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Selective Membranes with Biologically Active Surface

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Abstract—Composite membranes have been developed for media where accumulation of pathogenic microorganisms on the membrane surface is possible. It has been proposed to use as membrane skin layer a polymer nanocomposite modified with detonation nanodiamonds containing surface-bound dibutyltin dilaurate as biologically active substance, which should ensure self-cleaning of the membrane surface.

Keywords: Composite membranes, detonation nanodiamonds, surface modification, polymer nanocomposites.

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Search for new efficient agents against pathogenic microorganisms is the most important aspect of problems related to safe environment, protection of technosphere from biodeterioration, and food preservation. Radically new approaches for solving these problems are now actively developed. In this respect, a promising line is wide implementation of membrane technologies.

Membrane technologies are effectively used in biology, medicine, and health protection. Processes based on membrane filtration have been implemented most widely. Primarily, such processes include purification of water from both colloidal organic and inorganic matter and various microorganisms. The use of filtration membranes in analytical and diagnostic microbiology and virology for the isolation and concentration of biological matter should also be noted.

Apart from processes based on membrane filtration, those involving diffusion membrane separation are important for biology and health protection. For example, creation of controlled gas media, which is based on diffusion membrane separation, underlies the solution of one of the most urgent problems of modern civilization, preservation of foods.

A combination of filtration and diffusion modes of membrane separation is used in the creation of sterile rooms. The need of the latter sharply increases during technological and natural disaster management when necessary material and energy supply is lacking; in these cases membrane technologies have almost no alternative. The use of membranes for the treatment of wastewater from medical facilities is based on entrapment of various pathogenic species on the membrane surface.

Nowadays, tolerance of pathogenic microorganisms and viruses to newest antibiotics has raised a serious problem for human health protection. Furthermore, synthesis of new highly efficient agents for protection from biodeterioration is often accompanied by discharge of highly toxic substances into the environment, thus further increasing extremely high chemical load on the biosphere.

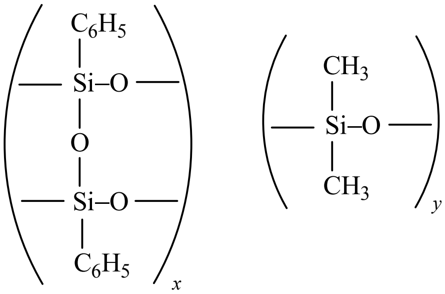
The goal of the present work was to elaborate "green" composite membranes with antibiotic properties of the surface. Environmental safety of such membranes is ensured by the lack of free migration of the bioactive component to the environment.

EXPERIMENTAL

Materials

As base membrane we used a polyethylene terephthalate (PET) track membrane (thickness 12 μm, pore diameter 0.6 μm) manufactured by the Cyclotron Laboratory at the Ioffe Physical Technical Institute, Russian Academy of Sciences.

The skin layer was prepared from a polysiloxane multiblock copolymer with a length ratio of rigid (*x*) and flexible (*y*) unit sequences of 25:61. The fraction of flexible polydimethylsiloxane (PDMS) blocks was 42 wt %.



Detonation nanodiamonds ASUD-99 were obtained from the Bakul Institute for Superhard Materials (Kiev, Ukraine). Dibutyltin dilaurate $Bu_2Sn(OCOC_{11}H_{23})_2$ (R_b–Sn) was used as modifier.

Procedures

Modification of the DND surface. A sample of DNDs was mixed with a slight excess of R_b–Sn on stirring for 15 min, and the suspension was heated for 3 h at 100°C under stirring. The modified DNDs were separated by decanting and transferred into excess toluene, The resulting suspension was subjected to ultrasonic treatment and was then centrifuged at 6000 rpm. The modified DND sol was separated by decanting.

Modification of the track membrane surface. The polysiloxane copolymer was dissolved in toluene to a concentration of 40 wt %), and the modified DND sol was added under stirring (5 wt % with respect to the polymer). A track membrane was placed in a Büchner funnel and fixed by suction. The nanocomposite solution was applied on the membrane surface, filtered, and dried until the absence of toluene odor. This procedure ensured the pore surface remaining unchanged. The modified membrane was finally dried for 4 h at 100°C. Depending on the particular goal, partly or completely covered pore surface can be obtained.

RESULTS AND DISCUSSION

The long history of biology has led to the discovery of a huge number of biologically active substances which can be used to control pathogenic microorganisms. However, direct application of biologically active substances on a surface to be protected involves the risk of their discharge into the environment. Therefore, to achieve "green" membrane operation, it is necessary to immobilize active substances in a polymeric skin layer.

Nowadays, biological activity of nanosized particles and their application as antiseptics are widely discussed in the literature. In particular, metal nanoparticles and some nanocarbons are studied in this respect. In recent time increasing attention is given to prospects in medical and biological applications of detonation nanodiamonds (DNDs)[1] [1].

Small particle size, fractal structure, and the presence of surface functional groups constitute those properties which underlie almost all attempts to implement DNDs in practice. The formation of DND complexes with physiologically active molecules has attracted much interest. A combination of high dispersibility and physiological activity of DND particles may give rise to a pronounced effect on pathogenic microorganisms.

The algorithm applied for the manufacture of composite membranes included (1) immobilization of active substance on the DND surface, (2) dispersion of the modified sorbent in polymer matrix, and (3) application of the nanocomposite onto a porous support.

It is known that organic tin compounds are highly toxic for living matter. For instance, an efficient agent has been designed on the basis of triphenyltin acetate Ph_3SnOAc for control of potato and sugar beet fungal diseases. Tributyltin hydroxide is used to protect equipment in the pulp-and-paper industry from micromycetes. Dibutyltin dilaurate is widely used in practice [2], e.g., to ensure antifungal protection of memorials and other architectural objects [3, 4]. From the chemical viewpoint, R_b–Sn is capable of reacting with functional groups possessing a labile proton [5]. Figure 1 shows a scheme of such reaction. We have already performed functionalization of DND surface with dibutyltin dilaurate with a view to make it hydrophobic [6]; however, the reactant ratio was not rigorously controlled, so that the final product could contain unreacted R_b–Sn. Therefore, the probability for discharge of R_b–Sn into the environment could not be excluded. In order to achieve quantitative functionalization it is necessary to reliably determine the concentration of labile proton-containing groups on the DND surface. For this purpose we used the

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[1] Detonation nanodiamonds constitute a crystalline component of products formed by detonation of oxygen-deficient explosive mixtures.

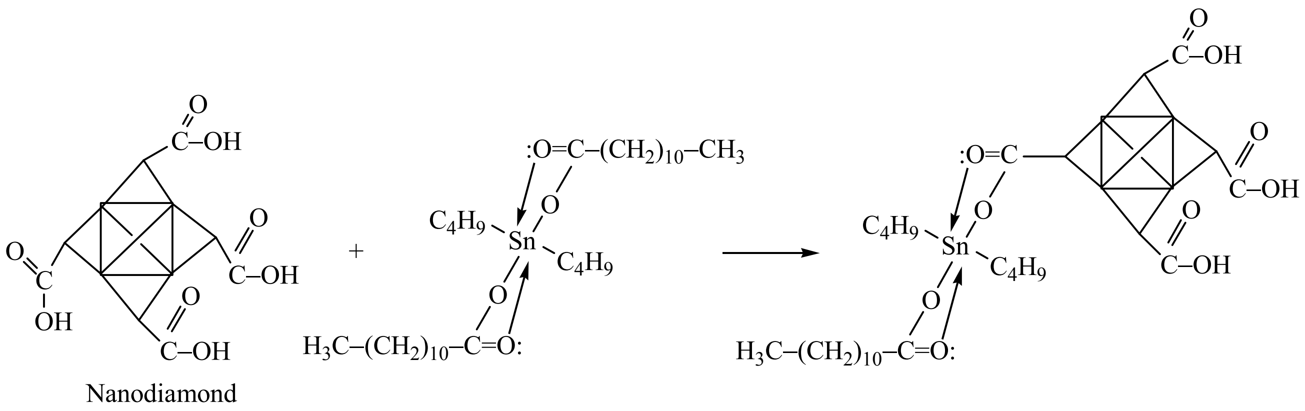

Fig. 1. Functionalization of DND surface with dibutyltin dilaurate.

Tserevitinov–Chugaev method [7] based on measurement of the gas volume liberated in the reaction of alkylmagnesium halide with a substance containing reactive protons. The results of such measurements can be affected by the presence of adsorbed water on the DND surface. Therefore, DNDs were preliminarily dried in a high vacuum (0.5 mm) at 250°C. The initial sample contained 2.78 mol of labile protons per gram of DND, and their concentration after vacuum drying was reduced to 0.45 mol per gram of DND. These data show that the amount of covalently bound groups containing a labile proton is much lower than the amount of labile protons in molecules adsorbed on the DND surface, i.e., vacuum drying is an important step in the DND surface functionalization process.

Detonation diamonds prepared in such a way were modified with dibutyltin dilaurate according to the scheme shown in Fig. 1. The efficiency of this scheme was estimated by studying the structure of suspensions of the initial and modified DNDs in polar (water) and nonpolar (toluene) medium, respectively. Figures 2 and 3 show the size distribution curves obtained by dynamic light scattering. It is seen (Fig. 2) that even in nonpolar medium a part of unmodified DND particles is transferred to the suspension, i.e., their surface is hydrophobic. According to the weight-average size distribution, micron-sized particles constitute the main fraction of DNDs, and the resulting suspension is unstable (sedimentation is observed in ≤15 min).

Modification of DNDs with R_b–Sn ensures efficient dispersion of almost all DND particles in toluene (Fig. 3). Special experiments showed complete absence of labile proton-containing groups on spatially accessible DND surface, which well supports the conclusion that

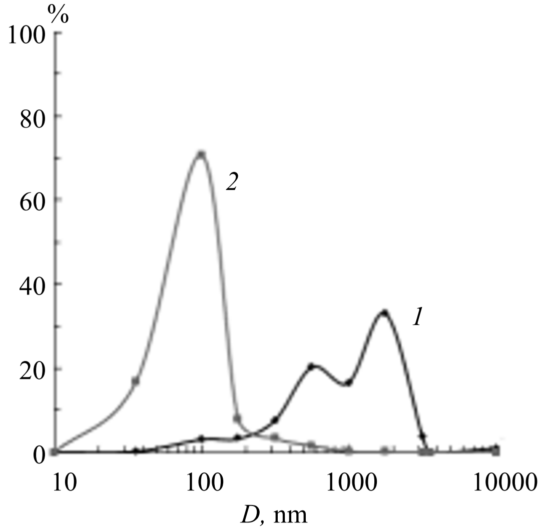

Fig. 2. Unmodified DND size distribution in a toluene suspension: (*1*) weight-average size distribution and (2) number-average size distribution.

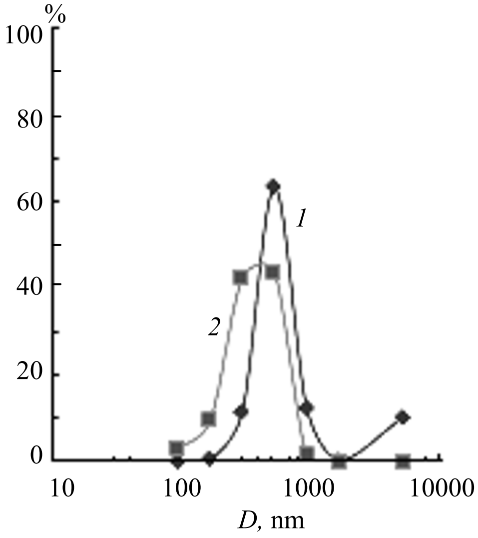

Fig. 3. Dibutyltin dilaurate-modified DND size distribution in a toluene suspension: (*1*) weight-average size distribution and (2) number-average size distribution.

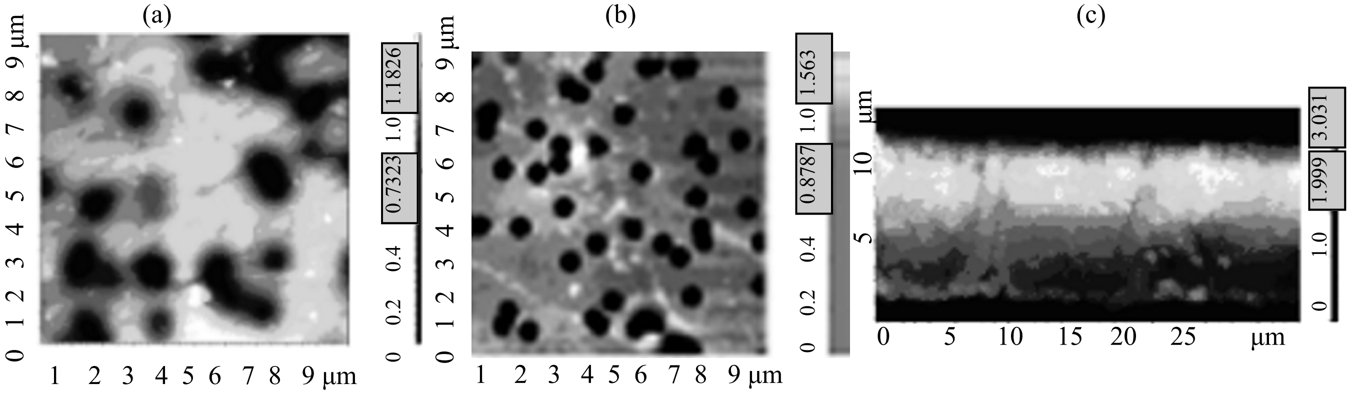

Fig. 4. Atomic force microscopy images of the modified composite membrane: (a) top, (b) bottom, and (c) section.

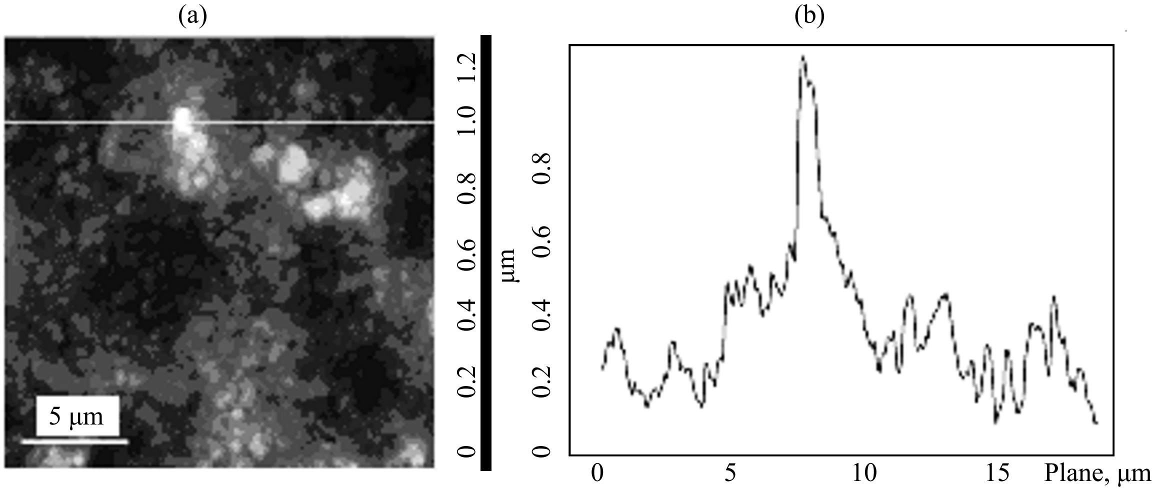

Fig. 5. Atomic force microscopy images of (a) modified composite membrane and (b) its surface profile.

chemical grafting of R_b–Sn makes the surface hydrophobic. It should be noted that modification of DND particles changes not only the character of their surface but also the structure of DND suspension. The resulting suspension becomes more uniform with respect to the particle size. The effect of surface modification on the structure of DND suspensions in polar and nonpolar media will be the subject of a particular study.

Our experiments showed that R_b–Sn should be taken in 25 wt % excess with respect to DND to achieve stoichiometry of the reaction given by Fig. 1. After washing with toluene, the unreacted R_b–Sn residue is immobilized during the process of dispersion of DND←R_b–Sn particles in polymer solution. The immobilization mechanism involves coordination of dibutyltin dilaurate to hydroxy groups in the polymer chains [8].

Figure 4 shows AFM images of the prepared composite membranes. The described procedure for membrane preparation makes it possible to obtain a defect-free thin-film coating with a thickness of 1 µm (Fig. 4c). The bottom membrane surface remains uncoated, so that the pore space also remains unaffected. The absence of open pores was checked by applying an air pressure of 1.0 bar to the membrane (no air bubbles was observed at the bottom side).

The track membrane surface was hydrophobized by passing the polymer solution through the membrane. Change of the membrane porosity was monitored by measuring the mass transfer parameters for simple gases. The thickness of the skin layer was additionally estimated by comparing the air efficiencies of the initial and modified membranes in the dead-end filtration mode under a definite pressure drop using a static cell. The efficiency was calculated using the known formula [9], in which the total gas flow rate J is determined by the Knudsen and Poiseuille flows:

$$J = a(P_2 - P_1)/\sqrt{M} + b(P_2^2 - P_1^2)/\sqrt{\eta},$$

Here, a and b are parameters of the membrane pore space, $\Delta P = P_2 - P_1$ is the pressure drop, M is the molecular weight, and η is the dynamic viscosity of gas. We have found that the skin layer thickness is 0.8 μm, which is very consistent with the AFM data.

The membrane selectivity is determined by the polymer nature. The selectivity factor determined by our experiments for the nitrogen/oxygen system was $P(O_2/N_2) = 2.4$, which agrees well with the data of [10].

Figure 5 shows an AFM image of the upper part of the composite membrane at higher magnification (Fig. 5a) and its surface profile (Fig. 5b). It is seen that the DND particle size ranges from 200 to 1000 nm, in keeping with the dynamic light scattering data.

The prepared membranes were tested for biological activity. For this purpose, the membrane surface was inoculated with *Penicillium glaviform*. A membrane with unmodified polymeric skin layer was used as control. It was found that membranes with DND-R_b–Sn-modified polymeric skin layer efficiently inhibited growth of micromycetes on the surface.

REFERENCES

1. Shugalei, I.V., Sudarikov, A.M., Voznyakovskii, A.P., Tselinskii, I.V., and Ilyushin, M.A., *Khimiya poverkhnosti detonatsionnykh nanoalmazov kak osnova sozdaniya produktsii biomeditsinskogo naznacheniya* (Chemistry of Detonation Nanodiamond Surface as a Basis for the Design of Materials for Biomedical Applications), St. Petersburg: Leningr. Gos. Univ. imeni A. S. Pushkina, 2012.
2. Mel'nikova, E.P., Smolyanitskaya, O.L., Slavoshevskaya, L.V., Lebedeva, E.V., and Panina, L.K., Abstracts of Papers, *Vsesoyuznaya konferentsiya "Biopovrezhdeniya v promyshlennosti"* (All-Union Conf. "Biodeterioration in Industry"), Penza, 1993, p. 18.
3. Vlasov, D.Yu. and Dement'ev, A.A., *Infstroi*, 2005, vol. 5, no. 13, p. 22.
4. Vlasov, D.Yu., Arkhipova, M.A., Dolmatov, V.Yu., Frank-Kamenetskaya, O.V., and Shilova, O.A., *Probl. Med. Mikol.*, 2006, vol. 8, no. 2, p. 26.
5. Kocheshkov, K.A., Zemlyanskii, N.N., Sheverdina, N.I., and Panov, E.M., *Metody elementoorganicheskoi khimii. Germanii, Olovo, Svinets* (Methods of Organometallic Chemistry. Germanium, Tin, Lead), Moscow: Nauka, 1968.
6. Voznyakovskii, A.P., Kalinin, A.V., and Fursenko, A.V., Abstracts of Papers, *Pyataya Vserosiiskaya konferentsiya (s mezhdunarodnym uchastiem) "Khimiya poverkhnosti i nanotekhnologiya"* (5th All-Russian Conf. with Int. Participation "Surface Chemistry and Nanotechnology"), St. Petersburg: Sankt-Peterb. Gos. Tekhnol. Inst., 2012, p. 218.
7. *Methoden der organischen Chemie (Houben–Weyl)*, Müller, E., Bayer, O., Meerwein, H., and Ziegler, K., Eds., Stuttgart: Georg Thieme, 1953, 4th ed., vol. 2. Translated under the title *Metody organicheskoi khimii*, Moscow: Gos. Nauch.-Tekh. Izd. Khim. Lit., 1963, vol. 2, p. 307.
8. Shan-Yang Lin, Wen-Jin Tsayb, Ying-Liang Chenb, and Chau-Jen Leeb, *J. Controlled Release*, 1994, vol. 31, no. 3, p. 277.
9. Ageev, E.L., *Membrany*, 2001, no. 9, p. 42.
10. Vorotyntsev, V.M., Drozdov, P.N., Vorotyntsev, I.V., and Smirnov, K.Yu., *Inorg. Mater.*, 2009, vol. 45, no. 11, p. 1263.