

Chapter 1

General Introduction

The nanocomposite science concerning the class of composite materials, whose typical feature is nanometer size of their structural elements (metal particles, their oxides, chalcogenides, carbides, nitrides, etc.) has appeared in the last decades of twentieth century at the junction of different fields of knowledge: physical, organic, colloid, polymer chemistry, biology, and materials science. One of the driving forces of this is that extensive ways of materials science development have undergone essential depletion, giving way to searching for methods of improvement and modifying of materials properties, miniaturization of their structural elements. Along with continuous perfection of the known composites, which provide technical and economic effect due to unique combination of properties, some trends appear in development of new materials actively interacting with environment. These materials are called “intellectual”, “smart”, “wise”, “integral”, etc. due to their ability to “sense” their physical state, environmental impacts, and react in special way to these “sensations”, i.e. self-diagnose nucleation and growth of a defect, make its correction, and stabilize a material state in critical zones. Due to variety of properties of the “intellectual” materials they can be used in different structural elements, for example in air-space technique (cases, fairings, compartments, frictional units, etc.), and they will allow one to control and predict a state of different articles and structures in a required time and even in difficultly accessed parts, to improve significantly life time of the systems, as well as reliability [1].

Successes in chemistry and technology of nanometer materials science have brought to outbreaking development in many fields in science and industry. General laws of formation of nanoparticles, methods of their optimization and manipulation, special methods of fabrication of articles based on these materials, main fields of their applications have become clear. It follows from expertise of specialists that in the following 20 years 90 % of contemporary materials used in industry will be replaced by new ones, in particular, “intellectual”, which will allow development of structures and devices, and will provide technical progress in twenty-first century. We shall highlight three main advantages of the nanocomposites as compared to conventional composites: they have lighter weight due to lower content of a filler; lower cost due to

less amount of a filler, improved properties (including mechanical, thermal, optical, electric, barrier, etc.) [2]. While having higher operating characteristics, they envisage weight reduction of articles by 30–50 %. Under given operating conditions and increase in loading an element based with the same weight on these materials provides increment in rigidity by 60–80 %, increment in reliability by 20–25 %, and increase in guarantee term by 60–70 % as compared to conventional composites. The key advantage of nanocomposites is that a possibility of improvement of their properties without change in technological conditions, and procedures of surface modifying can be quite easily integrated into the technological process. Providing that, the surface treatment methods are preferred, because often particularly the surface characteristics determine quality of a whole article [3]. Besides, with account for economic aspects, modifying of a surface is more attractive as compared to the ways of change in bulk characteristics of materials and articles. This approach makes it possible to use most efficiently combination of properties of a basic material and the modified surface layer or modification of articles.

Though definitions “nanocomposites”, “nanomaterials”, “nanofillers” used for description of materials are introduced relatively recently, these materials exist for a long time. For example, soot is used as reinforcing filler for rubber since 1904. Roman masterpiece of fourth century known as Lykurgus cup is made of glass with suspended nanometer (~ 70 nm) gold and silver particles in the ratio 3:7. The cup shows unusual properties of dichroism, which appears in green in reflected rays and in red in transmitted light [4]. It has recently been shown that Maya blue dye used from ancient times is nanostructural hybrid material: needle-shaped palygorskite crystals $H_{10}Mg_2Al_2Si_7O_{24}\cdot 4H_2O$ form superlattice with the period 1.4 nm, and Mg crystal nanoparticles are impregnated in this matrix. Beautiful blue light appears only in presence of Mg nanoparticles, indigo molecules, and palygorskite superlattice. Sizes of the nanoparticles are also important, in many cases it can be found by a change in color of solution. For example, in the systems with Faraday red gold sol stabilized with formaldehyde color of the solution changes from red to blue due to aggregation of the nanoparticles [5]: red (Au particle size is 23.7 ± 0.9 nm), violet (24.3 ± 0.7 nm), lilac (32.5 ± 1.4 nm), and blue (33.2 ± 2.0 nm). Since 1940 SiO_2 nanoparticles are widely used in many articles, and since 1960 metal nanopowders have been developed [6]. In 1989 [7] it was shown that compacts of fine crystallites (~ 10 nm) have unique physical properties, which can be used in engineering. The term “polymer nanocomposite” has a clear definition. Nanocomposite is a product of combination of at least two different materials with a distinct interface boundary; at least one of them should have nanometer sizes (1–100 nm) no less than in one direction. This also concerns distances between layers and nets formed by polymer and inorganic ingredients [8]. In other words, polymer nanocomposite is a two-phase material in which organic and inorganic phases are mutually distributed at the nanolevel. Although dimensional range of structural elements of the particles is to some degree conditional, it is comparable with correlation radius of one or other chemical or physical phenomenon (for example, free path of electrons, phonons, coherence length in a superconductor, sizes of magnetic domain, or nuclei of a new phase, etc.), in these systems so called dimensional effects manifest themselves. Nowadays many

materials can be obtained at the nano-level with usage of high-energy impacts, electric deposition, spray-pyrolysis, gas phase, vacuum and sol-gel technique, hydrothermal and aerosol processes, intercalation, and micellar templates, chemical reducing agents, etc.

Hybrid organic-inorganic nanostructural materials occupy more and more free space remained between inorganic and polymer chemistry and biology, progress in this area depends significantly on competence of materials scientists for development of contemporary nanomaterials, the task is not only in creation of nanostructures, and in reaching the best knowledge of properties of these ensembles, but in processing and controlling of their assembling in any form, in knowledge of its structure at different spatial levels. Thus, the main key to development of new hierarchically organized hybrid materials is not only in control of the origin, but also of sizes of the nanoparticles, availability of interior interfaces of a nanocomposite. Despite variety of methods of production of nanocomposites it has been found that all versatility of synthetic approaches to preparation of nanometer particles and their self-assembling can be reduced to two principally different ways: “top-down” (descending way) and “bottom-up” (ascending way). The first of them appears in various ways of grinding of coarse particles to nanometer, the essence of the “bottom-up” way is in assembling of nanoparticles from different atoms (or ions with the following reduction) to nanoparticles of a given size in presence of polymer matrix (or its precursor). The latter method, which is considered in this monograph, is more widely used due to its variability and potential abilities than the dispersion method. A researcher can predict in advance properties of obtained nanoparticles: he can choose a content and properties of initial components, stabilizing agents, can estimate their role, predict conditions of nucleation and growth of the nanoparticles at each stage, thus constructing designed materials. Properties, which can be reached in these materials, depend strictly in synergetics between organic and inorganic origin of components and are, undoubtedly, defined by nano/microstructure and degree of its ordering.

In turn, formation of metal-polymer nanocomposites can be implemented by two main methods: “wet” and “dry”. The first of them is characterized by one component (or at least at one stage of the multistage process) being used as a solution or dispersion in a solution. The dry method is characterized by entire elimination of a solvent from the technological process. Due to poor solubility of the components, and in some cases chemical instability of them, and due to difficulties of the following removal of some solvents, including ecological aspects, the “dry” method of producing metal polymer nanocomposites is preferred.

Most scientific works are focused on synthesis of polymer nanocomposites and studying of their physical and mechanical characteristics required by operating conditions. Nanocomposites based on thermoplasts or reactoplasts reinforced by nanometer particles or intercalated layers, are actively studied. Nanofillers can present in significant amounts in the interface zone providing strong interaction due to interatomic binding forces: Van-der-Waals in chemical (metal) bond, while in the case of micron particles the fillers concentration in a transition layer is considerably lower. Realization of chemical bond in a contact is a thermomechanical activation

process, which goes due to fluctuations of groups or individual atoms in a solid phase topochemical reaction. A structure of semi-crystalline polymer matrix depends not only on prehistory of the treatment, but on presence of nanoparticles having effect on kinetics of crystallization and final morphology. Understanding of the composite reinforced by nanoparticles phenomenon requires profound studies, and will advantage reinforcement of more complicated anisotropic structures in polymer composite systems.

Though many fields of their application are based on properties of individual nanoparticles (sensors, medical diagnostics, homogeneous catalysis, etc.), there are many important fields in which self-organized nanoparticles are needed (nanoelectronics, optoelectronics, heterogeneous catalysis, etc.). The same also concerns bio-inspired strategies of imitation (“simulation”) of growth in biomineralization processes, development of innovated multi-scaled structural hybrids (from nano- to multimeter scales) hierarchically organized at the level of structures and functions.

Historically reduction of metal ions to nanoparticles is related to Faraday, who discovered chemical reduction of gold ions in presence of gelatin in 1857, which has still a great value, another important stage in development of this approach is connected with Turkevich name [9], who for the first time realized reproducible synthesis of Au nanoparticles (20 nm) via reaction of cytrate reduction of $[\text{AuCl}_4]^-$, etc. [5]. Among the most widely used contemporary methods there is “diborane” method of production of $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ (1.4 nm) nanoclusters stabilized with phosphine ligands, the method of reduction by alcohols (so called polyolic process) with usage of polyvinyl pyrrolidone, polyvinyl alcohol, etc. as stabilizers.

On the whole, synthesis of nanoparticles of a given diameter with almost monodisperse size distribution and low degree of agglomeration is limited by two boundary conditions: precise control over nucleation and growth of a nucleus and efficient suppression of agglomeration. The most important task of increasing resistance to aggregation of highly reactive nanoparticles with highly developed surface is their surface passivation by different stabilizers. At early stage of the studies low molecular organic compounds (carbonic acids, alcohols, amides, etc.) and natural polymers (gelatin, cellulose, starch, gummiarabic, agar-agar, etc.) were used. A new stage in materials science deals with usage of synthetic polymers: a possibility of steric stabilization is caused by the fact that spatial dimensions of even relatively low-molecular compounds are comparable with the radius of action of London attraction forces or even greater. On the one hand, regulation of stability of nanoparticles by polymer surfactants is the most important part of the polymer colloids modern science which studies laws of formation of disperse systems with highly developed interface surface, various surface phenomena on interface boundaries and adsorption of macromolecules from liquid media on solid surfaces [10]. As a result of steric stabilization the nanoparticles will be surrounded by a protective barrier, a continuous layer of solvated polymer links, and a colloid system becomes unlimitedly stable as long as the protective layer remains undamaged. In the systems with high concentration of disperse phase thermodynamically stable spatial structures form spontaneously as a result of particles

linking in dispersion medium: liophobic nanometer particles are allegedly arranged in a web of protective polymer. On the other hand, at this stage already the main demands to structuring and optimizing of metal polymer nanocomposites can be taken into account. Chemical reduction of metal ions in water and non-water solutions in presence of polymers playing a role of stabilizing matrix and/or reducing agents is the most widely spread method in strategy of condensation synthesis of nanocomposites. Very attractive are the methods simultaneously using a stabilizing polymer ligand also as a reducing agent. Advantages of this approach are obvious. It is replacement of some toxic reducing agents, lower cost, higher efficiency, etc. Most often for these purposes are used polymers whose molecules contain a great deal of different functional groups (polysaccharides [11], humic substances [12], peptides, etc.). Promising systems for these purposes are block-co-polymers, polymer linked hydro-gels working as nanoreactors in synthesis of colloid metal particles.

One of universal condensation methods of fabrication of nanoparticles stabilized by oxide inorganic or polymer matrix is sol-gel method based on hydrolysis and condensation of metal alkoxides including different modifications of the method. A special interest is in materials, which are obtained by combination of sol-gel chemical methods with aerosol and spray processes, combination of reactions of polymerization and sol-gel synthesis in which inorganic phase, monomers and polymer links are captured inside oxide net. These self-organizing systems are characterized by strong interface interactions between inorganic and polymer components, they are convenient methods for preparation of organic-inorganic nanocomposites of different types. Polymer-inorganic materials in which nanoparticles can reach 10 nm have high mechanical strength and thermal stability. They have already found their place in various contact lenses, optical wave-guides, printing lithography, heat-resistant coatings, memory and printing units, chemical filters, solid electrolytes, biosensors, semiconductors, catalysts of different reactions, etc. The sol-gel process is very flexible and versatile by types of possible reaction products, motivation of this direction is structuring at the stage of fabrication of materials with given properties, in the recent years special attention has been focused on composites based on heteroelemental ceramics.

The methods of production of hybrid nanocomposites from polymer solutions and *in situ* polymerization in combination with delamination and exfoliation, special type of topo-chemical reactions were discovered in the mid of the last century. In early 1990s a convenient method of their fabrication was obtained on example of PEO (polyethylene oxide) and MMT (montmorillonite), which advantageously demonstrated intercalation process in a polymer melt and potential applications of the formed products in solid phase electrolytes of recharging lithium accumulators.

However, a promising commercial strategy in this problem formed after a team of researchers from Toyota had found unprecedented strengthening of mechanical properties of polymer layered nanocomposites based on nylon, which had extremely big surface contacts of ingredients and high aspect ratio reached in intercalation/exfoliation process, and high homogeneous dispersion of silicate

plates in polymer matrix. These functional materials relate to nanocomposites, on the one hand, because of nanometer (1–5 nm) galleries of layered silicates, distances between nets and layers formed by polymer and inorganic ingredients, and, on the other hand, because of sizes of exfoliated fragments. A polymer is integrated into interlayer space of a smectite by penetration from a solution/melt with the following delamination and exfoliation with *in situ* formation of mineral nanoparticles, which are individually distributed in the polymer. Exfoliation is accompanied by formation of monolayers of nanometer thickness with high shape anisotropy. Thus, in this process formation of three main types of hybrid phase composites is possible: microcomposite with separated phases (traditional material), intercalated (including a flocculated one), and exfoliated nanocomposites. Intercalation of organic ingredient in inorganic materials with limited interlayer space, which preserves a layered structure, is, on one hand, a perfect way of structuring of organic-inorganic ensembles, and, on the other hand, proposes additional possibilities for studying of physical-chemical properties of these systems. Nanocomposites of intercalation type based on polyamides are of great interest due to their special properties and they are used as structural, flame-resistant materials; their enhanced barrier characteristics, chemical resistance, low penetrability for solvents, flame-resistance attract interest not only from scientific but from industrial point of view. The driving force of intercalation process is a decrease in free energy of a system: enthalpy changes due to intermolecular interactions, while entropy changes due to configuration interactions, and enthalpy is a dominant factor. Special place have *host* lattices with electron conductivity (semiconductors based on layered metal oxides, their chalcogenides, etc.), which undergo redox reactions with electron or ion transport causing substantial change in physical properties during intercalation.

Typical methods of production of intercalated composites, which are analyzed in this book, can be reduced to *in situ* polymerization (solution mixing); mixing in suspension, latex compounding, and direct intercalation in a polymer melt (reactor mixing). The simplest methods of intercalation of polymers into inorganic structures are one-staged emulsion and suspension polymerization, interlayer blocked radical poly- and co-polymerization of traditional monomers in presence of different organophilic minerals. A special place in this problem have orientation control of a guest-molecule in intercalation system of a host, inter-lamellar catalytic, oxidizing-reduction polymerization, intercalation assembling, reactor mixing, etc. Architecture and morphology of intercalated nanocomposites are studied in detail. Many original approaches are developed for obtaining of nanocomposites based on epoxy resins and layered silicates, a balance between intercalation and solidification rates is optimized. However, many problems of intercalation chemistry of reactoplasts are yet to be solved. Hybrid self-assembling nanocomposites formed as multilayers are developed substantially; very different approaches to layered assembling are realized. This strategy allows fabrication of very different combinations of materials of semiconductor metal-insulator structures with nanometer sites and unusual properties, which is favored by a close contact between components and strict molecular ordering. And finally, a special attention is attracted to

hybrid nanocomposites with periodic nanostructure of semiconductors based on dichalcogenides of metals of MS_2 type. They have special optical, electric, and other properties making them promising for applications in microelectronics.

Intercalation chemistry has a great potential for structuring of hybrid polymer-inorganic nanocomposites, which is far from its realization, and this is a reason for intense development of research work in this field.

Many-sided, convenient and well-reproduced method of formation of nanocomposites is thermolysis of suitable precursors. Under certain conditions this process is ecological and easily controlled. One of practical directions of pyrolysis is polymer waste utilization. Its most interesting application is production of carbon nanomaterials, various ceramics, nanocomposites with “core-shell” structure. On the other hand, thermolysis is a complicated process in which all spectrum of chemical transformations of polymers takes place: destruction, linkage of chains, transformation of functional groups and intermolecular regrouping. At the stage of thermolysis it is convenient to integrate different dopants in polymers, including metal containing, which change mechanism of thermolysis, and bring to obtaining of a range of interesting products. The same concerns metal-forming precursors (metal containing monomers), including the ones chemically bound with polymers containing “active” functional fragments (carboxyl, amino-, amido-, imino-, nitrilo-, oxy-, and other groups). Thermal transformations of these macromolecular metal complexes have begun being studied just recently, as does thermolysis in conjugated processes, on examples of self-regulated stabilization of highly dispersion metal particles in the *metal containing precursor—monomer* system with the following polymerization and thermolytic transformations. These systems are characterized by general picture of transformations consisting of a consequence of three main different by temperature macrostages: dehydration (desolvation) of initial metal-monomers (403–473 K); the stage of solid phase homo- and co-polymerization of dehydrated metal-monomer (monomers) (473–573 K); decarboxylation of formed metal-polymer to metal containing phase and oxygen-free polymer matrix at the temperatures >523 K.

Kinetics of thermal transformations of metal polymer systems is described by macro kinetic equations with account for mechanisms of reactions (decomposition model) in low and high temperature areas (including reactions accompanying burning of polymers, components of solid propellants, polymer bindings for thermal protection of spacecrafts, etc.). These processes go with external or internal heating, either under isothermal or non-isothermal conditions in closed or open system. Depending on the solving problems, different methods of control over a degree of transformation are possible, which predetermine a choice of instrumentation for experimental study of thermolysis: thermogravimetry, linear pyrolysis, volumetry, impact of high energy irradiations, spray (spattering pyrolysis), the processes are studied in precursors and in polymer matrices, in which they are integrated. A significant interest is in mono-disperse magnetic heterostructures like MFe_3O_4 ($M = Ag, Au, Pt, Pd$), polymer-mediated thermosynthesis of multimetal alloys and ceramics, and computer modeling of kinetics of nanoparticle formation during solid state thermolysis for obtaining nanocomposites of a given content.

Gas phase methods of synthesis are based on homogeneous nucleation of supersaturated vapor and the following growth incited by encountering and condensation. Supersaturated vapor can be generated in different ways depending on chemical origin of a precursor, but most often this is realized by heating of a solid matter. Depending on a character of heating and cooling, the methods of flame pyrolysis, heating and evaporation in continuous reactors (Ag, Ga, Al, PbS, Pb, Si, Ge), methods of pulsed laser evaporation of metals in inert gas atmosphere (He or Ar) and reacting gases (O_2 , N_2 , NH_3 , CH_4) with forming of nanocrystalline oxides, carbides or nitrides, etc. Content and size of the nanoparticles in them can be controlled by change in pressure, content of atmosphere, power of a laser pulse, temperature gradient between evaporated target and a surface, on which the vapor is condensed. Due to high temperatures of synthesis strong aggregates often form, which are not easily separated to initial particles. There are also limitations to formation of multicomponent phases because of significant fraction of segregation processes at high temperatures.

Plasmochemical methods are widely used. High rates of formation and condensation of a compound and quite high efficiency are provided by plasmochemical synthesis. The main drawbacks of this method are wide spread size distribution and high content of impurities in a powder. Very fine powders of titanium, zirconium, hafnium, vanadium, niobium, tantalum, boron, aluminum and silicon, titanium nitrides; titanium, niobium, tantalum, tungsten, boron, and silicon carbides; magnesium, yttrium, and aluminum oxides are produced.

Production of metal nanoparticles and nanostructured materials under impact of high energies on a chemical system is related to generation of highly active reducing agents such as electrons, radicals, and excited particles. The main advantage of photo and radiation-chemical reduction is a possibility of synthesis of nanoparticles in different media, including solid ones (for example, polymer matrices, films), and at low temperatures with high reproducibility. Methods of production of nanocomposites using the effect of microwave or sonic-chemical impact give rather short reaction times, provide fine particles with narrow size distribution. For example, rapid and uniform heating under microwave irradiation causes efficient reduction of Au and Pd nanoparticles on the surface of oxides in presence of poly(ethylene glycol) and poly(vinyl-2-pyrrolidone) with homogeneous dispersion [13].

Therefore, the “bottom-up” synthetic strategy provides production of hybrid nanocomposite materials including a way from molecular precursors or nanostructuring blocks of a given structure to final products in shape of fibers, films, or monolith. Design of these materials can be supplied by formation of complicated hierarchical structures in combination with usage of a template technology (micropatterning) and “bottom-up” methods (Fig. 1.1). Combination of different approaches provides unlimited possibilities for design of hybrid architectures and new materials for various application fields, smart membranes, new catalysts and sensors, new generations of photovoltaic and solar batteries, micro-optical and optoelectronics components and systems, drug delivery systems, etc. [14].

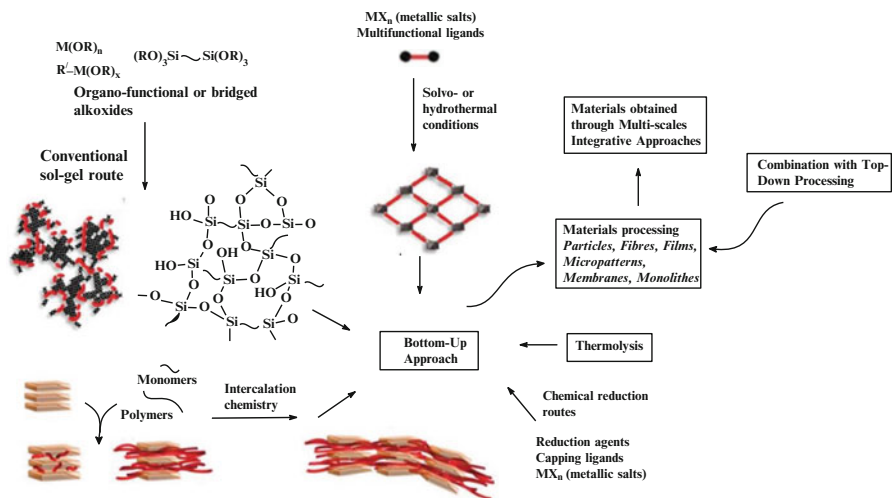


Fig. 1.1 The main synthetic strategies for production of nanocomposite materials

In the recent years particles, which take place in different biologic processes, play a special role in nanometer composites. Interaction of nanoparticles with biopolymers is very important in fermentative catalysis, biosorption, biohydrometallurgy, geobiotechnology, etc. For this purpose are used: peptides and natural or synthetic proteins obtained by chemical methods or genetic modification of microorganisms or plants, nucleic acids (including synthetic ones), biodecomposed complex polyethers, such as poly lactic acid and its derivatives, oligo-hydroxyalkanoates, hydroxyapatites, synthetic and natural (vegetable or animal) polysaccharides, cellulose and its derivatives, alginates, dextrans, gummiarabic, etc.

Almost all synthetic and nano-materials science approaches considered in this book are more or less typical of production of biocomposites. Especially important their application is in medicine, this is a basis for progress in diagnostics and therapy at cellular and genetic levels. Thus, vegetable biomasses and extracts are widely used in the methods of metal ion reduction in mass and extra-cellular production of nanobiocomposites. At that molecular components of biomasses stabilize simultaneously the formed nanoparticles. And, though rates of biogenic syntheses are, as a rule, lower than in reactions of chemical reduction, their advantage is simplicity and minimization of a number of technological cycles, realizing of green chemistry principles at all stages including formation of biocompatible non-toxic products applicable in biomedicine. Soft conditions for synthesis, aqua media, and quite high product yield make plant-mediated processes attractive for scaling, including disposal of toxic metals and radionuclides from wastes. The processes with bacteria participation, oppositely to those involving vegetable objects, demand special stage of cellular cultivation and they are characterized by high selectivity and molecular control over metabolic processes providing reproducible synthesis of nanoparticles. The same relates to highly specific structures

such as enzymes and proteins incorporated in bacterial membranes. Processes of biosorption of metal ions by microorganisms are characterized by rather high rates, and bioreduction goes far slower. However, methods of molecular engineering make it possible to design templates which have high affinity to some type of metal ions, for example, to Au(III). Development of integrated materials based on biomolecules and inorganic nanoobjects and assembling of these systems into functional devices makes a basis for nanobiotechnology.

There is an interesting usage of sol-gel technologies providing production of biotechnologically important ferments, biosensor constructions, and ferment electrodes, components of bioactive optical detectors, lipid bi-layer vesicles, encapsulating agents for drug delivery and adsorbents for pharmaceuticals and cosmetics, etc. Sol-gel method is realized for immobilizing of ferments acting as bioreactors. Organic polymers are widely used materials for replacement of soft tissues, though they do not have biological activity, they are most often bio-tolerant. At that, intermediate temperatures and soft conditions of hydrolysis and condensation – polymerization of monomer metal alkoxides allow capturing of proteins at the stage of matrix formation without their denaturation. Coating of implants surface made of metal alloys advances their integration in bone tissue and binding with it. Nanocomposites form bioactive ceramics and resolved polymer implant are successful in regeneration of bone tissue, in development of frames in bone tissue engineering.

Bioactive materials based on calcium phosphates (hydroxyapatite and tri-calcium phosphate) and glass/glass-ceramics are widely clinically used in dentistry and orthopaedics. Reconstruction of a damaged tissue, artificial substrate for cell growth, locally active drug delivery system with regulated loading and releasing kinetics are the most widely used application fields of bionanocomposites.

Sol-gel processes are the most widely spread ways of formation of structural bionanocomposite materials in living nature, preferably similar to polymer sol-gel synthesis. Moreover, many of them are borrowed from living nature and are used by it for many different bioprocesses, biosorption, biomineralization, construction of natural composite materials having hybrid structure, for example, bone, borosilicate glasses, etc. During bio-concentration—biomineralization organic matrix (template) performs control over nucleation, growth processes and formation of inorganic materials with perfect morphology; this is used for creation of complicated hierarchic structure of composites with unusual chemical and physical properties.

Intercalation of biostructures, including commercially available ones, in layered materials is accompanied by specific traits. Integration of nanoparticles and biomolecules with unique properties of each object, on the one hand, and present at same nanometer length scale, on the other hand, (enzymes, antigens, and antibodies have typical sizes of nanoparticles 2–20 nm), i.e. both classes of these materials are structurally compatible. One of the interesting directions of this approach is obtaining of biodegrading “green” nanobiocomposites in a variant of reinforcing of polymer matrix for preparation of a framework for development of a tissue, therapy of periodontal bone defects, drug delivery, etc. For example, in montmorillonite (MMT) only some polymers can penetrate into interplanar distance (linear polymer amylose, oppositely to gigantic globes of branched amylopectin), gallery space gives

an opportunity for big starch molecules to diffuse between layers and thus promotes interphase interactions, which causes more intense strengthening effect. At that tearing load and edge wetting angle increments are higher for exfoliated than for intercalated nanocomposite, which is related to higher degree of interaction between biomacromolecules and MMT particles in it. These nanocomposites are important in medicine (drugs), genetic engineering (DNA, RNA), biotechnology (proteins, individual cells, enzymes) and in food industry. Antimicrobial properties of modified clays destroy bacterial cellular membranes, suppressing their metabolic activity, and with time cause destruction (lysis) of bacterial cells. Synthetic nanometer apatite crystals manifest increased physiological affinity to host tissues or biological activity, they advance increase in compatibility of materials due to their chemical and structural similarity with natural apatite crystals. A special place has development of magnetically controlled drugs of chemotherapeutic, diagnostic, and hyperthermal activities. Hybrid superparamagnetic nanocomposites are used in MRI for localization of brain and heart infarctions, liver flaws or tumors, where nanoparticles have a tendency to accumulate in high concentration due to a difference in content of a tissues and/or endocytosis channel processes, magnetic hyperthermia. Usage of hybrid nanoparticles and nanocomposites in biocatalytic processes is one of main-streams of development of bionanocomposites.

We have focused on outline of achievements and problems in the nanocomposite science, which would be filled periodically with new experimental and theoretical data thus forming a complete pattern.

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