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The stability of Poly(ether sulfone) membranes treated in hot water and hypochlorite solution

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Abstract

In order to improve hydrophilic property and filtration performance, a membrane has been modified by addition of polymeric additives in polymer solution. In the practical application, it is necessary to control the stability of the modified membrane. This study discusses filtration stability and hydrophilic property of four types of polyethersulfone hollow fiber membrane prepared with and without polymeric additives. The effect of membrane treatment (soaked in hot water and hypochlorite solution) on the filtration performance and hydrophilic property was investigated. Membrane consists of original PES membrane (M1), and three types of PES modified membrane with three different additive (M2, M3, and M4). The stability investigation was designed by using single module of hollow fiber membrane filtrated with deionized water during 10 days of filtration time. The hydrophilic property change of membrane was analyzed by measuring water contact angle. It was found that hydrophilic property and ultrafiltration performance of membrane M1 does not change after treated in water at temperature of 40^{o} C and in NaOCl solution. The treatment of membrane has also showed no impact on the hydrofilic property and ultrafiltration performance of membrane M2, M3, and M4. A significant change of filtration performance of membrane M2, M3, and M4 was obtained after membrane soaked in hypochlorite solution. Water permeability of those membrane increased up to 50% after ten days of filtration.

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Keywords: membrane stability, polyethersulfone, Ultrafiltration, water contact angle

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Nomenclature

UF	ultrafiltration
NIPS	non-solvent induced phase separation
PES	polyethersulfone
MWCO	molecular weight cut-off
ID	inner diameter
AFM	atomic force microscopy
Ra	mean roughness
RMs	root mean-square roughness
Rz	difference between the average highest peaks and the average lowest valleys
P	transmembrane pressure
V	volume of permeate
Jw_1	water permeability in the first day filtration
Jw_n	water permeability in the n^{th} day filtration
CTAB	cetyle three methyl ammonium bromide

1. INTRODUCTION

In recent years, ultrafiltration (UF) has been widely applied for water purification process. With the increasing requirement of membrane on the market, manufacturer and researcher have been developing a high performance of UF membrane. In order to improve the membrane life time as well as fouling resistant properties, porous polymeric membranes were prepared and modified in several methods including treatment of polymer materials[1-2], addition of the second polymer (blending) into polymer solution as pore modifying agent[3-5], modification of preparation condition[6], and surface modification of fabricated membrane[7]. Blending of polymer solution is an attractive option because it offers simple procedure and possibility of modifying the properties including pore size, pore distribution, skin layer thickness and surface hydrophilicity in a single step operation of non-solvent induced phase separation (NIPS) methods. In case of hollow fiber membrane, spinning condition via NIPS procedure such as polymer flow rate, air-gap distance, inner coagulant flow rate, and take-up speed winder also affect the performance of membrane[8-9]. In addition, properties of polymer materials, i.e. mechanical strength, flexibility, chemical resistance, and degree of hydrophilicity determine the membrane structure.

Property and performance of the modified membrane is expected to be better in regard of anti fouling, permeation and stability on caustic chemicals. In the aspect of filtration performance, membrane permeation has to be stable and durable, so that membrane life time could be longer. This research investigates ultrafiltration-stability characteristic by blending PES membrane modified with three types of polymer additives, and compared to profile of original PES membrane. The effect of types of membrane-modifying material on both water permeability and hidrophilic membrane property was subject of the study. Both water temperature at 40^{o} C and NaOCl solution as testing media of membrane stability are used.

2. METHODOLOGY

2.1. Materials

Four types of PES membrane of hollow fiber used in this experiment were produced in Membrane Research Center, Kobe University, Japan. The characteristic of membranes was listed in Table 1. Sodium hypochlorite solution (available chlorine 11%) used for membrane stability test was purchased from WAKO Pure Chemical Industries, Ltd. (Japan). High quality of pure water produced by an Elix-5 system (Millipore) was used in the membrane preparation and ultrafiltration experiment.

Table 1. The characteristic of membrane.

Membrane	Materials	MWCO (k·Da)	Length/ID (mm)
M1	PES	27	1550/0.96
M2	PES/PluF127	42	150/0.96
M3	PES/PVP	50	150/0.96
M4	PES/Tet1307	60	150/0.96

2.2. Membrane Characterization

The morphology of membrane surface was analyzed by using atomic force microscopy (AFM) (SII NanoTechnology, Inc., Tokyo, Japan, SPA400). For AFM measurement, a single piece of membrane was dried in oven drier at 70°C overnight. The outer surfaces of original and blended PES membranes were depicted in a scanning area of 4 μm × 4 μm. The surface roughness parameters of membrane such as mean roughness (Ra), root mean-square roughness (RMs), and difference between the average highest peak and the average lowest valleys (Rz) of fabricated membrane were analyzed from AFM photo processed by Spicel 32 software.

2.3. Membrane Stability

Filtration experiments were conducted by using a laboratory scale ultrafiltration of single hollow fiber module at transmembrane pressure (P) 0.5 atm, as the method reported in our previous paper[10]. The stability of the PES membrane was measured by the procedure described by Susanto and Ulbricht[11]. The membrane was immersed into deionized water for 10 days at 40° C. Another membrane sample was soaked in 200 ppm NaOCl solution at 25° C for 10 days. The stability performance of both membrane treatments was observed by measuring water permeability of the membrane every day until the experiment was stopped after 10 days. The stability performance of all membranes was determined based on membrane permeability which was calculated from volume (V) of permeating water every 5-minutes filtration time (t) by using the following equation:

$$\text{Relative permeability} = \frac{Jw_n}{Jw_1} \quad (1)$$

where, Jw_1 and Jw_n are water permeabilities in the first day and in the n^{th} day filtration, respectively.

2.4. Membrane Hydrophilicity

Hydrophilic level of membranes was analyzed by measuring water contact angle of all membranes that were original, immersed in hot water at 40°C, as well as in NaOCl solution of 200 ppm. Water contact angle was measured by water contact angle meter (Kyowa Kaiwenkagaku, CA-A) with 10 times repetition for each sample. One water drop was dropped onto membrane surface in wet condition. Immediately after the water touched membrane surface, angle formed between water bubble and membrane surface was recorded.

3. RESULT AND DISCUSSION

3.1. Surface Morphology

Detail observation on membrane surface morphology was done by AFM measurement. Fig. 1 shows three-dimensional AFM image of the outer surface of membranes without and with addition of membrane modifying agents. It can be seen that membranes have nodular structures formed as peak path and valley region. Generally, membranes prepared via NIPS process have this type of surface structure[12-13]. As clearly shown in Fig. 2, brightest

areas indicate the highest nodular peaks of the membrane surface and the dark regions mean valleys or pores of the membrane. Mean roughness (Ra), root mean-square roughness (RMs), and difference between the average highest peaks and the average lowest valleys (Rz) obtained from AFM images with Spicel 32 software are tabulated in Table 2.

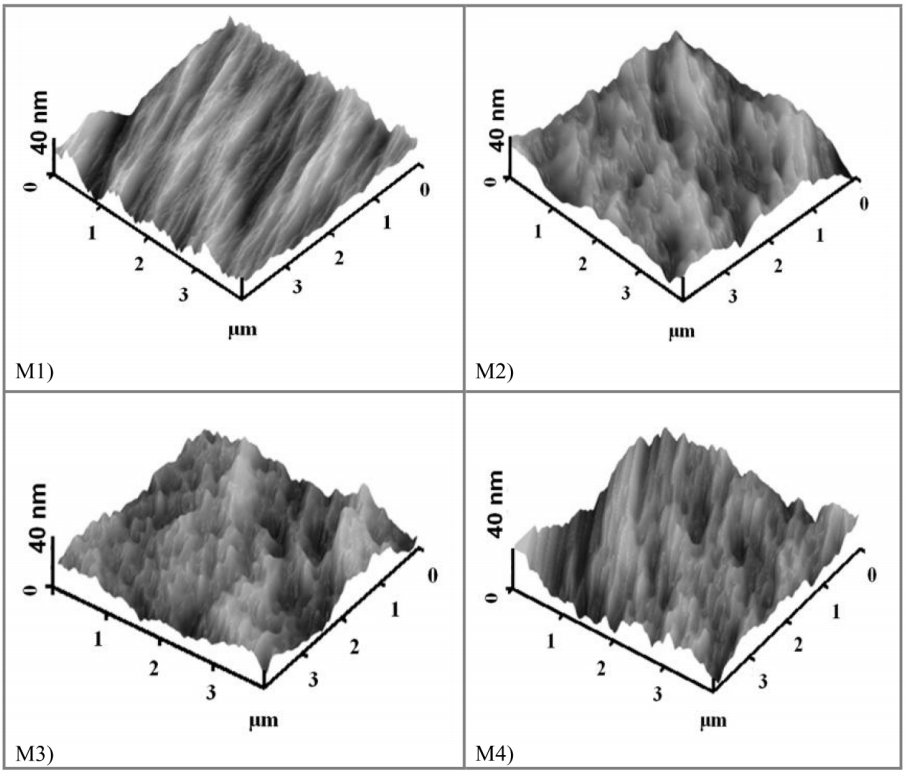

Fig. 1. Outer surface structure of membrane.

Table 2. Surface roughness of hollow fiber PES membrane.

Membrane system	Roughness parameters		
	Ra (nm)	RMs (nm)	Rz (nm)
M1	2.96	3.80	11.53
M2	7.65	9.30	26.89
M3	5.50	6.97	13.71
M4	5.89	7.01	16.25

It is confirmed that the surface roughness of all PES modified membrane is higher than the unmodified membrane. Addition of polymeric additive into dope solution may affect porous structure of PES membrane surface. The appearance of nodules structure on the membrane surface may attribute to the increase of membrane roughness. Such tendency was also reported in the previous studies. Research group of Ochoa found that the surface roughness of flat PES membrane modified with PVPK360 was higher than the unmodified PES membrane[14]. Rahimpour and co-worker[15] summarized the surface roughness changes of PES flat membrane after blended with PVP, cetyle three methyl ammonium bromide (CTAB), and Triton x-100. In all cases, the surface roughness of modified PES membrane was higher compared to unmodified PES membrane.

3.2. Membrane Stability

Fig. 2 indicates the performance of membrane filtration in terms of relative permeability during stability test. As clearly shown in Fig 2, the permeability of all membrane systems does not change after immersed in water at 40°C. A slightly decrease of the relative permeability of PES membrane M2, and M4 are detected, but still in the range of tolerable experimental data error. Fig. 3 shows results of membrane stability test after soaked in hypochlorite solution of 200 ppm. Relative permeability of the original PES membrane (M1) shows constant up to 10 days filtration. No change was found in relative permeability of the system of PES original membrane. Polyethersulfone has high chemical resistances, good mechanical and thermal properties[16]. Therefore, it is hard to decompose by hypochlorite treatment in this experiment. The same experimental results was also reported by our research group[12,17]. Another hypochlorite aging investigation was done by research group of Jung[18]. Polyacrylonitrile (PAN) membrane with and without addition of PVP were soaked in hypochlorite solution of 5000 ppm. They found that the permeability of PAN membranes without PVP were kept constant before and after treated with hypochlorite solution.

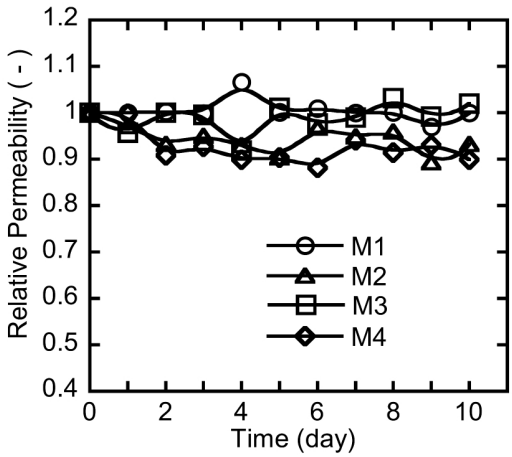

Fig. 2. The stability of membranes soaked 10 days in water at 40°C.

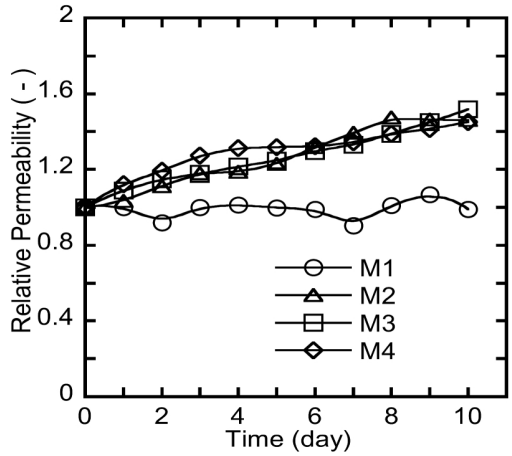

Fig. 3. The stability of membranes soaked 10 days in hypochlorite solution of 200 ppm

Relative permeability of the membrane M2, M3 and M4 increases remarkably when an aqueous hypochlorite solution of 200 ppm was applied (Fig. 3). During contact with hypochlorite solution, some parts of polymeric additives were leached out from the membrane matrix, resulting more porous morphology. Thus, membranes with higher relative permeability were achieved. The results was in agreement with other experiments reported by some authors[11, 19-20]. The improvement of water permeability sometimes may lead to reduction of solute rejection. It depends on diameter size of substantial particle in the solution. In order to overcome this problem, it is necessary to consider the appropriate composition between polymer and additive. Leaching of the additive particle while contacting with extreme solution is also influenced by compatibility interaction between polymer and additive material. Therefore, in the case of membrane modification, it is necessary to select membrane modifying agent with good stability and resistant to extreme solution

3.3. Membrane Hydrophilicity

Membrane hydrophilicity before and after treatments in water of 40^{o} C, and in NaOCl solution of 200 ppm were confirmed by water contact angle measurement. As shown in Fig. 4, membrane M1 has the highest water contact angle i.e. 73^{o}. Treatment in water of 40^{o}C, and in NaOCl solution does not influence on the water contact angle of the membrane M1.

Water contact angles of membrane M2, M3 and M4 are 63, 61 and 62^{o}, respectively. It indicates that hydrophilic property of these three membranes is better than that membrane M1. Immersion of these membranes in water at temperature of 40^{o}C during 10 days does not change the water contact angle. It means membrane treatment in hot water does not effect on membrane hydrophilicity. On the other hand, the slightly change in water contact angle was detected when membranes of M2, M3 and M4 were soaked in NaOCl solution. As described in section 2.1, membrane M2, M3, and M4 are prepare from blended polymer solution with additive. Some part of the additive particle is destroyed due to contacting with NaOCl solution. Reducing of additive content in the membrane matrix may result in increases of water contact angle. Therefore, the hydrophilicity of membrane became decreases.

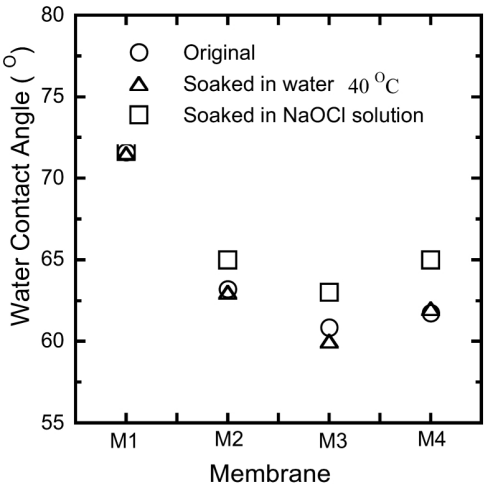

Fig. 4. Water contact angle of membrane before and after treated in water at 40°C, and in NaOCl solution

4. CONCLUSION

Filtration stability of four types of PES hollow fiber membranes was evaluated by using laboratory scale of single hollow fiber module. Permeation of deionized water was investigated after immersion of membrane in water at temperature of 40^{o}C. On the other series of experiment, all membranes are soaked in hypochlorite solution. The results of experiment concluded that ultrafiltration performance of membrane M1 which was prepared from PES

does not change in both treatment. Nevertheless, the modified PES membranes with additive (M2, M3 and M4) respond to change of hydrophilic property and UF performance after soaked in NaOCl solution. There was no effect of hot water treatment on hidrophilic property and UF performance of membranes M2, M3 and M3.

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