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APPLICATION OF THE MULTILAYER ASSEMBLY (LBL) METHOD IN ENGINEERING TECHNOLOGIES FOR OBTAINING PERSPECTIVE COMPOSITE MATERIALS WITH PURPOSE PROPERTIES

Abstract. This report provides an overview of the use of the multilayer assembly method to obtain a new type of composite materials with physical-chemical and chemical-biological properties. Polyelectrolyte multilayer (PEM) technology alone covers the entire widespread spectrum of functionalization possibilities. The method is based on the adsorption of successively alternating oppositely charged macromolecules and makes it possible to obtain ultrathin films of a given thickness and composition from a large number of diverse systems on a charged surface of any geometry both in air and at room temperature, illustrating the large versatility of the PEM technology.
Key words: composite materials, ultrathin films, multilayer assembly method.

Nowadays potentially promising scientific direction from the point of view of theory and practice to date is the creation of composite materials with purposeful optical, electrical, biochemical and many other useful properties. A special place among them belongs to thin polymer films exhibiting catalytic, magnetic, antibacterial, biosensory, electrochromic and photoluminescent properties.

In [1], the author describes several methods for obtaining such thin films: deposition on a rotating disk substrate, thermal deposition, chemical assembly, Langmuir-Blodgett method, layer-by-layer deposition of polyions. Depending on the method of obtaining, thin films differ in their physicochemical characteristics, such as the quality of the applied coating, roughness, stability, thickness, arrangement of molecules and have various practical applications [2].

One of the cheapest and easiest ways to obtain such films is the multilayer assembly method, the so-called layer-by-layer method, which attracts the attention of many researchers in connection with the formation of uniform organized surface coatings with controlled thickness and roughness [1]. This method is based on the adsorption of successively alternating oppositely charged macromolecules and makes it possible to obtain ultrathin films of a given thickness and composition from a large number of diverse systems, moreover, the assembly can be performed on a charged surface of any geometry both in air and at room temperature.

At present, many polymeric materials are used by researchers to obtain multilayers, beginning with biopolymers such as proteins [3] or DNA [4], as well as inorganic substances such as clays, microcapsules, colloidal particles and even biological cells [5].

Until recently, it was believed that the bond in the layers of such films is mainly electrostatic. Later it was found that the bonds can also be provided by hydrogen [6], hydrophobic and other forms of interaction [7-9].

There are two main types of growth of such polymer films [10]: linear and exponential. The linear dependence of the thickness (optical density) on the number of layers is explained by the constant amount of polyelectrolyte adsorbed at each stage of bilayer production. Several models have been proposed to substantiate the exponential growth.

The authors of [11] explain the growth pattern of the film roughness, which increases with the number of deposited layers. Macromolecules adsorbed to the initial layers are strongly attracted to the surface, resulting in a smooth configuration. With an increase in the number of deposited layers, the effect of the substrate decreases, and polyelectrolyte molecules begin to adsorb in a more coil-like (entangled) state, increasing the surface area of the film. In this connection, a greater number of macromolecules can be adsorbed at subsequent stages of the obtaining of multilayers. Another less common explanation of nonlinearity is based on the diffusion of free polyelectrolyte chains in multilayers upon adsorption [12-13].

In addition to polymer molecules, low-molecular compounds, for example, dyes, can participate in the multilayer assembly method, which makes the method more universal in terms of creating thin polyelectrolyte multilayers (PEMS) with the desired useful properties [14-15]. The assembly of films containing dyes can be attractive when studying their electrochromic and optical properties. For example, in a number of works phthalocyanine dyes exhibit good optical properties [16] and optical memory [17], so that the electrochromism of dyes of this class can be used to create materials of a new generation.

In [12] the films were obtained from poly (vinyl alcohol) (PVA) with hydrophobic polymers - polymethylmethacrylate, polystyrene, poly-D, L-lactide, polydimethylsiloxane. As is known, PVA is insoluble in organic matter, while other components are insoluble in water. During the assembly process, the intermediate drying of the film proved to be an important factor: PVA adsorbed on the surface of the plate becomes insoluble in the aqueous solution due to the formation of hydrogen bonds between hydroxyl groups and, possibly, water molecules.

The authors of [13], when obtaining films from organosoluble polymers, confirm the necessity of drying (in contrast to the usual electrostatic assembly) and for other systems, where the chemistry of the formation of films is also due to hydrophobic interactions and hydrogen bonds.

Metal-containing polyelectrolyte multilayers have been widely studied and found application in the manufacture of polyelectrolyte membranes, in the creation and obtaining of nanoparticles, electronic and optical materials, and in the preparation of nanoscale capsules for the controlled delivery of biologically active compounds. One of the most important features of multilayers is their selective permeability for various substances. The permeability of a multilayer film depends on the thickness of the layer, its porosity, the structure, the chemical composition of the composition and the size of the penetrant. The authors of [18] established that such films are impenetrable for macromolecules of large molecular weight and size, but they are completely permeable to small polar molecules.

Tiake et al. [19] showed that PEMS can serve as a multifunctional membrane and can be used to soften and distil the sea water. They obtained ultra-thin membranes by the LbL method by applying various polymer compounds such as polyelectrolytes, calixarenes, hexacyanoferrate metal salts and Berlin azure. It has been shown that polyelectrolyte multilayers can be used as nanofilters, molecular and ionic sieves for the size-selective separation of neutral and charged aromatic compounds. Specific interaction in such polymeric compositions goes by the guest-host mechanism, which transmits ions with hybrid membranes from p-sulfonato-calixarenes and cationic polyelectrolytes. Membranes have a high selectivity to various metal ions and can find application in various innovative technologies for separation of ions of different nature. The authors also demonstrated the possibility of obtaining purely inorganic membranes from Berlin azure and similar metal salts by successive adsorption of cations of transition metals and hexacyanoferrate of the anion. Thanks to the porous structure of the Berlin azure, the membranes can be used as an ion filter capable of separating, for example, cesium ions from sodium ions.

The authors of [20] used complexes of transition metals with polyelectrolytes to control the charge density in PEPS films for the obtaining of ion-selective membranes. The method of alternative deposition of oppositely charged polyelectrolytes on a porous carrier obtained ultra-thin ion-selective membranes. Cu^{2+} ions were used as a nucleus in PAK/PAA membranes to control the charge density and, therefore, to increase the selectivity of anion transfer. Alternative deposition of PAA, partially bound to complexes with Cu^{2+} and PAA on a porous aluminum carrier followed by removal of copper ions and deprotonation, allowed the formation of - COO^- positions in these films. A comparative analysis of two membranes obtained under identical conditions showed that the Cu^{2+} -containing PAA/PAA membrane has four times the selectivity for Cl^-/SO_4^{2-} transfer as compared to the conventional PAA/PAA membrane.

In paper [21], the LbL method was used to incorporate ZnO nanoparticles into multilayer polymer films from the polymer matrix PDDA-PSS on a quartz plate. A multilayer film containing ZnO nanoparticles was prepared by multiple adsorption of zinc nitrate and subsequent precipitation with ammonium hydroxide. UV-Visible spectroscopy studies indicate the regular growth of ZnO nanoparticles.

The authors have shown that by changing the number of precipitation cycles, can control the morphology of nanoparticles. Increasing the number of cycles of precipitation of zinc oxide on the film (PDDA/PSS) 3.5 to 6, the authors succeeded in obtaining crystalline nanoparticles with better morphology and with a diameter of 20 to 60 nm. A further increase in the number of cycles of precipitation of the reaction to 8 showed that most of the particles grew in a one-dimensional direction, forming nanostructures, and the particle sizes remained practically unchanged. Changes in the number of bilayers also turned out to affect the morphology of the particles. So, for example, with an increase in the number of PDDA-PSS bilayers to 5.5, the results differ from data on a film with 3.5 bilayers PDDA-PSS. After four cycles of precipitation, the particles remain dispersed in the matrix. However, with a further increase in the number of cycles of the precipitation reaction to 8, the growth of individual particles in chips of crystals is not observed.

Thus, the multilayer assembly method, being one of the simplest and cheapest, makes it possible to obtain thin films from a large number of different systems, which can potentially have unique properties. Interesting work in this regard was proposed by Wang and Lee [22] in which they obtained nanoscale Pd catalysts attached to magnetic ferrite nanoparticles by LbL films and investigated the relationship between the structure of these hybrid nanocomposites and their catalytic activity in the hydrogenation of olefinic alcohols. To obtain nanoscale palladium catalysts, polyacrylic acid and polyethyleneimine-Pd (II) complex (PEI-Pd (II)) were applied on the surface of magnetic nanoparticles ($CoFe_2O_4$, average size = 20 nm), followed by reduction of Pd (II) with sodium borohydride to Pd (0). Based on the results of studies of the catalytic activity of these hybrid core-shells of nanocomposites with different numbers of bilayers for hydrogenation of olefinic alcohols, it was concluded that palladium nanoparticles act as a catalyst only in the upper layers, probably because of the difficulty of diffusion of olefinic alcohol molecules into the crosslinked multilayered film. In this case, the catalyst is easily separated from the reaction mixture by an external magnetic field and can be reused.

Makanas and others created a catalytic reactor by modifying microfiltration membranes from hollow fibers by LbL adsorption of polyelectrolytes and stabilization by metal nanoparticles [23].

As the results of these studies have shown, metallic nanoparticles have unique physico-chemical and catalytic properties, unlike conventional microfiltration membranes. For this purpose, the authors synthesized metal nanoparticles stabilized by polymer inside functional polymeric membranes. For this purpose, polymeric matrices with functional groups (for example, containing sulfonic acids) were used, which primarily bind the nanoparticles and create the conditions for the growth of metal particles within the polymer matrix. Two different strategies were used in the work. First, polyether sulfone microfiltration hollow fibers were modified with polyelectrolyte multilayers. Subsequently, the polysulfone ultrafiltration membranes underwent UV photocoupling, using p-styrene sodium sulfonate as vinyl monomers. The catalytic properties of the fibers were tested by a model reaction-reduction of p-nitrophenol in the presence of sodium borohydride and a metal catalyst, which is widely used to evaluate new catalysts for reactions in the aqueous phase. The use of such catalysts could lead to the abandonment of many costly catalysts, such as platinum, palladium and others. However, the use of catalysts of this type is not entirely limited to this particular field of application. Synthesis of new metal-polymer ligand-type catalysts in polyelectrolyte multilayer films deposited on solid carriers also opens up a huge field of application, ranging from simple exchange reactions in inorganic and organic technology to sophisticated processes in biotechnology.

In modern biotechnology, various methods of obtaining nanocapsules are used. Among them recently use the method of encapsulation of medicinal substances using LbL technology, successively applying polyelectrolytes to a special substrate. The capsules obtained in this way with a very small size and an ultrathin wall suggest great prospects for their use in pharmaceutics. The main advantage of such multilayer nanocapsules is the ability to vary the wall of thickness and diameter, using various polyelectrolytes and different combinations and the nature of the solvents, as well as the growth conditions of the polylayers. Depending on the type of polyelectrolyte, when applying layers, the driving force can be due to electrostatic bonding, or due to the hydrogen bond.

In medical practice, there is a method for obtaining nanocapsules based on the nature of hydrogen bonds. In particular, Kumar et al. propose the obtaining of a capsule by the complexation of polyacrylic acid with non-ionized polyvinylpyrolidone in an aqueous solution [24]. The complex is formed in acidic medium at pH 2 and is destroyed in alkaline at pH 7. The properties of such hydrogen-bound films are well described in the work of Sukhishvili et al. [25].

In Kumar's work, the anti-tuberculosis drug rifampicin is loaded into multilayer capsules, several microns in size at pH 2. At 37 °C and pH 7.4, the drug is released almost 90 %. Carrying out experiments in vivo and in vitro, it was found that encapsulated and free drugs have the same effect.

Zhao and others have automatically loaded nanocapsules from biocompatible and biodegradable polymers like chitosan and alginate [26]. Calcium carbonate microparticles containing carboxymethylcellulose with a porous structure were used as a backing core for the obtaining of hollow capsules. The multilayers obtained in this way were crosslinked with a solution of glutaraldehyde at room temperature. The $CaCO_3$ particles were dissolved in a solution of sodium ethylenediaminetetraacetate. The obtained hollow microcapsules were immersed in a solution of the antitumor drug dexorubicin.

The potential for the use of polyelectrolyte multilayers for biomedical purposes has been discussed in reviews [27-28]. Very often, clay particles are used as one of the constituents of LbL films [29]. LbL films were obtained by the authors from positively charged polyelectrolytes, such as polydiallyl dimethyl ammonium chloride, polyallylamine hydrochloride, polyethyleneimine and copolymers containing quaternary acrylic ammonium monomers. The components were applied in a certain sequence to negatively charged clay particles, and it was found that after the application of each layer of the surface, the charge varies from positive to negative, and vice versa.

Hybrid organo-inorganic nanocomposites based on polymers and clayey plates enable the preparation of advanced materials with new applied properties in pharmacy [30] for the obtaining of nanocapsules with controlled release of drugs, biosensors [31], as well as for the obtaining of fireproof materials [32] for fuel cells.

Thus, the use of the LbL method in modern nanotechnologies implies great potential in the field of obtaining new multifunctional polymer compositions with the necessary physico-chemical and medical-biological properties and have a great future especially in medicine.

Modern medicine in medical practice faces such negative problems as inflammatory processes, the treatment of which requires great moral and material costs. Most often, inflammatory processes occur against the background of hospital infections in traumatology, dentistry, surgical operations, etc. [33-36]. Hospital-acquired infections are often the result of bacterial colonization of biomedical products and their devices. If colonization of the medical implant with bacteria occurs, it is often necessary to change it, which leads to an increased incidence of patients and an increased cost of treatment for the health care system not only in Kazakhstan but also in other countries. The high cost and high death rate of patients associated with hospital-acquired infections led to the need to conduct research in the development of conditions for obtaining antibacterial coatings for biomedical implants, bandages and sutures.

Timely prevention of the consequences of such processes can be solved using various antibacterial and anti-inflammatory techniques at the initial stage of treatment. In this regard, modern medicine is keen to develop optimal conditions for the obtaining of multifunctional antibacterial and anti-inflammatory nanomaterials and nanocoats for medical and biological purposes, for which the use of the multilayer assembly method will help solve important theoretical and applied problems.

One of the most promising varieties of antibacterial coatings in scientific and applied terms is thin polymer films that release biological active substances in response to the appearance of bacteria. In this respect, scientific achievements of US scientists have made great strides. For example, the results of US Pat. № 5520664 ("Catheter with a surface permanently emitting antimicrobial agents"), US Pat. № 6261271 ("Medical devices with anti-infectious and antithrombogenic agents"), US Pat. № 5902283 ("Impregnated with Antibacterial Drugs Catheters and Other Medical Implants") have significant theoretical and applied achievements in this field. In [37] reported the conduct of infection-prophylactic coatings on silicone urinary catheters. The catheter surface was first sonochemically treated in a nanosphere to improve its antibacterial potential, then combined with a polyanion with hyaluronic acid (HA) to create a step-by-step construction on silicone surfaces using the multilayer assembly method. The antibacterial effect of the multilayers of the aminocellulose nanosphere was 40 % higher than that of the coatings based on the aminocellulose solution. To prevent the formation of a biofilm of bacteria, 5 hyaluronic acid/aminocellulose nanoferrous bilayers were sufficient. Currently, a number of researchers are trying to solve this problem by applying coatings with various antibiotics or silver deposition on the implant surface [38]. The authors [39] developed a method for obtaining silver antibacterial coating of medical implants (Patent of the Russian Federation № 2536293, IPC A61L 27/30, A61C 8/00, published on 20.12.2014, bulletin № 35). The method consists in the electrochemical coating of the surface of the implant with silver ions, which have an antimicrobial effect. The cathode material and the anode material are connected to each other in a conductive manner and form a plurality of local electrochemical cells, thereby increasing the antimicrobial effect of the coating. In [40] work describes a method for the obtaining of an antimicrobial coating based on silver in the manufacture of interstitial endoprostheses on a titanium base (Patent of the Russian Federation № 2504349, IPC A61F 2/30, A61K 33/06, A61P 31/04, C23C 4/12, published on 20.01. .2014, bulletin № 2). For this, a certain preparation of the silver-containing solution, the implant surface and the formation of the coating itself is carried out. Preliminary preparation of the surface of the implant is carried out by blasting the surface with powder of electrocorundum under pressure. The coating is formed by plasma spraying first of a titanium sub-layer, then a silver-containing hydroxyapatite powder. Such implants exhibit good and long-lasting antibacterial activity. In [41] work, a method for coating with an antibacterial effect on a medical device was carried out on the basis of a high molecular weight compound (Patent of the Republic of Belarus № 13256, IPC C08J 7/00, A61L 27/00, A61L 29/00, published on 30.06.2010). The antibacterial agent is layerwise deposited on the surface of the article by a physicochemical method. In all the above methods, surface activation is rather complex and expensive. Using the same multilayer assembly method is more economical and environmentally beneficial. In this regard, modern innovative nano technologies use this method to obtain antibacterial and anti-inflammatory nano coatings not only for biomedical products, but also dressings. Modern bandage materials contain various active compounds that are useful for wound healing [42]. Dressings can be made by multilayer assembly in such a way that biologically active ingredients such as antimicrobial, antibacterial and anti-inflammatory agents of prolonged action are adsorbed and fixed on the surface of nanocoatings, which greatly facilitates the healing of wounds.

For example, magnetic nanoparticles Fe_3O_4 (NPs) were used in Ref. [43] to improve the mechanical and antibacterial properties of composite nanofibrous films (membranes) based on chitosan (CS) and gelatin (GE). The authors found that the inhibitory zones of Escherichia coli and Staphylococcus aureus were significantly expanded by the addition of Fe_3O_4. In general, membranes made of Fe_3O_4/CS/GE composite nanofibers with individual mechanical and antibacterial properties are a promising material for wound dressing.

Wound healing is a long and painful biological process and the ideal wound dressing should be able to absorb excess exudate, maintain a wound layer moist, provide adequate gas exchange and act as a mechanically strong barrier to the environment and have excellent antimicrobial properties to prevent wound infection and speed up the process healing. Analysis of the authors' studies [44, 45, 46] showed that dressings with silver nanocoating have antiseptic, antimicrobial and anti-inflammatory properties when applied even to chronic diseases. Bandages with honey coating also showed an anesthetic properties exceeding their effectiveness in antimicrobial action.

The authors of ref. [47] developed the physicochemical basis for the obtaining of polyelectrolyte multilayers by the LBL method with catalytic and biological properties. Regularities of growth of PEI/PAK, PEI/PSS, QPVP/PAK and QPVP/PSS multilayers were established by the LbL method of applying oppositely charged polyelectrolytes on the surface of a solid carrier. For the first time, the possibility of obtaining catalysts with multiple activity based on PMC $Co2^{+}$ and Cu^{2+} in the above polyelectrolyte multilayer films was demonstrated. The influence of various factors on the formation of multilayers has been studied: the pH, the nature of the polymer, the temperature, the mechanism of formation of layers, and the absorption of metal ions on their surfaces. The dependence of the amount of absorbed metal on PEMS films on the pH of solutions of applied polyelectrolytes and on the degree of quaternization of QPVP was investigated. The catalytic activities of immobilized catalysts have been investigated as a function of the number of bilayers and application conditions. It has been established that between the components of the systems there is an acid-base interaction with the formation of double and triple PMCs, the chemistry of their formation depends on the nature of the metal-complexing agent ion, ligands, and also on pH, ionic strength, and temperature.

For the first time, ultra-thin coatings of clay/PAA with a large value of capacity with respect to the antibacterial agent gentamicin were obtained. It was found that in a strongly acidic medium, binding of clay and PAA plates in multilayers is realized mainly due to the dipole-cation interactions between positively charged clay functional groups and protonated carboxyl groups of PAA. It is shown that the obtained films are capable of exhibiting antibacterial activity, to isolate gentamicin in response to a decrease in the pH environment, while the features of the pH-stimulated behavior of the film are due to the presence of a weak polyacid PAA in their composition. A mechanism is proposed for the pH of the stimulated release of gentamicin from the clay / PAA film.

SEM and AFM methods, the structure and surface properties of PEMS (clay / PAA) n, (clay / PAA), n-gentamicin and (clay / gentamicin) n were studied. A layered structure of clay-containing multilayers is shown. They also showed that they have high antibacterial activity against gram-positive and gram-negative bacterium bacteria S. aureus, and are cytocompatible with osteoblast cells.

Thus, the given far from complete list of works in this area points to the potential prospect of using the multilayer assembly method to obtain a new type of composite materials with targeted properties and is a general strategy of an innovative approach to the creation of new biotechnologies and tissue engineering.

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