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Dialysis Performance of the Modified Poly(vinyl alcohol) Membranes

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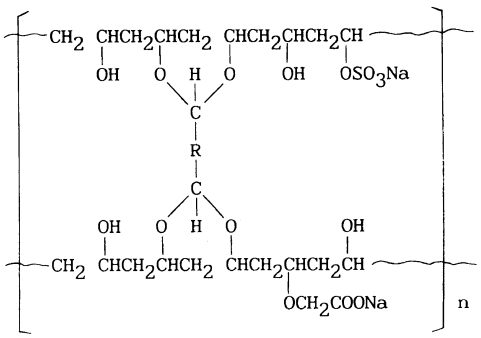
ABSTRACT: Based on the anionic groups which appear in heparin, sulfonated poly(vinyl alcohol) (S-PVA), and carboxymethylated poly(vinyl alcohol) (C-PVA) were synthesized. Cross-linked blendmer (XSC-PVA)s were obtained by mixing two aqueous solutions of the anionic charged PVA, whose degrees of substitution were 25%, respectively, using glutaraldehyde as the cross-linking agent. These XSC-PVA membranes were prepared under various conditions in order to determine a suitable mixing ratio of S-PVA to C-PVA and concentration of cross-linking agent. Effect of amount of cross-linker on permeability and mechanical property of the membranes was also examined.

KEY WORDS Sulfonated Poly(vinyl alcohol) / Carboxymethylated Poly-(vinyl alcohol) / Cross-Linked Blendmers / Dialysis Membrane /

The structure of water in membranes is very important when a diffusion takes place through membranes swollen with water.[1] A solute permeation is not taken place in the bound water region that has strong hydrogen bond but in the free water region. Factors that affect to the hydrogen bond of water to the membrane material can be defined as chemical structure of membranes, *i.e.*, hydrogen bonding ability of functional groups.

Polar groups such as $-SO_3H$, $-COOH$, $-NH_2$, and $-CHO$ make hydrogen bond with water but have tendency to combine with themselves. This effect weakens the coherence of water cluster, which cause diffusion of solute efficiently.[2-5]

Poly(vinyl alcohol), that has a good membrane property, mechanical strength and easily cross-linkable hydroxy groups, has been widely used as membrane and biomedical material. Cross-linked PVA membrane also has a good hydrophilic character that causes efficiently diffusion of solutes, and the ability of hydrogen bond with water and the degree of crystallinity can be controlled with the variation of cross-linking density, and thus it is supposed that owing to these variations the diffusion character of solute through the membrane could be controlled.[6-11] Two types of modified PVA containing sulfate and carboxylic group were prepared respectively, and they were blended and cross-linked under various conditions to make membranes which can be supplied with a test of dialysis performance, because these cross-linked blendmers showed more improved anticoagulation activity.[12]



Cross-linked blendmer

EXPERIMENTAL

Material

Urea, creatinine, and poly(ethylene glycol) (PEG) were obtained from Wako Pure Chemicals and was used without purification. Vitamine B_{12} (V_B12) was supplied from Rhone Poulence Co. All other materials were same as a previous paper.[12]

Modification of Poly(vinyl alcohol)

Preparation of PVAs containing carboxymethyl groups (C-PVA),[13] sulfate groups (S-PVA),[14,15] and their cross-linked blendmer (XSC-PVA) were same as a previous paper.[12]

Measurement of Physical Properties

The degree of swelling, tensile strength and elongation were measured according to the methods of previous paper.[12]

Dialysis Performance and Ultrafiltration Rate

Dialysis performance was measured by the continuous flow dialysis apparatus as shown in Figure 1, which contains the flat plate type dialysis cell as illustrated in Figure 2.

The dialyzer consists of two compartments, each of which contains a flow channel and baffles to obtain uniform flow patterns through the cell. One compartment of the cell is connected *via* a centrifugal micro pump to a small reservior containing the solution to be dialyzed. The other compartment is connected to a reservior containing deionized water as a dialysate. All the dialysis cell and two reserviors are immersed in water bath at 37°C.

Ultrafiltration rate was measured by the ultrafiltration cell (Amicon model 8050). Data on dialysis performance and ultrafiltration rate were obtained using aqueous solutions of 100—2,000 ppm with various solutes. Solute concentrations in the feed and product solutions were determined by means of refractometer (Waters R 403). The effective area of the membrane used in the cell was 26 cm^2 for dialysis and 13.4 cm^2 for ultrafiltration experiment.

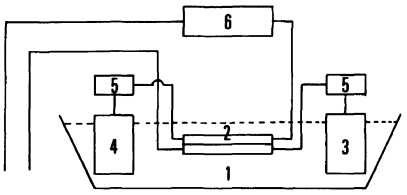


Figure 1. Schematic diagram of continuous flow dialysis apparatus: 1, water bath; 2, dialysis cell; 3, deionized water reservoir; 4, dialyzing solution reservoir; 5, centrifugal pumps; 6, refractometer.

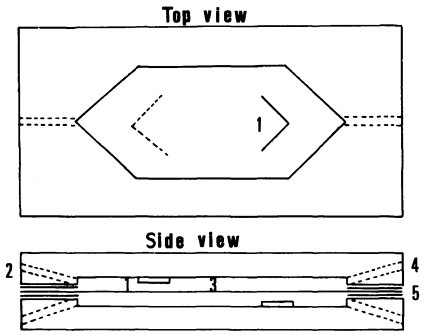


Figure 2. Schematic diagram of flat plate type dialysis cell: 1, flow baffle; 2, inlet port; 3, membrane; 4, outlet port; 5, O-ring.

RESULTS AND DISCUSSION

Carboxymethyl group in the C-PVA was confirmed by FT-IR spectroscopy and the degree of substitution was measured with acid-base titration method. It was shown that the degree of substitution of the carboxymethyl group was increased with increasing the concentration of monochloroacetic acid. The degree of substitution in the S-PVA was determined by sulfur analysis and elementary analysis. The degradation of PVA accompanied by the sulfonation was confirmed by solution viscometry. Though the substitution ratio was increased with increasing the concentration of sulfur acid, the degradation was increased. In order to diminish the degradation, substitution ratios of two anionic groups were controlled at 25%, respectively.

Table I. Characteristics of modified PVA samples

Sample	Degree of swelling/%	Tensile strength/ kg mm^{-2}		Elongation/%		Urea permeability[a]/ $\times 10^{-1}$ cm min^{-3}
		Dry	Swollen	Dry	Swollen	
PVA	—	7.03	—	—	—	—
X-PVA	420	12.43	2.38	27	82	10.0
XS-PVA	382	0.73	0.33	12	46	22.5
XC-PVA	297	3.76	1.14	180	319	17.7
XSC-1	314	4.48	0.70	160	290	15.1
XSC-2	326	3.98	0.66	146	270	15.8
XSC-3	33	2.71	0.61	126	207	12.5
XSC-4	344	1.55	0.46	122	173	12.0

[a] Concentration of urea, 1,000 ppm.

X-PVA, cross-linked PVA; XS-PVA, cross-linked sulfonated PVA; XC-PVA, cross-linked carboxymethylated PVA; XSC-1, cross-linked blendmer (S : C = 1 : 4); XSC-2, cross-linked blendmer (S : C = 2 : 3); XSC-3, cross-linked blendmer (S : C = 3 : 2); XSC-4, cross-linked blendmer (S : C = 4 : 1).

XSC-PVA was confirmed by IR spectra. Figure 3 shows that an absorption band at 1140 cm^{-1}, which based on the crystallinity of PVA, is decreased with increasing the concentration of glutaraldehyde. On the contrary, the absorption based on carbonyl of acetal group around 1100 cm^{-1} is increased gradually.

The characteristics of samples are shown in Table I. In the case of XSC-PVA, the degree of swelling is increased with increasing the concentration of S-PVA, in the order of XSC-1, XSC-2, XSC-3, and XSC-4. The tensile strength and elongation of XSC-PVA are decreased with increasing the concentration of S-PVA. This effect can be explicable because the S-PVA has brittle mechanical property which was caused by losing its molecular weight by the degradation during sulfonation.[12,17] As compared with dry state, tensile strength of all swollen samples shows a trend of decrease, but have more improved values of elongation than those of dried samples. The phenomena that cross-linked blendmers have decreased permeation properties than those of sulfonated and carboxylated PVA, result from side reactions such as esterification[17] and lactonization[18] between hydroxy group and two polar groups, and then free water content in the XSC-3 PVA membrane is changed.

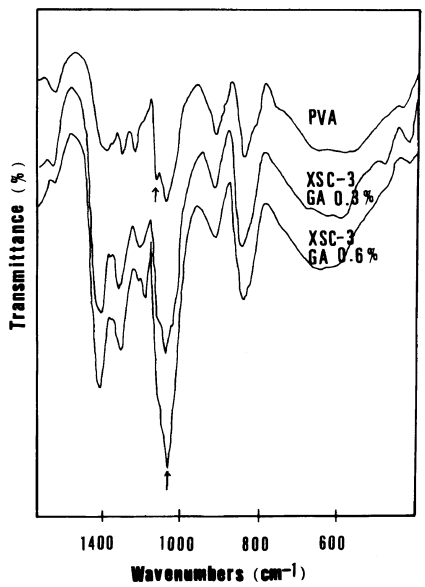


Figure 3. IR spectra of cross-linked blendmer.

The urea permeabilities of the XSC-PVA membranes varied slightly. Since XCS-PVA, however, showed the best anticoagulation activity in previous paper[16] and has average mechanical property and permeability, this was selected for intensive study.

Concentrations of the cross-linking agent,

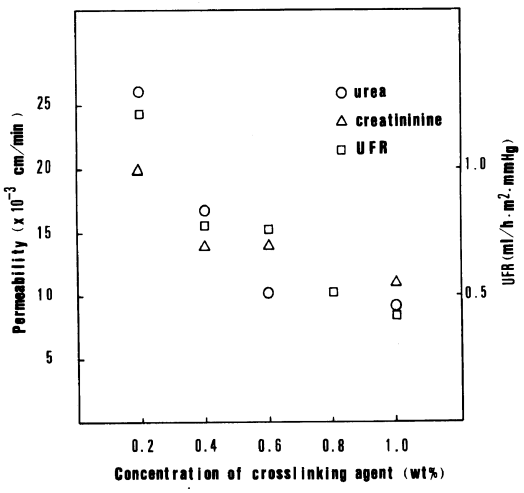


Figure 4. The effect of concentration of cross-linker on solutes permeability and ultrafiltration rate of XSC-3 membrane.

Table II. Solute permeability of XSC-3 membranes

Solute	M.W.	Concentration / ppm	Permeability / $\times 10^{-3}$ cm min^{-1}
Urea	60	100	7.8
		200	12.8
		500	14.3
		1000	15.0
		2000	17.9
Creatinine	113	1000	14.8
V_B12	1355	1000	13.2
PEG 200	200	1000	12.8
400	400	1000	7.1
600	600	1000	6.8
800	800	1000	4.9
1000	1000	1000	3.8

glutaraldehyde, for preparing XSC-3 were varied and the optimal value was selected for the dialysis membrane. Urea permeabilities and ultrafiltration rates (UFR) of XSC-3 PVA membranes with various concentrations of cross-linking agent are shown in Figure 4. As the concentration of cross-linker to XSC-3 PVA membrane decreases, the urea permeability and UFR increases. But by considering the mechanical strength of membrane, suitable concentration of glutaraldehyde was 0.6 wt% to the weight of polymer solution.

Table II represents permeation performance of XSC-3 PVA membrane for various solutes and the urea permeability of XSC-3 PVA membrane at different concentration. With increasing molecular weight of PEG, the permeability is decreased. But with different solutes, they showed no confirmative result in relation with the molecular weight of different solute. It is supposed that these results were due to different movement of various solutes in an aqueous solution.[19] On the other hand, the urea permeability is increased gradually with increasing the concentration of urea. This is explained by Fick's second law.

The effect of membrane thickness on the solute permeability of XSC-3 PVA membrane was also studied. The solute permeability was increased with decreasing thickness of the membrane.

CONCLUSIONS

It has been shown that the mechanical properties and dialysis performance of XSC-PVA membranes were varied by adjusting the mixing ratio of S-PVA and C-PVA, and the amount of cross-linking agent added.

The mechanical properties and solute permeabilities are increased with decreasing the amount of S-PVA in XSC-PVA membrane. In the case of XSC-3 PVA membrane, the solute permeability is increased with decreasing the amount of cross-linking agent. It was supposed that the reason is due to the change in hydrogen bond between hydroxy groups and free water region in the cross-linking network of XSC-3 PVA. These anionic charged membranes showed the possibility to have appropriate mechanical strength and solute permeability enough to produce blood contacting membrane.

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