Romanian Reports in Physics, Vol. 66, No. 4, P. 1165–1179, 2014

FORMATION OF COMPOSITE POLYMER 'DIODE-LIKE' MEMBRANES*

L. I. KRAVETS[1], S. N. DMITRIEV[1], V. SATULU[2], B. MITU[2], G. DINESCU[2]

[1] Joint Institute for Nuclear Research, Flerov Laboratory of Nuclear Reactions, Joliot-Curie Str. 6, 141980 Dubna, Russia; E-mail: kravets@lnr.jinr.ru
[2] National Institute for Laser, Plasma and Radiation Physics, Atomistilor Str. 111, 77125 Magurele, Bucharest, Romania

Received June 30, 2013

Abstract. The method of formation of the composite polymer 'diode-like' membranes, that possess asymmetry of conductivity in electrolyte solution – a rectification effect similar to that of a p-n junction in semiconductors, is described. To prepare the 'diode-like' membranes, a thin polymer layer synthesized in plasma was deposited on the one side of a poly(ethylene terephthalate) track membrane. Study of electrotransport properties of composite membranes using the voltammetry and impedance spectroscopy techniques is presented. Physicochemical aspects of the arising of the conductivity asymmetry for the developed membranes are discussed.

Key words: polymer 'diode-like' membranes, plasma polymerization, conductivity asymmetry.

1. INTRODUCTION

Membrane processes have found wide application in many areas of science and technology, such as gas separation, desalination of water, pervaporation, separation and isolation of individual solutes, and purification and concentration of biologically active substances [1]. Prominent among the variety of the membranes used in these processes are polymer membranes. However, the properties of existing membranes are frequently inconsistent with the requirements of industrial processing technologies, since the range of polymers suitable for the manufacture of membranes is limited. To extend the application area of commercial membranes, research works on the modification of their properties are performed. The most popular technique used for this purpose is the treatment of membranes in low-temperature plasma [2]. An important advantage offered by this process is the possibility for modifying a thin surface layer, which alters membrane properties,

* Paper presented at the 16th International Conference on Plasma Physics and Applications, June 20–25, 2013, Magurele, Bucharest, Romania.

namely, the adsorption, transport, and selectivity properties. This possibility substantially extends the application area of membranes. The bulk of the membrane matrix remains intact in this case, which is undoubtedly very important from the viewpoint of retention of its mechanical and physicochemical properties.

The low-temperature plasma treatment entails a number of physicochemical processes, depending of the discharge type and the nature of the plasma-forming gas, which make it possible to control in the targeted mode the structure and the chemical composition of the surface of polymer membranes. When various organic vapors are used for the plasma treatment of membranes, a thin polymer film is deposited on their surface as a result of polymerization. In this case, composite membranes consisting of the porous substrate (parent membrane) and a plasma deposited polymer layer are produced. Depending on the plasma treatment time and the pore diameter of the parent membrane, composite ultra-, nanofiltration and reverse-osmosis membranes can be obtained. In the latter case, a thin polymer layer, which completely covers the pores, is deposited on the membrane surface. The possibility for controlling the thickness of the plasma-deposited layer, which determines the selective properties of membranes, and a wide choice of organic compounds suitable for this process make this method especially promising. Note that the structure and properties of the plasma-deposited polymer layer substantially differ from those of the polymer obtained by conventional chemical polymerization processes. Macromolecules of a conventional polymer are composed of repeating units of the reactant monomer and are quite mobile in the surface layer. The polymer obtained in plasma has a highly cross-linked structure in which the mobility is retarded. This determines characteristic changes in the transport properties of plasma modified membranes and, first of all, their permeability for water and selectivity.

The surface properties of composite membranes obtained *via* plasma polymerization depend on the chemical compound used. For example, when hydrocarbons or fluorinated organic compounds are used as a plasma-forming gas, a hard, chemically resistant polymer film without functional groups is formed [3, 4]. This treatment makes it possible to prepare hydrophobic composite membranes, which are widely used in distillation processes. Plasma modification of membranes in a mixture of hydrocarbons with nitrogen leads to the incorporation of nitrogen atoms into the polymer film though the formation of nitrogen-carbon bonds [5, 6]. As a result, the membrane surface acquires the hydrophilic character. For example, the treatment of a polytetrafluoroethylene membrane, which had an initial water contact angle (Θ) of 126°, in an acetylene-nitrogen plasma caused a decrease in Θ to 34° [5]. This significantly improved the hydrodynamic properties of the produced composite membrane. Improvement in the hydrodynamic properties of a poly(ethylene terephthalate) (PET) membrane was observed after the deposition of a thin polymer film onto its surface in cyclohexane-nitrogen plasma [6]. A decrease in the concentration of COOH-groups on the surface did not result in a

considerable decline in the water permeability of the modified membrane; thus, the volume of the filtrate was increased. When acrylic acid is used for polymer layer deposition, hydrophilic composite membranes with a high concentration of carboxyl groups in the surface layer are formed [7–9]. The surface wettability of the membranes substantially increases in this case; in addition, membranes manufactured in this way exhibit a high cation-exchange capacity and permselectivity. During membrane treatment in allylamine, butylamine, dimethylaniline, plasma, a polymer film with nitrogen-containing functional groups (NH_2, NH, etc.) is deposited on the surface [10–12]. Such composite membranes have a hydrophilic surface and are characterized by high biocompatibility with blood and a decreased protein adsorption from solutions. When a poly(vinylidene fluoride) membrane is treated in mixed tetramethylsilane-ammonia plasma, an organosilicon film containing a considerable amount of amino groups is deposited on the surface [13]. This results in a composite membrane with a high anion-exchange capacity and permselectivity. Polymer film deposition on the membrane surface in allyl alcohol plasma improves the hydrodynamic properties of the obtained hydrophilic composite membranes [14, 15]. In addition, a high concentration of hydroxyl groups in the surface layer noticeably enhances the immobilization of biologically active compounds.

In this paper, the structure and electrotransport properties of track membrane (TM) from poly(ethylene terephthalate) modified by plasma polymerization method have been investigated. Pyrrole and acetylene were used as monomers to obtain the polymer layer on the membrane surface. The poly(ethylene terephthalate) track membrane (PET TM) was chosen for the study because it has possesses excellent material properties and is characterized by the presence of cation-exchange carboxyl groups on the surface. Moreover, the pores of PET TM are cylindrical channels, cross-sections of which are practically independent of the depth. This allows use of PET TM as a model system in theoretical description of the mass transfer processes across the membranes. Pyrrole was chosen as a monomer due to opportunity of obtaining a polymer layer with nitrogen-containing functional groups which can exchange the anions. Acetylene was chosen as a monomer due to the possibility of obtaining a polymer coating containing no anion-active functional groups.

2. EXPERIMENTAL

In the present experiments, PET TM with an effective pore diameter of 125 nm (pore density of 10^9 cm^{-2}) was 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 to ~ 1 MeV/nucleon at the cyclotron. Then the ion-irradiated film was additionally sensitized by ultraviolet radiation from a

source (LE-30 lamp, Russia) that provided about 3 $W \cdot m^{-2}$ of electromagnetic power in the range of 280-315 nm on the specimen surface. Chemical etching of the latent tracks to obtaining the pores of the required size was performed in an alkaline (NaOH) aqueous solution with concentration of 1.0 mol/L at 80°C for 5 min. The technique to produce the track membranes is described in more detail in [16].

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. Pyrrole and acetylene (99% purity specified for synthesis applications) from the Aldrich Chemical Co. were used as monomers for plasma polymerization. Disk-shaped membrane samples, with an area of 56 cm^2, were positioned on the grounded electrode at a 4 cm distance from the powered electrode. Before treatment, the chamber was vacuumed down to a residual pressure of 6.5 Pa. The discharge power was 20 W in all experiments. The gas pressure for the deposition of polymer film from pyrrole vapors was 90 Pa and from acetylene was 12 Pa. Argon was used as a carrier gas. Only one side of the membrane was subjected to the plasma treatment. The deposition time was varied. The scheme of a plasma-chemical setup and treatment technique are described in detail in [7].

The chemical composition of the polymers obtained by plasma polymerization of organic compounds was studied by X-ray photoelectron spectroscopy (XPS) and FTIR-spectroscopy. The XPS spectra were recorded with a Riber SIA-100 spectrometer using the MAC-2 analyzer (MgK_α, 100 W). The positions of peaks (the binding energy values) were calibrated to the C_{1s} standard peak (285.0 eV) [17]. FTIR reflection spectra were measured on a Bruker Equinox 50S Fourier-transform IR spectrometer with a MIRacle™ single reflection horizontal ATR attachment, using a ZnSe crystal, over the range 400–4000 cm^{-1}; data of 500 scans were collected with a scanning step size of 2 cm^{-1}. The absorption bands were referenced according to [18]. In order to record the XPS and FTIR-spectra of the plasma polymers, the polymers were deposited on a 10×15 mm silicon plate.

The characteristics of the initial membranes and modified ones were determined through a series of complementary procedures. The amount of polymer deposited on the membrane surface was determined gravimetrically on the basis of the sample mass gain. The change in the membrane thickness was measured with an electronic counter of thickness Tesa Unit (Austria). The gas flow rate through the membranes was determined at an adjusted pressure drop by a float-type flow meter. From the obtained data, the gas-dynamical pore diameter (an effective pore diameter) was calculated using the Knudsen equation as described in [19]. The error of measurements of the effective pore diameter did not exceed 2%. The study of the membrane microstructure and the definition of the pore diameter on the membrane surface was conducted by SEM using a JSM-840 (JEOL, Japan). Before scanning, a thin layer of gold was deposited by thermal evaporation in a vacuum. The changing of the membrane surface properties was evaluated by static contact

angle measurements at room temperature based on a sessile drop method [20] using a goniometer (Rame-Hart, Model NRL 100) equipped with a digital camera and a programmable system. Double distilled water was used as a test liquid. The average value was obtained from at least six measurements tested for each membrane sample. The measurement accuracy was ± 1°.

The electrotransport properties of membranes have been investigated by voltammetry and impedance spectroscopy [21] measurements. Current-voltage characteristics of the membranes were measured in the dc mode over the range of –1 to +1 V using a computer-controlled potentiostat Elins P-8S (Russia) on a scan rate of 50 mV/s. The membranes conductivity was measured by an impedance meter Z-3000X (Russia) in the frequency range 10 Hz – 3 MHz with signal amplitude of 20 mV at a temperature of 23 ± 1°C. For the measurements of the current-voltage curves and impedance spectra a two-chambered cell with Ag/AgCl electrodes, containing a water solution of potassium chloride (KCl) of identical concentration on both sides of the membrane was used. The concentration of KCl ranged from 10^{-4} to 1 mol/L. Prior to measurements, the samples were held in the electrolyte solution for 30 min.

3. RESULTS AND DISCUSSION

The parameters of the membrane subjected to the plasma are presented in Table 1. The results show an increase of membrane mass during plasma treatment due to deposition of a polymer obtained by pyrrole or acetylene polymerization. The membrane thickness increases and the effective pore diameter decreases in this process. This points to polymer deposition both on the membrane surface 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 effective pore diameter on the surface are observed (Table 1). However the pores on the membrane surface are open in this case because the thickness of the deposited polymer layer it is small enough (Fig. 1b and d). From the electron microscopy data, it also follows that the pore diameter on the untreated side remains unchanged relative to the initial value (Fig. 1f). An increase in the plasma treatment time leads to an increase in the thickness of the deposited polymer layer. Examination of the surface (Fig. 1c and e) and cross-section (Fig. 2c and e) of such membranes with the help of electron microscopy shows that a plasma polymer layer completely covering pores is formed on its surface. Herewith, gas permeability of the membrane decreases considerably (Table 1). The performed calculations show that the effective pore diameter of the composite membrane formed in this process is 35 nm. This means that the pore diameter in the plasma-deposited polymer layer is much lower than the pore diameter in the initial membrane and is apparently only several nm.

As may be seen from the data of electron microscopy presented in Fig. 2, the plasma-formed polymer films grow comparatively fast in the thickness and cover the pores on the membrane surface. However, it is difficult to determine on the basis of these data how the plasma-formed polymers are distributed inside the membrane pores. It is also difficult to determine the pore geometry in the polymer layer deposited on the membrane surface. We may only assume how these processes actually occur. We assume that the polymer is deposited in the pore channels at a certain depth from their inlet, but this cannot be seen in microphotographs of the membrane cross-sections. Further investigations could give more complete information. Here, we wanted to present only a schematic representation of the proposed model of filling the PET TM pores during a plasma polymerization process. In the case of short treatment time, only formation of a thin polymer film on the membrane surface and internal pore surface at a certain depth from the inlet is observed (Fig. 3b). As a result, insignificant reduction of the effective pore diameter for the modified membranes is observed. An increase in the treatment time results in an increase in the film thickness on the membrane surface and further decrease in the pore diameter in the deposited polymer layer (Fig. 3c). A longer deposition time causes additional polymer growth on the top and across the pore inlet, resulting in the channel closing (Fig. 3d). Extended growth of the polymer film (Fig. 3e) will result in the complete covering of the pore channels in the deposited polymer layer. Thus, the deposition of the polymer layer on the surface of the initial track membrane with cylindrical pores, a change in the pore structure takes place. Pores acquire an asymmetric (conical) shape: the pore diameter remains unchanged on the untreated side of the membrane and significantly decreases on the side exposed to plasma.

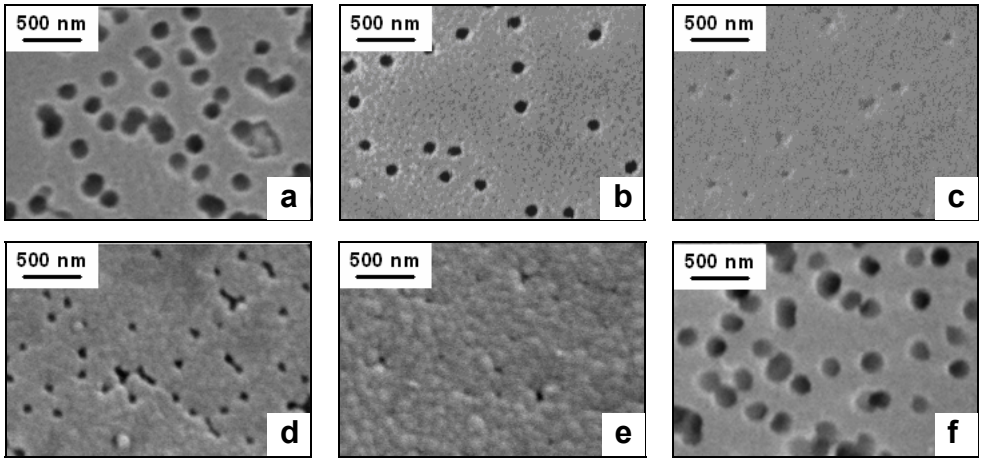

Fig. 1 – SEM photographs of the initial PET TM surface (a), membranes treated by pyrrole plasma for 1 (b) and 5 min (c) and membranes treated by acetylene plasma for 10 (d) and 20 min (e); (f) is the back side of the initial membrane (untreated in plasma).

The study of the surface properties shows that by processing the TM with pyrrole plasma, a slight increase of wettability is obtained. So, if the initial membrane is characterized by the value of the water contact angle equal to 65°, then for the plasma modified membranes the value of the water contact angle are on the average 51° (Table 1). For the membranes modified by acetylene plasma no improvement of the wettability of the surface is observed. Indeed, the values of the water contact angle are approximately similar and are on the average 64°. The results of the analysis of the XPS spectra of the films deposited by plasma are shown in Table 2. The analysis of the XPS spectrum of the plasma polymerized pyrrole (PPPy) film shows the presence of peaks related to atoms of carbon, nitrogen and oxygen. 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 polymers synthesized by plasma [22]. For pyrrole, the carbon-nitrogen atoms ratio is equal to 4. For the polymers obtained by plasma, this ratio is higher, because part of the nitrogen is lost. This effect is more pronounced at longer deposition times. A detailed analysis of N_{1s} spectra of PPPy films shows they are of complex character due to the presence in polymer of =N− (397.1 eV) and −NH− (399.1 eV) bonds and a higher binding energy (401.6 eV) tail due to positively charged nitrogen $-N^{+}-$. Analysis of the C_{1s} spectra of the PPPy films shows the presence of β-C in a pyrrole ring (283.3 eV) and α-C in the ring (285.3 eV) C−H bonds, and C=N, C=O or C−O (288.1 eV). The presence of the oxygen-containing groups means that a part of the carbon atoms is in the oxidized state. High-resolution spectra of the O_{1s} peak indicates that the predominant groups are O−C (533.9 eV) and O=C (531.8 eV). There is a small amount of O−N groups (528.8 eV) in the polymer. The presence of O−N bonds indicates that some of the nitrogen atoms are connected to oxygen. They apparently exist as functional end-groups.

Table 1

Change of the membrane characteristics in the process of plasma treatment

Plasma gas	Plasma treatment time [min]	Increase of the sample mass [%]	Thickness of the polymer layer [nm]	Effective pore diameter [nm]	Water contact angle [deg]	Rectification coefficient in KCl solution	
						10^{-2} [mol/L]	10^{-3} [mol/L]
–	–	–	–	125.0	65	1.0	1.0
Pyrrole	1	2.8	100	115.0	50	1.0	1.0
Pyrrole	5	6.3	400	55.0	52	8.1	6.3
Pyrrole	10	10.8	800	34.0	52	6.5	4.2
Acetylene	10	8.2	150	105.0	65	1.0	1.0
Acetylene	20	12.6	300	35.0	63	1.5	1.9
Acetylene	40	15.8	600	26.0	63	2.6	2.0

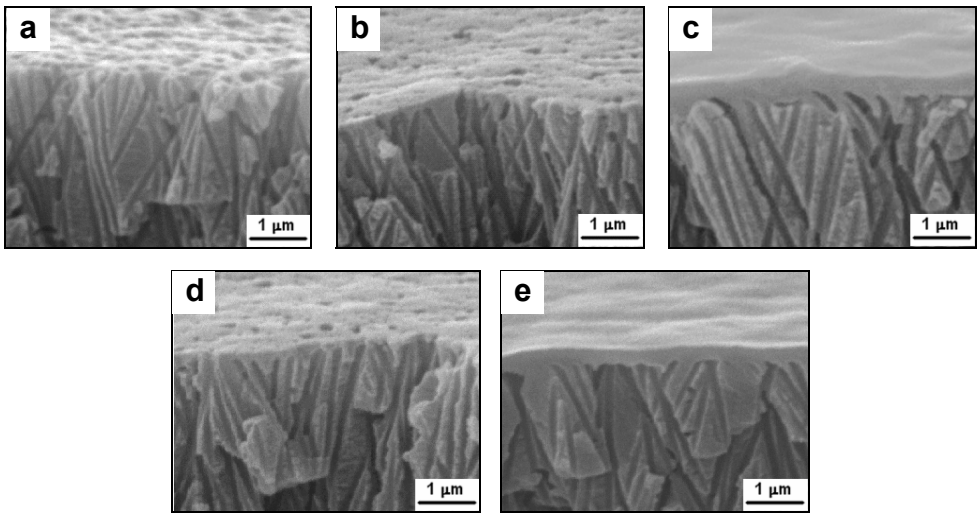

Fig. 2 – SEM photographs of the cross-sections of the initial PET TM (a) and membranes treated by pyrrole plasma for 1 (b) and 5 min (c) and membranes treated by acetylene plasma for 10 (d) and 20 min (e).

The investigation of the chemical composition of the PPPy film deposited on a silicon wafer sample directly in plasma reactor by FTIR-spectroscopy (Fig. 4a) shows absorptions compatible with the structure of polypyrrole synthesized by chemical or electrochemical methods; strong absorptions between 3350 cm^{-1} and 1642 cm^{-1} associated with N−H stretching and deformation bands and moderate absorptions at 1435 cm^{-1} (ring vibrations), 1075 and 1030 cm^{-1} (the aromatic C−H in plane bending) and 800 cm^{-1} (the C−H out of plane bending mode). Therefore, the pyrrole rings remain as an important part of the plasma synthesized polymer. Another observation is that the band at 3100 cm^{-1} representing C−H stretching and the bands at 1030 and 1075 cm^{-1} representing C−H in plane bending have become relatively weak in comparison of the polymer with monomer [23] and chemically synthesized polymer [24]. This decreasing in intensity of these bands indicates a corresponding reduction in the number of C−H bonds in the plasma polymer. From this study it is reasonable to conclude that polymerization has taken place through hydrogen abstraction of the C−H bands under the action of charged particles and vacuum UV-radiation of plasma. However, the existence of aliphatic C−H stretching absorptions (2800–3000 cm^{-1}) and −C=N stretching absorptions (2250 cm^{-1}) indicates that some of the pyrrole rings in the polymer are fragmentized. Moreover, in the spectra, absorption band is observed at 1270 cm^{-1} due to stretching vibrations of groups C−O. It specifies that part of carbon atoms is in an oxidized state. Apparently, they also will exist as functional end-groups.

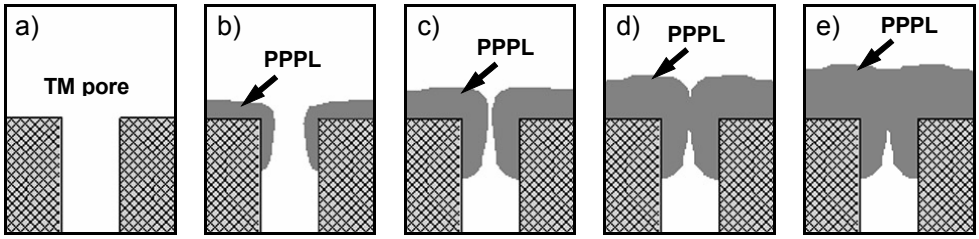

Fig. 3 – Schematic representation of the pore of the initial PET TM (a) and membranes with plasma polymerized polymer layer (PPPL) formed during plasma polymerization process.

Table 2

Relative content of atoms in the plasma polymers

Plasma-forming gas	Plasma treatment time [min]	Relative content of atoms [%]			Formula
		C	N	O	
Pyrrole	5	76.6	11.7	11.7	$C_4N_{0.6}O_{0.6}$
Pyrrole	10	78.5	11.2	10.3	$C_4N_{0.6}O_{0.5}$
Acetylene	5	80.9	–	19.1	$C_2O_{0.47}$
Acetylene	10	81.9	–	18.1	$C_2O_{0.44}$

The analysis of the XPS spectrum of the plasma polymerized acetylene (PPAc) films shows the presence of peaks related to atoms of carbon and oxygen (Table 2). The presence of oxygen in polymer is possible also due to the presence of residual oxygen in the vacuum reaction chamber and subsequent oxidation of PPAc on air. A detailed analysis of C_{1s} spectrum of the PPAc samples shows that it has a complex character due to the presence in the polymer of C−C/C−H (284.4 eV) and $-CH_2-$ (283.5 eV) bonds as well as some bonds of C–O (286.1 eV) and O–C=O (288.9 eV). The presence of the last two groups means that part of the carbon atoms could be bound to oxygen. High-resolution spectra of the C_{1s} peak indicates that the predominant groups are O=C (531.4 eV), C−O−C (532.8 eV) and −O−C− (534.6 eV). There is a small amount of ions O^{2-} (529.9 eV) in the spectrum. This also means that part of carbon atoms is bonded to oxygen. Apparently, these groups of atoms exist as functional end groups. Evaluation of the chemical composition of the plasma polymer by FTIR-spectroscopy (Fig. 4b) shows absorptions compatible with the structure of ethylene. So, there are a band at 1600 cm^{-1} in the spectrum which corresponds to stretching vibrations of the bonds C=C in olefins, a band at 1300 cm^{-1}, corresponding to in-plane bending of C−H in $-CH=CH_2$, a band at 900 cm^{-1}, corresponding to in-plane bending of the bond C–H in $RCH=CH_2$. Besides, in the spectrum there are absorption bands which are characteristic for acetylene. So, the spectrum contains a band at 3300 cm^{-1} which corresponds to stretching vibrations of the bond C−H in H−C≡; bands at 2198 cm^{-1} and 2102 cm^{-1} corresponding to stretching vibrations of triple bond C≡C in

R'−C≡C−R and H−C≡C−R as well as a band at 609 cm^{-1} which can be related to in-plane bending of groups H−C≡C−. Apparently, these groups exist as end ones on the polymer macromolecules. Data of the FTIR-spectroscopy thus confirm that fact that olefin groups are the basic structural element of the polymer synthesized from acetylene plasma. In addition to that, in the spectrum one can observe an absorption band corresponding to stretching vibrations of bond C−H in satiated hydrocarbons: at 2953 cm^{-1} – asymmetric vibrations in CH_3-groups, at 2928 cm^{-1} – asymmetric vibrations in CH_2-groups and 2870 cm^{-1} – symmetric vibrations in CH_3-groups. The spectrum also has the absorption bands corresponding to in-plane bending of CH_3 and CH_2-groups: 1452 cm^{-1} and 1376 cm^{-1}, and a band at 750 cm^{-1} which answers rocking vibrations of CH_2-groups. Apparently, these groups are formed as a result of cross-linking and recombination processes in the discharge. In the spectrum one can observe also an absorption band at 1020 cm^{-1} due to the stretching vibrations of groups C−O, a band at 1150 cm^{-1}, corresponding to stretching vibrations of C−O−C and absorption at 1720 cm^{-1}, corresponding to stretching vibrations bond C=O, most likely, of carboxyl groups. The presence of the carboxyl groups in the surface PPAc layer is proved also by the results of research by the XPS method.

So, the deposition of the polymer films on the surface of PET track membrane by plasma polymerization method leads, to formation of composite membranes consisting of two layers. One of the layers corresponds to the initial membrane. A second layer is thin polymer film synthesized in plasma. The results of measuring the current-voltage characteristics of the membranes show that the conductivity of the initial membrane does not depend on the current direction (Fig. 5a) because the pores have symmetric (cylindrical) form. On the contrary, the analysis of the current-voltage characteristics of the plasma-modified membranes shows that their conductivity depends on the current direction (Fig. 5c and d). It means that the formation of the composite membranes possessing asymmetry of conductivity in electrolyte solutions (an effect of current rectification) takes place in this case. It should be noted however that appearance of conductivity asymmetry for the composite bilayered membranes is observed only in the case when a plasma polymerized layer covering pores is formed on the initial membrane surface. Thus, the thickness of the PPPy layer deposited under plasma treatment for 1 min is quite small (only 100 nm) and pores on the surface are not covered by plasma polymer. Therefore, the conductivity is not asymmetric for this membrane (Fig. 5b). On the contrary, plasma treatment for 5 and 10 min produces a polymer layer that completely covers the pores on the membrane surface. For this membrane the conductivity is asymmetric (Fig. 5c), *i.e.*, the membranes of such type can rectify a current. The size of rectification effect can be characterized by a rectification coefficient (k_r) calculated as the ratio of values of the current in the opposite directions at a potential of +1 and −1 V. The conducted research shows that the rectification coefficient for the membrane treated by pyrrole plasma for 5 and 10 min in KCl solution with concentration 10^{-3} mol/L are 6.3 and 4.2 respectively.

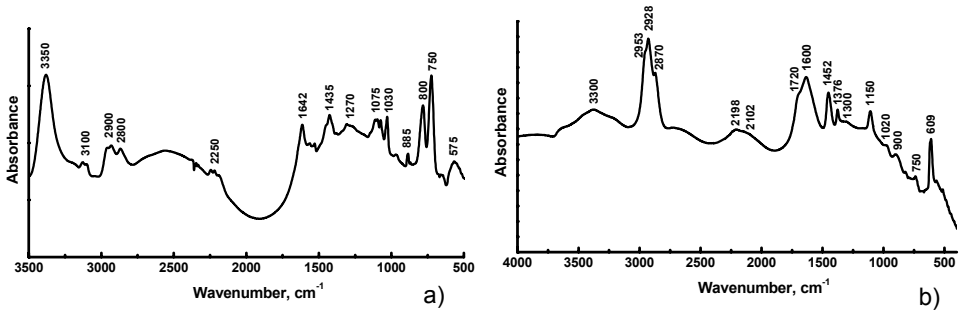

Fig. 4 – FTIR spectra of the plasma polymerized pyrrole (a) and acetylene (b) films deposited for 5 min on silicon plate.

For the membrane treated by acetylene plasma the same results are observed. The occurrence of the conductivity asymmetry for the composite membranes with a PPAc layer appears only in case when on the surface of the initial membrane there is a formation of a plasma polymer that closes the pores. So, at plasma treatment of membrane for 10 min the thickness of the deposited PPAc layer is quite small, and the pores are not covered on the surface and, as consequence, the asymmetry of conductivity in the electrolyte solution does not arise (Fig. 5b). On the contrary, at plasma treatment of the membrane for 20 and 40 min, on its surface a plasma polymerized layer of polymer is obtained that completely covers the pores. For the membranes of this type the asymmetry of conductivity is observed (Fig. 5d). The rectification coefficient for the membranes treated by acetylene plasma for 20 and 40 min in KCl solution with concentration 10^{-2} mol/L are 1.5 and 2.6 respectively.

The appearance of conductivity asymmetry for the PET track membranes with a plasma polymerized 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, as our results have shown. They have positive charge in electrolyte solutions due to a protonation of nitrogen atoms. 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 pyrrole 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 for which the effect of conductivity asymmetry is well-known [25]. The contact of two layers with antipolar conductivity, apparently, plays important role in appearing the conductivity asymmetry for composite membranes in the electrolyte solution under the electric field. The layer synthesized by the plasma polymerization of acetylene contains some amount of the cation-exchange oxygen-containing (apparently, 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 too. Certainly, the concentration of COOH-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 with different concentrations of the same functional groups plays important role in appearing the asymmetry of conductivity too. Besides, for the composite 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. For PET TM with conical pores, the effect of conduction asymmetry is well-documented [26]. According to the published data, the conduction asymmetry is due not only to the pore geometry, but also to the presence in the narrow part of the pores of a gel phase that results from swelling of the membrane surface layer or the presence of fixed charged groups on the pore surface. In other words, the appearance of the asymmetry of conductance in PET TM with a plasma polymerized layer of polymer, formed by plasma polymerization, on the surface can result from both the contact of two layers and a significant decrease in the pore diameter in the polymer layer synthesized in plasma, which changes the pore geometry.

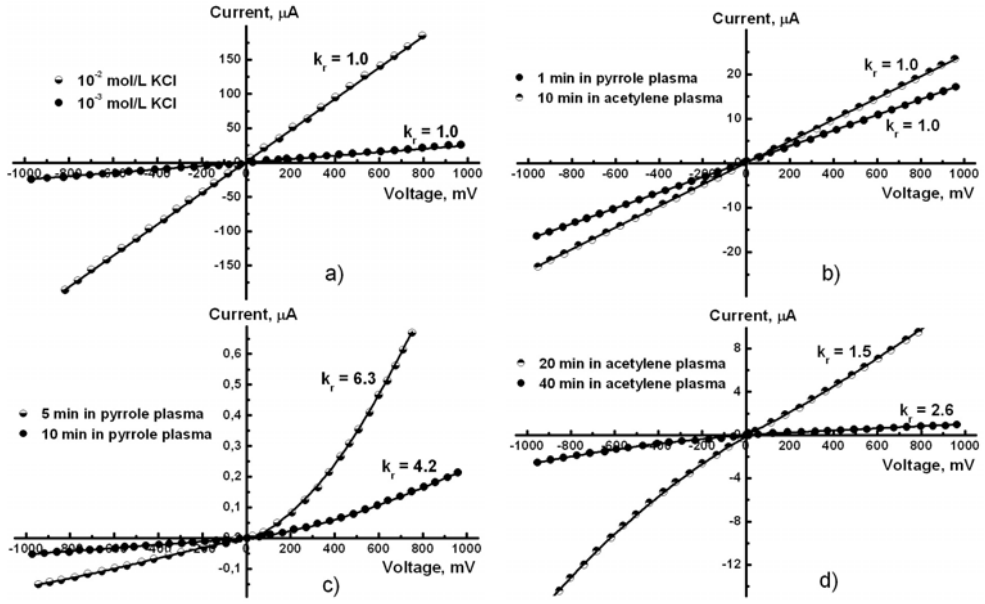

Fig. 5 – Current-voltage characteristics of the initial membrane (a), membranes treated by pyrrole plasma for 1 min and acetylene plasma for 10 min in KCl solution with concentrations of 10^{-3} mol/L (b), membrane treated by pyrrole plasma in KCl solution with concentrations of 10^{-3} mol/L (c) and membrane treated by acetylene plasma in KCl solution with concentrations of 10^{-2} mol/L (d).

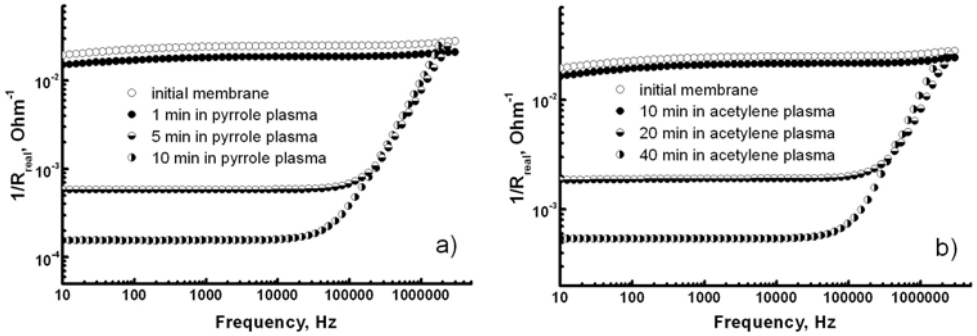

Fig. 6 – Dependences of the real admittance components on the frequency for the initial PET TM and membranes treated by pyrrole (a) and acetylene plasma (b) in KCl solution with concentrations of 1 mol/L.

Thus, our research has shown that the deposition of the layer of the polymer synthesized in plasma on the PET TM surface, leads to formation of composite membranes possessing the asymmetry of conductivity – the current rectification effect. In this respect, the obtained membranes are similar to the well-known semiconductor diode, but in the liquid state. There is a formal analogy between the conductance of the developed membranes in water solution of an electrolyte and of electrons and holes in a semiconductor. Hence, the PET TM with the PPPL on the surface can be considered as a matrix (diode) where the each layer contains the fixed on the pore surface charges one sign neutralized by mobile ions of the opposite sign (counter-ions). The appearance of the conductivity asymmetry for PET TM with a plasma polymer layer on the surface is observed not only in case of forming bipolar membranes, *i.e.* the membranes having two layers with antipolar conductivity. When forming composite membranes having two layers with different concentration of carboxyl groups in the surface layer, the produced composite membranes also possess the asymmetry of conductivity. 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 different concentrations of carboxyl groups.

Research on the process of ion transport in the membranes under the action of electric current has been performed by the method of electrochemical impedance spectroscopy. Experimental data of the measurement of frequency spectra for the membranes studied in a KCl solution with concentration of 1 mol/L are presented as dependences of the real admittance components on the frequency in Fig. 6. One can see that in case of the modified membranes the increase of resistance is observed, which is the most essential at increasing the processing time in plasma. The obtained experimental data were processed with the help of the model suggested in [27]. According to this model, three components can be allocated during the ion transport through the membrane (both the initial and modified ones).

First, ion transport in pores; secondly, ion transport through the interface membrane/electrolyte and, finally, ion transfer through the diffusion layers existing near the membrane surface. The ion transfer through the membrane under action of the current according to the given model is a mixed-diffusion one, and the resulting rate is determined by the ion transport through the membrane and through the interface membrane/electrolyte as well as through the diffusion layers of the solution near the membrane surface. Analysis of the experimental data shows that resistance of ion transfer in pores for composite membranes (determined by the sum of resistances of each layer) at an increase in the thickness of the plasma-deposited polymer layer grows, which may be explained by narrowing of the pore channels and growing membrane thickness. A significant increase in the resistance of ion transfer through the interface is also observed for composite membranes. Most probably, this value for modified membranes should be considered as resistance of ion transfer through the membrane/electrolyte interface combined with resistance of ion transfer through the interface between the initial membrane and plasma-deposited polymer layer, where there is the potential jump caused by occurrence of the concentration polarization phenomenon.

4. CONCLUSION

Summarizing the obtained results, one can conclude that the conductivity of the initial PET track membranes in the electrolyte solutions does not depend on the current direction. The deposition of the polymer layer by the plasma polymerization method, resulting in formation of a polymer layer that covers the pores on the membrane surface, leads to the creation of a composite bilayered membranes possessing asymmetry of conductivity in electrolyte solutions – a rectification effect similar to that of p-n junction in semiconductors. This effect is due to the plasma-deposited polymer layer producing the change of membrane pore geometry and the formation of an interface between two layers with oppositely charged functional groups or with different concentrations of carboxyl groups. Studies of composite membranes using the impedance spectroscopy technique have shown that they are characterized not only by increase in the ion transfer resistance in pores, but also by a significant increase in the resistance of ion transfer across the interface between the initial membrane and plasma-deposited polymer layer.

REFERENCES

1. T. D. Brock, *Membrane Filtration: A User's Guide and Reference Manual*, Science Tech., Inc., Madison, 1983.
2. F. Garbassi, M. Morra, E. Ochiello, *Polymer Surface from Physics to Technology*, John Wiley & Sons, New York, 1994.

3. B. Bae, B.-H. Chun, D. Kim, Polymer, **42**, 7879–7885 (2001).
4. Ch. L. Chapman, D. Bhattacharyya, R. C. Eberhart, R. B. Timmons, Ch.-J. Chuong, J. Membr. Sci., **318**, 137–144 (2008).
5. Ch.-Yu. Tu, Yi.-Ch. Wang, Ch.-L. Li, K.-R. Lee, J. Huang, J.-Y. Lai, Eur. Polym. J., **41**, 2343–2353 (2005).
6. L. I. Kravets, S. N. Dmitriev, G. Dinescu, A. Lazea, V. V. Sleptsov, V. M. Elinson, J. Phys.: Confer. Ser., **63**, 012032 (2007).
7. Lazea, L. I. Kravets, S. N. Dmitriev, G. Dinescu, Rom. Rep. Phys., **57**, 413–417 (2005).
8. H. I. Kim, S. S. Kim, J. Membr. Sci., **286**, 193–201 (2006).
9. D. E. Weibel, C. Vilani, A. C. Habert, C. A. Achete, J. Membr. Sci., **293**, 124–132 (2007).
10. M. Bryjak, G. Pozniak, I. Gancarz, W. Tylus, Desalination, **163**, 231–238 (2004).
11. L. I. Kravets, S. N. Dmitriev, A. B. Gilman, A. I. Drachev, G. Dinescu, J. Membr. Sci., **263**, 127–136 (2005).
12. D. T. Tran, S. Mori, M. Suzuki, Thin Solid Films, **516**, 4384–4390 (2008).
13. S. Roualdes, N. Kourda, J. Durand, G. Pourcelly, Desalination, **146**, 273–278 (2002).
14. L. Kravets, S. Dmitriev, G. Dinescu, V. Sleptsov, V. Elinson, Mater. Sci. Forum, **636-637**, 805–811 (2010).
15. M. Bryjak, I. Gancarz, K. Smolinska, Adv. Coll. Interf. Sci., **161**, 2–9 (2010).
16. G. N. Flerov, Vestn. Akad. Nauk SSSR, **4**, 35–48 (1984).
17. G. Beamson, D. Briggs, *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*, John Wiley & Sons, Chichester, 1992.
18. H. Kuptsov, G. N. Zhizhin, *Handbook of Fourier Transform Raman and Infrared Spectra of Polymers*, Elsevier Science, The Netherlands 1998.
19. M. Mulder, *Basic Principles of Membrane Technology*, Kluwer Acad. Publ., Dordrecht, 1996.
20. *** *Surface Characterization Methods: Principles, Techniques, and Applications*, Ed. by A. J. Milling, Marcel Dekker, Inc., New York, 1999.
21. Ch. M. A. Brett, A. M. O. Brett, *Electrochemistry: Principles, Methods, and Applications*, Oxford University Press Inc., New York, 1994.
22. H. Yasuda, *Plasma Polymerization*, Academic, Orlando, 1985.
23. J. Zhang, M. Zh. Wu, T. Sh. Pu, Zh.Ya. Zhang, R. P. Jin, Z. S. Tong, D. Z. Zhu, D. X. Cao, F. Y. Zhu, J. Q. Cao, Thin Solid Films, **307**, 14–20 (1997).
24. J. Wang, K.G. Neoh, E.T. Kang, Thin Solid Films, **446**, 205–217 (2004).
25. S. Mafe, P. Ramirez, Acta Polym., **48**, 234–250 (1997).
26. P. Ramirez, P. Yu. Apel, J. Cervera, S. Mafe, Nanotechnology, **19**, 315707 (2008).
27. L. I. Kravets, A. B. Gilman, M. Yu. Yablokov, V. M. Elinson, B. Mitu, G. Dinescu, Plasma Process. Polym., **10**, 603–618 (2013).