RSC Nanoscience & Nanotechnology

Edited by Qasim Chaudhry, Laurence Castle and Richard Watkins

Nanotechnologies in Food

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Preface

Rapid advancements in the fields of nanosciences and nanotechnologies in the past decade have not only led to a lot of hopeful anticipation, but have also raised some concerns. The current global market impact of nano-enabled products is in many billions of US$ and it is estimated by some to cross the 1 trillion US$ mark in a few years time. For such a rapidly expanding set of cross-cutting technologies, an obvious and prime target of new applications is the food sector, which itself is worth around 4 trillion US$ per annum globally. However, even at such an early stage, when the food and health food markets are only being 'tested' by market forces for new materials and products of nanotechnologies, they seem to have opened a new Pandora's box. There are mixed voices that are raising expectations and concern among the general public at the same time. Projections of enormous benefits are equally matched by calls for a moratorium or outright ban on the technologies until they are proven safe for human health and the environment. The same distinctive chemical and physical properties of nanomaterials that make them so attractive for new product development have raised fears over their safety to consumer health. A debate over how best to define nanomaterials, and whether they should be treated as new materials under the regulatory frameworks is still ongoing. Questions have also emerged over the adequacy and appropriateness of existing risk assessment paradigms, testing methodologies, detection and monitoring tools, as well as over the possible societal impacts of the new technologies.

Despite all this, it seems that many nano-sized materials have been a part of our everyday lives all the time, in the form of biological entities and processes that happen naturally at a nanoscale. Since the development of probe microscopes in the 1980s, food structures have been studied close to the molecular level. It is now known that most of our food materials are either composed of nanostructures, or are broken down into them during digestion. The concerns

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over deliberately added insoluble and bio-persistent nanoparticles in food do, however, seem justified. The prospect of being exposed through consumption of food and drinks to free, insoluble and possibly bio-persistent nanoparticles, which may have large reactive surfaces, and which may cross biological barriers to reach otherwise protected sites in the body is a legitimate worry. Such concerns, combined with the in-built scepticism of the general public towards any technologically derived food, have led to a call for more knowledge and understanding before such applications can be given what David Bennet has regarded in this book 'a license to produce' by the general public.

Against this contentious and rapidly changing background, this book puts the various views into perspective and analyses the pros and cons of the new technologies in an objective and realistic manner. The book presents the state-of-the-art in chapters written by leading experts in their respective fields. The subject areas cover science and technology, new product innovations, health and safety, consumer perception, risk assessment, risk management and regulatory aspects. The book aims to inform both non-specialist and specialist readers who are either new to the area or who want information and understanding from outside their immediate specialism. The Editors believe that this book, and of course the contributors to it, bring clarity to a number of issues and help move the debate on the new technologies forward in a more pragmatic manner.

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CHAPTER 1

Nanotechnologies in the Food Arena: New Opportunities, New Questions, New Concerns

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1.1 Background

It has been suggested for sometime that materials and substances may be manipulated at the very small size scale through atom-by-atom assembly.[1] The advent of nanotechnology in recent years has provided a systematic way for the study and 'fine-tuning' of material properties in the nanometer size range. Nanotechnology is a broad term used to represent an assemblage of processes, materials and applications that span physical, chemical, biological and electronic science and engineering fields. The common theme amongst them is that they all involve manipulation of materials at a size range in the nanometer scale. One nanometer (nm) is one-billionth of a meter. A nanomaterial has been defined as a 'material having one or more external dimensions in the nanoscale or which is nanostructured',[2] where the nanoscale size range is approximately 1–100 nm (Figure 1.1). Materials with all three external dimensions in the nanoscale are classed as nanoparticles. Nanomaterials also exist in other forms, such as nanorods or nanotubes with two dimensions in the nanoscale, or nanolayers, coatings or sheets with just one dimension in the nanoscale.

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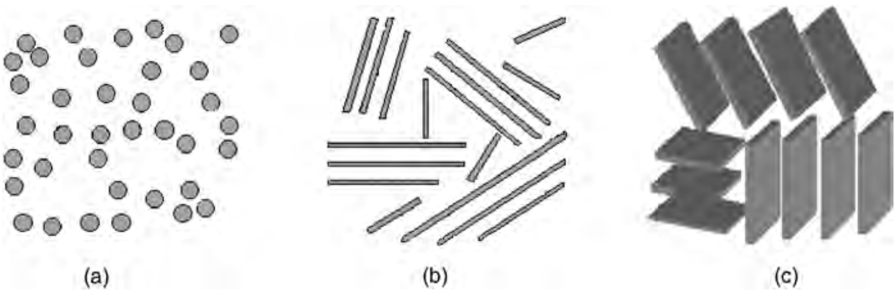

Figure 1.1 Nanomaterials as (a) particles; (b) rods; (c) layers.

Of particular interest to most nanotechnology applications are engineered nanoparticles (ENPs) that are manufactured specifically to achieve a certain material property or composition. Although ENPs are produced in free particulate forms, they tend to stick together to form larger agglomerates due to enormous surface free energies. In final applications, ENPs may be in fixed, bound or embedded forms in different matrices, such as food packaging plastics. Other applications, such as certain cosmetics, personal care products and functional foods may contain free ENPs. The chemical nature of substances used to manufacture ENPs can be inorganic (e.g. metals and metal oxides) or organic (e.g. food additives and cosmetics ingredients). Some nanomaterials are also obtainable from natural sources, most notably montmorillonite (also known as bentonite) that are nanoclays commonly obtained from volcanic ash/rocks. To help visualise nanomaterials in context, organic life is carbon based, and the C–C bond length is about 0.15 nm. So placed in a food context, most ENPs are bigger than molecules such as lipids, are a similar size to many proteins, but are smaller than the intact cells in plant- and animal-based foods (Figure 1.2).

The fundamental driver at the heart of most nanotechnology applications is the promise for improved or new functionalities of materials, and a possible reduction in the use of (chemical) substances. On an equivalent weight basis, ENPs have much larger surface to mass ratios (also known as the aspect ratio) due to their very small sizes compared to the conventional bulk forms. Thus, a relatively small amount of an ENP may provide a level of functionality that would otherwise require a much greater amount of the conventional material. The notion 'a little goes a long way' is probably the single most powerful reasoning behind many of the nanotechnology applications in different sectors. The very small size of ENPs can also offer other benefits. For example, nanosizing of water-insoluble substances can enable their uniform dispersion in aqueous formulations. This makes it possible to reduce the use of solvents in certain applications such as cosmetics, paints and coatings, and allows the dispersion of food additives such as water-insoluble colours, flavours and preservatives in low-fat systems. Nano-sized nutrients and supplements have also been claimed to have a greater uptake, absorption and bioavailability in the body compared to bulk equivalents. This aspect alone has attracted a lot of

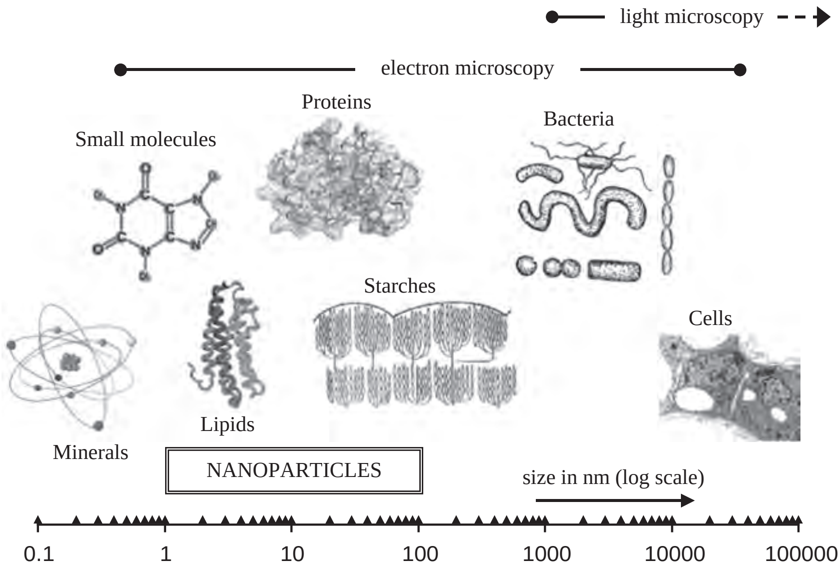

Figure 1.2 Nanomaterials placed in the context of other components in foods.

commercial interest in the use of nano-sized ingredients, supplements and nutraceuticals in (health)food applications.

The current applications of nanotechnology span a wide range of sectors, predominantly cosmetics and personal-care, health-care, paints and coatings and electronics. As in these sectors, nanotechnology is also promising to revolutionise the food industry – from food production, processing, packaging, transportation and storage to the development of new food tastes and textures and innovative food packaging applications. Nanotechnology has also emerged as one of the major converging technologies, offering the potential for further new developments through integration with other sciences and technological disciplines. Already there are examples where integration of nanotechnology with biotechnology and information technology is enabling the development of miniaturised devices, such as nanobiosensors. The use of the latter to detect pathogens and contaminants during food processing, transportation and storage is expected to enhance safety and security of food products. In view of the new technological developments, it is not surprising that the food industry is amongst the main sectors eagerly seeking ways to realise the potential benefits offered by nanotechnology.

This book is aimed at providing an impartial view of the potential prospects, benefits and risks that nanotechnology can bring to the food sector and its customers, and it also aims to discuss some of the main questions and concerns that the new technological developments have started to raise. In turn, this first chapter sets the scene for the subsequent chapters on individual application areas that are written by acknowledged experts in their respective fields.

1.2 Evolution of New Technologies in the Food Sector

The main driver that has shaped our present-day food industry is the basic human need for a sustained supply of safe, nutritious, affordable and enjoyable food throughout the year. Our food has gone through a long history of transformations over the centuries, from hunting and gathering to highly mechanised farming and technologically advanced processing and preservation methods. Agricultural food production during early human settlements is known to have started off with little knowledge, elementary tools and at the mercy of climate, pests and pathogens. The knowledge gained over generations enabled different civilisations to live off the land, and paved the way for systematic farming and animal breeding. The basic food production methods, however, then seem to have remained more or less unchanged over many centuries. By the early 1900s, agriculture was still run as a family-controlled or community-owned affair in most countries. The norms of food production, transportation and trade, however, started to transform in the 20th century with the introduction of mechanised farming, high-yielding crop varieties and, later on, with the availability of synthetic fertilisers, pesticides and other agrochemicals (antibiotics, hormones). The so-called 'green revolution' of the mid-20th century succeeded in substantially increasing the global food production. As the production of food reached industrial scales, new ways were found to transport, store and preserve foodstuffs. This laid the foundations of the modern-day food industry. The advancement in DNA technology in the past few decades has led to further advances in our understanding of the fundamental biological principles and genetic mechanisms, and enabled a big leap from protracted conventional breeding methods to faster knowledge-based improvements of crops and farm animals.

The history of food processing is also as old as that of food production. Throughout the centuries, foodstuffs have been processed and treated in various ways, and blended with different ingredients and additives to kill off pests and pathogens, to enhance nutritional value, taste, flavour and texture, and to keep and store foodstuffs for longer periods. In that respect, many of the processes used by the modern-day food industry, e.g. heat-treatment, fermentation, acid-hydrolysis, kilning, curing, smoking, drying etc, are not new to the consumer. However, the current consumer-driven food industry has to constantly look for innovative and novel products that not only offer new tastes, textures and flavours but are also wholesome, nutritious and value for money. The food sector now has a multitude of sub-sectors and branches that span from farm to fork. The global food retail market alone has been estimated to be worth between 3 and 4 trillion US$.[3] With globalisation of trade and industry worldwide, the rigid national boundaries that once existed in relation to food production and consumption have also become gradually obscure, and the supply and demand are now largely determined by global market forces. In this context, the introduction of nanotechnology is likely to make new waves in the already very competitive and technologically advanced food industry. These aspects are discussed in more detail in Chapters 2 and 7.

1.3 Public Perception of Nanotechnology Food Products

Before being successfully established, any new technology has to cross a number of technological, societal and regulatory barriers. This is especially true when the technology relates to such a sensitive area as food. The new nanotechnology-derived materials and applications for the food sector are not likely to face any lesser a challenge in this respect. Despite the infancy of nanotechnology applications for food, there are already demands for demonstrations that the new technological developments will have some real benefits for the consumer and not for the industry alone, and that the promised benefits will outweigh any risks to the consumer and/or the environment.

Like any new technology, public confidence, trust, and ultimately acceptance will be the key determinants for the success or failure of nanotechnology applications for food. Nanotechnology-derived food products will also be new to consumers, and it remains to be seen how they will be viewed by the general public. It is, nevertheless, obvious that uncertainties and lack of knowledge in regard to any new technology, or a lack of clear communication of the risks and benefits, can raise concerns amongst the public. In the present era of heightened consumer awareness, nanotechnology applications in the food sector seem to have already opened up a new debate amongst the stakeholders. There are, variously, calls ranging from a moratorium to an outright ban on the use of nanotechnologies for food. A recent report on the survey by the German Federal Institute of Risk Assessment[20] has shown that the current consumer opinion in the EU, whilst conducive to many nanotechnology applications, is not entirely favourable in regard to its use in food. This bears some resonance with similar issues of food irradiation and of genetically modified (GM) crops in the past, where a lack of clear demonstration of consumer safety and benefits resulted in a negative public response in many countries.

Public perception of a new technology is, however, influenced by an array of complex factors. In developed countries, where food is currently plentiful and affordable, there is a degree of public scepticism towards the food products that are (or perceived to be) unduly over-processed, or that lack wholesomeness, freshness or 'naturalness'. It also appears that even though food production is becoming increasingly globalised, public perceptions and priorities on food quality and safety do have more of a national characteristic, based partly on economic and cultural reasons. Thus, even within a single trading block, such as Europe, consumer priorities differ from country to country, some placing pesticides, for example, at the top of the agenda, some animal welfare, whilst others consider genetically modified organisms most worrying, etc. A similar heterogeneity in the perception and acceptance of nanotechnology is likely. Indeed, the public opinion in Europe seems to contrast with that in the USA. A survey carried out in 2008 for the Woodrow Wilson Institute for Scholars[21] has shown that, whilst a large majority of Americans has little or no knowledge of nanotechnology, the respondents expressed positive expectations when told about the potential benefits and risks of the technology. The consumer perception of nanofood in less well-off parts of the world may also be different from that in the developed world. (The recently coined term 'nanofood' refers to the use of nanotechnology techniques, materials or tools for production, processing or packaging of food.)

In this regard, it is logical to think that some applications will be seen *per se* as less acceptable than others. These aspects have been discussed in detail in Chapters 2 and 3, and analogies have been drawn from experiences with other technologies introduced into the food sector in the past.

1.4 Natural Nanostructures in Food

Whilst nanotechnologies offer exciting opportunities for the development of new tastes and textures through the development of nanostructures, emulsions and micelles in foodstuffs, it is known that our food already contains certain natural nanostructures. The three basic food constituents are proteins, carbohydrates and fats. Many food proteins and carbohydrate starches exist naturally in the nanoscale and simple triglyceride lipids are about 2 nm long. Food substances are also metabolised in the body at a nanoscale. Although proteins, carbohydrates and lipids are each digested in the gastrointestinal tract (GIT) in a different way, a common factor is that they are all broken down to nanostructures before assimilation. It has, therefore, been argued that our body is already used to dealing with nanostructures in the GIT, and that foods processed at the nanoscale would simply be more readily digestible, absorbed and bioavailable in the body. However, it remains to be seen whether nanoscale processing of food materials might produce structures that are different from those that occur naturally. These aspects are discussed in more detail in Chapter 4.

1.5 Potential Benefits and Market Drivers

Like any other sector, the food industry is also driven by innovations, competitiveness and profitability. The industry is, therefore, always seeking new technologies to offer products with improved tastes, flavours, textures, longer shelf-life, better safety and traceability. Other pressures, such as increased health consciousness amongst consumers and tighter regulatory controls, have also driven the industry to look for new ways to reduce the amount of salt, sugar, fat, artificial colours and preservatives in their products, and to address certain food-related ailments, such as obesity, diabetes, cardiovascular diseases, digestive disorders, certain types of cancer (e.g. bowel cancer) and food allergies. The needs for food packaging have also changed with time, to stronger but lightweight, recyclable and functional packaging materials. Food labels are now expected to provide much more than a mere list of ingredients and cooking instructions, and 'Smart' labels are finding an increasing use in monitoring food quality, safety and security during transportation and storage. Other 'newer' societal and technological pressures are affecting the food industry, such as the need to control pathogens and certain toxins in food, to reduce the amount of packaging, food waste and carbon footprint in the life cycle of food products. In this context, the advent of nanotechnology has raised new hopes that it can address many of the industry's needs (Figure 1.3). These aspects are discussed in more detail in Chapters 5, 6 and 7.

A number of recent reports and reviews have identified the current and short-term projected applications of nanotechnology for the food sector.[4–7] Although such applications are relatively new and emergent, they appear to have started to make a global impact. A current niche for such applications is in the areas where there is an overlap between the food, medicines and cosmetics sectors. Many food products are marketed as a means to enhance nutrition for different lifestyles and age groups, and as an aid to health, beauty and wellbeing. This has resulted in certain hybrid sub-sectors that include nutritional supplements, health foods, nutraceuticals, cosmeceuticals and nutricosmetics. These hybrid sectors have so far been the first focus of nanotechnology applications, which have only recently started to appear in the mainstream food sector. Thus a large majority of the currently available nanotechnology products falls in the areas of supplements, health foods and nutraceuticals, with only a few products in the food and beverage areas. The main tenet behind the development of nano-sized ingredients and additives appears to be the enhanced uptake and bioavailability

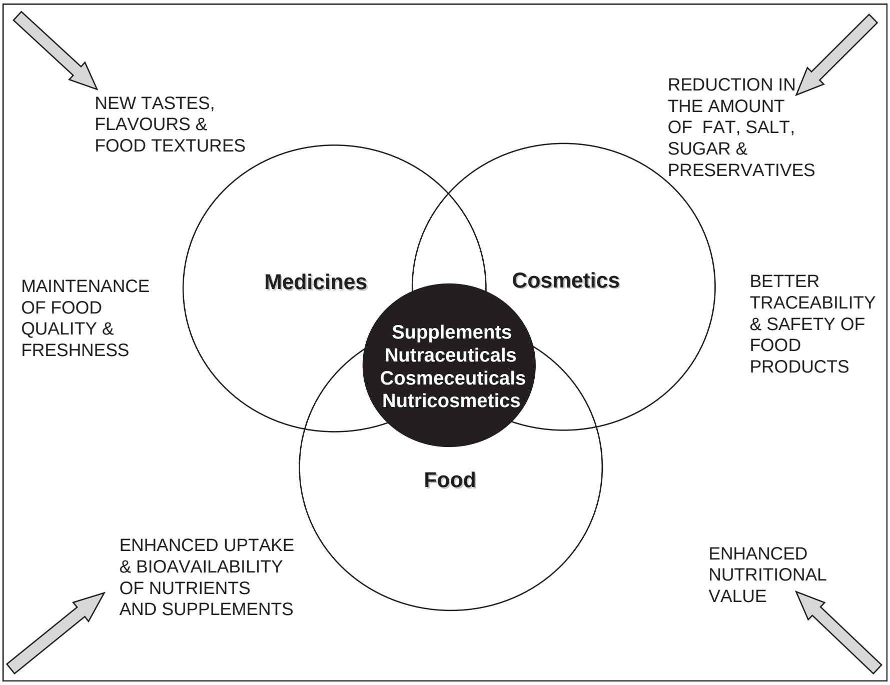

Figure 1.3 The main projected benefits of nanotechnology applications for food and related sectors.

of nano-sized substances in the body, although other benefits such as improvement in taste, consistency, stability and texture, etc. have also been claimed. A major current area of application for ENPs is in food packaging, in the form of innovative nanoparticle/polymer composites that offer improved mechanical or antimicrobial properties.

The number of companies undertaking research and/or using nanotechnology for food applications has been estimated to be between 200 (ref. 8) and 400 (ref. 9). These almost certainly include some of the major international food and beverage firms. However, accurate information on the true scale of industrial activity in this area is difficult to obtain because of commercial and other sensitivities. A number of major food corporations, who had been at the forefront of food nanotechnology R&D until a few years ago, now disown any involvement in this area. This has made it difficult to gauge the accurate level of commercial activity in this area. The absence of any quality scheme for nanofood products makes it even more difficult to segregate 'real' nano products from those that are based on unsubstantiated claims to project the 'magic' of nanotechnologies for short-term commercial gains. This has also raised concerns that at least some, if not many, of the products claimed to have derived from nanotechnology may in fact not be so. Conversely, some products may contain a nano component, but may not be claimed for its presence. In this context, some market forecasts for a dramatic future growth in the nanofood sector need to viewed with caution. It is, nevertheless, noteworthy that the number of nano (health)food products has been on a steady increase over the past few years. It is also likely that many more products and applications are currently in the R&D pipeline, and will appear on the market in coming years.

It is evident from available reports that the current nanofood sector is led by the USA, followed by Japan and China.[10] Despite the infancy of the nanofood sector, the overall size of the global market in 2006 has been estimated at between US$410 million (ref. 9) to US$7 billion (ref. 10). Future estimates vary between US$5.8 billion in 2012 (ref. 9) to US$20.4 billion by 2010 (ref. 10). Thus despite the current uncertainties, it appears that the upward trend in the nanofood sector will continue and may gather pace in the coming years.[5,9] The commercial exploitation of nanotechnology is also almost concurrent with that of the start of online marketing of consumer products through the internet. Thus virtually all of the currently available nanotechnology-derived consumer products can be bought by the consumer via the internet anywhere in the world.

1.6 Current and Projected Applications of Nanotechnology for the Food Sector

The applications of nanotechnology for the (health)food sector are potentially numerous, and are discussed in detail in Chapters 5 and 6. The main focus of developments has so far been on innovative food packaging, smart labels, nano-sized or nano-encapsulated ingredients and additives, and nanocarriers for delivery of nutrients and supplements.[5]

1.6.1 Innovative Food Packaging Materials

Whilst most nanotechnology applications for food and beverages are currently at R&D or near-market stages, the applications for food packaging are rapidly becoming a commercial reality.[5,9] A contributing factor to the rapid commercial developments in this area appears to be the expectation that, due to the fixed or embedded nature of ENPs in plastic polymers, they are not likely to pose any significant risk to the consumer. Nanotechnology applications for food contact materials (FCMs) already make up the largest share of the current and short-term predicted nanofood market.[9] It has been estimated that nanotechnology-derived packaging (including food packaging) will make up to 19% of the share of nanotechnology products and applications in the global consumer goods industry by 2015.[11] The main developments in the area of nanotechnology-derived FCMs include the following.

- 'Improved' FCMs in terms of flexibility, gas barrier properties and temperature/moisture stability. Typical examples include polymer composites with nanoclay (gas barrier), silicon dioxide (abrasion resistance), titanium dioxide (UV absorption) and titanium nitride (processing aid, mechanical strength). Also under research are nanocomposites of biodegradable polymers, such as nanoclay composites with polymers of starch and polylactic acid, for improved mechanical and moisture barrier properties.
- 'Active' FCMs incorporating metal or metal oxide nanoparticles (e.g. silver, zinc oxide, magnesium oxide) for antimicrobial properties. They are claimed to prevent microbial growth on the surface of plastics and hence keep the food within fresher for relatively longer periods.
- 'Intelligent' and 'Smart' packaging incorporating nano-sized sensors that can monitor the condition of the food during transportation and storage. Of particular interest in this regard are the safety and quality indicators that can be applied as labels or coatings to add an intelligent function to food packaging. These could, for example, monitor the integrity of the packages sealed under vacuum or inert atmosphere by detecting leaks, freeze-thaw-refreeze scenarios by detecting variations in temperature with time, or microbial safety by detecting the deterioration of foodstuffs.
- Nanocoatings for FCMs with barrier or antimicrobial properties, and for 'active' or self-cleaning surfaces in food processing facilities such as abattoirs.

The currently available FCMs include multi-layered PET bottles with nanoclay composite for gas barrier. The technology is understood to be already used by some large breweries. Other examples include food containers made of plastic/nano-silver composite and wrapping film containing nano-zinc oxide for antimicrobial protection of food. As mentioned before, market estimates for the current and short-term predicted applications suggest that nanotechnology-derived food packaging materials already make up the largest share of the overall nanofood market.[9] Chapter 6 covers the nanotechnology processes, products and applications for food packaging materials in detail.

1.6.2 Nano Ingredients and Additives

A key application area of nanotechnology for food processing is the development of certain nano-structured (also termed as nano-textured) foodstuffs, such as spreads, mayonnaises, creams, yoghurts and ice creams. The nano-structuring of food materials has been claimed for new tastes, improved textures, consistency and stability of emulsions, compared to equivalent conventionally processed products. A typical product of this technology could be in the form of a low-fat nano-textured product that is as 'creamy' as the full-fat alternative, and hence would offer a 'healthy' option to the consumer. Currently, there is no clear example of a proclaimed nano-structured food product that is commercially available, although some products are known to be at the R&D stage.[5] One such example under R&D is that of a mayonnaise which is composed of nanomicelles that contain nanodroplets of water inside. The mayonnaise would offer taste and texture attributes similar to the full-fat equivalent, but with a substantial reduction in the amount of fat intake by the consumer.

Another area of application involves the use of nano-sized or nano-encapsulated food additives. This type of application is expected to exploit a much larger segment of the (health)food sector, encompassing colours, preservatives, flavourings and supplements. The main advantage is said to be a better dispersability of water-insoluble additives in foodstuffs without the use of additional fat or surfactants, and enhanced tastes and flavours due to enlarged surface area of nano-sized additives over conventional forms. A range of consumer products containing nano-sized additives is already available in the supplements, nutraceuticals and (health)food sectors. These include minerals, antimicrobials, vitamins, antioxidants, etc. Virtually all of these products also claim enhanced absorption and bioavailability in the body compared to their conventional equivalents.

Nano-encapsulation is the technological extension of micro-encapsulation that has been used by the industry for (health)food ingredients and additives for many years. Nano-encapsulation offers benefits that are similar to, but better than, micro-encapsulation, in terms of preserving the ingredients and additives during processing and storage, masking unpleasant tastes and flavours, controlling the release of additives, as well as enhanced uptake of the encapsulated nutrients and supplements.

Following food packaging, nano-encapsulation is currently the largest area of nanotechnology applications in the (heath)food sector. Nano-encapsulation in the form of nanomicelles, liposomes or protein-based carrier systems has been used to develop delivery systems for additives and supplements in food and beverage products. A growing number of (health)food and nutraceutical products based on nanocarrier technology are already available on the market. These include a number of food additives and supplements. Other products containing nano-antimicrobials and nano-antioxidants, etc., are also commercially available. The concept of nanodelivery systems seems to have originated from research on targeted delivery of drugs and therapeutics. However, the use of similar technology in foodstuffs is interesting in the sense that whilst