

Plasma-Modified Porous Membranes*

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The presented paper shows some possible ways for alteration of membrane properties. The used method of plasma treatment allows to tailor membranes according to a particular demand. The action of plasma on porous membranes results in polymer ablation (an increase of pore diameter), deposition of polymer layer (plugging of pore lumen) and/or rebuilding of surface functional groups. These effects place plasma treatment among the most versatile modification methods. Having in stock one ultrafiltration membrane one is able to obtain various micro-, ultra-, and nanofilters, some membranes designated for immobilization of biological components, hydrophobic membrane for membrane distillation, or gel-like membranes for dialysis. Several possible ways of that modification are presented in the paper.

Modern polymers to be used in some high-tech applications have to be surface-modified. The nature of surface functional groups and surface roughness are the most frequently altered parameters. Among several modification procedures, a low-temperature plasma treatment seems to be the most versatile technique. The excited species created in the plasma state may activate the surface layer of polymer and significantly modify its properties. Due to some limitations in a penetration depth, the rest of the material remains unchanged. Additionally, one is able to control the modification extent by simple manipulation of process parameters; among them kind of gas and exposition time are used commonly. Two more issues of plasma treatment are worthy to be noted here [1]:

Plasma technique meets most of the ecological limitations. Amounts of produced wastes are minimized to an acceptable level.

Plasma treatment belongs to the fastest methods used in nowadays technology. The operation lasts usually no more than one minute.

When polymer is plasma-treated, three various phenomena may take place. They are as follows [2]:

Ablation. This term describes the whole bunch of destruction processes that appear when excited gas molecules interact with surfaces. As a result, some

volatile molecules are freed and treated polymer loses its own mass.

Modification of surface chemical structure. New functional groups are created. Some others undergo qualitative reconstruction. This phenomenon does not affect the mass of modified sample.

Deposition of polymer film. The deposit consists of plasma-polymerized gas molecules and the same amount of impurities that were created during ablation of sample and/or parts of a reactor material.

In this place some comments are needed to explain an ambiguous term "plasma-deposited polymer". There is a vital difference between conventional polymer molecule and macromolecule obtained in the plasma polymerization step. When the former is built from repeated units (monomers) and one can find a periodic sequence along the chain, the latter is an ensemble of highly cross-linked chaotic structural units. Schematically, both these structures are shown in Fig. 1 [3].

The increasing interest of industry in separation rises the demand for new membrane techniques. Unfortunately, the number of appropriate polymers that can be used in membrane production is limited. Hence, the available extent of membrane properties does not cover the whole range of industrial needs. To face this

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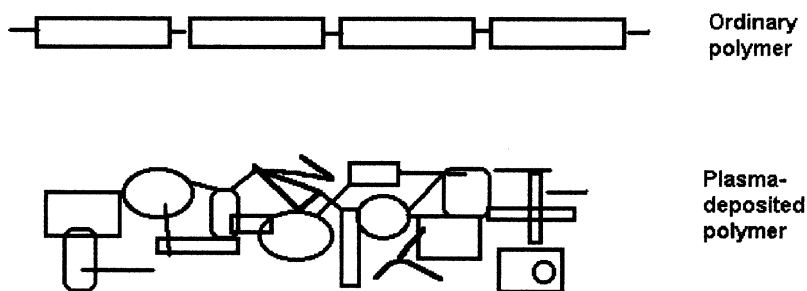


Fig. 1. Schematic presentation of conventional polymer chain and plasma-deposited polymer.

Table 1. Properties of PAN Membranes Treated by Air Plasma

Plasma power	Average pore diameter	Surface tension	Polar contribution to surface tension
W	nm	mN m ⁻¹	mN m ⁻¹
0	3.4	52.2	23.0
12	5.4	66.8	41.3
30	10.4	64.1	40.9
60	27.7	70.0	61.0
120	37.7	62.6	45.8
180	22.0	61.6	40.8

problem, an intensive work on modification of existing polymers is being performed. The presented paper summarizes our experience on plasma treatment of porous polymer membranes and should be considered as our contribution to the search for new polymer membranes.

In membrane business, plasma treatment was used so far to improve gas separations [4, 5] or decrease membrane ability to be fouled [6, 7]. In other cases, plasma action was used to obtain membranes for pervaporation [8, 9] or ultrafiltration [10, 11]. However, according to the authors' best knowledge, the idea of transforming one membrane to the whole bunch of various separators has not been presented. We believe that this paper fulfils that gap.

ABLATION OF POROUS MEMBRANES

Poly(acrylonitrile) (PAN), Membrane in Air Plasma [12]

In this case, as well as for other examples presented herein, we have used microwave plasma (2.45 GHz, duty time 25 %, pulse frequency 125 Hz). In the case of PAN treatment with air plasma the most important results are juxtaposed in Table 1.

It is obvious that any increase of the plasma power makes the pore diameter larger. It happens because PAN macromolecules are susceptible to degradation. However, when plasma power reaches a particular value, in our case 120 W, the polymer deposition process is switched on. The plasma-polymerized layer cov-

ers membrane face – pores' diameter reduces and the surface tension drops down. The deposit is built from volatile fragments that were freed in the preliminary stages of plasma treatment.

Polysulfone (PSU), Membrane in Carbon Dioxide Plasma [13]

The action of CO₂ plasma onto PSU membranes is in fact similar to oxidative etching of PAN membranes. Pores become larger with wider size distribution. Taking into account ATR-FTIR spectroscopy and surface wettability studies, the following steps have been suspected to participate in ablation:

- Bombardment of surface by ionized gas molecules. As a result free-radicals sites are created on the surface;
- Polymer chain destruction with formation of volatile fragments that can vaporize;
- Reaction of volatile species in the gaseous phase followed by deposition of plasma-polymerized macromolecules;
- Reaction of surface radicals with carbon dioxide and/or freed species;
- Post-reactions, when surface radicals are exposed to air.

Surface tension, being the most sensitive measure of surface oxidation, increases during the first 30 s of the process and then it remains unchanged. It means that the reconstruction of surface groups appears within the first half minute of the process. By increasing reaction time we could perform etch-

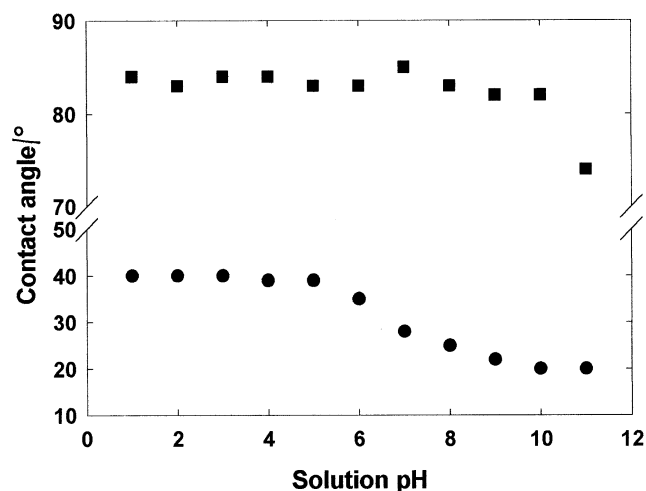


Fig. 2. Change of surface wettability with the course of solution pH. ■ Virgin polysulfone, ● polysulfone modified in CO₂ plasma.

ing of some polymer layers only. The kind of surface groups did not alter at all. Considering the character of surface one may note its acidity. The presence of carboxylic groups is well documented by ATR-FTIR spectroscopy for sample subjected to plasma action. The same conclusion comes from observation of surface wettability when aqueous solutions of various pH have been applied as testing liquids (see Fig. 2).

Virgin polysulfone does not show any change of contact angle with the course of the pH value. Its surface does not bear any groups that can dissociate. In the case of plasma-modified membrane, surface carboxylic groups can dissociate when solution changes within the range of 7–10 pH units. The reader, who wants to know why surface carboxylic groups behave in different way in comparison with their “bulk solution” analogue, is asked to refer to our paper [14] or to an excellent review of *Whitesides et al.* [15]. Hence, it is not difficult to predict that a modified membrane is negatively charged when it is immersed in solution of pH 9.0 and almost uncharged for pH 3.0. Consequently, both membranes should differ in fouling ability when bovine serum albumin (pI = 4.9) is being used as foulant. The comparative studies of these membranes are summarized in Table 2.

When a membrane is in the off-charge state, pro-

tein molecules foul it more effectively than its charged analogue. Moreover, the fouling layer deposited on the charged membrane is easily removable, which means that all protein deposits are dissolved in acid or basic solutions. In case of solution pH 9.0, the deposit is weakly bound to the membrane surface. We have observed similar phenomena in the case of ultrafiltration membranes modified according to conventional chemical routes [16–18]. The unique properties of charged ultrafilters have forced us to specify a new class of membranes. We called them Porous Ion-Exchange Membranes (PIEM). As one notes, PIEM may be also obtained in plasma treatment.

Polysulfone (PSU), Membranes in Nitrogen Plasma [19]

The action of N₂ plasma onto PSU membrane resulted in creation of amphoteric surface (see Fig. 3). Nitrogen plasma affected polysulfone membrane weakly. Hence, pore size distribution function was not altered so dramatically as it was observed for oxidative plasma. The process of polymer ablation was caused by the presence of some oxygen amount in gas used (gas impurity) and in the polymer (oxygen dissolved in polymer or freed from vaporized polymer fragments). Simultaneously to ablation, some acidic and basic sites were anchored to the surface in the time of reaction. The obtained bifunctional membrane was less prone to protein fouling than its monofunctional analogue. The filtration indices of nitrogen-modified membrane are collected in Table 3. As one can see, the modified membrane is not so strongly fouled in both solutions. The repulsive effect between the protein molecule and membrane when both bodies bear the same charge, raises the obtained membrane at the top of engineers' interest.

PLASMA-DEPOSITED POLYMERS

PAN Membranes in Perfluorohexane Plasma [20]

In the paper [20] we have shown that the PAN membrane was coated with the Teflon-like polymer within 30 s of plasma action. When the modification time was extended to 10 min, all pores

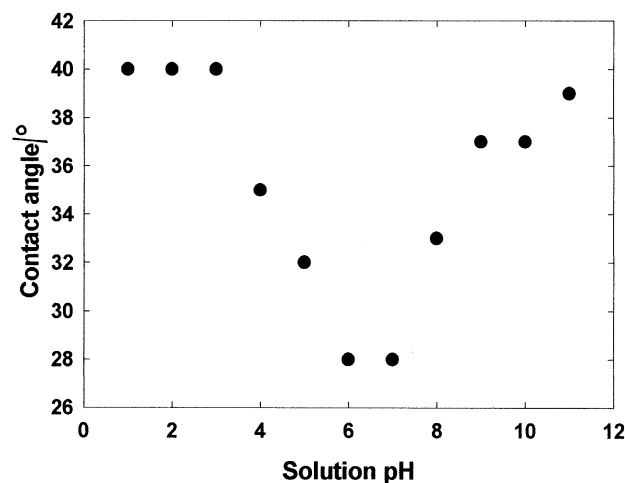
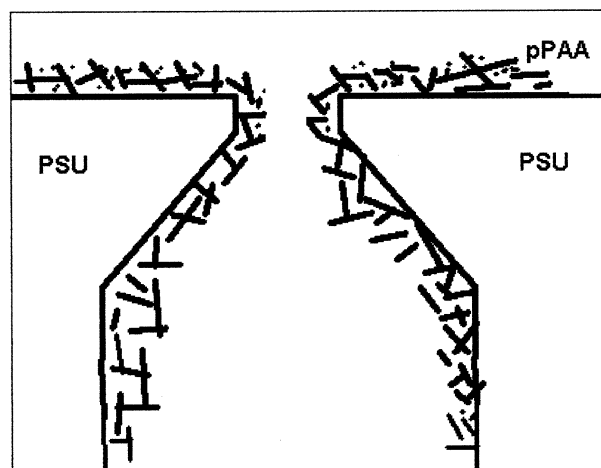
Table 2. Fouling Indices for PSU Membrane Modified in Carbon Dioxide Plasma

	pH = 3.0		pH = 9.0	
	Virgin PSU	Modified PSU	Virgin PSU	Modified PSU
Fouling index/%	59.9	60.9	53.5	22.1
Flux recovery/%	53.2	88.2	68.4	100

Fouling index expresses a decrease of flux caused by membrane fouling after 1 h of the process. Flux recovery expresses the ability of fouled membrane to be regenerated by the conventional acid-base cleaning procedure.

Table 3. Fouling Indices for PSU Membrane Modified in Nitrogen Plasma

	pH = 3.0		pH = 9.0	
	Virgin PSU	Modified PSU	Virgin PSU	Modified PSU
Fouling index/%	59.9	47.5	53.5	45.5
Flux recovery/%	53.2	87.2	68.4	89.5

**Fig. 3.** Change of surface wettability with the course of solution pH. Polysulfone modified in N₂ plasma.**Fig. 4.** Schematic presentation of asymmetric polysulfone (PSU), membrane coated by plasma-deposited poly(acrylic acid) (pPAA).

of the membrane were filled with plasma-deposited poly(perfluorohexane). It was also found that the deposition rate depended on pore diameter; large pores were plugged quicker than the smaller spaces.

PSU Membranes in Acrylic Acid Plasma [21]

As one can suspect, plasma-deposited poly(acrylic

acid) has shifted the pore size distribution towards smaller pore values. The scheme below rationalizes this phenomenon (see Fig. 4). Evaluation of surface tension for virgin and modified membranes showed that the deposit has a character of poly(acrylic acid). The total surface tension of PSU was estimated at 43.3 mN m⁻¹ with a small polar contribution (1.0 mN m⁻¹) while these values for the deposited polymer were as follows: 67.6 mN m⁻¹ in total and 42.6 mN m⁻¹ for polar component. Additionally, it was observed that the amount of deposited polymer has linear correlation with the reaction time and the power of plasma.

Sulfonated Polysulfone Membrane in Butylamine or Allylamine Plasma [22]

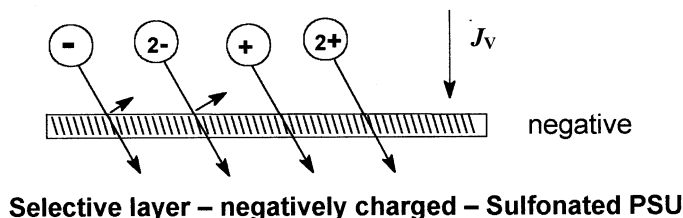
The idea of preparation of bipolar nanofiltration membrane is shown in Fig. 5. For the negatively charged nanofilter (called herein monopolar nanofiltration membrane), most of small inorganic cations are poorly rejected. That situation turns when one uses the bipolar membrane. The double layer exclusion phenomenon may affect significantly permeation flux and one observes improvement in salt rejection behaviour. The obtained data are shown in Table 4.

An increase of water flux for bipolar against to monopolar membranes may be caused by an enlargement of pore diameter (polymer ablation mechanism). However, the salt rejection coefficient keeps still an interesting value. It takes even the level of 60–70 % for magnesium sulfate, the salt mostly responsible for water hardness.

GRAFTING OF POLYMERS ONTO SURFACE-ACTIVATED MEMBRANES

Entirely different form of plasma use is a process of surface activation followed by grafting of acrylic monomers. Such method is also discussed in our paper [21]. According to the obtained data, it is possible to manipulate the grafting yield by selecting the grafting conditions (monomers come from vapour or liquid phase) and time of the process. In both cases brush-like surface structures are obtained. Long grafted chains of poly(acrylic acid) are formed when the process is conducted in aqueous solutions while grafting in a vapour phase results in dense-packed short poly-acid chains. The obtained membranes were tested in

Monopolar nanofiltration membrane



Bipolar nanofiltration membrane

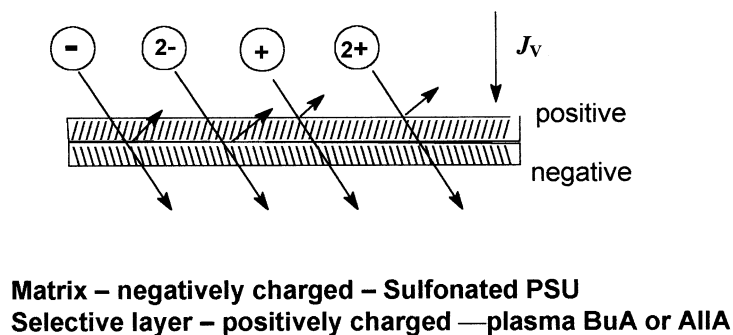


Fig. 5. Salt rejection for monopolar and bipolar nanofiltration membranes.

Table 4. Transport Properties of Mono- and Bipolar Nanofiltration Membranes

Plasma to obtain bipolar membranes	Time of treatment	Water flux	NaCl rejection	MgSO ₄ rejection
	min	dm ³ m ⁻² h ⁻¹	%	%
Butylamine	2	6.3	36	41
	4	4.9	35	56
	6	4.5	38	52
Allylamine	2	8.4	37	56
	4	7.5	35	60
	6	4.6	26	69
Monopolar membrane		2.5	57	42

nanofiltration. Membranes obtained in vapours were more effective for that purpose.

CONCLUSION

Plasma treatment of porous polymer membranes results in obtaining of some brand new materials useful for separation processes. Taking the plasma modification method one is able to obtain a membrane with requested pore diameter. The creation of membranes with demanded surface character is not so a difficult task. One should put a piece of membrane into a plasma reactor, switch a device on, and obtain the requested membrane within seconds. Additionally, amounts of produced wastes are considerably limited (modification is carried out in the vapour phase). It seems that the described method allows to prepare a

great number of new membranes having in stock one kind of an ultrafilter.

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