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Preparation and Characterization of Chemically Stable PVDF-HFP Asymmetric Microfiltration (MF) Membranes

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Abstract: Chemically stable Polyvinylidene fluoride-hexa-fluoropropane (PVDF-HFP) copolymer asymmetric membranes were prepared by the conventional phase inversion process, using Dimethyacetamide (DMAc) as a solvent and water as a non-solvent. To control the pore size and porosity of the PVDF-HFP membranes, tetra-ethoxysilane (TEOS) was used as a pore-forming agent. The prepared membranes were characterized, using several analytical methods such as Fourier Transform Infrared spectroscopy (FTIR), Thermo-gravimetric analyzer (TGA), Field Emission Scanning Electronic Microscopy (FESEM). TEOS turned out to increase porosity and make homogeneous pores on the membranes. Depending on the composition of the dope solutions, the pore size was ranged from 0.1 to 1.0 μm. The flux of the PVDF-HFP membranes prepared by using TEOS as a pore forming agent was increased substantially without much decrease in the rejection. When 15 wt% PVDF-HFP solution was blended with 13 wt% TEOS solution at composition ratio of 70/30 in wt%, the water flux at 2 bars was about 2 m^3/m^2day.

Keywords: *Polyvinylidenfluoride-hexafluoropropylene copolymer, Microfiltration Membranes, Tetra-ethoxysilane, Pore-forming agent, Chemical stability*

1. Introduction

The water treatment by the membrane is one of the significant technologies most often used [1-13]. Of the many different types of membranes for the water treatment, such as microfiltration (MF) membranes, ultrafiltration (UF) membranes, nanofiltration (NF) membranes and reverse osmosis (RO) membranes, MF- and UF-membranes have significant application areas. Especially they have been used for the filtration of particles or colloids, and many times used as a support layer for the formation of NF and RO-membranes. For such a wide application, they need to have a strong chemical stability. When considering the frequent cleaning with corrosive chemicals such as perchloric acids for the long time use of the membranes, they specially need to have a strong chemical stability. Though the membranes prepared from engineering plastics with mechanical properties such as polysulfone and polyethersulfone have relatively strong chemical stabilities, they are not strong enough to endure such strong corrosive chemicals for a long time. And also the membrane of polyethylene (PE) and polypropylene (PP) show very good chemical stabilities, but they are not easy to be prepared as membranes by simple phase inversion process, eventually becoming expensive membranes.

Knowing such difficulties in the preparation of chemically stable MF- and UF-membranes by the simple phase inversion process, poly (vinylidene fluoride)-hexa-fluoropropylene copolymer (PVDF-HFP) was used in this study as a membrane material to prepare chemically stable MF-membranes by the economically favorable process. PVDF-HFP is one of the chemically very stable polymers due to its large number of fluoride atoms composing the main chain. Also an advantage of this polymer is its high solubilityin polar aprotic solvents such as N-methylpyrrolidone (NMP) and N,

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N-dimethylacetamide (DMAc) that make it possible to prepare PVDF-HFP MF-membrane by the simple conventional phase inversion process, using water as a coagulant. However, this polymer is so hydrophobic due to its hexafluoropropylene (HFP) moieties that it is not easy to form micropores on the membrane surface by the phase inversion process of the PVDF-HFP dope solution in NMP or DMAc without addition of additives. Therefore, in this study Tetra-ethoxysilane (TEOS) was used as a pore forming agent. TEOS has been known to have the characteristics of being hydrolyzed by the small amount of water into tetra-hydroxysilane that is very soluble in water and expected to help form small pores to the PVDF-HFP membrane when used as an additive. The detailed procedure for the formation and the effect of the TEOS on the porosity and pore size are elaborated in the following section.

2. Experimental

2.1. Materials

PVDF-HFP and TEOS purchasedfrom Aldrich Co. were used as a membrane material and as an additive, respectively, for the formation of PVDF-HFP MF membranes. DMAc and Ethyl alcohol bought from Junsei Co. were used as solvents of dope solutions. PEG 35,000 and PEO 100,000 from Aldrich Co. were used for the preparation of feed solutions for the membrane tests. Glycerin was used to prevent the membrane from being dried, after purchasing from Aldrich Co. Other chemicals used in this experimental were used as purchased without a further purification.

2.2. Preparation of Membranes

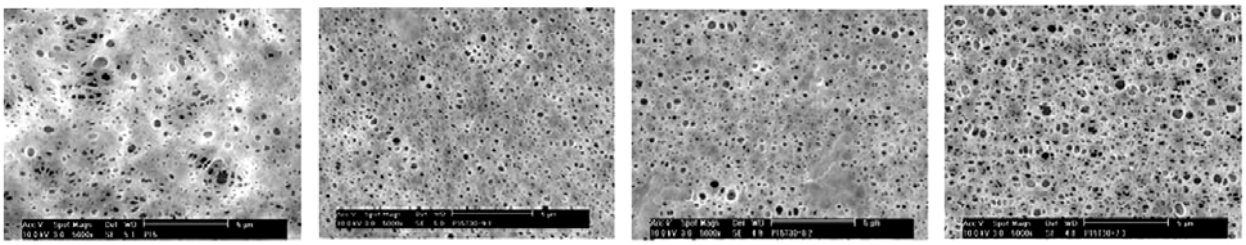
Asymmetric PVDF-HFP MF membranes were prepared by the conventional phase inversion process of the PVDF-HFP dope solutions that contain different amounts of TEOS, using DMAc as a solvent and water as a non-solvent. The detailed procedure is as follows: Certain amounts of PVDF-HFP was dissolved in DMAc at elevated temperature with constant stirring to form dope solutions with different solid contents 15 wt% (named P15) and 20 wt% (named P20). For the preparation of a homogeneous TEOS solution, water, hydrochloric acid, ethanol and TEOS in a molar ratio of 4 / 0.1 / 0.7 / 0.3 were well mixed. The concentration of HCl used here was 0.01 M in distilled water. Then certain amounts of TEOS solutions were added into each PVDF-HFP dope solution with stirring to form dope solutionswith different amounts of TEOS; 0, 10, 20, and 30 vol%. The prepared dope solutions were cast on the Polyester non-woven fabrics using a casting knife, and followed by dipping into a water bath at 20°C for 24 hr for solidification. The PVDF-HFP membranes prepared so were kept in distilled water before their use.

2.3. Characterization

The prepared PVDF-HFP membranes were then characterized using various analytical methods: The morphologies of the surface and cross-section of the membranes were examined with a Field Emission Scanning Electron (FESEM) (Model : XL 30, Philips Co., USA) to study the effect of TEOS on the membrane structure. Fourier transform infrared (FT-IR) spectra of the membranes were takenusing (Bio-Rad, Digilab Division, Model FT-80, FT IR) to figure out the effect of TEOS on the chemical property of the membrane surface. The FT-IR measurements were performed with an attenuated total reflectance method. To know whether the TEOS remained in the membrane or not, if yes, how much TEOS was remained, thermo gravimetric analysis (TGA, TA Instruments DMA 2980)was used. The TGA measurements were carried out under a nitrogen atmosphere at a heating rate of 10°C/min from 50 to 700°C.

2.4. Permeation Test

The PVDF-HFPmembranes were tested with 1,000 ppm aqueous solutions of PEG 35,000 and PEO 100,000, using a general RO test set-up and a Dia-frame pump (Hydro-cell Model-13, Wanner Engineering INC., MN, USA), controlling the feed flow rate at 1 L/min. to characterize their permeation properties.



(a) (b) (c) (d)

Fig. 1. FESEM photographs of the surface of the membranes with different compositions: 15 wt% PVDF-HFP sol./ 13 wt% TEOS sol. (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30.

The flux of pure water and feed solution was determined by measuring the amount of solution that penetrated through the membrane for the certain period of time. The operating pressure was controlled from 2 to 4 bars, using back pressure regulators. Before measuring the flux, the membrane compaction was completed by running the pump at 4 bars for 2 hrs, using just distilled water. Solute rejection was calculated from the concentrations of the feed and permeatesusing the following equation;

$$Rejection(\%) = \frac{C_f - C_p}{C_f} \times 100$$

Where C_f and C_p are the concentrations of the feed solution and permeate, respectively. The C_f and C_p were measured by using a high-performance liquid chromatograph (HPLC) (Model Waters 501) that was attached to a differential refractometer R401 as a detector.

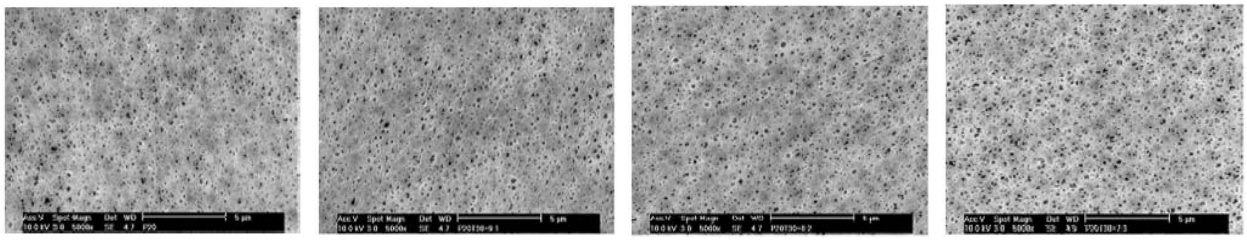
3. Results and Discussion

3.1. Membrane Preparation

PVDF-HFP asymmetric MF membranes were prepared by the phase inversion process using PVDF-HFP dope solutions with different contents of TEOS as a material helping form pores. The hydrophilicity of PVDF-HFP was so high that the dope solution composed of PVDF-HFP alone in DMAc was not good enough to form a membrane with micropores in the MF range. The SEM photograph of Fig. 1(a) shows the pores of the membrane prepared from the dope solution composed of PVDF-HFP alone. For the formation of pores by the phase inversion process, the non-solvent, in this case water, has to go into the dope solution layer by the solvent-non-solvent exchange mechanism in the stage of phase inversion when cast dope solution was immersed into the nonsolvent, however, the PVDF-HFP dope solution was so hydrophobic that the nonsolvent (water) could not go homogeneously into the dope solution toreplace the spaces that were occupied by the solvent prior in the cast dope solution layer. As a result, the pores formed on the surface of the resulting membrane were heterogeneous and the number of pores was relatively low.

This kind of problem was solved by using TEOS as an agent for helping formation of pores. It was found that when certain amount of TEOS solution was added into the PVDF-HFP dope solution to make the composition of PVDF-HFP/TEOS was 90/10 in wt%, the pores started to become homogeneous and the porosity of the membrane seemed to increase as shown in Fig. 1(b). And with further increasing contentsof the TEOS in the dope solution, more homogeneous pores were formed in the membrane. This kind of behavior of the formation of pores in the PVDF-HFP membranes by the TEOS was almost same regardless of the concentrations of the dope solutions used. When the 20 wt% PVDF-HFP solution in DMAc was used, the same trend was found (Fig. 2).

The reason for the formation of homogeneous, large number of micro-pores in the PVDF-HFP membranes by the TEOS canbe explained by the characteristics of

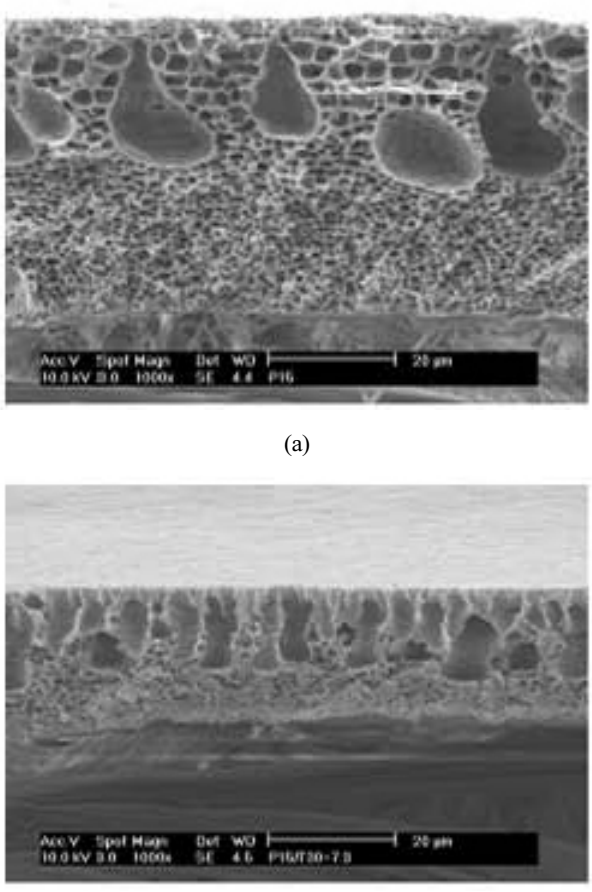


(a) (b) (c) (d)

Fig. 2. FESEM photographs of the surface of the membranes with different compositions : 20 wt% PVDF-HFP sol./ 13 wt% TEOS sol. (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30.

the TEOS shown in Fig. 3. TEOS is a material that can be hydrolyzed easily by water into Tetra-hydroxysilane that is very soluble in water. In other words, the TEOS mixed with PVDF-HFP homogeneously increased the hydrophilicity of the dope solution, making the dope solution thermodynamically unstable, and made it easy to form small pores by the phase inversion process. It is well known that as the dope solution is thermodynamically unstable, phase inversion process is usually faster and smaller pores are formed on the surface of the asymmetric membranes. So, it was expected that the TEOS added into the dope solution increased the porosity and made the pore size more homogeneous.

However, the morphology of the cross-sections of the membraneswas not affected substantially by the TEOS. All the membranes prepared from different composition of PVDF-HFP and TEOS showed a finger-like structure mixed with sponge structure as shown in Fig. 3. The prepared membranes were physically stable and strong enough to be used as MF-membranes.



(a)

(b)

Fig. 3. FESEM photographs of the cross-section of the membranes with different compositions: 15 wt% PVDF-HFP sol./ 13 wt% TEOS sol. (a) 100/0, (b) 70/30.

3.2. Characterization

3.2.1. FESEM

Fig. 1 shows the surface morphologies of the PVDF-HFP membranes prepared from the dope solutions with different blend ratios between the 15 wt% PVDF-HFP solution in DMAc and the TEOS solution. The Fig. 1(a), the surface morphology of the PVDF-HFP membrane prepared without use of TEOS, shows that the pores formed are very heterogeneous in size and shape, indicating that the 15 wt% PVDF-HFP solution in DMAc alone is not proper for the formationof a MF membrane with good membrane performances. How- ever, when the TEOS solution was blended with

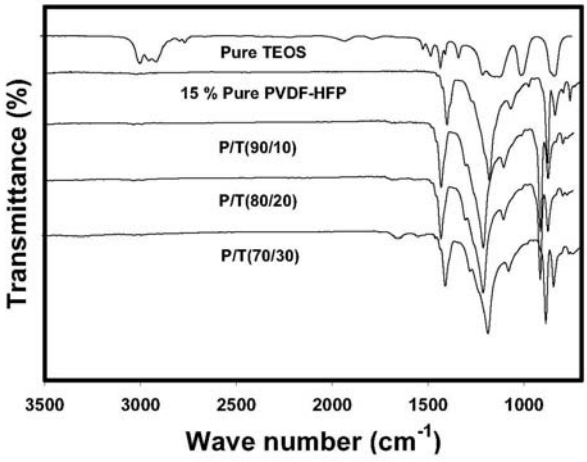
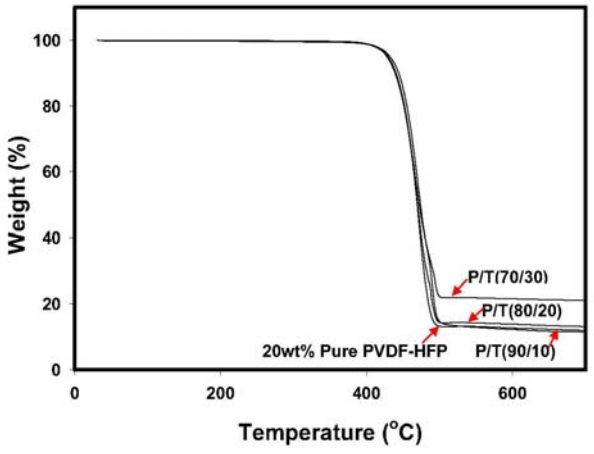
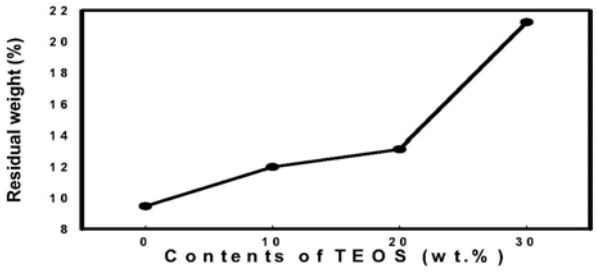


Fig. 4. FT-IR spectra of membranes.



(a)



(b)

Fig. 5. (a) TGA curves, (b) Residual weight percent of membrane at 700°C.

the PVDF-HFP polymer solution, the resulting membranes showed much better membrane surface morphologies. As the contents of TEOS solution in the dope solution increased from 10 to 30%, the number of pores formed on the membrane surface seemed to be increased. But when the content of the TEOS was 30 wt%, because of the much less concentration of the PVDF-HFP in the dope solution, the homogeneity of the pore size decreased and became less homogeneous than the membrane prepared from the dope solution with 10 wt%. The homogeneity of the pore size and shape turned out to be very dependent on the amounts of the TEOS used, but collectively speaking it became much better by blending the PVDF-HFP solution with TEOS solution. From these results, it might be possible to say that the TEOS helps formation of pores of the PVDF-HFP membranes. The permselective properties of those membranes that will be discussed in the later section will give more detailed understanding on the effect of the TEOS on the formation of PVDF-HFP membranes.

The morphologies of the membrane surface when 20 wt% PVDF-HFP solutions, instead of 15 wt% solution, were used are shown in Fig. 2. With increasing concentration of the PVDF-HFP in the dope solution, the pore size decreased and homogeneous, and porosity increased. As compared Fig. 2(a) with Fig. 1(a), it is evident that 20 wt% of PVDF-HFP dope solution is much better for the formation of a MF membrane. In this case the TEOS seemed also to increase the porosity of the membrane but not very clear from the SEM pictures. Same as the prior case, as the amount of TEOS was 30 wt%, the pore size seemed to be increased a little by the same reason.

3.2.2. FTIR (ATR)

In order to know if the TEOS used as an additive to help form pores were remained in the resultant membrane, FTIR spectra of the PVDF-HFP membranes prepared from dope solutions with different amount of TEOS were taken and compared with that of pure TEOS as shown in Fig. 4. The pure TEOS showed a characteristic bands at 792 cm^{-1} (symmetric Si-O-Si stretching), 1,082 and 1,170 cm^{-1} (asymmetric Si-O-Si stretching), and 934 cm^{-1} (Si-OH stretching), but the spectra of the membranes prepared by using the TEOS

did not show any distinctive TEOS characteristics peaks. They are just very similar to the spectrum of pure PVDF-HFP membrane prepared, showing only bands at 877 cm^{-1} (CF_2 symmetric stretching) and 839 cm^{-1} (CH_2 rocking). These results suggest that the TEOS used did not remain in the resulting membrane, being washed out by the excess water used as a coagulant.

3.2.3. TGA

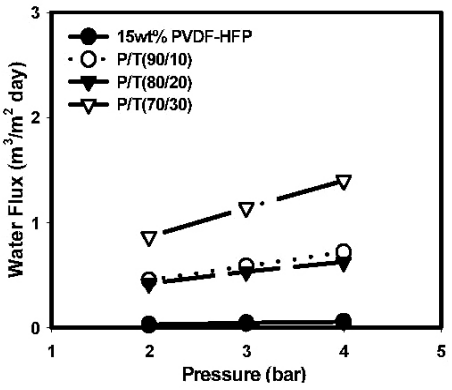
To confirm the results obtained from the FTIR study, TGA measurements were performed. The TGA curves of the membranes under nitrogen are shown in Fig. 5(a). The TGA measurements were carried out under a nitrogen atmosphere at a heating rate of 10°C/min from 50 to 700°C. A major weight loss of the membranes was at onset temperature of about 430°C, which is attributed to the decomposition of the PVDF-HFP.When the sample was the membrane prepared from 20 wt% PVDF-HFP solution without use of TEOS was used, residual weight was about 10 wt%. Up to the content of TEOS solution of 20 wt% in the dope solution, the residual weights of the membrane after heating to 700°C was about 12 wt%, suggesting not substantial amount of TEOS remained in the membranes, but when the content of TEOS solution was 30 wt%, it became over 20 wt%. From these results, it was proved that even though from the FTIR study, there was no difference in the FTIR spectra, some of the TEOS remained in the membrane and increased the residual weights in the TGA study. But this fact did not affect on the thermal stability of the membranes.

3.3. Permeation Performance

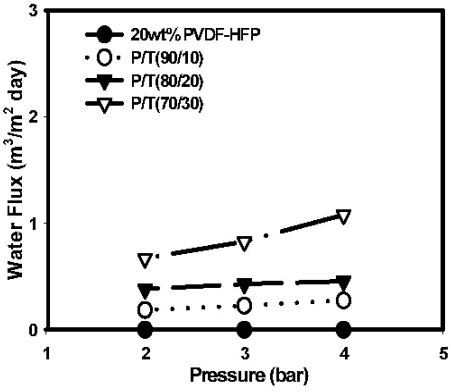
3.3.1. Test with Pure Water

To Fig. out the effect of the TEOS on the pore formation of the PVDF-HFP membranes, the permselective properties of the PVDF-HFP membranes were studied using water and 1,000 ppm aqueous solutions of PEG 35,000 and PEO 100,000 as feed solutions.

Fig. 6 shows the pure water flux as a function of operating pressure of the PVDF-HFP membranes prepared from the different compositions of PVDF-HFP and TEOS. As one can see, the water flux of the membrane prepared without use of TEOS from both 15 and 20 wt% of PVDF-HFP solutions was almost nothing. Considering the heterogeneous, relatively large pores formed on the surface of the membrane as shown in Figs. 1(a) and 2(a), it is kind of surprising to know that they showed almost no flux.



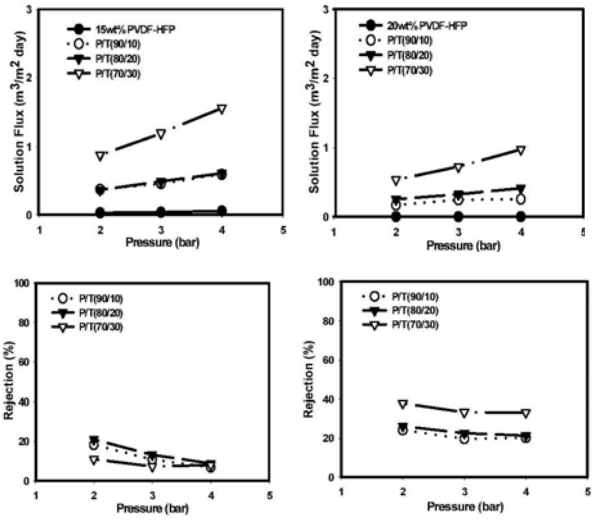
(a)



(b)

Fig. 6. Water flux of the PVDF-HFP membranes prepared from the PVDF-HFP dope solutions with different compositions: (A) the dope solutions prepared by blending 15 wt% PVDF-HFP solution in DMAc with 13 wt% TEOS solution in different blending ratios, and (B) the dope solutions prepared by blending 15 wt% PVDF-HFP solution in DMAc with 13 wt% TEOS solution in different blending ratios in which P/T (90/10) means 90 wt% of PVDF-HFP solution and 10 wt/% of TEOS solution, P/T (80/20) 80 w% of PVDF-HFP solution and 20 wt/% of TEOS solution, and so on.

However, when TEOS was used for the preparation



(a) (b)

Fig. 7. Permeation properties of the PVDF-HFP/TEOS membranes as a 1,000 ppm aqueous solution of PEG 35,000 was used as a feed solution : P/T = compositions of (a) 15 wt% PVDF-HFP sol./ 13 wt% TEOS sol., (b) 20 wt% PVDF-HFP sol./ 13 wt% TEOS sol.

of the membranes, the water flux of the membranes prepared increased with the amount of the TEOS used. The membrane prepared from the dope solution that contained 90 of 15 wt% PVHF-HFP solution and 10 wt% of TEOS solution showed muchhigh flux than the PVDF-HFP membrane prepared without use of TEOS. However, that was more or less same as the flux of the membrane prepared by blending with 20 wt% of TEOS solution. Then with further increase in the content of TEOS solution of the dope solution to 30 wt%, the flux increased to as high as almost 1.0 m^3/m^2day at 2 bar.

When the 20 wt% PVDF-HFP solution was used, the same tendency in the flux of the membrane was found. The water flux was gradually increased with increasing contents of TEOS in the dope solution. As the content of TEOS solution reached to 30 wt%, that was about 0.7 m^3/m^2day at 2 bar.

This kind of behavior of the membrane flux can be explained by the changes in the concentrations of PVDF-HFP and TEOS in the dope solution. With increasing contents of TEOS solution in the dope solution from 0 to 30 wt%, for example of the 15 wt% PVDF-HFP solution, the concentration of PVDF-HFP decreased from 15 to 10.5 wt%, while that of TEOS increased from 0 to 3.9 wt%. Generally speaking,for the membranes prepared by the phase process of the polymer solution, with decreasing polymer concentration, bigger pores inclined to be formed on the surface of the resulting membranes. On the other hand, the TEOS was found in this experiment to help the formation of large number of small pores on the membrane. So, with the increase in the contents of TEOS, the number of pores was increased (high porosity) substantially, but the pore size was not increased as much as the increase in the porosity. This kind of phenomenonwill be more evident in the Fig. 7 obtained from the tests with a 1,000 ppm aqueous solution of PEG 35,000.

3.3.2. Test with a 1,000 ppm Aqueous Solution of PEG 35,000

Fig. 7 exhibits the permselective properties of the PVDF-HFP membranes prepared, when a 1,000 ppm aqueous solution of PEG 35,000 was used as a feed.

The flux of the solution was found to be very dependent on the contents of TEOS used for the formation of the membranes as well in this case. The membrane prepared from withoutuse of TEOS showed almost no flux, but with the increasing contents of TEOS of the dope solutions used for the preparation of the membranes, the flux gradually increased. The behavior and values of the flux of the membranes as a function of operating pressure was more or less same as the case where pure water was used as a feed. For the membranes prepared from the dope solution consisted of 70 of 15 wt% PVDF-HFP solution and 30 wt% of TEOS solution, it was about 1.0 m^3/m^2day at 2 bars.

The rejection of the membranes ranged from 10 to 40%, depending on the membranes used. Even though the flux was highly improved by the use of TEOS, the rejection was not decreased substantially. For the membranes prepared by using 15 wt% PVDF-HFP sol-

utions, it ranged between 10 to 20%, decreasing with increasing flux. However when 20 wt% PVDF-HFP solution was used, the membranes prepared showed totallydifferent behavior in their rejections. For the membrane prepared from the dope solution composed of 70 of 20 wt% PVDF-HFP solution and 30 wt% of TEOS solution, it appeared to be about 40% at 2 bars. It is much higher than that of the membranes prepared by using 10 or 20 wt% of the TEOS solution. It is quite interesting result, considering the much higher flux of that membrane than that of the others.

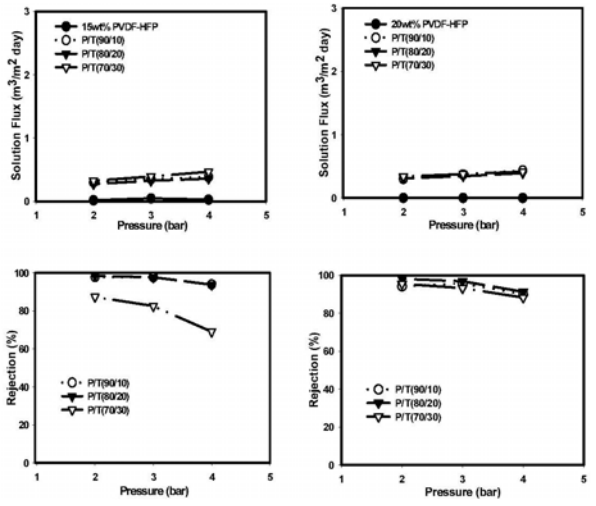
From these result, it became evident that the TEOS used for the preparation of the PVDF-HFP membranes tend to decrease the pore size but increasethe porosity of the membranes, improving the flux without or less hampering the rejection.

3.3.3. Test with a 1,000 ppm Aqueous PEO 100,000 Solution

Fig. 8 shows performance of the PVDF-HFP membranes as a 1,000 ppm aqueous PEO 100,000 solution as a feed. The rejection was high in this case, over 90% at 2 bars, and decreased with an operating pressure, but the flux was substantially low, and not affected by the operating pressure probably by the serious fouling effect. The flux of the membranes prepared from different conditions show almost the same value, about 0.3 at 2 bars. The slope of the flux as a functionof the operating pressure was very slow, indicating the serious membrane fouling. However still the membranes prepared by using TEOS as an additive showed much higher flux than the membranes prepared without TEOS. From these result, it is assumed that the molecular weight cut off (MWCO) of the membranes prepared is about 100,000 or less.

4. Conclusions

Asymmetric PVDF-HFP membranes can be prepared by the phase inversion process of the PVDF-HFP solutions in DMAc whose concentration was ranged from 15 to 20 wt%, using water as a coagulant. However,



(a) (b)

Fig. 8. Permeation properties of the PVDF-HFP/TEOS membranes as a 1,000 ppm aqueous solution of PEO 100,000 was used as a feed solution: P/T = compositions of (a) 15 wt% PVDF-HFP sol./ 13 wt% TEOS sol., (b) 20 wt% PVDF-HFP sol./ 13 wt% TEOS sol.

when the concentration of the PVDF-HFP solution was low such as 15 wt%, without use of TEOS as pore forming agent, the surface pores of the PVDF-HFP membranes prepared were heterogeneous with low porosity. Blending of the PVDF-HFP solution with TEOS solution with 13 wt% of solid content, composition ratio between 90/10 to 70/30, improved the porosity of the membrane, and made the pores homogeneous, approving the blending TEOS with PVDF-HFP solutions to be helpful for the formation of asymmetric PVDF-HFP MF membranes with good permselective performances. The MWCO of the membranes was turned out to be about 100,000.

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