REVIEW ARTICLE

Application of nano technology in dairy industry : prospects and challenges — A Review

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Abstract Nano technology applications are expected to revolutionize the food and dairy sector in the near future. The potential applications include superior processing techniques, improved food contact materials, better quality, shelf-life and safety of dairy and food products and novel packaging materials with better mechanical, barrier and antimicrobial properties. Recently, there is considerable interest in exploring the potential of nanotechnology in encapsulation and delivery of biologically active substances, enhancing the flavour and other sensory characteristics of foods and introduce antibacterial nanostructures into packaging. By reducing particle size, nanotechnology can improve the properties of bioactive compounds like delivery properties, solubility and absorption through cells. However, consumer concerns about the potential negative effects of nanotechnology-based delivery systems on human health will need to be addressed before commercial exploitation. This article comprehensively reviews the application of nanotechnology in dairy and food-related systems, focusing specifically on applications which are most likely to be commercialized in the immediate future.

Keywords : Nano particles, Nanosensors, Nano food additives, Nano encapsulation, Nano- packaging

Introduction

Nanotechnology is the design, production and application of structures, devices, and systems through control of the size

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and shape of the materials at the nanometer (10^9 of a meter) scale where unique phenomenon enables novel applications (Ravichandran and Sasi, 2006). When particle size is reduced below this threshold, the resulting material exhibits physical and chemical properties that are significantly different from the properties of macro scale materials composed of the same substance. This technology was introduced by Richard Feynman in 1959. Since then, it has been developed into a multidisciplinary field of applied science and technology which is expected to impact almost all areas of daily life. Research in the nanotechnology field has skyrocketed over the last decade, and different types of nanosized materials are available in many countries. In food and dairy industries, the major applications of nanotechnology include Nano particulate delivery systems, packaging, food safety and bio security etc (Chen *et al.*, 2006). A variety of food ingredients, additives, encapsulation systems and food contact materials are already available in many countries and the market for nanotechnology-derived food products and food contact materials is expected to grow worldwide. The nano scale food additives may be used to influence texture, flavour, provide functionality and even to detect pathogens. Food packaging involves edible, nano wrapper which will envelope foods, preventing gas and moisture exchange, 'smart' packaging (containing nano-sensors and anti-microbial activators) for detecting food spoilage and releasing nano-anti-microbials to extend the shelf life (Miller, 2008; Richardson and Piehowski, 2008).

Milk proteins are natural materials with high nutritional value and excellent functional and sensory properties. In addition, they have many structural features and functionalities that make them suitable for the construction of nano materials, where interactions can be controlled in a very precise way to modulate functionality. The potential of milk proteins as natural nano-vehicles for bioactive compounds has already received considerable research attention. Casein micelle has been designed by nature itself as a self-assembled nano scale system that delivers calcium and protein in dairy foods. Similarly, whey proteins have been designed to bind and transport hydrophobic molecules. Milk fat globule membrane material

has been found to be a suitable material for making liposomes. Nano-tubes and nano-fibrils can be produced from whey proteins using enzymatic and heat treatments.

Approaches for nano material production

There are two major approaches to attain nano materials, that is top-down and bottom-up approach. The "top-down" approach involves physically machining materials to nano meter size range by employing processes such as grinding, milling, etching and lithography. By contrast, self-assembly and self-organization are concepts derived from biology that have inspired a bottom-up food nanotechnology. Bottom-up techniques build or grow larger structures atom by atom or molecule by molecule. These techniques include chemical synthesis, self-assembly and positional assembly (Sozer and Kokini, 2008).

Owing to the greater surface area of nano particles per mass unit, they are expected to be more biologically active than larger sized particles of the same chemical composition. This offers several perspectives for functional food applications. Nano particles can be used as bioactive compounds in functional foods.

Applications

Nanotechnology will play a vital role in the food and dairy processing in near future and would involve three forms of nano food applications viz, food additives, delivery systems and food packaging.

Food additives

Nanotech companies are trying to fortify processed dairy and food products with nano encapsulated nutrients. The nano scale food additives may be used to influence texture, flavour, functionality, nutritional quality and even to detect pathogens. The appearance and taste of the food can be boosted by nano-developed colours, and the fat and sugar content can be reduced by nano-modification. In some countries food additives with nano ingredients are being produced keeping view of sports and health food market. They contain mainly minerals with nano formulation and particle size of these minerals is less than 100 nm. Hence, they can cross stomach wall into body cells more quickly than minerals with larger particle size.

Nanoceuticals

Nutraceutical compounds such as bioactive proteins are used in functional foods to impart health benefits to consumers in addition to the nutrition that the food itself offers. Nanomaterials can be used as bioactives in functional foods (Chau *et al.*, 2007). The biological activity of a substance depends on its ability to be transferred across intestinal membranes into the blood (Shegokar and Muller, 2010). Reducing the particle size of bioactives will improve the
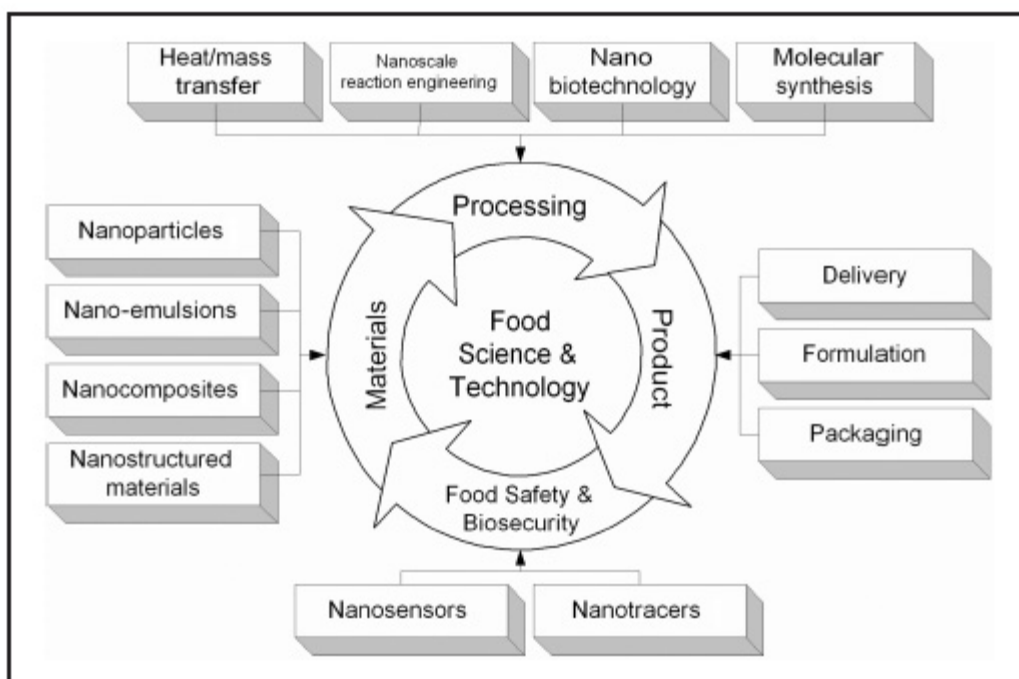

Fig.1. Potential applications of Nanotechnology
(Adapted from Moraru *et al.*, 2003)

availability, delivery properties and solubility of the bioactives and thus their biological activity. Further, Nanotechnology can also be utilized to improve the stability of nutraceuticals during processing, storage and distribution (Chen *et al.*, 2006). The prospect of the production of nutraceuticals at the nanoscale, which will have increased stability throughout the processing chain, will be of significant interest to food processors and will ultimately benefit the consumers.

The concept of nanoceuticals is gaining popularity and it includes the commercial food/dairy supplements containing nano particles like carotenoids, minerals, Omega-3 fatty acids, certain probiotic bacterial species, lycopene and Vitamin D_2 (Neethirajan and Jayas, 2011; Qureshi *et al.*, 2012). Ivanov and Rashevskaya (2011) developed functional butter with nano sized herbal supplements like polysaccharides, pectin, inulin, cryo powders of red beets, carrots, black currants buds with surface active properties. They studied the micro and nano structure of butter by scanning electron microscopy and observed that introduction of small amounts of pectin reduces the structural elements of butter to 5-25 times and is in the range of 1-100 nm. The nature and properties of the herbal additive significantly affected by the formation of nano structure of butter, morphology and architecture of its nano elements.

Nano encapsulation

Nano encapsulation is incorporation of ingredients in small vesicles or walled material with nano (or submicron) sizes. These nano materials offer several advantages such as, delivery vehicle for lipid soluble ingredients, protection from degradation during processing or in gastro intestinal tract, controlled site specific release, compatibility with other food constituents, greater residence time and greater absorption (Chen *et al.*, 2006). The protection of bioactive compounds, such as vitamins, antioxidants, proteins, and lipids as well as carbohydrates may be achieved by using this technique for the production of functional foods with enhanced functionality and stability. Nano encapsulation can make significant savings for formulators, as it can reduce the amount of active ingredients needed (Huang *et al.*, 2011).

Delivery systems used in food and Dairy industry

The different delivery systems used in food nanotechnology include the association colloids, biopolymeric nanoparticles, nanoemulsions, nanofibers, nanocapsules etc. These systems will serve as a vehicle for carrying functional ingredients, protect functional ingredient from degradation and control the release of functional ingredients (Weiss *et al.,* 2006).

Association colloids

A colloid is a stable system of a substance containing small

particles dispersed throughout. An association colloid is a colloid whose particles are made up of even smaller molecules (5 to 100 nm). Surfactant micelles, vesicles, bi layers, reverse micelles, and liquid crystals are some examples of association colloids which have been used to encapsulate and deliver polar, non polar, and amphiphilic functional ingredients (Flanagan and Singh, 2006).

Bio polymeric nano particles

Nanometer range particles can be produced by using food grade biopolymers such as proteins or polysaccharides through self-association or aggregation or by inducing phase separation in mixed biopolymer systems (Gupta and Gupta, 2005). Biopolymeric nanoparticles were first designed by using albumin and non biodegradable synthetic polymers such as polyacrylamide and poly methylacrylate. Poly lactic Acid (PLA) is a common biodegradable nano particle which is often used to encapsulate and deliver drugs and micronutrients like iron, vitamin, protein etc. It has been shown that PLA need an associative compound such as polyethylene glycol for successful results and the functional ingredients can be encapsulated in nano particles and released in response to specific environmental triggers (Riley *et al.,*1999).

Nano-emulsions

Emulsions are referred to as "nano emulsions", when the droplet diameter is reduced to 100 to 500 nm by the use of high-pressure valve homogenizers or micro fluidizers. The functional food components can be incorporated within such droplets, the interfacial region, or the continuous phase (Mc Clements, 2011). The small droplet size gives nanoemulsions unique rheological and textural properties which render them transparent and pleasant to the touch (Sonneville-Aubrun *et al.*, 2004). These unique features are desirable in the food and cosmetic industry. It is possible to develop smart delivery systems by engineering the properties of the nano structured shell around the droplets. This interfacial engineering technology would utilize food-grade ingredients (such as proteins, polysaccharides, and phospholipids) and processing operations (such as homogenization and mixing) that are already widely used in the manufacture of food emulsions (Weiss *et al*. 2006). Using nanoemulsions in food products can facilitate the use of less fat without a compromise in creaminess, thus offering the consumer a healthier option. Products of this type include low fat nanostructured mayonnaise, spreads and ice creams (Chaudhry *et al*. 2008). As the size of the droplets in an emulsion is reduced, the less likely the emulsion will break down and separate. In this way nano emulsification may reduce the need for certain stabilizers in a product. Nano size emulsion-based ice cream with a lower fat content has been developed by Nestle and Unilever.

Nano fibers

Nano fibers with diameters from 10 to 1000 nm, makes them ideal for serving as a platform for bacterial cultures as well as structural matrix for artificial foods. Electro spinning is a manufacturing technology capable of producing nano fibers from solution by applying a strong electric field to a spinneret with a small capillary orifice. The food industry can use electro spun microfibers as a building/reinforcement element of composite green food packaging material, as building elements of the food matrix for imitation/artificial foods, and as nano structured and micro structured scaffolding for bacterial cultures.

Nanotubes

Certain globular proteins from milk can be made to self assemble to form nano tubes under appropriate conditions. α-lactalbumin is a milk protein which is beneficially used in the production of nanotubes. α-lactalbumin nano tubes are formed by self-assembly of the partially hydrolysed molecule. At neutral pH and in the presence of an appropriate cation, these building blocks self-assemble to form micro meter long tubes with a diameter of only 20 nm (Otte et al., 2005). These features of the α-lactalbumin nano tube make it an interesting potential encapsulating agent. Nanotubes of α-lactalbumin have a cavity diameter of 8 nm which enables the binding of food components such as vitamins or enzymes (Srinivas et al., 2010). The cavities can also be used to encapsulate nutraceuticals or to mask undesirable flavour/aroma compounds

(Bikker and Kruif, 2006). Since, α-lactalbumin is a milk protein it will be fairly easy to apply the nano tubes in foods or pharmaceutics.

Nanocapsules

Casein micelles (CM) are nano-capsules created by nature to deliver nutrients such as calcium phosphate and protein to the neonate (Uricanu et al., 2004). CM plays a role as natural nano-capsular vehicle for neutraceuticals. The micelles are important due to their biological activity and good digestibility. They are very stable to processing and retain their basic structural identity through most of the processes (Gouin, 2004). A novel approach is to harness CM for nano-encapsulation and stabilization of hydrophobic neutraceutical substances for enrichment of non-fat or low-fat food products. Such nano-capsules may be incorporated in dairy products without modifying their sensory properties.

Food packaging

Food packaging is considered to be one of the earliest commercial applications of nanotechnology in the food sector. Reynolds (2007) reported that about 400-500 nano-packaging products are estimated to be in commercial use, while nanotechnology is predicted to be used in the manufacture of 25% of all food packaging within the next decade. The significant purpose of nano-packaging is to set longer shelf life by improving the barrier properties of the food packaging materials (Sorrentino et al., 2007).
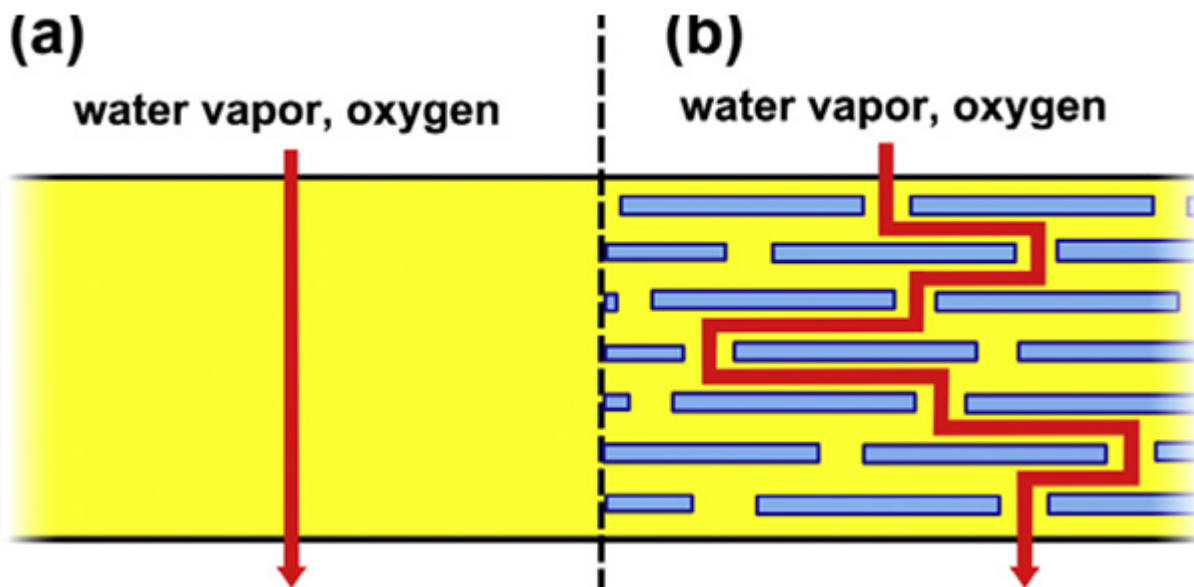

Fig.2. Illustration of the "tortuous pathway" created by incorporation of exfoliated clay nanoparticles into a polymer matrix film. (a).Diffusing gas molecules migrate via a pathway that is perpendicular to the film orientation in a film composed only of polymer. (b). In a nanocomposite film, diffusing molecules navigate around impenetrable particles and through interfacial zones which have different permeability characteristics than those of the virgin polymer. The tortuous pathway increases the mean gas diffusion length and, thus, the shelf-life of foods (Adapted from Duncan, 2011).

Success of packaging materials for fresh products totally depends on the control of internal gas composition and water loss in packaging. The incorporation of oxygen scavengers into food packages modifies atmosphere with controlled gaseous exchange, so that the shelf life of fresh products may be increased to weeks. Xiao *et al.* (2004) successfully made oxygen scavenger films by adding titania nano particles to various polymers. The surface of an ordinary packaging material such as plastic or paper can make suitable for food by coating it with one or more sharply defined layers of nanometer thickness. The plastic packaging material of drink bottles can contain clay nano particles to keep oxygen or water vapour in or out. Furthermore, nanomaterials are being developed with enhanced mechanical and thermal properties by adding reinforcing compounds (Azeredo, 2009).

Nano-packaging can also be designed to release antimicrobials, antioxidants, enzymes, flavours and nutraceuticals (Cha and Chinnan, 2004). Nano composite films with antimicrobial activity could help to control the growth and development of pathogenic and spoilage organisms in food items. Antimicrobial properties can be developed by impregnating natural antimicrobial agents to nano composite matrix (Rhim and Ng, 2007). The antimicrobial property of silver has been known for thousands of years and the extremely small size of silver nano particles even increases their antimicrobial efficiency. Packaging material incorporating silver nanoparticles are reported to be commercially available. Nano silver, Nano magnesium oxide, nanocopper oxide, nano titanium dioxide and carbon nanotubes are also predicted for future use in antimicrobial food packaging (Doyle, 2006; Chaudhry *et al.,* 2008 and Miller and Sejnon, 2008).

Nano-Coatings

Waxy coating is used widely for some foods such as apples and cheeses (Park, 1999). Recently, nanotechnology has enabled the development of nano scale edible coatings as thin as 5 nm wide, which are invisible to the human eye. Edible coatings and films are currently used on a wide variety of foods, including fruits, vegetables, meats, chocolate, cheese, candies, bakery products, and French fries (Rhim, 2004). An edible antibacterial nano-coating was developed in the United States which can be applied directly to bakery goods (El Amin, 2006).

Nano-coatings will serve as moisture, lipid and gas barriers as well as carriers of agents like colors, flavors, antioxidants, nutrients and antimicrobials and could increase the shelf life of manufactured foods, even after the packaging is opened (Qureshi *et al.*, 2012).

Nano laminates

Nanotechnology offer food scientists with a number of ways to create novel laminate films suitable for use in the food and dairy industry. A nano laminate consists of two or more layers of materials with nanometer dimensions that are physically or chemically bonded to each other. Weiss *et al.* (2006) reported that nano laminates have some advantages for the preparation of edible coatings and films over conventional technologies and may thus have a number of important applications within the food and dairy industry. A variety of different adsorbing substances could be used to create the different layers, including natural poly electrolytes (proteins, polysaccharides), charged lipids (phospholipids, surfactants), and colloidal particles (micelles, vesicles, droplets). It would be possible to incorporate active functional agents such as antimicrobials, anti browning agents, antioxidants, enzymes, flavors, and colors into the films. These functional agents would increase the shelf life and quality of foods. These nano laminated coatings could be created entirely from food-grade ingredients (proteins, polysaccharides, lipids) by using simple processing operations such as dipping and washing.

Biodegradable packaging materials

The conventional materials used for food packaging are practically undegradable which causes serious global environmental problem. New technologies and bio- based materials are emerging to alleviate the environmental pollution caused by non degradable packaging polymers. Biodegradable plastics are polymeric materials in which at least one step in the degradation process is through metabolism in the presence of naturally occurring organisms without generation of toxic or environmentally harmful residues. Biodegradable polymers include polymers that are directly extracted or removed from biomass such as polysaccharides, proteins, polypeptides and poly nucleotides. The use of biodegradable films for food packaging has been strongly limited because of the poor barrier properties and weak mechanical properties shown by natural polymers. The application of nanocomposites promises to expand the use of biodegradable as well as edible films (Lagaron *et al.*, 2005 and Sinha Ray and Bousmina, 2005). The application of nanotechnology to these polymers may open new possibilities for improving not only the properties but also the cost-price efficiency. So far, the most studied biodegradable nano composites suitable for packaging applications are starch and derivatives, poly lactide, poly hydroxyl butyrate, and aliphatic polyesters as polycaprolactone. Biodegradable-starch based polymers have poor moisture barrier properties due to their hydrophilic nature, and inferior mechanical properties compared to plastic films. The incorporation of clay nano particles in starch polymers has been reported to improve moisture barrier and mechanical properties (Avella *et al.*, 2005). Poly lactide is a biodegradable thermoplastic polymer that has a high mechanical strength, but low thermal stability and low moisture and gas barrier properties compared to plastic polymers. Incorporation of clay

nano particles into poly lactide has been reported to improve tensile modulus and yield strength, and to reduce permeability to oxygen.

Nano sensors

A nano sensor is a device consisting of an electronic data processing part and a sensing part, which can translate a signal such as light or presence of organic substance or gas into an electronic signal. These sensors can be integrated into food processing equipment or refrigerator or into the food itself and will help to improve food safety by enabling faster quality control and testing up to the consumer level. To ensure food safety, packaging materials incorporated with nano structured biosensors or DNA-based biochips are being developed. The embedded sensors in a packaging film will be able to detect pesticides, allergens, toxins, food-borne pathogens and food-spoilage organisms and trigger a colour change to alert the consumer about these facts. "Electronic Tongue" consists of an array of nano sensors which are extremely sensitive to gases released by food as it spoils, causing a sensor strip to change colour which gives a clear visible signal whether the food is fresh or not. To be incorporated directly into packaging, the sensors need to be made from cheap and flexible materials. Nano scale-sensing devices are also under development that, when attached to food products and packaging, would act as electronic barcodes. They would emit a signal that would allow food to be traced from field or farm to factory to supermarket and beyond. Among the near-market developments are nano material based next-generation packaging displays that include Radio frequency identification display (RFID). The technology consists of microprocessors and an antenna that can transmit data to a wireless receiver. Unlike barcodes, which need to be scanned manually and read individually, RFID tags do not require line-of-sight for reading and it is possible to automatically read hundreds of tags in a second. Kodak is using nanotechology to develop antimicrobial packaging as well as active packaging, that absorbs oxygen, to keep food fresh that will be commercially available in near future (Clark, 2006). The Netherlands Researchers are developing intelligent packaging that will release a preservative if the food within begins to spoil. This "release on command" preservative packaging is operated by means of a bioswitch developed through nanotechnology (Ravichandran, 2010).

Probable adverse effects:

The additives universally accepted as GRAS will have to be re-examined when used at nano scale level. Owing to the increased surface area of nano materials, studies should be conducted for the identification of possible ill effects in the body which could be caused by the use of nano materials in food products. The nano particles are more reactive, more mobile, and likely to be more toxic. Toxicity is the most important issue that must be addressed before the commercial exploitation of nano particles. Further, detailed studies are required to determine the effects of these materials on the normal micro flora of the alimentary canal of the consumers. Currently no regulations exist for specific control or limit for the production of nano sized particles (Sozer and Kokini, 2008). Particle size, mass, chemical composition, surface properties, and aggregation of individual particles are the properties of nano materials that determine the impact on the body (Nel et al.,2006). The nano toxicity can be assessed by several criteria like toxicology of nano particles, exposure assessments, environmental and biological fate, recyclability and overall sustainability of nano materials. Laboratory safety guidelines have been provided by the Committee on chemical safety of American chemical society for appropriate handling of nano materials.

The extent to which nano particles enter the human body, penetration sites, accumulation and translocation in body are the factors determining the potential risks of nano scale materials. Dermal exposure, inhalation and ingestion are the three possible routes of nano particles to cause harm inside the body (Chau et al., 2007). The epidermis of healthy intact skin will provide excellent protection against nano structured particles and the impact of nano particles on the body depends on their ability to penetrate through outer protective layers of the skin (Nel et al., 2006). Materials with less than 10 mm diameter can pass through nasal cavity into lung and particles with less than 4 mm diameter is having greater probability of penetrating the alveolar region. Inhaled nanoparticles may accumulate in lungs and induce chronic pulmonary diseases like pneumonia, granuloma oxidative stress (Kim et al., 2003). Exposure to some engineered nano particles can increase production of oxyradicals that may lead to oxidative damage and inflammatory reactions. Nanoparticles has a prolonged gastric retention time by decreasing intestinal clearance mechanisms, increased surface area of exposure and efficient delivery to target sites in the body (Chen et al., 2006).

The verified nano products comes with the certificate of nanomark, which is the first certification system implemented by ministry of economic affairs in Thaiwan (Chau et al., 2007). The European Union regulations for food and food packaging have recommended that for the introduction of new nanotechnology, specific safety standards and testing procedures are required (Halliday, 2007). In the United States, nanofoods and most of the food packaging are regulated by the United States Food and Drug Administration (US FDA) (Badgley et al., 2007), while in Australia, nanofood additives and ingredients are regulated by Food Standards Australia and New Zealand (FSANZ), under the Food Standards Code (Bowman and Hodge, 2006). However, there is an urgent need for a common regulatory system capable of managing any

risks associated with nanofoods and the use of nanotechnologies in dairy and food industry.

Conclusions

Nanotechnology is a very promising area in food and dairy industry and it is expected to offer technological advantages in production, processing, storage, transportation, traceability and safety of food. This principle can be used in the dairy industry for the delivery of bioactive components, development of new tastes, textures, sensations and consistencies; potential reduction in the amount of fat, salt and other additives; enhancements in the absorption and bioavailability of nutrients and supplements; preservation of product quality and freshness and better traceability and security of food products through innovative packaging applications. Currently, food packaging applications make up the largest share of nanofood market, followed by nano-sized and/or nano-encapsulated ingredients and additives for health food applications. Nevertheless, detailed research should be carried out to study the possible adverse effects before commercial application of nano food additives. Nanomaterials used as food additives or food packaging materials must not cause any health risks for consumers or to the environment. Further, research studies are required to investigate the hazards of nanomaterials, taking the size as a main factor even though some of the chemical materials in the form of large particles are safer than when they are in the nano state. Hence, commercial application of nanotechnology derived products can be done only after the safety issues are resolved. There is also an immediate need for regulation of nanomaterials before their incorporation into food and dairy processing including packaging. In addition, nanotechnology-derived products need to demonstrate their economical competitiveness prior to commercialization. Until now information related to the economical competitiveness of nanotechnology-derived products is almost lacking.

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