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The nanostructure's management is the basis for a functional fatty foods' production

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Abstract

For the first time the functional types of butter with herbal supplements (HS) are developed. The effect of HS on micro-and nanostructure of developed types of butter was studied. It was established that the introduction of HS reduces the value of nanostructure's elements of butter in a 5 - 25 times. The nature and properties of HS influence the formation of the butter's nanostructure, the architecture and morphology of its nanoelements. According to comprehensive studies it was found that the decreasing of the size of butter's nanostructure's elements improves the structure, texture and rheological parameters of butter - it increases the thermal stability and plasticity, the ability of the structure to retain the liquid phase of fat and a structure's connection, prevents the formation of layered and brittle consistency of butter, promotes the formation of coagulation-crystallization structure dominated by coagulation, inhibits microbiological and biochemical spoilage of butter. According to the results of clinical trials and the conclusions of the Ministry of Health developed the kinds of butter are recommended to use in health care and dietary nutrition. Based on the results of the study it was recommended to use HS to control the formation of the butter's nanostructure and its quality, physical and chemical properties.

Keywords: functional food products; butter; nanostructure; nanoelements; herbal supplements.

1. Introduction

One of the main problems of the modern food industry is to create functional food products that will not only satisfy human needs for essential nutrients and energy, but also have health, preventive and curative properties. Functional properties can be given to traditional foods by enriching them with biologically active substances and thereby making medicine from food, and medicine – is going to be a meal, as it was recommended by Hippocrates.

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At the 25 and 26 International Dairy Congresses scientists paid attention to the creation of functional foods and developing their concept, which includes the main provisions: the development of functional foods with regard to the nature and specificity of ethnic cuisine, familiar to the population; enriching food products with functional components must have nutritional and medical justification; dairy products can be classified as functional only by the Ministry of Health on the results of clinical studies.

Butter has a significant place in the diet of the population in Ukraine; it is included in the diet of health and child care centers, which makes the feasibility of butter's establishing a functional purpose. In recent years, the physicians and food industry workers pay attention to the use of herbal supplements that have health and medical-preventive properties. This indicates the feasibility of their usage in the development of functional types of butter. Nowadays, the world's leading scientists connect the creation of functional materials with nanoscience and nanotechnology. A number of scientific conferences held in New York, Paris, Tokyo, Seoul, Los Angeles, and Russia were devoted to this problem. It was noted that nanotechnology's creation is the priority areas of science and food industry. Nanotechnology is based on the ability to create a nanostructure materials with desired properties, which are regulated in the nanoscale range (1 nm = 10^{-9} m). Therefore, today it is especially important to study the formation of the nanostructure of food products. The implementation of nanotechnology requires deep knowledge of nanostructured systems' functioning (butter is such a system) and processes of their molecular self-organization.

We were the first who developed the functional types of butter with herbal supplements (HS) such as polysaccharides, pectin and inulin cryopowders of red beets, carrots, black currant's buds, topinambour, which have the properties of surface-active substances (SAS). The purpose of the work is study the effect of plant food additives on the micro-and nano-structures and physicochemical properties of functional types of butter.

2. Materials & Methods

There are the results of a study of the functional types of butter with apple pectin (BP), cryo powder of red beet (BB), the control sample was butter without additives (BC). The samples of fresh prepared butter (BC_f, BP_f, BB_f) and butter stored at 5 °C (BC_5, BP_5, BB_5) and at -18 °C (BC_{-18}, BP_{-18}, BB_{-18}) for 6 months were studied. Micro-and nanostructure of butter was examined by scanning electron microscopy, which is the most effective way of getting images of the sample surface and determining the size of nanoparticles [1]. To prepare the butter samples for the study we used a frosting-break technique that allows capturing the true structure of the butter. Structure of butter was fixed at the temperature of its storage.

3. Results & Discussion

Fat phase in the structure of butter is represented by two kinds of structures: continuous emulsion water/fat and the fat globules with d ≈ 1-8 micrometers, distributed it in. We were the first who studied the nanostructure of butter [2-4]. The results showed that the butter is nonostruktured nanocrystalline material. Electron microscopy studies showed that the microstructure of BC_f consists of a continuous fat phase, in which there are the dispersed droplets of the plasma with a diameter d ≈ 1 ... 10 micrometers and there are distributed single partially destroyed fat globules of d ≈ 1,5-3,5 micrometers (Fig. 1). Interglobular structure contains a number of crystalline layers of 1000-2600 nm, their high is a 30-100 nm. They consist of glyceride monomolecular layers of thickness ~ 5 nm.

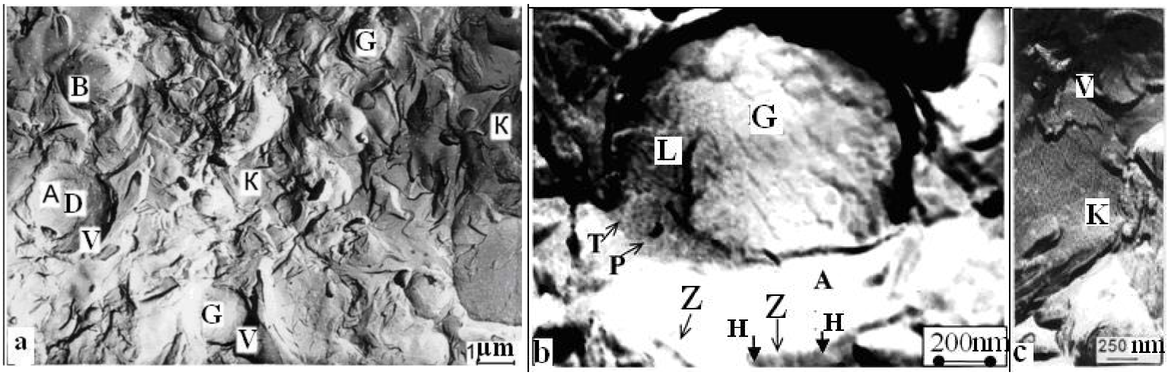

Fig..1 Micro-and nanostructure BC_f (a) and its fragments (b, c): B, G, D - fat globules; K - crystalline layer, A - surface amorphous layer, V - layer of the aqueous phase, L - lamellas , Z - rough surface rupture, P - nanobumps, T - tubular nanocrystals, H – nanocapillarie.

The crystalline aggregates formed from the individual crystal layers. Superficial layers of fat globules, crystalline layers and amorphous aggregates are composed of fatty phase, which is formed by cell nanostructure which we can see on the surface of the fat globules **G** (Fig. 1, b). Crystalline layers have different nanostructure (lamellas), formed of alternating lamellae of glycerides crystalline nanograins with d ~ 5 ... 10 nm and the lamellae of the nanoparticles of moisture with d ~ 3 ... 10 nm, or from layered tubular crystals. Phase boundary of the crystal layers and units have a rough surface with a layer of aqueous phase in the form of nanofilms or quasi-one-dimensional chains of nanodroplets, located between the roughness and in the nanopores of a butter's fatty phase. We first identified the presence of nanopores in the structure of milk by locally sensitive method for the electron-positron annihilation [5]. Nanocapillaries **H** are formed from nanopores parallel to the crystal layers. The aqueous phase diffuses on the nanocapillaries, which proves its continuity in the butter on the nanoscale.

In the BC_5 there is the division of the crystal layers of units on the multifaceted nanoblocks with a size of 300 ... 1000 nm and a height of 30 ... 80 nm, on the surfaces of their division the nanocapillaries **H** that contain nanoparticles or films of the aqueous phase are formed. While butter storage with the temperature -18 ° C (BC_{-18}) an extremely layered nanostructure is formed (Fig. 2), that is due to its self-organization.

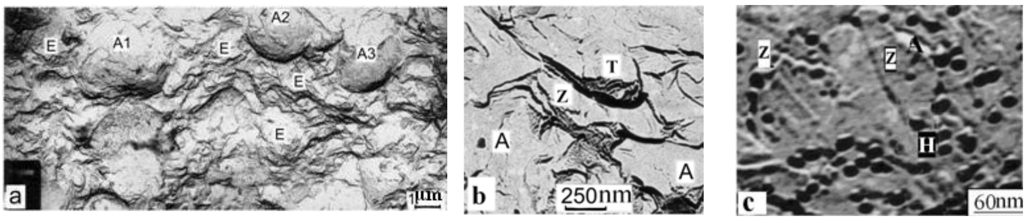

Fig. 2. Micro-and nanostructure of the BC_{-18}(a) and its fragments: b - amorphous-crystalline layer, A1, A2, A3 - the fat globules and their surface (b); E - crystal unit, A - amorphous layer, T - terrace, Z - rough surface section; H - moisture nanodroplets.

The mechanism of self-organization is based on the phase transformations in fat: a discrete low-melting crystallization of glycerides, glycerides redistribution in the solid amorphous and crystalline phases, and polymorphic transformations of glycerides. The surface of the fat globules, aggregates and nanoblocks has amorphous-crystalline layers. Layers of water nanodroplets (d ~ 3 ... 50 nm) are formed between the crystalline layers. The diameter of nanodroplets decreases when the distance of the layers of the initial layer formation of aggregates and nanoblocks is larger, i.e. with an increasing of fusibility of glycerides that form the crystalline layers. Electron microscopy studies showed that the introduction of small amounts of pectin reduces the structural elements of the quantity of butter to 5-25 times and is in the nanoscale range, including the 1-100 nm. Grinding mechanism is based on the Rehbinder effect and is associated with surfactant adsorption of the pectin on interphase surfaces and nanoelements' interfaces that promotes the adsorption reduction of strength of their structure and formation of micro-and nanocracks, forming a new phase.

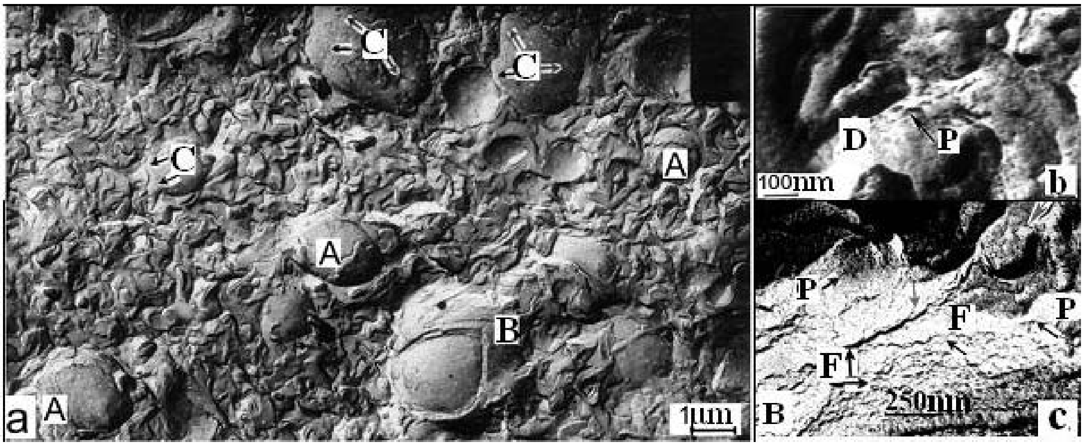

Fig. 3. Micro-and nanostructure of BP_f (a) and its fragments: b - interglobular space, c - the surface of the fat globules B: A, B, C - the fat globules, D - unit with pectin-lipid membrane, P - nanobump, F - surface fracture.

Fig. 3 shows that pectin influences the nanostructure of butter, the morphology and architecture of its nanoelements. The introduction of pectin increases the number and size of fat globules, which is connected with the formation of polysaccharide-lipid membranes on their surface. In BP_f and BP_5 the pectin-lipid layers of membranes are composed of plate-like nanocrystals, mostly rhombic shape with the parties size of 8 ... 10 nm and nanoparticles of moisture on the rough boundaries of the section (Fig. 3, c). interglobular nanostructure consists of a three-dimensional polyhedral, spherical and cylindrical aggregates and nanoblocks with a size of 100-800 nm (Fig. 3, b), which are formed on the basis of small cellular mesh three-dimensional structure of pectin solution in the plasma of butter, which contributes to a decreasing of the structural elements of BP compared to BC [4]. Nanobumps' formation on the shells of fat globules and aggregates indicates on the elasticity of pectin-lipid layers. In interglobular nanostructure of BP_{-18} (Fig. 4) the pectin-lipid layers with a thickness 10 ... 40 nm are formed, which can be attributed to the liquid crystal systems with the structural organization of the smectic phases. It contains crystalline nanograins with d ~ 40 ... 60 nm and units that have the form of a low cylinder with base d ~ 200 ... 280 nm and a layer of adsorptive bounded moisture on the lateral surface, as well as individual nano globules - d ~ 60 ... 150 nm, separated from the fat globules in which they were emerged. The nanoglobul extraction of fat globules **C** you can see in Fig. 3, a.

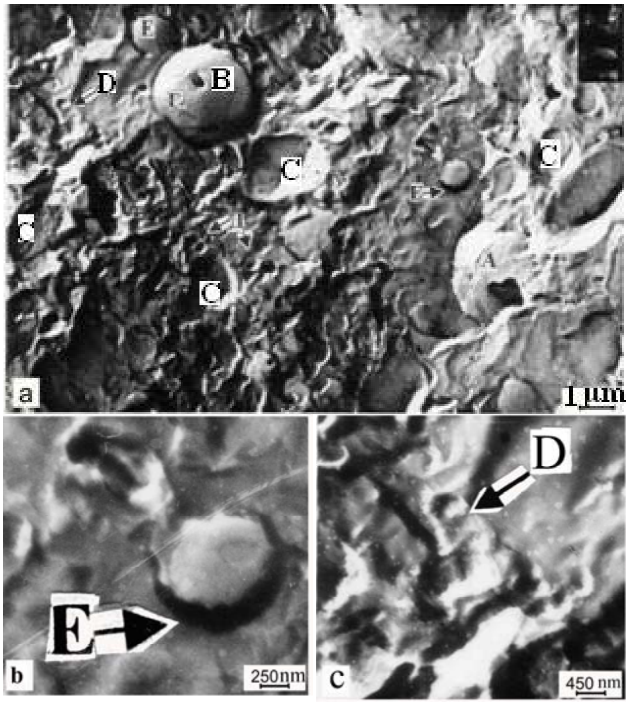

Fig. 4. Micro-and nanostructure of BP_{-18} (a) and fragments of its interglobular space (b, c): B, C - the fat globules, A – amorphous-crystalline surface layer, D - crystalline nanograins.

Electron microscopy studies showed that the microstructure of BB differs significantly from the BC samples. In BB_f it contains a significant amount of intact fat globules d ~ 1,4 ... 4,2 micrometers and crystalline aggregates with the size (300-800) x (150-400) x (100-300) nm (Fig. 5), having the shape of the polyhedra . Elements of interglobular nanostructure of BB_f and BC_f significantly differs in shape, size, morphology and architecture. In BB_f they are 5-25 times lower than in BC_f. We can see a layer of emulsion on the surface of the fat globules and crystalline aggregates in the sample of BB_f. Images show that the formation of structural elements in BB_f goes at the nanoscale in the process of self-organization of butter's nanostructure. Emulsion (solution of the components cryopowder/milk fat) is formed in the process of butter formation. In the photos (Fig. 5) there is the stage of formation and self-organization of the nanostructure of the surface fat globules and nanoelements: aqueous phase's nanoparticles, dimensional chains of nanoparticles from the aqueous phase, interfacial rough surface of their division with a continuous fat phase and nanobumps with d ~ 40 ... 100 nm. Bumps' nanostructure consists of concentric layers of glycerides' nanograins with d ~ 3 ... 6 nm and the layers of aqueous phase's nanoparticles with d ~ 3 ... 12 nm, which are heterogeneously formed on rough interfaces section, formed as a result of phase transformations in the continuous fat phase of the emulsion.

Microstructure of BB_5, stored at 5 ° C, contains fat globules that are larger than BB_f (their diameter is ~ 1,8-5,0 micrometers), crystalline aggregates of polyhedra form, cylinders and bumps. On the surface of the fat globules and aggregates the amorphous-crystalline layers are formed, there nanostructures are formed; they are such like bumps with d ~ 20-30 nm and have nanodroplets of the aqueous phase on the formation's top. Crystalline layers have a mixed structure that consists of areas with cellular and lamellar nanostructure. The latter is formed by short lamellae (60-360 nm) of crystalline nanograins and layers of nanoparticles of aqueous phase. On the shell of fat globules there forms additional surface layer, which increases their size and strength.

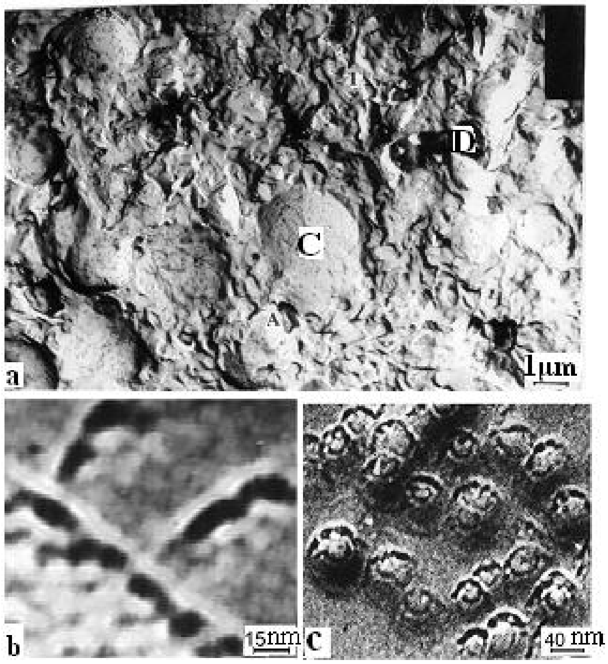

Fig. 5. Micro-and nanostructure BB_f (a) and its fragments: b - rough interphase interface of dimensional chains with a fat phase; c - nanostructure bumps, on the surface of the fat globules B; C – fat globule, A - amorphous layer, D – particles of cryopowder.

The nanoblocks in the shape of nanobumps (height of 400 ... 470 nm) are formed in interglobular nanostructure. This shows viscoelastic properties of BB_f and BB_5, which they get from the components of cryopowder, especially - pectin. Microstructure of BB_{-18} (Fig. 6) contains undefeated fat globules with d ~ 2,0 ... 5,0 micrometers with well-formed peripheral crystalline membranes, which have a cellular nanostructure. In the BB_{-18} the value of the nanostructure's elements decreases in 5 ... 25 times relative to the BC_{-18}. Interglobular microstructure is composed of crystalline nanoaggregates that are formed from crystalline layers with a thickness of 10 ... 50 nm, they also have a cellular nanostructure, the width of the cells is 60 ... 100 nm. Cells consist of monomolecular crystalline layers and have a convex or concave shape. They are joined on a "guide to depression," which strengthens the membrane of fat globules and crystalline aggregates. The surface layer of the cell has an amorphous state, and the crystal layers are also composed of cells, their width is 8 ... 15 nm (according to the principle of "like in like"). This indicates the hierarchical subordination of nanoelements and fractal forms in the formation of nanostructures of BB_{-18}. Cells are in the form of polyhedra and their faces are a four-, five-and hexagons (Fig. 6, c). Square faces have a crystal form of octahedra, pentagonal - dodecahedron, and the pentagonal profile with apex at the center has a form of icosahedra. It is established [6] that at the edges of nanoparticles there is an aqueous phase with d ~ 6 ... 8 nm, and at their tops there are parts with d ~12 ...16 nm. The moisture in the nanostructure BB_{-18} is distributed in the form of nanoparticles with d ~ 3 ... 16 nm, also there is moisture in the form of thin films at an interface section of the individual crystal layers and structural elements. The highest concentration of moisture nanoparticles with d~3 nm is in the amorphous layer.

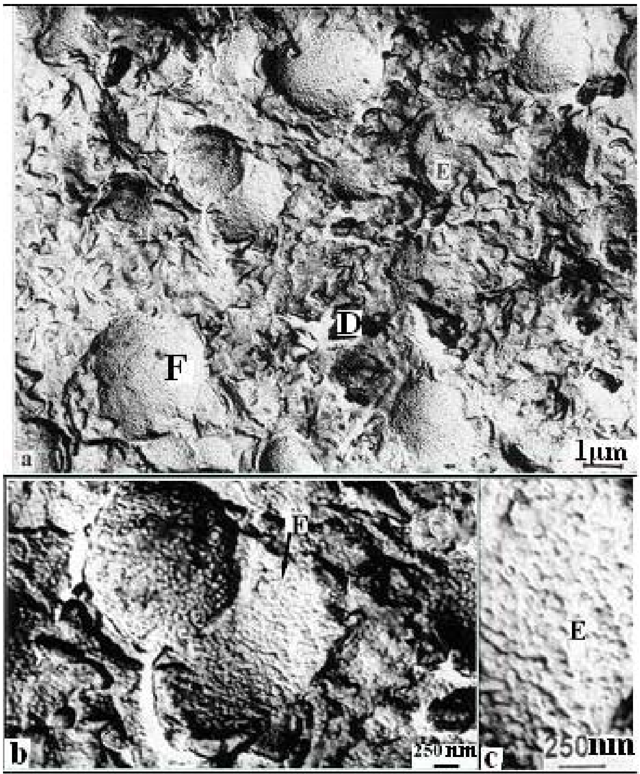

Fig. 6. Micro-and nanostructure of BB_{-18} (a) and its fragments (b, c): F - fat globules, D - particle of cryopowder, E - cellar nanostructure.

So, the results of electron microscopic studies have shown that the formation of the nanostructure of butter, the morphology and architecture of its nanoelements significantly affects the nature and properties of the herbal additive.

According to comprehensive studies it was established [2-4, 7] that the decreasing the nanostructure's elements of butter with HS improves the structure, texture and rheological properties of butter: increases its thermal stability and connectivity of the structure, as well as the ability to retain the liquid phase of fat, decreases the hardness of butter and increases its flexibility, promotes the formation of crystallization-coagulation structure with a predominance of coagulative one, changes the mechanism of destruction of the structure of butter from crumbled to viscous, which is typical for ductile systems. It prevents a defect of consistency as bedding and crumbling; simultaneously inhibits microbiological and biochemical damage to butter that increases its biological value. According to the results of clinical trials and the conclusions of the Ministry of Health, the developed kinds of butter are functional, they are recommended for usage in health care and dietary nutrition.

The foregoing indicates that the polysaccharides and cryopowders of herbal supplements are multifunctional. They not only give butter medical and dietary properties, but also contribute to crumbling of the structure's elements; their size is in the nanoscale range, including the 1-100 nm that improves the structure, texture and ability for product's keeping. It is established [8, 9] that the introduction of small doses of HS with the properties of surfactants, allows you to control the nanostructure and physicochemical and functional properties of butter. The results of the studies are used to develop a scientific basis for the formation and self-organization of butter's nanostructure with HS, which are the theoretical basis for the creation of nanotechnology food products with functional purpose that will have predetermined properties, especially butter.

4. Conclusion

1. It was established that the introduction of herbal food supplements (polysaccharides and cryopowders) reduces the size of the nanostructure's elements of butter in 5-25 times. The nature and properties of the additives significantly affect the formation of the nanostructure of butter, the architecture and morphology of its nanoelements.

2. It was established that the introduction of small doses of herbal supplements that have the properties of surfactants, are useful for controlling the nanostructure formation of butter and, accordingly, its quality and physical and chemical properties. The influence of nanostructure on the functional properties of the product was studied for the first time.

3. Theoretical data of the nanostructure's formation of butter are the scientific bases to the new direction of creation the food nanotechnology of functional products with desired properties, primarily butter.

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