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PLASMA MODIFICATION OF POROUS POLYACRYLONITRILE MEMBRANE

The process of plasma modification of porous ultrafiltration membrane by deposition of perfluorohexane is discussed. It is shown that teflon-like polymer is deposited in the form of a film of the thickness dependent on the pore diameter. Distribution of pores becomes narrower when the extent of deposition increases. Polyacrylonitrile membrane, PAN 1514, is clogged totally after 6-7 min treatment of plasma.

1. INTRODUCTION

The increasing interest of industry in search for more profitable processes and growing demand for clean environment have pushed the researchers towards the use of new technologies. As a consequence, the dynamic development of large-scale membrane processes has been observed in the last decades. By the same token, a great deal of effort has been devoted to seeking some new materials for preparation of semipermeable membranes. However, the number of appropriate materials to be applied in this production is limited. The only way to overcome this drawback is modification of currently used membranes to change their properties in desired direction. Plasma techniques are very useful and effective for that purpose; by changing the gases or plasma parameters one can get practically unlimited number of materials with great deal of various properties of surface. From membranologist point of view it is possible to produce various classes of membranes (i.e., for reverse osmosis, dialysis, electrodialysis, filtration, membrane distillation or liquid extraction) having in stock only a few kinds of porous material.

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Generally, gas plasma can react with organic polymers in three ways:

1. Ablation – both physical etching and chemical reaction form volatile products at the surface. In the case of porous membrane, the process gives an increase in pore diameter [1].

2. Surface reactions – both substitution and addition reactions can appear. The process provides entirely different membrane surfaces [2]–[4].

3. Deposition of polymer film. For a porous membrane as a support the last method results in formation of a membrane with totally different surface and lower porosity [5]. Finally, the deposited polymer may plug pores and form solid phase between both membrane surfaces. Hence one porous support may be used in production of either porous or solid membranes.

This paper is addressed mainly to such possibilities. Typical ultrafiltration membrane serves here as a porous support. Evaluation of pore size distribution functions is used to follow the progress and extent of deposition of plasma polymerized polyperfluorohexane.

2. EXPERIMENTAL

2.1. MEMBRANE

Membrane PAN 1514 supplied by Deutsche Carbon G, Membran Trenverfahren GFT was used in this study as a porous support. The membrane was characterized elsewhere [1].

2.2. PLASMA TREATMENT

Small pieces of membrane were modified in a plasma apparatus described previously [6]. A dry membrane was put on a teflon table in a plasma reactor, at distance of 66 mm from the lower edge of plasma. Plasma was formed by a 2.45 GHz generator in a quartz tube at the top of a reaction chamber. Pulsed plasma with pulse frequency of 500 Hz and 25% duty cycle was used. Mixture of argon (99.99% of purity) and perfluorohexane (95%, Aldrich Chem. Co.) was applied as the plasma gas. The following parameters were selected: argon flow rate (19 cm³/min), perfluorohexane flow rate (10 cm³/min), total pressure (1.5 hPa), power (60 W). In the experiment, the time of plasma treatment was changed in the range of 0–10 min.

2.3. MEMBRANE EVALUATION

Each membrane was soaked with 30 ml of 96%-vol. ethanol (30 min). Then water was added gradually up to 200 ml (60 min). Finally, a membrane was immersed in

water for the next 30 min. After the soaking procedure, membrane was fixed in an ultrafiltration cell and subjected to evaluation of pore size distribution functions according to the procedure described previously [1]. Water solutions of narrow fraction of dextrans (2.5 mg/cm^3) were used for this purpose. The flux of water was determined for membranes fixed in the unit just before the experiment.

2.4. CONTACT ANGLE MEASUREMENTS

For the measurements of water contact angle, the polymer samples were prepared as follows: 1) polyacrylonitrile was extracted from membrane by dimethylformamide, 2) the solution was poured on clean microscopic glasses and cut into 0.2 mm samples, 3) the samples were dried at ambient temperature for 3 days and then under vacuum for 1 day, 4) the samples were exposed to appropriate plasma conditions. Advancing contact angle of water droplets was detected by means of TM 50 System (Technicome, France). Each measurement was repeated 10 times.

3. RESULTS AND DISCUSSION

It is known from the literature that plasma of fluorocarbons can cause etching of polymeric substrate, perfluorination of surface layer or deposition of plasma polymers. The final result for a given polymer substrate depends mainly on plasma gas composition and F/C ratio of the fluorocarbon used. The presence of oxygen in the gas mixture gives rise to the ablation rate [7]. This process is widely applied in electronics for etching and removing polymer resists. The presence of hydrogen in the plasma gas mixture, on the other hand, enhances the deposition process [8]. Fluorocarbons with low F/C ratio polymerize and deposit effectively, while those with higher F/C ratios cause etching and surface fluorination only [8]. YASHUDA [9] has investigated the plasma behaviour of perfluorohexane and found that this fluorocarbon was deposited on smooth surfaces and the thickness of plasma polymer increased linearly with time. For this reason, perfluorohexane monomer was especially selected by us to be deposited on porous substrate.

The evaluation of the pore size distribution function for membranes coated with plasma polymerized perfluorohexane (pPFH) is shown in table 1. The changes of average pore diameter and standard deviation show that the pores become smaller and their distribution narrower when the time of polymer deposition is longer. The observed results may be explained by the disappearing of population of small pores and clogging of large pores by pPFH formed. Now there is the time to put open the following question: *Does the plasma polymer deposit to the same extent in all pores?*

Table 1

Pore size distribution function for PAN1514 membrane
modified by deposition of plasma polymerized perfluorohexane

Time of deposition [min]	Average pore diameter [nm]	Standard deviation	Pore size distribution function
0	3.69	1.7638	$0.2262 \exp[-(\ln R - 3.6090) \wedge 2/6.2218]$
0.5	2.52	1.2535	$0.3183 \exp[-(\ln R - 3.2265) \wedge 2/3.1427]$
1	1.83	1.1747	$0.3396 \exp[-(\ln R - 2.9087) \wedge 2/2.7598]$
2	1.29	0.9476	$0.4210 \exp[-(\ln R - 2.5609) \wedge 2/1.7957]$
3	1.11	0.9730	$0.4100 \exp[-(\ln R - 2.4073) \wedge 2/1.8936]$
10	N/D	N/D	N/D

N/D – not determined due to pore plugging.

Or in other words: *Do pores clog in the same way independently of their diameter?* The problem may be resolved by comparison of pore size distribution functions in the way described by BELFORT et al. [10] for various times of polymer deposition. Nevertheless, the simple method of determination of the deposition course is the comparison of average pore diameters. The correlation is shown in figure 1. The curve presented here is far away from a straight line. Hence, it is suspected that all pores cannot clog in the same manner. The thickness of the deposited polymer must depend on pore diameter.

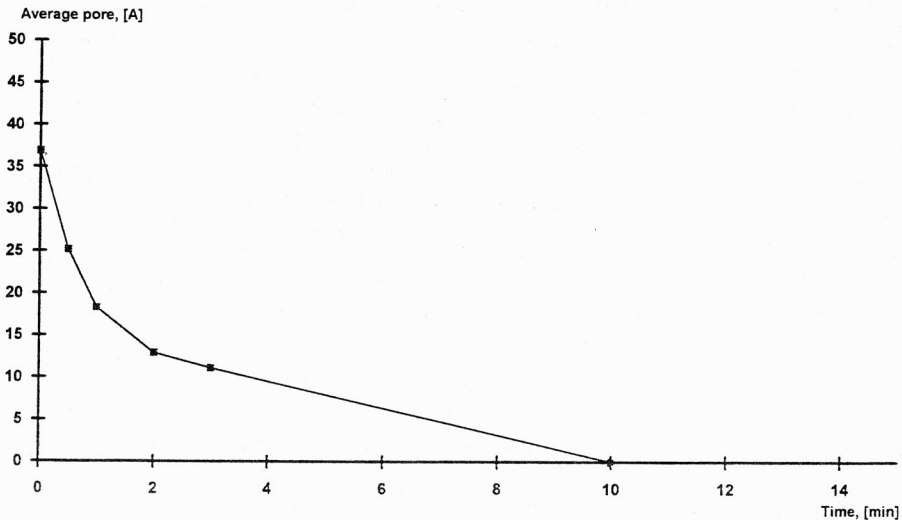


Fig. 1. Effect of plasma treatment time on average pore diameter

Another point for discussion is available when one compares the fluxes of water through the membranes. According to Hagen–Poiseuille equation water flux may be expressed as follows:

$$j(R) = \frac{\pi \Delta p}{8l\mu} R^4$$

where Δp is the driving pressure, μ denotes the kinematic viscosity, l is the mean thickness and R is the membrane average pore diameter.

Hence the correlation $\ln j(R)$ vs. $\ln R$ should be a straight line. The relationship in figure 2 shows quite good linearization except the point for Ar-modified membrane. This behaviour indicates that membrane changes its surface properties just after 0.5 min of deposition. Membranes activated in Ar-plasma do not follow this relationship. Their surface properties differ so much so the flux is higher. The measured water contact angles visualize this problem more accurately (table 2).

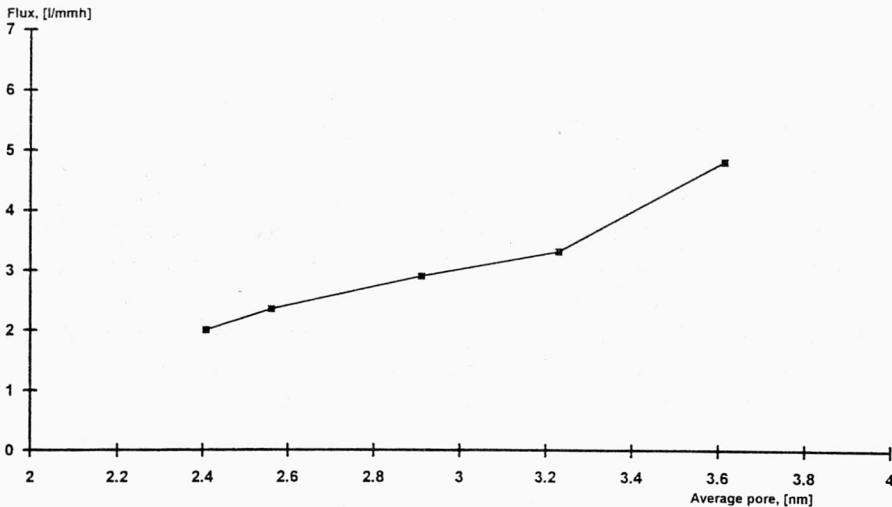


Fig. 2. Correlation between the average pore diameter of plasma modified membranes and permeate flux. Medium – water, pressure – 0.05 MPa

Etching by neutral gases or oxygen is accompanied by a mass loss and increase of wettability. In the case of polyacrylonitrile used in this study, argon plasma caused sharp decrease in wetting angle of water (from 65° for PAN to 38° for modificate). Perfluorination and deposition of fluorocarbons give as a result the surface of modified material – wetting angle of water can reach the value up to 175° [11]. For perfluorohexane polymer the contact angle of water reached the value of 120 – 122° . It shows that polymerizable fluorocarbon deposits on polyacrylonitrile support.

Table 2

Advancing contact angle for water on plasma modified polyacrylonitrile films

Time of deposition [min]	Contact angle [deg]	Standard deviation
0	37.8	1.56
0.5	122.3	2.3
1	122.4	1.5
2	122.6	1.4
3	118.8	1.6
10	122.2	3.0

4. CONCLUSIONS

Porous polyacrylonitrile membrane exposed to Ar-perfluorohexane plasma is coated by teflon-like polymer film. The process of polyperfluorohexane deposition prevails over the support degradation. The thickness of coating depends mostly on the diameter of the pore in which the polymer is deposited. Hence the assumption of uniform increasing of the thickness of the plasma deposited film seems to fail for the porous substrate. In the case of studied PAN 1514 membrane, a whole membrane is plugged after 6–7 minutes of plasma polymerisation. However, to obtain a membrane without any pinholes prolonged exposure to plasma is recommended. When one is interested in tailoring porous membranes with small pores and reduced polydispersity one should apply plasma for 0.5–2 minutes.

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MODYFIKACJA PLAZMOWA POROWATYCH MEMBRAN Z POLIAKRYLONITRYLU

Представлено процес плазмowej modyfikacji powierzchniowej porowatych membran z poliakrylonitrylu przez osadzanie poliperfluoroheksanu. Stwierdzono, że poliperfluoroheksan osadza się na ściankach porowatego podłoża w postaci filmu, przy czym jego grubość zależy od wielkości porów, w których zachodzi osadzanie. Zmierzony rozkład wielkości porów zawęży się wraz ze zwiększaniem ilości osadzonego polimeru. Pory w badanej membranie PAN 1514 zostają wypełnione poliperfluoroheksanem po ok. 6–7 minutach procesu. Przedstawiona metoda umożliwia otrzymywanie jakościowo innych membran (porowatych lub litych), przydatnych w różnych procesach membranowych.

ПЛАЗМОВАЯ МОДИФИКАЦИЯ ПОРИСТЫХ MEMBRAN ИЗ ПОЛИАКРИЛОНИТРИЛА

Представлен процесс плазмовой поверхностной модификации пористых мембран из полиакрилонитрила посредством осаждения полиперфторогексана. Было установлено, что полиперфторогексан оседает на стенках пористого основания в виде фильма, при чем его толщина зависит от размера пор, в которых происходит осаждение. Измеренное распределение размеров пор сужается вместе с повышением количества осажженного полимера. Пory в исследуемой мембране PAN 1514 заполняются полиперфторогексаном после ок. 6–7 минут процесса. Представленный метод дает возможность получения разных по качеству мембран (пористых или монолитных), пригодных в разных мембранных процессах.

