Plasma Deposition Modified Nylon 4 Membranes for Hemodialysis

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SYNOPSIS

The purpose of this research is to prepare high solute permeability membranes for hemodialysis by plasma depositing hydrophilic monomers onto chemically treated or O_2 plasma etched Nylon 4 substrate. The factors that affect the performances of membranes, such as deposition conditions and chemical or plasma etching conditions, were studied. The monomers used in this study were 1-vinyl-2-pyrrolidone (VP), 2-Hydroxyethyl methacrylate (HEMA), and Methyl methacrylate (MMA). The permeabilities of NaCl, urea, vitamin B_{12}, and albumin were measured, as were the water content, hydration, diffusivity, partition coefficient, and protein adsorption ratio of fibrinogen to albumin by membrane surface of plasma deposited membranes.

The permeabilities of NaCl, urea, vitamin B_{12}, and albumin of HEMA 5 w–1 h plasma deposited onto chemical treated Nylon 4 membranes were 2.896 ± 0.192, 3.301 ± 0.325, 0.010 ± 0.007, and 0.000×10^{-5} cm^2/min, respectively. The mole ratio of adsorbed fibrinogen to adsorbed albumin (F/A) is 0.26 ± 0.05, which is much lower than that of the pure Nylon 4 membrane (0.94 ± 0.06) and the Gambro® membrane (0.90 ± 0.15). The HEMA deposited membrane possesses the highest feasibility as hemodialysis material among those plasma deposited membranes considered.

INTRODUCTION

Previous work on Nylon 4 membranes has been carried out by Lonsdale et al. and by Orofino (cited by Huang et al.[1,2]), who found that Nylon 4 membranes behaved erratically in terms of their transport fluxes. Use of the improved poly(pyrrolidone) synthesis and membrane preparation method to improve performance of Nylon 4 membranes was reported by Huang et al.[1,2]

To improve the performance of Nylon 4 membranes, Lai et al.[3] utilized ^{60}Co r-ray irradiation, which induced hydrophilic vinyl monomers to be grafted onto Nylon 4 membranes for reverse osmosis desalination purposes. Jong et al.[4] used the chemical method to graft different hydrophilic monomers onto Nylon 4 membranes for reverse osmosis, ultrafiltration, and electrodialysis. Nylon 4 membranes were plasma modified to improve the surface energy, water content, and transport fluxes for dialysis by Lai et al.[5,6] Lai et al. used plasmas to induce hydrophilic monomers to graft onto Nylon 4 membranes for reverse osmosis desalination.

Plasma deposition has been utilized to increase surface energy, plasma polymerization, etching in membrane modification,[7–9] and biomedical applications.[10–11] Plasma polymerized surfaces are in both smooth and textured configurations, and tend to be relatively nonthrombogenic.[12]

The purpose of this study is to improve the permeability hemodialysis and the mole ratio of adsorbed fibrinogen to adsorbed albumin of membranes by plasma depositing the hydrophilic monomers, such as 1-Vinyl-2-pyrrolidone (VP), 2-Hydroxyethyl methacrylate (HEMA), and Methyl methacrylate (MMA), onto chemical or O_2 plasma treated Nylon 4 substrate. The dialysis permeability, hydration, water content, diffusion coefficient, partition coefficient, and protein absorption ratio of fibrinogen to albumin by membrane surface of plasma deposited membranes are measured. The solutes

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considered for the dialysis system are NaCl, urea, vitamin B_{12}, and albumin.

EXPERIMENTAL

Polymer Synthesis

Nylon 4 was synthesized by CO_2-initiated polymerization of 2-pyrrolidone using potassium 2-pyrrolidonate as a catalyst.[3] The molecular weights of the samples, measured by a Cannon-Fenske viscometer with m-cresol as a solvent, at 25°C, are about 38,000–46,000.

Membrane Preparation

Dialysis membrane was prepared from a formic acid casting solution of Nylon 4 added with n-PrOH as a swelling agent.[2,3] The detailed procedure of the membrane preparation was presented in our previous report.[3] The casting condition for the membrane was heated at 30°C for 40 min to evaporate solvent and it provided suitable pore size of membranes. The membrane thickness was in the range of 15–30 μm.

Annealing of the Membrane

Membranes were immersed in 25% formic acid aqueous solution at a temperature of 30°C for 4 h before testing.

Plasma Treatment

Bell jar type plasma deposition system PD-2S (Samco Ltd., Japan) was used in this study as in the previous report.[5] After the system had been pumped down (less than 0.06 mKg/cm^2), gas (O_2) or monomers (VP, HEMA, and MMA) are introduced into the reactor through the system, which is allowed to equilibrate at the desired pressure. The plasma is then ignited at the required power for a fixed time interval. The membranes are treated by O_2 plasma 20 W, 20 min at a pressure of 0.2 mKg/cm^2, then by monomers (VP, HEMA) plasma at a pressure of 0.08 mKg/cm^2 (1–10 W, 1 h), and by monomer (MMA) plasma at a pressure of 0.1 mKg/cm^2 (5–20 W, 20 min), and at a frequency of 13.65 MHz.

Dialysis Permeability

The dialysis appartus and calculation of the permeability has been reported in our previous report.[5]

Concentration of the vitamin B_{12} and albumin were determined by a UV-spectrophotometer (Milton Roy spectronic 1201).

Hydration, Water Content, Partition Coefficient, and Diffusion Coefficient

All those properties were measured and determined by the methods that were reported in our paper.[5]

Density

Density of the plasma-treated membrane was measured at 25°C using a density gradient column filled with mixtures of varying solutions of carbon tetrachloride/acetone for VP plasma deposited membranes, and carbon tetrachloride/ethanol for MMA plasma deposited onto Nylon 4 membranes.

The Mole Ratio of Adsorbed Fibrinogen to Adsorbed Albumin

The membranes of 8 cm^2 in area were immersed into CPBS buffer solution[13] (0.01 M sodium citrate, 0.01 M sodium phosphate, 0.12 M sodium chloride, pH 7.4) for 12 h. The membranes surfaces were quickly blotted with absorbent paper to remove surface buffer solution, and then were fixed. The membranes were next filled with 2 mL of protein solution at 30°C for 1 h. Concentration of albumin and fibrinogen were 1.0 and 0.1 mg/mL, respectively, in CPBS buffer solution. After desorption, the membranes were rinsed by deionized water. The sorbed proteins were desorbed with 1% Triton X-100 and 1% SDS in 0.01 N NaOH at 30°C with shaking (100 rpm) for 1 h.[14] Of the boric acid buffer solution, 1.5 mL (0.1 M H_3BO_4 and KCl, pH 9.3), was added into the desorbed proteins (1 mL) and was mixed. Mixed in next was 0.5 mL of fluorescamine in acetone (20 mg/100 mL) with vigorous stirring. The protein quantity was determined by a fluorescence spectrophotometer (Hitachi Co., F-2000), and the fluorescence intensity was measured at 392 nm with excitation and at 491 nm with emission comparison with calibration curves.

RESULT AND DISCUSSION

Effect of Maturation Time on NaCl Permeability

It was observed that Nylon 4 molecular chains could not be extended thoroughly if the dissolving time in the 90% formic acid aqueous solution was not suf-
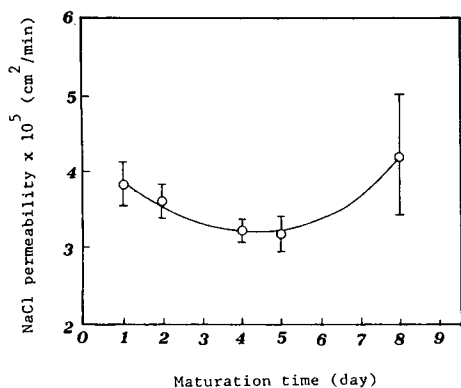
Figure 1 Effect of maturation time on NaCl permeability of pure Nylon 4 membrane. Solvent: 90% formic acid.

Figure 2 Effect of supply power on NaCl permeability of VP plasma deposited membrane. Plasma deposition condition: 1 h-0.08 mKg/cm^2; (●) membrane substrate with chemical treatment; (○) membrane substrate with O$_2$ plasma treatment.

ficient. But a serious degradation effect exists in Nylon 4 with 90% formic acid that has a longer maturation time.

Figure 1 shows that the sodium chloride (NaCl) permeability decreases with increasing maturation time and levels off at about 4 or 5 d, however, the permeability increases over 5 d. This suggests that the proper maturation time for a casting solution is about 4 d in order to achieve better reproducibility of the permeability of the membrane.

Effect of Monomers Plasma Deposition

After chemical treatment or O$_2$ plasma etching, Nylon 4 membranes are treated by plasma VP deposition. The plasma deposition time is considered to fix in 1 h in order to discover the most suitable power supply for plasma deposited VP. From Figure 2 and
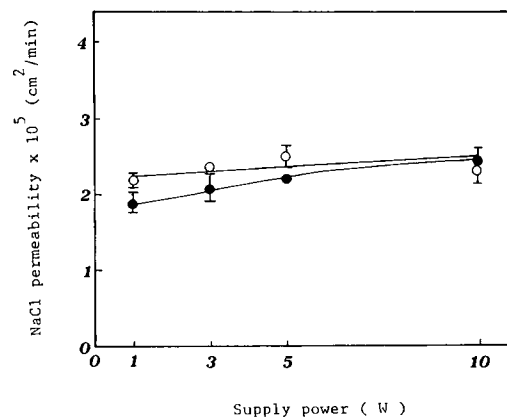
Tables I and II, it is shown that the permeability of NaCl for VP plasma, deposited onto chemical treating or plasma etching Nylon 4 membrane, increases as supply power increases from 1 to 10 W. The membrane is not only deposited but also etched in the range of 3 to 10 W. The permeabilities of NaCl and urea solutes (low molecular solutes), for VP deposited membrane with plasma etching, are about the same with chemical treating. The permeability of albumin (high molecular solute) for deposited membrane by 25% formic acid aqueous solution is almost zero. But the permeability of albumin for deposited membrane by O$_2$ plasma etched is 0.068–0.496 × 10^{-5} cm^2/min.

The second monomer considered is 2-Hydroxy-ethyl-methacrylate (HEMA). From the results, as

Table I Effect of Plasma Etching and VP Deposition on Membrane Performances

Untreated Nylon 4	O$_2$ Plasma Etching (20 W–20 min)					Plasma Deposited (VP) after Plasma Etching (Deposited Time: 1 h)[a]			
$P_{NaCl} \times 10^5$ (cm^2/min)	$P_{NaCl} \times 10^5$ (cm^2/min)	$P_{Urea} \times 10^5$ (cm^2/min)	$P_{B12} \times 10^5$ (cm^2/min)	$P_{Oval} \times 10^5$ (cm^2/min)	Power (W)	$P_{NaCl} \times 10^5$ (cm^2/min)	$P_{Urea} \times 10^5$ (cm^2/min)	$P_{B12} \times 10^5$ (cm^2/min)	$P_{Oval} \times 10^5$ (cm^2/min)
2.408 ± 0.370	3.130 ± 0.097	2.693 ± 0.400	0.351 ± 0.085	0.426 ± 0.242	1	2.427 ± 0.187	2.650 ± 0.474	0.312 ± 0.157	0.068 ± 0.030
2.993 ± 0.264	3.307 ± 0.235	2.910 ± 0.180	0.394 ± 0.230	0.418 ± 0.194	3	2.818 ± 0.046	2.901 ± 0.454	0.205 ± 0.065	0.140 ± 0.191
2.889 ± 0.586	3.494 ± 0.266	2.896 ± 0.156	0.746 ± 0.561	0.860 ± 0.747	5	3.002 ± 0.323	2.998 ± 0.620	0.183 ± 0.086	0.158 ± 0.113
2.605 ± 0.470	3.468 ± 0.360	2.786 ± 0.222	0.728 ± 0.218	0.603 ± 0.081	10	2.581 ± 0.330	2.731 ± 0.465	0.195 ± 0.033	0.496 ± 0.423

[a] Plasma depositing pressure: 0.08 mKg/cm^2.

Table II   Effect of Chemical Treating and VP Deposition on Membrane Performances

Untreated Nylon 4	25% Formic Acid Treating (30°C-4 h)				Plasma Deposited (VP) after Chemical Treating (Deposited Time: 1 h)[a]				
$P_{NaCl} \times 10^5$ (cm²/min)	$P_{NaCl} \times 10^5$ (cm²/min)	$P_{Urea} \times 10^5$ (cm²/min)	$P_{B12} \times 10^5$ (cm²/min)	$P_{Oval} \times 10^5$ (cm²/min)	Power (W)	$P_{NaCl} \times 10^5$ (cm²/min)	$P_{Urea} \times 10^5$ (cm²/min)	$P_{B12} \times 10^5$ (cm²/min)	$P_{Oval} \times 10^5$ (cm²/min)
1.583 ± 0.103	3.169 ± 0.266	2.572 ± 0.425	0.058 ± 0.039	0.003 ± 0.004	1	1.799 ± 0.298	1.893 ± 0.273	0.002 ± 0.003	0.000 ± 0.000
1.850 ± 0.099	3.037 ± 0.168	2.600 ± 0.267	0.187 ± 0.129	0.064 ± 0.052	3	2.188 ± 0.429	2.154 ± 0.179	0.104 ± 0.017	0.049 ± 0.038
1.830 ± 0.115	3.568 ± 0.793	2.452 ± 0.135	0.240 ± 0.200	0.141 ± 0.120	5	2.380 ± 0.097	2.437 ± 0.037	0.124 ± 0.033	0.004 ± 0.005
2.242 ± 0.477	3.411 ± 0.265	2.824 ± 0.319	0.351 ± 0.348	0.309 ± 0.210	10	2.801 ± 0.470	2.965 ± 0.485	0.137 ± 0.022	0.000 ± 0.000

[a] Plasma depositing pressure: 0.08 mKg/cm².

shown in Figure 3 and Tables III and IV, the permeability decay of NaCl decreases as the supply power increases. For HEMA plasma deposited onto O_2 plasma etching Nylon 4 membrane, the permeability of NaCl (low molecular solute) is about $2.321-2.756 \times 10^{-5}$ cm²/min, the permeability of vitamin B_{12} (moderate molecular solute) is $0.101-0.185 \times 10^{-5}$ cm²/min, and the permeabilities of albumin (high molecular solute) are 0.112, 0.030, 0.010, and 0.186×10^{-5} cm²/min for supply power of 1, 3, 5, and 10 W, respectively. There is a more significant result from HEMA plasma deposited onto chemical treating Nylon 4 membrane. The permeabilities of NaCl, urea, and vitamin B_{12} are obtained about $2.574-2.896 \times 10^{-5}$ cm²/min, $2.646-3.010 \times 10^{-5}$ cm²/min, and $0.010-0.465 \times 10^{-5}$ cm²/min, respectively. The permeability of albumin is zero except that the supply power is 1 W. The permeability of albumin is 0.148×10^{-5} cm²/min. More improved permeability of plasma deposited HEMA is obtained by using chemical treating than by using plasma etching.

For MMA plasma deposited membrane, it is shown that the permeability decay decreases as supply power increases, as shown in Figure 4 and Tables V and VI. The result obtained from MMA plasma deposited onto chemical treating or plasma etching membrane is similar to that from HEMA plasma deposited onto chemical or plasma etching membrane.

An ideal hemodialysis membrane contains high permeabilities of low molecular solutes, medium permeabilities of moderate molecular solutes, and low permeabilities of high molecular solutes. VP, HEMA, and MMA monomers respectively plasma deposited onto chemical treating membrane, which preferred that they be plasma deposited onto O_2 plasma etching membrane. On the basis of the permeability of NaCl, the permeabilities of the chemical treating membrane by plasma deposited HEMA at 5 W supply power are $P_{NaCl} = 2.896 \times 10^{-5}$ cm²/min, $P_{urea} = 3.301 \times 10^{-5}$ cm²/min, $P_{vitamin\ B_{12}} = 0.010 \times 10^{-5}$ cm²/min, and $P_{albumin} = 0.000$; the permeabilities of VP plasma deposited onto chemical treating Nylon 4 membrane at 10 W supply power are $P_{NaCl} = 2.801 \times 10^{-5}$ cm²/min, $P_{urea} = 2.965 \times 10^{-5}$ cm²/min, $P_{vitamin\ B_{12}} = 0.137 \times 10^{-5}$ cm²/min, and $P_{albumin} = 0.000$. The results are improved the most.
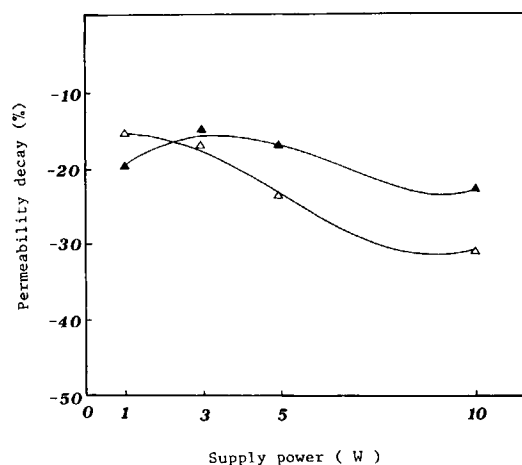

Figure 3 Effect of supply power on NaCl permeability decay of HEMA plasma deposited membrane. Plasma deposition condition: 1 h-0.08 mKg/cm²; (▲) membrane substrate with chemical treatment; (△) membrane substrate with O_2 plasma treatment.

Table III   Effect of Plasma Etching and HEMA Deposition on Membrane Performances

Untreated Nylon 4	O_2 Plasma Etching (20 W–20 min)				Plasma Deposition HEMA after Plasma Etching (Deposited Time: 1 h)[a]				
$P_{NaCl} \times 10^5$ (cm²/min)	$P_{NaCl} \times 10^5$ (cm²/min)	$P_{Urea} \times 10^5$ (cm²/min)	$P_{B12} \times 10^5$ (cm²/min)	$P_{Oval} \times 10^5$ (cm²/min)	Power (W)	$P_{NaCl} \times 10^5$ (cm²/min)	$P_{Urea} \times 10^5$ (cm²/min)	$P_{B12} \times 10^5$ (cm²/min)	$P_{Oval} \times 10^5$ (cm²/min)
2.618 ± 0.033	3.258 ± 0.106	2.543 ± 0.301	0.363 ± 0.211	0.083 ± 0.047	1	2.756 ± 0.062	2.667 ± 0.198	0.174 ± 0.141	0.112 ± 0.146
2.600 ± 0.034	3.303 ± 0.184	2.635 ± 0.164	0.476 ± 0.164	0.536 ± 0.360	3	2.745 ± 0.372	3.275 ± 0.573	0.189 ± 0.099	0.030 ± 0.042
2.838 ± 0.492	3.524 ± 0.246	2.801 ± 0.176	0.207 ± 0.130	0.052 ± 0.060	5	2.696 ± 0.298	3.025 ± 0.746	0.159 ± 0.081	0.010 ± 0.014
2.754 ± 0.259	3.374 ± 0.296	2.735 ± 0.164	0.508 ± 0.235	0.244 ± 0.314	10	2.321 ± 0.373	2.699 ± 0.308	0.101 ± 0.028	0.186 ± 0.262

[a] Plasma depositing pressure: 0.08 mKg/cm².

The HEMA plasma 3 W, 1 h deposited onto chemical treating Nylon 4 membrane, possesses the high vitamin B_{12} permeability of 0.274×10^{-5} cm²/min.

Water Content and Hydration

For VP deposited membrane, Figure 5 shows that its water content and hydration increases with increasing the supply power. This is due to the increase of the amount of the highly hydrophilic grafted polymer. The hydration values are almost the same both for testing in 0.85 wt % of NaCl aqueous solution and for testing in 0.5 wt % urea aqueous solution.

Figure 6 shows that the water content of HEMA plasma deposited membrane decreases with increasing the supply power. It is assumed that membrane crosslinking exists.

From Figure 7 one can see that MMA is not a hydrophilic monomer, so the result is that water content and hydration decreases with increasing the supply power.

Partition Coefficient and Diffusion Coefficient

The relation between solute permeability, partition coefficient, and diffusion coefficient is expressed in the following equation:

$$D_{2,13} = P_{2,13}/K_2 \tag{1}$$

where the subscripts 1, 2, 3, and 13 refer to water solute, polymer, and water-swollen polymer, respectively. The diffusion coefficient D was calculated by using eq. (1). Figures 8, 9, and 10 show that when

Table IV   Effect of Chemical Treating and HEMA Deposition on Membrane Performances

Untreated Nylon 4	25% Formic Acid Treating (30°C–4 h)	Plasma Deposited (HEMA) after Chemical Treating (Deposited Time: 1 h)[a]				
$P_{NaCl} \times 10^5$ (cm²/min)	$P_{NaCl} \times 10^5$ (cm²/min)	Power (W)	$P_{NaCl} \times 10^5$ (cm²/min)	$P_{Urea} \times 10^5$ (cm²/min)	$P_{B12} \times 10^5$ (cm²/min)	$P_{Oval} \times 10^5$ (cm²/min)
1.662 ± 0.267	3.415 ± 0.383	1	2.717 ± 0.722	2.964 ± 0.442	0.465 ± 0.331	0.148 ± 0.209
2.041 ± 0.241	3.039 ± 0.174	3	2.574 ± 0.211	2.646 ± 0.130	0.274 ± 0.260	0.000 ± 0.000
2.279 ± 0.205	3.504 ± 0.262	5	2.896 ± 0.192	3.301 ± 0.325	0.010 ± 0.007	0.000 ± 0.000
2.153 ± 0.204	3.482 ± 0.129	10	2.672 ± 0.207	2.845 ± 0.086	0.061 ± 0.062	0.000 ± 0.000

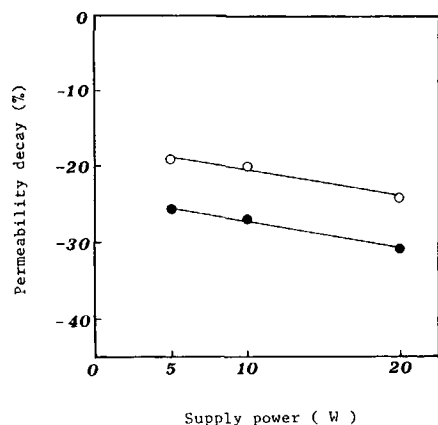[a] Plasma depositing pressure: 0.08 mKg/cm².

Figure 4 Effect of supply power on NaCl permeability decay of MMA plasma deposited membrane. Plasma deposition condition: 20 min–0.1 mKg/cm^2; (■) membrane substrate with chemical treatment; (□) membrane substrate with O$_2$ plasma treatment.

hydration increases, the partition coefficient decreases, but the diffusion coefficient increases. This is the same result as that obtained by Yoon et al.[15]

The Mole Ratio of Adsorbed Fibrinogen to Adsorbed Albumin

Albumin had thromboresistant ability, whereas fibrinogen promoted platelet adhesion onto the polymer surfaces. Therefore, the mole ratio of adsorbed fibrinogen to adsorbed albumin was used to evaluate blood compatibility of membranes in our research.

Figure 11 shows the desorption isotherms of fibrinogen and albumin on Nylon 4 membrane. Untreated Nylon 4 membranes are adsorbed with albumin at a concentration of 1 mg/mL at 30°C for 1 h. The maximum desorption appears in 10 min, then decreases with time until equilibrium in 30 min. Desorption requires a short time, possibly because of a weak interaction between Nylon 4 membrane and protein, or because of the degree of solubility with albumin used in eluting agent changed with time. But for the fibrinogen desorption isotherm, a larger amount of fibrinogen desorption from adsorbed fibrinogen Nylon 4 is obtained compared with albumin desorption. The desorption reaches the maximum in 10 min when it is in the state of equilibrium.

Table V   Effect of Plasma Etching and MMA Deposition on Membrane Performances

Untreated Nylon 4	O$_2$ Plasma Etching (20 W–20 min)	Plasma Deposited (MMA) after Plasma Etching (Deposited Time: 20 min)[a]				
$P_{NaCl} \times 10^5$ (cm^2/min)	$P_{NaCl} \times 10^5$ (cm^2/min)	Power (W)	$P_{NaCl} \times 10^5$ (cm^2/min)	$P_{Urea} \times 10^5$ (cm^2/min)	$P_{B12} \times 10^5$ (cm^2/min)	$P_{Oval} \times 10^5$ (cm^2/min)
2.539 ± 0.223	3.106 ± 0.089	5	2.504 ± 0.143	2.830 ± 0.194	0.332 ± 0.203	0.230 ± 0.154
2.483 ± 0.405	3.174 ± 0.091	10	2.544 ± 0.195	2.825 ± 0.082	0.504 ± 0.356	0.014 ± 0.020
2.454 ± 0.075	3.478 ± 0.240	20	2.641 ± 0.382	2.565 ± 0.346	0.335 ± 0.007	0.167 ± 0.139

[a] Plasma depositing pressure: 0.10 mKg/cm^2.

Table VI   Effect of Chemical Treating and MMA Deposition on Membrane Performances

Untreated Nylon 4	25% Formic Acid Treating (30°C–4 h)	Plasma Deposited (MMA) after Chemical Treating (Deposited Time: 20 min)[a]				
$P_{NaCl} \times 10^5$ (cm^2/min)	$P_{NaCl} \times 10^5$ (cm^2/min)	Power (W)	$P_{NaCl} \times 10^5$ (cm^2/min)	$P_{Urea} \times 10^5$ (cm^2/min)	$P_{B12} \times 10^5$ (cm^2/min)	$P_{Oval} \times 10^5$ (cm^2/min)
2.467 ± 0.360	3.318 ± 0.550	5	2.462 ± 0.354	2.867 ± 0.264	0.055 ± 0.064	0.000 ± 0.000
2.347 ± 0.164	3.241 ± 0.491	10	2.362 ± 0.776	3.333 ± 0.493	0.075 ± 0.060	0.013 ± 0.018
2.184 ± 0.131	3.330 ± 0.342	20	2.309 ± 0.310	3.327 ± 0.281	0.142 ± 0.108	0.066 ± 0.066

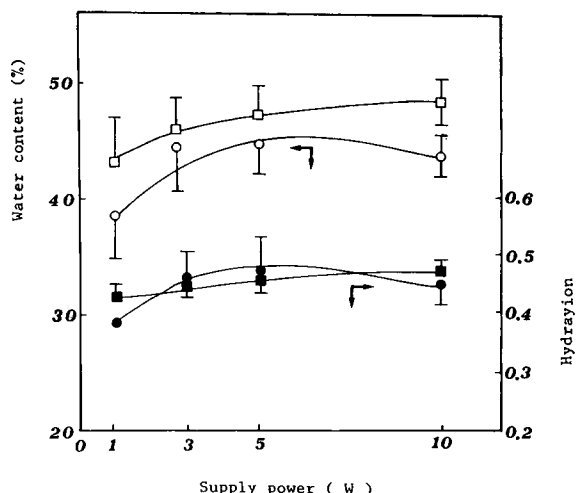[a] Plasma depositing pressure: 0.10 mKg/cm^2.

Figure 5 Effect of supply power on water content and hydration of VP plasma deposited membrane. Deposited time: 1 h, hydration testing in 0.85 wt % NaCl aqueous solution. (□) membrane substrate with chemical treatment; (○) membrane substrate with O_2 plasma treatment.

Table VII shows that the mole ratios of adsorbed fibrinogen to adsorbed albumin on untreated Nylon 4 membranes and commercialized Gambro® membrane are 0.94 ± 0.06 and 0.9 ± 0.15, respectively. The mole ratios of adsorbed fibrinogen to adsorbed albumin of Nylon 4 membranes with chemical treatment or O_2 plasma etching are 0.53 and 0.46, respectively. It is found that for both the above examples, treated Nylon 4 membranes have a lower mole ratio than the untreated and commercialized Gambro® membranes.

Furthermore, for the O_2 plasma treatment process, the blood compatibility of the membranes are better than the membrane with 25% formic acid
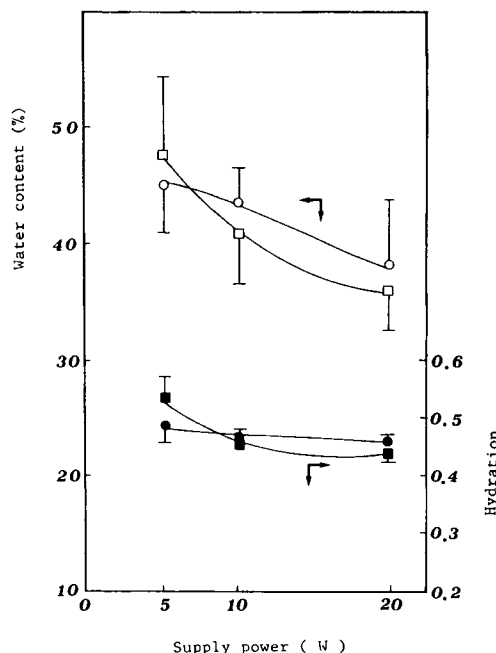

Figure 7 Effect of MMA plasma deposition supply power on water content and hydration. Deposited time: 20 min, hydration testing in 0.85 wt % NaCl aqueous solution. (□) membrane substrate with chemical treatment; (○) membrane substrate with O_2 plasma treatment.

treatment. This is due to the increasing hydrophilic functional groups on the membrane surface, such as ether, hydroxyl, and ketone.

Nylon 4 membranes are treated with 25% formic acid or O_2 plasma and then are plasma deposited by HEMA, VP, and MMA monomers, respectively. The mole ratio of adsorbed fibrinogen to adsorbed albumin on HEMA plasma deposited Nylon 4 membranes decreases to a minimum, then increases with
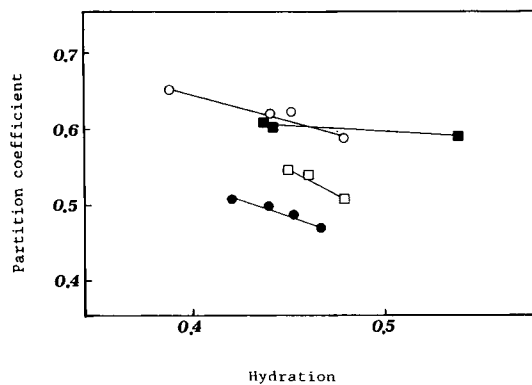

Figure 6 Effect of supply power on water content of HEMA plasma deposited membrane. Deposited time: 1 h, water content testing in water. (▲) membrane substrate with chemical treatment; (△) membrane substrate with O_2 plasma treatment.

Figure 8 Effect of hydration on partition coefficient. (●) VP deposited onto chemical; (○) plasma treating membrane; (■) MMA deposited onto chemical; (□) O_2 plasma treating membrane.
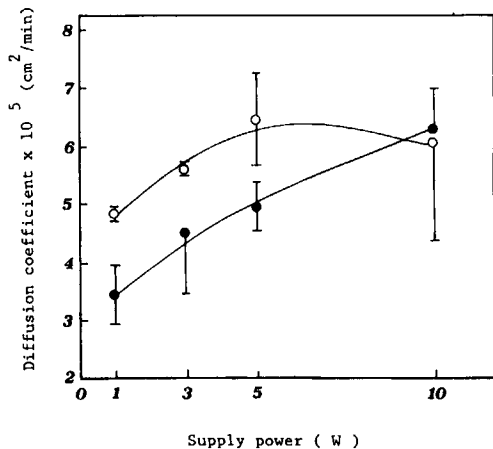
Figure 9 Effect of VP plasma deposition supply power on diffusion coefficient. (●) membrane substrate with chemical treatment; (○) membrane substrate with O_2 plasma treatment.

the supply power increasing, as shown in Figure 12. In other words, the surfaces of the membranes are well modified by the increase in the amount of HEMA plasma deposition. This is similar to the trend for MMA plasma deposited membrane, with the relationship between the mole ratio of adsorbed fibrinogen to adsorbed albumin with supply power increasing, as shown in Figure 13. However the relationship does not change for the mole ratio of adsorbed fibrinogen to adsorbed albumin onto VP plasma deposited membrane, as shown in Figure 14.

As shown in Table VII, the blood compatibility is significantly improved by HEMA deposition, for example, HEMA deposited chemical treated Nylon 4 membrane at 5 W supply power possesses a fibrinogen/albumin absorbed ratio of 0.26 ± 0.05.
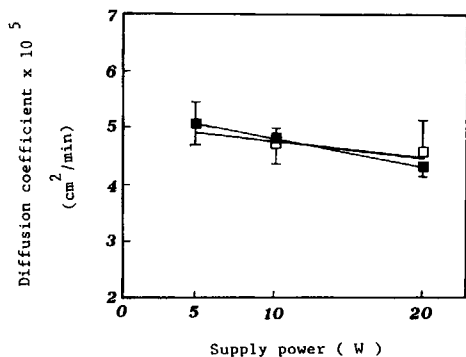

Figure 10 Effect of MMA plasma deposition supply power on diffusion coefficient. (■) membrane substrate with chemical treatment; (□) membrane substrate with O_2 plasma treatment.
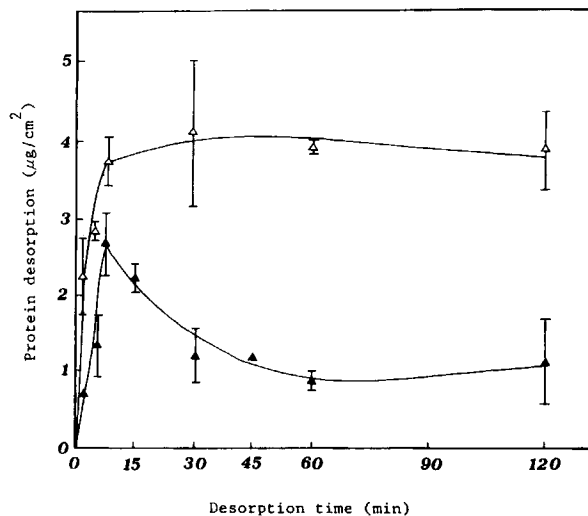

Figure 11 Desorption isotherms of fibrinogen and albumin on Nylon 4 membranes. Nylon 4 membranes were adsorbed with proteins at concentration 1 ug/mL for 1 h at 30°C. The membranes were rinsed and then desorbed with 1% SDS and Triton X-100 in 0.01 N NaOH at 30° with shaking (100 rpm). (△) fibrinogen; (▲) albumin.

CONCLUSION

This study suggests that the maturation time of casting solution is about 4 days for better reproducibility of the solutes' permeability of membranes.

The relationships of water content or hydration and plasma power supply are different for VP, HEMA, and MMA deposited membranes due to hydrophilicity and crosslinking. The results show that
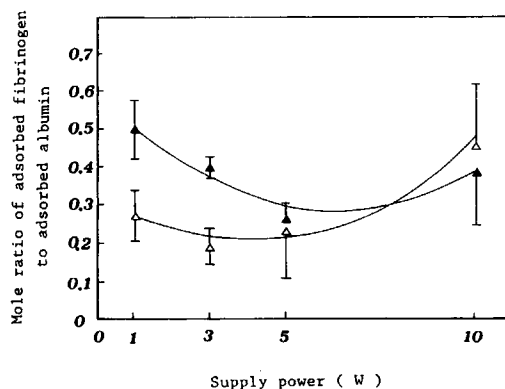

Figure 12 Effect of supply power on the mole ratio of adsorbed fibrinogen to adsorbed albumin for HEMA plasma deposited membranes. Plasma deposition condition: 1 h–0.08 mKg/cm²; (▲) membrane substrate with chemical treatment; (△) membrane substrate with O_2 plasma treatment.

Table VII   Effect of Various Membranes on the Mole Ratio of Adsorbed Fibrinogen to Adsorbed Albumin

Materials	Treated Conditions	Γ_F (ug/cm^2)	Γ_A (ug/cm^2)	Mole Ratio (F/A)
Nylon 4	Untreated	3.03 ± 0.56	0.67 ± 0.13	0.94 ± 0.06
	[a]	1.45 ± 0.33	0.61 ± 0.09	0.53 ± 0.05
	[b]	1.09 ± 0.39	0.55 ± 0.34	0.46 ± 0.09
	[c]	0.82 ± 0.08	0.67 ± 0.15	0.26 ± 0.05
	[d]	0.90 ± 0.23	1.01 ± 0.10	0.19 ± 0.05
	[e]	0.86 ± 0.30	0.61 ± 0.06	0.29 ± 0.11
Gambro® Dialysis Membrane		3.54 ± 0.82	0.79 ± 0.08	0.90 ± 0.15

Adsorbed condition: Total albumin and fibrinogen concentration, 1 mg/mL and 0.1 mg/mL, respectively. Adsorption was done for 1 h at 30°C in a CPBS buffer solution, pH 7.40, was rinsed, and then desorbed for 1 h in 1% SDS, 1% Triton X-100, and 001N NaOH.
[a] 25% formic acid aqueous solution treatment.
[b] O_2 plasma 20 W–20 min etching.
[c] HEMA plasma 5 W–1 h deposited onto 25% formic acid aqueous solution treated membrane.
[d] HEMA plasma 3 W–1 h deposited onto O_2 plasma 20 W–20 min etching membranes.
[e] VP plasma 10 W–1 h deposited onto 25% formic acid aqueous solution treated membranes.

when hydration increases, the partition coefficient decreases, and the diffusion coefficient increases for the prepared composite membranes.

Reasonable permeabilities of NaCl, urea, vitamin B_{12}, and albumin, and the mole ratio of adsorbed fibrinogen to adsorbed albumin on membrane surface for plasma deposited Nylon 4 membranes, can be obtained.

For example, the permeabilities of NaCl, urea, vitamin B_{12}, and albumin of HEMA 5 w–1 h plasma deposited onto chemical treated Nylon 4 membranes are 2.896 ± 0.192, 3.301 ± 0.325, 0.010 ± 0.007, and

0.000×10^{-5} cm^2/min, respectively. The mole ratio of adsorbed fibrinogen to adsorbed albumin (F/A) is 0.26 ± 0.05, which is much lower than that of the pure Nylon 4 membrane (0.94 ± 0.06) and the Gambro® membrane (0.90 ± 0.15). The HEMA deposited membrane possesses the highest feasibility as hemodialysis material among those plasma deposited membranes considered.

The permeabilities of NaCl, urea, vitamin B_{12}, and albumin of HEMA 5 w–1 h, which are plasma deposited onto chemical treated Nylon 4 membranes, are 2.896 ± 0.192, 3.301 ± 0.325, 0.010 ± 0.007, and 0.000 × 10^{-5} cm^2/min, respectively. The mole ratio of adsorbed fibrinogen to adsorbed
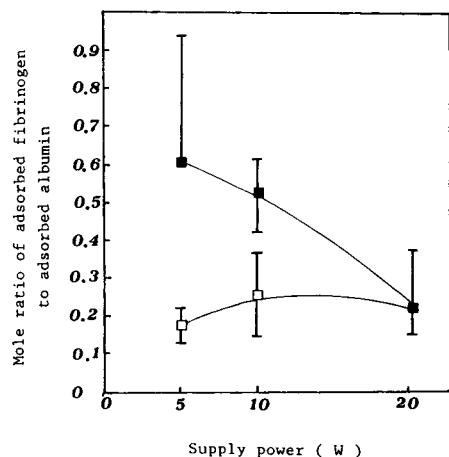

Figure 13   Effect of supply power on the mole ratio of adsorbed fibrinogen to adsorbed albumin for MMA plasma deposited membranes. Plasma deposition condition: 20 min–0.1 mKg/cm^2; (■) membrane substrate with chemical treatment; (□) membrane substrate with O_2 plasma treatment.
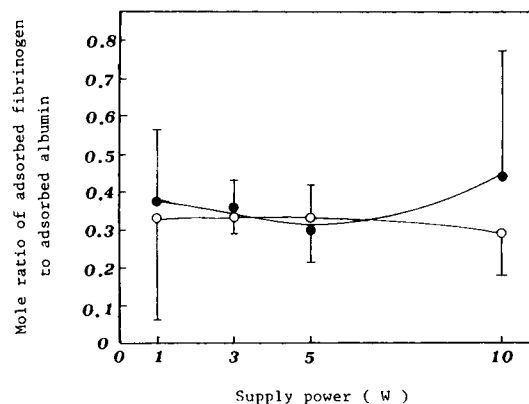

Figure 14   Effect of supply power on the mole ratio of adsorbed fibrinogen to adsorbed albumin for VP plasma deposited membrane. Plasma deposition condition: 1 h–0.08 mKg/cm^2. (●) membrane substrate with chemical treatment; (○) membrane substrate with O_2 plasma treatment.

albumin (F/A) is 0.26 ± 0.05, which is much lower than that of the pure Nylon 4 membrane (0.94 ± 0.06) and the Gambro® membrane (0.90 ± 0.15). The HEMA deposited membrane possesses the highest feasibility as hemodialysis material among those plasma deposited membranes considered.

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