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Controlled change of transport properties of poly(ethylene terephthalate) track membranes by plasma method

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Abstract. A process of plasma polymerization of dimethylaniline and acrylic acid vapours on the surface of poly(ethylene terephthalate) track membranes has been investigated. The surface and hydrodynamic properties of the composite membranes produced in this case have been studied. It is shown that the water permeability of the obtained polymeric membranes can be controlled by changing the filtrate pH. Membranes with such properties can be used for controllable drug delivery and in sensor control.

1. Introduction
Our work is related to a problem of obtaining the so-called ‘smart’ or ‘intelligent’ membranes, that is, such membranes whose permeability can be adjusted by changing external conditions. These investigations are of major practical and scientific importance as they allow one not only to gain a wide spectrum of membranes with unique properties, but also to discover synthesis opportunities for membranes that imitate the biological ones. In order to create membranes with controllable transport properties, one can use the ability of the macromolecules at the surface in response to environmental stimuli such as temperature [1], solution pH [2], electric [3] and magnetic [4] fields, solvent composition [5] and pressure [6] to make reversible conformational transitions from hydrated (swollen) state to dehydrated (compact) ones. One of the approaches is the preparation of hydrogel membranes by traditional methods of polymerization or copolymerization [3, 4]. Another direction in this field consists in the modification of the surface of the industrially produced membranes. The research in this area is related to forming a chemical structure with desired properties on the membrane surface. For this purpose, various physicochemical methods are employed: chemical [1], plasma-induced [2] or radiation-induced [5] graft polymerization of monomers, plasma [6] deposition of thin polymeric layers on the surface of membranes.

In this paper we report on the surface and transport properties of composite membranes consisting of a porous substrate – a poly(ethylene terephthalate) track membrane (PET TM) and a polymer layer obtained by plasma polymerization of organic vapours. As monomers for plasma polymerization, dimethylaniline (DMA) and acrylic acid (AA) were used. In some experiments poly(acrylic acid) was grafted from the gas phase and this procedure followed after treatment in plasma of AA.
2. Experimental

Poly(ethylene terephthalate) track membranes of thickness of 9.5 µm with an effective pore diameter of 0.215 µm (pore density was $2 \times 10^8$ cm$^{-2}$) were used as objects of the investigation. To produce the membranes, PET films were irradiated with ~ 3 MeV/nucleon positively ionized atoms of krypton accelerated on the cyclotron U-400 (Flerov Laboratory of Nuclear Reactions), and then subjected to physicochemical treatment on a standard procedure [7]. The pores in this type of membranes are the cylindrical channels intersecting a membrane through.

As an initial substance for membrane modification by the plasma polymerization, $N,N$-dimethylaniline and acrylic acid (Fisher Scientific Co, USA) were used. Deposition of the polymer from dimethylaniline was realized in DC glow discharge at the pressure of DMA vapours 26.6 Pa and the discharge current density 0.1 mA/cm$^2$ during 20-180 s. The treatment procedure and the schematic of the plasma reactor set-up are detailed elsewhere [8]. Deposition of the polymer from acrylic acid was performed in a plasma-chemical installation realizing a RF-discharge in parallel plate configuration at the frequency of 13.56 MHz at gas pressure of 26.5 Pa in the vacuum chamber and discharge power 60 W during 60–900 s. The treatment procedure and the schematic of this installation described previously in [9]. Only one side of the membranes was subjected to the plasma treatment.

The graft polymerization of AA was conducted from gas phase during 1 h. For this purpose membranes were placed over the 25 % water solution of AA which had a temperature 75°C. To suppress a homopolymerization process, divalent copper ions were introduced in the solution. After the graft polymerization PET TM were washed with distilled water.

The characteristics of the initial and modified membranes were determined through a series of complementary procedures given in [10]. The polymer composition deposited by plasma was studied by ESCA and FTIR spectroscopy. The ESCA spectra were recorded with the spectrometer Riber SIA-100 with MAC-2 analyzer (MgKα, 100 W, 15 kV, 20 mA). FTIR-spectra were recorded with a Bruker Equinox 50S spectrometer in the range of 400 – 4000 cm$^{-1}$, working with 500-fold accumulation of data and a scanning step of 2 cm$^{-1}$. Permeability of water solutions with various pH values was measured with the help of the standard filtration installation FMO-2 on samples of membrane by the area of 254 mm$^2$. Solutions of hydrochloric acid and sodium hydroxide of various concentrations were used as working solutions.

3. Results and discussion

The research on the process of modification by plasma polymerization of vapours of dimethylaniline and acrylic acid on the PET TM surface shows that with the treatment time an increase of the mass of the sample is observed (tables 1, 2). This increase is connected with the deposition of the polymeric layer on the surface. Thus, the thickness of the membrane increases, while the effective pore diameter decreases. This testifies that the deposition takes place both on the surface of the membranes and on the walls of its pores. The polymer deposition in pores by plasma treatment is confirmed by the ESCA method. According to ESCA data, nitrogen atoms were detected both on the treated and on the untreated sides of the membrane modified by DMA plasma. This finding proves that polymer deposition during plasma treatment takes place in the pore volume, reaching the back side of the membranes.

Table 1. Change of the membrane characteristics during treatment by DMA plasma.

| Plasma treatment time (s) | Relative increase in the mass (%) | Thickness (µm) | Effective pore diameter (µm) | Water contact angle (deg) |
|--------------------------|---------------------------------|----------------|----------------------------|--------------------------|
| Control                  | –                               | 9.5            | 0.215                      | 65                       |
| 20                       | 9.5                             | 9.8            | 0.210                      | 45                       |
| 60                       | 11.5                            | 10.0           | 0.205                      | 45                       |
| 180                      | 13.5                            | 10.2           | 0.200                      | 45                       |
Table 2. Change of the membrane characteristics during treatment by AA plasma.

| Plasma treatment time (s) | Relative increase in the mass (%) | Thickness (µm) | Effective pore diameter (µm) | Water contact angle (deg) |
|--------------------------|---------------------------------|----------------|-----------------------------|--------------------------|
| Control                  | –                               | 9.5            | 0.215                       | 65                       |
| 60                       | 3.7                             | 9.8            | 0.190                       | 15                       |
| 300                      | 5.2                             | 9.9            | 0.175                       | 15                       |
| 600                      | 6.5                             | 10.0           | 0.170                       | 15                       |
| 900                      | 7.2                             | 10.1           | 0.160                       | 15                       |

The detailed analysis of the ESCA spectrum of the polymer obtained by dimethylaniline plasma (PPDMA) shows the presence of peaks related to carbon and nitrogen atoms, and small content of oxygen. The ratio of nitrogen atoms to carbon atoms in the PPDMA equal 12.3 %, and it is practically the same that the initial DMA. This makes possible to conclude that the structural unit in the polymer formed by dimethylaniline plasma is identical to that of the initial DMA. A small amount of oxygen in PPDMA can be explained by the presence of residual oxygen in the plasma-forming gas and also by a subsequent oxidizing of PPDMA after plasma treatment on air that is characteristic for polymers synthesized by plasma polymerization. Accordingly, the ESCA spectra of the polymer obtained by AA plasma (PPAA) show that with increasing the plasma treatment time the intensity of peak O₁s increases too, and the ratio of oxygen atoms to carbon increases in the polymer and for the membrane treated in plasma during 900 s equals 65.5 %, that is practically coincides with the simulated value for the monomer: the ratio of oxygen atoms to carbon in acrylic acid is equal to 66.7 %. This gives the basis to believe that the structural segment in the PPAA on the PET TM surface at its plasma treatment during 900 s is similar to the AA structure.

The study of the TM surface properties shows that after plasma treatment the wettability of the surface increases. So, if the initial membrane is characterized by the water contact angle (Θ) value equal to 65°, then for the membranes modified by DMA plasma the Θ value, irrespective of the plasma treatment time, does not exceed 45° (table 1) and for all modified membranes the value Θ is 15° (table 2). It means that in all cases, independently of the quantity of relative increase in the membrane mass, there is a complete coating of the membrane surface by a layer of the deposited polymer. Electron-microscopic observations indicate the absence of erosion of the membrane surface under plasma treatment; so, the increase of wettability can be related to the formation of additional hydrophilic groups on the surface. It is confirmed by the FTIR spectroscopy. It was shown that the PPDMA IR-spectrum contained the absorption bands at 1373, 1348 and 1323 cm⁻¹ connected with the stretching vibrations of CN-groups in tertiary amines, and so the PPAA IR-spectrum contains the absorption bands at 1720 cm⁻¹ connected with the stretching vibrations of carbonyl in carboxyl groups.

It is known that the main contribution introducing the restriction of ions transport through membranes is provided by the electrochemical mechanism related to the presence of ionized functional groups on the pore surface. The interaction of these groups of polymeric chains of the membrane matrix with the flow of molecules of the sliding phase and the change of local states of the segments of these chains causing various conformation and structural modifications, explain the change of the transport characteristics of the membrane and, first of all, its permeability. Obviously, these changes will appear to a larger degree when the changes in the value of the surface pore charge and the conformation mobility of their surface macromolecules are important. So, the treatment of PET TM in air plasma, as we have shown in [10], results in changing the hydrodynamic characteristics of the membranes as their water permeability depends in a large measure upon pH of the filtrated solution. This is insured by the increasing of the content of carboxyl groups in the surface layer of the membranes and by the greater conformational mobility of macromolecules of this layer. In this connection, research on the water permeability of the membranes on the surface of which the others functional groups are presented, is of particular interest.
The research of water permeability of membranes modified by plasma of DMA and AA vapours demonstrates their abnormal behaviour (figures 1–4). So, for the initial PET TM we can observed that dependence of the flow rate on the applied pressure in acidic media (pH = 1.2) has a linear character (figure 1, line 1), which is typical for membranes with a hard structure at a viscous character of filtrate flux (when the pore diameter is larger than the size of water molecules [11]). Observations of the plasma modified membranes have shown that the dependence of water permeability upon the pressure in the same filtrate is not linear (figure 1, curves 2 and 3). This effect is caused by decreasing the pore diameter of the membranes that is explained by changing a conformation of PPDMA macromolecules. At low pH values due to protonation of the nitrogen atoms, the segments of the macromolecules of the plasma deposited polymer acquire a positive charge that results in its swelling – formation of gel [12], causing a partial membrane pore contraction. The PPDMA macromolecules in this case represent an expanded ‘coil’ (figure 5a). Such a conformational state of macromolecules resulting from the electrostatic interaction of charged segments with molecules of water is steady. So, increase of pressure up to 0.15 MPa for a membrane with relative increase of mass 11.5 % does not change the value of its water permeability (figure 1, curve 3). It should be noted that the value of pores contraction depends essentially on the relative increase of the mass of the sample. Thus, for a membrane with elative increase of mass 9.5 % a smaller deviation from a linear dependence of the flow rate on the applied pressure is observed (figure 1, curve 2).

Increase of filtrate pH essentially changes the character of dependence of water permeability on the value of applied pressure for the modified membranes. So, at the pH = 4.6 for the PET TM with deposited layer of PPDMA the increase of water permeability (figure 2, curve 2) is observed which is connected to reduction of concentration of protons in a filtrate. In the medium with higher pH the content of positively charged atoms of nitrogen in the PPDMA layer decreases; therefore, the electrostatic interaction gets weaker. With decreasing this interaction, the non-electrostatic interaction of hydrophobic groups, in this case, of non-polar \( \text{CH}_2 \) groups increases. It results in a collapse of gel – transition of macromolecules of PPDMA in a compact conformational state of a ‘globule’ (figure 5b). A similar state of macromolecules does not cause an appreciable decrease of the pore diameter, and consequently for modified membranes one can observe a viscous character of the filtrate flow – dependence of water permeability on the applied pressure has practically a linear character.

The study of the hydrodynamic characteristics of PET TM with the PPAA layer showed that for all modified membranes, as compared to the initial one, a significant decrease in the water flow in the pH region near 4 occurred (figure 3). On this figure, curves 2 and 3 show the pH dependence of the water flow rate for the membranes treated by plasma during 60 and 900 s, accordingly. The pH dependence of the flow rate for the membranes modified by plasma during 300 and 600 s is not
presented here. It should be noted that the water flow rates for these membranes are of intermediate values. Decrease in the water flow rate for the plasma treated membranes is caused by decreasing (contraction) of their pore diameter which can be explained by the change of the conformational state of macromolecules of PPAA layer. At low pH values of the solution, dissociation of carboxyl groups is suppressed, i.e. monomer units of macromolecules of the deposited in plasma layer are in a neutral state. Absence of the charge is accompanied by a weak electrostatic interaction and a strong non-electrostatic interaction of hydrophobic groups, in this case \( \text{CH}_2^- \) and \( \text{CH}^- \)-groups, which leads to a collapsed gel – a transition of PPAA macromolecules to a compact conformation state of ‘globule’ (figure 5b). Such a state of the macromolecules does not cause decreasing the pore diameter, so for the modified membranes high values of the water flow are observed. A similar dependence at low pH values is observed for the initial membrane also (figure 3, curve 1), in this case at the pH range from 4 to 6 decrease of its water permeability also takes place. It is caused by increasing the degree of dissociation of carboxylic groups – \( pK_{\text{COOH}} \) in PET is 3.6 – 3.7. However, this change is less defined as compared to the modified membranes. The latter is explained by a lower concentration of carboxylic groups on the surface of the initial membrane and their lower mobility.

\[ \text{Figure 3. pH-Dependence flow rate for initial TM (1) and membranes modified by AA plasma during 60 (2) and 900 s (3).} \]

\[ \text{Figure 4. pH-Dependence flow rate for initial TM (1) and membrane with polymeric layer that was grafted from the gas phase after modification by AA plasma (2).} \]

Increase of filtrate pH leads to changing the conformation state of the macromolecules of the deposited layer by AA plasma. At pH in the region of 4, dissociation of carboxyl groups takes place – \( pK \) of poly(acrylic acid) is equal to 4.28. Therefore the monomer units of the macromolecules of the deposited in plasma polymeric layer get a negative charge. Thus, on the membrane surface a gel is formed. In this case the PPAA macromolecules look like an expanded ‘coil’ (figure 5b). Such a conformation state of the macromolecules leads to an essential decreasing of the membrane pore diameter and thus causes a sharp decrease in the value of water flow. Notice, the complete pore contraction is not observed in these experiments that are, probably, caused by the following factors: insufficient thickness of the polymeric layer deposited in plasma; a significant degree of lacing of the given layer (complicating conformation mobility of macromolecules); the large pore diameter of membrane subjected to the investigations. Probably, varying the discharge parameters at plasma treatment or the rational choice of the pore diameter of the initial membrane will cause a complete pore contraction in a particular range of pH value that will lead to preparation of composite mechanochemical membranes with ‘chemical valve’, i.e. when in a specific range of the pH filtrate the membrane will be fully impermeable for water molecules. Nevertheless, full contraction of pores can be achieved by additional treatment of the modified membranes. So, the grafting of poly(acrylic acid) from a gas phase on the membrane modified by plasma results in formation of a mechanochemical membranes with ‘chemical valve’ (figure 4, curve 2). Apparently, in this case the process of graft polymerization causes increase of length of macromolecules of poly(acrylic acid) layer. For this
membrane at pH values more than 8 the full pore contraction is observed due to negative charge on the segments of the macromolecules of the grafted polymer that results in its swelling – formation of gel. The membrane pores are ‘closed’ in this state (figure 5a). Decrease of filtrate pH leads to loss of charge on the segments of the macromolecules of the grafted polymer. That results in a collapse of gel – transition of macromolecules in a compact conformational state. The membrane pores are ‘open’ in this state (figure 5b) that leads to increasing the membrane pore diameter, thus, its water permeability increases. For the membrane with a grafting polymer at pH ~ 8 one can observe change-over to an operation mode of a ‘chemical valve’ i.e. at higher pH values of the filtrate the membrane gets non-permeable for molecules of water. At smaller pH values of the filtrate the membrane gets permeable for molecules of water.

![Porous Membrane Diagram](image)

**Figure 5.** Schematic illustration of changing in the conformation state of a deposited polymeric layer by plasma in medium with various pH values.

### 4. Conclusion

The performed investigations have allowed us to make the following conclusions. The presence of the polymeric layer of PPDMA or PPAA on the surface of PET track membranes results in changing their transport properties – the water permeability of the formed composite membranes substantially depends on the value of filtrate pH. These changes are caused by convertible conformational transitions of macromolecules of a deposited polymer layer by plasma which are in turn caused by the degree of ionization of functional groups of this layer. Membranes with such properties can be used in biotechnology and medicine, for example, for bioseparation and biocatalysts immobilization. They also can be used for controllable drug delivery, in biosensor controls, for modelling processes of regulation in the cell, etc.

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