Plasma-chemical modification of the structure and properties of poly(ethylene terephthalate) track membranes

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Abstract. A process of extraction of the low-molecular products of the synthesis from the poly(ethylene terephthalate) track membranes modified by plasma has been investigated. It is shown that the deposition of a thin polymeric hydrocarbon film by cyclohexane plasma on the membrane surface with preliminary treatment in a plasma of non-polymerizing gases, for example oxygen, allows one to produce membranes possessing a high productivity. Their advantages are much better hydrodynamic properties and a small amount of the low-molecular products of the synthesis extracted by organic solvents.

1. Introduction

The investigations on the effect of plasma discharge on poly(ethylene terephthalate) track membranes (PET TM) have allowed us to find out that the main processes at treatment of the membranes by plasma of non-polymerizing gases are the gas-discharge etching of a polymeric matrix and its hydrophilization [1, 2]. We have shown that the result of gas-discharge etching is decreasing a thickness and increasing an effective pore diameter of the membranes. The etch rate depends on a discharge parameters, i.e. gas pressure and discharge power and on the contents of the plasma-forming gas – rise of the discharge parameters and introduction of oxygen into the gas leads to increase of the etch rate [3]. Moreover, the result of the gas-discharge etching of the polymeric matrix is a formation of asymmetric track membranes, i.e. the pore shape of membranes changes. Thus by the gas-discharge etch method it is possible to change directly the TM structure. Depending on the choice of the discharge parameters, etching can be executed either in a part of the channel or along the whole length of the pore channels; anyway, asymmetric track membranes possessing high porosity and flow rate are formed [1, 3].

The process of the hydrophilization of the membrane surface is connected with the formation of functional; in particular, carboxyl groups the appearing of which results from oxidation the end groups where the chemical bounds break down due to the active plasma particles effect [4]. The increase in the concentration of the surface carboxyl groups at plasma treatment leads to increase in the density of the negative charge on the pore walls of the membranes. As a result, the water permeability resulting
from the gas-discharge treatment quickly decreases [4]. This causes a slower increase in the filtrate volume in the filtration process. To make the hydrodynamic properties of the membranes better, a treatment by plasma of polymerizing gases was applied [3, 5]. As a result, the following processes have been demonstrated: the deposition of a thin polymeric hydrocarbon film from plasma of cyclohexane [3] or allyl alcohol [5] on the membrane surface allows one to minimize the concentration of the surface functional groups. Moreover, this does not cause a drastic decrease of water permeability and results in a considerable increase in the filtrate volume in the filtration processes.

However it is well known that any polymeric material has some quantity (up to 2 – 4%) of low-molecular products of synthesis – oligomers which are dissolved quite well in solvents. For example, the influence of a number of organic compounds (halide-produced hydrocarbons, dioxane, dimethylformamide and some others) on PET TM leads to extraction of the low-molecular products consisting, mainly, of cyclic oligomers [6, 7]. The influence of these solvents on PET TM seems to lead to extraction of both the oligomers and the products of destruction of the poly(ethylene terephthalate) macromolecules which are formed in the course of the chemical etching. In the polymeric films obtained by plasma polymerization one can see two fractions too: the dissolved one (less than several percents) consisting of the compounds possessing a low-molecular mass, and not dissolved one consisting of a polymer with a large number of crosslinks [8]. It should be supposed that the effect of the solvents capable of dissolving the low-molecular products, on the plasma polymerized films will lead to their extraction and, thus, a pollution of the filtrate when using the membranes modified by plasma. This makes actual the research on the processes of extraction of low-molecular products from the plasma polymerized films deposited on the surface of the track membranes.

In this paper we studied a process of extraction of the low-molecular products of synthesis from PET TM modified by cyclohexane plasma. In some experiments the non-polymerizing gases were used for modification.

2. Experimental

Poly(ethylene terephthalate) track membranes of thickness of 10.0 μm with an effective pore diameter of 85 nm (pore density was $1.25 \times 10^9$ cm$^{-2}$) were used as the objects of 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 [9].

The plasma treatment was performed at a plasma-chemical installation providing the RF-discharge on a frequency 13.56 MHz at gas pressure of 22.5 Pa in a vacuum chamber and discharge power of 400 W. The membrane samples of the size of 10x10 cm were placed on a flat holder in the active plasma zone of the vacuum chamber. Only one side of the membrane was exposed to plasma. Such inorganic gases as nitrogen, oxygen and air were used as plasma-forming gases. Cyclohexane was used for the deposition of the polymeric hydrocarbon film on the membrane surface. Duration of the plasma treatment was varied. The technique of the treatment and the scheme of the plasma-chemical device are described in detail in [1].

The low-molecular products from the membranes were extracted at room temperature during 24 h. Chloroform and dimethylformamide were used as solvents. Sometimes we used distilled water, but the extraction process lasted 10 days in this case. The amount of extracted products was determined with the help of the UV-spectrophotometry method [10]. A spectrophotometer Specord M-40 (Carl Zeiss Jena) was used. The content of the low-molecular products was calculated with the formula:

$$m = \frac{D \cdot V \cdot M}{\varepsilon \cdot l},$$

where $D$ – an optical density of the extraction at $\lambda = 288$ nm; $V$ – the extract volume; $l$ – a thickness of the photometric layer; $\varepsilon$ – experimentally found value of the molar coefficient of absorption, referred to one ethyleneterephthalate group equal to $1.35 \times 10^3$ l/mol-cm; $M$ – a molecular weight of one
ethyleneterephthalate grouping equal to 192. The characteristics of the initial and modified membranes were determined through a series of complementary procedures given in [1].

3. Results and discussion
The experimental data describing the extraction of the low-molecular products, soluble in organic solvents and water, from PET TM with a layer of the polymeric hydrocarbon film of various thicknesses which was deposited by cyclohexane plasma are given in table 1. As it follows from the data, the effect of organic solvents on modified PET TM leads to extraction of the soluble low-molecular products. The appearance in the UV-spectra of extracts of the absorption band for the wave length of 288 nm corresponding to the absorption of a phenyl radical testifies it. Matching the UV-spectra of the extracts from the samples of the membranes exposed to plasma (figure 1, curves 2–5) and the spectrum of the initial sample PET TM (figure 1, curve 1) does not reveal new absorption bands. This gives the idea about availability in the modified membranes of only oligomer products. The calculation of a mass share of the extracted products shows that if modifying the membranes by cyclohexane plasma, an increase in the contents of the low-molecular products is not observed. Quite the reverse, deposition the polymeric hydrocarbon film by a thickness of 100-120 nm on the membrane surface results in some decrease of the mass share of the extracted products. Apparently this effect to be connected with the fact that the polymeric hydrocarbon film deposited on the membrane surface interferes extraction of the low-molecular products into the solvent. The absence of the absorption band for $\lambda = 288$ nm in spectra of water extracts allows one to conclude that the effect of water at room temperature during 10 days does not result in extracting low-molecular products from the initial and modified membranes. The insignificant loss in the weight of the membrane samples in this case is less than 0.1% that can be referred to a measurement error. The use of the PET TM modified by cyclohexane plasma during filtration water solutions, thus, does not result in pollution of the filtrates. When filtering the organic solvents, the weight of the low-molecular products, extracted from the modified membranes, does not exceed the weight of the low-molecular products extracted from the initial membrane.

In addition, when recording the UV-spectra of the chloroform extracts from the membrane samples, deposition the polymeric hydrocarbon film on the surface of which was performed after a preliminary treatment by plasma of non-polymerizing gases (the duration of the plasma effect in these experiments was selected arbitrary), a noticeable decrease of intensity of the absorption band for the wave length of 288 nm was revealed in comparison with the spectrum of the extract from the initial membrane. Table 2 presents the results of valuation of the contents of the extracted products from PET TM with the deposited layer of a 100 nm polymeric hydrocarbon film. One can see the treatment by the plasma of inorganic gases results in decreasing a mass share of the extracted products that is stipulated by a gas-discharge etching of a surface layer of the membranes (a large part of oligomers, as was found in [6, 7], is on the surface of the polymer). The essential decrease of the contents of low-molecular products in the modified membranes is observed in case of using oxygen as a plasma-forming gas, that is connected to a greater etch rate in the plasma of this gas [3].

| Thickness of the polymeric hydrocarbon film (nm) | Amount of extracted products in membrane (%) |
|-----------------------------------------------|------------------------------------------|
|                                               | extraction by chloroform | extraction by dimethylformamide | extraction by water |
| –                                             | 2.20                       | 2.45                       | < 0.1            |
| 50                                            | 2.35                       | 2.55                       | < 0.1            |
| 80                                            | 2.30                       | 2.45                       | < 0.1            |
| 100                                           | 1.90                       | 2.30                       | < 0.1            |
| 120                                           | 1.75                       | 2.20                       | < 0.1            |
Figure 1. UV-spectra of chloroform extracts of low-molecular products from initial PET TM and membranes with deposited by plasma layer of a polymeric film of thickness 100 nm (the numbering of curves corresponds to numbering the membranes in table 2).

Figure 2. Dependence of content of extracted products from PET TM upon duration of plasma of air (1) and oxygen (2). Discharge parameters: gas pressure 22.5 Pa, discharge power 400 W.

Table 2. Amount of the low-molecular products extracted by chloroform from PET TM with a deposited by cyclohexane plasma layer of the polymeric hydrocarbon film.

| No | Plasma-forming gas | Plasma effect duration (min) | Amount of extracted products in membrane (%) |
|----|---------------------|-------------------------------|---------------------------------------------|
| 1  | –                   | –                            | 2.45                                        |
| 2  | Cyclohexane         | 10                           | 1.90                                        |
| 3* | Nitrogen            | 3                            | 1.75                                        |
| 4* | Air                 | 3                            | 1.00                                        |
| 5* | Oxygen              | 3                            | 0.60                                        |
|    | Cyclohexane         | 10                           |                                             |

*In experiments No 3-5 the deposition of a polymeric film was carried out with a preliminary treatment of the membrane surface by non-polymerizing gas plasma.

The detailed research on the process of extracting soluble products from the PET TM exposed to the plasma of non-polymerizing gases, allows one to make the following conclusions: increase of the treatment duration leads to a more complete deleting of low-molecular products from the membrane surface (figure 2), as the value of the polymer layer etched from the surface increases in this case (see table 3). However, a durable plasma effect could result in a noticeable decrease of the mechanical strength of the membranes (table 3). Such a phenomenon can be explained by the presence of a thin damaged superficial layer on the modified membranes (with a small molecular weight of the macromolecules) forming in the plasma process with the results given in [1]. More significant difference in the mechanical strength of the TM treated for long duration treatment, if compared with the samples not treated in plasma, witnesses the formation of the deeper damaged layer. The loss of their strength is essential. This can be taken into account, if choosing the optimal parameters of plasma treatment. Thus, one can see that the choice of the plasma treatment has two aspects. First of all, the discharge parameters should provide a significant decrease of the content of the low-molecular products. Secondly, the plasma treatment should be short enough to prevent a damage of the
membrane. We have come to a compromise when the loss in mechanical strength is of 15 – 20 %, whereas the content of the low-molecular products in PET TM is four times lower. So, the treatment PET TM by oxygen plasma during 3 min leads to decrease of the content of low-molecular products in PET TM up 0.6 %, while the loss in mechanical strength of membrane comes to 20 %.

The experimental data given in table 3 show also that the treatment by the oxygen plasma of the initial membrane leads to increasing the effective pore diameter. It is a result of the gas-discharge etching of polymeric matrix. As shown in [1], the membrane structure changes, i.e. pores, become asymmetric. At the discharge parameters selected, only a part of the channel is etched. Part of the pore channel is not etched here. This is proved by the data of the electron-microscopic analysis. If the pore diameter on the side of the membrane treated by plasma increases, on the back (not treated) side the pore diameter remains at an initial level. The preserving of the initial pore size in this part of the pore channels does not leads to a decrease of the membrane selectivity during the separation of dispersed media. This property of the modified membranes is their big advantage.

Table 3. Change of the membrane characteristics during treatment by oxygen plasma. Discharge parameters: gas pressure 22.5 Pa, discharge power 400 W.

| Plasma treatment time (min) | Thickness (µm) | Effective pore diameter (nm) | Porosity (%) | Burst strength (MPa) | Water contact angle (deg) | Initial water flow rate at ∆P = 0.1 MPa (ml/min cm²) |
|----------------------------|----------------|-------------------------------|--------------|----------------------|--------------------------|---------------------------------------------|
| –                          | 10.0           | 85                            | 7.1          | 0.23                 | 65                       | 0.50                                        |
| 1                          | 9.9            | 100                           | 9.8          | 0.22                 | 35                       | 0.85                                        |
| 2                          | 9.8            | 110                           | 11.9         | 0.20                 | 30                       | 1.60                                        |
| 3                          | 9.7            | 125                           | 15.3         | 0.18                 | 25                       | 2.30                                        |
| 4                          | 9.6            | 145                           | 20.6         | 0.16                 | 20                       | 4.25                                        |
| 5                          | 9.5            | 165                           | 26.7         | 0.12                 | 15                       | 7.00                                        |

Figure 3. Change in water flow rate (a) and filtrate volume (b) of initial PET TM (1), membrane treated by oxygen plasma during 2 min (2) and membrane treated by cyclohexane plasma during 2 min followed oxygen plasma (3). Discharge parameters: gas pressure 22.5 Pa, discharge power 400 W.

An increase in the effective pore diameter leading to increasing a volume porosity of the modified membranes causes an increase in their water permeability. As experimental data show (table 3), the initial flow rate of asymmetric membranes are higher than that of the initial one. Concentration of carboxyl groups while treating the membranes in plasma of non-polymerizing gases, to what reduction of a water contact angle of the membrane surface testifies (table 3), however, leads to increasing a
density of negative charge of the pore surface. That is reflected on the behaviour of the membrane
during filtration process – the water flow rate of the membrane quickly decreases (figure 3, curve 2). This
result, in turn, leads to a slighter increase of the filtrate volume as compared to the initial membrane (figure 4, curve 2), that causes deterioration of the membrane performance characteristics. However, the deposition of a polymeric hydrocarbon film by a subsequent treatment of the asymmetric membranes by cyclohexane plasma leads to changing of the surface properties of the membrane. The value of the water contact angle of the surface of the composite membrane in this is 70°, i.e. it increases and becomes compatible with that of the initial PET TM. Certainly, the modification of the surface properties of the asymmetric membrane leads to changing its hydrodynamic characteristics. One can observe (figure 3, curve 3), decreasing the concentration of polar functional groups into the membrane surface layer leads to increasing the flow rate. This, in turn, causes a much high filtrate volume (figure 4, curve 3). Using cyclohexane as a plasma-forming gas allows one to improve hydrodynamic characteristics of the asymmetric track membranes that were formed by a gas-discharge method.

Thus, the performed investigations show that the deposition of a thin polymeric hydrocarbon film by cyclohexane plasma on the surface of poly(ethylene terephthalate) track membranes with preliminary exposed to a gas-discharge etching by plasma of non-polymerizing gases, for example oxygen, allows one to produce asymmetric membranes possessing a high productivity. Besides, the investigations have shown that the proposed method of manufacturing membranes results in forming track membranes with a low content of the low-molecular products of PET synthesis. Even in case of a unilateral treatment of the membranes in plasma, an essential decrease of the mass share of the low-molecular products in the membranes is observed. Using such membranes will allow one both to increase the efficiency of the processes and to reduce pollution of the filtrates by low-molecular products of the synthesis of PET.

4. Conclusion
The performed investigations have allowed one to make the following conclusions. The effect of non-polymerizing gases plasma on PET TM resulting from a gas-discharge etching of the membrane surface layer leads to decreasing a mass share of low-molecular products. The deposition of a polymeric hydrocarbon film by cyclohexane plasma on the PET TM surface does not cause an increase in the mass share of the low-molecular products of synthesis of poly(ethylene terephthalate). The deposition of the polymeric hydrocarbon film by cyclohexane plasma on PET TM surface with a preliminary treatment of the membrane surface by plasma of non-polymerizing gases can serve as a basis for a method of production PET track membranes with a small mass share of low-molecular products of synthesis of poly(ethylene terephthalate) possessing a much higher productivity.

Acknowledgement
This work was supported by grant (No 06-02-90878) from Russian Foundation for Basic Research.

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