Chapter 11

Laser-Assisted 3D Printing of Functional Graded Structures from Polymer Covered Nanocomposites: A Self-Review

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/63565

Abstract

As a method for conservation of nanoparticles with perspective properties, the three-dimensional (3D) printing is a promising technique for modeling, fabricating of functional graded structures (FGS) with nanoadditives and functional devices. The stabilization of nanoparticles in a polymeric matrix and additionally reinforced porous structure makes it possible to arrange a desired distribution of the nanoparticles in the polymer and thus to protect them from oxidation and corrosion and even to design not only the FGS but also micro/nanoelectromechanical systems (M/NEMS) devices. The synthesized nanocomposites with controlled porosity and large-specific surface may also find their application in implantation, catalysis, lab-on-chips, drug delivery systems, and 3D crystalline structures for hydrogen storage devices.

Keywords: 3D printing, functional nanoparticles, selective laser sintering/melting (SLS/M), functional graded structures (FGS), micro/nano – electromechanical systems (M/NEMS)

1. Introduction

The additive technologies (ATs) (three-dimensional (3D) printing, selective laser sintering/melting (SLS/M), etc.) are promising techniques for modeling, fabricating of functional graded structures (FGS) with nanoadditives and functional devices, but a direct SLS/M fabrication of the nanopowders by multilayered techniques is a difficult technological task. Laser sintering and melting are known to be thermally activated processes accompanied by the coagulation of nanoparticles into micro-sized conglomerates. However, a real challenge is the aggregation prevention during the 3D printing, which significantly levels the potential advantages of using the materials in the nano- or submicron state. One of the ways to solve this problem is the isolation of nanoparticles into the inert matrices where they do not undergo any aggregation or "aging" and can be controllably released with the retained of chemical and phase composition [1–3].

Stabilization of nanoparticles in a polymeric matrix and additionally reinforced porous structure makes it possible to arrange a desired distribution of the nanoparticles in the polymer and thus to protect them from agglomeration, oxidation, and corrosion and even to design the FGS. The results indicate that nanoparticles mechanically reinforced the polymer matrix and elastic modulus and the maximum stress significantly increased. Finally, the correlations "prehistory of obtaining (i.e., "background") - chemical composition of the nanoparticles volume and surface condition - phase/structural composition - morphology - perspective properties" will determine the nanoparticles behavior in further applications.

The present review will demonstrate how laser-assisted techniques of the 3D synthesis could be used to prepare a porous core-shell polymer structures containing different encapsulated nanoparticles distributed heterogeneously over the sintered polymer and dangerous for cancer tissue account of thermal hyperthermia or cytotoxic effect. We demonstrated a principal feasibility for fabrication of functionally graded 3D parts with the structural ordering of iron oxide particles and determined corresponding laser optimal regimes. The SLS-fabricated 3D samples of biocompatible iron oxide core/(polyetheretherketone (PEEK) or polycaprolactone (PCL)) shell magnetic nanocomposites have potential medical application for the tissue engineering scaffolds and cell targeting systems [4].

Functionally graded 3D parts with alternating ferromagnetic Ni-PC and nonmagnetic Cu-PC layers [5] exhibited hysteresis phenomena that can probably be used in microelectromechanical systems (MEMS)-nanoelectromechanical systems (NEMS) applications [6] also, where the time response must depend on the relaxation rate. The synthesized nanocomposites with high porosity and large-specific surface could also find their application in catalysis, lab-on-chips, drug delivery systems, and 3D crystalline structures for hydrogen storage devices [7].

2. Inkjet 3D printing of optical nanostructures

The inkjet 3D printing has already been used for more than 20 years. Up to now, this method remains to be one of the most popular due to its low price both for home using, and for commercial applications. During this period, the techniques of the inkjet 3D printing made an incredible progress [8]. The step of drop resolution advanced from 500 μm (30 dpi) to several micrometers (9000 dpi), reaching the value boundary to the nanoscale range. The absence of high temperatures and a wide variety of inks made a revolution in the field of biosensor and print electronic devices. This method was used for printing first organic light-emitting diode (OLED) displays and panels.

The possibility of the point deposition of thin layer coatings is often used to create conductive layers [9]. Under an intensive study is the possibility of applying the inkjet 3D printing for the

http://dx.doi.org/10.5772/63565

graphene electronics fabrication, production of ordered arrays with metallic conductivity and high transparency, for deposition of electrodes of a predetermined shape to a substrate, and also for generation of 2D microarrays in printing electronics. A well-known method is printing of metal precursors (the most popular are Au^{+}, Ag^{+}, Ni^{2+}, Cu^{2+}), followed by the deposition of a reducing agent from another cartridge. These approaches are widely used in industrial printing of electrochemical sensors and combined differential thermocouples, as well as in deposition of substrate electrodes on the conductive polymeric panels.

No less revolutionary is the application of the inkjet 3D printing in the bioengineering field. For example, for the first time the selective bacterial test systems for the analysis of drinking water quality were researched and developed, mechanisms of diagnosing pancreatitis were studied with the aid of biosensors applied to the inkjet 3D printing substrate. Just that very method was used to obtain noninvasive high-sensitive biochips estimating the content of hydrogen peroxide and glucose, as well as to design colorimetric sensors aimed to detect neurotoxins and pesticides [5, 10]. However, the use of the inkjet 3D printing mechanism for bioengineering basically reduced to finding of new approaches to the biomolecules fixation into porous matrices that ensure a stable trapped substance for a long period of time after its deposition on the substrate and drying. Thus, the fabrication of highly inert colloids capable of biomolecules capturing is the most important task for the 3D bioprinting.

The optical nanostructures designed to control the photons flow are of a high practical and fundamental importance. Studies on the interaction of electromagnetic radiation (EMR) with low-dimensional semiconductor and dielectric media suggest the occurrence of a whole set of multifactor processes that jointly determine the probability of photon transport as a key mechanism for the quantum communication. Hence, the control of light flows in nanostructure constructions brings closer to the developing of new photonic devices. Thus, the development of widely available 3D inkjet printing technology for getting optical nanostructures and construction applicable in quantum communications is a pressing problem. This method proved to be successful in the field of electronics and biosensor engineering, including the generation of microchips and microintegrated circuits. The use of the nano-oxide-based system ensures a high stability and repeatability of 3D process. Earlier, we have shown the crystalline phase obtained from liquid solutions with the following condensation of boehmite, anatase, and magnetite under temperatures not exceeding 100°C and without annealing of the samples obtained [11].

Hence, it is possible to fabricate photon-induced panels with a uniform spreading of the light wave in the thin layer. These objects are unique both from the standpoints of the effect proper, and from the viewpoint of their fabrication by 3D methods of a soft chemistry. Such heterostructures will allow to carry out the uniform photon transport (for the specified wavelength) by the whole area perimeter and irrespective of the excitation point. The substrate structure can serve the base for transfer and reading of information in the new PC generation operating by the photon-signal principle. The deposition of planar waveguides on flexible polymeric substrates by the inkjet methods from solutions will greatly simplify and accelerate machine-readable signals pickup on carriers. However, the deposition of transparent dielectric structures with the accuracy of several nanometers by the 3D inkjet technology is still inaccessible.

A complex "structure—property" correlation is required to be determined, ensuring the controllability of optical characteristics of the sample being formed at the stage of the "ink" preparation for the jet printing.

The question of the materials and 3D inkjet technology use for optics remains open. This is due to the fact that the droplet coating aimed to form a solid phase on the substrate surface can embrace a predetermined range of 10^{-3}–10^{-6} m with a high accuracy, while the transition to nanoscale remains uncontrollable. But this nanorange is of a particular importance for the optical use, since nanostructures are commensurable with the wavelength of light in the visible range (400–700 nm).

On the other hand, printing of photonic materials and optical structure is still gaining in popularity, and is solely determined by the development of printing technologies and by increase in their accuracy. The size effect has a major impact on the photon flow control thus imposing many restrictions to the used ink. Still unsolved is the problem of a high heterogeneity of morphology in the drying process (coffee-ring effect). The maximal achievements were obtained under the controlled application of photonic crystals. However, in this case, the light control does not depend on the 3D inkjet technology and is exclusively resulted by the dimensions of spherical particles composing the ink.

As the universal method to control the photon flow, the use of layers with a high refractive index (RI), encased into a core with a low RI can serve. Classically, these approaches are often used for the creation of antireflective coatings and planar waveguides. However, the formation of the high RI transparent layers (more than 2.0 in the visible range) it is not an easy task. To solve this task, attempts were made to modify the polymers by using various nanoscale crystalline additives improving the optical properties of the polymers. In addition to this, the adjustment of 3D printing parameters implies the evaluation of viscosity and surface tension, as well as fine-tuning of the printer for a specific composition. Generally, in order to change the rheology, the additives increasing viscosity, such as glycerin, and surfactants decreasing the surface tension are used [9, 12].

Now only a few of inorganic materials among a great variety of those adapted to the 3D inkjet printing and widely used, can be attributed to highly refractive ones, having high transparency and not expensive, they are for example, ZrO_2, TiO_2, ZnO, and several mixed oxides. TiO_2 and magnetite are considered to be the most versatile for the obtaining of ink with high RI. This soft chemistry approach is well presented in publications, due to known values of the RI for TiO_2 in the anatase phase (2.61), and for Fe_3O_4 (3.2). At the same time, TiO_2 is completely transparent in the visible range, and its colloids are readily formed in an aqueous medium, and Fe_3O_4-based films are magnetically controlled. Printed aluminum and silicon oxides can be used in the polymer environment with a low RI. Now they are the most common matrixes for the storage and delivery of biomolecules. The alumina is used in microelectronics for deposition of dielectric layers, including the use of the 3D inkjet technology. Due to the tendency of these two systems to spontaneous and uncontrolled polycondensation it is necessary to study the influence of sonication on the particles stabilization. For planar waveguides obtaining by the inkjet technology, the multipass printing should be applied. For this, the ink combinations with different RI from cartridges of different types should be

http://dx.doi.org/10.5772/63565

alternated. This approach concept consists in using of a layered heterostructure wherein the layer with the minimum RI is formed of spherical nanoparticles with a narrow distribution by size. If the sphere diameter is commensurable with the wavelength of the external light excitation, then the effect of the critical angle of total reflection will be minimized.

3. 3D-printing of polymer nanocomposites, characterized by a tailored viscosity and biodegradability

Nowadays there is no polymer processing treatment capable of competing with the SLS with respect to the fabrication flexibility and complexity of the 3D shapes obtained. The priority of such processing for the construction of new complex parts is clear. However, the advancement of polymer laser sintering technologies is obviously hindered by several factors, such as:

1. Insufficient repeatability and control of the process, which stems from a lack of fundamental understanding. Indeed, the intricate relations between the polymer properties and processing conditions on the one hand, and the final microstructure of the material and/or physical properties of the object on the other hand, are far from being completely understood.

   Polymer powdered materials are characterized by complex physical mechanisms involved in the heating processes by a laser radiation source followed by their coalescence and melting, and then by crystallization during cooling, therefore they require the advanced experimental techniques allowing to study them in real time and at the adequate space resolution [13, 14].

2. Difficulties in developing of polymer matrices with optimized parameters of the melting transition and melt viscosity.

   Since for pure polymer matrices the fine-tuning of these parameters can hardly be achieved, the use of polymer with nanocomposite inclusions is very promissory.

The above-mentioned conclusions are based on the recent studies of the nanocomposite rheology [12–14]. Earlier, in most studies on the polymer nanocomposites, the filler particles of 10–20 nm and even bigger were used. But of highest interest is the case when the size of the particles is still lower than 10 nm. In this case, the particles size becomes commensurable with the polymer ball dimensions, individual polymer coils are approached and the interparticle half-gap is comparable with their gyration radius (R_g) or even smaller than this [15]. This produces chain confinements and distortion that can result in the depletion-driven phase segregation, or unusual properties—if segregation can be avoided. Thus, it is well known that the melt viscosity of polymers can be significantly reduced by adding a small amount of fine nanoparticles. This phenomenon is explained by the increase in the free volume owing to adding nanoparticles that is confirmed in some cases by the decrease in the glass-transition temperature. It should be noted that the viscosity reduction was observed only in cases when the interparticles half-gap was smaller than the R_g of the polymer coil.

The self-healing effect is another interesting example observed in a multilayered nanocomposite polymer structure [16]. The study showed that nanoparticles dispersed in a polymer matrix migrated to cracks generated at the interface between the polymer and glass fiber layer. According to the results of computer simulations, nanoparticles in a polymer can segregate to the surfaces and into the cracks due to the polymer-induced "depletion attraction" between the particles and the surface. In this case, only the particles comparable by their size to the polymer R_g were driven from the matrix to the surface in the crack area. Importantly, a homogeneous dispersion of the nanoparticles in the polymer matrix is a prerequisite for achieving the above-mentioned properties.

The surface enrichment with nanoparticles may result in the improvement of several practically important properties (i.e., friction, wear resistance, flame retardation, chemical resistance, touch feeling, and optical properties). This phenomenon was not taken into account in most studies of the polymer nanocomposites. In recent years, polymer composites are used increasingly for tribological applications, and the effectiveness in tribological performance of nanocomposites over microcomposites has been verified in many systems [17]. However, the specific role of nanoparticles in this case remains an open question. In particular, the tribological properties have rarely been related to the nanocomposite morphology, i.e., the distribution of particles in the polymer (bulk vs. surface). Yet, the improvements of properties can be attributed in this case to the surface enrichment with the nanoparticles.

The selection of new bioresorbable nanocomposites is feasible by the SLS approach. The polymer materials became widely used in various biomedical applications such as design of synthetic tissues and organs from biocompatible materials and stem cells, testing of new drug delivery systems, researches on tissues and organs in normal and abnormal states. The ability to form controllable regular structures from polymer molecules is used for the development of biomedical materials such as porous matrixes for tissue engineering and therapeutic agents' delivery [18]. The fabrication of polymer matrices from biodegradable polymers can facilitate the solution of environmental issues related to the 3D printing industry and promote its further development.

In spite of a great amount of works devoted to the development of polymer nanocomposites, including biocompatible and/or bioresorbable polymers, a clear insights into their structure—property relations is still extremely deficient. This is partly due to the tendency of nanoparticles toward the agglomeration inside the polymer matrix. The fabrication of polymer-based matrix nanocomposites with a homogeneous distribution of particles sized from tens to hundreds of nanometers, affords to systematically study the influence of the ratio of interparticles distance to the polymer coil size on the melt rheology and performance properties of the nanocomposites.

Nanoparticles of different sizes are to be surface-modified and mixed with polymer, so that to ensure a homogeneous particles distribution. Earlier, we received mesocomposites based on PA/PC etc. containing different amounts of inert inclusions (including those of nanosizes) [3, 6]. The use of the nanoparticles is expected to enhance the control over the melt viscosity, crystallization kinetics (e.g., nucleation effect of the nanoparticles), and preferable formation of certain polymorphic modifications of PA/PC (e.g., γ-phase vs. α-phase), which is highly

http://dx.doi.org/10.5772/63565

important for SLS processes [13]. The use of ultrasmall nanoparticles for obtaining control over the nanocomposite melt viscosity is original and is based on recent researches of the melt viscosity decrease due to the addition of such nanoparticles to the polymer matrix.

Consideration of the polymer matrices based on biodegradable polymers such as polycaprolactone (PLC) is another interesting issue for the practical medicine [19, 20]. This last issue is of high importance for all the 3D printing technologies, as it can solve the problem of growing concerns related to the environmental threat of the 3D printing industry development. We were among those first who experimentally studied the optical characteristics of polymer systems (PC, PA, etc.), impregnated with metallic particles [21]. We used an advanced strategy of determination the beam part, which was subjected to absorbing, scattering, and transmission. We offered original decisions for the characterization of thermophysical properties of such metal—polymer powdered mixtures also [22]. However, there is an obvious need to continue this work with nano-sized additives.

While studying the heat transfer and phase transformation processes, it is highly demanded to analyze the microstructural model of semicrystalline polymer, which is usually forming the nano-sized crystals (lamels) that have a very small depth but a significantly larger lateral size. The polymer structure formation under laser sintering is described in papers [23, 24]. However, for the comprehensive theoretical description of the process, the knowledge of a great number of parameters is demanded, such as temperature of phase transformation, enthalpy changing and thermochemical properties of materials. Moreover, rheological parameters of the polymer melt will influence the sintering process, which in detail described by the molecular dynamic theory [25]. Besides, the particles aggregation depends on viscoelastic properties of the polymer matrix, which are, in turn, crucially dependent on the environment conditions, as well as on degree of crystallinity and crystal texture of the material. The modeling of the melted particles aggregation behavior can be conducted by using simplified models of Frenkel, Maxwell, Kelvin-Voigt, or Bingham.

Therefore, the study of the nanoparticle influence on the final material properties gains special importance. Oxides nanoparticles are most widely used nano-sized additives for polymers and their synthesis and surface modification are well known. Nevertheless, nanoparticles aggregation is still hardly avoidable. It is known that presence of silicon dioxide nanoparticles in the polymer matrix increases the Young modulus but decreases its ultimate elongation, as to the data on the nanoparticles influence on others properties, the data about it is contradictory and inconsistent.

4. FG nanostructures with different connectivity types, obtained by hybrid SLS technology

The search and synthesis of new electro- and magneto-active materials are almost exhausted due to the almost complete use of the existing chemical compositions and processes of their preparation in various solid states, and also due to the limited functions of samples. Therefore, it is an urgent problem of today to switch over to the multicomponent mesoscopically inhomogeneous (i.e., functional graded, FG) nanostructures with different types of orderings (and different thermal, magnetic, piezoelectric, ferroelastic properties, etc.) [25].

The most promising materials are lead-free phases (involving niobates of alkali metals and alkaline earth metals, bismuth ferrite, etc. with various additives) [26, 27]. These materials have giant macroresponses including ultrahigh Curie ($T_C \geq 1400$ K) and Neel ($T_N \geq 1000$ K) temperatures providing a wide range of practical applications. They are ferroelectric, antiferroelectric, piezo- (magneto) electric solid solutions, and/or their based compositions due to greater polyfunctional characteristics in vicinity of new structured phases appearance with their accompanying extreme electro-(magneto-) physical parameters.

However, there are some negative factors impeding their application, which are related to the physical and chemical features of these objects (decomposition during the process of heat treatment, problems with poling, high volatility of the starting components, excessive grain growth due to recrystallization, low thermal stability, and mechanical strength, etc.), which could be solved by additive technologies. An urgent and significant problem of modern physical material science is the development of experimental and theoretical base of functional (and FG) materials fabrication which are free from the abovementioned drawbacks. A hybrid technology is based on the combination of traditional techniques (solid-phase synthesis, hot isostatic pressing (HIP)) and SLS/M technologies and uses dispersion—nanocrystallite powders and CAD of specific (M/NEMS) devices on the base of obtained materials [28, 29].

Fundamentals of the active elements creation were developed at the Samara branch of LPI [25] from functional (smart) materials by the SLS method with a hybrid combination of some traditional processes. The laser influence (LI) on multicomponent (including reaction capable) powdered compositions was studied. Well-known piezoelectric, hexaferrite, and high-temperature superconductivity (HTS) systems ($PbTi_{1-x}Zr_xO_3$—named as PZT; $Li_{0.5}Fe_{2.52x}Cr_xO_4$ and $BaFe_{12-x}Cr_xO_{19}$—spinels; $SrFe_{12}O_{19}$ and $CoFe_2O_4$—HTS) were fabricated [26, 30]. A hybrid layerwise SLS-SHS process (SHS is self-propagated high-temperature synthesis) was realized by means of the laser-controlled combustion reaction inside the oxide stoichiometric mixtures of the above said systems. The main achievement was a production of the 3D parts during the SLS-SHS hybrid process, as well as determination of optimal regimes for their following annealing and polarization (magnetization). The X-ray analysis of the sintered and annealed samples revealed the main phases, responsible for the ferroelectric, antiferroelectric, piezo- (magneto) electric activity of these ceramics. The possibility of association of several approaches (we used PZT as a filler for poly(vinylidene fluoride) (PVDF) polymer) into a united technological process for layerwise syntheses of the FG structures and 3D parts with ferroelectric characteristics of different types of connectivity were also shown [28, 29]. The use of nano-PZT particles in PVDF matrix (which has its own piezoelectric properties) will allow to create such types of connectivity into hybrid AT, which do not exist in the nature, but can possess unique features. Regrettably, density of the synthesized ceramics reached only 3–4 g/cm^3 (that makes up ~40–50% from the theoretical value for PZT) and, as an effect, instead of completely synthesized products, we received only mixture of the initial oxides with partly formed given active phases.

So, the development of the hybrid SLS-HIP technology facilitates manufacturing of ferroelectric ceramics hardly obtainable by conventional methods, of multiferroic and FG materials with giant macroresponses including infinite anisotropy of properties and ultrahigh working temperatures.

5. SLS/M formation of local zones of given configuration possessing magnetic properties

Mechanisms of formation of local zones of a specified configuration with magnetic characteristics during the melting (SLM/S) of nanoparticles additives of transition and/or rare-earth metals with a HTS ceramics in a polymer matrix are of great interest [11, 31].

However this issue was not given a sufficiently thorough study yet. Parts and/or tools of a complex configuration with selective local magnetic properties and multidirectional magnetic poles, which cannot be obtained by the machine treatment, can be easily reproduced by the SLM process. But the mechanisms of formation of such zones and the interaction of materials at the zones boundary have been studied partially only.

If at the moment of a rapid crystallization from the liquid phase into the solid one, the melted pool is influenced with a strong static magnetic field, then the resultant alloy microcrystallines will be arranged along the power lines and after cooling will keep their magnetization. This approach allowing to create local magnetic zones inside a solidified matrix in the longitudinal, transverse, or vertical direction, was proposed by us earlier [32]. By means of the passage by passage consistent cladding, it is possible to form in the vertical direction an overall solid coating of 3D parts with magnetic properties. The obtainment of the 3D part with volume zones of the predetermined magnetic properties is a challenge in materials science and manufacturing. The microstructure of the resultant material is determined by the joint mutual influence of the processes of rapid solidification and crystallization, directional cooling and phase transitions caused by repeated thermal cycles, and chemical composition of the initial powders.

The rapid solidification may cause a volumetric heterogeneity of chemical elements that can lead to the metastable phases formation. The directional heat removal can determine both the preferred direction of the grains growth and crystallographic texture, thereby affecting the magnetic properties of the part [32]. The LI enables to choose the regimes of energy influence on the cladded layers of materials, ensuring the maintenance of the crystalline structure and a given grains size. The orientation of the grains in an external magnetic field characterizes the residual magnetic properties of the obtained material.

Other interesting tasks are the obtainment on nonmagnetic (polymer) substrates of quasi-zero-dimensional points (local zones) [11], quasi-one-dimensional magnetic passages from rare-earth nanoadditives (e.g., Samarium-based alloys) with different composition, two- and three-dimensional arrays based on them; determination of their morphology, crystalline and magnetic structure, the saturation magnetization, residual magnetization, and coercive force.

In the paper [33], a model was considered allowing numerical determination of a resulting field velocity under the laser melting of aluminum in the external magnetic field. The model included heat-dependent characteristics of the material (surface tension and viscosity). A heterogeneous distribution of the magnetic flow density was determined by the experimental Hall data measured for the prototype. It was shown that a constant magnetic flow applied coaxially with the LI, exerts its influence upon the direction of the melted material flow and can be explained as a heterogeneity of electromagnetic destruction.

6. Osteoconductive bioresorbable implants, fabricated via 3D printing with nanoadditives

In the process of fabrication of the source materials for the bone implants capable of providing a sufficiently reliable biological integration with the bone tissue, it is important to search for new phase composition of these materials, to improve their microstructure, to create new architectural types of a macroporous structure, to develop approaches for generating materials with a specified surface roughness of the material, and macropores surface of the material. The material science aspect of the problem is connected with the choice of the chemical and phase composition of the composite based on of the synthesized powders. The backbone of the composite should be a biopolymer degradable in the body environment. The biopolymer can also be with functional nanoadditives [34].

One more method of obtaining strong implants by means of the 3D printing is their hardening by ceramic nanoadditives (Al_2O_3, ZrO_2, AZO, HA) [14, 18, 19, 35–38]. The crucial parameter that determines the suitability of this method for making real bone implants and tissue engineering scaffolds is the print resolution. The polymer matrices framing the macropores must be of a specific architecture that, under the given pores fraction, ensures the following: (a) maximizing of permeability, (b) maximizing of the mechanical characteristics such as strength, hardness (elastic modules), (c) obtaining of the surface where to the cells of osteogenic type could be attached, divided, and differentiate. The task of the powder synthesis of spatially ordered complex structures with a connected system of macropores (not smaller than 100 μm) is quite solvable. These structures determine the osteoconductive properties of the implant.

The best resorption characteristics are observed for tricalcium phosphate β-$Ca_3(PO_4)_2$ (β-TCP, Ca/P = 1.5) [39–43]. The increase of the resorption speed and level, obtaining of a more available environment for the bone tissue development can be achieved by lowering of the Ca/P ratio values below 1.5, while the pH level of the implant environment is maintained close to neutral. A further increase of the resorption limit and speed is associated with the decrease of the Ca/P ratio, i.e., in the transition to the materials, including calcium phosphates phases with condensed phosphate ions, i.e., calcium pyrophosphate and polyphosphate. The presence of condensed phosphates improves the surface hydrophily of the composite and promotes the adsorption of special signaling proteins from the interstitial fluid, resulting in the acceleration of the implant integration in the body.

The task of forming a surface roughness is solved by regulating the system composition, CAD structures and choice of the SLS/M regimes which ensures the fabrication of the specific microporous surface. It is known that smooth matrixes ensure a high proliferative osteoblast potential, while the osteogenous cytodifferentiation is hampered [18]. The increase in the 3D print resolution for matrix in the form of a filled polymer with a given architecture, and then with a given microstructure and phase composition in a porous ceramic material is an important problem [44]. The surface modification by nanoparticles is a perspective approach to the microstructure management for different types of functional implants and tissue engineering scaffolds.

Permeability optimization with the conservation of a sufficient toughness can be realized by the directed obtainment of the given porosity architecture of a 3D part. Topological structures (3D minimum surfaces) occurring in nature ensure the achievement of the maximum permeability under the maximum toughness obtainable for the porous samples. Under the comparable porosity (50%) the most permeable models are cubic, tetrahedral and gyroidal cell models [45, 46]. The gyroidal model has a reasonable compromise between permeability and toughness. Roughness can be introduced as a term with higher angular frequency. This will change the curvature locally, as required for the optimal cell adhesion and growth. A porosity gradient can be easily modeled by adding a linear term. Algebraic form for the function describing the gyroid surface is not complicated and can be represented as trigonometric function, thus allowing the generation and scaling of computer models for such architectures.

Osteoconductivity is the ability of the material to provide the possibility of biological flows, intergrowth of blood vessels into the implant (vascularization), adhesion and binding of osteogenic cells [47]. These characteristics are correlated with the physical permeability of a porous body (bone implants or tissue engineering scaffolds) and are provided by means of the inherent bimodal porosity.

Permeable pores of a large size provide permeability for the flow of necessary biological substances, while the pores of a small size are accountable for the roughness of the surface, giving the signal to spreading and proliferation of bone cells [35, 48, 49]. In order to fabricate a chaotic macroporous structure, different approaches could be used, but only the regular spatial architecture of porous-structured materials allows to increase the permeability and strength of the product to the desired values. The task of designing a regular architecture of the porous space can be only solved with the use of additive technologies, the 3D printing in particular.

Tissue engineering scaffolds possess a certain structured organization, capable to form a framework of life space for the bone-cells predecessors and thus stimulate their functional activity. The scaffolds themselves or in combination with other components exert a direct regulatory effect on the cells predecessors and hereby induce the osteogenesis within the implantation zone. The design of 3D scaffolds must stabilize mechanical loads in the place of contact and prevent the formation of a fibrous capsule around the implant [50].

7. 3D printing of magnetic polymer nanocomposites for medical applications

Magnetic nanoparticles in their pure form are rarely used for therapeutic purposes. Usually, they are encapsulated and/or placed in biologically inert matrixes (oligomers or polymers, including those of natural origin) with the view of reducing a possible toxic influence of the magnetic phase, raising its physicochemical stability and creating of the immobilization conditions on the surface of drugs capsules or matrixes. This problem is successfully solved by the AT methods [51]. The capsulation is usually conducted in ultrafine ferri-, ferro- and superparamagnetic particles, containing stabilizing reagents called "magnetic liquids" [52, 53]. Magnetic nanodots are essentially the same class of nanoparticles, that are respondent to the magnetic field influence. Such particles usually consist of magnetics, such as iron, nickel, and cobalt, and of their chemical mixtures. The increased interest to these objects is explained by their possible application in the catalysis, biomedicine, magnetic-resonance (MR) spectroscopy, and data storage.

Physicochemical characteristics of the magnetic nanoparticles are strongly dependent on the method of their preparation and chemical structure. In most cases, these are particles of the size ranging from 1 up to 100 nm with the apparent superparamagnetism.

During their motion by the blood flow, the nanoparticles could become coated with the blood plasma protein, or absorbed by the immune protectors (macrophages). In order to extent the nanoparticles lifetime in the organism, the polymeric chains are fastened to the nanoparticles. Another method consists in the attachment to nanoparticles of antibodies for malignant tumorous cells since they "know" the pathway to the target (the cancer tumor). The magnetic nanoparticles behavior inside the organism is caused by the surface phenomena, size of nanoparticles and their magnetic characteristics (magnetic moment, remanent magnetism) [54]. The surface phenomena chemistry is particularly important for the elimination of the influence of reticular-endothelial system (RES) being the part of the immune system, and for the elongation of the nanoparticles lifetime within the bloodstream. The nanoparticle coating by a neutral and hydrophilic compound (i.e., polyethylene glycol (PEG), polysaccharides, etc.) enlarges the circulating time of the particle existence from minutes to hours and even days [55].

One more possible way is the reduction of the particles size. However in spite of all the efforts, the RES effect has not been completely avoided, and toxicological problems due to the undesirable displacement into other organism areas are still remaining.

Magnetic nanoparticles have found a lot of efficient applications in biomedicine that open new possibilities for therapy and diagnostics of a number of heavy diseases. Alive organisms are built of cells with a typical size of about 10 μm. And in turn, the cell components are much smaller and have the size less than 1 μm. For medical applications, it is important that nanoparticles have controllable sizes within the range of several nanometers to hundreds nanometers, which are comparable with the sizes of intracellular biological objects—(10–100 nm), viruses (20–450 nm), proteins (5–50 nm), and genes (about 2 nm in the transverse direction

http://dx.doi.org/10.5772/63565

and 10–100 nm lengthwise). By their size (from 4 to 1000 nm) and their mass, nanoparticles are intermediate between molecules and alive cells.

This size range opens great freedom for promissory medical application of nanoparticles at the AT.

7.1. Magnetic hyperthermia

Magnetic nanoparticles can be incorporated into a bioresorbable polymer matrix so that they could reverberatory respond on the alternating external magnetic field (EMF) of a certain frequency and amplitude, and concurrently effectively absorb the EM energy and transfer it as a heating to the surrounding biological tissues. For instance, a magnetic nanoparticle can be used as hyperthermia agent heated in the applied EMF and delivering mortal doses of thermal energy to the tumors cells [56]; or as facility capable of increasing the efficiency of chemotherapy, beam and laser therapy, where magnetic nanoparticles lead to a moderate degree of heating resulting in a more efficient destruction of the malignant tissue. For the magnetic hyperthermia the particles are to possess high SAR (specific absorption rate) allowing their fast heating in the alternating magnetic field. The cancerous cells are known to be ruined under 42–43°C.

Study on the absorption rate of the EME by the magnetic liquid SAR with nanoparticles is important for the certification of fluid-magnetic hyperthermia (FMH) drugs. Along with the parameters, such as Curie point, value of saturation-specific magnetization, and toxicity, the SAR as an attribute of the magnetic liquid determines the possibility and efficiency of medical applications. For the FMH, it is necessary to develop in polymers the magnetic nanoparticle compositions, capable of releasing a dosated portion of magnetic particles. At present, superparamagnetic particles on the magnetite base have been developed, with the substitution of Fe^{2-} by manganese and zinc, and Fe^{3-}—by the gadolinium. At a slight decrease in the specific magnetic receptivity and specific magnetization saturation, the Curie temperature reduction from 575°C (magnetite) to 70°C was achieved. A similar problem was also solved for manganites.

The tendency to reducing the size resulted in a dominating use of superparamagnetic systems (for instance, superparamagnetic iron nano-oxides (SPIO)) without a hysteresis loop. The magnetic nanoparticles used for therapeutic purposes, can consist of ferromagnetic, ferrimagnetic, or superparamagnetic materials. Their main advantage is the possibility of contactless control of their displacement in the organism under the EMF. In our researches, it was shown that promissory materials are iron oxide nanoparticles with spinel structure (magnetite, maghemite) and even high-temperature superconducting ceramics ($SrFe_{12}O_{19}$) [31].

7.2. Radio-absorbing coatings from polymers with nano inclusions

To protect against the EMF, radioabsorbed materials (RAM) are widely used, in particular polymer composites with ferrimagnetic or ferromagnetic nanoadditives are used as RAM. Efficient RAM should satisfy a number of requirements: maximum absorption of electromagnetic waves within a wide frequency range, minimum reflection and lack of harmful fumes, fire safety, small dimensions, and light weight.

Two types of RAM are distinguished: interference type, wherein the electromagnetic waves are weakened due to the destructive interference, and absorbing type in which the electromagnetic energy is converted into thermal one due to scattered currents, dielectric or magnetic relaxation. Depending on the main source of relaxation, the RAM can be of dielectric or magnetodielectric types, and depending on the operating range of the absorption frequencies, there exist narrow band or wide band RAM.

As the alternative, the transparent in visual light materials (glass, polymer) can be used with embedded magnetic nanoparticles (particularly, magnetite Fe_3O_4 nanoparticles and hexagonal strontium ferrite $SrFe_{12}O_{19}$ nanoparticles) [11, 31]. It is known that spinel ferrites and their composites effectively absorb EMR within the frequency band of 0.8–2.0 GHz. Hexagonal ferrites intensively absorb in the range of tens of GHz. So, by combining the nanoparticles of magnetite and hexaferrites (e.g., strontium hexaferrite), it is possible to improve the RAM performance at the edges of the frequency band, i.e., at few GHz and at tens GHz, thus significantly increasing the operating range of RAM.

Earlier, we have obtained the 3D parts from polymers with nano inclusions of Fe_3O_4 and $SrFe_{12}O_{19}$ by the SLS/M. By the proposed method, it is possible to fulfill easy polymer coatings with nanoparticles of the above-mentioned ferrites on the surface of medical equipment thus providing its protective covering [57, 58].

7.3. Magnetic nanoparticles for targeted drug delivery systems

The targeted drug delivering (TDD) is one more promissory sphere for the medical application of magnetic nanoparticles [49]. Its main advantages are significant reducing of the drug toxic effect on other organs and systems, possibility to direct and retain the drug-containing nanoparticles in a certain place with the help of magnetic field, and to visualize them by the magnetic resonance imaging (MRI) methods. An important property of magnetic nanoparticles is a possibility of their local heating by the high-frequency magnetic field for the initiating of the drug desorption/decapsulation mechanism or for magnetic hyperthermia. Usually for the TDD, the superparamagnetic particles are used as the magnetic carrier since after the magnetic field influence they are not aggregating. However, there exists the problem of the reduction of magnetic influence power after the drug delivery, resulting in complicating of the particles retaining in close proximity from the target object, particularly under the powerful blood flow effect.

For a long time, already various one- and multicomponent liposomes generating in lipid solutions have been well known. For the practical purposes, liposomes with sizes of 20–50 nm are of interest since they are used as drug delivering systems to a biological target [59]. There is also a whole set of natural nanocarriers, for instance, viruses. Especially, processed adenoviruses can effectively be used for vaccination through the skin. Other examples of biogenic nanoparticles capable of the targeted delivering are lipid nanotubes, nanoparticles and nanoemulsion of natural origin, some cyclical peptides, chitozans, and nucleic acids [60].

http://dx.doi.org/10.5772/63565

“Magnetic” bacteria can deliver drugs, for instance they can be used as a system for the point delivery of drugs to the diseased tissues also. The MC-1 bacteria are capable of a fast moving owing to the rotating of their own flagellums. Besides, they contain magnetic nanoparticles and are therefore sensitive to the magnetic field and are enforced to move along the lines of force. As a generator of these lines of force the MRT device, for instance, can serve.

Nanospheres and nanocapsules are referred to the polymer nano objects. The nanospheres are solid matrixes with an active material spread over their polymer surfaces, while in nanocapsules the polymer coatings form the cavity filled with liquid. Hence, the active material is released into the organism by different mechanisms—the release from the nanospheres is of an exponential nature, whereas from the nanocapsules it happens with a constant velocity and for a long time. Polymer nanoparticles could be received via the SLS/M process as core/shell composites. They are polysaccharides, polyglycolic acids, polylactides, polyacrylates, acrylic polymers, polyethyleneglycol (PEG), etc. Polymer materials are characterized by a whole number of useful properties for the medical transportations, such as biocompatibility, ability to be biologically decomposed, and multifunctionality.

Dendrimers are becoming of a high interest. This is a new type of polymers, having a branching, dendrite-like structure instead of the usual linear one. Dendrimers are often mentioned in the context of their nanotechnological and medical applications. Dendrimers are a unique type of polymers since their size and shape can be superaccurately specified under the chemical synthesis that is extremely important for the TDD. Dendrimers are obtained from monomers by conducting their consequent convergent and divergent polymerization (including the use of the peptide synthesis methods), thus determining the pattern of branching.

Typical monomers used in the synthesis are polyamide-amine and amino acid—lysine. The “target” molecules are linked with dendrimers either by means of forming complexes with their surface, or by means of embedding deep between their separate chains. It is also possible to place in a stereo-specific way the necessary functional groups on the dendrimers surface so that they could interact with viruses and cells.

Carbon nanoparticles (fullerenes and nanotubes) are well known material for the TDD. Nanotubes can be used as microscopic containers introduced by the SLS/M process for the transporting of many chemical or biologically active materials: proteins, poisonous gases, fuel components, and even melted metals. For medical applications, the nanotubes possess an important increased affinity to lipid structures, they are able to form stable complexes with peptides and DNA-oligonucleotides and even encapsulate these molecules. Taken together, all these characteristics and properties provide their application as efficient drug delivering systems for vaccines and genetic material.

Promissory platform technologies are microcapsulation, technology for manufacturing of matrix, multilayered, and coated tablets and capsules. Designed and described in the literature are the platform technologies for making the nanosize complexes of active materials with biocompatible and biodegradable synthetic and natural polymers [6, 18]. The nanosize may result in the increase in a drug activity by several times and also in the reinforcement of therapeutic characteristics. Preclinical studies of known drugs in new nanopacking are already carried out (e.g., taksol or nurophene of a prolongation effect). Platform technologies for a controllable drugs release are very important for the targeted delivery of high toxic antineoplastic drugs.

Traditional cancer drugs are evenly distributed by the whole organism, thus reaching both the diseased and healthy organs. This problem can be solved with the help of directed DDS (drug delivery system) when the drug is delivered along with a biodegradable polymer used as transport. In this case, the drug is released not immediately, but gradually, in the process of the polymer degradation.

There exist the target drugs delivering by nanoparticles of a genetic material, DNA or RNA. For the magnetic target influence, the drug or therapeutic radionuclide is attached to magnetic compound, which is entered into the organism, and then concentrated in the area of the target influence by means of a magnetic field (here the implanted constant magnet or the EMF could be used).

The magnetic DDS in its current state is mostly applicable to well-studied tumors, whereas the medical treatment of metastatic and/or small tumors at their early stage of development still remains an unsolved problem. The therapy of emerging tumors implies the development of a new generation of nanoparticles of teradiagnostics type, capable of recognizing small clusters of cancerous cells and delivering the elements (drugs or hyperthermia materials) required for their destruction. Teradiagnostics will ensure a permanent control of the course of treatment with a concurrent checkup of the drug delivery results and influences.

7.4. Magnetic resonance imaging

Lately, a number of directions in the molecular visualization sphere have got a wide development via the 3D printing. MRI is one of the most powerful noninvasive methods of visualizations intensively used in clinical medicine [61]. Contrast agents based on the magnetic nanoparticles are one of the most perspective medical applications and are considered as the following MRI-agents generation. Magnetic SPIO are also actively researched as contrast agents for the MRI. New biological applications of these contrast agents are the following: checking of a bloodstream, cancer and tissue engineering scaffolds agents, the MRI contrasts, checking the cells motion, and biomolecular study. In contrast to paramagnetic ions, the SPIO nanoparticles have a higher molecular relaxation. Therefore, in case of their use under low concentration for the bloodstream checkup, they can have some advantages. The MRI yields to positron spectroscopy in its resolution but it gains in its cost. An inexpensive MRI procedure with the SPIO nanoparticles use, distinguishes tumor metastasis of approximately 1 mm size.

8. Conclusions

In this chapter, we reviewed the modern tendency to fabricate the 3D printing of functionally graded structures from the polymer-covered nanocomposites: inkjet 3D printing of optical nanostructures; 3D-printing of polymer nanocomposites with specific viscosity, osteoconductivity and biodegradability; FG nanostructures with different connectivity types, obtained by a hybrid SLS technology; opportunities of the SLS/M formation of magnetic local zones of the specified configuration; and 3D printing of magnet polymer nanocomposites/objects for medical applications.

Numerous problems have been identified and some solutions have been proposed and assessed. Still, a lot of further researches are required to implement a true industrial process, providing the rapid fabrication of high quality net-shaped MEMS/NEMS devices—implants, catalytic filters and membranes, lab-on-chips and drug delivery systems, magnetic hyperthermia systems and 3D crystalline structures for hydrogen storage, and/or optical devices.

Acknowledgements

Prof. I. Shishkovsky is grateful for the financial support provided by the Russian Science Foundation (grant no. 15-19-00208).

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