

Bipolar Nanofiltration Membranes Based on Plasma Modified Microfilters

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ABSTRACT: Track-etched membranes were used as support for deposition of plasma polymerized layers and formation of bipolar nanofiltration membranes. The 75 KHz plasma reactor was applied for that purpose. Three kinds of monomers were plasma polymerized. They were as follows: *n*-butylamine, allylamine, and acrylic acid. For each monomer, the best polymerization parameters were selected. It was determined that acrylic acid deposited at the highest rate, then deposited allylamine and finally *n*-butylamine. Among the electrodes, the grounded one offered more stable layer and can be used for plasma polymer deposition. The obtained membranes showed good rejection properties toward bivalent ions. It was shown that the sequence of deposited layers did not affect the separation properties. For some investigated membranes, rejection reached 50–80% value. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 39790.

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INTRODUCTION

Bipolar membrane (BPM) is a composite membrane comprising a cation-exchange and an anion-exchange layers. Due to its specific properties, the membranes have attracted the growing attention of scientists and industry engineers for their application in electro dialysis mostly. This technique called EDBM (electrodialysis with BPM) has found a large number of new applications in chemical industry, in food and drug industry as well as in waste water treatment or production of high quality water. Among EDBM processes described so far one can find: production of specific organic compounds, mainly acids,^{1–12} removal of boron from aqueous solution,¹³ regeneration of CO₂ or other chemicals,^{14–16} recovery of amino acids,¹⁷ water electrolysis for H₂ production,¹⁸ inactivation of the enzymes in juice manufacturing,¹⁹ and others.

There are various methods of BPMs preparation.²⁰ Some of them are based on pressing together the cation- and anion-exchange membranes (sandwich-like membrane), some other on deposition of polyelectrolytes on modification of commercially available membranes. The last method is constituted by depositing or grafting of polymer layer with oppositely (to the supporting membrane) charged functional groups. Both methods can be performed with the help of plasma techniques that are often used for membranes modification.^{21,22} Plasma polymerization is characterized by number of essential advantages. It is simple to control the thickness of the deposited layer, it

makes strong adhesion of the layer, the time of modification is short, and the method can be applied for different organic monomers.²³ Plasma-deposition of pyrrole²³ or aniline²⁴ on the poly(ethylene terephthalate) track-etched membrane gave BPMs of interesting electrochemical properties. Plasma induced grafting is also the method to prepare thin layers. A work of Hung et al.¹⁸ can serve as the example. The authors grafted 2-methacrylic acid 3-(biscarboxymethylamine)-2-hydroxyl-propyl ester onto porous poly(vinylidene fluoride) membrane.

Track etched polyester membranes (PET TM) were often used as a substrate for BPMs manufacturing. They have excellent material properties and are characterized by the presence of cation-exchange carboxyl groups on the surface. Hence, the plasma polymerization of pyrrole²³ or thiophene²⁵ led to composite membranes characterized by asymmetric distribution of electrolytes and bipolar character; the layer synthesized by both monomer polymerization in plasma has anion-exchange nitrogen- or sulfur-containing groups.

There are limited numbers of works describing the use of BPMs in filtration processes. Zhu et al. obtained polyamide bipolar nanofiltration membranes by interfacial polymerization.²⁶ BPMs based on the sulfonated poly(phenylene oxide) covered with plasma polymer of allylamine were very efficient in ultrafiltration and micellar-enhanced ultrafiltration of organic compounds.²⁷ The theoretical evaluation of the effect of BPM on nanofiltration has been presented by Zhu et al.²⁶ The authors

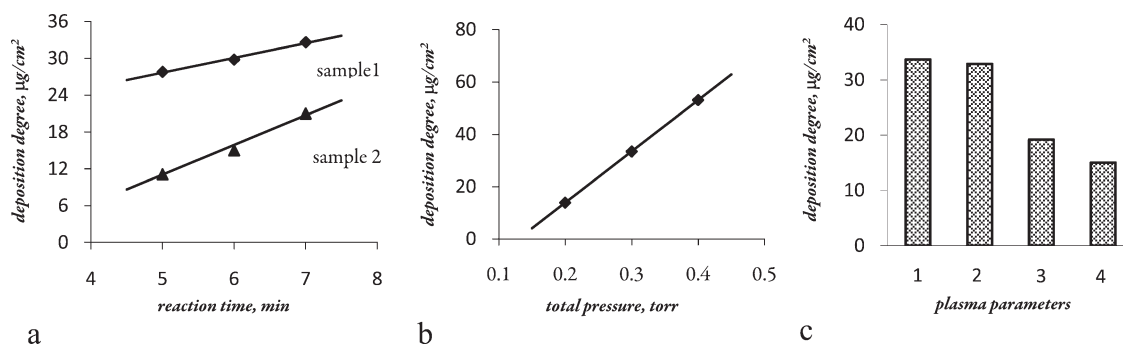


Figure 1. Effect of: (a): polymerization time, (b): pressure, (c): power-current (W-A) adjustment on deposition degree on deposition of pp-acrylic acid. W/A: 1-0.005/0.014, 2-0.018/0.018, 3-0.042/0.045, and 4-0.062/0.063.

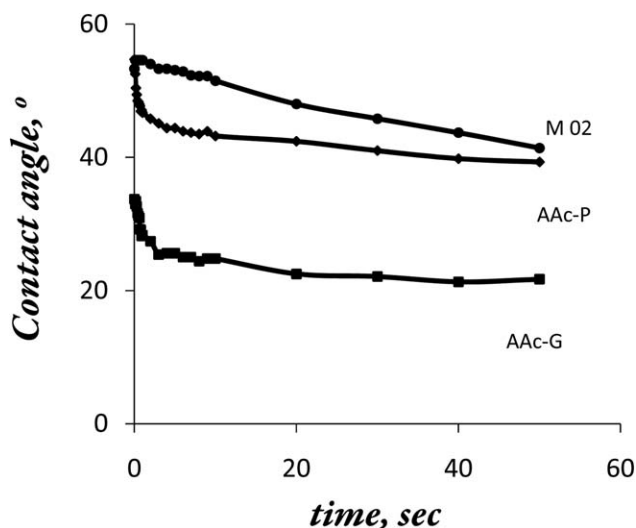


Figure 2. Dynamic water contact angle of pp-acrylic acid. M 02—membrane PET, AAC-G—membrane modified on the grounded electrode, AAC-P—membrane modified on the powered electrode.

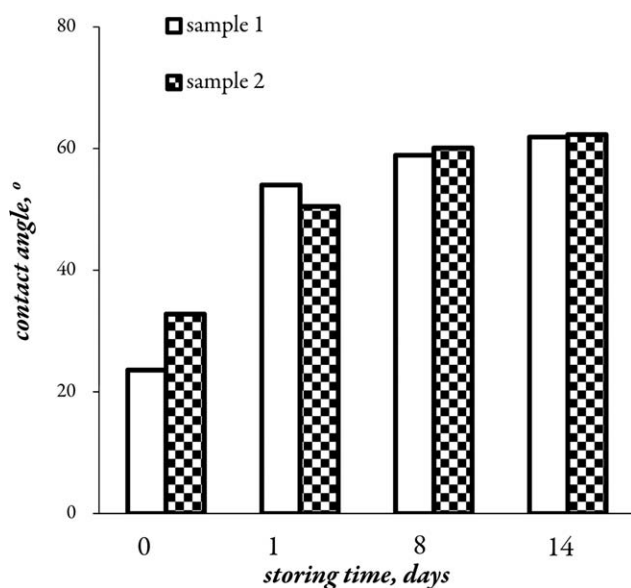


Figure 3. Water contact angle of pp-acrylic acid with storage time.

proved that asymmetric distribution of functional groups along the pores can effectively reduce the transport of multivalent ions and improve membrane rejection.

In this work, we tried to obtain bipolar nanofiltration membranes from commercial microfiltration membranes poly(ethylene terephthalate) track etched membranes. To do that plasma polymerization of acrylic acid and butylamine or allylamine on their surface was conducted. The work was directed to the search on a new method of nanofilters production that can be used for water softening.

EXPERIMENTAL PART

Materials and Equipment

Discs of poly(ethylene terephthalate) track etched membranes (PET TM) of 47 mm of diameter and 0.4 and 0.2 μm pore size were purchased from SterliTech. Aldrich supplied acrylic acid and allylamine and Loba Feinchem delivered *n*-butylamine. Argon was supplied by Linde Gas. A 75 KHz frequency plasma generator (Dora Systems, Wroclaw, Poland) was used throughout the study.

Plasma Polymerization Protocol. Plasma was generated between two electrodes in the glass reactor. Membrane weighted with the accuracy of 10^{-5} g was attached to the lower

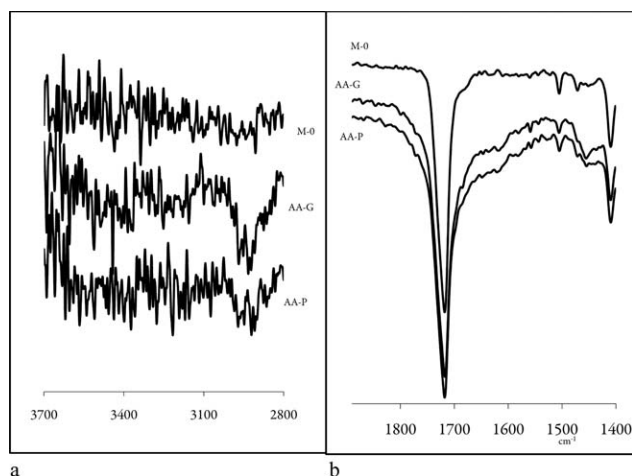


Figure 4. The FTIR ATR spectra for PET TM neat membrane, M-0 and membrane modified with acrylic acid at grounded AA-G and at powered AA-P electrodes.

Table I. Permeation of Water Through the pp-AAc Modified Membranes

Grounded electrode					Powered electrode				
Deposition degree ($\mu\text{g cm}^{-2}$)		Water flux ($\text{dm}^3 \text{m}^{-2} \text{h}^{-1}$)			Deposition degree ($\mu\text{g cm}^{-2}$)		Water flux ($\text{dm}^3 \text{m}^{-2} \text{h}^{-1}$)		
After plasma	After wiping	Pressure (MPa)			After plasma	After wiping	Pressure (MPa)		
		0.005	0.02	0.1			0.005	0.02	0.1
PET TM 0.4 (μm)									
		419							
17.3	12.9	346	-	-	20.2	6.3	154	-	-
36.9	23.1	120	-	-	41.0	38.1	107	-	-
42.7	36.3	254	-	-	46.1	41.5	52.0	-	-
47.3	32.9	111	-	-	50.2	43.2	119	-	-
61.1	39.8	95	-	-	58.2	49.6	14.4	-	420
99.2	79.6	0	-	18.5					
PET TM 0.2 (μm)									
		96.1	1946						
2.9	2.9	53	1476	-	22.5	22.5	0	56	78
20.8	10.4	86.4	1853		45.0	45.0	0	814	
21.9	20.0	0	166	-					
24.2	22.2	22.1	495	-					
36.9	36.9	0	26	220					

(grounded, G) or upper (powered, P) electrode. Distance between electrodes was changed. When the reactor chamber was evacuated to 0.02 Torr vacuum, argon was switched to flow through. The pressure rose to 0.06 Torr. At this stage vapor of monomer was introduced to the reactor up to demanded total pressure. Plasma was then ignited and sustained for the desired time. The amount of pp-polymer deposited on the membrane was determined gravimetrically on the basis of the sample mass gain and shown as degree of deposition N.

Where,

$$\Delta m - \text{mass gain, } \mu\text{mg} \quad S - \text{membrane area (17.34 cm}^2\text{)}$$

CONTACT ANGLE MEASUREMENTS

Dynamic contact angles were measured at room temperature using goniometer PG-X (FibroSystem AB) and mili-Q water as

a liquid. For comparative studies, the values of angle at time zero were given in the tables. The contact angle value was averaged from 6 to 8 independent measurements.

Fourier Transform Infrared Spectroscopy

Spectra were obtained using a Perkin-Elmer System 2000 spectrometer with horizontal ATR device (Ge, 45°). Sixty-four scans were taken with 4 cm^{-1} resolution.

Water Permeability

Membranes were immersed in ethyl alcohol (half an hour) then in ethyl alcohol/water 50/50 vol % mixture (half an hour) and left in water for the next day. The volumetric flux was determined through timed collection of permeate at 0.005, 0.02, or 0.01 MPa, using Amicon 8200 filtration cell. Flux J was calculated according to the formula:

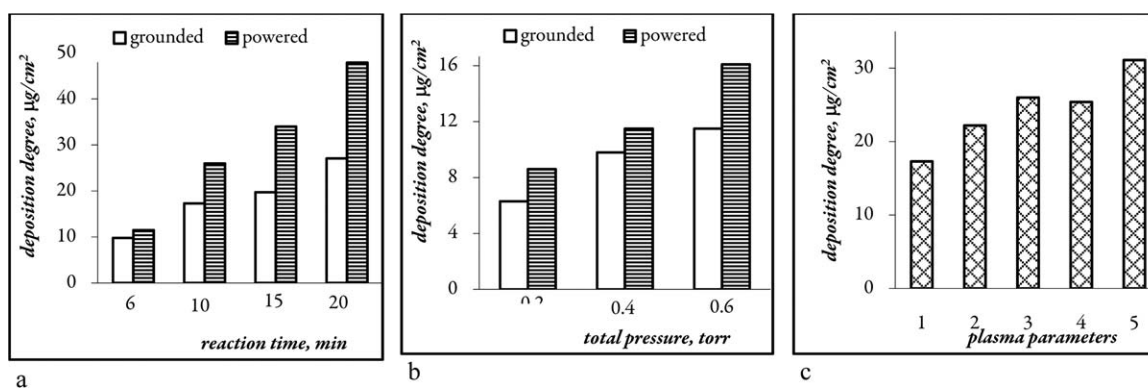


Figure 5. Deposition degree as the function of: (a): polymerization time, (b): total pressure, and (c): power-current. (W/A) adjustment: 1-0.003/0.021, 2-0.005/0.025, 3-0.032/0.039, 4-0.018/0.059, and 5-0.019/0.067.

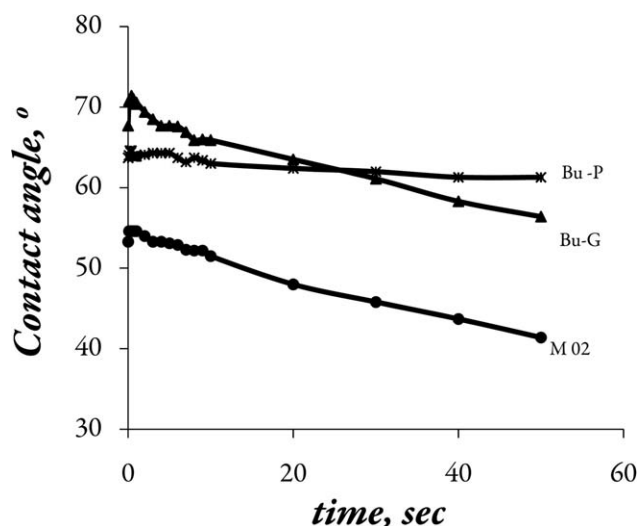


Figure 6. Dynamic water contact angle of pp-N-butylamine. M 02—membrane PET, Bu-G—membrane modified on the grounded electrode Bu-P—membrane modified on the powered electrode.

$J = V/st \text{ dm}^3 \text{ m}^{-2} \text{ h}^{-1}$, where:

V = volume of the permeate (dm^3), s = area of membrane surface (m^2), t = time (h).

Nanofiltration Properties of BPMs

Fluxes of water and 0.01M aqueous solutions of Na_2SO_4 , MgCl_2 , Na_2CO_3 , and MgCO_3 were measured by timed collection of 25 mL of permeate at pressure ranging from 0.005 to 0.1 MPa. Conductivity of permeate was measured and recalculated to salt concentration. That value served to calculation of salt retention.

RESULTS AND DISCUSSION

Plasma Polymerization

To check the efficiency of plasma deposition process, the membranes with pores size of 0.4 μm were selected. They served as supports for recognition of the critical parameters for plasma

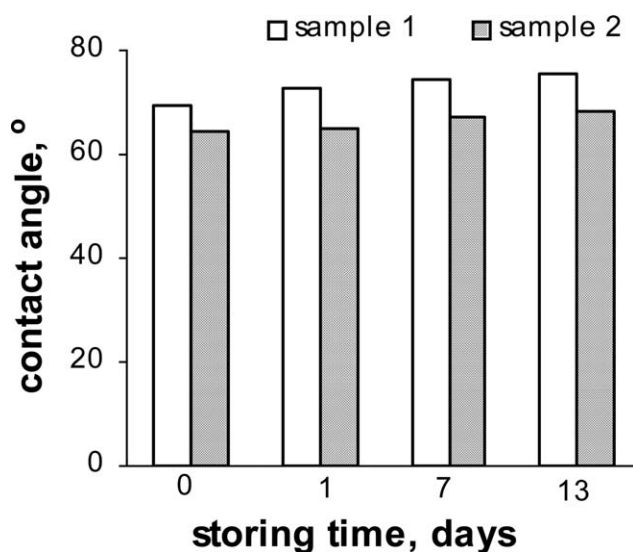


Figure 7. Water contact angle of pp-N-butylamine with storage time.

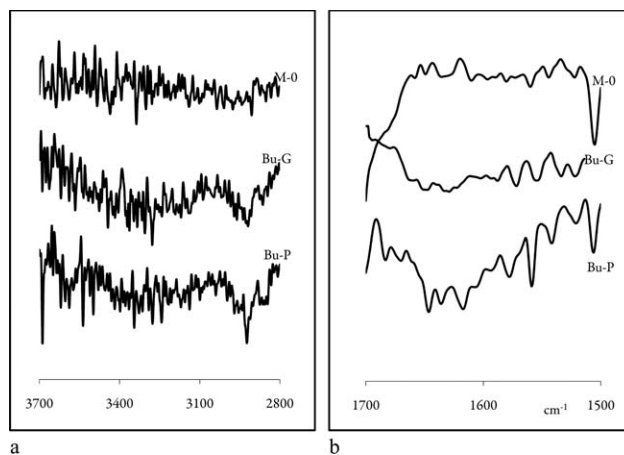


Figure 8. The FTIR ATR spectra for PET TM neat membrane, M-0 and membrane modified with *n*-butylamine at grounded Bu-G and at powered Bu-P electrodes.

deposition of each one monomer separately. The following parameters were selected: current-voltage of generator, reaction time, monomer pressure in the reactor, electrode to which the membrane was attached and distance between the electrodes. The modified membranes were characterized by:

- Deposition degree, immediately after reaction and after dry and wet wiping,
- Water contact angle; in most cases the reading of static contact angle was impossible due to pore structure of membrane substrate. For this reason, the value of static angle was estimated as the angle at the beginning of dynamic measurement,
- FTIR-ATR, to see if monomer functional groups retained in the deposited layer,
- Water flux measurements, to see if the membrane was suitable for nanofiltration.

Acrylic Acid. Acrylic acid polymerizes in plasma with good rate. In the selected parameters, the deposition degree from 17 to $>100 \mu\text{g}/\text{cm}^2$ was detected. In all cases, more polymer was deposited onto powered electrode than onto the grounded one. The deposited layer could not be removed by dry wiping, however, after wetting some samples lost 10–70% of gained mass. It meant that for them the outer layer was not tightly connected to the membrane surface. The time course of deposition degree (for two various plasma parameters), and effects of other plasma parameters are shown in Figure 1(a–c).

Water contact angle of freshly deposited pp-acrylic acid varied from 20 to 35° for samples modified on the grounded electrode and from 24° to 52° for those on the powered one. The typical shape of dynamic contact angle of membrane surface is shown in Figure 2.

The contact angles however were not stable—the storage of samples caused slow increase of surface hydrophobicity. In Figure 3, this process is shown for two samples with different zero time contact angle. The first sample had 23° while the second one 33°. The increase of surface hydrophobicity means that hydrophilic

Table II. Permeation of Water Through the pp-BuNH₂ Modified Membranes

Grounded electrode				Powered electrode		
Deposition degree ($\mu\text{g cm}^{-2}$)		Water flux ($\text{dm}^3 \text{m}^{-2}\text{h}^{-1}$)		Deposition degree ($\mu\text{g cm}^{-2}$)		Water flux ($\text{dm}^3 \text{m}^{-2}\text{h}^{-1}$)
After plasma	After wiping	Pressure (MPa)		After plasma	After wiping	Pressure (MPa)
	0.005	0.02	0.1			0.005
0	-	419	-	0		419
6.3	-	103	-	11.5		175
11.0	-	228	-	26.0		392
17.3	-	203	-	33.4		110
20.2	-	260	-	36.3		394
22.9	-	193	-	39.2		59
PET TM 0.2 (μm)						
0	96.1	1946				
17.3	20.2	54	1377	36.3		168
20.2	17.3	41	1360			
24.0	0	14.9	20.5			

groups on the surface were immersed into the bulk polymer. That phenomenon generally is known as hydrophobicity recovery.

IR spectra of plasma treated membranes are shown in Figure 4. For pp-acrylic acid, in the range of $3600\text{--}3000 \text{ cm}^{-1}$ [Figure 4(a)], one can see the wide band with two maxima, around

3500 cm^{-1} (OH ... OH) and around 3200 cm^{-1} (OH ... C=O). Between 3000 and 2900 cm^{-1} appears a new band that probably comes from stretching CH vibrations of poly(acrylic acid). The peak for carboxylic group (O=C-O) at 1716 cm^{-1} , detected in the virgin membrane also, is much wider after modification, it

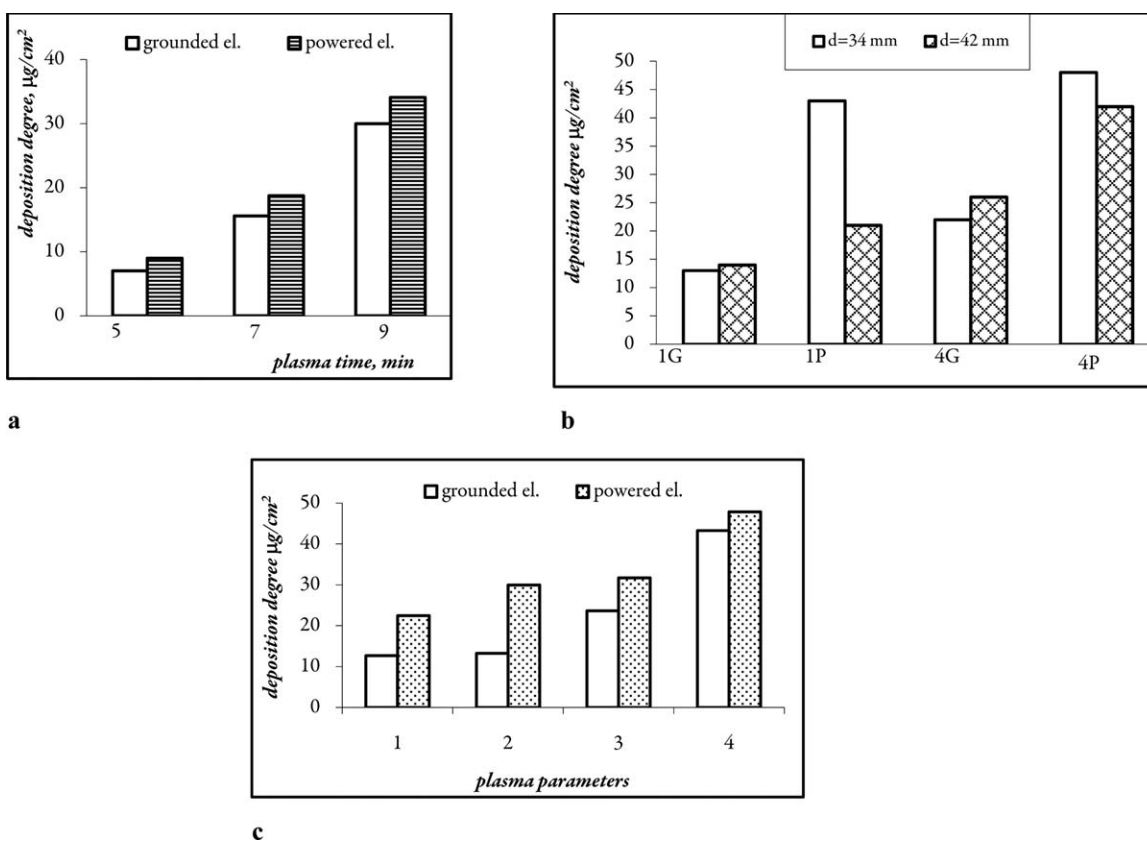


Figure 9. Deposition degree as the function of (a): polymerization time, (b): electrode distance, and (c): power-current. (W/A) adjustment: 1-0.018/0.021, 2-0.031/0.038, 3-0.047/0.060, and 4-0.066/0.080.

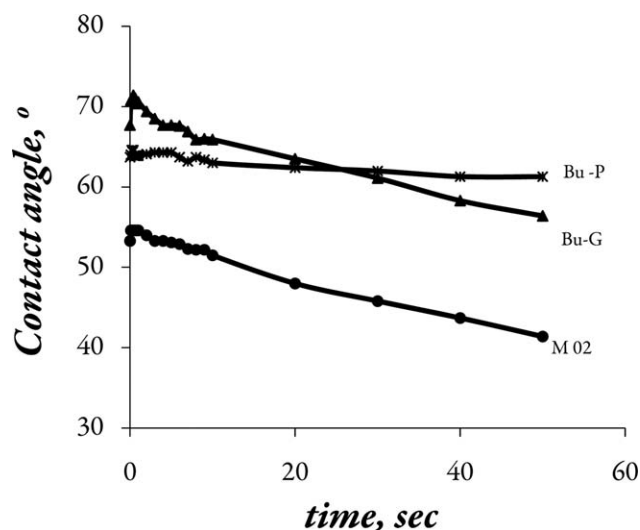


Figure 10. Dynamic water contact angle of pp-allylamine. M0: membrane PET, Al-G: membrane modified on the grounded electrode, Al-P: membrane modified on the powered electrode: deposition degree P2 > P1.

proves the presence of other than PET carboxylic functionalities [Figure 4(b)].

In all studied cases, plasma modification caused the decrease of water flux through the membranes (Table I). However, the flux through the modified PET membranes was still very high even when measurements were done under 0.005 MPa pressure. It can be noted that value of water flux through modified membranes with pores of 0.2 μm is much lower than through membranes obtained by modification of 0.4 μm support.

***n*-Butylamine.** Plasma polymerization of *n*-butylamine is much slower than acrylic acid what is caused by the lack of double bonds in the monomer structure. The higher monomer concentration and longer polymerization time were required. In the selected plasma condition, the range of deposition degree was 6–31 $\mu\text{g}/\text{cm}^2$ on the grounded electrode and 9–49 $\mu\text{g}/\text{cm}^2$ on the powered one. In the case of *n*-butylamine plasma, like in the case of pp-AAc, the higher deposition efficiency was observed for powered electrode. In the most cases, 19 of 22

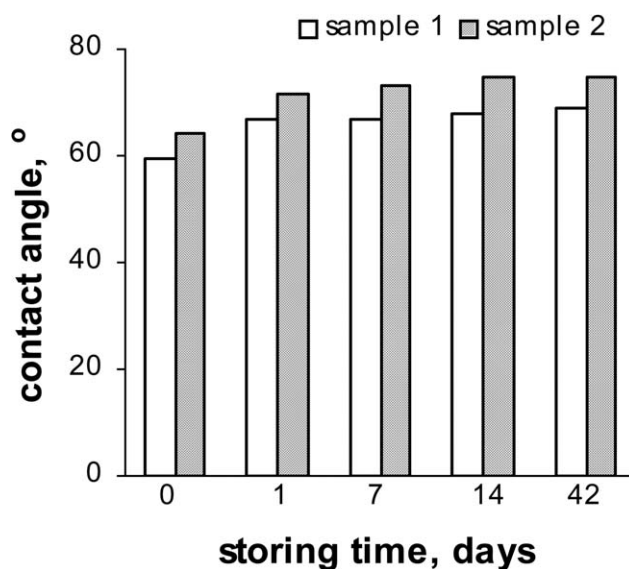


Figure 11. Water contact angle of pp-allylamine with storing time.

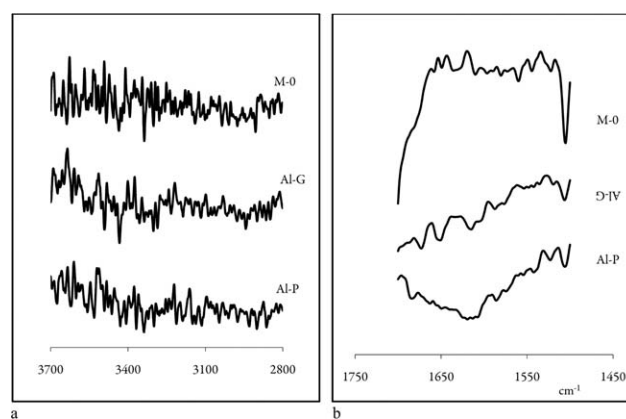


Figure 12. The FTIR ATR spectra for PET neat membrane and membrane modified with allylamine plasma on the grounded (Al-G) and powered (Al-P) electrodes.

Table III. Permeation of Water Through the pp- AlNH_2 Modified Membranes

Deposition degree ($\mu\text{g}/\text{cm}^2$)	Grounded electrode			Deposition degree ($\mu\text{g}/\text{cm}^2$)	Powered electrode		
	Water flux ($\text{J dm}^3/\text{m}^2\text{h}$)				Water flux ($\text{J dm}^3/\text{m}^2\text{h}$)		
	Pressure (MPa)				Pressure (MPa)		
	0.02	0.05	0.1		0.02	0.05	0.1
0	1946	-	-	0	1946	-	-
12.7	895	1679	-	23.1	-	-	64.4
14.5	-	-	-	30.0	960	-	-
18.4	-	-	-	31.7	555	1119	-
21.3	-	-	-	33.5	199	253	-
23.6	187	274	463	42.1	809	1679	-
				47.9	819		

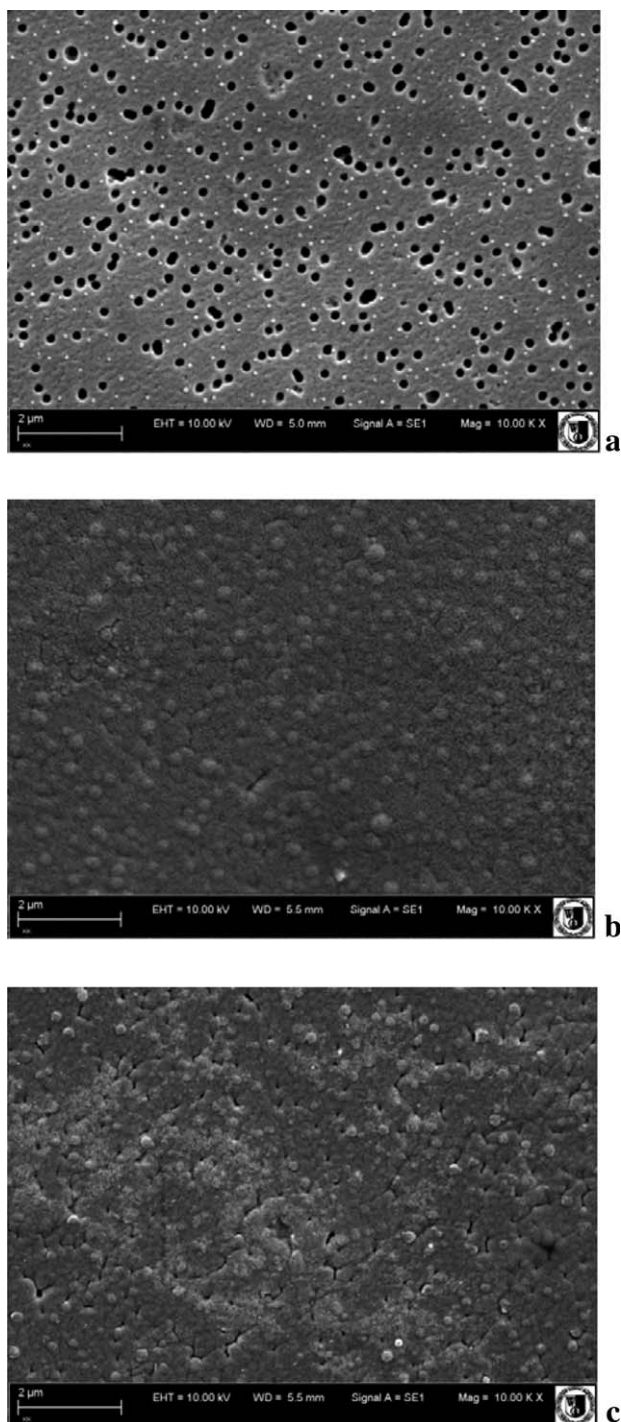


Figure 13. SEM of neat membrane (a), membrane with deposited poly(acrylic acid) (b), and deposited poly(allylamine) (c).

experiments, the deposited layer was resistant to the wet wiping. In three cases, the mass loss was marginal and did not exceed 6%. The time course of deposition degree (for two localization of membranes), the effects of polymerization pressure, and other plasma parameters are shown in Figure 5(a–c).

For all modified samples, water contact angles were higher than for virgin membrane. It proved that the prepared surface became more hydrophobic (Figure 6) after deposition. In all

cases, the layer deposited on the grounded electrode had higher contact angle ($64\text{--}73^\circ$) than that on the second electrode. The differences however were not so significant and took usually $3\text{--}5^\circ$. The surface character did not change with time of storage (Figure 7).

The FTIR ATR spectrum of plasma-polymerized *n*-butylamine (Figure 8) seems to prove the presence of amine groups on the surface. The wide band with maximum around 3300 cm^{-1} [Figure 8(a)] ascribes presence of amine groups (stretching vibrations of NH group). The new band around 2900 cm^{-1} , not visible for virgin membrane, also proves the presence of new aliphatic group. In Figure 8(b) one can see the wide band between 1650 and 1600 cm^{-1} that can be assigned to deformation vibration of NH functionalities.

For $0.4\text{ }\mu\text{m}$ PET membranes measure of water permeability through modified pp-*n*-butylamine membranes was limited as the value was high for pressure larger than 0.005 MPa . For $0.2\text{ }\mu\text{m}$ PET membranes, water flux was much lower and some membranes were completely not permeable (see Table II).

Allylamine. In selected conditions of plasma polymerization, allylamine gave layers with deposition degree of $13\text{--}43\text{ }\mu\text{g}/\text{cm}^2$ for grounded electrode and of $23\text{--}47\text{ }\mu\text{g}/\text{cm}^2$ for powered one. As for other investigated monomers, deposition on powered electrode was much higher than on grounded one. Figure 9(a,b) show the effect of polymerization time and distance between electrodes on deposition extent. Figure 9(c) shows the effect of plasma power-current adjustment. It is clearly seen that when plasma is stronger the degree of deposition gets higher value.

The hydrophilicity of the membrane with pp-allylamine layer depended on the place of modification. Water contact angle for membranes modified on the grounded electrode achieved values from 50° to 65° while those from powered one were higher $\text{--}61^\circ$ to 70° . Typical picture of dynamic contact angle measurement is shown in the Figure 10. The modified membranes can be stored practically without any change of contact angle (Figure 11).

In the FTIR-ATR spectrum of pp-allylamine membrane (Figure 12) two new wide bands, absent in spectrum of membrane substrate, can be observed. The first one, $3500\text{--}3300\text{ cm}^{-1}$, might come from asymmetric and symmetric stretching of NH bonds. The second one, $1660\text{--}1550\text{ cm}^{-1}$, expresses the NH deformation vibrations. The participation of $\text{C}=\text{C}$ vibration however cannot be excluded.

Taking into account the results of flux measurements for previously investigated monomers, only PET TM 02 membranes were considered for filtration. The results are shown in Table III. Water flux of the most of the modified membranes was high and could be measured under 0.005 MPa only. Some samples were permeable to water much more than the untreated membrane was. It means that intensive etching during plasma treatment took place.

Structure of Modified Membranes

To evaluate the morphology of modified samples, scanning electro-microscopic studies were performed. The pictures

Table IV. Properties of BPMs Prepared on PET TM 0.2 μm Support

Sample symbol	Deposition degree ($\mu\text{g cm}^{-2}$)		$J_{\text{H}_2\text{O}}$ ($\text{dm}^{-3} \text{m}^{-2} \text{h}^{-1}$)	$J_{0.01\text{M Na}_2\text{SO}_4}$ ($\text{dm}^{-3} \text{m}^{-2} \text{h}^{-1}$)	R (%)	$J_{0.01\text{M Na}_2\text{CO}_3}$ ($\text{dm}^{-3} \text{m}^{-2} \text{h}^{-1}$)	R (%)
	pp-acid	Total					
BMB	0	34.0	473.0	310.0	3.2	229.2	12.3
ALMAL	0	41.0	337.5	116.2	1.9	23.5	8.8
MAB	31.7	45.0	373.1	390.5	0.8	325.8	3.0
MBA	30.0	46.7	6.27	5.60	17.3	1.64	23.8
MAAL	34.6	55.9	0.10	-	-	-	-
MALA	25.4	48.5	2.24	1.75	48.2	1.19	82.0
AMB	25.3	52.5	137.6	106.6	4.9	66.6	6.3
BMA	28.1	40.4	550.5	83.4	7.3	68.1	10.0
AMAL	32.1	56.3	12.6	8.4	18.3	6.1	22.3
ALMA	36.9	61.7	16.8	5.44	16.7	7.8	26.8

Pressure 0.005 MPa.

collected in Figure 13 clearly show that plasma deposited poly(-acrylic acid) layer cover the support without any cracks. Such pinholes can be seen on the photo of deposited poly(allylamine). It is untestable as the polyamine deposit is not as thick as polyacid one. However, both deposited layers fill pores and decrease pore diameter dramatically.

The above described studies allowed to find the proper conditions for preparation of BPMs. All bipolars were prepared at the mild power parameters to preserve as many monomer functionalities as possible. They were modified on the grounded electrode as layers prepared there were more stable in water. Due to the fact that during plasma action the powered electrode was hotter than the grounded one, the deposited polymer was subjected to the thermal stress and had tendency to crack after prolonged storage in water.

Bipolar Membranes

Poly(ethylene terephthalate) support has some number of carboxylic group. Theoretically, the deposition of the layer with amine group should result in BPM. In this study, two types of BPMs were prepared. They were as follows:

- BMB-both sides of membrane covered with plasma polymer of *n*-butylamine.
- ALMAL-both sides of membrane covered with plasma polymer of allylamine.

The other samples were composed from two plasma deposited polymer layers—one acidic (pp-acrylic acid) and one basic (pp-*n*-butylamine or pp-allylamine). They were deposited successively on one side of membrane:

- MAB-deposition of pp-acrylic acid and pp-*n*-butylamine,
- MAAL-deposition of pp-acrylic acid and pp-allylamine,
- MBA-deposition of pp-*n*-butylamine and pp-acrylic acid,
- MALA-deposition of pp-allylamine and pp-acrylic acid, or on both sides of membrane:

- AMB-membrane covered with pp-acrylic acid and with pp-*n*-butylamine.
- BMA-membrane covered with pp-*n*-butylamine and with pp-acrylic acid.
- AMAL-membrane covered with pp-acrylic acid and with pp-allylamine.
- ALMA-membrane covered with pp-allylamine and with pp-acrylic acid.

These membranes were evaluated for the salt rejection. Table IV contains fluxes of water and salt as well as rejection values for the investigated membranes. The first look at the collected data shows that plasma deposition of pp-butylamine or pp-allylamine on both sides of PET membranes, namely membranes BMBM and ALMAL, has resulted in creation of nanomembranes that slightly rejects sodium sulfate and carbonate. What was more interesting-permeate flux was still high enough. Pores of membrane were not plugged completely and they were able to reject salt. When pp-acrylic acid was deposited, independently on the same or other side than polyamine, rejections were improved significantly. However, a decrease of membrane permeability was observed. Fluxes diminished to hundreds of liters per square meter, hour, and bar. Such phenomenon was noted for MBA, MALA, AMAL, or ALMA membranes. It is expected that the effect was caused by narrowing pores by second layer and increase of membrane resistivity. In the case of MAAL membrane, the pores were filled with deposited polymers and membrane was almost impermeable. However, it should be stressed that the typical NF membranes have fluxes of tens liters per square meter, hour, and bar.

Table V. Separation Properties of MALA Membrane Towards 1-1, 1-2, 2-1, and 2-2 Electrolyte

Salt	NaCl	Na ₂ CO ₃	MgCl ₂	MgCO ₃
Rejection (%)	15.3	82.0	68.3	84.5

Pressure 0.005 MPa.

It is worthy to add here that all studies were conducted at 0.005 MPa pressure, far away from the transmembrane pressure usually applied for nanofiltration. The best separation properties were achieved for MALA membrane, when pp-allyloamine forms the first layer and it was coated with pp-acrylic acid. This membrane were subjected for detailed studies on separation of 2 : 1, 1 : 2, and 2 : 2 type salts. The results are shown in Table V.

The obtained data allowed to consider BPM as more effective in separation of divalent cation and anion salts. Similar conclusion was presented by Ba and Economy for BPM obtained by putting sulfonated poly(ether ether ketone) on positively charged nanofilter.²⁸ Water permeate through these membrane with a flux of about 3 L/(m² h bar) and its value was typical for commercial nanofiltration membranes when the flux changed from 1 to 15 L/(m² h bar).²⁹ The recalculated permeate flux through plasma deposited membranes varies from 22 to 45 L/(m² h bar). It is expected that after optimization of the plasma deposition process it can be obtained membranes with flux as high as 100 L/(m² h bar).

FINAL REMARKS

These studies allow making two groups of conclusions. In the field of plasma modification in can be noted that (i) at investigated conditions, the rate of plasma deposition is as follows: *n*-butylamine < allylamine < acrylic acid, (ii) the deposition degree is higher at the powdered electrode however the grounded electrode offers more stable layer, (iii) extending the time of polymerization and pressure one is able to increase amount of deposited polymer, and (iv) the stronger plasma the higher deposition degree for both investigated amines but the lower degree of pp-acrylic acid deposition.

In the case of filtration properties the evaluated membranes can be used for softening of water as they are able to: (i) reject sulfate and carbonate ions in the reasonable extent, (ii) well separate salts with divalent cation and anion, (iii) keep still large permeate flux, and (iv) the separation properties of membrane does not depend on the sequence how layers were deposited.

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