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Thin Film Net Metal–Polymer Composites

V. I. Shadrina[a], I. A. Bashmakov[b], V. E. Agabekov[a], and F. N. Kaputskii[b]

[a] *Institute of Chemistry of New Materials, National Academy of Sciences of Belarus, ul. F. Skoriny 36, Minsk, 220141 Belarus*
e-mail: ShadrinaVictoria@mail.ru

[b] *Research Institute of Physicochemical Problems of Belarus State University, Minsk, Belarus*

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Abstract—On the basis of carboxylated nitrocellulose were formed ordered micronets containing nanoparticles of nickel in their surface layer. The optimal conditions for a uniform coating with nickel of the polymer net film are as follows: activating the surface with solutions of tin(II) and palladium chlorides for 30–60 s and the action of the nickel developer for at least 3 min at 20ºC.

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Nanoheterogeneous composite materials with the metal nanoparticles incorporated into a dielectric polymer matrix are of interest in the areas like electronics and photonics due to the unusual photo and electrical properties caused by the mutual influence of the matrix and the nanoparticles [1]. The ordered metallic structures are also of interest in optics as substrates for recording the Giant Raman Scattering spectra [2, 3].

The methods of forming metal coatings on polymeric materials are quite varied: thermal vacuum [4], electrolytic [5–7], and chemical deposition of metals [1–4, 8]. One of the promising methods is the chemical metallization [1, 4], which allows to obtain a uniformly thick coating on the surface of products of not only simple, but of complex form, as well as to apply a metal selectively by selective surface activation.

The purpose of this work was obtaining composite microstructures as thin polymer net films containing nickel nanoparticles fixed on their surface, and studing their morphology with scanning probe microscopy.

As known, chemical metallization of polymer materials requires prior activation of the surface, consisting essentially in the application of a metal-catalyst on the covered sample. The most common method is the senso-activation, which includes two consecutive operations: sensitizing (coating the polymer surface with a compound that can reduce the metal-catalyst ions, in particular, processing the sample with a solution of tin(II) chloride), and activation (treatment of the sensitized surface with a solution of a compound of catalytically active metal such as palladium) [1, 4].

At the processing the film with tin chloride solution, the presence of carboxy groups in carboxynitrocellulose causes formation of the salt form of the modified cellulose and Sn^{2+} cations fixed on the sample. At the subsequent processing of such film with palladium chloride redox reaction occurs resulting in formation of catalytically active palladium nanoparticles on the polymer net. According to published data [1] the solution for the chemical deposition of nickel has a high dissipating power, namely, it ensured the formation of a uniform metal coating on the entire sample surface. For finding the optimal conditions of selective nickel precipitation on the microstructured net film duration of the stages of sensitization, activation, and the nickel precipitation was varied, as well as the temperature of the process of nickel deposition on the polymer micronet.

It is known [4] that for obtaining a durable, uniform metallic coating a certain optimal amount of Sn^{2+} on the surface should be provided. At the insufficient amount, a cover nonuniform by thickness and density is formed on the surface; excess of tin makes the cover loose, with poor adhesion to polymeric materials. We found that at prolonged (15–60 min) processing of carboxynitrocellulose micronet with tin(II) chloride and palladium chloride solutions at the step of activation, the palladium nanoparticles are formed both on the surface of the net film and inside the cells, like

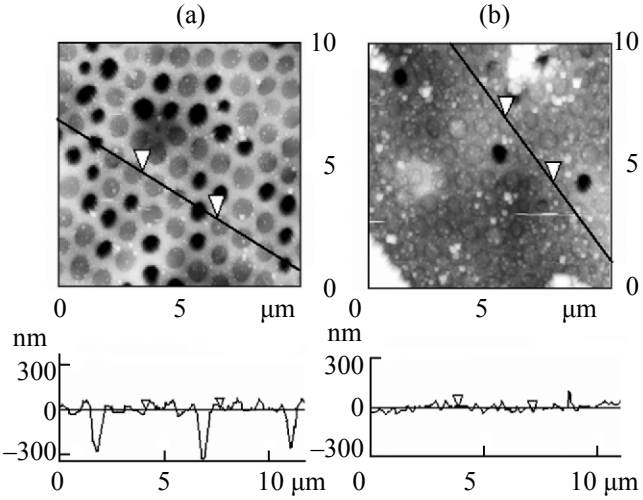

Fig. 1. AFM images of Ni nanoparticles in the polymer matrix of carboxynitrocellulose (activation surface with $SnCl_2$–$PdCl_2$ for 30 min, temperature of the nickel physical developer solution 40°C). Duration of nickel deposition, min: (a) 2 and (b) 7.

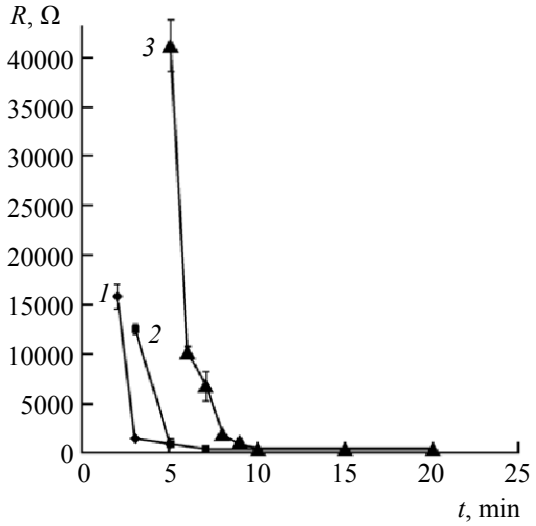

Fig. 2. The dependence of the linear resistance of carboxynitrocellulose-Ni micronet on the duration of the nickel deposition. Temperature in the process of the nickel deposition, °C: (*1*) 40, (*2*) 30, and (*3*) 20.

at the metallization of such samples with nickel (Fig. 1). For example, nickel deposition for even 0.5–2 min leads to filling with nickel not only the links of the micronet, but also its cells (Fig. 1a). Increase in the duration of the metallization process to 7 min results in obtaining a continuous nickel film, the formation of large aggregates of nanoparticles, and virtually in the disappearance of the initial net structure (Fig. 1b), therewith the size of the nickel nanoparticles formed is about 40 nm.

The degree of filling the polymer micronet with nickel nanoparticles is affected by the temperature of the solution of the nickel physical developer. Thus, the increase in temperature from 20 to 40°C increases the degree of nickel deposition that causes a change in resistance of the samples (Fig. 2). Initial carboxynitrocellulose net film is an insulator ($R > 2$ GΩ), and in the process of nickel deposition occurs a gradual decrease in its resistance. The resistance 10^4 Ω at a temperature of the nickel physical developer solution 20°C is achieved after 5–6 min of nickel deposition, at 40°C in 2 min. Then a sharp drop in resistance of the sample occurs, which within 7–10 min becomes equal to the value characteristic of metals (~50 Ω). Accord-ing to the AFM data, such samples are characterized by almost complete filling with nickel of all micronet cells (Fig. 1b).

In order to form the nickel nanoparticles selectively on the links of the net film, the stages of the film sensitization and activation were shortened, and to prevent the tin(II) chloride hydrolysis we used hydrochloric acid solution. Nickel deposition was carried out at 20°C. We showed that the reduction in the course of processing carboxynitrocellulose film with tin(II) chloride and palladium chloride solutions to 30–60 s leads to a more selective formation of the catalyst nanoparticles on the micronet surface. According to AFM examinations, when the micronet was activated by this procedure, at the increase in duration of processing with nickel developer at the nickel deposition the degree of filling the polymer film surface with the metal nanoparticles increases (Fig. 3). Thus, at the nickel deposition for 2 min, the aggregates of nickel nanoparticles are observed on the micronet (Fig. 3a). A dense homogeneous layer of metal nanoparticles on the polymer matrix is formed at the action of nickel developer on the sample for more than 3 min (Fig. 4b). It should be noted that with this method of activating the surface, at the nickel deposition of the samples even for 90 min filling the cells with the metal nanoparticles does not occur. Uniform covering with nickel of the links of microstructured net film takes place at 20°C, which is significantly lower than the typical temperature (~60°C) of its chemical deposition [1, 4].

Thus, we found that selectivity of nickel deposition on the carboxynitrocellulose net film depends mainly on the duration of the stages of sensitization and activation of its surface.

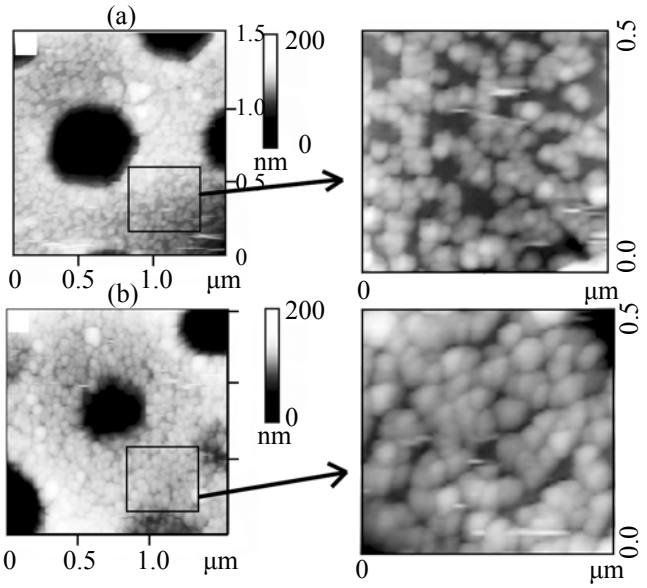

Fig. 3. AFM images of Ni nanoparticles on the carboxynitrocellulose polymer matrix (activation of surface with $SnCl_2$–$PdCl_2$ for 30 s). Duration of nickel deposition, min: (a) 2 and (b) 10.

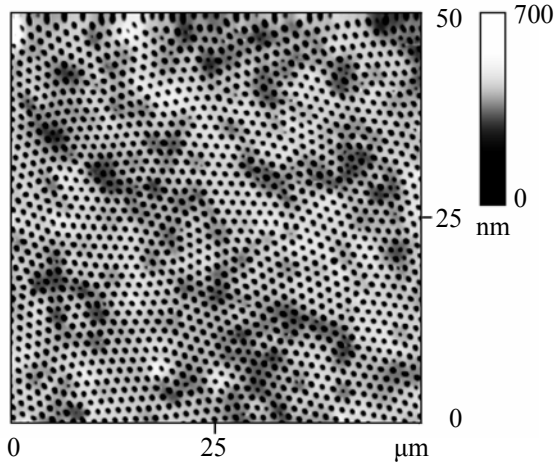

Fig. 4. Microstructure of carboxynitrocellulose net film.

A rapid (~30–60 s) processing of the carboxynitrocellulose micronet with the activating solutions of tin(II) and palladium chlorides followed by the nickel deposition for 3 min or longer leads to the formation of a dense uniform layer of nickel nanoparticles on the surface of the polymer matrix. With an increase in the duration of the stages of sensitization and activation up to 15–60 min, the metal nanoparticles at the nickel deposition are formed not only on the surface of the net film, but also within its cells.

EXPERIMENTAL

For the formation of thin film structure, as the starting polymer was used a chemically modified cellulose containing nitroester and carboxyl groups. Synthesis of carboxynitrocellulose was carried out by the method [9] that includes oxidation of C^2 and C^3 atoms of the cellulose macromolecule monomer unit with the subsequent nitration of carboxylic derivative.

Formation of microstructured cross-linked films was carried out as in [10]. To the surface of water cooled to 0–2°C was applied 20 μl of 2% solution of carboxynitrocellulose in the binary solvent (isoamyl acetate – butanol in 3 : 1 ratio by volume). After 5–10 s onto the formed liquid polymer film a flow of air was directed with relative humidity 75% at a rate 2.3 l min^{-1}. Then the film was left for 5–10 min for the complete evaporation of the solvent, and the ordered carboxynitrocellulose micronet (Fig. 4) was transferred onto a solid substrate. Obtaining the cellular structure of the film is based on the process of "self-organization" in it of water microdroplets into a dense hexagonal packing [10].

Modification of polymer matrix with the nickel nanoparticles was carried out by chemical reduction of Ni^{2+} with a solution of sodium hypophosphite. Preliminary, a metal catalyst (Pd) was introduced to the net film. Palladium was introduced in the polymer micronet in two ways: (a) the carboxynitrocellulose film fixed on a polycor substrate was immersed into freshly prepared saturated solution of tin(II) chloride, then washed with distilled water, and treated with a saturated solution of palladium chloride (pH 5.5); (b) the carboxynitrocellulose film fixed on a polycor substrate was immersed in 10 wt % solution of tin(II) chloride acidified with hydrochloric acid to pH 3, then washed with distilled water, and treated with 0.1 wt % solution of palladium chloride, acidified with hydrochloric acid to pH 3.

Then the micronet activated by one of the above methods, containing the catalytically active palladium particles, was placed into a solution of nickel physical developer, that is, to a mixture of two solutions: (1) nickel chloride (30 g l^{-1}) and (2) sodium hypophosphite (10 g l^{-1}), sodium citrate (88 g l^{-1}), ammonium chloride (50 g l^{-1}), and ammonia (25%) in the ratio 1:4 by volume [7].

The duration of the carboxynitrocellulose film processing with the solutions of tin(II) chloride and

palladium chloride ranged from 30 to 60 min, with the nickel developer, from 0.5 to 90 min. The electrical resistance of the films was measured on a combined digital device SHCH-300.

The morphology of the films formed was studied by means of atomic force microscopy (AFM) on a scanning probe microscope MultiMode III (Vecco, USA). Conditions of scanning: speed 3.5 Hz; cantilever of silicon nitride with a stiffness constant 0.12 N m^{-1}. The density of information was 512 × 512 pixels. Images were processed using the software "Nanoscope 5.31r1."

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