

Ion-Plasma Modification of Polyvinylchloride Microfiltration Membranes

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ABSTRACT: Here we present how the surface and some filtration properties of PVC microfiltration membranes are affected by controlled and well-defined modification by ion-plasma treatment in the kinetic region of the high voltage (HVGD) or normal glow discharge (NGD) in air. The surface energy and work of adhesion of the samples were calculated from the contact angle with both polar (H₂O) and nonpolar (CH₂I₂) liquid measurement data. The surface morphology was observed by SEM and the surface chemical composition was analyzed by ESCA. The trans-membrane water flux, the average pore size, and the pore-size distribution as well as the "bubble point" were used to control the effect of the ion-plasma treatment on the filtration properties of the PVC

microfiltration membranes. Two characteristic regions of the ion-plasma treatment in air were found in our experiments where the surface properties and filtration characteristics of the membranes are extremely changed: at a pressure of 10–15 Pa in the region of the HVGD and at a pressure of 100–120 Pa in the region of the NGD. It was shown that the ion-plasma treatment in air is an effective technological method for regulation of some important surface and filtration properties of PVC microfiltration membranes. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2433–2440, 2003

Key words: PVC membranes; surface modification

INTRODUCTION

There is an increasing interest to the hydrophobic porous polymeric materials in the membrane technologies because of their stability during the work. The surface/fluid interface interaction is of great importance in this case. There is an increasing belief in the ability of the surface modification to change this interaction in a desirable direction. A lot of chemical methods for temporary or continuous hydrophilization of polymer surfaces have been developed up to now aiming at combining the stability of the hydrophobic porous materials with the advantages of the hydrophilic ones.^{1–8}

The plasma treatment has turned lately into one of the basic methods of the polymer surface modification, changing the whole complex of surface physicochemical properties, including the hydrophilic/hydrophobic balance. Particularly, the porous polymeric materials are very suitable for such modification due to their plasma penetrability. For example, plasma treatment in air glow discharge (GD) of poly(vinylthreemethylsilane) thermopervaporation membranes leads to an increase of their hydrophylicity and

possesses effective transport and selective properties for thermopervaporative separation of inorganic substances, including volatile acids.⁹ Plasma treatment of PVC membranes changes their separation coefficient for binary mixtures benzene/cyclohexane or *n*-hexane.¹⁰ Acrylic acid grafting on ultrafiltration PVC membrane in glow discharge has been reported also.¹¹ Kim and Fane¹² have established that the hydrophilization increases the permeability but does not change the protein sedimentation on similar ultrafiltration membranes. The effect of ion-plasma treatment in high voltage (HVGD) or normal glow discharge (NGD) on high porous PVC materials is not been studied up to now. These discharges are easily realized in conventional plasma treatment equipment, and the effect of ion-plasma treatment under defined conditions could be equal to that of the ion beam.¹³

We present here how some important surface properties and filtration characteristics of PVC microfiltration membranes are affected by controlled and well-defined modification by cold low-pressure ion-plasma treatment in air.

Expecting significant differences in the modifying effect of the ion-plasma treatment in HVGD or NGD, our study includes treatment in the negative (kinetic) region of the both discharges, at Paschen's factor $p \cdot d > 8 \text{ Pa} \cdot \text{cm}$ for HVGD or $p \cdot d < 8 \text{ Pa} \cdot \text{cm}$ for NGD, where d is the distance between the electrodes and p is

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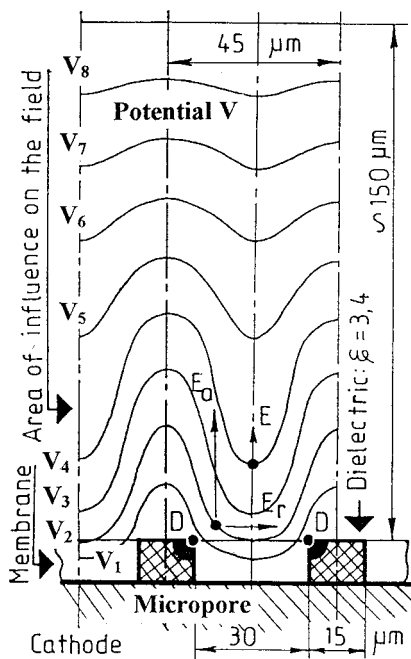


Figure 1 Area of influence of the membrane material on the electrical field intensity.

the pressure. Such an experimental set offers the following original elements in the surface modification of polymer membrane: intensive chemical activation and etching in the ion-plasma kinetic region of direct current GD (glow discharge); a possibility to transform the treatment from intensive chemical activation to intensive etching through a change of the pressure at a constant interelectrode distance (in our case $d = 380$ mm) going from NGD to HVGD; localizing the impact, that is, the etching at the pore outline [Fig. 1(D)] where the intensity of the electrical field is maximal.

EXPERIMENTAL

Membranes preparation

PVC microfiltration membranes with an average pore size of $0.3 \mu\text{m}$ made by PVC-S 6858, a product of "Polychim," Devnya, Bulgaria (mol wt 7.8×10^4 , density 1.38 g/cm^3), were employed in our experiments. They were prepared on the phase-inverse method¹⁴ by casting under the following conditions: solvent—dimethylformamide, p. a. (Merk); concentration of the forming PVC solution of 9 mass %; time of reforming in air—180 s; air humidity—55–60%; forming and coagulation temperature of 22°C at 1 atm. The coagulation was made in a water bath, and the membranes were cleaned through multiple rinsing in bidistilled water. After that, they were kept in a water bath containing 20 mass % glycerin, for 30 min and dried in air.

Ion-plasma treatment

Ion-plasma treatment was performed in the kinetic region of HVGD or NGD in air at a temperature of 20°C and at a variable pressure, 2–180 Pa, putting the samples directly on the cathode.

Surface wettability measurement and surface energy calculation

H_2O (polar liquid) as well as CH_2I_2 (nonpolar liquid) contact angle was measured at a temperature of 21°C , and the surface energy and its components were calculated using a modified method of Bikerman.^{15,16} All parameters, determining the wetting and adhesion of our low-energy PVC surfaces: contact angle, θ (or $\cos\theta$), surface tensions, γ_{st} and its polar, γ_s^p and nonpolar (disperse), γ_s^d components, free energy of adhesion W_{ar} and its components as well as interface tension, γ_{sl} , were determined using the following parameters of the test liquids; water: $\gamma_{lv} = 728.0 \text{ J} \cdot \text{m}^{-2}$, $\gamma_{lv}^d = 218.0 \text{ J} \cdot \text{m}^{-2}$, $\gamma_{lv}^p = 510.0 \text{ J} \cdot \text{m}^{-2}$, and CH_2I_2 : $\gamma_{lv} = 508.0 \text{ J} \cdot \text{m}^{-2}$, $\gamma_{lv}^d = 495.0 \text{ J} \cdot \text{m}^{-2}$, $\gamma_{lv}^p = 13.0 \text{ J} \cdot \text{m}^{-2}$.

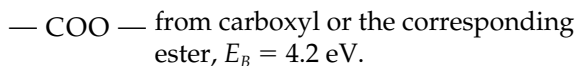
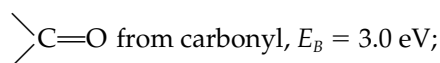
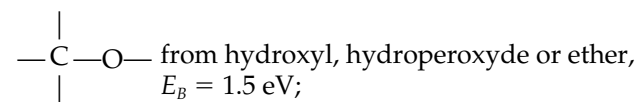
Surface morphology

The surface morphology of the untreated and ion-plasma treated membranes was observed with SEM, Philips-515.

Surface chemical composition

The surface chemical composition was investigated by means of ESCA, using a Leybold-Heraeus instrument. The excitation X-ray source was $\text{AlK}\alpha$ (excitation energy: 1486.6 eV). The binding energy scale was fixed by assigning $E_B = 285.0 \text{ eV}$ to the $-\text{CH}_2-$ carbon (1s) peak.

According to previous studies,¹⁷ and using this $-\text{CH}_2-$ reference carbon peak, the chemical shifts of different oxygen-containing groups are:



Flux measurement

All the membranes were subjected to a water pressure of 0.5 MPa before the permeation experiment. The quantity of water permeated through the membrane was determined with a microfiltration cell (Sartorius

TABLE I
Contact Angle, Surface Energy, and Polarity of Various Surfaces

Substrate		Water		CH ₂ I ₂		γ_s J · m ⁻²	γ_s^d J · cm ⁻²	γ_s^p J · m ⁻²	Polarity, p
		θ	cos θ	θ	cos θ				
PVC membrane	nontreated	100.2	-0.1771	62.2	+0.4664	278.1	266.4	6.7	0.024
	HVGD treated at 10 Pa	87.2	+0.0489	20.8	+0.9348	476.0	468.4	7.6	0.016
	NGD treated at 120 Pa	73.9	+0.2772	14.1	+0.9697	502.2	458.9	43.3	0.086
PVC control nonpore sample	nontreated	116.2	-0.4415	101.2	0.1942	86.1	75.0	11.2	0.130
	HVGD treated at 10 P	109.0	-0.3256	31.4	+0.8536	481.9	470.9	11.0	0.023
	NGD treated at 120 Pa	115.8	-0.4352	24.8	+0.9078	548.6	515.6	33.0	0.060

type) with a working area of 17.34 cm² and at an operational pressure of 0.1 MPa. The pore-size distribution was determined with a Coulter porometer, England.

RESULTS AND DISCUSSION

We have studied the effect of ion-plasma treatment in the negative region of HVGD or NGD (at a pressure of 2 to 160 Pa) and a constant temperature of 21°C on some important surface and technological properties of PVC microfiltration membranes. Some theoretical prerequisites give us reason to expect surface etching and oxygen-containing groups accumulation during such ion-plasma treatment,¹³ and hence, affecting the surface wettability, morphology, and chemical composition as well as the filtration characteristics of the membranes. In Table I are represented the surface energy and its components for some of the most interesting surfaces whose free energy of adhesion, W_a (reversible work of adhesion), and its components are shown in Tables II and III. As it was shown by our measurements, the liophylization is the most effective; respectively, the decrease of the water as well as of the nonpolar liquid, CH₂I₂ contact angle, θ is the most significant, when the sample was treated at 10 Pa in the region of HVGD or at 120 Pa in the region of NGD.

Therefore, the surfaces parameters of these samples are represented in the above-mentioned tables. PVC control nonpore sample, prepared under conditions similar to those of the PVC membrane preparation, was included in our experiments to evaluate the influence of the porosity (the pore capillary effect) on the studied surface properties. Also, the porosity could be accepted as an additional roughness. Hence, in the comparison of the surface properties of PVC, both membrane and corresponding nonpore sample would provide information about the contribution of the roughness to the value of the measured parameter. As it is evident from Table II, the transition from nonpore to pore nontreated PVC surface (rows 4 and 1) is characterized by a strong increase of the surface tension, γ_s —from 86.1 of the nonpore sample up to 278.1 J · m⁻² of the membrane, mainly due to a sharp increase of its disperse (nonpolar) component, γ_s^d —from 75.0 of the nonpore sample up to 266.4 J · m⁻² of the membrane, whereas the polar component, γ_s^p decreases almost twice. Evidently, the differences in the surface tension (and its components) of nonpore and pore sample are associated with the porosity and the higher roughness of the membrane. The transition from nonpore to the pore nontreated PVC sample is characterized also by an increase of the work of adhesion, W_a mainly due to a significant increase of its

TABLE II
Work of Adhesion of Various Surfaces to Water

Substrate		W_a^d J · m ⁻²	W_a^p J · m ⁻²	W_a J · m ⁻²	W_a^d/W_a %	Z_a	θ	γ_{sl} J · m ⁻²
PVC membrane	nontreated	482.0	116.8	598.8	80.5	0.4114	0.6654	407.3
	HVGD treated at 10 Pa	639.1	124.5	763.6	84.0	0.5244	0.6803	440.4
	NGD treated at 120 Pa	632.6	297.2	929.8	68.0	0.6386	0.7689	300.4
PVC control nonpore sample	nontreated	255.7	151.2	406.9	62.8	0.2792	0.8126	407.2
	HVGD treated at 10 Pa	640.8	149.8	790.6	81.0	0.3372	0.6674	419.3
	NGD treated at 120 Pa	670.5	259.5	930.0	72.1	0.2824	0.7358	346.6

TABLE III
Work of Adhesion of Various Surfaces to CH₂I₂

Substrate		W_a^d J · m ⁻²	W_a^p J · m ⁻²	W_a J · m ⁻²	W_a^d/W %	Z_a	θ	γ_{sl}^{-2} J · m ⁻²
PVC membrane	nontreated	726.3	18.7	745.0	97.5	0.7332	0.9910	41.1
	HVGD treated at 10 Pa	963.0	19.9	982.9	98.0	0.6751	0.9994	1.1
	NGD treated at 120 Pa	953.2	47.4	1000.6	95.2	0.9850	0.9907	9.6
PVC control nonpore sample	nontreated	385.4	24.1	409.5	94.1	0.4029	0.9790	184.6
	HVGD treated at 10 Pa	965.6	23.9	989.5	97.6	0.9268	0.9999	0.4
	NGD treated at 120 Pa	1014.0	41.4	1051.8	96.1	0.9539	0.9962	4.8

nonpolar component, W_a^d , whereas the polar component, W_a^p decreases (Table II, rows 4 and 1; Table III, rows 4 and 1). In the nontreated PVC surfaces, both nonpore and membrane are low energetic (their surface tension is lower than 1000 J · m⁻²) and low polar (Table I). It is well known that the interactions of such surfaces are dominated by nonpolar, disperse forces. Therefore, it is not a surprise that the predominant part of their work of adhesion to the nonpolar liquid, CH₂I₂ (Table III, rows 4 and 1) and even to the polar liquid, H₂O (Table II, rows 4 and 1) is due to a dispersion, nonpolar interactions as shown by the ratio W_a^d/W : of over 94% for the nonpore or of over 97% for the membrane sample to the CH₂I₂ or, respectively, over 62 and 80% to the H₂O. The relative work of adhesion, Z_a , increases and approaches to 1 at full wetting of a surface by a liquid. The relative work of adhesion, Z_a , of the PVC membrane, is significantly higher compared to that of the PVC control nonpore sample (H₂O: about 1.5 times, Table II; CH₂I₂: about 1.8 times, Table III), which indicates its better wettability compared to the nonpore sample.

The ion-plasma treatment in both HVGD or NGD causes some increase of the hydrophylicity of the studied membrane and nonpore materials: their water contact angle, θ decreases in both cases (Table I). This effect is more strongly expressed at the pore material because of its better plasma permeability. The water contact angle of the nontreated nonpore control sample of 116.2° decreases only to 109.0° after HVGD treatment (Table I, rows 4 and 5), whereas the water contact angle of the nontreated membrane of 100.2° decreases to of 87.2° or 73.9° after the ion-plasma treatment in HVGD or NGD, respectively (Table I, rows 1, 2, and 3). The sharp decrease of the CH₂I₂ (nonpolar liquid) contact angle, θ of the nonpore PVC control sample (from 101.2° down to 24.8°) or PVC membrane (from 62.2° down to 14.1°), indicates a sharp increase of the liophylicity to nonpolar liquids after their ion-plasma treatment (Table I, rows 4 and 6; 1 and 3). These results show that the surface modification of PVC membrane or nonpore material by ion-

plasma treatment in HVGD or NGD is associated with significant changes of the disperse forces and interactions. It is confirmed also by the increase of the surface tension, γ_s of the ion-plasma-treated samples due to a sharp increase of its disperse component, γ_s^d , as it is evident from Table I, rows 2, 3, and 1; 5, 6, and 4. At the same time, the polar component, γ_s^p also demonstrates an increase: from 11.2 J · m⁻² for the nontreated nonpore PVC sample up to 33.0 J · m⁻² for the NGD treated one (Table I, rows 4 and 6); from 6.7 J · m⁻² for the nontreated membrane up to 43.3 J · m⁻² for the NGD treated one (Table I, rows 1 and 3). The increase of the polar component, γ_s^p simultaneously with the

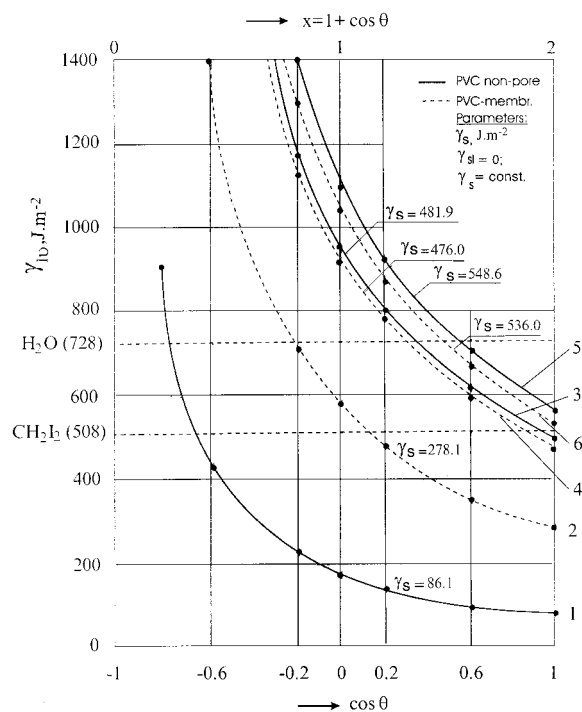


Figure 2 The surface tension γ_s (at $\gamma_{sl} = 0$) as a function of $\cos \theta$ at different wetting liquids, that is, different γ_{lv} for PVC-nontreated nonpore (1) or membrane (2) sample as well as for HVGD-treated samples at 10 Pa (3 and 4) or NGD-treated samples at 120 Pa (5 and 6).

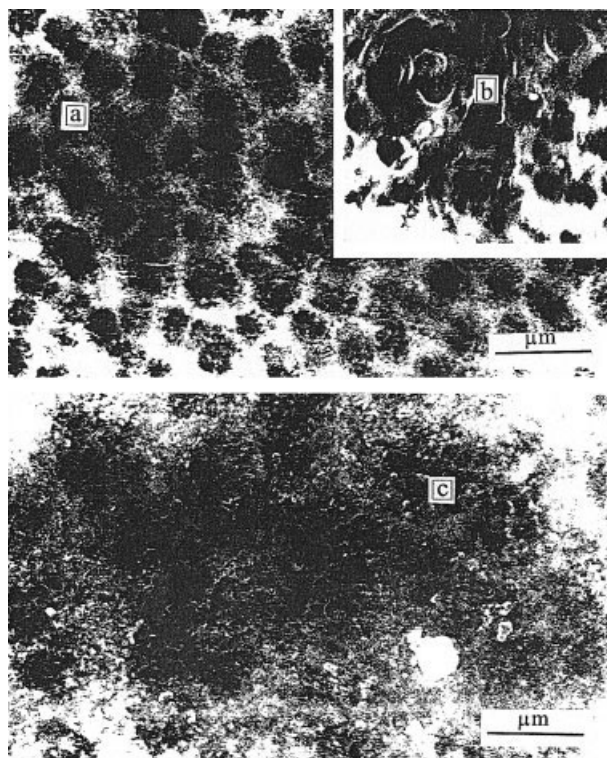


Figure 3 SEM photographs of the surface of untreated (a), ion plasma treated in HVGD at pressure of 10 Pa (b) and in NGD at 120 Pa (c) PVC microfiltration membrane.

sharp increase of the disperse component indicates a simultaneous development of two processes: surface etching and formation of chemical active centers. A comparison of row 3 to row 2 or of row 6 to row 5 in Table I shows that the increase of the polar component of the surface tension, γ_s^p is better expressed for NGD-treated compared to the corresponding HVGD-treated PVC membrane or nonpore sample. This gives us reason to conclude that the surface polar groups' accumulation at the NGD-treated PVC surface (nonpore or membrane) is higher compared to that of the corresponding HVGD treated material. The factor Φ , giving notion about the contribution of disperse (nonpolar) interactions in the adhesion and wetting, is almost 1 for all PVC surfaces (membrane and nonpore, nontreated or ion-plasma treated) contacting with the nonpolar liquid, CH_2I_2 (Table III). Thus, it confirms that the adhesion and wetting of PVC both nontreated and ion-plasma-treated samples in contact with non-

polar liquids are dominated by disperse interactions. The sharp increased lyophylicity to nonpolar liquids combined with a slightly increased hydrophilicity is of a great interest for the practical application of the NGD- or HVGD-treated PVC pore materials in the membrane technologies. The dependence of surface tension, γ_s on $\cos\theta$ at wetting by different liquids, represented in Figure 2, demonstrates that the ion-plasma treatment leads to similar liophylicity/hydrophylicity balance on PVC membrane surface. It is evident from the figure, that the surface tension, γ_s of the nontreated both nonpore (curve 1) and membrane (curve 2) material, is quite different and shows the strong influence of the porosity (the roughness) on the wetting. The surface tension of the nontreated both, nonpore (curve 1) and membrane (curve 2) material is not high enough for their full wetting by water (H_2O : $\gamma_{lv} = 728.0 \text{ J} \cdot \text{m}^{-2}$) or CH_2I_2 (CH_2I_2 : $\gamma_{lv} = 508.0$) that occurs when $\cos\theta$ approaches 1 or γ_s approaches γ_{lv} (full wetting at $\cos\theta = 1$ or $\gamma_{lv} = \gamma_s$). The surface tension, γ_s of all ion-plasma treated (in HVGD or NGD) samples (curves 3–6) is much higher compared to that of the nontreated one (curves 1 and 2), and demonstrates their improved wettability to different liquids. At any rate, the surface tension, γ_s of the ion-plasma treated samples is not high enough for their full wetting by water. The interface tension, γ_{lv} of the nonpolar liquid, CH_2I_2 , is lower and the surface tension, γ_s of all ion-plasma-treated materials reaches or closely approaches the interface tension, γ_{lv} of the CH_2I_2 , which indicates a full or almost full wetting of the corresponding surface by this nonpolar liquid. In addition, the dependence of γ_s on the $\cos\theta$ presented in Figure 3 offers a possibility to predict the behavior of our ion-plasma-treated materials in contact with other liquids, knowing the corresponding interface tension, γ_{lv} . All results of our study give us reason to accept that the surface modification of PVC membranes by ion-plasma treatment is due to an etching accompanied by a surface polar groups accumulation. The etching should be better expressed at HVGD treatment, whereas the polar group accumulation should be more intensive at NGD treatment.

The mass loss and SEM observation were used to monitor the etching effect of the ion-plasma treatment in HVGD or NGD. The mass loss of PVC membranes as well as of PVC control nonpore samples treated in

TABLE IV
Mass loss of Ion-Plasma-Treated PVC Both Membrane and Nonpore Samples

Sample	Pressure, Pa	2	10	15	40	60	80	100	120	160
PVC membrane	Mass loss, %	0.89	1.03	0.92	—	0.86	0.84	0.76	0.79	—
PVC control non pore sample		—	1.16	1.0	0.93	0.90	0.87	0.82	0.83	0.85

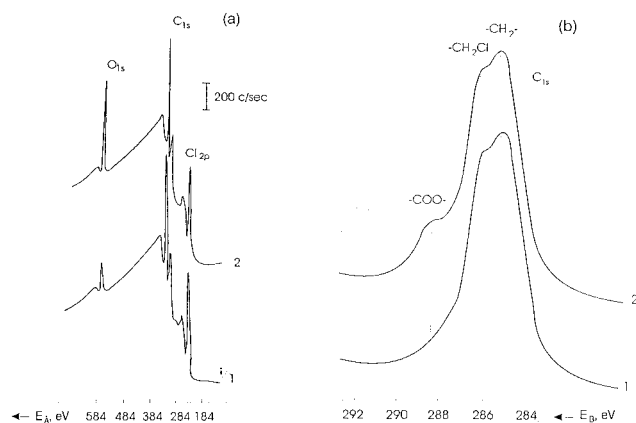


Figure 4 Complete spectral scans (a) and detailed C(1s) ESCA spectra (b) of untreated (1) and plasma treated in NGD at a pressure of 120 Pa (2) PVC microfiltration membrane.

ion-plasma at a pressure of 2–160 Pa is relatively low, as is evident from Table IV. The mass loss of HVGD (below 40 Pa)-treated PVC membrane or PVC nonpore sample is the highest at 10 Pa, and that of NGD (over 40 Pa)-treated samples is the highest at 120 Pa, that is, the maximal etching ability of the HVGD and the NGD is respectively at about 10 Pa or 120 Pa. In addition, the mass loss of the HVGD-treated samples is higher compared to that of the NGD-treated one, which is in correspondence with the theoretical prediction and all results of the surface properties study. Our SEM observation confirmed the expected surface morphology changes due to an etching during the ion-plasma treatment in HVGD or NGD in air. It was found that the surface morphology is maximally changed when the membrane was treated in HVGD at a pressure of 10 Pa that is in accordance with the maximal mass loss of this same membrane. Circle-oriented formations with a changed surface pore outline on the background of the typical cell-globular structure of the untreated membrane are observed in this case [Fig. 3(a) and (b)]. The changes of the pore surface structure were less pronounced for the NGD-treated membranes. The spreading of the pore outline only observed in this case is illustrated by the SEM picture of ion-plasma treated in NGD at a pressure of 120 Pa membrane [Fig. 3(c) and (d)].

A comparative surface chemical analysis of the untreated and plasma-treated PVC microfiltration membranes confirmed our suggestion that the modification

effect of the cold ion plasma is due not only to an etching effect but also to a surface oxygen-containing groups accumulation, more strongly expressed in the region of NGD. In Figure 4(a) and (b) are shown, respectively, the complete spectral scan and detailed C(1s) ESCA peaks of a nontreated (1) and ion-plasma-treated (2) NGD at a pressure of 120 Pa PVC microfiltration membrane as an example. The complete spectral scan and detailed C(1s) ESCA spectra of all ion-plasma-treated membranes were very similar, and therefore, they are not shown here. A comparison of the complete scan and detailed C(1s) ESCA spectrum of the untreated membrane to the corresponding spectrum of the ion-plasma-treated one clearly shows an accumulation of oxygen-containing groups as a result of such ion-plasma treatment: chemical shifts between 1.3 and 4.2 eV from the side of the higher binding energy, corresponding to different oxygen-containing groups appear in the detailed C(1s) peak of the treated membrane together with the $-\text{CH}_2-$ signal [Fig. 4(b), curve 2]; in addition, an intensive O(1s) peak appears in the complete scan spectrum of the treated membrane [Fig. 4(a), curve 2] and its intensity depends on the treatment conditions as it is evident from Table VI, where is represented cross-section corrected relative intensity of the O(1s) peak. The relative intensity, O(1s)/ $-\text{CH}_2-$ is higher for the NGD-treated membranes (at a pressure over 40 Pa) compared to that of HVGD-treated samples (at a pressure below 40 Pa), and it is maximal for the NGD treated at a pressure of 120 Pa membrane. The higher oxygen-containing groups accumulation on the surface of the NGD ion-plasma-treated membranes is probably due to the expected higher concentration of chemically active species in the NGD ion-plasma.

The trans-membrane water flux, used to evaluate their relative hydrodynamic productivity, is represented in Table V. It is evident that the relative hydrodynamic productivity of all ion-plasma-treated (in HVGD or NGD at a pressure of 2–160 Pa) membranes (all columns of Table V, excluding the last one) is significantly increased compared to that of the nontreated one (the last column of the Table V). The increase is of over twice for the region of the HVGD at 10 Pa or over three times for the region of NGD at 120–160 Pa. The increased productivity of the ion-plasma-treated membranes could be ascribed to the membrane surface etching and hydrophyllization, leading to the change of the water flux turbulence but

TABLE V
Trans-membrane Water Flux of Ion-Plasma-Treated and Nontreated PVC Membranes

Pressure, Pa	2	10	15	40	60	80	100	120	160	Nontreated membrane
water flux, $\text{m}^3/\text{m}^2 \cdot \text{s}$	1.9×10^{-4}	3.8×10^{-4}	2.3×10^{-4}	2.0×10^{-4}	3.2×10^{-4}	3.9×10^{-4}	4.3×10^{-4}	5.0×10^{-4}	4.8×10^{-4}	1.5×10^{-4}

TABLE VI
Cross-section Corrected Relative Intensity of the O(1s) Peak for Ion-Plasma-Treated PVC Membranes

Pressure, Pa	2	10	15	40	60	80	100	120	160	Nontreated membr.
O(1s)/—CH ₂ —	0.15	0.33	0.26	0.21	0.34	0.40	0.46	0.62	0.50	0.05

also to some opening of the pores. Fortunately, it appeared that it is not due to a change of the pore dimensions. As it is evident from Figure 5, the differential curve of a pore-size distribution of the ion-plasma-treated membrane at 120 Pa (curve 2) is almost the same compared to that of the nontreated membrane (curve 1). The only difference observed is some opening of the small-size pores. The porograms of all plasma-treated membranes were similar, and therefore, only one of them is shown here, as a sample. The maximal deviation of the average pore size does not surpass 10% in all cases, as showed our calculations. The measured pressure, corresponding to appearance of the first bubble (so called "bubble point") was almost equal for all ion-plasma-treated membranes, and the same compared to that for the nontreated membrane. Thus, it indicated that the maximal size of the membrane pores stays unchanged after the ion-plasma treatment under the chosen conditions. Consequently, no significant change in porosity of the PVC microfiltration membranes causes the ion-plasma treatment in HVGD or NGD in air. This result does not contradict the conclusions from SEM about a significant change (more strongly expressed at HVGD-

treated membranes) of the membrane surface morphology. This indicates that the observed change in the morphology of the ion-plasma-treated membranes is not widespread in the whole thickness of the membrane material. It is localized at the surface pore outline, as was expected according to our mathematical model of the electrical field intensity distribution around the PVC membrane (Fig. 1, outline D). That is why it could be accepted that the strongly (up to threefold) increased flux by the ion-plasma treatment is due to a hydrodynamic reason. Both the hydrofilycity of the ion-plasma-treated membranes and the round outlines of their pores [see Fig. 1(D)] (nontreated membranes are hydrophobic with sharp outlines of their pores) lead to a transition from the turbulent to laminar flux. This usually results in an increased flux.¹⁸

All results of our investigation show two characteristic regions at a slight change of the pressure—before 40 Pa, a region of HVGD and over 40 Pa, a region of NGD where the parameters of the modified membranes are extremely changed. They are in accordance with the results of a former our investigation on ion-plasma treatment of polyethyleneterephthalate nonwoven textile.^{19,20}

CONCLUSIONS

Ion-plasma treatment of PVC microfiltration membranes in the kinetic region of HVGD or NGD was carried out, and the potential ability of these discharges to modify effectively the membrane surface properties is shown. The possibility to regulate the membrane properties thorough a transition from NGD to HVGD by a slight pressure change has been demonstrated. The different ability of both HVGD and NGD for etching and surface chemical activation of PVC microfiltration membranes has been experimentally proven. It was found that the etching is more significant at ion-plasma treatment in HVGD, whereas the chemical activation and surface oxygen-containing groups accumulation are more intensive at NGD. The etching is localized at the surface pore outline, and does not change significantly the pore dimensions.

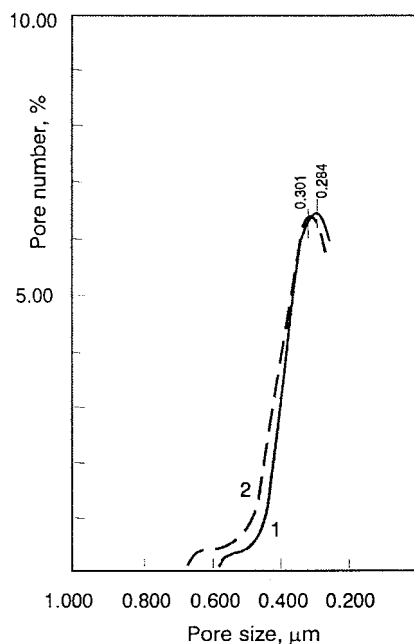


Figure 5 Porograms of an untreated (1) and ion plasma treated in NGD at a pressure of 120 Pa (2) PVC microfiltration membrane.

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