Structure and electrottransport properties of track-etched membranes modified by plasma polymerization of organic compounds

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Abstract: Structure and electrottransport properties of poly(ethylene terephthalate) track-etched membranes modified by plasma polymerization of organic compounds were studied. Physicochemical aspects of the conductivity asymmetry arising from the contact of two layers with functional groups differing in chemical constitution and properties are discussed.

Keywords: composite membranes, plasma polymerization, asymmetry of conductivity

1. Introduction

Plasma treatment is a convenient technique for the surface modification of polymer membranes. Treatment by plasma involves a number of physicochemical processes depending on the discharge type and nature of the gas used that allow directionally controlling the structure and chemical composition of the surface layer of polymer membranes [1]. Chemical processes occurring under modification in the membrane surface layers are largely determined by the composition of the working plasma vapor phase. Two plasma types are used: plasma of simple gases resulting in no formation of polymers (non-polymerizable gases) and plasma in the atmosphere of vapors of some organic compounds leading to polymer formation. In the second case, plasma treatment of membranes causes deposition of a thin polymer film on their surface as a result of the polymerization process. Herewith, composite membranes are formed that consist of a porous support (the initial membrane) and plasma-deposited polymer layer. As dependent on the duration of plasma treatment, one may obtain composite membranes for ultra- and nanofiltration, and also for reverse osmosis. In the latter case, a thin polymer layer is deposited on the surface and completely covers the pores. The possibility of regulating the thickness of the plasma deposited layer determining selective properties of membranes and a wide choice of organic compounds for such process makes this method especially promising. New properties of the composite membranes obtained in this process depend on the chemical compound used.

In this paper, the structure and electrottransport properties of poly(ethylene terephthalate) track-etched membranes (PET TMs) modified by plasma polymerization method have been investigated. Pyrrole, acetylene, thiophene, hexamethyldisilazane, hexamethyldisiloxane and 1,1,1,2-tetrafluoroethane were used as precursors to obtain the polymer layers on the membrane surface.

2. Experimental details

In the present experiments PET TMs with an effective pore diameter of 125 and 215 nm were used. To produce the membrane, poly(ethylene terephthalate) film with a thickness of 10.0 µm (Lavsan, Russia) was irradiated by krypton positive ions, accelerated at ~1 MeV/nucleon in the cyclotron U-400 (Dubna, JINR), and then subjected to the physicochemical treatment on a standard procedure [2]. Pyrrole (Py), hexamethyldisilazane (HMDSN), 1,1,1,2-tetrafluoroethane (Tf), hexamethyldisiloxane (HMDSO), acetylene (Ac), and thiophene (Th) (99% purity specified for synthesis applications from the Aldrich Chemical Co.) were used without additional purification. The deposition of the plasma polymerized films on the membrane surface was done in a plasma-chemical reactor using a RF-discharge in a parallel plate configuration at the frequency of 13.56 MHz. Only one side of the membrane was subjected to the plasma treatment. The deposition time and discharge parameters were varied. The scheme of a plasma-chemical setup and treatment technique are described in detail in [3]. The characteristics of the initial membrane and the membranes with a deposited layer of plasma polymer were determined through a series of procedures detail given in [3]. Measurements of the membrane current-voltage characteristics were carried out with a direct current regime in the voltage range of −1 to +1 V using a PC-controlled potentiostat “Elins P-8S” (Russia) with a scan rate of 50 mV/s. A two-chambered cell with Ag/AgCl electrodes, containing a water solution of potassium chloride of identical concentration on the both sides of the membrane, was used for this purpose.
3. Results and discussion

The parameters of the membranes subjected to the plasma are presented in Table 1. The results show an increase of membrane mass during plasma treatment. The thickness of the membranes increases, and the effective pore diameter in this process decreases. The increasing thickness and decreasing effective pore diameter indicate that the deposition of polymers takes place both on the surface of the membranes and on the walls of its pores. Electron-microscopic research of the surface of modified membranes (Fig. 1) shows that deposition of the polymers occurs predominantly on the sample surface. Herewith for the membranes treated for the short time, only a negligible decrease in the pore diameter is observed (Fig. 1b). The membrane pores are open in this case because the thickness of the deposited polymer layer on the surface is small enough. An increase in the plasma treatment time leads to an increase in the thickness of the deposited polymer layer and the membrane pores on the plasma treated side are covered by a plasma polymer layer (Fig. 1d). SEM investigation of the cross-sections of this kind membranes shows that a thin polymer layer is formed on its surface that blocks the pores. From the electron microscopy data, it also follows that for the modified membranes the pore diameter on the untreated side remains unchanged relative to the initial membranes. Moreover, results of the testing of modified membranes show that an effective pore diameter of the membranes formed at the short plasma treatment time decreases insignificant. On the contrary, for the membranes formed at the longer plasma treatment time, an effective pore diameter reduction is quite essential (Table 1). It is indicates that the pore diameter in the polymer layers deposited by plasma is much smaller than the ones of the initial membranes and pores get the asymmetric (conical) shape in this case.

The study of the surface properties shows that by processing the TM with plasma-polymerized pyrrole layer, a slight increase of wettability is obtained. So, if the initial membrane is characterized by the value of the water contact angle equal (Θ) to 65°, then for the plasma modified membrane the value of the water contact angle is 50° (Table 1). For the membranes modified by acetylene plasma no improvement of the wettability of the surface is observed. Indeed, the Θ value is almost the same at 64° on average in this case. The layers synthesized by plasma polymerization of Th, HMDSO, HMDSN and Tf have a hydrophobic character. So, for the membranes with plasma-polymerized thiophene layer, the Θ value is 88°. For the membranes treated by plasma of 1,1,2,2-tetrafluoroethane, the Θ value by water is 90°, for the membranes treated by plasma of HMDSO or HMDSN the Θ value is 98° on average.

The analysis of the XPS spectrum of the plasma-polymerized pyrrole film shows the presence of peaks related to atoms of carbon, nitrogen, and oxygen. For pyrrole, the carbon-nitrogen atoms ratio is equal to 4. For the polymer obtained by plasma, this ratio is higher, because part of the nitrogen is lost. The analysis of the XPS spectrum of the plasma-polymerized thiophene film shows the presence of peaks connected to carbon, sulfur, and oxygen atoms. For thiophene, the carbon-sulfur atoms ratio is equal to 4. For the polymers obtained by plasma, this ratio is higher in view of sulfur removing. The analysis of the XPS spectrum of the plasma-polymerized acetylene film shows the presence of peaks related to atoms of carbon and insignificant contents of oxygen. The analysis of the XPS spectrum of the plasma-polymerized 1,1,2,2-tetrafluoroethane film shows the presence of peaks related to atoms of carbon, fluorine and insignificant contents of oxygen. The analysis of the plasma-polymerized HMDSO and HMDSN films spectrum shows the presence of insignificant contents of oxygen also. The presence of oxygen in plasma polymers is possible due to the presence.
of residual oxygen in the vacuum reaction chamber and subsequent oxidation of polymers on air that is characteristic for polymer synthesized by plasma [4]. So, the deposition of the polymer films on the surface of PET track-etched membranes by plasma polymerization method leads to formation of composite membranes consisting of two layers. One of the layers corresponding to the initial membrane is characterized by presence on the surface of end carboxyl groups, which in the electrolyte solutions can exchange the cations. A second layer is the thin polymer film formed by the plasma polymerization method.

The results of testing the current-voltage characteristics of the membranes show that the conductivity of the source track-etched membranes does not depend on the current direction (not presented here) because the pores have cylindrical (symmetric) form. On the contrary, the analysis of the current-voltage characteristics of the bilayered membranes shows that their conductivity depends on the current direction (Fig. 2). It means that the formation of the composite membranes possessing asymmetry of conductivity in electrolyte solutions takes place in this case. However, it should be noted, that appearance of conductivity asymmetry for the composite bilayered membranes is observed only in the case when a plasma polymer layer covering pores is formed on the membrane surface. Thus, the thickness of the polymer layer deposited under plasma treatment for 1 min is quite small (only 100 nm) and pores on the surface are not blocked. Therefore, the conductivity is not asymmetric for this membrane. On the contrary, plasma treatment for 5 min produces a polymer layer that completely blocks the pores on the membrane surface. For this membrane the conductivity is asymmetric (Fig. 2a), i.e., the
membrane of such type can rectify a current. The value of rectification effect may be characterized by rectification coefficient $k_r$, that is calculated as the ratio of current values in the two opposite directions at the potentials of $+1$ V and $-1$ V. The conducted research shows that the rectification coefficient, for example, for the membrane with pore diameter of 125 nm treated by pyrrole plasma for 5 min in KCl solution with concentration $10^{-2}$ mol/L is equal to 8.1, and in the solution with concentration $10^{-3}$ mol/L is 6.3. For the membranes treated by acetylene, 1,1,1,2-tetrafluoroethane thiophene, HMDSO and HMDSN plasma the same results are observed. The occurrence of the conductivity asymmetry for the composite membranes does not appear unless a plasma polymer layer that blocks the pores forms on the surface of the initial track-etched membrane. So, at treatment of membrane with effective pore diameter of 215 nm by thiophene plasma for 1 min the thickness of the deposited polymer layer is quite small, and the pores are not blocked on the surface and, as consequence, the asymmetry of conductivity does not arise. On the contrary, at plasma treatment of the membrane for 5 or 10 min, on its surface a layer of plasma polymer is obtained that completely blocks the pores. For the membranes of such type the asymmetry of conductivity is observed (Fig. 2c).

The appearance of conductivity asymmetry for the PET track-etched membranes with a plasma polymer layer on the surface can be interpreted as follows. In the treated by pyrrole plasma membranes there are both negatively and positively charged layers. Really, in a layer synthesized by plasma polymerization of pyrrole there are the nitrogen-containing groups. They have positive charge in electrolyte solutions and they can exchange the anions. A layer of PET TM has a negative charge on the macromolecular segments due to dissociation of surface COOH-groups. Thus, in the treated by plasma membranes there are both negatively and positively charged layers, i.e., the deposition of polymer film on the membrane surface by plasma polymerization of pyrrole vapors leads to creation of the bipolar membranes. The layers synthesized by the plasma polymerization of thiophene, 1,1,1,2-tetrafluoroethane, acetylene, HMDSO and HMDSN contain some amount of the cation-exchange oxygen-containing (mainly, carboxyl) groups, as our results have shown. In the electrolyte solutions, dissociation of surface COOH-groups leads to formation of negatively charged segments on the polymer chains.

![Fig. 2. Current-voltage characteristics of the PET TM treated by pyrrole plasma in KCl solution with concentration of $10^{-3}$ mol/L (a), acetylene (b) and thiophene (c) plasma in KCl solution with concentration of $10^{-3}$ mol/L (b), and hexamethyldisiloxane plasma in KCl solution with concentration of $10^{-4}$ mol/L (d).](image-url)
too. Certainly, the concentration of carboxyl groups on the surface of plasma polymers is smaller than the concentration of these groups on the surface of PET TM. Thus, in this case in the treated by plasma membranes there are two layers with different concentrations of carboxyl groups. The contact of two layers, apparently, plays important role in appearing the asymmetry of conductivity for composite membranes in the electrolyte solution under the electric field. Besides, for the bilayered membranes a significant decrease in the pore diameter in the plasma deposited polymer is observed that is the cause for a change in the pore geometry. In other words, the manifested effect of conductivity asymmetry for PET TMs with a polymer layer on the surface produced by plasma polymerization method may be due both to a significant decrease in the pore diameter in the plasma deposited polymer layer resulting in a change in the pore geometry and also existence of an interface between the source membrane and plasma polymer layer.

4. Conclusions

The deposition of the polymer layer on the PET TMs surface by the plasma polymerization method, resulting in formation of a thin polymer layer that blocks the pores, leads to the creation of a composite bilayered membranes possessing asymmetry of conductivity – a rectification effect. This effect is caused by an important reduction of the pore diameters in the plasma polymer that results in changing the pore geometry, as well as an existence of an interface between two layers with oppositely charged functional groups or with different concentrations of carboxyl groups on their surface. Such membranes can be used for creation of chemical and biochemical sensors.

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6. References