ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 3, pp. 630–642. © Pleiades Publishing, Ltd., 2010.
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Food Nanotechnologies

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Received January 10, 2009

Abstract—The authors of the present review are the first to collect, systematize, critically analyze, and summarize the information on food nanotechnologies, published over 2000–2008.

DOI: 10.1134/S1070363210030436

INTRODUCTION

The first publications concerning nanotechnologies in food industry appeared as late as the end of XX and beginning of XXI centuries. [1, 2–7]. This delay is to a certain extent explained by the fact that the food market is fairly conservative and food industry and food quality are rigidly regulated. Actually, recent research shows that the food safety of nanomaterials is still a poorly explored issue [1, 8–10]. The fact that high dispersity of a food material is not always a positive factor should also be borne in mind. For example, an increase in the dispersity of flour, powered sugar, or instant coffe to the nano level increases the share of dust fractions and entails prepackaging losses. At the same time, a lot of foods inherently contain particles 1–1000 nm in size and are traditionally considered as classical colloidal objects [11]. For instance, 50-nm fat droplets are contained in ordinary milk**,** food protein globules are tens and hundreds nanometers in size, linear polysaccharides can be considered as one-dimensional structures 1 nm in thickness, whereas starch polysaccharides contain small three-dimensional nanostructures of about 10 nm in size.

Thus, at first glance, there is no urgent need in developing special food nanotechnologies. At the same time, according to our records, the growth of publications on food nanotechnologies have acquired an avalanch-like character. This is explained by the recent progress in technologies for manufacturing dispersed systems containing nanoparticles (1–100 nm) and for controlling their structure and fractional composition. It was shown that nanoparticles, having much larger specific surface area than their coarse analogs, exhibit enhanced biological activity [12] and present undeniable interest as carriers for biologically active substances (BAS) in foods for improving health function [13]. There`are other reasons for enhanced interest in food nanotechnologies. The payment of humankind for motorization and computerization is a slow-moving lifestyle and, as a consequence, obesity. The demand for low-fat foods (milk, quark, sour cream, cheese, confectionery creams, ice cream, etc.) has enhanced considerably. However, decreasing fat content decreases the content of fat-soluble vitamins and other BAS. Therefore, to produce a low-fat but balansed and vitamin-rich food is an urgent problem. Nanotechnologies should play a key role in approaching this problem.

The global market of nanoproducts in the food sector and the sector of beverage packaging is continuously growing, and this tendency is expected to be preserved in future [1]. At the same time, it is still early to declare that nanotechnologies have already been introduced in food industry. The initiation of this process can be dated back to 2000, when Kraft Foods set up the first nanotechnological laboratory and NanoteK Consortium comprising 15 universities in differerent countries and national research laboratories [14]. Already in 2004 more than 180 nanotechnological developments at different stages of implementtation in food industry are known [15]. In March 2006, more than 200 foodstuffs marked “nano” by their producers were present at the world market. Of them 59% related to the Health and Fitness category and 9% to the Food and Beverages category [16].

Among food nanoproducts which have already entered or are ready to enter the market we can mention a milk product containing nanoparticles for faster calcium digestion (Campina). It was targeted to aged people. However, the latter did not show enough interest, and the product was removed from the market. Another company, NutraLease, developed new carriers for food additives (lycopene, β-carotene, lutein, and phytosterins) as nanosized structures and natural macromolecular aggregats suspended in water together with food additives [10]. In Australia, an experimental batch of bread cotaining nanocapsules with tuna fish oil. According to producers, these nanocapsules endow bread with additional nutrients, but therewith the product has no fish smell [10].

In general, about 200 companies all over the world are involved in an active research and development in the field of nanofood [1, 10]. At the same time, even though the progress is obvious, it’s still more right to say that the potential of nanotechnologies in food industry is only coming to be recognized [1].

Application Fields of Nanotechnolories in Food Industries

The applications of up-to-date nanotechnologies in food industry are quite diverse and by far promising (see table) [17–114]. First of all this relates to purposeful search for new-generation foods on the basis of finely dispersed particles and a narrow fractional composition. The demand for such foods is dictated by a changed consumer’s attitude to food which is increasingly considered to be not only a source of nutrients with certain organoleptic properties, but also as an important component of health maintanance [17]. In this context, research aimed at gaining insight into interrelationship between and fuction of nano- and supramolecular, and larger structural elements of food.

Nanodispersions of foods themselves have still scarcely been reported and are limited to traditinal edible plants consumed as nanopowders and emulsions [97]. They include green tee containing nanoparticles with enhanced antioxidant activity [18], as well as nanodispersions of propolis as a powder or pellets [98]. It was shown that the antioxidant activity of green tea with a particle size less than 1000 nm is two orders of magnitude higher compared with the same tea brands with a normal particle size; a technology for manufacturing such nanodispersions was developed [18].

Food additives and their enriched foods have received much wider acceptance. It was found that both the food product itself and food additive radically change properties when reach the nanosize level. An example is provided by selenium. This vitally important element is not normally digested by human organism in an elemental form. To enrich food, fairly comlex organic selenium compounds are needed. However, it was found that elemental selenium nanoparticles can be stabilized as aqueous dispersions which are readily digested [19]. This facilitates and makes less costly the manufacture of the corresponding bioadditive.

At present products with microencapsulated ingredients have gained the widest recognition [20, 21]. Microencapsulation allows controlled release of bioadditives, which enhances their efficiency, extends the application field and optimizes the dose. This approach offers best advantages in the case of unstable and volatile additives (vitamins, flavoring agents). These quite unstable substances can convert with time in fairly stable food components. Considerable effort in this field has been focused on nanoparticle microencapsulation [19–27].

Up-to-date technologies for manufacturing nanoemulsions make it possible to obtain aromatized beverages, juces, and milk enriched with controllably released vitamins, minerals, and functional components [25, 26]. Moreover, taste or flavor bioadditives and their shells can be combined so that release occurs only when the product comes into contact with tongue receptors during food intake. This property solves the problem of taste loss on food preparation, handling, and consumption. The nearest perspective is development of so-called interactive foods and beverages. Such products will be capable of “tuning” to an individual taste and demands of each consumer. For example, it may be beverages changing color to meet consumer’s preferences or food additives that recognize allergy for one or another component of the product [10].

Expenses for microencapsulation and enrichment should not raise essentially the cost of the final product. By rough estimates, if the content of functional additives will be no more than 1–5 wt %, the cost rise will make €0.1 per 1 kg of the product [20].

Of considerable interest are microemulsions stabilized with cyclodextrins. These cyclic carbohydrates have a cavity about 0.5–0.8 nm in diameter, capable of accomodating 6–17 water molecules. Small organic molecules can replace water in the cyclodextrin cavity to form host–guest inclusion compounds (supramo-

Application of nanotechnologies in food industries

Technology	Examples and results
Dispersion of a traditional macro product	Preparation of nanopowders or emusions of traditional edible plants [18, 97, 98]
Creation of functional nanoadditives, food ingredients and their-enriched prod-	
– inorganic nanoadditives as powders and tablets	Nanodispersed Al, Ca, Mg, Fe [99], Se [19, 100], Zn [100], and S [101] oxides (particle size < 100 nm) with much enhanced bioavailability
– natural nutriceutical, antioxidant, taste, flavor, and vitamin nanoadditives	Nanotechnologies allow to convert hydrophobic substances into water-soluble, producing nanodispersions of valuable food ingredients (carotenoids, phtosterols, antioxidants) in water and fruit beverages and enhancing the bioavailability of the latter [13, 16, 21–33, 102–106, 113], protecting them from oxidation and photodestruction [107], and improving their transport properties [13, 109]; the desired food flavor and taste can be provided immediately before use [15a]
– functional preservative and bactericidal nanoaditives	New-generation silver nanopreservatives [35, 36, 111, 114]
– nanocoatings	Antibacterial silver and protein coatings for wide-range food applications [37]
Nanofiltration	A unique technique for isolation of pure food ingredients and fine purification of liquid food systems [27–49]
Creation of a new-generation packaging	Introduction of nanoparticles (silver, titanium dioxide, silicon dioxide, clays) allows essential modification and improvement of food packaging qualities [1, 7, 64–76]. Multilayer nylon nanocomposites are used for manufacturing bottles, including those for alcoholic beverages, provide protection from oxygen and carbon dioxide, and preserve freshness and flavor [112]
Creation of biosensors for food quality control	New class of ultramicroscopic nanosensors for express identification of viruses, bacteria, and other pathogens [110]; biocatalytic sensors [54–57, 90]

lecular encapsulation). In essence, here we deal with molecular design of food ingredients. This provides a way of generating dispersions of particles encapsulated in molecular cavities no less than 1 nm in size. The thermodynamic stability of supramolecular associates of cyclodextrin with inclusion molecules is fairly high, and they are also exhibit a fairly high thermostability (up to 200°C).

The advantage of such compositions is a unique character of release of food additives: Flavor substances encapsulated in the cyclodextrin cavity can be replaced by other components of the medium, which have a higher affinity to the cyclodextrin molecule. In particular, such release can invove natural biocomponents of human oral cavity [20, 28]. The use of cyclodextrins for encapsulation of flavoring food additives [20, 29, 30] and hydrophobic vitamins of the A, D, E, and K groups have been reported [20].

The Chair of Biotechnology, Moscow State University of Food Industries (MSUFI) together with the Bioenginnering Center, Russian Academy of Sciences, and Institute of Biology, Ufa Research Center, Russian Academy of Sciences, has implemented to success the Enzymatic Systems and Technologies for Manufacturing Cyclodextrins Project. The principal results of the research are as follows. A new halophilic strain identified as *Paenibacillus maceranns 1 AMB* was obtained. This enzyme was used to obtain from starch α-, β-, and γ-cyclodextrins, and the latter were further used to produce a wide range of nanoproducts for food and medical applications. Procedures for preparing cyclodextrin complexes with CO_2 extracts of carnation by ultrasound treatment and vanillin complexes with hydroxypropyl cyclodextrin. A possibility to produce biologically active inclusion complexes from β- and γ-cyclodextrins and their hydroxypropyl derivatives and elemental sulfur nanoparticles which exhibit a true water solubility (see figure). A stable nanosuspension of a complex of β-cyclodextrin with β-carotene was obtained. A procedure for preparing vitamin E powder as an inclusion β-cyclodextrin comples was developed, and a series of β-cyclodextrin derivatives with low-molecular chitosan for microbiologic hydroxylation and dehydrogenation of steroid medicines were synthesized [113].

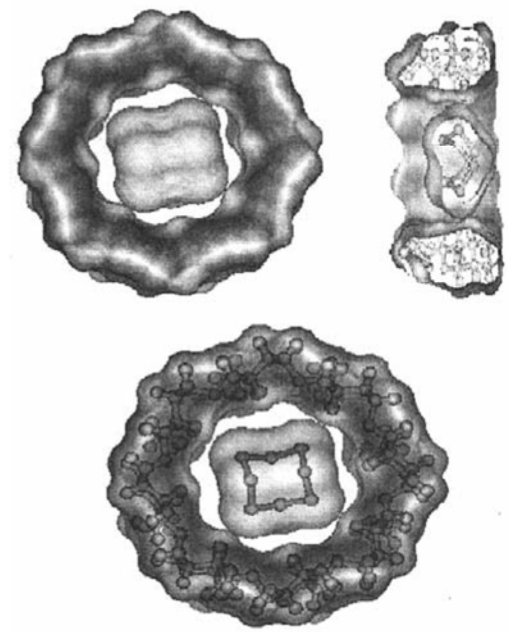
The formation of inclusion complexes of vitamins with cyclodextrin was confirmed by thermal and fluorimetric analyses, and NMR. The above BAS included in the cyclodextrin cavities exhibit enhanced stability and bioavailability. In particular, the room-temperature solubilities of vitamins E and B_2 in the inclusion complexes are 25.9 and 81 mg/100 ml and that of vanillin is 14 g/100 ml. These values are 3–6 times higher than the respective values for native BAS.

Most of the synthesized inclusion complexes were used for enrichment of such mass consuption products as confectionery. In particular, the vitamin E:β-CD complex was introduced into the recipe of sugar fudge, the vitamin B_2:β-CD complex, in the recipe of jelly marmalade, and the vanillin:α-CD and orange ether oil:α-CD complexes, in the recipes of cream and sugar fudges. Analysis of the confectionery for BAS immediately after preparation and 2 months after storage in ambient conditions gave evidence for stability of the cyclodextrin complexes.

Of no little importance is that the inclusion complexes of BAS with cyclodextrins have no negative impact on the shape, structure, and consistency of confectionery, enhanicing their nutritional value and extending their storage life. For such products no changes in technological parameters are required.

The disadvantage of cyclodextrins as additive carriers consists in their low volume and the reversibility of inclusion complex formation. Thus, for instance, the cavity size in six-membered α-cyclodextrins (MW 1135 Da) allows for the latter to include no more than 11 wt % of target flavor additive. It should also be noted that biologically active compounds whose molecular size is larger than the cyclodextrin cavity size quite rarely form inclusion compounds. Further disadvantage of cyclodextrins is associated with their still high price [20]. In view of these circumstances, wide use of cyclodextrins in medicine and food industry is unlikely to be expected in the near future.

Simple proteins hold the greatest promise as carriers for BAS (vitamins, probiotics, bioactive peptides, antioxidants, etc.). Regardless of the fact that the



Molecular models of the complex of γ-cyclodextrin with S_8 in different projections [113]. Solvated surfaces of the complex are shown. Geometry optimization was performed using Hyperchem 7.5.

mechanisms of involvement of food additives in the metabolism of living organisms are still not conclusively established, an opinion has already formed that the consumption of their-based functional foods reduces the risk of diseases [31].

The efficacy of functinal products as prevention means for a wide spectrum of diseases is associated with prolongation of the bioavailability of the active ingredient. Generally, food bioadditives are only partially digested by human organism. The reason for this loss is their insufficiently long residence time in the stomach, low permeability or low solubility in the digestive tract, as well as degradation of the active ingredient during food preparation (effect of heat, oxygen, or light) or on the way through the digestive tract and esophagus (effect of pH and enzymes) [31]. Therefore, for enhanced efficacy of functional food certain protective mechanisms should be included to ensure preservation the active form of the additive until it has been digested and its directed transport. Such protective and transport functions can be fulfilled by globular proteins, specifically serum protein. Entrapping and encapsulating food additive particles, they substantially enhance the accessibity of nutriaceuticals. This is especially important for functional low-soluble lipids (carotenoids, phytosterols). Depending on processing conditions and the environment, globular proteins can form micro- and nanoparticles 40 to 2 nm in size [31].

It was found that nanoglobules exhibit unique advantages over microglobules. Both types of particles are readily adsorbed on intestine walls, thus much prolonging the residence time of bioadditives to the body and enhancing the probability of their resorption. However, unlike microglobules, their nano analogs are capable of penetrating into the intracellular space, providing additional and quite an efficient delivery of the target product [31].

The promise held by globular nanocarriers has obtained experimental evidence. At the same time, a lot of questions concerning the properties and behavior of such associates on their way from a vitamin-enriched product to vitamin release from globules in human organism are still have to be answered and require large-scale and labor-consuming research efforts.

Along with spherical food additive carriers, a unique tubular milk protein was described [33]. It was found that the milk protein α-lactalbumin in certain conditions can undergo self-assembly to form tubular nanostructures. Such tubes are thousands of nanometers long, their diameter is 20 nm, and the inner cavity diameter is about 8 nm. Such structures are formed in several stages. At the first stage α-lactalbumin is partially hydrolyzed under the action of a protease from *Bacillus licheniformis*. Therewith, along with other components, several derivatives with molecular masses varying from 10 to 14 kDa are formed. This mixture in the presence of calcium ions self-assembles into a helical tube.

These tubes exhibit unique properties. First of all, they are highly resistant to external actions. In particular, they can withstand heat treatment at 72°C for 40 s. They are also resistant to freezing and drying. Moreover, the α-lactalbumin nanotubes are fairly stiff: Their Yuong's modulus is about 0.1 GPa, which is much higher than in whole living cells (10^{-2}–10^{-4} MPa) or casein micelles (10^{-1} mPa). In was found possible to cut the nanotubes, punch holes in their walls, or cut-out nanotube fragments. The nanotubes filled with biologically active components hold much promise as carriers for the delivery of such substances to the body.

One more practically important property of the α-lactalbumin nanotubes is their reversible assembly–disassembly, which allows controlling this process in the body or food products. The disassembly starts at the nanotube ends and is induced by decreased Ca^{+2} concentration or varied pH. Thus, the assembly–disassembly process is fairly easy to control. The disassembly processes can also be induced at pH < 3 and pH > 9, when proteins acquire an electrostatic charge. Cross-linking the nanotubes by transglutaminase or glutaldehyde enhances their resistance to disassembly.

A no less interesting property of the nanotubes proved to be their capacity for gel formation. Such gels are quite stable to linear deformation. At the same time, simply shaking a cuvette with the gel made the latter immediately completely liquid. However, when shaking was ceased, the gel structure self-recovered within a few hours.

The above-mentioned properties suggest wide-spectrum application of tubular nanostructures in food industry. First of all, they can be used as hardeners with a high protein concentration. They present undeniable interest as new-generation gelling agents. The unique properties of such gels are their controlled reversibility and absolute transparency. Finally, what is of the greatest importance, the nanotube cavities can be filled with medicines and food additives (vitamins, enzymes), which makes them candidate means for the delivery of target components to target organs in the human body and for protection of such components from untimely degradation. At present approaches to controlled opening and closing nanotube holes with lipid "caps" are being developed.

To complete the picture, we should also mention inorganic carriers for food additives [34]. The use for this purpose of elemental silicon nanopowders has been described. Such powders readily biodegrade in the intestinal tract but are extremely stable in foods and beverages. They have already been used as carriers for such bioadditives as vitamins, fish oil, lycopene, and coenzyme Q_{10}. The nutrients and medicines sorbed by the carrier acquire, due to a combined effect of the nanostructure and solid phase, kinetic characteristics favoring their adsorption in the body. Moreover, the orthosilicic acid formed by biodegradation of the carrier exerts a positive effect on the skeletal tissues.

Along with functional food additives, active effort is focused on food preservatives possessing bacericidal properties. In the first turn we should mention here technologies using silver nanoparticles [35, 36], for example, as stabilizers of vegetable juces [37]. The evidence obtained at the MSUFI shows that silver nanoparticles incorporated in custers in a micellar solution exhibit a higher bactericidal activity toward yeast cells than silver ions in a true solution [114].

Thus, the manufacture of food nanodispersions and functional food additives and preservatives is a vitally important, high-tech, and rapidly progressing field of food industry of XXI century.

A no less important application field of food nanotechnologies is nanofiltration. Nanofiltration occupies a niche between ultrafiltration and reverse osmosis, operating by pressures ranging from 5 to 50 bar [38]. Natomembranes usually cut off molecules with the molecular masses 200–1000 Da and higher. Polymeric nanofiltration membranes generally much worse pass charged particles compared to neutral molecules. They are widely used for separation of enzymes and glutamine from cultural liquor [38], aspartam production [39], fractionation of protein hydrolyzates [40, 41], separation of biogenic amines from fermented and unfermented beverages [42], production of functional food ingredients [43], and demineralization of vines, juces, milk serum, and well as production of drinking water [44–46].

A comprehensive analytical study of polymeric nanofiltration membranes for separation of organic media (production and properties) is presented in [44]. A procedure for calculating the surface interaction energy of charged particles in a dilute electrolyte solution with charged walls of membrane pores [45]. This energy determines the equilibrium distribution coefficients which, in their turn, determine the degree of membrane retention of charged particles. Modeling porous structures (membranes) in themselves was reviewed by Vasin et al. [46]. It was shown that modeling makes it possible to assess the permeability of complex porous nanofiltration membranes by introducing in the calculation of two additional structural physicochemical parameters. According to [47], fermented food prepared with a slightly salted water preliminarily passed through a nanofiltration membrane possesses excellent organoleptic properties.

Let us consider the use of nanofiltration on an example of the preparation and purification of xylose [48]. Xylose is as sweet as saccharose, but, unlike the latter, does not cause teeth caries and, therefore, is used as an alternative sweetener in confectionery industries [49]. Xylose, along with other monosaccharides, lignosulfonates, and inorganic substances, is a product of cellulose hydrolysis. Finnish researchers showed that nanofiltration is an economically competitive, less complicated, and easier realizable separation technique for xylose [48]. Using Desal-5 DK, Desal-5 DL (GE Osmonics, USA) and NF270 (Dow Liquid Separations, USA) hydrophobic nanofiltration membranes they could isolate D-xylose from cellulose hydrolysate.

Nanofiltration is frequently used together with ultrafiltration and microfiltration. For example, the isolation of a natural food dye from sweet potato could be accomplished to success by successive filtration on a cascade of membranes with pore sizes of 0.01–0.20 μm (ultrafiltration), 2–10 nm, and 1 nm [50]. Analogous cascades were used to separate carbohydrates, specifically, lactose from milk [51], as well as bacteria and enzymes in beverage production [52]. Of considerable practical interest is membrane surface modification by nanoparticles. It was demonstrated at the MSUFI that beer can be pasteurized by filtration through metal ceramic membranes with silver nanoparticles on pore surface [114].

One more promising application of nanotechnologies in food industry relates to food analysis for pathogenic bacteria [53–58]. To this end, biosensors for *Campylobacter jejuni*, salmonella, *Listeria monocytogens,* and *Escherichia coli* O157 10-20 after incubation of a food product for 24–48 h [53]. Biosensors involve pathogen antibodies bound to nanoparticles. In certain cases they allow to detect single pathogen cells in food products. However, such biosensors still remain very complex, expensive, and require a highly qualified pesonnel to operate with them in specialized laboratories.

An example of successful use of nanotechnology is provided by the development of an amperometric biosensor with gold nanoparticle-modified electrodes for the determination of the polysaccharide inuline in foods [56]. The choice of electrodes with gold nanoparticles applied on their sufrace is motivated by the fact that the surface should ensure preservation of the processing properties of immobilized biomolecules and good performance of the electrode.

Inuline is a key source material for flructose and oligofluctose which is a valuable prebiotic. Furthermore, inuline is a component of dietary and children's food products. Therefore, analysis of technological mixtures for inuline is a necessary operation in food industries. The analysis involves measurement of fructose formed by the enzymatic hydrolysis of inuline.

There is a multistep procedure for making such an electrode. First cysteamine is applied on the surface of a gold electrode, after which gold nanoparticles readily sorbing inuline, enzyme, and mediator for biological sensor response are precipitated from above. The final operation is fixing the enzyme and mediator by means of a cross-linking agent, glutaraldehyde, which forms a three-dimensional network entrapping and retaining the mediator. A stable-in-time multilayer electrode (service life 35 days) is thus obtained, having the inuline detection limit of 6.6×10^{-7} M (in express analysis).

A new class of ultramicroscopic protein-coated silicone nanosensors for express identification of viruses, bacteria, and other pathogens was obtained [110].

Finally, the fourth major direction in the development of nanoindustry is improvement of food packageing qualities [58–72]. Here, too, a few application fields of nanotechnologies can be recognized. One of the fast progressing fields is the modification of packaging surface with bactericidal agents, first of all silver nanoparticles. A bactericidal paper packaging for foods, cigarettes, and hygienic means (blankets, paper towels) containing 50-nm silver nanoparticles was suggested [59, 67]. A laminated packaging film made of a transparent polymer coated on one side with a silver nanolayer was developed [62]. Of potential interest is a highly bactericidal material on the basis of silver bromide nanoparticles [70]. A no less impressive result was obtained when titanium dioxide nanoparticles were introduced in an ethylene–vinyl chloride copolymer to obtain a material possessing an unprecedently high biocidal activity and photodegrading on exposure to sun light [58].

One more approach to improving the quality of food packaging involves the use of nanocomposites. Nanocomposites on the basis of dispersed clays (kaolinite, montmorillonite) introduces in ethylene–vinyl alcohol copolymers or a poly(lactic acid) biopolymer were found to improve such packaging material characteristics as oxygen permeability barrier and mechanical and thermal stability and, therewith, preserve the major characteristics of the base packaging material. There is a certain concentration range, when the composite can even preserve its transparency [65]. Montmorillonite nanodispersions were suggested as additives capable of improving the quality of biolopymeric packaging coatings on the basis of starch [68]. Clay nanodispersions are usually added at a level of 2–10 wt % [65, 69].

Quite urgent is the problem of environmental protection from the wasteful food packaging made of poorly degradable plastics. An alternative for such packaging materials is provided by materials based on such readily biodegradable biopolymers as polysaccharides, proteins, etc. However, these materials, too, generally have serious disadvantages, namely, poor mechanical characteristics and high water permeability. A solution can consists in a combination of biopolymers with silicate nanodispersions, which allows increase the durability and water permeability and decrease gas permeability of a biopolymeric packaging. The potential of such systems is indeed huge [70, 71]. A nanofiber material on the basis of starch and poly(vinyl alcohol), which has nanopores (respiratory function) and capable for biodegradation, was obtained [61].

Multilayer nylon nanocomposites are used to success in manufacturing bottles for alcoholic beverages. These materials provide protection from oxygen and carbon dioxide, maintain freshness, and preserve flavor of the product [112].

Finally, we have to mention the so-called smart packaging on the basis nanomaterials [72–75]. This term relates a wide spectrum of functional packagings for food products, beverages, pharmaceuticals, and household goods. Smart packaging preserves a product from disintegration and spoilage (prolongs lifetime), improves its properties (appearance, color, taste, flavor, etc.), actively responds to changes in the product itself or in its environment, provides consumers with information about the product (history and current state), helps to uncover the product and provides information about lid defects, evidenced the authenticity of the product, and even prevents its theft [72]. Smart packaging is capable of controllably renewing natural antioxidants and bactericides consumed on storage. However, the latter are not infrequently either too fast or too slowly released from up-to-date packaging materials [74, 76]. Before smart packagings will be widely introduced in practice, a great deal of basic research has to be done, since there is still no complete understanding of antioxidant and bactericide release processes and interrelationships between the rate of such processes and the nature of a concrete polymer. One of the ways to attacking thy problem of smart packaging is to use a mixture of polymers instead of a single polymer. This, too, opens up great persectives for nanotechnologies. In this respect of interest are cyclodextrins that are capable of encapsulating active ingredients at the molecular level. Their embedding into packaging materials allows to improve aromatic properties of beverages, slow down lipid oxidation, and suppress pathogen development [77].

Certain Safety Issues of Nanotechnologies

Safety of nanotechnologies and nanomaterials either used or recommended for use in food industry is the subject of hot discussions and puclic concern [1, 6, 8, 9, 12, 78, 115–117]. Actually, nanomaterials on the basis of carbon, silver, silicon, titanium dioxide, and zinc oxide show properties untypical of their macro- and microsized analogs. This can entail predictable risks. For example, aluminum oxide is widely used in dentistry due to its high inertness but can self-explode when ground to the nano level. At present Al_2O_3 is studied to find out whether it is useful as a component of rocket fuel [15a]. Thus, very little is still known on potential threats for a person dealing with newly developed particles, materials, and instruments [1, 78].

In a general case, the health impact of nanoparticles (nanotoxicity) depends on their size, mass, chemical composition, surface properties, and aggregation modes [79, 80]. Of importance are also the degree to which nanoparticle can penetrate in the body, penetration sites, and possibility of accumulation. The following criteria are suggested for nanotoxicity assessment [1, 81]: exposure time; intrinsic toxicity of nanoparticle material; possibility of extrapolation nanotoxicity assessment using existing databases for macromaterials; environmental behavior, ability for transformations and migration; regenerability and average stability.

Nanoparticles of 50 nm can penetrate to cells, of 70 nm to lungs, and of 30 nm even to blood and brain cells [1, 15a, 82]. Thus, they can migrate from lungs to the circulatory system, distribute over the whole body, and further enter some organs (liver, spleen, marrow, heart, brain, etc.) [12, 83]. As far back as 1994, Oberdörster et al. discovered that inhaling virtually insolubel and nontoxic titanium dioxide nanoparticles 20 nm in diameter can lead to pulmonary attacks [84]. Titanium dioxide nanoparticles are also capable of penetrating through skin into cells and initiate formation of free radicals that cause intracellular damage [85]. According to [86, 87], long-term contact of living organisms with an environment containing nanocarbon aerosols cause lung inflammation, whereas diffusion of carbon nanoparticles from lungs to the circulatory system leads to vascular diseases.

In view of the possible negative impact, nanoparticles can be considered as potentially hazardous materials [16]. The Chemical Safety Committee of the Americal Chemical Society have developed safety guidelines on handling nanomaterials (http://membership.acs.org/c/ccs/nano.html). At the same time, the information on negative effects is still scarce and many statements on this issue are obviously speculative in nature [88].

In our opinion, nanofood should be differentiated in that it contains inorganic nanoparticles introduced in a foo product as an additive (zinc oxide, selenium, elemental sulfur) or natural ingredients dispersed in nanoparticles (propolis, green tea, caritenoids, etc.). As mentioned above, a lot of food systems inherently contain nano- and microobjects (globular proteins, oligosaccharides), and their dispersion should not entail any negative consequences. Moreover, dispersion of inorganic substances which are foreign for living organisms may lead to unexpected results. In particular, it was shown that toxic substances when enter the body in the nanodispersed state not always exhibit toxicity. For instance, elemental nickel gets much less toxic when its particle size reaches the nano level [89]. It was also shown that carbon nanotubes introduced intratracheally in laboratory mice cause death, whereas the same nanotubes with nitrogenous compounds applied on their surface are much less toxic, which can be used to develop new food packagings [90].

Public, Legal, and Legislative Facets of Food Nanotechnologies

The public, legal, and legislative problems of food nanotechnologies inevitably arise when a food product marked “nano” enters the market. These problems are the subject of research and discussions [1, 91–97, 115–119].

Among countries whose consumer market has products marked “nano” the leading position belongs to the USA (126 items), followed by Asian Region (42) and European countries (35), and the production of all other countries is represented by as little as 7 items [1, 16]. Therewith, some Asian companies put the mark “nano” exclusively for marketing purposes. It is usually reported that finely dispersed ingredients are better digested, possessing new qualities and functions, but actually they meet the severe criteria for nano products in terms of neither size nor function [1].

It is only in a few countries, specifically the USA, Great Britain, Japan, and China, legislation regulating, to a greater or lesser estent, food nanotechnologies are available. Thus, in the USA these are the Toxic Substances Control Act, Occupational Safety and Health Act, Food Drug and Cosmetic Act, and principal environmental protection laws. At the international level, such acts should be developed by the Codex Alimentarius Commission, but still (by the end of 2006) no documents regulating application of nanotechnologies in food industry and agriculture have been issued [1].

Therefore, the most comrehensive review on this issue [1] analyzes local interpretations of the terms nanotechnology and food nanotechnology. Let us consider some of them.

The US National Nanotechnology Initiative (NNI) defines the nanotechnology as "the understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications" (http://www.nano.gov/html/facts/whatIsNano.html). The US Food and Drug Administration (FDA) gives a slightly different definition of the nanotechnology, including: (a) research and development of technologies at the atomic, molecular, and macromolecular levels within the 1–100 nm size range, (b) creation of structures, apparatuses, and syatems possessing new properties and functions due to their small size, and (c) ability to create and manipulate materials at the atomic level (www.fda.gov/nanotechnology/faqs.html).

As readily seen, these definitions are fairly general and relate mostly to non-food materials. It is still unclear whether such definitions apply to nanofood. Note that the FDA considers the existing drug testing protocols quite suitable for nanomaterials, and, therewith, size is not taken into account as an essential factor until a concrete new product is found to pose health threat.

In the European Union, too, regulatory documents, protocols, and definitions are under development. And here fairly strange circumstances arise. Thus, any chemical compounds in the nano state is recommended to be taken as a completely new product subject to large-scale testing, even though its macro form is safe [93, 94]. From this it follows that any new nano product canot be allowed to enter the market without stringent safety tests. At the same time, the very interpretation of the term "new nano product" cannot be considered noncontradictory. In particular, all nanomaterials, depending on their production way, can be divided into two categories: existing and new. The first are produced by dispersing a macro product, while the second are formed by atomic or molecular aggregation [95]. A paradoxical situation therewith arises, when titanium dioxide which gains in toxicity when dispersed to the nano level will be considered as an existing product, and no certificates for its nano forms will be required. By contrast, fairly "harmless" fullerenes formed due to aggregation of several tens of carbon atoms will be considered as a new product subject to certification [93].

There is also active effort on the regulation and standardization of nano products in China and Japan [1].

It should be noted that in most countries major attention is focused on nanofood itself, but, according to estimates in [1], nanotechnologies, too, will come foreground in the nearest future.

Official certification of nanoproducts at the state level traces back to the development of the Nano Mark Certificate in Taiwan in 2005. The production having such mark should meet with garanty at least two requirements: (1) One of the dimensions of the principal product or its additive should fall the range 1–100 nm; (2) nano products should exhibit radically new consumer attributes or improved characteristics specifically because its size fits the above range. Up to January 2007, there were only three product categories certified in the described system: antimicrobial photocatalytic fluorescent lamps, antimicrobial photocatalytic tile, and photocatalytic coatings for deodoration. The major ingredient of all these products is nanodospersed titanium dioxide, and no one of these products belong to food. However, the range 1–100 nm will probably also be applied to foods.

In Taiwan, a non-governmental association "Nano Manufacture and In-spection Union" was established in 2006 (http://www.nanounion.com.tw). At present this association is developing a protocol for testing dispersed pearl powder, a traditional Chinese Medicine product, which is advertized as a nano product. Therewith, the range chosen here for the nano size criterion is 100–500 nm. Thus, even in such a small country as Taiwan, there is a controversy between state and business concerning what to take for nanoproducts.

Passing to an analysis of the situation with food nanoproducts, we would like to mention the following issues. On the one hand, the use of nanotechnologies in food and food packaging industries is steadily growing. On the other hand, the obligatory requirement to mark such products, as is the case with genetically modified products, is still lacking. As a result, no regulatory stanards are still available. One can face different marks in the food market, say "nanofood" or "ultrafine food." Therewith, it is hard to find out what products can indeed be classed with nano products. West European consumers are more informed and demandive, and the rule for declaring new products are more stringent. Therefore, only few producers mark their goods "nano product" or "nanotechnology product." This information is safer to keep in secret. Obviously, there are much more goods containing nano components than this is officially declared. Quite a different situation is characteristic of Asian countries. Here the mark "nano" is very popular and favors better marketing of the product. Profiting by the lack of stringent criteria, producers mark "nano" even those products that by no means fall into this category. This picture is especially characteristic of China, Hong-Kong, and Taiwan [1].

In the absence of clear understanding of risks associated with nanofood, clear definitions for the term "nanoproduct," public debates, and risk assessments, a real threat arises that nanofood will be quite difficult to enter the market, and the food industry will never take avantages offered by nanotechnologies: Legal aspects can presently play the role of a brake. Thus, we consider of urgent to develop a system of standards and rules for detailed and comprehensive regulation of nanofood production. This system should provide clear definitions, standards, analytical procedures, safety assessment rules, and guidances for introducing the mark "nano" in good labels.

Real and imaginable advantages and disadvantages of food nanotechnologies will probably be debated for a few decades. Regardless of the fact that at present no evidence for the negative impact of food nanothechnologies is available, we consider it expedient to play safe and to put the introduction of nanotechnologies under control. This task is consistent with the "Development of the Regulatory and Methodical Basis and Control Means for Handling and Safety of Nanoparticles in Agriculture and Food Products and Packaging Materials" Program initiated in November 2008 in the framework of a Federal Targeted Program. To implement this project, the MSUFI will establish the first analytical reference laboratory for control of nanomaterials in food products. First publications on the metrology of food nanosystems have appeared [120].

At the same time, the regulation of the application of nanotechnologies in food industry should favor rather than hinder this process. In developing standards and definitions, a "golden mean" have to be found between too stringent and too liberal approaches.

CONCLUSIONS

In general, the preparation for introduction of nanotechnologies in food industry proceeds at a fast pace. A leader in terms of the quantity of marketed food products lebeled "nano" is the USA, whereas China and South Korea are leading in terms of the quantity of patents. However, inspite of large-scale research effort, most developments are still at the stage of laboratory experiments and far from being introduced into practice. In particular, nobody has still managed to fill protein nanotubes with an active ingredient and to test their transport characteristics. At the same time, there is no doubt that most of these developments hold great promise.

In selecting material for this review we experienced a sharp deficit of information but tried to cover as wide range of problems as possible: from properties of food nanodispersions to their toxicology and from definitions and certification problems to assesment of the market of food nanoproducts. The present review is the first attempt to systematize and summarize the information accumulated over the past years. Unfortunately, for the reasons of space, we could not consider in detail the methods for manufacturing food nanodispersions. For information on this subject, see [14, 19].

ACKNOWLEDGMENTS

The present review was prepared with financial support from the *Nanoindustry Infrastructure Development* in the Russian Federation for 2008–2010 Federal Targeted Program in the framework of the *Development of the Regulatory and Methodical Basis and Control Means for Handling and Safety of Nanoparticles in Agriculture and Food Products and Packaging Materials* Project (project no. 2008-3-3.1-065-008).

The authors express their gratitude to the Honored Professor of the MSUFI, Rector of the University of Oulu (Finland) Lauri Lajunen for the presented possibility to use the library fund in the framework of the bilateral agreement on collaboration.

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