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OBTAINING THREE-DIMENSIONAL NANOSIZE OBJECTS ON A "3D PRINTER + ELECTROSPINNING" MACHINE

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The possibility of obtaining three-dimensional nanosize polymeric fibers has been shown. The obtained fibers are oriented, which makes it possible to create three-dimensional objects. The proposed method allows alignining strongly directive nanofibers from a polymethylmethacrylate polymer with a diameter of 50 to 500 nm. The use of different types of electrodes enables one to vary the nanofiber size. Oriented polymeric nanofibers were used to construct bioskeletons for biological cells.

Keywords: *3D printer, electrospinning, nanosize fibers, nanoobjects.*

Introduction. At present, there are various methods to obtain nanomaterials. In turn 3D printing has reached a stage where the desired product can be made irrespective of the complexity of its shape. The application of such technology to nanofabrication will permit obtaining nanosize substances with a necessary geometric structure. We propose the most novel method that involves the process of electrospinning of nanofibers under the action of a high-voltage electric field and 3D technologies. The central problem with using electrospinning for nanofabrication is internal instability of electrified nanojets experiencing mutual Coulomb repulsion. In our method, we solve this problem by employing electrodes of different types, which represent modifications of the H shape, and also two parallel II electrodes. This approach enables us to reverse the directions of the lines of electric field, which is necessary to obtain oriented nanofibers. The proposed method permits aligning strongly directive nanofibers of diameter of 50 to 500 nm by building "nanowalls" of them. This technology of nanofabrication with a 3D printer will find its application in various fields, such as the production of nanofilters, nanorobotics, nanoelectronics, and medicine, in particular, obtaining a skeleton for biological cells.

The application of 3D technologies to nanofabrication will enable one to produce nanosize objects. Furthermore, nanostructures or microstructures can be used as substrates, and thus the complexity of the object's shape can be implemented at a nanolevel. An example of direct processes of deposition at a nanolevel is dip pen nanolithography (DPN). This method enables one to "draw" collections of molecules in a line with a width of tens of nanometers [1]. Electrospinning is an attractive process for applying nanosize objects that use nanofibers emitted from a liquid droplet on exposure to a strong electric field [2]. It should be noted that the shape of the jet and the rate of diffusion of polymer molecules contained in a bounded volume of the solvent are very difficult to monitor.

Manufacture of 3D objects by direct deposition of functional materials has been the subject of active study in the macroscale production in the past few years. 3D printing is a promising production technology, permitting obtaining products of any degree of complexity and making the production more attractive economically.

The electrospinning method is a simple and available technique for obtaining nanosize objects by using nanofibers emitted from a liquid droplet on exposure to a strong electric field. The central problem with using electrospinning for nanoproduction is internal instability of electrified nanojets experiencing mutual Coulomb repulsion [3, 4].

The interest in nanosize materials is provoked by the fact that their mechanical properties, such as ultimate strength, tensile strength, bending strength, and compressive strength, as well as elastic moduli, grow as the particle size decreases, and reach a theoretical limit once a nanolevel has been attained [5]. Using various structures and modifications of the equipment, by the electrospinning method one obtains at present nanofibers from highly diverse materials: polymers, composites, semiconductors, metals, and ceramics [6].

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In the process of electrospinning, the jet is stretched by electrostatic forces and gravitational forces, whereas surface tension, viscosity, and inertia also play a role. In the process of thinning of the jet, the surface density of the charge changes, which in turn affects the electric field. Once the jet changes from the Taylor cone to a nearly straight line, the motion of the liquid jet is acted upon by various forces, such as the Coulomb electric-field force applied by the external electric field, surface-tension forces, gravitational force, and air resistance force [7]. Relying on D. A. Saywell′s work on electrohydrodynamic processes that occur in a Taylor cone, we can represent the jet′s state in the form of four stead-state equations: the laws of conservation of mass and electric charge, the force-moment equation, and the Coulomb law for an electric field. Thus, the electrospinning jet can be represented by the following equations [8]:

the law of conservation of mass is written by the expression

$$\pi R^2 v = Q \,, \tag{1}$$

where Q is a constant volumetric rate of flow, R is the jet radius, and v is the axial velocity of the liquid within the jet;

the law of conservation of charge can be expressed by the formula

$$\frac{d}{dz}\left(2\pi R\sigma v + \pi R^2 KE\right) = 0 \,, \tag{2}$$

where σ is the surface density of the charge, K is the conductivity of the jet, and E is the electric field strength;

the moment equation is of the form

$$\frac{d(\pi R^2 \rho v^2)}{dz} = \pi R^2 + \frac{d}{dz}\left(\pi R^2(-P + \tau_{zz}) + \frac{\gamma}{R}\left(2\pi R\left(\frac{dR}{dz}\right)\right) + 2\pi R\left(t_z^{\mathrm{e}} - t_z^{\mathrm{e}}\left(\frac{dR}{dz}\right)\right)\right), \tag{3}$$

where ρ is the liquid density, τ and t are the indices of viscosity in the axial direction and of the tangential component respectively, and γ is the surface tension.

The Coulomb integral for tangential electric forces in the jet is determined by the following expression:

$$E - \ln\frac{1}{x}\left[\frac{\beta}{2}\frac{d^2(R^2E)}{dz^2} - \frac{1}{\varepsilon_{\mathrm{air}}}\frac{d(\sigma R)}{dz}\right] = E_\infty \,. \tag{4}$$

As can be seen from the equations, the electric field strength is one of the basic parameters of formation of a jet; in our experiments, use is made of a pulse electric-current generator, which in turn hampers quantitative calculations.

Experimental. Polymeric fibers were obtained on a "3D printer + electrospinning" machine at the Institute of Combustion Problems and at the University of Texas at Dallas. The machine incorporated a 3D printer, a high-voltage source, a protective case, and a syringe pump. A 10 kV voltage was fed to the needle tip and to the electrode; the distance between them was 15 cm. In the work, we employed various types of electrodes, which enabled us to obtain oriented fibers with a thickness of the order of 200 nm. Figure 1 gives a diagrammatic representation of the "3D printer + electrospinning" machine. The 3D printer was modified, namely, the extruder was replaced by a capillary to which a polymer solution was delivered. High voltage was fed to two electrodes one of which was on the 3D printer′s printed-circuit board, and the other was the capillary.

It should be noted that the electrodes employed in our experiments had different geometric shapes. Figure 2 gives their diagrammatic representations. Modifications were necessary for changing electric-field lines, which in turn enabled us to obtain even "walls" from the polymeric fibers.

At this stage of work when fiber printing was implemented, we obtained the simplest figures. At a later time, there are plans to carry out experiments with three types of polymers, and also work on obtaining several layers from different types of polymers.

Results and Discussion. As a result of the work, the authors obtained nanosize films from different types of polymers. Figure 3 gives the images obtained on an electron microscope with three different types of substrate electrodes. The electrodes differed only in geometric shape. The difference of the obtained fibers is attributed to the fact that the electric field changes with different types of electrodes, which in turn affects the formation of nanosize polymeric fibers. In the images, we can see the orientation of the fibers whose size is ~200 nm. The dimension of the obtained film depends just on the dimension of the first electrode; in our experiment, we obtained 5 × 5 cm films.