006, Chaudhry et al. 2008, Abbas et al. 2009, Acosta 2009, Augustin and Hemar 2009, Da Pieve et al. 2009, Sozer and Kokini 2009, Srinivas et al. 2010). According to the definition commonly used today, nanomaterials exhibit a size in the order of 1-100 nm in at least one dimension. Therefore, spherical particles (3 dimensional) in the above mentioned size range are defined as nanomaterials as well as films (2 dimensional) and fibres (1 dimensional). In addition, agglomerates or aggregates with sizes above 100 nm are defined as nanomaterials, as long as they still retain their characteristic nano-scale properties. Compared to their larger-scale counterparts, nanomaterials exhibit altered properties or functionalities due to their very large surface area. ENMs are deliberately produced in this size range or size distribution. This distinction is necessary since structures in the range of 1-100 nm also occur naturally in foods. For example, the different protein fractions of milk exhibit sizes of a few nanometres (whey proteins) or 50-300 nm (casein micelles). Furthermore, nanostructures could be introduced by conventional food processing such as grinding, emulsification and gelation possibly resulting in novel textures, consistencies or stabilities of the food. Especially in the food sector it should be noted that production technologies in a precise nanometre range can in principle be used to generate larger-scale structures and materials; conversely, traditional processing methods can create nano-scale structures and materials. Therefore the boundaries between conventional processing and nanotechnology become blurred and terms such as “nanomaterial” or “nanotechnology” could be easily misinterpreted.

In the food sector, nanomaterials can be the food or an ingredient itself (nano inside) or as part of a food contact material such as food processing equipment or packaging (nano outside). The aim of this review is to provide an overview of the state of knowledge and the market situation regarding the use of ENMs in the food sector. Analytical issues, security issues and the legal framework are also briefly addressed.

Production of Nanomaterials

The production of ENMs can either be top down, which means reducing the size of structures to the nano-scale such as grinding large structures (e.g., crushing plant parts) by the application of mechanical and / or thermal energy, or bottom up whereby individual atoms and molecules are manipulated into nanostructures using various chemical reactions (enzymic crosslinking), electrostatic interactions (ionic cross-linking), or self-association (micelles, liposomes) (Taylor et al. 2005, Liu et al. 2008, Augustin and Hemar 2009, Sagalowicz and Leser 2010). As examples of the bottom up approach, starting materials may be fats, proteins and carbohydrates. It is also possible to create mixed structures, for example by applying different layers on a particle surface. Even with identical starting materials a variety of sizes and size distributions are obtainable, because size or size distribution of the nanoparticles generated are dependent on the production parameters; difference in size or size distributions of two to three orders of magnitude are possible. All components used in the production of nanomaterials for food application need to be food grade. This is a significant difference in terms of technological possibilities compared to, for example, pharmaceutical applications.

Improvement of Product Quality

From a technological perspective nanomaterials are interesting since their small size may result in different properties compared to their larger scale counterparts. For example, the temperature range of solid fats could be decreased by up to 20°C when present in the form of nanomaterials (Weiss et al. 2008). Nanoparticles, generally, do not scatter visible light such that their presence in clear beverages does not cause the impression of turbidity. Suspended nanoparticles are less prone to sedimentation, and nanoemulsions exhibit a higher kinetic stability than conventional emulsions (Gutierrez et al. 2008).

Structuring of Food

The specific design of certain food structures using ENMs can be used to improve consistency and texture of food. This is particularly advantageous in low-fat products since these products often find low consumer acceptance due to their insufficient creamy consistency. The specific generation of nanostructures consisting of fibres or organogels could be an approach to end up with semi-solid fats with the physiological properties of oils without the need of hydrogenation, the classical way of fat hardening (Marangoni et al. 2012). Due to interactions between nanoparticles and interfaces, a stabilisation of foams and emulsions can be obtained. Such stabilisation is difficult to achieve by conventional methods (Dickinson 2010, Gupta and Rousseau 2012).

Encapsulation of Additives

Encapsulation of additives provides benefits such as protection against external factors (e.g. pH, temperature), a better distribution in the food matrix or optimised interaction of the bioactive compound with food components. The choice of the material for the carrier system depends on the desired application and the bioactive compound to be encapsulated.

Structures composed of micelles are often encountered in food products and consist of a mixture of surfactants which form association colloids (self-associated surfactants) due to hydrophobic interactions. These micelles are composed of a hydrophobic core and a more or less water-rich shell facing the aqueous phase. They typically have diameters of about 30 nm and are characterised by very high capacities to solubilise and encapsulate low molecular mass lipophilic additives that can be introduced into aqueous food. For example, natural dyes could replace synthetic water-soluble dyes. Flavouring and colouring compounds in the form of product micelles have also been shown to be suitable for use in meat products (Yusop et al. 2012).

Preservatives in the form of solid lipid nanoparticles, nanoemulsions and liposomes exert a better effect in certain products and/or are more stable than other formulations (da Silva Malheiros et al. 2010, Donsì et al. 2011, Prombutara et al. 2012). The majority of the formulations studied so far in this area are lipid-based, but also carbohydrate-based edible coatings are currently in development (Campos et al. 2010).

A technological challenge is the stabilisation and formulation of volatile aroma compounds. For example, a significant stabilisation of carvon, an oily aroma compound, by encapsulation in spray-dried chitosan-coated nanoemulsion droplets was reported (Kaasgaard and Keller 2010). In addition, complexes between aroma compounds and cyclodextrins has been shown to be promising (Marques 2010).

Masking of Off-flavours

Complexes of substances with nanoscale structures can also be used to mask off-flavours. By using cyclodextrins the undesirable odour or flavour of omega-3 fatty acid-rich products, soy products or sweeteners can be reduced (Astray et al. 2009,Zimet and Livney 2009). Phospholipid-coated iron phosphate nanoparticles exhibit a comparable bioavailability as iron supplements such as iron sulphate, but without having their typical metallic taste (Rohner et al. 2007).

Functional Foods

“Foods that provide health benefits beyond basic nutrition” is a widely used definition for functional foods. In the development of functional foods, nano-encapsulation of the bioactive compounds can yield numerous benefits such as increasing the stability of the bioactive compound in the food matrix during storage or processing and in the stomach in order to delay or control release of the bioactive compound, and to improve the transport of the bioactive compound through the intestinal wall (Ubbink and Krüger 2006, Acosta 2009, Huang et al. 2010, Sagalowicz and Leser 2010).

It was shown in several studies that by nano-encapsulation an increase in the stability of bioactive compounds in food model systems (Jee et al. 2006, Kim et al. 2006, Hentschel et al. 2008, Barras et al. 2009, Zimet and Livney 2009, Almeida et al. 2010, Zimet et al. 2011) and in the gastro-intestinal tract (Dube et al. 2010a, b) is possible. This is due to the fact that the capsule material acts as a physical barrier to oxygen, unfavourable pH conditions, free radicals or light. It is particularly important that not only the nano-carrier system itself as well as every component of the formulation may determine the stability of the encapsulated bioactive compound (Helgason et al. 2009). Therefore, in order to protect the encapsulated bioactive compound in the digestive tract the capsule material must remain intact until it reaches the site of absorption of the encapsulated compound, i.e. no degradation of the capsule material by digestive enzymes occurs within the stomach. Digestibility of encapsulated nanomaterials as well as the release of the encapsulated bioactive compounds have been investigated in in vitro models where, in lipid-based formulations, the physical state of the fat matrix and in particular the choice of the emulsifiers are crucial (Bonnaire et al. 2008).

A problem with many bioactive compounds is their low bioavailability, which is due to their low solubility and/or membrane permeability. It was observed that bioactive compounds in a comminuted amorphous form exhibited an improved bioavailability due to a higher solubility (Onoue et al. 2010). Furthermore, substances increasing the contact time between bioactive compound and intestinal mucosa are favourable with respect to bioavailability. For example, chitosan exhibits muco-adhesive properties and forms spontaneously nanoparticles via ionic crosslinking (Dudhani and Kosaraju 2010). Very few human studies on bioavailability of nano-encapsulated bioactive compounds, in which exclusively food-grade materials were used, have been reported. Presently, studies have been reported for coenzyme Q10 (Terao et al. 2006,Wajda et al. 2007), vitamin E (Back et al. 2006, Wajda et al. 2007), pearl powder (Chen et al. 2008) and iron supplements (Fidler et al., 2004a,b, Roe et al. 2009). In general, a 2-5 fold higher plasma concentration of the bioactive compounds over time could be achieved by nano-encapsulation. In most of the studies, a modification in the kinetics of absorption was also observed. The highest plasma concentrations of the bioactive compounds were achieved earlier or later compared to the non-encapsulated form of the bioactive compound. The effect on biokinetics strongly depends on the formulation used and even the ability to make general predictions about the suitability of certain formulations to increase the bioavailability of a bioactive compound cannot be made. Bioavailability of a certain bioactive compound is dependent on the various interactions of capsule material, bioactive compound and also other components used in the formulation. In addition, the method used for encapsulation and the food matrix for which the nanocarrier systems are incorporated play a crucial role with respect to absorption of the encapsulated bioactive compound.

The above mentioned texture optimisation by nano-structuring of low-fat products can also be advantageous from a nutritional point of view, especially because industrially produced food is in general energy dense and worldwide the problem of obesity is increasing. The above mentioned low-fat products are expected to result in the same mouth-feel as their full fat counterparts. In addition, a reduction in sugar or salt could be achieved by encapsulation of flavour compounds. Due to a sudden release of those flavour compounds close to the flavour receptors a more intense flavour impression is possible compared to the soluble counterparts.

Food Contact Materials

The term food contact material is used for various applications such as packaging, food storage containers, dishes, refrigerators, and food processing equipment. Gas permeability, microbial growth and mechanical stability are issues that are the focus of nanomaterials in the food sector.

By applying nano-silver on the surfaces of storage containers microbial growth can be significantly reduced (Appendini and Hotchkiss 2002). The mechanism of the antimicrobial effect has yet to be resolved and may be either an intrinsic property of the nano-silver itself or the release of the silver nanoparticles from the surface (Tolaymat et al. 2010). In addition, nano-scale coatings are being developed for kitchen utensils and food processing equipment. The aim is to reduce biofilm formation and to facilitate cleaning of the surfaces. Feasibility of such approaches was shown for heat exchangers in the dairy processing industry (Kananeh et al. 2010).

Nano-composites such as nanoclay could be incorporated into polyethylene terephthalate polymer (PET) or other polymers to improve barrier properties of bottles, boxes or films. This effect is due to the staggered arrangement of the nanoplatelets, whereby gases and vapours are forced to use a longer path to diffuse through the polymer layer. Furthermore an increase in mechanical strength could be achieved by incorporating nanomaterials without increasing the weight of the polymer (Sorrentino et al. 2007, de Azeredo 2009, Arora and Padua 2010). Since biodegradable packaging systems often lack the mechanical stability and often poorer barrier properties than conventional materials, the potential use of nanomaterials would be great (Tang and Alavi 2011).

Food packaging systems with integrated nanosenors or indicators are in development. Such sensors or indicators may facilitate traceability of the food products, monitoring freshness of foods, their contamination with spoilage microorganisms, pathogens, and allergens or toxins during transport and storage (Zhang et al. 2009).

Safety Aspects

Up to now, extensive data on human exposure to ENMs via the oral route are not available. It is estimated that with a Western diet 1012 to 1014 nano- and microparticles are consumed daily (Powell et al. 2010). There are major gaps in knowledge with regard to the behaviour, fate and effects of nano-sized material via the gastro-intestinal route. It is not known whether nano-sized materials bind to other food components, agglomerate, or remain as free particles in the gastro-intestinal tract. It is possible that they will not remain in a free form in the lumen and hence not be available for absorption. As with other food components, interaction of nano-sized materials is very likely to change during passage through the gastro-intestinal tract. Nano-sized material may also affect gut function or gut microflora. Solubility and digestibility are two factors that largely determine the fate of nanomaterials in the gastrointestinal tract. When dissolved or digested it can be assumed that nanomaterials lose their nano-scale properties. Due to the large variety of nanomaterials that could be used in the food sector, general statements on the behaviour of nanomaterials in the gastro-intestinal tract are not possible. For example, for nano-scale lipid particles it was reported that very small modifications in the formulation strongly affected their digestibility in an in vitro model (Olbrich et al. 2002). Indigestible and insoluble nanoparticles can be either excreted or absorbed intact. From studies with predominantly organic and inorganic, insoluble nanoparticles it is known that absorption of intact particles is size-dependent and depending on the nature of the nanoparticles different mechanisms are involved (Powell et al. 2010). Besides absorption of the intact nanoparticles, their interaction with the intestinal epithelium may pose a health risk. It is discussed that this interaction might facilitate absorption of compounds that otherwise cannot enter the body ("Trojan Horse Effect") (Limbach et al., 2007). Therefore, such questions as raised above need to be answered case-by-case.

As soon as nanomaterials have been absorbed, they can be distributed throughout the body via the bloodstream or the lymphatic system. Interactions of nanomaterials with blood components can have a significant impact on their distribution and excretion. Nanomaterials are filtered out by the liver and spleen, but this is dependent on size and nature as they may also reach other organs and tissues (Jani et al. 1994). Moreover the question as to whether nanomaterials can overcome natural barriers such as the blood-brain barrier is seen as a major issue in respect to safety.

Analytical Approaches

There are several methods suitable for identifying nanomaterials in simple systems. However, when applying those methods to complex matrices such as food, many analytical challenges arise. In addition, the different analytical methods require different sample preparation methods and every sample preparation may produce its intrinsic artefacts. Therefore, the application of different analytical approaches to detect nanoparticles in the same sample will result in different results with respect to particle size and size distribution. A complete characterisation of the nanomaterials would include particle shape, surface charge, surface chemistry / reactivity, chemical composition, purity, crystallinity and aggregation or agglomeration state in addition to size and size distribution (Luykx et al. 2008). Up to now, there are no routine analytical approaches available to identify and characterise nanomaterials in complex matrices such as foods or cosmetics. Therefore, it is extremely difficult to obtain data about exposure or data in respect to hazard identification and characterisation. Thus, risk assessment of nanomaterials is a challenge (www.nanolyse.eu/).

Legal Obligation

The definition for ENMs laid down in the above mentioned regulation will need to be adjusted and adapted to the technical and scientific progress or to definitions agreed at an international level. According to a recommendation of the European Commission, ENM is defined as a nanomaterial if at least 50% of the number particle size distribution is in the size range between 1 and 100 nm. In addition, it was recommended to re-examine necessary modifications of the Novel Food Directive in order to be applicable for nanomaterials or materials derived from nanotechnology

Nanomaterials or changes caused by a modified particle size in the nano range are also covered in some other European Regulations, such as the regulation on enzymes (Regulation No. 1332/2008), on food additives (Regulation No. 1333/2008)], on active and intelligent food contact materials (Regulation No. 450/2009) and on plastic food contact materials (Regulation No. 10/2011)

Current Market Situation

There are a few product databases for nanotechnology products from independent institutions accessible via the internet (BUND 2012, Woodrow Wilson International Center 2012). The recent NanoRelease Project is currently in the process of developing a database of products containing ENMs (http://www.ilsi.org/ResearchFoundation/RSIA/Pages/FoodAdditiveMainPage.aspx). Since there is no compulsory registration for nanomaterials existing, those databases may be incomplete or contain products which do not contain or consist of nanomaterials. Meanwhile, some products in the food sector that were indicated a few years ago as containing or consisting of nanomaterials, were withdrawn from the market or advertising was changed in a way that no conclusions about the presence of nanomaterials in the products could be made. Validation of products entries will be required for any credible database of nanomaterials.

The German Patent Office has currently 30 inventions concerning nanomaterials for the food sector notified (Deutsches Patent- und Markenamt 2012). Among these notifications, 16 deal with the use of nanomaterials in the food matrix itself and 14 with application of nanomaterials in food contact materials. However, it cannot be predicted which of these notifications will be commercialised.

So far the majority of the applications of nanomaterials in the food sector are food contact materials. Within the European Union, the use of nano-scale titanium nitride is approved for use in PET bottles in concentrations up to 20 mg/kg. Furthermore, the use of nano clay for the inner surface of PET bottles as a nano layer was approved by the European Food Safety Authority (EFSA) (EFSA 2007). Due to economic considerations, however, the market share for such packaging is rising very slowly. Nano silver is neither approved nor in the assessment process within the European Union.

Dietary supplements containing nanomaterials is undoubtedly one of the most active areas of food nanoscience / technology. Application of nanomaterials or nanostructures aims to increase the bioavailability of bioactive compounds. Marketed products are for example, Easy Iron® (improved iron availability) or Nutri-NanoTM (improved co-enzyme Q10 availability). The product micelles marketed by Aquanova (NovaSOL®) or Frutarom (Nutralease®) and the nano-formulated lycopene (LycoVit®) developed by BASF could be found in liquid foods such as beverages. LycoVit® is authorised under the Novel Food Regulation as a novel food. Exact sales figures for all of these products or applications are not available.
In dry products, such as spices, silicon dioxide is used as an anti-caking agent for many years and its application is authorised as a food additive (E551). Silicon dioxide is composed of nano-scale silica particles that agglomerate to bigger particles before addition to foods. β-Cyclodextrin (E459), which displays a nano-scale molecule trap, is approved for use in certain foods and finds application as a carrier for flavour compounds in beverage powders and snack items.
In conclusion, if the application/use of food nanomaterials is to become a success, the issues raised above as well as an open and transparent dialogue among all stakeholders (public authorities, governments, the industry, NGOs, bench researchers) will be necessary as the technology / science progresses if the potential huge technological and economic benefits identified are to be realised.

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Dr Ralf Greiner and Dr Kathleen Oehlke are with the Max-Rubner Institut, Federal Research Institute of Nutrition and Food, Department of Food Technology and Bioprocess Engineering, Haid-und-Neu-Str. 9, 76131 Karlsruhe, Germany, e-mail: ralf.greiner@mri.bund.de; Professor Rickey Yada is Canada Research Chair in Food Protein Structure and Scientific Director, Advanced Foods and Materials Canada (AFM Canada), Department of Food Science, University of Guelph, Guelph, Ontario N1G 2W1, Canada, e-mail: ryada@uoguelph.ca