

膜特性改質剤として市販のフッ素系高分子を用いた 高性能塩素化ポリ塩化ビニル平膜の作製

Fabrication of high-performance chlorinated poly(vinyl chloride) flat-sheet membranes using commercially available fluoropolymers as membrane-property modifiers

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Abstract

The porosity, surface hydrophilicity, and morphology of membranes significantly affect their fouling propensity in membrane bioreactors (MBRs). The use of polymers as additives is an effective strategy for improving the properties of the membranes. In this study, we developed a new technique to improve the membrane properties by using Unidyne DSN-403N and Surfion S-420, which are fluoropolymers, as novel polymer additives to prepare chlorinated poly(vinyl chloride) (CPVC) flat-sheet membranes suitable for MBR applications. The blending of these fluoropolymers in the dope solution produced membranes that exhibited dense and smooth surfaces and were suitable for use in MBRs. The membrane prepared using Surfion S-420 showed a higher pure water permeability than that of the membrane with Unidyne DSN-403N. Thus, it can be expected that the former membrane would exhibit better antifouling properties. This method of blending a fluoropolymer is useful for preparing high-performance CPVC flat-sheet membranes for MBRs.

Key words : Chlorinated poly(vinyl chloride); fluoropolymer; membrane-property modifier

1 Introduction

Membrane bioreactors (MBRs) have been adopted widely in different types of wastewater treatment plants all over the world, resulting in a significant in-

crease in their market share. However, MBRs continue to be plagued by membrane fouling which can significantly reduce the permeation flux. In the case of extreme membrane fouling, it becomes necessary to clean or replace the membrane module, which can increase the operation and maintenance costs.¹ In general, the fouling propensities of membranes are deter-

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mined by their characteristics such as the type of material used, surface hydrophilicity, pure water permeability, pore size and distribution, surface porosity, and surface roughness. Therefore, to mitigate membrane fouling, it is essential to develop techniques for controlling the properties of the membranes.

Chlorinated poly(vinyl chloride) (CPVC) flat-sheet microfiltration membranes with a nonwoven polyester fabric as a support layer are used extensively in MBRs²⁻⁴ because of their excellent chemical and mechanical properties. CPVC flat-sheet membranes are generally prepared via water vapor induced phase separation (VIPS), which results in the formation of a symmetric structure both within and on the support layer.^{3,4} On the other hand, several studies have reported that blending an amphiphilic polymer in ultrafiltration and microfiltration membranes can improve the membrane properties such as the surface hydrophilicity and antifouling characteristics.⁵⁻⁸ Pluronic polymers such as poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer are typical commercially available amphiphilic polymers. Therefore, Pluronic polymers are often used as additives in membranes.^{5,7,8} However, apart from Pluronic polymers, numerous other types of polymers are also commercially available that can be used as polymer additives in membranes. Therefore, to develop a suitable technique for controlling the membrane properties and optimizing their fabrication procedure, it is important to elucidate the differences in the properties of membranes that are prepared using different polymers as additives. In this study, we focused on fluoropolymers whose chemical structures are significantly different from those of Pluronic polymers.^{9,10} Thus, fluoropolymers may show unique characteristics as membrane-property modifiers.

With the aim of developing an effective method for controlling the properties of membrane, in this study, CPVC flat-sheet membranes containing commercially available fluoropolymers as additives were prepared by the VIPS method, and their effects on the membrane properties were analyzed.

2 Experimental

2.1 Membrane fabrication

The membranes were prepared from a dope solution containing CPVC, tetrahydrofuran (THF), 2-propanol (IPA), and different types of additive polymers. The corresponding solution compositions are listed in Table 1. Unidyne DSN-403N (a perfluoroalkyl poly(ethylene oxide) adduct compound) and Surflon S-420 (a perfluoroalkyl compound) were used as the additive polymers. For comparison, Pluronic F-108 and L-64 were used as the Pluronic polymer additives. The dope solution was prepared by the following procedure. CPVC was dissolved in THF, and the mixture was stirred at 40°C for 8 h in a water bath to obtain a homogenous solution. This solution was subsequently cooled to 25°C, followed by adding IPA and the polymer additives to it. The resulting solution was stirred for more than 24 h until a homogenous solution was obtained.

The membranes were prepared via the VIPS method in a room under constant temperature and humidity. A nonwoven polyester fabric was used as the support layer. This fabric was dipped into a vessel containing the dope solution and then removed through a clearance gap between two stainless steel rolls that were adjusted to be at a constant distance. The nonwoven polyester fabric impregnated with the dope solution was kept in the room for more than 2 h till it was completely dry, and the membrane structure had solidified.

The viscosities of the dope solutions were measured by a viscometer (BL II, Toki Sangyo Co., Ltd., Japan).

2.2 Membrane characterization

The hydrophilicities of the membranes were determined by measuring their contact angles via the sessile

Table 1 Compositions of the dope solutions used for preparing CPVC/polymer-additive membranes

CPVC (g)	THF (g)	IPA (g)	Polymer additive	
			Type	Amount (g)
20	125	55	Control	0
20	125	55	F-108	5
20	125	55	L-64	5
20	125	55	DSN-403N	5
20	125	55	S-420	5

sile drop method by using a contact angle goniometer (DMs-401, Kyowa Interface Science Co., Japan).

The pure water permeabilities of the membranes were measured by wetting the membranes and using them to filter distilled water. The fabricated membranes were placed in a dead-end filtration unit, and distilled water was filtered under a constant pressure of 0.5 bar and temperature of 25°C. Subsequently, the filtration time for a 100 mL permeate volume was measured. The pure water permeability, L (mL/cm²·bar·min), was calculated using the following equation¹¹:

$$L = \frac{Q}{A \times \Delta t \times \Delta P} \quad (1)$$

where Q is the permeate volume (mL), A is the effective membrane area (cm²), Δt is the filtration time (min), and ΔP is the applied transmembrane pressure (bar).

The pore sizes and size distributions of the fabricated membranes were measured by a capillary flow porometer (CFP-1200A, Porous Materials Inc., USA). This apparatus was used to determine the pore diameters of the membranes via the liquid-gas displacement process. The membranes were fully wetted with Galwick which has a low surface tension. The fully wetted membrane was then placed in the sample chamber, and the liquid was extruded from the membrane pores by gradually increasing the air pressure. The flow rate of the air extruded from the membrane pores was measured by a flow meter placed in the apparatus. The mean flow pore diameter, d , was calculated by using the following equation¹²:

$$d = \frac{C}{\gamma p} \quad (2)$$

where C is a constant, γ is the surface tension of Galwick, and p is the differential pressure when the wet flow is half of the dry flow.

The surface morphologies of the fabricated membranes were observed via a scanning electron micro-

scope (SEM, TM3030, Hitachi High-Technologies Co., Japan). The surface porosities of the membranes were calculated by binarizing the SEM images of the membrane surfaces by using an image processing software (Image J, National Institutes of Health, USA). In the binarized images, the open-pore areas were designated with black color and the nonporous areas were designated with white color. The surface porosity was determined by the ratio of the total open-pore area to the total surface area.

The surface roughness of the fabricated membranes were measured by using a portable surface roughness tester (Surftest SJ-410, Mitutoyo Corp., Japan) which uses a contact stylus to make physical contact with the membrane surface. The measurements were performed at a contact force of 7.5×10^{-4} N and a measurement speed of 0.5 mm/s. The sampling length was 4 mm. Furthermore, the surface roughness also were analyzed in a narrow area by atomic force microscopy (AFM, AFM5100N, Hitachi High-Technologies Corp., Japan) in the dynamic force mode. The scan area was $5 \times 5 \mu\text{m}$.

3 Results

3.1 Viscosities of dope solutions

Table 2 lists the viscosities of the used dope solutions which consisted of CPVC, THF, IPA, and one of the polymer additives. The viscosities of all the dope solutions containing the polymer additives were higher than that of the control solution. Moreover, the viscosities of the dope solutions containing the fluoropolymers as additives were higher than those of the dope solutions containing the Pluronic polymers as additives. In particular, the dope solution containing Surfion S-420 exhibited the highest viscosity.

3.2 Hydrophilicities of fabricated membranes

Table 3 lists the water contact angles of the membranes fabricated with and without the different polymer additives. The contact angles of the membranes containing the polymer additives were significantly

Table 2 Viscosities of the dope solutions

Polymer additive	Control	F-108	L-64	DSN-403N	S-420
Viscosity (mPa·s)	60	66	65	70	84

Table 3 Water contact angles of the fabricated membranes after 0 and 180 s

Polymer additive	Contact angle (°)	
	time 0 s	180 s
Control	119	117
F-108	33	0
L-64	10	0
DSN-403N	14	0
S-420	35	0

lower than that of the control membrane. Moreover, the contact angles of all the membranes containing polymer additives reduced to 0° after 180 s. Therefore, it can be concluded that the hydrophilicity of the membranes enhanced due to the polymer additives. However, the hydrophilicities of the membranes with the fluoropolymers were not significantly different from those of the membranes with the Pluronic polymers.

3.3 Pure water permeability of fabricated membranes

Fig. 1 shows the pure water permeabilities of the membranes with and without the different polymer additives. The pure water permeability of the membrane containing Surflon S-420 was the highest. In contrast, the pure water permeabilities of the membranes with the other polymer additives were lower than that of the control membrane. However, the difference was slight, with the exception of the membrane with Pluronic F-108. According to the Hagen-Poiseuille law, for a constant transmembrane

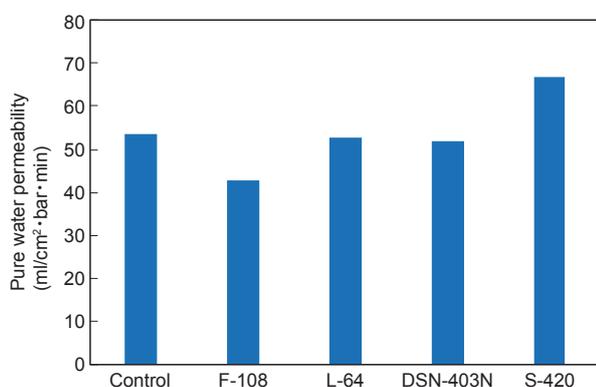


Fig. 1 Pure water permeabilities of membranes fabricated using different polymer additives

pressure, water viscosity, and membrane thickness, the pure water permeability of a membrane is determined by its porosity. In our case, the transmembrane pressure was constant. Furthermore, the viscosity of the water during the measurements also was constant because the measurements were performed at the same temperature. In addition, the membrane thicknesses were also similar (data not shown). Therefore, it can be assumed that the enhanced pure water permeability of the membrane containing Surflon S-420 additive is due to an increase in the porosity of the membrane.

3.4 Pore size and distribution of fabricated membranes

Fig. 2 shows the mean flow pore sizes of the membranes with and without the different polymer additives. In general, the mean flow pore size is indicative of the average pore size. The pore sizes of all the membranes with the polymer additives were larger than that of the control membrane with the exception of the Pluronic F-108-added membrane. In particular, the pore size of the membrane with Surflon S-420 was significantly larger than those of the other membranes. In contrast, the pore size of the membrane with Pluronic F-108 was slightly smaller than that of the control membrane. The pore size distribution curves of the membranes with and without the polymer additives are shown in Fig. 3. The membrane with Surflon S-420 exhibited a broad size distribution, whereas the membranes with the other polymer additives exhibited narrow size distributions.

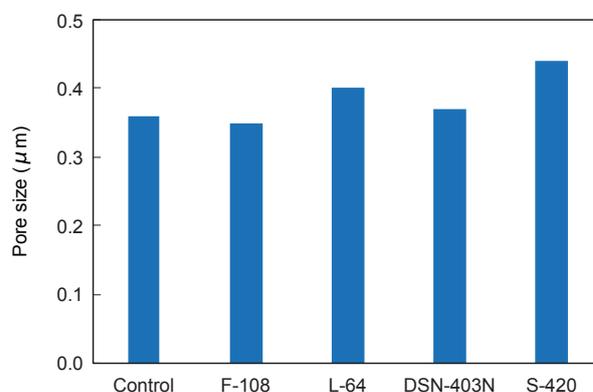


Fig. 2 Pore sizes of membranes fabricated using different polymer additives

3.5 Surface morphologies and porosities of fabricated membranes

Fig. 4 shows the surface morphologies of the membranes with and without the polymer additives. The SEM images show that all the membranes exhibited porous surfaces. In addition, the surface pores of the fluoropolymer-added membranes were much smaller than those of the other membranes. Furthermore, the widths of the additive polymers surrounding the open pores on the membrane surfaces were greater in the case of Pluronic polymer-added membranes than that in the control membrane.

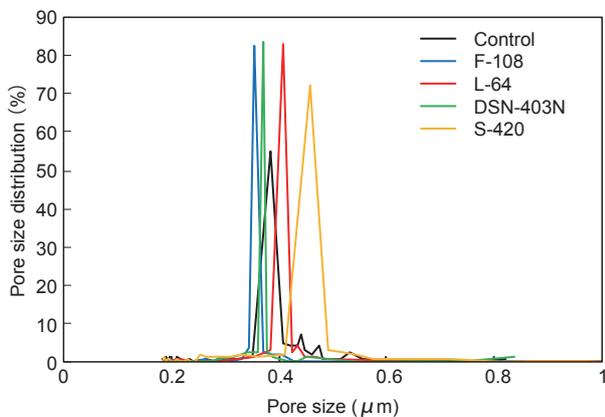


Fig. 3 Pore size distributions of membranes fabricated using different polymer additives

The surface porosities of the fabricated membranes as calculated from their binarized images are shown in Fig. 5. It was observed that the surface porosities of all the membranes containing the polymer additives were lower than that of the control membrane. This indicates that the area occupied by the pores on the membrane surface decreased. In particular, the surface porosities of the membranes with the fluoropolymers were significantly lower than those of the other membranes containing different additives.

3.6 Surface roughness of fabricated membranes

Fig. 6 shows the surface roughness line profiles of

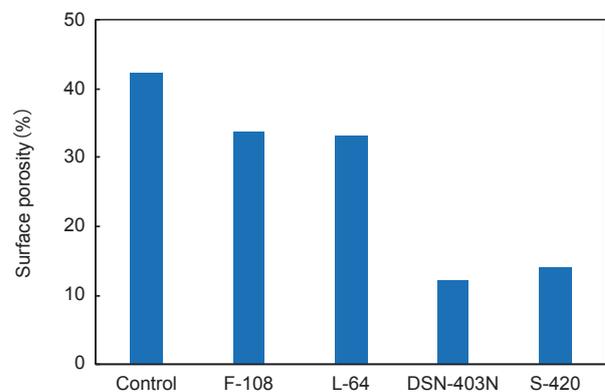


Fig. 5 Surface porosities of membranes fabricated using different polymer additives

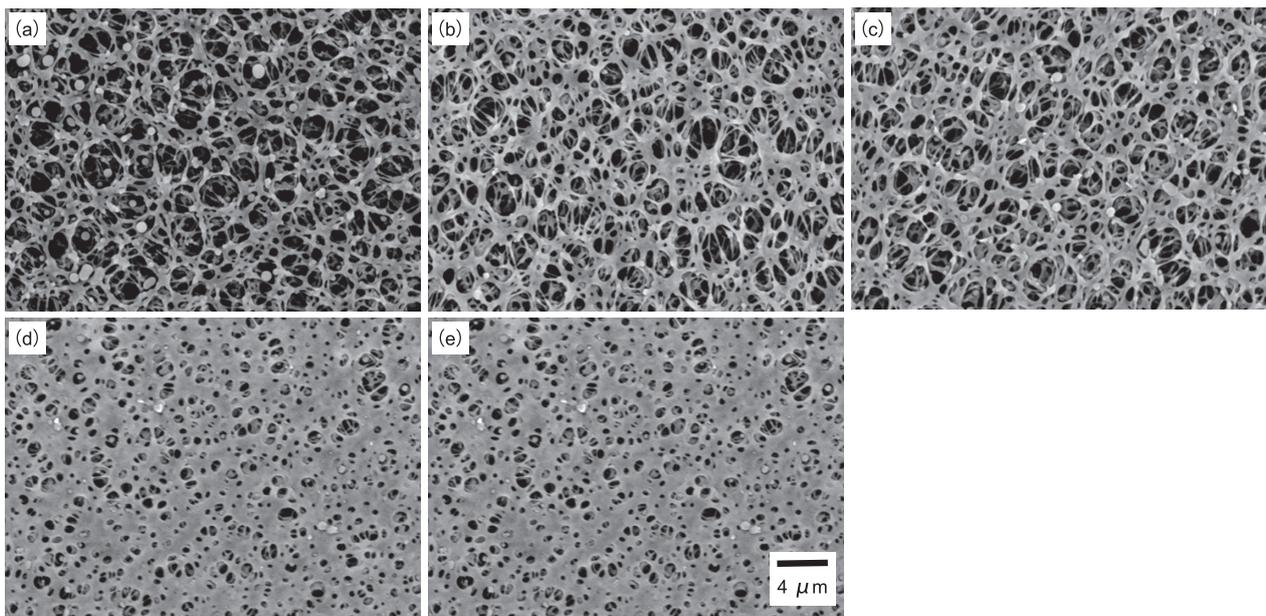


Fig. 4 SEM images of the surfaces of membranes fabricated using different polymer additives: a) control membrane, b) Pluronic F-108, c) Pluronic L-64, d) Unidyne DSN-403N, and e) Surfion S-420

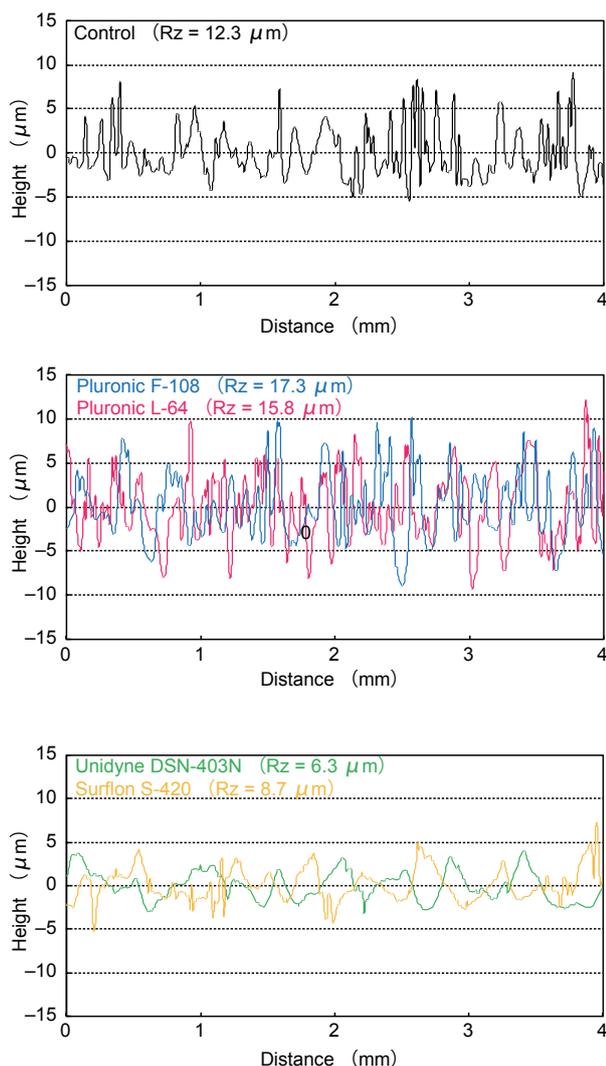


Fig. 6 Surface roughness line profiles of membranes fabricated using different polymer additives as determined by using a surface roughness tester

the membranes with and without the different polymer additives. The surface roughness of the membranes containing the Pluronic polymers were more pronounced than that of the control membrane. Conversely, the fluoropolymer-added membrane surfaces were smoother than that of the control membrane. In particular, the membrane containing Unidyne DSN-403N exhibited the smoothest surface. Fig. 7. shows AFM images of the fabricated membranes. It is clear that the membranes prepared using the fluoropolymers have smoother surfaces. These results are similar to those of the line profile measurements using portable surface roughness tester.

4 Discussion

The membranes that were prepared using the fluoropolymers exhibited structures different from that of the control membrane as well as those of the membranes prepared using the Pluronic polymers. When Surfion S-420 was used as the additive, the surface porosity of the membrane was lower (i.e., the surface was denser), and the surface was smoother than those of the control membrane and the membranes prepared using the Pluronic polymers. This was observed despite the fact that the Surfion S-420-added membrane showed the highest porosity. Conversely, when Unidyne DSN-403N was used as the additive, the surface porosity of the membrane was the lowest (i.e., the surface was the densest), and the surface was the smoothest, even though this membrane was as porous as the control membrane. In addition, the surface pore sizes of these two membranes were smaller than those of the other membranes. Therefore, it can be concluded that the addition of the fluoropolymers produced membranes that have smoother and denser surfaces as well as show high porosity. We believe that the phenomenon of the formation of a dense membrane surface observed in this study is similar to the evolution of the pore structure because of the coarsening of the polymer-rich phase, as observed in a previous study.⁸ The viscosities of the fluoropolymer-mixed dope solutions were higher than those of the other solutions; this may have also contributed to the formation of a dense surface. It is likely that the high viscosities of the former solutions hindered the diffusion of atmospheric water vapor into the dope solution, resulting in a delay in the phase separation and consequently the formation of a denser membrane surface. However, it is known that, when used as leveling agents, fluoropolymers can significantly lower the surface tension in solvent systems. Therefore, this functionality of the fluoropolymers may have aided the formation of smoother membrane surfaces. In general, membranes with denser and smoother surfaces are considered less susceptible to membrane fouling.^{13,14} Thus, it can be expected that the membranes containing the fluoropolymers as additives would show excellent antifoul-

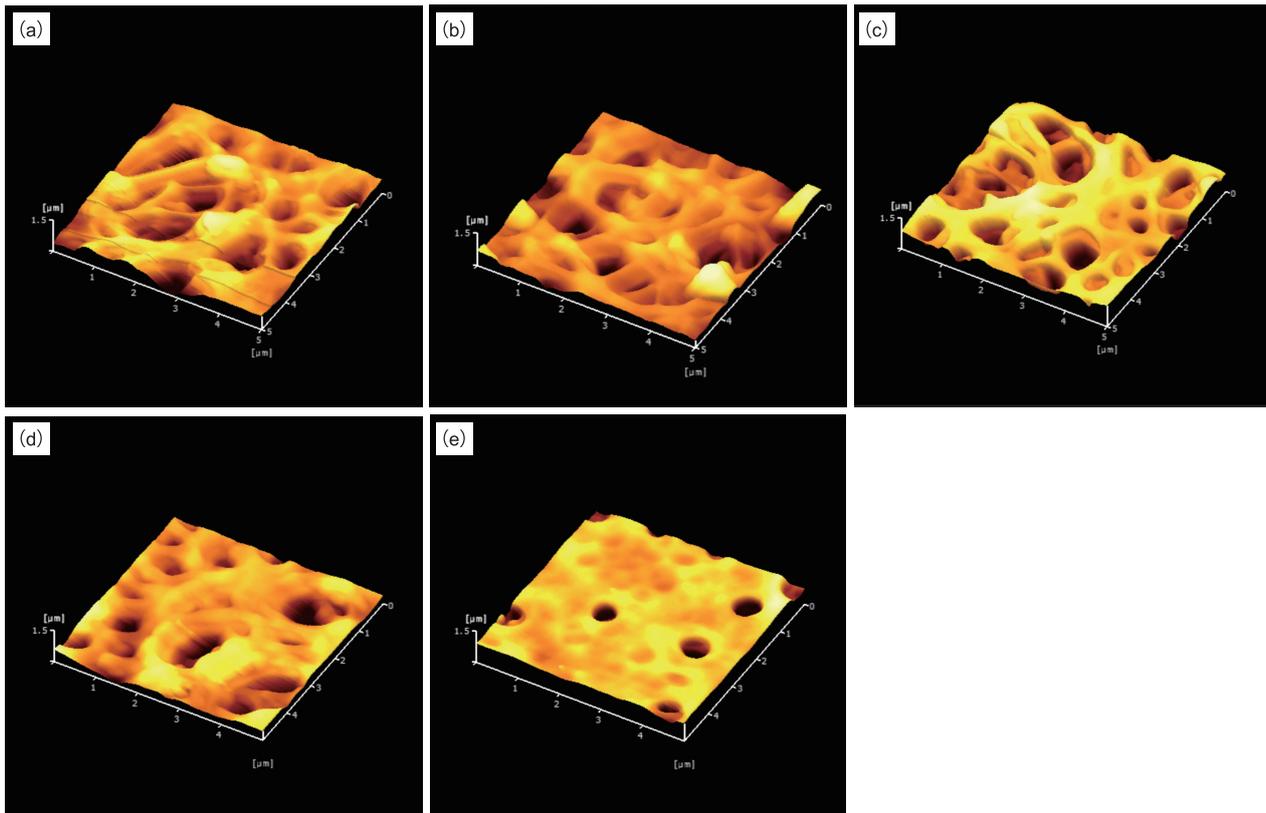


Fig. 7 AFM images of membranes fabricated using different polymer additives: a) control membrane, b) Pluronic F-108, c) Pluronic L-64, d) Unidyne DSN-403N, and e) Surfion S-420

ing properties in MBRs. The primary purpose of blending Pluronic polymers in membranes is to improve their surface hydrophilicity.^{5,7} Considering this aspect, the addition of the fluoropolymers also improved the hydrophilicity of the membrane surfaces.

Numerous studies have investigated the relationship between the properties of membranes and their fouling propensity. Based on the results of such studies, it is believed that membranes with a higher pure water permeability have a lower fouling propensity in MBRs.^{11,14} In our case, only the membrane prepared using Surfion S-420 as an additive showed a higher pure water permeability than that of the control membrane; therefore, it can be expected that of all the membranes fabricated in this study, the Surfion S-420 added membrane would exhibit the best anti-fouling characteristics in MBRs.

5 Conclusions

In this study, we investigated the effects of different

polymer additives on the properties of membranes for MBR applications. We used commercially available fluoropolymers instead of the commonly used amphiphilic polymers such as Pluronic polymers to prepare CPVC membranes by the VIPS method. The addition of fluoropolymers such as Unidyne DSN-403N and Surfion S-420 to the dope solution resulted in membranes that had dense and smooth surfaces and thus would be suitable for MBR applications. Furthermore, it was confirmed that the blending of the fluoropolymers in the dope solution improved the surface hydrophilicity of the fabricated membranes, similar to the case when Pluronic polymers are added. Therefore, this method of using fluoropolymers as additives is suitable for controlling the surface properties of membranes and can be used to fabricate high-performance CPVC flat-sheet membranes that show excellent antifouling properties in MBRs. Thus, this method will aid in developing improved MBRs.

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