Preparation and Characterization of Pore-filled Membrane Based on Polypropylene with Poly(vinylbenzyl chloride) by Using *in-situ* Cross-linking Technique

Byeongmin Kwon, Moonyoung Ko, Byungpyo Hong, and Hongsik Byun[†]

Department Chemical System Engineering, Keimyung University, Daegu, Korea

Abstract: Water softening is a very promising field for membranes and especially ultra low pressure membranes. Nanofiltration membranes based on pore-filling technology was prepared by using a new technique : the *in-situ* cross-linking. This route involves introducing a pre-formed polymer into the pores of a host membrane and then locking the polymer in the pores by *in-situ* cross-linking with an appropriate reagent. By this way, it is possible to make robust and competitive, pore-filled, anion-exchange membranes with excellent control over the properties of the incorporated gel without affecting the host membrane. In this paper, the possibilities of tuning such membranes for ultra low pressure water softening was examined by altering pore-filling chemistry (by changing cross-linking and aminating reagents). The results showed that tuning the chemistry of the pore-filling has important effects. In particularly, it had been shown that the correct selection of cross-linking reagent was not only essential to get pore-filled membranes but it could control their properties. Moreover, the aminating reagent could improve membrane performance. It was found that an increase in hydrophobicity could improve the Darcy permeability.

Keywords: *pore-filled membrane, aminating reagent, in-situ cross-linking, Poly(vinylbenzyl chloride)*

1. Introduction

A membrane is a barrier that is capable of separating materials as a function of their physical and chemical properties when a driving force is applied across the membrane. Membrane processes, while not new, are currently undergoing a major expansion in use as a method of separation. Thus membrane filtration was not considered a technically important separation process until 25 years ago. Today, membrane processes are used in a wide range of applications and the number of such applications is still growing [1].

Water softening is one of these promising applications. Water hardness is due to the presence of divalent ions of calcium and magnesium. The traditional methods for water softening include lime-soda and ion-exchange processes. Membrane water softening is becoming an attractive alternative presenting many advantages : superior water product quality, no sludge disposal, ease of operation [2,3].

Polymeric membranes have been used for water deionization for over three decades. With the development of carefully designed membranes with prescribed pore structure and charge density, it is now possible to selectively separate mono and multivalent ions. In order for the membranes to compete with the conventional processes, they must be economically feasible. With the advent of "low-pressure nanofiltration charged membranes" in recent years, it is possible to selectively separate solutes with different charges at low pressure [4]. Furthermore, improvements in flux and separation during the past two decades have increased the number

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[†] Author for all correspondences
(e-mail : hsbyun@kmu.ac.kr)

- thickness = 79 μm
- porosity = 80.5%
- pore diameter = 0.82 μm
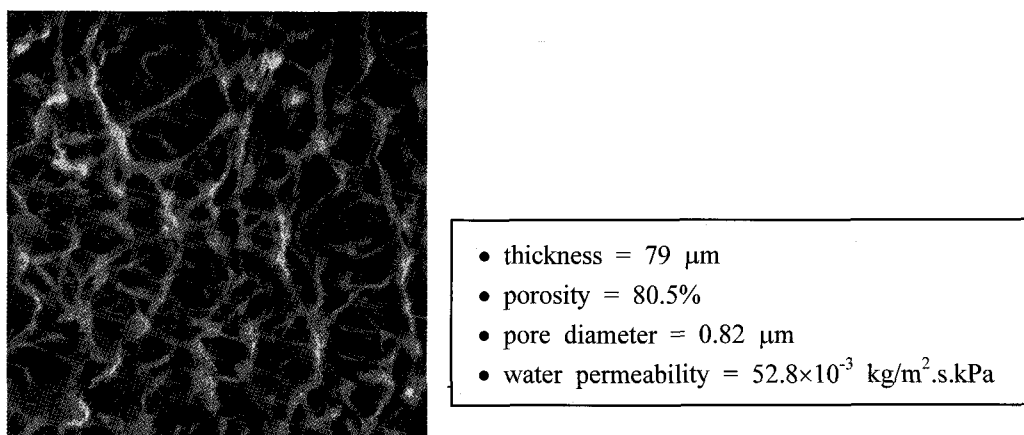- water permeability = 52.8×10^{-3} kg/m^2.s.kPa

Fig. 1. AFM picture and properties of PP3 nascent membrane.

of applications for which membranes are being used. However, there still remain some limitations for the general application of membrane technology : predominantly overall cost versus competitive technologies and the sensitivity of membrane elements to fouling (absorption of organics is a major cause for flux decline) [5,6]. The requirements for ideal water softening membranes are demanding.

A new preparation technique, *in-situ* cross-linking, has been recently developed [7]. This route involves introducing a pre-formed polymer into the pores of the host membrane and then lock the polymer in the pores by cross-linking. It has been previously reported that it is possible to make robust, pore-filled anion-exchange membranes with excellent control over the properties of the incorporated gel without affecting the host membrane [8]. In this work, the possibility of using such membranes for water softening at low pressure was examined with different pore-filling chemistry. The objective was to study the effect of chemistry on properties and performance.

2. Experimental

2.1. Materials

The porous substrate used in this study was a polypropylene (PP3) microfiltration membranes produced by a thermally induced phase separation process [9].

The properties of this nascent membrane are given in Fig. 1.

Poly(vinylbenzyl chloride) (PVBCl) (60/40 mixture of 3- and 4- isomers with average molecular weight M_n ca. 55,000, M_w ca. 100,000) was obtained from Aldrich. The chlorine content was determined by neutron activation analysis and found to correspond to 5.625 mmol/g of PVBCl which corresponds to 80% PVBCl and 20% styrene. Piperazine (PIP) (anhydrous, 99.8% purity), 1,4-diazabicyclo [2,2,2] octane (DABCO) (98% purity), dimethylamine (NHMe$_2$) (40% weight in water), trimethylamine (NMe$_3$) (40% weight in water), N,N-dimethybutylamine (NMe$_2$Butyl) (99% purity), N,N-dimethyloctylamine (NMe$_2$Octyl) (tech), N,N-dimethyldodecylamine (NMe$_2$Dodecyl) (97% purity) were obtained from Aldrich and pyridine (PYR) (99.9% purity) from Fisher Scientific. Methanol, N,N-Dimethylformamide (DMF) and tetrahydrofuran (THF) (from Caledon Lab. Ltd.) were used as supplied.

2.2. Membrane Preparation

A weight of poly(vinylbenzyl chloride) (from 0.1 to 0.3 g) and cross-linking reagent (piperazine or DABCO) (from 8 to 20 mg) was dissolved in 2.5 mL of DMF. The degree of cross-linking was kept constant and equal to 10% (0.1 mole of cross-linking reagent for 1 mole of PVBCl). The solution was prepared in a tube and rapidly mixed. The solution was spread across a

Table 1. Experimental Conditions for the Second Step

Aminating reagent	Solvent	Ratio*	t (h)	T (°C)
trimethylamine	water/methanol	20/40/40	24	20
dimethylamine	water/methanol	20/40/40	24	20
pyridine	methanol	20/80	24	20
DABCO	DMF	0.01 g/mL	24	20
dimethylbutylamine	DMF	20/80	24	20
dimethyloctylamine	none	100	24 + 1	20 + 75
dimethyldodecylamine	none	100	24 + 1	20 + 75

* ratio in volume of aminating reagent in solvent

host membrane (10×10 cm^2) placed on a glass plate. The solution was homogeneously distributed with a Teflon roller and another glass plate was placed on top of the filled membrane and left for 24 hrs. After removing the membrane from the glass plate, the membrane was rinsed with methanol and placed in an aminating reagent solution. Different functional groups were used in this step. The experimental conditions for all these reagents are shown in Table 1. Finally, the membrane was rinsed with methanol and deionized water and equilibrated over 2~3 days in NaCl 0.5 M before characterization and testing.

2.3. Membrane Characterization

The thickness of host microporous substrates and pore-filled membranes were measured with a digital micrometer model MDC-1P Mitutoyo Corp. The thickness of the nascent membrane was found to be 79±5 μm.

The mass gain (MG) is the percent mass increase after pore-filling and quaternization :

$$MG~(\%) = \frac{m_d - m_0}{m_0} \times 100 \qquad (1)$$

where m_d was the mass of a cross-linked, quaternized and dried sample and m_0 the mass of the nascent sample. The mass gain was converted to gel concentration (GC) which represents the filling density of polyelectrolyte :

$$GC~(g/cm^3) = \frac{m_d - m_o}{pore~volume} \qquad (2)$$

To determine the water uptake (WU), the membrane was thorough washed with deionized water, placed between 2 sheets of wet filter paper, gently pressed to remove surface water and weighed. WU was calculated by the following equation :

$$WU(\%) = \frac{m_w - m_d}{m_w} \times 100 \qquad (3)$$

where m_w was the mass of the water-swollen membrane sample and m_d the mass of the dry sample. Then, the water uptake was converted to volume fraction of water (VFW) :

$$VFW~(cm^3 water/cm^3 membrane) = \frac{m_w - m_d}{d_w \times V_{membrane}} \qquad (4)$$

where d_w was the density of water (d_w=997.07 kg/m^3 at 25°C) and $V_{membrane}$ the volume of the membrane.

The ion-exchange sites (IES) were measured by ion-exchange chromatography. The membrane sample in chloride form was kept in a 2,000 ppm sulfate solution during 24 h to exchange Cl⁻ with SO$_4^{2-}$. Then, the concentration of chloride in solution was measured by ion-exchange chromatography and the IES was calculated from the following relationship :

$$IES~(meq) = \frac{Cl^-(ppm) \times V}{35.5} \qquad (5)$$

where Cl⁻ was the chloride concentration given by ion-exchange chromatography, V the volume of the

sulfate solution (L) and md the mass of the dry membrane (g).

IES was converted to charge density (meq/cm^3 gel) which represents the effective charge of the gel in the membrane :

$$\text{charge density (meq/cm}^3\text{gel)} = \frac{IES}{VFW \times V_{membrane}} \quad (6)$$

2.4. Performance of Membrane

A dead-end cell was used for the test of flux. The membrane active area was 38.5 cm^2. The feed solution was stirred at a rate of 250~300 rpm. Permeate samples were collected over a given period and weighed. The flux at 25°C was calculated from the equation :

$$\text{flux (kg/m}^2 \cdot h) = \frac{m_x \cdot \alpha_T}{t \cdot A_m} \quad (7)$$

where m_x (kg) was the mass of permeate collected over the time t(h), α_T the experimental temperature correction factor (α_T = -0.575lnT (°C) + 2.85), t the time (h) and A_m the active membrane area (m^2). Reproducibility of flux measurements was within 5%.

3. Results and Discussions

3.1. Preparation and Characterization of Membrane

Several series of membranes were prepared by in-situ cross-linking of PVBCl with a cross-linking reagent (piperazine or DABCO). All the membranes were made with the same degree of cross-linking (0.1 mole of cross-linking reagent for 1 mole of PVBCl) but with different amounts of incorporated gel in the pores of microporous hosts and different aminating reagents. The cross-linked membranes were converted into positively charged ammonium membranes with different aminating reagents.

As shown in Fig. 2, the in-situ cross-linking process can be divided into 2 steps: the first one is the cross-linking reaction between PVBCl and a cross-linker
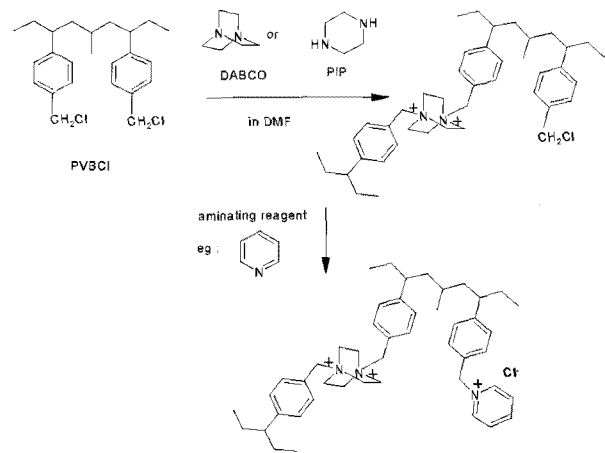

Fig. 2. Chemical reactions occurring during *in-situ* cross-linking with PVBCl, DABCO as cross-linking reagent and pyridine as aminating reagent.

reagent (PIP or DABCO) in DMF. The second step is the conversion of the remaining benzyl chloride groups into ammonium salts using an aminating reagent. The sequence of reactions proceeded smoothly to give membranes with pore-fillings that were predictable based on composition of the starting DMF solutions.

3.2. Effect of Cross-linker on Water Flux

In order to study the effect of cross-linking reagent, two series of membranes were prepared using piperazine and DABCO as cross-linking reagents with different amounts of incorporated gel (various mass gains). All the membranes were aminated in the same way with a pyridine solution (pyridine/methanol : 20/80) so that the second step of the process was kept constant. The following table shows the water flux at 100 kPa obtained for the two series of membranes.

These results show clearly that there is an important effect of cross-linking reagent on membrane properties : DABCO membranes exhibit typical nanofiltration fluxes irrespective of the mass gain. This is not the case with piperazine membranes where the flux becomes very high below a certain mass gain.

This difference between the two cross-linking reagents can be explained by the different chemical configuration of the two reagents. In cross-linked state, the nitrogens in DABCO are quaternized but not in

Table 2. Water Flux at 100 kPa Using Piperazine or DABCO as Cross-linker Reagent

| Cross-linker[1]	Mass gain (%)[2]	Water flux 100 kPa (kg/m$^2 \cdot$ h)
PIP	46	16920
PIP	56	12600
PIP	69	44
PIP	78	23
DABCO	40	31
DABCO	57	7
DABCO	69	6

[1] degree of cross-linking = 10%
[2] amination with pyridine

piperazine. As a consequence, when the gel is collapsed in a poor solvent (methanol or water used for the amination step), there is additional possible cross-linking between the di-reacted piperazine and PVBCl as shown in Fig. 3. Due to this additional cross-linking, the gel can not revert to swollen state when a good gel solvent is used. The pores are not filled but only coated and it leads to very high fluxes.

This possible additional cross-linking with piperazine can only occur when the amination reaction is very slow compared to collapse of the initial cross-linked gel so that there is a competition between the two reactions. This is typically the case with pyridine for which the amination reaction is slow and incomplete [10]. But, if trimethylamine is used instead of pyridine, the amination reaction is faster and collapse of the initial gel seems to occur, resulting in additional cross-linking. So, the gel can again swell and it leads to pore-filled membranes with low fluxes (typical nanofiltration membranes).

In the case of DABCO, the additional cross-linking is not possible because the nitrogens are already quaternized. Furthermore, the conformation of the direacted DABCO is very rigid and the gel will slowly collapse. Therefore, the DABCO cross-linked gels always lead to pore-filled membranes (typical nanofiltration fluxes).

This result shows that the use of DABCO as a cross-linking reagent is better to get pore-filled membranes and control the fabrication and the properties of these membranes. In the following part of the discus-
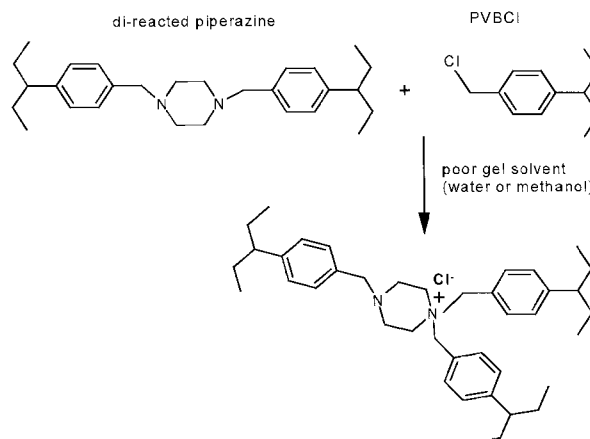
Fig. 3. Additional cross-linking reaction between di-reacted piperazine and PVBCl

sion, all the membranes have been prepared with DABCO.

3.3. Characterization of the Pore-filled Membranes

A series of seven membranes was prepared by *in-situ* cross-linking using identical first step (same mixture PVBCl/DABCO in DMF was incorporated in the pores of the polypropylene nascent membranes) but varying the aminating reagent in the second step. The objective was to study the effect of aminating reagent on performance.

All the membranes were first characterized by measurement of their thickness, mass gain and water uptake, Table 3.

It has been previously reported that the pore-filled membranes made by *in-situ* cross-linking were very robust, they could be dried in vacuo in order to obtain mass gains and then readily re-hydrated on immersion in water. It was possible to control with a good precision the degree of cross-linking, the expected mass-gain and the expected ion-exchange size assuming that the void volume of the membranes was filled with a polymer solution of known concentration. It was found that there were no dimensional changes in the pore-filled membranes : length, breadth and thickness were the same after treatment, which was not true with the previous fabrication of pore-filled membranes produced by *in-situ* polymerization [7]. These results confirm

Table 3. Characterization of the Pore-filled Membranes (series 1)

# mb[1]	Aminating reagent	Thickness (μm)[2]	Expected mass gain (%)	Experimental mass gain (%)	Water uptake (%)
1	NMe₃	77	49	49	77
2	NMe₂	79	48	50	67
3	PYR	73	56	57	78
4	DABCO	77	62	66	69
5	NMe₂Butyl	75	59	58	69
6	NMe₂Octyl	77	70	65	63
7	NMe₂Dodecyl	77	80	73	39

[1] starting concentration of PVBCl and DABCO is constant with a degree of cross-linking of 10%.
[2] thickness of nascent membrane = 79±5 μm.

that there is no dimensional change, especially for the thickness using *in-situ* cross-linking process.

The change in mass gain of the series of membranes shown in Table 3 is only due to the use of different aminating reagents : final mass gain depends on the molecular weight of the functional group used in the amination step. As reported previously, there is a good correlation between expected and experimental mass gains. This result shows that it is possible to control with accuracy the amount of gel incorporated in the pores of the membranes.

The water uptake represents the amount of water inside the pores of the membrane. This parameter is used to characterize the porosity of the membranes after filling. Fig. 4 represents the water uptake as a function of the gel concentration (amount of gel incorporated into the pores). This figure shows that there is an important effect of aminating reagent on water uptake : as expected, water uptake decreases with gel concentration. The difference in the four amines presented in Fig. 4 is only due to the size of the substituent (methyl, butyl, octyl and dodecyl). This result shows that the size of the substituent is correlated with hydrophobicity : as the size increases, hydrophobicity increases and water uptake decreases.

The amount of ion-exchange sites (IES) expected in these membranes can be calculated assuming that all the benzyl chloride groups are converted into ammonium sites :
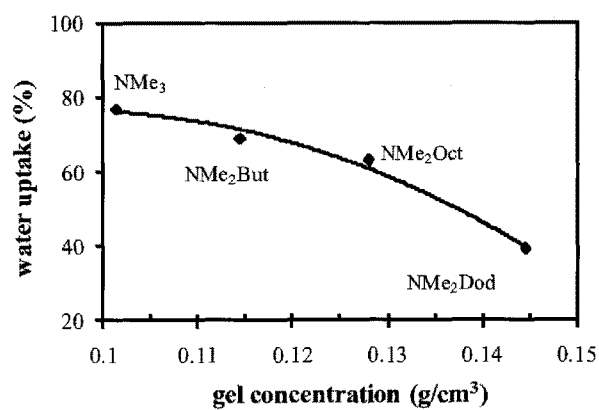
Fig. 4. Water uptake versus gel concentration.

Table 4. Characterization of the Pore-filled Membranes : Comparison between Expected and Experimental Ion Exchange Sites

#mb	Aminating reagent	Expected IES (meq)	Experimental IES (meq)	% conversion
1	NMe₃	0.28	0.24	86
3	PYR	0.28	0.16	57
4	DABCO	0.28	0.25	89
5	NMe₂Butyl	0.28	0.21	75
6	NMe₂Octyl	0.28	0.21	75
7	NMe₂Dodecyl	0.28	0.24	86

expected IES (meq Cl) =

$$\frac{\text{PVBCl (g)} \times 5.625 \text{ (meq/g)} \times \text{pore volume (cm}^3)}{\text{volume of solvent (mL)}} \quad (8)$$

The membrane with NHMe₂ as functional group is not in this table because the aminating reagent is a diamine and so doesn't produce charge during the amina-
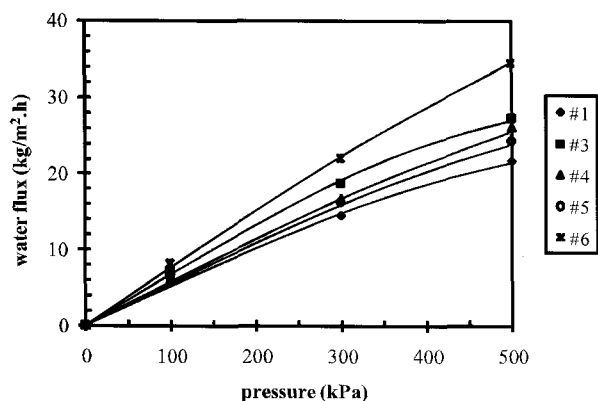
Fig. 5. Water flux versus pressure for the pore-filled membranes.

tion step. IES of this membrane is very low : the only charges are produced during the cross-linking step with DABCO which represents approximately 20% of the available chloride.

As the concentration of PVBCl in DMF and the pore volume are constant, IES should be the same. There are some differences but the conversion of the remaining chloride to ammonium is very good (about 75%) except for pyridine.

3.4. Water Flux of Anion Exchange Membranes

Pure water flux was measured for each membrane from 0 to 500 kPa. As shown in Fig. 5, all membranes showed a linear relationship with pressure until 300 kPa. Above this pressure, there is a drop off in flux as the pressure is increasing.

4. Conclusions

The work described here shows that *in-situ* cross-linking is a very efficient route to make robust, pore-filled anion-exchange membranes. This process allows good control over properties and performance. The chemical configuration has important effects on these properties. First of all, the choice of the cross-linking reagent is important to obtain pore-filled and not pore-coated membranes : several experiments have shown

that 1,4-diazabicyclo [2,2,2] octane (DABCO) is the best reagent. The aminating reagent used in the second step of the process has an effect on membrane performance. One of the most interesting results of this study is the increase of permeability with the increase of number of carbons present in the aminating reagent : it means that the permeability is increasing with the hydrophobicity of the functional group used in the amination step.

At least two mass gains have been tried with each aminating reagent, but some of these membranes can still be optimized in terms of performance. However, this preliminary work clearly indicates that this new series of pore-filled membrane exhibits very efficient water softening performance at ultra-low pressures (100 kPa).

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