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Modification of Polymer Membrane Properties by Low-Temperature Plasma

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Abstract—The results of investigations into the use of low-temperature plasma for modification of polymer membranes are considered. The basic lines of research in this area are highlighted. It is shown that plasma treatment is quite an effective tool for both improving properties of existing polymer membranes and manufacturing new composite membranes with unique characteristics. Examples of successful use of plasma-modified membranes in various branches of industry and medicine are given.

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INTRODUCTION

Membrane processes are widely used in many fields of science and technics, including gas separation, water desalination, pervaporation, separation and isolation of individual components of solutions, purification and concentration of biologically active compounds, etc. [1]. Polymer membranes occupy important place among a great diversity of membranes used in these processes. However, the properties of existing membranes not infrequently fail to meet demands of engineering processes, because the range of polymers suitable as membrane materials is quite limited.

To extend the range of commercial polymer membranes, research into modification of their properties, specifically, targeted variation of the composition and structure of the surface layer, is being performed. A number of physical and chemical methods for modification of polymer materials (including membranes) have been reported [2–16].

Of the physical methods for surface modification of polymers, wide acceptance has been gained by low-temperature plasma treatment [17]. An important advantage of this technology is that it allows one to modify a thin surface layer and thus affect such membrane properties as adsorption and transport capacity and selectivity. This essentially extends the range of possible applications of membranes. The bulk of the membrane matrix remains intact in this case, and this is quite important in terms of preservation of its mechanical and physicochemical properties.

Low-temperature plasma treatment involves a number of physicochemical processes depending on the type of the discharge (plasma frequency) and the nature of the plasma-forming gas, which allows targeted alteration of the structure and chemical composition of the surface layer of polymer membranes.

Low-temperature plasma can be generated by low-frequency, radiofrequency, and microwave discharges, as well as a dc discharge.

The chemical processes involved in surface modification of membranes, are primarily determined by the plasma gas composition. Two types of plasma are used: a simple gas plasma, when no polymer formation occurs on the surface being treated (nonpolymer-forming gases: H_2, He , Ar, O_2, N_2, air, halogens) and organic and organoelement vapor plasma. In the latter case, a polymer film is formed on the surface being treated.

Of special interest is low-temperature plasma treatment of porous polymer membranes, which makes it possible to create new materials for modern membrane processes (membranes for bioreactors, fuel cells, catalytic processes, etc.).

The present review covers Russian and foreign works on the modification of porous polymer membranes by low-temperature plasma treatment, reported over the past decade.

Treatment of Polymer Membranes by Plasma of Inorganic Gases

The main process that occurs on treatment of membranes with a low-frequency inert-gas plasma is cross-linking of the polymer surface layer [18] and cyclization of macromolecules [19], which impart enhanced stability to the modified membranes (Table 1).

Treatment of polymer membranes by RF (including pulsed) and microwave discharges in nonpolymer-forming gases results in etching (physical sputtering or oxidation) of the polymer matrix [20–50], the rate of which depends on the nature of the plasma-forming gas. For example, the surface etching of membranes in inert-gas or hydrogen plasmas by physical sputtering is inconsiderable [20, 21], whereas in nitrogen, oxygen, or air plasmas the rate of etching (primarily oxidative) in analogous conditions is several times higher [22–39]. Surface etching of polymer membranes entails increased pore diameter [24–30].

Figure 1 shows the micrographs of the surface of polypropylene track membranes, both starting and treated in argon, air, and oxygen plasmas. As seen, the pores on the surface of modified membranes are larger compared to the control sample. According to our experimental results [38], the pore size increases in membranes etched in air and oxygen plasmas (by 13 and 42%, respectively) is larger compared to membranes etched in a nitrogen plasma. In addition, plasma treatment of track membranes, whose pores are cylinder-shaped channels, changes the shape of the pores to form asymmetric membranes [32–35]. With such membranes, the efficiency of the filtration process is much higher.

Etching of a polymer matrix reduces the weight fraction of low-molecular products (oligomers) in the membrane [36], because the most part of such products is present on the polymer surface. Thus modified membranes are suitable for filtering organic solvents.

The rate of plasma etching is also dependent on the parameters of the discharge (as a rule, it is proportional to its power [24, 27, 28]), as well as the nature and crystallinity of the polymer (amorphous areas are etched slightly faster due to their lower density and higher diffusion of reaction gases [27, 28]). Because of the different etching rates of amorphous and crystalline polymer areas, the relief pattern of the surface changes, specifically, it becomes rougher [27–29, 32–34, 38]. Thus, the estimated rms deviation of the surface profile R_q for the starting polypropylene track membrane (see Fig. 1) is 50.7 ± 3.3 nm. Exposure to an air and, especially, oxygen plasma essentially affects the morphology of the membrane surface. The R_q value for a membrane modified by an air plasma is 78.6 ± 5.2 nm, whereas for a membrane modified by an oxygen plasma this value increases to 196 ± 12 nm [38]. Such structuring of the surface of membranes essentially improves their adhesion characteristics [30].

Exposure of polymer membranes to a nonpolymer-forming plasma alters the chemical composition of the surface layer (Table 1). Thus, treatment by an oxygen or air plasma forms on the surface oxygen-containing functional groups, in particular, carbonyls and carboxyls, as a result of oxidation of end groups arising from cleavage of chemical bonds [24–31]. As a result, the membrane surface becomes much more hydrophilic, which is quite useful for certain applications. The wettability of membranes is therewith much enhanced. For example, if the contact angle (θ) of the starting polypropylene track membrane is 120°, then after treatment by nitrogen, air, and oxygen plasmas this angle decreases to 75°, 65°, and 60°, respectively [38]. The enhanced wettability of the surface of hydrophobic membranes favors better penetration of water into pores, which enhances the water permeability of plasma-treated membranes. Thus, we found [38] that the starting polypropylene track membrane is water impermeable at pressure differentials of up 10^5 Pa, whereas plasma-treated membranes containing polar groups in the surface layer become water-permeable.

Increasing concentration of surface polar groups enhances the hydrophilicity of pores in modified membranes and, furthermore, enhances the electrical conductivity of the membranes. Measurement of current-voltage characteristics in [38] showed that plasma-treated polypropylene track membranes have a better electrical conductivity. Thus, the transmembrane current I_t at the potential 1 V for the starting membrane

Table 1. Examples of application of nonpolymer-forming gas plasma treatment for membrane modification[a]

Membrane	Plasma-forming gas, discharge type and frequency	Effect of plasma treatment	Properties of modified membranes	Reference
PA	Ar, glow discharge (20 kHz)	Cross-linking of the surface layer	Increased chemical stability	[18]
PAN	He, He/H_2O, glow discharge (20 kHz)	Cyclization of the surface layer	The same	[19]
PAN	Ar, He, RF discharge (13.56 MHz)	Destruction of polymer macromolecules, surface etching	Increased surface wettability and water permeability	[20]
PDMS	Ar, Ar/H_2, Ar/O_2 , microwave discharge (2.45 GHz)	Membrane and pore surface etching, formation of oxygen-containing groups	Increased surface wettability and adsorption capacity to dyes	[21]
PVC, PP	Air, dc discharge	Surface etching, formation of COOH groups	Increased surface wettability and water permeability	[22, 23]
PAN, PS	Air, microwave discharge (2.45 GHz)	Membrane and pore surface etching, formation of oxygen-containing groups	The same	[24, 25]
PP	O_2, microwave discharge (2.45 GHz)	Membrane and pore surface etching, formation of oxygen-containing groups	Increased surface wettability and water permeability, increased ionic conductivity	[26]
PAN, PS, PP, PU	O_2, air, RF discharge (13.56 MHz)	Membrane and pore surface etching, change of surface morphology, formation of oxygen-containing groups	Increased surface wettability and water permeability, decreased adsorption capacity to albumin	[20, 27–31]
PET, PP	O_2, air, N_2, RF discharge (13.56 MHz)	Membrane and pore surface etching, formation of oxygen-containing groups	Changed pore shape, increased surface wettability and water permeability, decreased content of oligomers in the polymer matrix	[32–38]

Table 1. (Contd.)

Membrane	Plasma-forming gas, discharge type and frequency	Effect of plasma treatment	Properties of modified membranes	Reference
PP, PS, PET	N_2, NH_3, RF discharge (13.56 MHz)	Membrane and pore surface etching, formation of polar nitrogen-containing groups in the surface layer	Increased surface wettability, decreased adsorption capacity to proteins	[39–43]
PA, PS, PVDF, PP	N_2, microwave discharge (2.45 GHz)	Etching of the surface layer in amorphous regions	Increased crystallinity of membrane matrix	[44, 45]
PS	N_2, NH_3, microwave discharge (2.45 GHz)	Membrane and pore surface etching, formation of polar nitrogen-containing groups in the surface layer	Increased surface wettability and water permeability, decreased adsorption capacity to proteins	[46–48]
PS	NH_3, Ar/NH_3, O_2/NH_3, RF discharge (13.56 MHz)	Membrane and pore surface etching, formation of polar groups in the surface layer	Increased surface wettability and water permeability, decreased adsorption capacity to proteins	[49]
PVDF	NH_3, RF discharge (13.56 MHz)	Formation of polar NH_2 groups in the surface layer	Creation of membrane catalysts with surface-immobilized tungsten	[50, 51]
PS, PES, PE, PC, PET	H_2O, RF discharge (13.56 MHz)	Change of surface morphology and chemical structure	Increased surface wettability and roughness	[52–54]
PS	CO_2, microwave discharge (2.45 GHz)	The same	Increased surface wettability and roughness, decreased adsorption capacity to proteins	[24, 25, 48, 55]
PS, PP	CO_2, RF discharge (13.56 MHz)	Formation of polar oxygen-containing functional groups in the surface layer	Increased surface wettability, decreased adsorption capacity to proteins	[56–59]
PA, PES	CO_2, dc discharge	Formation of polar oxygen-containing functional groups in the surface layer	Increased surface wettability, decreased adsorption capacity to proteins	[60]

[a] (PA) Polyamide, (PAN) polyacrylonitrile, (PDMS) polydimethylsiloxane, (PVC) poly(vinyl chloride), (PP) polypropylene, (PS) polysulfone, (PES) poly(ether sulfone), (PE) polyethylene, (PU) polyurethane, (PET) poly(ethylene terephthalate), (PC) polycarbonate, (PI) polyimide, (PVDF) poly(vinylidene fluoride), (PTFE) polytetrafluoroethylene.

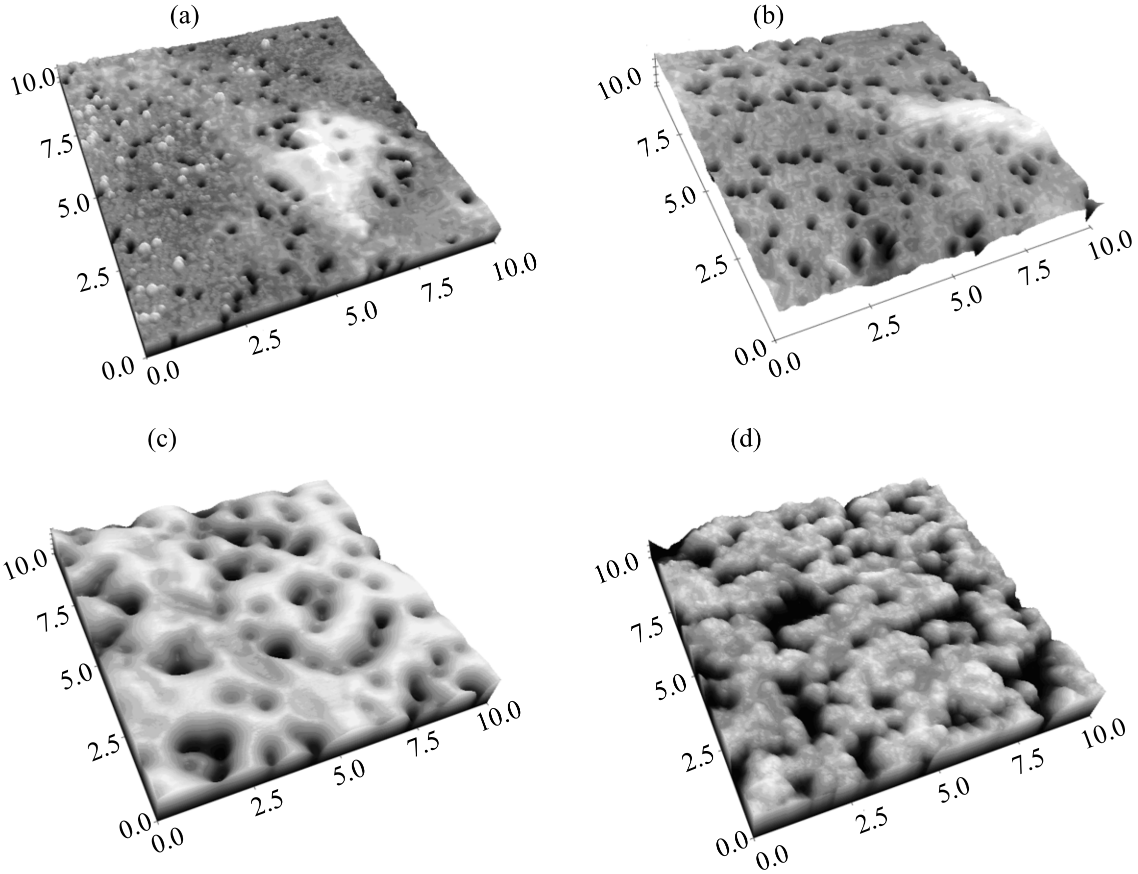

Fig. 1. Three-dimensional images of the surface of polypropylene track membranes: (a) starting membrane and (b) nitrogen, (c) air, and (d) oxygen plasma-modified membranes. Atomic force microscopy. Scan area 10 × 10 μm [38].

is 40 μA and for the membrane modified by a nitrogen plasma this value is double as high. The transmembrane current for the membrane treated by an air plasma is 300 μA (1 V), which is 7 times as high as that for the starting polypropylene track membrane. The I_t for the membrane modified by an oxygen plasma is even higher (355 μA at 1 V), specifically, 9 times as high compared to the starting membrane. The electrical conductivity of the modified membranes obtained by plasma oxidation is directly related to the concentration of oxygen-containing groups in the surface layer of the membranes (Fig. 2). The best correlation of I_t with the concentration of surface functional groups is reached if only polar groups (carbonyls plus carboxyls) are taken into account.

Under the action of hydrogen or inert-gas plasmas, oxygen-containing groups are mostly formed in sites where chain cleavage forms polymer radicals which are further oxidized in air [20, 21]. Treatment by a nitrogen-containing plasma (N_2, NH_3) results, along with etching and polymer radical formation, in insertion of nitrogen atoms into the surface layers of membranes to form N–C bonds [39–51]. The wettability of membrane surface is therewith improved and their protein adsorptivity is decreased. Modification by treatment in water vapor [52–54] or carbon dioxide plasmas [24, 25, 55–60] alters the surface morphology of polymer matrices, as well as their chemical structure, namely, oxygen-containing functional groups, in particular, carboxyls, are formed.

As an example of practically important applications of polymer membranes treated in a simple gas plasma, we would like to mention our works [61, 62] on the use of air plasma–modified poly(ethylene terephthalate) track membranes (PET TM) as a drainage material for surgical treatment of refractory glaucoma (Fig. 3). It was shown that the plasma treatment of track membranes forms asymmetric track membranes with improved filtration characteristics and a nanostructured surface layer. The presence of a nano-

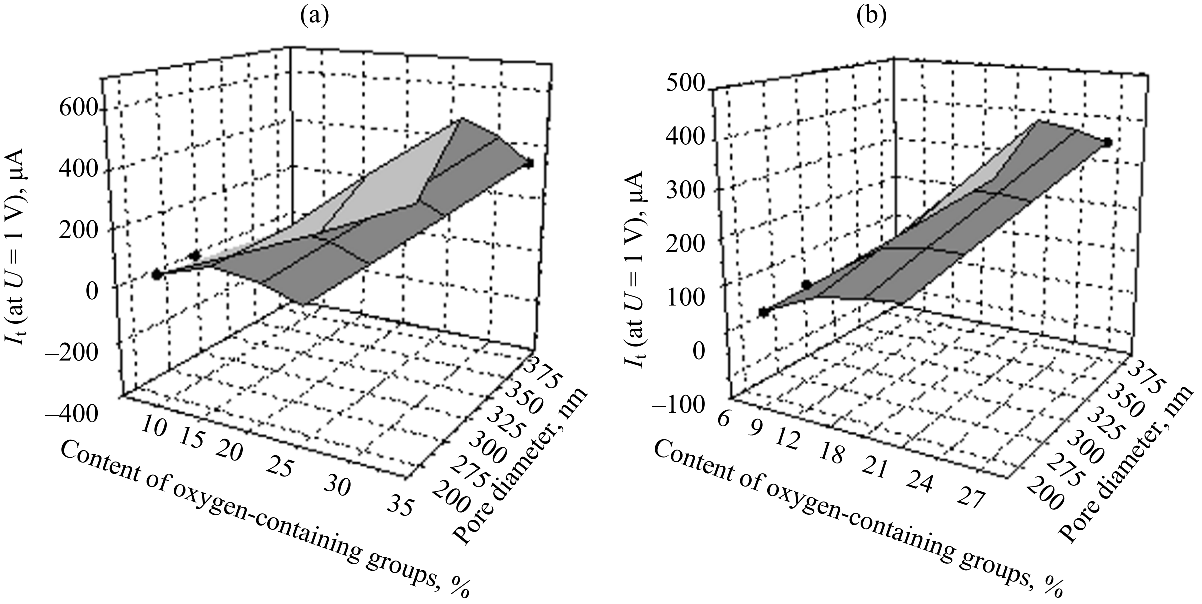

Fig. 2. Dependence of transmembrane current (I_t) on pore diameter and (a) total content of oxygen-containing functional groups and (b) total content of the carbonyl and carboxyl groups in the membrane surface layer [38].

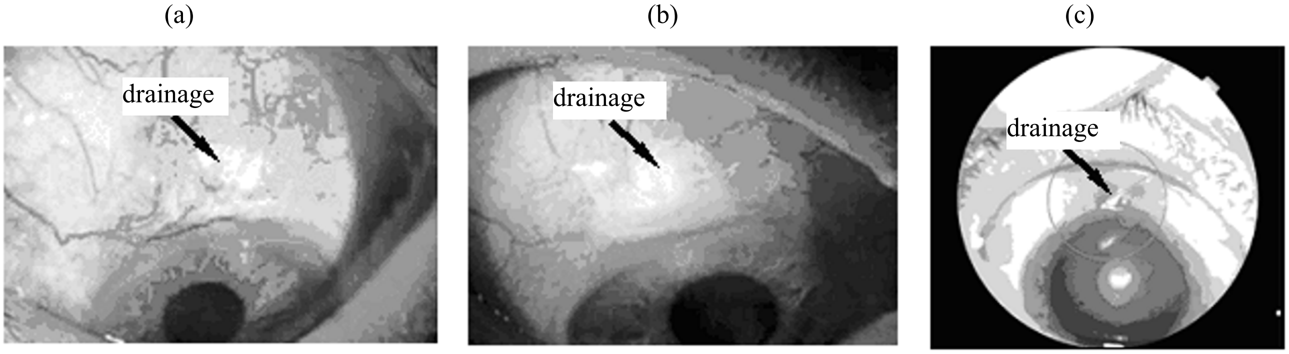

Fig. 3. (a, b) Eyes of patients and (c) optical coherent tomogram of an eye after glaucoma surgery.

structured surface layer affects some properties of these track membranes. Increased content of surface carboxyl groups enhances hydrophilicity of the membranes. Surface erosion and hydrophilization of PET TM enhances their wettability. Enrichment of the surface layer with carboxyl groups increases the negative pore charge in the solution and enhances roughness of the membrane surface, thereby preventing formation of a hard fibrous capsule around drainage and preserving ways for intraocular fluid during glaucoma surgical operations. The developed drainage causes no local irritation and sensitization, as well as no expressed reactive inflammatory changes in tissues surrounding the implant. One year after implantation the drainage showed no signs of biodegradation and completely preserved its functional properties. According to the results of clinical trials, PET TM with a nanostructured surface can use to success as drainage in surgical treatment of refractory glaucoma.

Treatment of Polymer Membranes by Plasma of Organic Gases

Organic plasma treatment of membranes results in the deposition on their surface of a thin polymer film. As a result, composite membranes comprising a porous support (the starting membrane) and a plasma-deposited polymer film are formed. By selecting starting membranes with a definite pore diameter and varying the time of plasma treatment one can produce

Table 2. Examples of application of plasma polymerization for membrane modification

Membrane	Plasma-forming gas, discharge type and frequency	Effect of plasma treatment	Properties of modified membranes	Reference
PET	Cyclohexane, RF discharge (13.56 MHz)	Deposition of a hydrophobic hydrocarbon film	Increased surface wettability	[63]
PP	Hexafluoroethane, RF discharge (13.56 MHz)	Deposition of a hydrophobic fluorocarbon film	The same	[64]
PS	Perfluoroheptane/Ar, RF discharge (13.56 MHz)	The same	The same	[65]
PC, PET	Perfluorohexane, RF discharge (13.56 MHz)	The same	Decreased O_2 and CO_2 permeability	[66, 67]
PET	Perfluoro-1-octene, RF discharge (13.56 MHz)	Deposition of a chemically stable hydrophobic fluorocarbon film	Decreased surface wettability, control of pore geometry	[68]
PTFE	Acetylene/N_2, RF discharge (13.56 MHz)	Deposition of a polymer film, nitrogen insertion	Increased surface wettability	[69]
PET	Cyclohexane/N_2, RF discharge (13.56 MHz)	Deposition of a polymer film, nitrogen insertion	Improved hydrodynamic properties	[70]
PET, PS	Acrylic acid, microwave discharge (2.45 GHz)	Deposition of a hydrophilic COOH-containing film	Increased surface wettability	[71, 72]
PET, PP, PS, PU	Acrylic acid, RF discharge (13.56 MHz)	Deposition of a hydrophilic COOH-containing film	Increased surface wettability and separation selectivity, creation of cation-exchange membranes, decreased adsorption capacity to rhodamine	[73–78]
PC	Acrylic acid, allylamine, RF discharge (13.56 MHz)	Deposition of hydrophilic COOH- and NH_2-containing films	Control of water permeability and separation selectivity	[79]
PP	Acrylic acid, allylamine, RF discharge (13.56 MHz)	Deposition of hydrophilic COOH- and NH_2-containing films	Control of water permeability by varying pH of the solution	[80]
PET, PP, PS, PI	Allylamine, RF discharge (13.56 MHz)	Deposition of a hydrophilic NH_2-containing film	Increased surface wettability, improved biocompatibility with blood	[76–83]
PET, PS	Allylamine, butylamine microwave discharge (2.45 GHz)	Deposition of a hydrophilic NH_2-containing film	Improved hydrodynamic properties in acid media, decreased adsorption capacity to proteins	[84–89]
PVDF	Diaminocyclohexane, RF discharge (13.56 MHz)	Deposition a hydrophilic NH_2-containing film	Increased surface wettability and separation selectivity	[90]

Table 2. (Contd.)

Membrane	Plasma-forming gas, discharge type and frequency	Effect of plasma treatment	Properties of modified membranes	Reference
PES	Acrylamide, RF discharge (13.56 MHz)	Deposition of a hydrophilic film	Decreased adsorption capacity to proteins	[91]
PET	Dimethylaniline, RF discharge (13.56 MHz)	Deposition of a hydrophilic NH_2-containing film	Control of water permeability by varying pH of the solution and pressure	[74, 92, 93]
PVDF	Tetramethylsilane/NH_3, glow discharge (40 kHz)	Deposition of a hydrophilic NH_2-containing film	Creation of highly selective anion-exchange membranes	[94]
PET	Allyl alcohol, RF discharge (13.56 MHz)	Deposition of a hydrophilic OH-containing film	Improved hydrodynamic properties	[95, 96]
PS	Allyl alcohol, microwave discharge (2.45 GHz)	The same	Improved enzyme immobilization	[97]
PET	Aniline, ac discharge (50 Hz)	Deposition of an electroconductive polymer film	Creation of composite membranes with conductivity asymmetry	[101, 102]
PET	Thiophene, pyrrole, acetylene, RF discharge (13.56 MHz)	Deposition of an electroconductive polymer film	The same	[103–108]
PET	1,1,1,2-Tetrafluoroethane, RF discharge (13.56 MHz)	Deposition of a hydrophobic fluorocarbon film	The same	[105, 109]
PA, PP, PET	*N*-Isopropylacrylamide, RF discharge (13.56 MHz)	Deposition of a hydrophilic film containing peptide bonds	Creation of thermosensitive composite membranes	[110–112]

composite membranes for ultra- and nanofiltration and reverse osmosis applications [35, 48]. In the latter case, a thin semipermeable film completely coating membrane pores should be formed on the surface of the membrane. The possibility to control the thickness of the plasma-deposited layer which is responsible for the selectivity of the membrane, as well as the wide range of organic compounds suitable for use as a plasma medium make this method of the production of composite membranes especially promising.

It should be noted that plasma-deposited polymer films much differs in structure and properties from polymers produced by traditional chemical polymerization. Unlike traditionally produced macromolecules which contain repeating units of the starting monomer and are fairly flexible in the surface layer, the polymer synthesized by plasma is a highly cross-linked structure with limited-mobility chain units. This predetermines the transport properties of plasma-modified membranes and, first of all, their water permeability and selectivity.

The surface properties of the composite membranes obtained by means of plasma chemical modification depend on the nature of the plasma-forming gas (Table 2). For example, if the plasma-forming gases are hydrocarbons or fluorinated organic compounds, a solid, chemically stable polymer film containing no functional groups is deposited on the surface of the membrane [63–68]. In this case, hydrophobic composite membranes with enhanced mechanical and chemical strength are produced. Such membranes are widely used in distillation processes.

The modification of membranes by a hydrocarbon–nitrogen plasma results in insertion of nitrogen atoms into the polymer film to form C–N bonds [69, 70]. As a result, the membrane surface becomes hydrophilic.

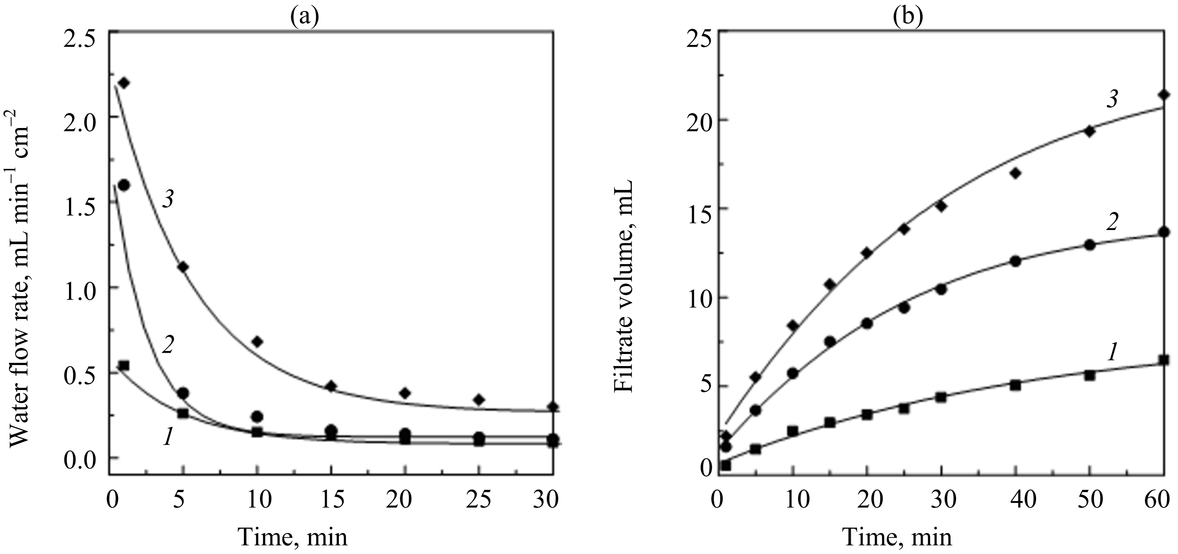

Fig. 4. Changes in the (a) water permeability anf (b) filtrate volume for PET TM: (*1*) starting membrane (pore diameter 0.1 μm) and (*2*) nitrogen and (*3*) nitrogen-cyclohexane plasma-treated membranes. Time of plasma treatment 3 min [70].

For example, treatment of polytetrafluoroethylene membranes by an acetylene–nitrogen plasma decreases their contact angle from 126° to 34° [69], which should improve the hydrodynamic properties of the resulting composite membrane. Actually, we observed an improvement of the hydrodynamic properties of PET TM after the deposition on their surface of a thin polymer film by a cyclohexane–nitrogen plasma [70]. Reduced concentration of surface COOH groups did not reduce considerably the water permeability of the modified membranes and increased the volume of the filtrate (Fig. 4). Hydrophilic composite membranes with a high surface concentration of COOH groups were produced by the deposition of plasma-polymerized acrylic acid films [71–80]. The wettability of the membrane surface is therewith much enhanced and, moreover, the modified membranes show high cation-exchange capacity and separation selectivity.

Treatment of membranes by allylamine, butylamine, diaminocyclohexane, acrylamide, and dimethylaniline plasmas results in the deposition of polymer films containing nitrogen-containing functional groups (NH_2, NH, etc.) [76–93]. Such composite membranes have a hydrophilic surface are characterized by a high biocompatibility with blood and reduced adsorption of proteins from solutions. Treatment of poly(vinylidene fluoride) membranes by plasma generated in a mixture of tetramethylsilane and ammonia forms an organosilicon film containing a lot of amino groups [94]. As a result, a composite membrane with a high anion-exchange capacity and separation selectivity is formed. Hydrophilic composite membranes with polymer films deposited on their surface by an allyl alcohol plasma exhibit improved hydrodynamic characteristics [95, 96]. Moreover, due to the high concentration of surface OH groups, such membranes show enhanced capacity for immobilization of biologically active compounds [97].

Adhesion of a plasma-deposited polymer film to membrane surface is frequently increased by pretreatment with in nonpolymer-forming gases to form polymer radicals in the polymer layer of the membrane. Thus, Toufik et al. [76] prior to depositing plasma-polymerized acrylic acid and allylamine films pretreated a PET TM by an oxygen plasma, and Hamerli et al. [85] used argon instead of oxygen as the plasma-forming gas. It was shown that such technology is the most efficient to produce composite materials on the basis of hydrophobic membranes, because it provides better adhesion of the plasma-deposited polymer film. Wavhal and Fisher [91] used argon for surface preactivation of poly(ether sulfone) membranes, and Roualdes et al. [94] pretreated PET TM by an oxygen plasma prior to deposition of an organosilicon film to their surface.

Pretreatment by an oxygen plasma used not only for activation of the surface of PET TM [95, 96]. It

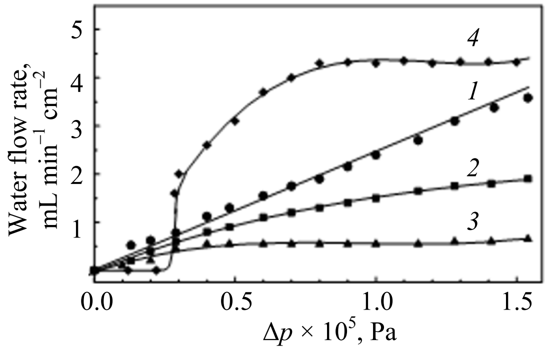

Fig. 5. Dependence of the water permeability of PET TM on pressure (Δp) for the filtration of a solution (pH = 1.2) through (*1*) the starting membrane (pore diameter 0.215 μm) and (*2–4*) membranes treated in a dimethylaniline plasma for (*2*) 20, (*3*) 60, and (*4*) 60 s and doped with iodine [93].

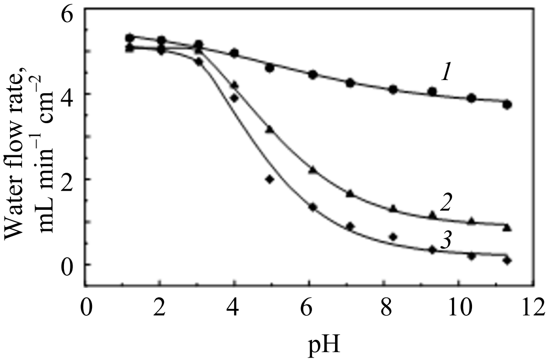

Fig. 6. Dependence of the water permeability of PET TM on solution pH: (*1*) starting membrane (pore diameter 0.215 μm) and (*2*, *3*) membranes treated in an acrylic acid plasma for (*2*) 60 and (*3*) 900 s [73].

was shown that such treatment forms an asymmetric membrane with increased porosity. The deposition of a plasma-polymerized allyl alcohol film on such membrane produces an asymmetric composite membrane with improved filtering capacity in a wide pH range.

Preparation of Smart Membranes by Plasma Polymerization

One of the most interesting directions of plasma chemical modification of polymer membranes is creation of smart (or intelligent) membranes [98], т.е. membranes, whose transport characteristics can be varied by varying external conditions (temperature, solution composition and pH, pressure, electric and magnetic fields, etc.). Smart membranes not only have unique water permeability, they are also capable of mimicking biological membranes. Smart membranes can be used for controlled drug release, in biosensors, and for simulation of regulatory processes in living cells. Furthermore, they have found application in isolation and purification of biologically active compounds and immobilization of biocatalysts.

To render a polymer membrane smart, i.e. to impart to it a high sensitivity to external conditions, i.e. ability to undergo a first-order phase transition accompanied by a sharp change of the specific volume of macromolecules. The primary condition for critical phenomena in swollen polymer networks or linear macromolecules is the presence of a “bad” solvent [99], i.e. a solvent where attractive forces between different segments of the polymer chain may overcome repulsive and thus induce polymer collapse.

Creation of smart membranes involves targeted construction of the chemical structure of the membrane surface layer. For example, plasma polymerization of dimethylaniline and acrylic acid on the surface of PET TM gave composite membranes whose water permeability is pH-dependent (Figs. 5 and 6). This property is associated with the reversible conformational transition in the macromolecules of the plasma-deposited polymer from the loose hydrated state with narrower pores to a compact dehydrated state with enlarged pore diameter.

It was shown that the film formed by plasma polymerization of dimethylaniline on the membrane surface can swell in solutions with low pH values [74, 93]. This process is induced by protonation of nitrogen atoms, as a result of which molecular units of the plasma-deposited polymer film acquire a positive charge and capacity to swell, forming a polyelectrolyte gel [100] and thereby decreasing membrane pore diameter. The dimethylaniline polymer macromolecules look here as loose coils (Fig. 7a). As the pH of the filtrate increases (H^+ concentration in the solution decreases), the nitrogen atoms lose charge, i.e. the macromolecules become neutral. As a result, the electrostatic interaction becomes weaker, whereas the nonelectrostatic interaction of hydrophobic groups, here CH_2, leads to gel collapse, specifically, transition of the plasma-polymerized dimethylaniline macromolecules into a compact conformational state “globule” (Fig. 7b). Macromolecules in this state do not decrease pore diameter, and, therefore, at increased pH values high water fluxes through the modified membranes are observed. Introduction of iodine into the film of plasma-polymerized dimethylaninile forms a polyelectrolyte whose swelling in an acid medium completely closes membrane pores. Such membrane is

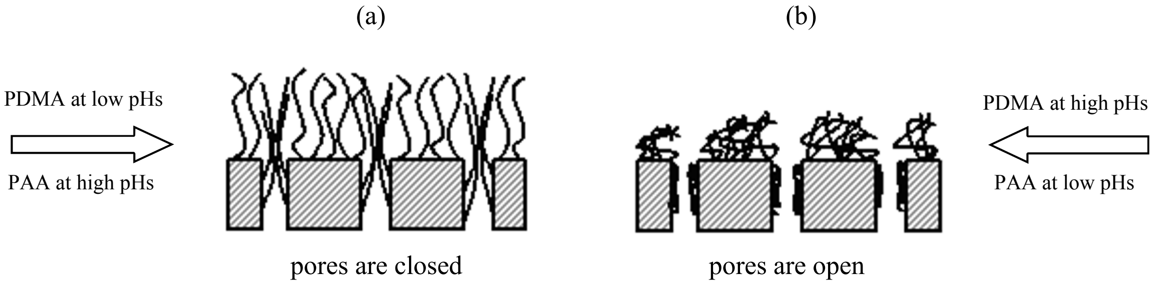

Fig. 7. Schematic representation of the conformational changes in the macromolecules by plasma-deposited polymer film in solutions with different pH values [74].

completely water impermeable at low pressures (Fig. 5, curve *4*). Increasing pressure leads to a collapse of the gel, as a result of which the water permeability of the modified membrane increases jumpwise, i.e. thus obtained composite membranes are pressure-sensitive.

A different situation takes place by an acrylic acid plasma. In this case, the polymer film that forms swells in solutions with high pH values [73, 74]. Therefore, the composite membrane by a plasma-polymerized acrylic acid film has a low water permeability in an alkaline medium. The decreased water permeability of the composite membranes is explained by their decreased pore diameter, which, in its turn, is explained by a conformational change in the macromolecules of this polymer. At low pHs, the COOH groups do not dissociate, the monomeric units of the macromolecules of the plasma-deposited polymer are neutral. As a result, the electrostatic interaction becomes weaker and the nonelectrostatic interaction between hydrophobic groups (CH_2– and CH–) becomes stronger, which makes the gel to collapse, specifically, the plasma-polymerized acrylic acid macromolecules undergo transition to the compact state “globule” (Fig. 7b) which does not decrease pore diameter. Therefore, in acid media high water fluxes through the modified membranes are observed. As the pH of the solution increases, the conformational state of the polyacrylic acid macromolecules changes. At pH > 4.28, the COOH groups dissociate (the pK_{COOH} in polyacrylic acid is 4.28), and the monomeric units of the plasma-deposited macromolecules acquire a negative charge, which gives rise to gel formation on the membrane surface [100]. In this case, the macromolecules are present in a loose, coil conformation (Fig. 7a), and the membrane pore diameter and, consequently, water permeability are decreased.

Composite membranes with unique properties were also obtained on the basis of PET TM by polymer film deposition in aniline [101, 102], thiophene [103–105], and pyrrole plasmas [105–107]. A characteristic feature of such membranes is that they have two layers (Fig. 8) with functional groups differing in chemical structure and properties. For example, if the surface of the starting membrane contains cation-exchange COOH groups, in the layer synthesized by aniline or pyrrole plasma polymerization there are anion-exchange nitrogen-containing groups, and in the layer synthesized by thiophene polymerization, sulfur-containing groups. On the contact of such layers with the bulk membrane, a unique property arises: conductivity asymmetry (Fig. 9). Such composite membranes are similar to a semiconductor diode. A formal analogy takes place between the conductivity of such membranes in aqueous electrolyte solutions and the conductivity of semiconductors, associated with electrons and holes. In other words, PET TM with a polymer surface layer can be considered as a matrix (diode), where each layer contains charges fixed on pore surface and neutralized by mobile ions (counter ions) of the opposite sign.

Our recent experiments [105] showed that composite membranes show conductivity asymmetry only if they have on the surface a semipermeable polymer film which closes their pores. For example, the polymer film formed on treatment of PET TM by a pyrrole plasma for 60 s is too thin to close pores (Fig. 10b), and, as a result, no conductivity asymmetry is observed in electrolyte solutions. At the same time, 300-s treatment forms a semipermeable polymer film which closes pores completely (Fig. 10c). Such membranes show conductivity asymmetry (the rectifying effect). The strength of this effect can be characterized by the rectification factor (k_r) which is calculated as the ratio of two mutually opposite currents at the potentials +1 and –1 V. It was shown that the rectification factor for a membrane treated by

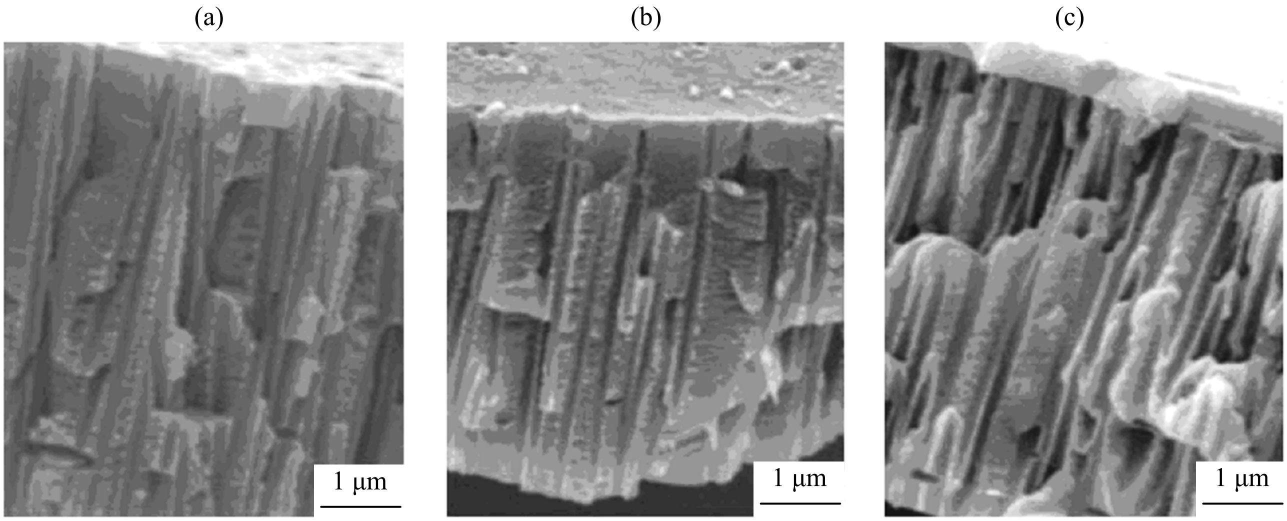

Fig. 8. Electron micrographs of the cross sections of PET TM: (a) starting membrane and membranes treated in a thiophene plasma for (b) 5 min and (c) 15 min [103].

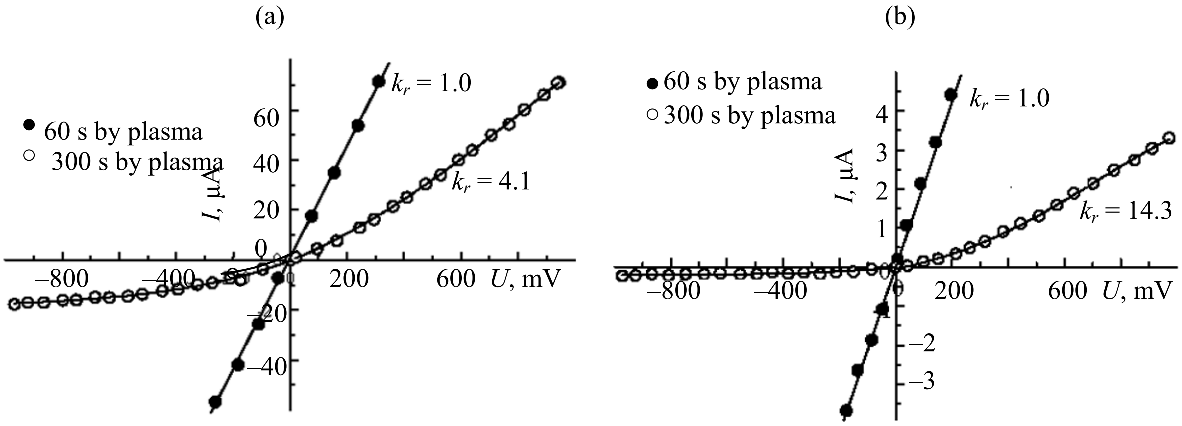

Fig. 9. Current-voltage characteristics of PET TM with a various-thickness plasma-deposited polypyrrole films, measured in (a) 10^{-2} M and (b) 10^{-3} M solutions of KCl [106].

plasma for 300 s in a 10^{-2} KCl solution is 4.1 and the respective values for a 10^{-3} KCl solution is 14.3 [106, 107].

The asymmetry effect in the two-layer composite membranes formed by treatment of PET TM by aniline, pyrrole, and thiophene plasmas is primarily associated with a contact between two layers with antipolar conductivity and is caused by different system resistances at different current directions. However, as we found in [108, 109], treatment of such membranes by acetylene and 1,1,1,2-tetrafluoroethane plasmas does not yield bipolar membranes, because the polymer films formed by the above plasmas contain no anion-exchange functional groups. However, here, too, two-layer composite membranes with properties similar to those of semiconductor diodes are formed. The asymmetry effect in two-layer composite membranes of this type arises on the contact of two layers with different surface concentrations of carboxyl groups. We also showed [107–109] that the deposition of a polymer film on the surface affects the structure of the initially cylindrical pores of the starting track membranes. The pores acquire an asymmetric (conic) shape: the pore diameter on a plasma-untreated side of the membrane remains unchanged, while the pore diameter on a plasma-treated side becomes much smaller. Thus, PET TM with a semipermeable polymer surface film acquire the property of conductivity asymmetry both as a result of a contact between two layers having either anti-polar functional groups or different COOH con-

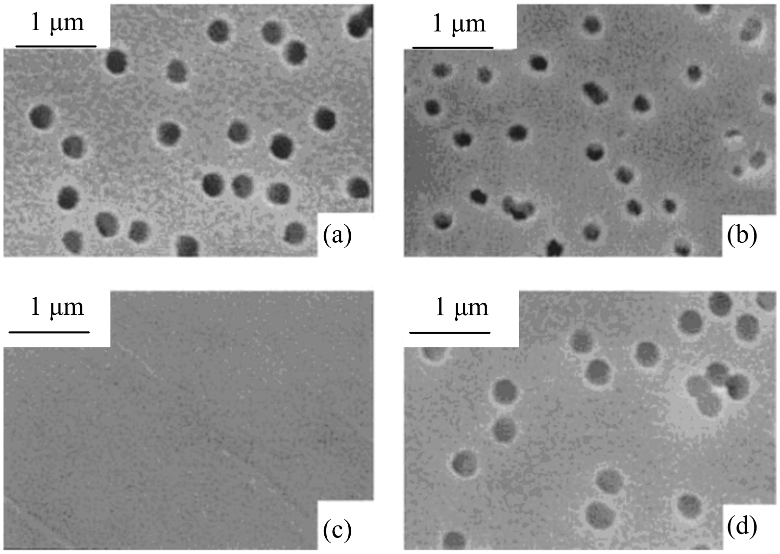

Fig. 10. Electron micrographs of the surface of PET TM: (a) starting membrane and membranes treated in a pyrrole plasma for (b) 60 s and (c, d) 300 s. (d) The back (plasma-untreated) side of the membrane [107].

centrations and as a result of a radical decrease in pore diameter in the polymer layer.

Smart thermosensitive membranes were prepared by depositing on the membrane surface a film formed by plasma polymerization of isopropylacrylamide [110–112]. The operating principle of such membranes is based on the phase separation (in the vicinity of the lower critical solution temperature) of the deposited thermosensitive polymer, caused by the reversible conformational transition of the macromolecules from the unfolded coil conformation to compact globule. This process is accompanied by decreasing volume of the polymer film deposited on the membrane surface and pore walls, which affects the water permeability of the composite membrane.

Plasma-Induced Polymerization of Organic Compounds

There are a number of examples of the use of the preactivation of the membrane surface by a nonpolymer-forming gas plasma for subsequent traditional vapor- or liquid-phase graft polymerization (Table 3). This so-called post process in which polymer is grafted onto the membrane surface due to the active centers formed under the action plasma. By varying the monomer, one can obtain both hydrophobic composite membranes (polystyrene grafting) [113] and membranes with a hydrophilic surface by poly(*N*-vinyl-2-pyrrolidone) grafting [114]. Hydrophilic composite membranes were synthesized by grafting poly(acrylic acid) onto polytetrafluoroethylene, poly(ether sulfone), and polyacrylonitrile membranes [115–119]. The use of such membranes in separation of biologically active substances makes it possible to reduce filtration losses.

Plasma activation of the membrane surface followed by polymer grafting can also be used to synthesize smart membranes. For example, mechanochemical membranes having a “chemical valve” function were obtained by grafting poly(acrylic acid) [74] and poly(2-methyl-5-vinylpyridine) [120] onto the surface of PET TM pretreated by an air plasma. Thus, the membrane with the poly(2-methyl-5-vinylpyridine) grafting yield of 7.2% at pH = 3 can change over to the “chemical valve” operating mode, specifically, at low pHs of the filtrate it becomes water-impermeable, whereas at higher pH values it is water-permeable (Fig. 11a). The membrane with the poly(acrylic acid) grafting yield of 7.4% changes over to the “chemical valve” operating mode at pH = 8. At pH > 8 this membrane is impermeable, whereas at lower pHs it becomes permeable (Fig. 11b). This property of the membranes is associated with swelling of the grafted layer due to the presence of a charge on its macromolecules.

Smart thermosensitive membranes were synthesized by grafting poly(isopropylacryalmide) [121–126] or its co-polymers [127] onto argon plasma-pretreated membranes.

Table 3. Examples of application of surface activation in a nonpolymer-froming gas plasma followed by traditional polymer grafting for membrane modification

Membrane	Plasma-forming gas, discharge type	Monomer used for traditional polymer grafting	Composite membranes with specific properties	Reference
PAN	Ar, RF discharge (13.56 MHz)	Styrene from the gas phase	Composite hydrophobic membranes for purification of organic solvents	[113]
PES	He, RF discharge (13.56 MHz)	*N*-Vinyl-2-pyrrolidone from aqueous solution	Composite hydrophilic membranes with decreased adsorption capacity to proteins	[114]
PTFE	H_2, RF discharge (13.56 MHz)	Acrylic acid from aqueous solution	Composite hydrophilic membranes with improved hydrodynamic properties	[115]
PAN, PES	Ar, RF discharge (13.56 MHz)	Acrylic acid from the gas phase	Composite hydrophilic membranes with improved hydrodynamic properties and decreased adsorption capacity to proteins	[116–118]
PC	Ar, RF discharge (13.56 MHz)	Acrylic acid from aqueous solution	pH-sensitive membranes	[119]
PET	Air, RF discharge (13.56 MHz)	Acrylic acid from the gas phase	Mechanochemical membranes having a “chemical valve” function	[74]
PET	Air, RF discharge (13.56 MHz)	2-Methyl-5-vinylpyridine from aqueous solution	The same	[120]
PA	Ar, RF discharge (13.56 MHz)	Acrylic acid and *N*-isopropylacrylamide from aqueous solution	pH- and thermosensitive membranes	[121]
PP, PE, PC, PVDF	Ar, RF discharge (13.56 MHz)	*N*-isopropylacrylamide from aqueous solution	Thermosensitive membranes	[122–126]
PVDF, PA	Ar, RF discharge (13.56 MHz)	Copolymer of *N*-isopropylacrylamide and butyl methacrylate from aqueous solution	The same	[127]
PE	Ar, RF discharge (13.56 MHz)	Glycidyl methacrylate from acetone, methyl metacrylate from toluene	Composite membranes for pervaporation	[128]
PP, PE	Ar, RF discharge (13.56 MHz)	Glycidyl methacrylate from ethanol	Highly selective cation-exchange membranes	[129]
PE	Ar, O_2, RF discharge (13.56 MHz)	Polyelectrolytes, adsorption from aqueous solution	Highly selective cation- and anion-exchange membranes	[130]

The described approach was also used to synthesize composite pervaporation and ion-exchange membranes. In the first case, the grafting yield should be high enough for closing all surface pores [128]. In the second case, one should choose a hydrophilic monomer whose polymerization provides a polymer with a high ion capacity. Thus, composite hydrophilic membranes with high cation-exchange capacity and

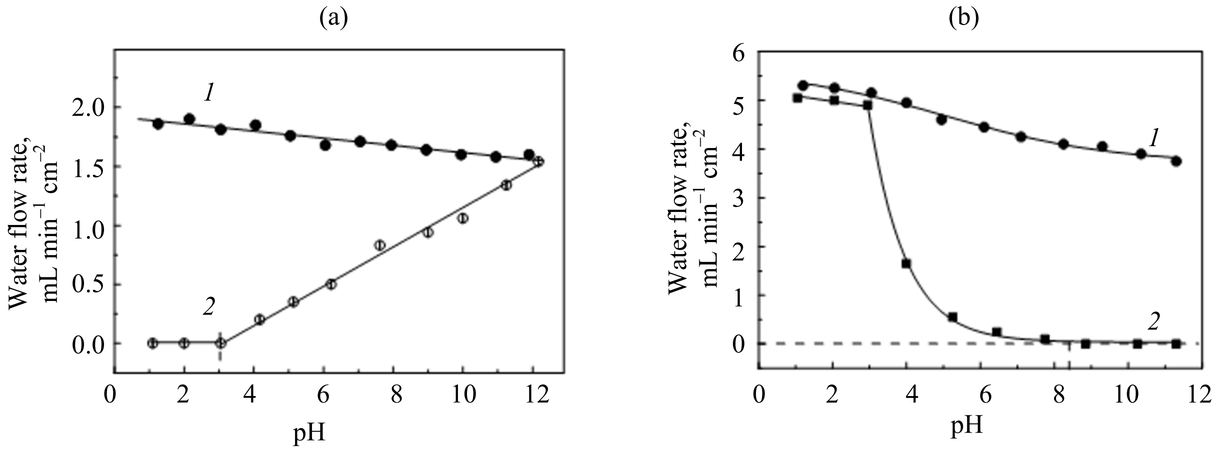

Fig. 11. Dependence of the water permeability of PET TM: (*1a, 1b*) starting membrane and membranes with grafted (*2a*) poly(2-methyl-5-vinylpyridine) [120] and (*2b*) poly(acrylic acid) layers [74].

separation selectivity were obtained by grafting poly(glycidyl methacrylate) onto polypropylene and polyethylene membranes [129]. Greene and Tannenbaum [130] to synthesize highly selective composite cation-exchange and anion-exchange membranes on the basis of polyethylene first treated by plasma and then performed adsorption of polyelectrolytes from aqueous solution.

Composite hydrophilic membranes were synthesized by directly grafting polymers [poly(ethylene glycol) or poly(vinylpyrrolidone)] preliminarily adsorbed on poly(ether sulfone) [131] and poly(vinylidene fluoride) or polypropylene membranes [132, 133] by a non-polymer-forming gas (nitrogen or air) plasma. This technology allowed strong immobilization of polymers on the surface, which much improved wettability.

CONCLUSIONS

The above-described examples of application of low-temperature plasma in the modification of porous polymer membranes show that plasma chemistry can be used to success not only for modifying their surface and structural characteristics but also for creating smart membranes with unique properties, which much extends the application range of membrane processes.

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