Formation of pH-responsive polymer composite membranes by plasma-induced graft polymerization method

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Abstract. The structure and the transport properties of polymer composite membranes consisting of a porous substrate and a polymer layer obtained by plasma-induced graft polymerization method were studied. It has shown that the presence of the polymer layer on the surface of porous substrate leads to changing its transport properties − the water permeability of the formed composite membranes substantially depends on the solution pH. These changes are caused by convertible conformational transitions of macromolecules of the grafted polymer layer from an expanded state into a compact one which is in turn caused by the degree of ionization of the functional groups on the surface of this layer.

Keywords: polymer composite membranes, plasma-induced graft polymerization, pH-responsive membranes

Introduction

The intense interest has been aroused recently in problem of obtaining the so-called 'smart' or 'intelligent' membranes, that is, such membranes whose transport properties can be adjusted by changing of 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 of the surface layer in response to environmental stimuli such as temperature [1, 2], solution pH [3], electric [4] and magnetic [5] fields, solvent composition [6] and pressure [7] 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 [4-6]. Another direction in this field consists in the modification of the surface of the industrially produced membranes. The research in this direction is related to a goal-directed formation of a membrane surface with tailored chemical structure. For this purpose, various physicochemical methods are employed: chemical [1], plasma-induced [2] or radiation-induced [3] graft polymerization of monomers, plasma [7] deposition of thin polymeric layers on the surface of membranes.

In the present paper we report on the transport properties of polymer composite membranes consisting of a porous substrate – a poly(ethylene terephthalate) track membrane (PET TM) and a polymer layer obtained by plasma-induced graft polymerization of 2-methyl-5-vinylpyridine (MVP) and acrylic acid (AA).

Experiments

The object of the investigation was PET TM with a thickness of 9.5 μm and an effective pore diameter of 215 nm (pore density of 2×10^8 cm^{-2}). In order to produce the membrane, the PET film was irradiated with krypton positive ions, accelerated at ~3 MeV/nucleon in the cyclotron U-400, and then subjected to the physicochemical treatment on a standard procedure [8]. The treatment of the membrane samples

by plasma was performed at the plasma-chemical set-up realizing a RF-discharge in parallel plate configuration at the frequency of 13.56 MHz at the air pressure in the vacuum chamber of 0.13 Pa and discharge power of 70 W. The treatment time was 2 min. Details on the treatment procedure and the scheme of the plasma reactor set-up have been described previously [9]. Only one side of the membrane was subjected to the plasma treatment. The graft polymerization of MVP was conducted using a 10% water solution of monomer at the temperature of 70°C for 1 h. The graft polymerization of AA was conducted from gas phase for 4 h. For this purpose membrane was placed over the 25% water solution of AA with temperature of 75°C. To suppress a homopolymerization process, divalent copper ions were introduced in the solution. After the graft polymerization, membranes were washed with distilled water using ultrasonic cleaner until the pH of the wash remained unchanged.

The characteristics of the initial and plasma modified membranes were determined through a series of complementary procedures given in [10]. The amount of the grafting polymer on the membrane surface was defined by the gravimetric method. The change of the membrane thickness was measured with an electronic counter of thickness 'Tesa Unit' (Austria). The gas flow rate through the membranes was defined at a pressure drop of 10^4 Pa. On the basis of the values obtained in these experiments an effective pore diameter was determined. For calculation we used the Hagen-Poiseuille equation. The water contact angle (as sessile drop method) was determined with a horizontal microscope equipped with a goniometer. Permeability experiments for water solution were carried out with the help of the standard filtration installation FMO-2 (Russia) at the pressure drop of 7×10^4 Pa on membrane samples with the area of 254 mm^2. pH of the solutions was varied by introducing the relevant quantity of hydrochloric acid or sodium hydroxide.

Results and Discussion

It is known that the main contribution introduced the delay of ions by membranes is provided by the electrochemical mechanism connected 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 a 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 greater degree when the changes in the value of the surface pore charge and the conformation mobility of their surface macromolecules are more essential. So, the treatment of PET TM in the air plasma results in changing its hydrodynamic characteristics. The water permeability of the modified membrane to the greater degree depends upon pH of the filtrated solution (Figure 1a). It is stipulated by increasing of the content of carboxylic groups in the surface layer of the membranes and greater conformational mobility of macromolecules of this layer [10]. Increase of the density of negative charge at the expense of increasing the concentration of the COOH-groups and increasing the degree of their dissociation at high values pH of the solution determines decreasing the water permeability in alkaline medium. But we did not observe the full contraction of the membrane pore in this case.

Table 1. Change of the membrane characteristics in the process of graft polymerization

Parameter	Initial membrane	Membrane with grafted polymer layer	
		PMVP	PAA
Grafting yield, %	—	7.2	7.4
Thickness, μm	9.5	10.5	10.1
Effective pore diameter, nm	215	160	190
Water contact angle, deg	65	45	20

The graft polymerization of MVP or AA induced by the air plasma on the PET track membrane surface leads to the formation of the composite membranes the water permeability of which can be controlled by changing the solution pH. These results can be explained by conformation transition of macromolecules of the grafted polymer layer from an expanded state 'coil' into a compact state 'globule', and vice versa. So, the research on water permeability dependence on the solution pH of the membrane with a grafted layer of poly(2-methyl-5-vinylpyridine) (PMVP) with a grafting yield of 7.2% demonstrates its abnormal behavior (Figure 1b). Note the effective pore diameter decreases in this case down to 160 nm (Table 1). This membrane is not penetrative in the region pH from 1 up to 3. If increasing pH, one can observe a linear increase of the water flow rate. Such a behavior of the membrane is explained by various conformational states of grafted PMVP macromolecules which cause changing the pore diameter. At low pH values of the solution due to protonating the nitrogen atoms of pyridine groups, the segments of the macromolecules of the grafted polymer acquire a positive charge that results in its swelling − formation of gel, causing a membrane pore contraction. The membrane pores are 'closed' in this state (Figure 2a). The macromolecules of PMVP have an extended conformation state 'coil'. Such a conformational state of macromolecules resulting from the electrostatic interaction of charged segments with water molecules is permanent. It leads to the complete contraction of pores in the acidic medium (at solution pH from 1 up to 3).
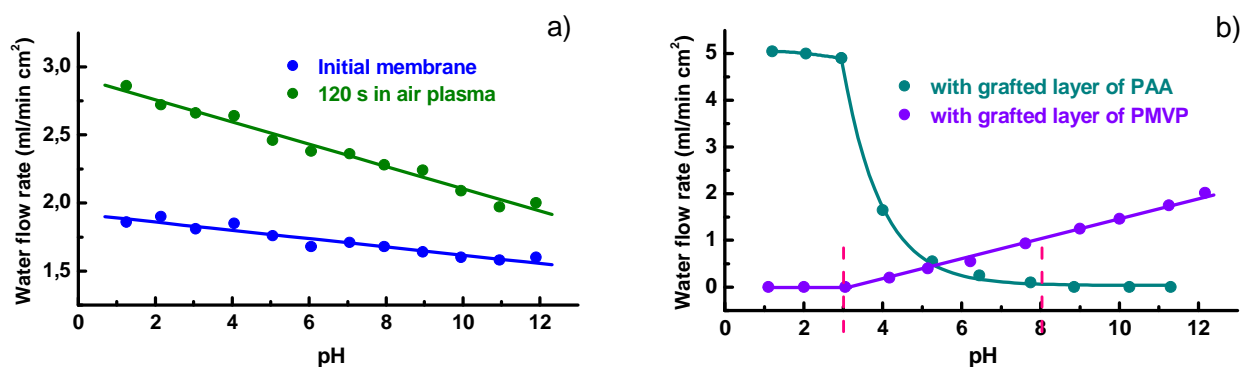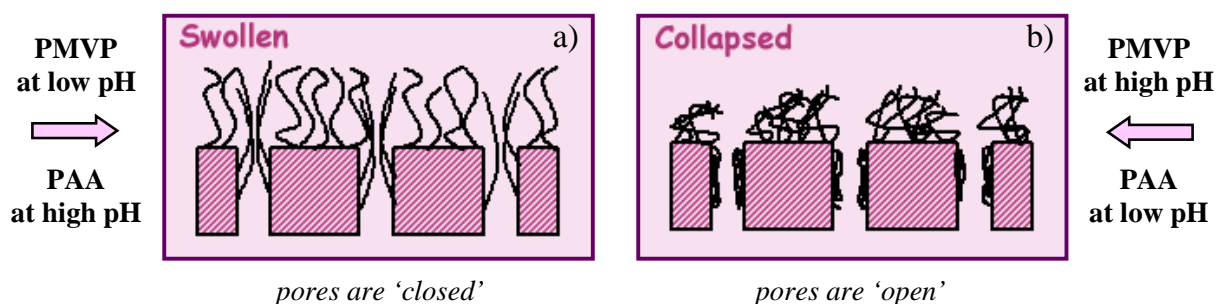

Figure 1. *pH dependence of flow rate for the: a − initial PET TM and the membrane modified by air plasma; b − composite membranes with the grafted layer of poly(acrylic acid) and poly(2-methyl-5-vinylpyridine).*

Increase of filtrate pH (the drop of ion concentration H^+ in the solution) leads to loss of the charge on the nitrogen atoms, i.e. transition of segments of the PMVP macromolecules to a neutral state. Therefore, the electrostatic interaction gets weaker. With decreasing Coulomb interaction, the non-electrostatic interaction of hydrophobic groups, in this case, of non-polar CH_3- and CH_2-groups increases. That results in a collapse of gel − transition of macromolecules in a compact conformational state 'globule'. The membrane pores are 'open' in this state (Figure 2b) that leads to increasing the membrane pore diameter, thus, its water permeability increases. The grafting of PMVP on the PET TM surface induced by plasma thus results in forming a composite mechanochemical membrane, the permeability of which is controlled by changing pH of the solution. For the membrane with a grafting yield of 7.2% at pH = 3 one can observe change-over to an operation mode of a 'chemical valve' i.e. at smaller pH values of the filtrate the membrane gets impermeable for water molecules. At higher pH values of the filtrate the membrane gets permeable for water molecules. Clearly, the boundary value of pH solution where the membrane changes for this mode will be determined by the properties of substrate and the grafted polymer layer.

The grafting of poly(acrylic acid) (PAA) on the membrane modified by plasma from a gas phase at elevated temperature results in formation of a mechanochemical membrane with 'chemical valve' too.

For the membrane that has a grafting yield of 7.4% and effective pore diameter of 190 nm (Table 1) at pH values more than 8 the full pore contraction is observed (Figure 1b) due to negative charge on the segments of the macromolecules of the grafted polymer macromolecules resulted from the dissociation of carboxyl groups. This leads to swelling the polymer layer and formation of gel. Such a conformational state of the macromolecules leads to the contraction of the membrane pores. The membrane pores are 'closed' under this condition (Figure 2a). Decrease of filtrate pH leads to loss of the charge on the segments of the grafted polymer macromolecules. That results in a collapse of gel − transition of macromolecules in a compact conformational state. The membrane pores are 'open' in this condition (Figure 2b) that leads to increasing the membrane pore diameter, thus, its water permeability increases. So, for the membrane with a grafted PAA layer change-over to an operation mode of a 'chemical valve' one can observe at pH = 8. I.e., at higher pH values of the filtrate the membrane gets impermeable for water molecules. At smaller pH values of the filtrate, the membrane gets permeable for water molecules.

PMVP at low pH → **PAA at high pH** a) Swollen — pores are 'closed'

PMVP at high pH ← **PAA at low pH** b) Collapsed — pores are 'open'

Figure 2. Schematic illustration of changing in the conformation state of the grafted macromolecules on the track membrane surface in medium with various solution pH.

Conclusion

The performed investigations have allowed us to make the following conclusions. The presence of the polymer layer of PMVP or PAA on the surface of PET track membrane results in changing its transport properties − the water permeability of the formed composite membranes substantially depends on the solution pH. These changes are caused by convertible conformational transitions of macromolecules of the polymer layer obtained by plasma-induced graft polymerization which is in turn caused by the degree of ionization of functional groups on the surface 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 modeling processes of regulation in the cell, etc.

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