

PLASMA POLYMERIZATION OF HYDROPHILIC AND HYDROPHOBIC MONOMERS FOR SURFACE MODIFICATION OF NUCLE-MICROPOROUS MEMBRANE

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ABSTRACT

Surface modification of nucle-microporous membrane by plasma polymerization of HEMA, NVP and D₄ has been studied. The hydrophilicity of membranes was increased with increasing of plasma polymerization time of hydrophilic monomers HEMA and NVP. The flow rate of water through the membrane was increased remarkably after plasma polymerization of HEMA on it.

INTRODUCTION

Plasma treatment or plasma polymerization method has been used as a useful approach in modification of surface properties for polymeric materials. This technique might give some new specific properties to the materials. Nuclepore is a kind of filter film developed in the early 60's and based on poly (bisphenol-A carbonate) as substrate with pores produced by irradiation of U²³⁵ fission fragments followed by etching process. This method is usually named as "nuclear tracks" technique. Standard pore sizes range from 0.015 — 0.80 microns. In the development of science and technology the nuclepore membranes have been used widely in many fields, such as electronics, chemical industry, chemistry, biology, drugs, environmental science, and food industry. In many cases more requirements in properties should be fulfilled for the microporous membrane in precision filtration. However, the polycarbonate film itself is a hydrophobic material. When the aqueous solution flows through the film, it must overcome large resistance force caused by surface tension. Therefore, surface modification is needed. Plasma treatment, especially plasma polymerization of different monomers on the nuclepore membrane is considered to be an effective method to promote the hydrophilicity, wettability, antistatical property and filtration rate of membrane for liquid or gases.

This paper deals with plasma treatment on surface of nucle-microporous membranous materials and the study on the structure and property of modified film.

EXPERIMENTAL

1. Materials and equipment

(1) Substrate: Poly (bisphenol-A-carbonate) nucle-microporous membrane

(NMPM) ($10\text{ }\mu\text{m}$ thick , pore diameter $0.4\text{ }\mu\text{m}$) made by " nuclear track " technique .

(2) Monomers : 2-Hydroxyethyl methacrylate (HEMA) , N-vinyl pyrrolidone (NVP) , Cyclooctamethylsiloxane (D_4) .

(3) Instrument : Plasma treatment and plasma polymerization were carried out on Plasma Deposition System model PD-2 .

2. Low temperature plasma treatment

NMPM was put on the lower electrode (sample plate) of plasma producer . Under vacuum of $6 \sim 10\text{ mbar}$, the air (or N_2 , Ar) was conducted into the chamber . Then the glow discharge was initiated in space between electrodes under 0.2 mbar with power of 50 w .

3. Preparation of plasma complex membranes (PCM)

NMPM was loaded on the lower electrode of plasma producer and was treated at first by air for 5 min . After that the glow discharge was initiated under 0.2 mbar and monomer was simultaneously pushed into the plasma chamber for a certain time .

4. Determination of properties

(1) Wettability

The contact angle was measured on FACE contact anglemeter model CA-D .

(2) Surface element composition

The element ratio O/C , N/C and Si/C of NMPM surface was analyzed by X-Ray photoelectron spectroscopy (XPS) .

(3) Surface morphology

Surface morphology and pore size were observed on Scanning Electron Microscopy (SEM) model S-530 .

(4) Water flow rate

It is determined on an apparatus installed in our laboratory .

RESULTS AND DISCUSSION

1. Effect of modification of NMPM by plasma treatment

The wettability of polycarbonate NMPM was increased markedly after low temperature plasma treatment . This was caused by chemical and physical interaction between membrane surface and free electrons , ions and neutral excited particles (i . e . low temperature plasma) produced by ionization of gas in reactor during glow discharge . When the membrane surface exposed under plasma , some new active points or groups were induced on it . So some new hydrophilic groups such as $-\text{OH}$, $-\text{COOH}$, $-\text{CONH}_2$ and $-\text{NH}_2$ would be produced on the surface of membrane just at these active points . Then the hydrophilicity of membrane was enhanced . The results of XPS analysis showed that the elements O/C ratio rose obviously after plasma treatment , indicating the generation of groups containing oxygen . However , this kind of active groups might disappear gradually upon standing for some time and the effect of modification could be lost completely .

2. Effect of modification of NMPM surface property by plasma polymerization

(1) Wettability

Tab. 1 shows the wettability of PCM formed from hydrophilic monomers (HEMA and NVP) and hydrophobic monomer (D₄). The contact angle of hydrophilic PCM was decreased with increasing of polymerization time , while the contact angle of hydrophobic PCM was increased with increasing of polymerization time and then reached to a constant value .

Table 1 Wettability of different PCM

Polymerization time (min) Contact angle Monomer				
	0	5	10	15
NVP	77.5 °	44 °	30 °	32 °
HEMA		44 °	5 °	5 °
D ₄		89 °	91 °	90 °

Table 2 Effect of polymerization time on flow through different PCM

Polymerization time (min)	Rate of water flow (ml / min · cm ²)		
	HEMA	NVP PCM	D ₄ PCM
0	70.9	70.9	70.9
5	106.3	100.7	slow
10	—	—	extreamly slow
15	147.2	100.7	don't flow
30	182.2	123.4	don't flow

(2) Surface element composition

The change of oxygen content on membrane surface determined by XPS was shown in Figs . 1 and 2 . It was revealed that the ratio of oxygen to carbon O/C of HEMA PCM was increased with prolongation of polymerization time , while O/C and N/C of NVP PCM were increased with increasing of polymerization time and then reached to a constant value .

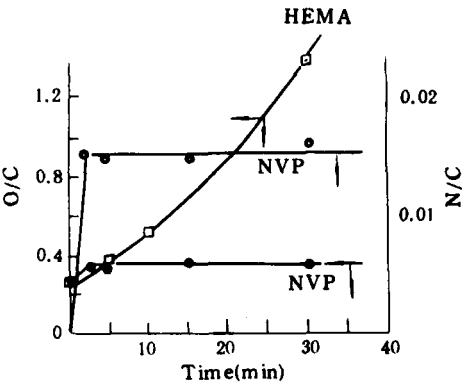


Fig. 1 Surface composition of HEMA PCM and NVP PCM , determined by XPS

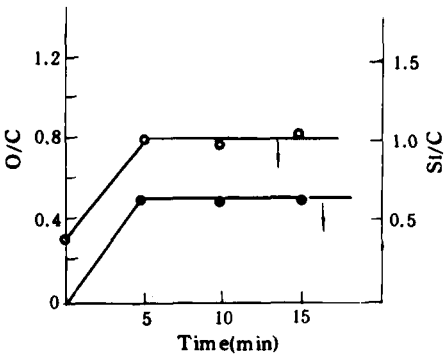


Fig. 2 Surface composition of D₄ PCM

Fig. 2 shows that O/C and Si/C of D₄ PCM were increased at first stage of polymerization and then go along a smooth curve . It can be seen that the results of XPS analysis and contact angle measurment were identical to each other , indicating that NVP and D₄ could produce stable PCM within very short time of glow discharge .

In Tabel 2 the results of plasma complex technique on membrane surface modification were illustrated .

(3) Water flow rate

Table 2 elucidates the flow rate of pure water through different porous

membranes with average pore diameter of 0.4μ under the same condition. It showed that the flow rate of water through HEMA PCM and NVP PCM was much higher than that of untreated membrane and flow rate was increased with increasing of polymerization time . In the case of D_4 PCM , the flow rate of water was quite slow , because the hydrophobicity of D_4 was much higher than that of untreated membrane .

(4) Surface morphology

The plasma polymer layer generated on NMPM surface can be clearly observed by SEM (Fig . 3) . The D_4 PCM formed quickly during plasma polymerization and micropores were covered at last by polymer . After 30 min . of polymerization the surface of NMPM PCM was piled up with granular polymer stack (Fig . 3-d) . However , HEMA and NVP deposited on the NMPM surface after 30 min . polymerization were very thin film around the micropores , providing good wettability to NMPM without any undesired effect to the pore size .

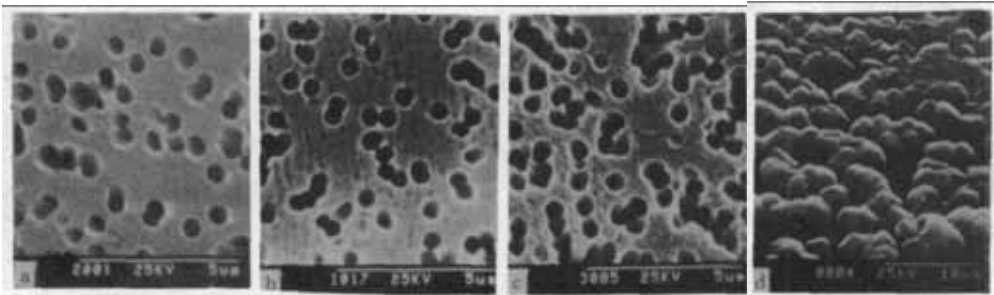


Fig . 3 SEM of NMPM before and after modification
a . Untreated ; b . HEMA PCM 30 ; c . NVP PCM 30 ' ; d . D_4 PCM 30 '

(5) Comparison of water flow rate through different membranes

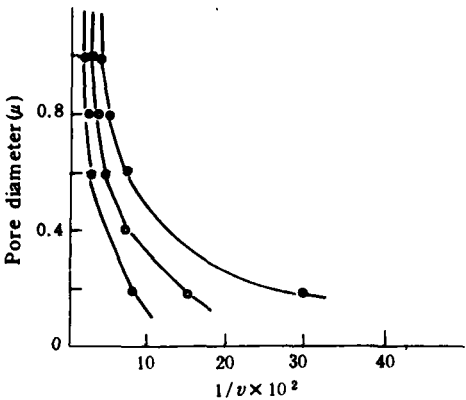


Fig . 4 Comparison of rate of water flow through different microporous membranes
• — untreated , ○ — nuclepore (G . E . of U . S . A .) ,
⊗ — modified by plasma polymerization of HEMA

Fig . 4 illustrates the flow rate of pure water passing through different NMPM .

The plasma modified HEMA PCM gives the highest water flow rate among the samples used in our experiments.

All of the results mentioned above indicate that the plasma polymerization of hydrophilic vinyl monomers on NMPM is a reliable method for improving the surface wettability of the micropore membrane.

Keywords :

Plasma polymerization ; Nucle-microporous membrane ; wettability

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