



Preparation and Characterization of Hydrophilic Hollow Fiber Microfiltration Membranes by Thermally Induced Phase Separation

Kitaura, Toshihiko

(Degree)

博士 (工学)

(Date of Degree)

2011-09-25

(Date of Publication)

2012-01-18

(Resource Type)

doctoral thesis

(Report Number)

甲5348

(URL)

<https://hdl.handle.net/20.500.14094/D1005348>

※ 当コンテンツは神戸大学の学術成果です。無断複製・不正使用等を禁じます。著作権法で認められている範囲内で、適切にご利用ください。



Doctoral Dissertation

**Preparation and Characterization of Hydrophilic
Hollow Fiber Microfiltration Membranes by
Thermally Induced Phase Separation**

(熱誘起相分離法による親水性中空糸精密ろ過膜の
作製と評価)

July 2011

**Graduate School of Engineering
Kobe University**

Toshihiko Kitaura

Acknowledgement

This thesis is the result of seven years of work whereby I have wished to develop new type membrane for a water purifier.

Foremost, I would like to express my deep and sincere gratitude to Professor Dr. Hideto Matsuyama for the support and the opportunity to perform my PhD study under his supervision. His advices, invaluable discussions, and teaching helped me to gain new perspectives and inspired me to undertake this challenge. I will never forget his encouragement over the years.

I sincerely thank Professor Dr. Takashi Nishino and Professor Dr. Naoto Ohmura for their kindness during the reviewing and examining of this thesis and giving many constructive comments to make it better. I am deeply grateful to Dr.. Yoshikage Ohmukai, for his kind support in the laboratory, helpful discussions during this research and help to draw up a thesis.

I sincerely thank to Dr. Tatsuo Maruyama, for his kind advise during examining of this thesis. I would like to extend my thanks to Dr. Tomohiro Sotani for his technical support throughout this work. I am also grateful to the fellow students I met during I have been studied in the laboratory for these seven years.

Finally, I would like to express special thanks to my wife for her understanding and cooperation.

Toshihiko Kitaura

Graduate School of Engineering

Kobe University, 2011.

Table of Contents

Chapter I General Introduction	1
I.1 Basis and uses of membrane separations	1
I.2 The history of membrane separation techniques.	6
I.3 Methods for preparing membranes	7
I.4 Fouling on separation membranes	10
I.4.1 Simplified fine pores occlusion model	11
I.4.2 Causes of fouling.....	12
I.4.3 Methods to avoid fouling and post-treatment after fouling.....	13
I.4.4 Development of an antifouling membrane	13
I.5 Polymer membrane materials	14
I.6 Purpose of this study	16
I.7 Scope of this thesis.....	18
References	19
Chapter II Effect of amphiphilic additives on properties of cellulose acetate butyrate hollow fiber membranes prepared by thermally induced phase separation	23
II.1 Introduction	23
II.2 Experimental.....	24
II.2.1 Materials.....	24
II.2.2 Phase diagram	25
II.2.3 Hollow fiber membrane preparation	26
II.2.4 SEM and AFM observation	28
II.2.5 Water permeability and mechanical strength.....	28
II.3 Results and discussion	29
II.3.1 Phase diagram	29
II.3.2 SEM observation.....	30
II.3.3 Water permeability.....	34
II.3.4 Mechanical strength	35
II.4 Conclusions	37
References	38
Chapter III Membrane fouling properies of hollow fiber membranes prepared from cellulose acetate derivatives	41
III.1. Introduction	41
III.2 Experimental	43

III.2.1 Materials	43
III.2.2 Phase diagram	44
III.2.3 Preparation of hollow fiber membranes	45
III.2.4 Characterization of the hollow fiber membrane	45
III.3. Results and discussion.....	48
III.3.1 Phase diagram	48
III.3.2 Membrane structure and characterization.....	50
III 3.3 Fouling experiment using membranes with similar water permeabilities	54
III.4 Conclusion.....	59
References	59
Chapter IV Preparation and characterization of several types of polyvinyl butyral hollow fiber membranes by thermally induced phase separation.....	65
IV.1 Introduction.....	65
IV.2 Experimental	66
IV.2.1 Materials	66
IV.2.2 Phase diagram.....	67
IV.2.3 Hollow fiber membrane fabrication	68
IV.2.4 SEM observation	68
IV.2.5 Water permeability	68
IV.2.6 Mechanical strength.....	69
IV.2.7 Exclusion of PS beads and bacteria.....	69
IV.3. Results and discussion	70
3.1 Phase diagram	70
3.2 SEM observation	71
3.3 Water permeability	73
3.4 PS bead and bacteria exclusion.....	76
3.5 Mechanical strength.....	78
IV.4. Conclusion	79
References	80
Chapter V General Conclusion.....	83
List of Publications.....	87

Chapter I

General Introduction

Water is essential to all living things and is said to be the origin of life. Specifically, it comprises approximately 65 percent of human body weight and about 2500 mL is metabolized per day. Therefore, as with air, it cannot be done without. Although air is equally available to everyone on Earth, water supplies depend heavily on geographic and meteorological conditions, and therefore are not equally available to each region. Because water shortages and pollution may lead to health problem and conflicts over water, they are a critical global issue. Although the planet is abundant in water, fresh water comprises only 2.5%, with the remainder being seawater, and water resources suitable for daily use amount to only 0.01% of the total. As this amount is insufficient to supply the current global population, the need for techniques that can efficiently filter impurities from raw water at low cost is increasing. Reverse osmosis (RO) membranes for seawater desalination and other separation membranes for river water purification and industrial sewage treatment, such as nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) membranes, suffer from a number of problem, although they have been put into commercial use and attracted significant attention.

I.1 Basis and uses of membrane separations

As shown in Fig. I.1, membranes used for separation have a porous structure, and membrane separation is a process wherein particles are separated from a liquid. Many types of particles of different sizes are present in water, including visible particles such as rust or mold, and invisible solutes, such as proteins, sugars and ionized inorganic

salts. Separation membranes filter these components through pores. Filtration membranes can be classified into four types in terms of their pore size and filtering ability: microfiltration membranes are used to remove yeast and bacteria; ultrafiltration membranes can filter proteins and viruses; nanofiltration membranes are used to remove divalent ions and agricultural chemicals; and reverse osmosis membranes are used in seawater desalination and manufacturing of ultrapure water [1]. The range of target sizes is summarized in Fig. I.2.

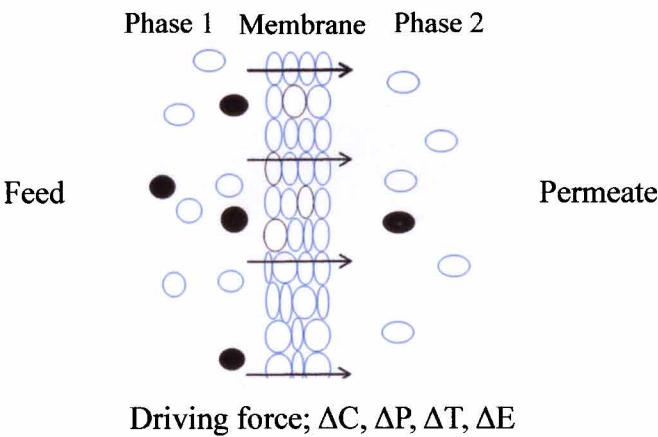


Fig. I.1 Image of molecular sieve.

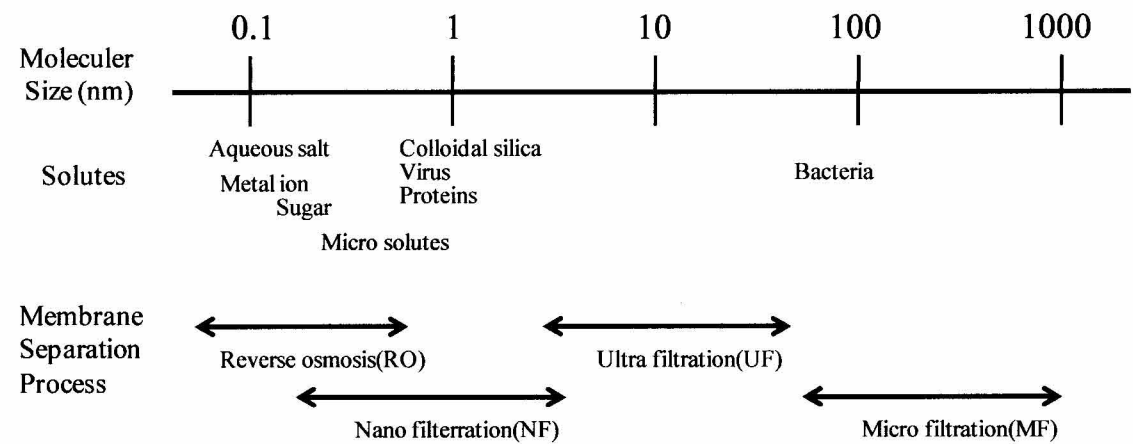


Fig. I.2 Application ranges of various processes.

Reverse osmosis membranes can separate ions that have been dissolved in water by permeating water through the membrane under high pressure. It has the smallest pore size of the four membranes, and is the only membrane that can desalinate seawater to produce fresh water. To produce desalinated water in practice, however, the specifications required of RO membranes are quite high: high water permeability, high NaCl rejection, and high mechanical strength to endure osmotic pressures greater than 24 atm. Since Loeb and Sourirajan succeeded in synthesizing the first asymmetric membrane using cellulose acetate in 1960 [2], many RO membranes have been developed. Reverse osmosis is essentially an energy-saving separation method because it consumes electric power mainly for hydraulic pressure, while conventional processes such as evaporation require enormous quantities of energy for phase change.

NF membranes can separate small matters, with diameter 1–2 nm, corresponding to molecular weights from 200 to 1000 Da. In NF membranes, mechanical separation through fine pores and electrostatic repulsion with electric charges on the membrane surface are combined. Thus, a membrane performance that is effective for the separation of divalent ions is possible. Because of this characteristic, NF membranes have attracted attention to satisfy the complex separation demands of the environmental and food fields. In Europe and the United States in particular, NF membranes are widely used in water purification processes, such as removal of organic solvents and pesticides from underground water and stream water. Applications of NF membranes in other fields are now being considered. Likely applications of NF membranes include the separation of mixtures of salts, amino acids and proteins in the food industry, desalination of whey in the dairy industry, separation of oligosaccharides from liquid saccharide mixtures, and separation of amino and organic acids such as lactic acid, amongst others.

Ultrafiltration membrane have fine pores with diameters from 2 nm to 0.1 μm and can separate materials with molecular weights from 100 to several hundred thousand Da. UF membranes can treat viruses, polymers, colloids, fine particles, enzymes and proteins, which cannot be separated by MF membranes. UF membranes have been used practically in the livestock industry, food processing and pharmaceutical industries, collection of electrodeposition lacquer, disposal of radioactive wastes from nuclear power plants, processing of sewage water, concentration of milk, and so on. Thus, the use of UF membranes in the water processing field is actively encouraged, in addition to MF membranes.

MF membranes vary the most amongst filtration membranes. They can capture particles with sizes larger than 0.1 μm on the membrane surface, and the fouling layer that accumulates on the membrane surface can be repeatedly washed. Therefore, MF membranes can be used long term. They can also be used long term in continuous processes using the cross flow filtration method. MF membranes are used practically in water treatment, the clarification of beverages and the manufacture of liquor. Moreover, MF membranes are extremely important for medical applications, because they can completely remove *E. coli* and pathogenic microorganisms with sizes from 0.2 to 0.4 μm if 0.1 μm microfilter membranes are used.

With regard to membrane morphology, hollow fiber membranes are gathering increasing attention because of needs for large volumes of water treatment, while flat membrane have been popular. The driving forces for mass transfer in membrane processes are mainly pressure difference, concentration difference and potential difference. Because membrane separation does not involve phase change, it is a fascinating method in terms of energy conservation. While other separation methods

that involve phase equilibrium, such as distillation and adsorption, require significant space and time, membrane separations efficiently separate large quantities of suspended solids in smaller devices within shorter times. For this reason, membrane separation technologies have developed into a wide field. They are used especially in food and biotechnology processes, for example separation or concentration of enzymes and proteins.

In the above, we explained the characteristics and some particular applications of four representative separation membranes. Next, we explain why membrane separation particularly excels over other methods in water purification. The distillation and adsorption processes used in the past required time for phase separation to occur and space for relatively large equipment. The driving forces for membrane separations depend on transmembrane differences in pressure, concentration or electric charge. Therefore, the process does not require phase change for separation. Because of the advantages mentioned above, membrane modules are of smaller size and can achieve shorter separation times, and thus, by definition, membrane processes are economical. Particularly recently, membrane separation is commonly used for seawater desalination or water purification to obtain safe, potable water. Although evaporation was the mainstream process for seawater desalination in the past, the method required huge amounts of energy. On the other hand, membrane separation methods using RO membranes gained attention because of the energy advantage and in the 90's, the construction of desalination plants using large RO membrane modules began all over the world.

In the field of water purification, water treatment using separation membranes have gained attention as an alternative to sand filtration, which was mainly used in the past.

Behind this trend were several reports of mass infection by protozoa (*Cryptosporidium*). Although these protozoa survive even disinfection by chlorine, they are removed by mechanical filtration. For these reasons, membrane separation is expected to become the main technology used in water treatment.

I.2 The history of membrane separation techniques.

Membrane separation is a relatively new technique. It is only 50 years since development and practical application started. However, new application fields are discovered every decade and each time, the technique is further developed. The history of membrane separation as a chemical engineering separation technique started when reverse osmosis membranes for seawater desalination were developed by S. Loeb and S. Sourirajan in 1960. In this year, a seawater desalination plant was built and put into use. On the other hand, the development of Loeb and Sourirajan type asymmetric membranes accelerated the development of other membrane techniques. In the 1970s, UF membranes were applied to the treatment of waste liquid from electrodeposition coatings of automobiles and to treatment of cheese whey (separation and collection of proteins). Huge separation plants were used at that time. In 1980s, UF membrane started to be applied to gas separation, hydrogen separation in chemical manufacturing plants, concentration of fruit juice, and sterilizing filtration in food processing.

Around 1990, as the semiconductor industry was developing, membrane processing contributed actively to making ultrapure water for manufacturing semiconductors. Nowadays, in the 21st century, membrane separation has gained attention in reverse osmosis for seawater desalination, for ultrafiltration in water purification plants, and the membrane bioreactor (MBR) process in sewage treatment. As mentioned above, the

history of water treatment is short indeed, and therefore the cumulative study and technique development is as yet insufficient. Universities and various research institutes are now making efforts to solve problems in water treatment.

I.3 Methods for preparing membranes

Porous membranes can be prepared by stretching, track etching, sintering, template, and phase separation methods. Among these, the phase separation method has been mainly adopted for industrial applications. Phase separation can be applied to various polymer substances to prepare membranes with various pore sizes and highly porous structures by controlling the operating conditions during the phase separation. Moreover, asymmetric membranes, which have a porosity distribution in the cross-sectional direction, can be prepared. There are two phase separation methods. The first is the nonsolvent induced phase separation (NIPS) method, in which the phase separation is induced by adding a nonsolvent. The other is the thermally induced phase separation (TIPS) method, in which phase separation is induced by cooling. Features of each technique are explained below.

[NIPS method]

In the NIPS method, a polymer solution is immersed in a nonsolvent to obtain a porous membrane. This method is the most widely used for membrane preparation. Fig. I.3 shows a phase diagram of the NIPS method. The exchange of the nonsolvent and the solvent occurs when a polymer solution (a mixture of polymer and solvent) is immersed in nonsolvent and the composition shifts toward the nonsolvent direction. Phase separation by nucleation and growth proceeds in the metastable region between the binodal line and the spinodal line. In contrast, the phase separation by spinodal

decomposition proceeds in the area inside of the spinodal line. The path of the composition change can be controlled by adding nonsolvent to the solution beforehand or adding the solvent to the nonsolvent. By controlling the path, membranes with various pore sizes and structures can be prepared.

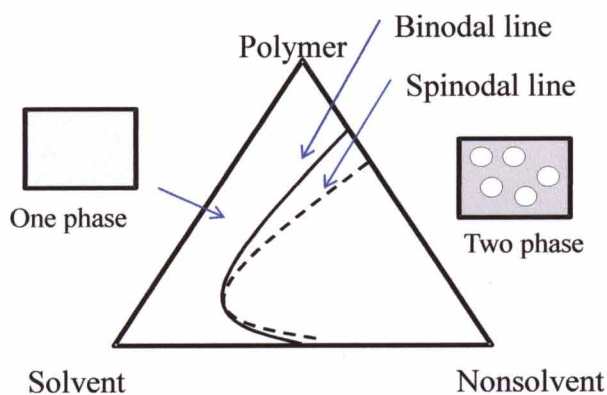


Fig. I.3 Phase diagram of the NIPS method.

[TIPS method][3,4]

In the TIPS method, the phase separation is induced by cooling a polymer solution that is homogeneous at higher temperatures, producing a porous membrane. It is an effective method for polymers that are not able to be dissolved in solvents at ambient temperature because the polymer is instead dissolved at higher temperatures. Fig. I.4 shows the phase diagram of the TIPS method. A homogeneous solution is prepared by stirring a mixture of polymer and diluent at higher temperatures. Phase separation is then induced by quenching the solution below the binodal line, which is the borderline between the one-phase and the two-phase region. Polymer crystallization occurs when the solution is cooled under the crystallization temperature of the system.

In the TIPS method, phase separation is induced by thermal migration, whereas it is induced by transfer of material in the NIPS method. It is said that TIPS method prepares

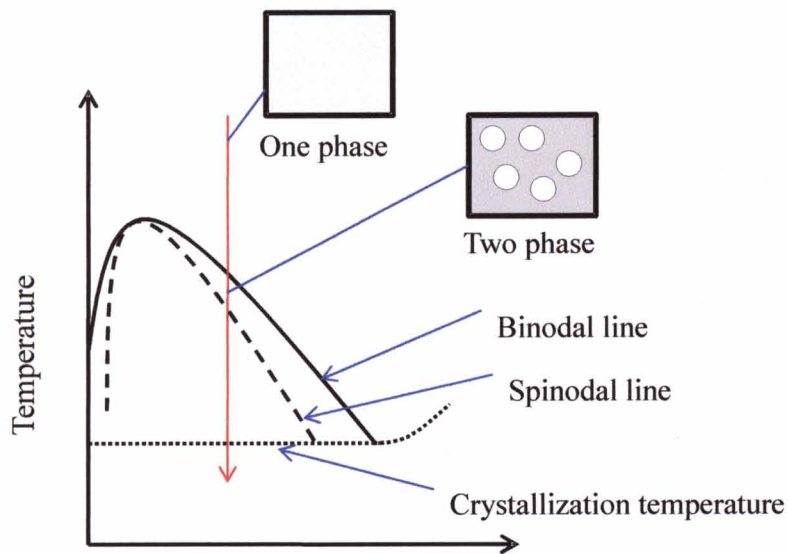


Fig. I.4 Phase diagram of the TIPS method.

membrane with a more uniform pore size, because heat transfer is extremely fast compared with the diffusion of material. The control of pore size has commonly been achieved by controlling the cooling rate. Moreover, the TIPS method is classified into three types, according to the phase separation: liquid-liquid phase separation (L-L TIPS); solid-liquid phase separation (S-L TIPS) where the polymer solidification (crystallization) occurs; and liquid-solid phase separation (L-S TIPS), where the crystallization of solvent occurs. Although TIPS is a comparatively new method for making porous membranes (the patent was granted for the first time in 1981). Porous membrane formation processes and the advantages of the TIPS method compared with the NIPS method are summarized as follows.

[Membrane formation using the TIPS method]

1. Make a mixture of polymer and diluent. The boiling point of the solvent must be high.

2. Cast the solution to form a flat membrane shape or extrude it from spinneret to form a hollow fiber.
3. To induce phase separation, the solution is cooled at an appropriate rate. To obtain a larger pore size, maintain a constant temperature and allow the droplets of polymer-lean phase to increase. Finally, the polymer is solidified by crystallization or glass transition.
4. The diluent is extracted by ethanol or another solvent.

[Advantages of the TIPS method over the NIPS method]

1. Compared with the NIPS method, TIPS method is suitable for polymers with low solubility, such as crystalline polymers, because the higher temperature of the solution enables greater solubility of polymer in the solvent.
2. Large, pore-like macrovoids are not formed in the membrane prepared by the TIPS method.
3. In the TIPS method, the membrane production process is easily controlled and has high reproducibility. In the NIPS method, the process is difficult to control because it involves diffusion of substances rather than heat transfer.
4. Membranes made by the TIPS method can be formed in various shapes, such as planar membranes, hollow fibers, tubes and blocks.

Given these factors, the TIPS method is superior to other methods and should be the main method used in the industrial field.

1.4 Fouling on separation membranes

The phenomenon of “fouling” is one in which solutes in water are adsorbed and

deposited on the membrane surface or within the pore, clogging the membrane pores. However, fouling is quite complex, where chemical, mechanical, electrical, and structural properties of the membrane affect the behavior. There is still debate about the theory regarding avoidance of fouling. In the past many studies have been conducted to overcome the fouling, which is the result of complex phenomena. [5–8]

I.4.1 Simplified fine pores occlusion model

To develop a highly effective membrane separation system, clarification of the mechanisms behind blockage of pores and the growth of the deposit layer is needed. Fouling is classified into four types, as shown in Fig. I.5.

- (a) Cake filtration: Foulant forms a cake layer over the membrane surface and the pores are covered.
- (b) Complete blocking: Foulant plugs the membrane pores.
- (c) Intermediate blocking: Foulant accumulates on membrane pores already plugged by foulant.
- (d) Standard blocking: Foulant is adsorbed in the membrane pores, reducing the diameter of the pores.

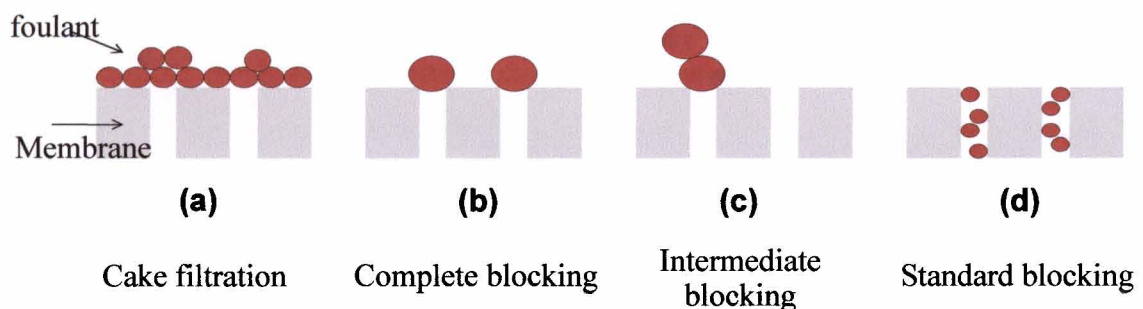


Fig. I.5 Fine pores occlusion model.

When the foulant is larger than the membrane pore, complete blocking occurs, in which the foulant clogs the membrane pore uniformly. Simultaneously, intermediate blocking and cake filtration proceeds. When the foulant is smaller than the pore diameter, standard blocking occurs. Many investigations have developed formulae for identifying which type of filtration dominates the water permeation from the relation between filtration velocity and unit area.

I.4.2 Causes of fouling

In terms of chemical properties, it is generally claimed that fouling occurs more often on hydrophobic membranes than hydrophilic ones. From a physical viewpoint, fouling occurs more easily on membranes with larger pores than membranes with smaller pores. It is also said that membrane with no charge does not easily adsorb foulant. Because the membrane characteristics affect the interaction of the membrane surface and foulants, each of the characteristics should be considered carefully for practical use. Typical foulant includes natural organic matters (NOM), such as humic substances, carbohydrates, proteins, inorganic substances and microorganisms. Because of hydrophobic interactions, a hydrophobic membrane surface tends to adsorb foulants such as proteins. Moreover, on the surface of the membrane, a phenomenon called "concentration polarization" occurs, in which the solute concentrations are higher than that of the bulk solution. The solute deposits and forms an adhesion layer when concentration polarization occurs, because the solute concentration on the surface of the membrane exceeds the saturation solubility. In particular, proteins interact with other proteins or substances, and sometimes creates a gel adhesion layer. In proteins that have SH and S-S groups including BSA, aggregation is promoted by the S-S exchange

reaction [9]. Biofouling, the propagation of microorganisms on the membrane surface, is also a serious problem in seawater desalination by RO membranes and MBR processes. After adhering to the membrane surface, microorganisms form colonies. As the number of colonies increase, the colonies are covered with polysaccharide slime called biofilm, and this causes fouling [10].

I.4.3 Methods to avoid fouling and post-treatment after fouling

To prevent fouling, pretreatment of the feed solution can be considered, such as pH adjustment, complexing agents, chlorination and adsorption. Once fouling has occurred, backwashing as a post-treatment is needed, such as hydraulic, mechanical, and chemical washes using acid, base, oxidant, enzyme and complexing agents.

I.4.4 Development of an antifouling membrane

Several washing techniques are well known for maintaining membrane function, as mentioned above. However, these washing methods complicate the membrane module, increase the running cost and may damage the membrane during treatment.

Therefore, to enhance the efficiency of the membrane separation process, the improvement of the membrane itself is essential. The suppression of adsorption and deposition of foulants on the membrane is the most important way to reduce fouling against various foulants. There are two ways to lower the possibility of fouling occurrence. One is surface modification, such as graft polymerization and coating of foulant-free materials. This kind of treatment requires additional processes for the prepared membrane, and therefore labor and operating costs will increase. The other method is modification of the dope solution by adding a hydrophilic additive or

modification of the polymer itself. This modification treats powder or liquid mixtures of polymer and additive, where the handling is easier compared with post-treatment of the membrane. Thus, the methods mainly reported are pretreatments, such as the addition of hydrophilic groups to the polymer substance, graft polymerization of hydrophilic monomers and the blending of hydrophilic materials into the polymer solution [11–13].

I.5 Polymer membrane materials

[Genealogy and problems of polymer membrane materials]

Membrane separation technology developed dramatically from the beginning of salt water desalination. Membrane separation processes are now applied in a wide range of fields by making various membranes. Membrane pore sizes can be controlled for separation of specific substances. Moreover, research has been carried out on synthetic polymers, including polyethylene, polypropylene, polyacrylonitrile, polysulfone, polyethersulfone, polytetrafluoroethylene and polyvinylidene fluoride. Because each synthetic polymer possesses advantages and disadvantages, however, studies on modification of the membrane materials themselves, using graft polymerization, copolymerization, and mixing of various additives have been carried out to overcome defects in practical applications. The features of representative polymers for membranes are explained as follows.

Cellulose acetate is a polymer that has been widely used in fibers and membranes, and is obtained through partial acetalization of the three hydroxyl groups on natural cellulose and subsequent solubilization in an organic solvent. RO and UF membranes are prepared from cellulose acetate by preparing a dense skin layer on one surface and an asymmetric structure beneath. Because the material is hydrophilic, the cellulose

acetate membrane has a relatively high antifouling property. On the other hand, cellulose acetate is biodegradable due to its natural origin, and has a relatively low long-term stability. Recently, because of its excellent hydrophilicity, a derivative in which a hydroxyl group is substituted by butyrate has gained attention [14].

Polyethylene and polypropylene are membrane materials used in the stretching method by which flat membrane and hollow fiber MF membranes are prepared. Because of their high hydrophobicity, they are used in membrane distillation, degassing membranes, and artificial lungs. Preparation of PE/PP hollow fiber membranes by the TIPS method has also been reported [15].

Polytetrafluoroethylene (PTFE) is a soft polymer that has an extremely high chemical resistance and is used in MF membranes. Because there is no solvent for PTFE, MF membranes are prepared by the stretching method.

PVDF is a polymer that has high chemical and mechanical strength. Therefore, it is used in many cases as a membrane for water purification. However, PVDF membranes have severe fouling properties due to its high hydrophobicity, and research has been carried out to improve its surface characteristics. PVDF membranes are also used for MBR because of its high mechanical strength, [16].

Polysulfone (PSf) is an engineering plastic with high mechanical strength and heat resistance. Thus, steam sterilization can be applied to this material. It also has high chemical resistance so strong washing agents can be used.

Polyethersulfone (PES) is not easily clogged by foulants because it is more hydrophilic than PSf, and therefore an asymmetric UF membrane has been prepared from this polymer. It is also used as the support for RO membranes [17].

Aromatic polyamide is a polymer created through amide bonds and is used as the

dense layer for RO and NF membranes. The material is hydrophilic and has a molecular gap. Due to these features, it works as a semipermeable membrane that can separate water from ions in a feed solution. Although it has both amino and carboxyl groups, its tolerance to chlorine is generally weak, because it is a charged membrane with excess anions [18].

Polyimide is a glassy polymer that has an excellent tolerance to heat and organic solvents. Membranes prepared from polyimide are used for gas separation.

In addition, many synthetic polymers with particular functionalities are studied as membrane materials: polyacrylonitrile has high hydrophilicity and chemical resistance; polyvinyl acetal has chemical resistance; copolymers of ethylene and polyvinyl alcohol, EVOH, has both hydrophilic and hydrophobic properties [19].

Recently, polyvinylacetal [20] has become more popular as a novel membrane material, while membrane development using polylactic acid obtained from plants has begun, with the aim of promoting petroleum-free industrial materials synthesis [21].

1.6 Purpose of this study

As mentioned above, the history of membrane separation for water treatment is very short and it is only 15 years since membranes started being used for water treatment. Therefore, the development of techniques for water treatment has been limited and there remain many problems, such as **1.** development and selection of polymers as membrane substances **2.** modification or processing techniques for materials **3.** membrane manufacturing techniques and **4.** decreases in water permeability through fouling during practical use. Amongst these problems, fouling is the most severe. The deposition and adsorption of foulant on the membrane surface or pores causes fouling of separation

membranes. Clogging of the pore results in a decline in water permeability. This phenomenon is affected by the hydrophilicity of the membrane material, the surface morphology, the size or shape of the membrane, the electrostatic properties of the membrane surface and the water permeability. Therefore, the analysis of fouling is difficult and the solution to avoid fouling has not yet been obtained. In the present circumstance, fouling leads to an increase in the running costs and a decline in membrane lifetime. Most research into fouling has been concerned with the improvement or modification of membranes to avoid fouling, while there have been few reports describing the fundamental investigation of correlations between membrane characteristics and fouling. Although it is claimed that membranes with high hydrophilicity are hardly affected by fouling, there is no report that mentions the relation between hydrophilicity and fouling mechanisms. For membranes made from hydrophobic materials, such as PDVF, PE, PP and PSf, various methods have been developed to improve the hydrophilicity of the membrane: graft polymerization or copolymerization of hydrophilic monomers, polymer blending of hydrophilic polymers, addition of polyethylene glycol or polymer surfactant, and coating or deposition of water soluble polymers. These hydrophilic additives in the membrane sometimes leach out due to its low compatibility with the hydrophobic membrane matrix, or are decomposed during washing treatment because of their low chemical resistance. However, no study has reported a solution to this problem currently.

First, the effect of membrane preparation conditions by the TIPS method and hydrophilic additives on the membrane characteristics were studied. To be more precise, we examined the effects of air gap between spinneret and coagulation water bath on water permeability, tensile strength and structure of membranes and the effects of three

hydrophilic additives on water permeability.

Second, to investigate the effect of membrane hydrophilicity on fouling, we prepared membranes with similar physical properties, water permeability, surface roughness, and zeta potential, but with differing contact angle measurements, which is an indicator of hydrophilicity. The fouling properties of each membrane and the behavior with backwashing was then examined through fouling experiments using humic acid and BSA as foulants.

Moreover, to develop MF membranes for water purification, membranes prepared from polyvinyl acetal (PVB) were examined. PVB is an acetalized polymer of polyvinyl alcohol, which is made from inexpensive polyvinyl acetate through partial saponification. The hydrophilicity of PVB can be controlled by the acetalization ratio, the choice of acetalization agent and the blending of polymers with similar structures. Because PVB has a high compatibility with the same type of polymer, membrane denaturation by leaching out of the additive is less likely to occur, compared with the case of blending the polymer with a completely different kind of additive. Moreover, PVB has tolerance to strong acids and bases, maintains its structure after repeated of wetting and drying, has a good balance of strength and elasticity, and maintains its strength at low temperature. In this study, we blended two PVBs to prepare hollow fiber membranes with high water permeability, hydrophilicity and mechanical strength.

I.7 Scope of this thesis

This thesis was divided into the following 5 chapters. Each part is described briefly below:

Chapter I introduces the background and purpose of this study. A review of previous

work and the scope of thesis are also given.

In **Chapter II**, the preparation of hollow fiber membranes from cellulose acetate butyrate by the thermally induced phase separation method is described. The effect of preparation conditions and amphiphilic additives on the membrane characteristics are evaluated for CAB membranes.

Chapter III discusses fouling properties of three hollow fiber membranes prepared from cellulose acetate, cellulose acetate butyrate, and cellulose acetate propionate. These membranes were prepared with similar membrane properties, including water permeability, surface roughness and zeta potential, so as to focus on the effect of hydrophilicity on the fouling properties.

In **Chapter IV**, the preparation of hollow fiber membranes from PVB by thermally induced phase separation method for a water purifier is described. The characteristics of PVB is controllable by partial modification of the molecular structure. The blended membrane had suitable properties for water treatment by microfiltration.

Chapter V summarizes the conclusions of this dissertation.

References

- [1] M. Mulder, Basic Principles of Membrane Technology, Kluwer Academic publishers, the Netherlands, (1996).
- [2] S. Loeb, S. Sourirajan, D. E. Weaver, Porous Membranes for Separating Water from Saline, US Patent 3133137 (1964).
- [3] D. R. Lloyd, K. E. Kinzer, H. S. Tseng, Microporous membrane formation via thermally induced phase separation. I. Solid-liquid phase separation, *J. Membr. Sci.*, **52** (1990) 239–261.

- [4] S. S. Kim, D. R. Lloyd, Microporous membrane formation via thermally-induced phase separation. III. Effect of thermodynamic interaction on the structure of isotactic polypropylene membranes, *J. Membr. Sci.*, **64** (1991) 13–29.
- [5] B. Mi, M. Elimelech, Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents, *J. Membr. Sci.*, **348** (2010) 337–345.
- [6] N. A. Ochoa, P. Prádanos, L. Palacio, C. Pagliero, J. Marchese, A. Hernández, Pore size distributions based on AFM imaging and retention of multidisperse polymer solutes: Characterisation of polyethersulfone UF membranes with dopes containing different PVP, *J. Membr. Sci.*, **187** (2001) 227–237.
- [7] L. E. S. Brink, S. J. G. Elbers, T. Robbertsen, P. Both, The anti-fouling action of polymers preadsorbed on ultrafiltration and microfiltration membranes, *J. Membr. Sci.*, **76** (1993) 281–291.
- [8] E. J. de la Casa, A. Guadix, R. Ibáñez, F. Camacho, E. M. Guadix, A combined fouling model to describe the influence of the electrostatic environment on the cross-flow microfiltration of BSA, *J. Membr. Sci.*, **318** (2008) 247–254.
- [9] S. T. Kelly, A. L. Zydney, Effects of intermolecular thiol-disulfide interchange reactions on bsa fouling during microfiltration. *Biotechnol. Bioeng.*, **44** (1994) 972–982.
- [10] H. Ivnitsky, D. Minz, L. Kautsky, A. Preis, A. Ostfeld, R. Semiat, C. G. Dosoretz, Biofouling formation and modeling in nanofiltration membranes applied to wastewater treatment, *J. Membr. Sci.*, **360** (2010) 165–173.
- [11] P. Wang, K. L. Tan, E. T. Kang, K. G. Neoh, Plasma-induced immobilization of poly(ethylene glycol) onto poly(vinylidene fluoride) microporous membrane, *J.*

- membr. Sci.*, **195** (2002) 103–114.
- [12] X. C. He, H. Y. Yu, Z. Q. Tang, L. Q. Liu, M. G. Yan, J. S. Gu, X. W. Wei, Reducing protein fouling of a polypropylene microporous membrane by CO₂ plasma surface modification, *Desalination*, **244** (2009) 80–89.
- [13] S. Kang, A. Asatekin, A. M. Mayes, M. Elimelech, Protein antifouling mechanisms of PAN UF membranes incorporating PAN-g-PEO additive, *J. Membr. Sci.*, **296** (2007) 42–50.
- [14] X. Fu, T. Maruyama, T. Sotani, H. Matsuyama, Effect of surface morphology on membrane fouling by humic acid with the use of cellulose acetate butyrate hollow fiber membranes, *J. Membr.Sci.*, **320**, (2008) 483–491.
- [15] H. Matsuyama, H. Okafuji, T. Maki, M. Teramoto, N. Kubota, Preparation of polyethylene hollow fiber membrane via thermally induced phase separation, *J. Membr. Sci.*, **223** (2003) 119–126.
- [16] A. K. Fritzsche, A. R. Arevalo, M. D. Moore, V. B. Elings, K. Kjoller, C. M. Wu, The surface structure and morphology of polyvinylidene fluoride microfiltration membranes by atomic force microscopy, *J. Membr. Sci.*, **68** (1992) 65–78.
- [17] Q. Shi, Y. Su, S. Zhu, C. Li, Y. Zhao, Z. Jiang, A facile method for synthesis of pegylated polyethersulfone and its application in fabrication of antifouling ultrafiltration membrane, *J. Membr.Sci.*, **303** (2007) 204–212.
- [18] M. D. Satre, N. D. Ghatge, M. P. S. Ramani, Aromatic polyamide–hydrazides for water desalination. I. Syntheses and RO membrane performance, *J. Appl. Polym. Sci.*, **41** (1990) 697–712.
- [19] M. Shang, H. Matsuyama, M. Teramoto, D. R. Lloyd, N. Kubota, Preparation and membrane performance of poly(ethylene-co-vinyl alcohol) hollow fiber membrane

via thermally induced phase separation, *Polymer*, **44** (2003) 7441–7447.

- [20] X. Ma, Q. Sun, Y. Su, Y. Wang, Z. Jiang, Antifouling property improvement of poly(vinyl butyral) ultrafiltration membranes through acid treatment, *Sep. Purif. Technol.*, **54** (2007) 220–226.
- [21] A. Moriya, T. Maruyama, Y. Ohmukai, T. Sotani, H. Matsuyama, Preparation of poly(lactic acid) hollow fiber membranes via phase separation methods, *J. Membr. Sci.*, **342** (2009) 307–312.

Chapter II

Effect of amphiphilic additives on properties of cellulose acetate butyrate hollow fiber membranes prepared by thermally induced phase separation

II.1 Introduction

Significant global climate changes and population growth are expected to cause worldwide water shortages in the immediate future, and this is now becoming a serious problem. Water purification processes using polymeric porous membranes prepared by phase separation are attracting significant attention as a method to preserve water resources [1,2]. Membrane separation is preferable in terms of resource conservation and energy saving because no phase transition occurs during the separation. Moreover, membrane separation is appropriate to treat water on a large scale because it proceeds at a rapid separation velocity because it does not reach phase equilibrium. This feature leads to another advantage of membrane separation, in that it needs a smaller plant size compared with conventional processes that require phase equilibrium such as distillation and adsorption [3]. Replacing precipitation and sand-filtration systems with a membrane separation system makes the site smaller, maintenance more manageable and the quality of the treated water more stable and satisfactory. For these reasons, the membrane separation process has been introduced into practical use. Hollow fiber membranes play a very important role in a water purification system because they have a larger surface area per unit volume of the module than other membrane configurations. Although there are several ways to prepare hollow fiber membranes, we adopted thermally induced phase separation (TIPS), which is a relatively new method [4–6]. We

used cellulose acetate butyrate (CAB) as the membrane substance, added polyethylene glycol and polymer surfactant to the polymer solution and investigated the effect of these additives on membrane characteristics.

II.2 Experimental

II.2.1 Materials

CAB (Daicel Chemical Industries, Ltd.) was used as a membrane material. Its structure is shown in Fig. II.1. The substitution ratios of functional groups by acetate ester and butyrate, shown as R in Fig. II.1, were 68% and 24%, respectively. Triethylene glycol was used as a diluent. Poly(ethylene glycol) ($M_w = 200,000$; Wako Pure Chemical Industries, Ltd., Tokyo, Japan), Tetronic[®] 1307 ($M_w = 18,000$, HLB value: 18–23, BASF) and Pluonic[®] F127 ($M_w = 13,000$, HLB value: 18–23, Sigma Aldrich) were used as additives. Molecular structures of Tetronic[®] and Pluonic[®] are shown in Fig. II.2.

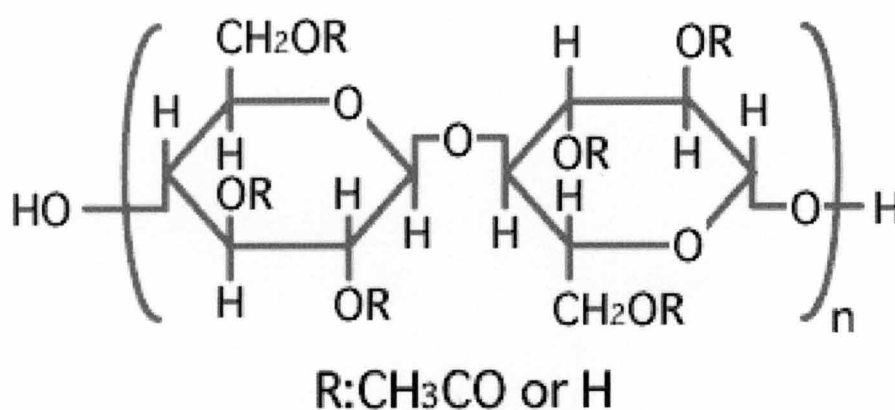
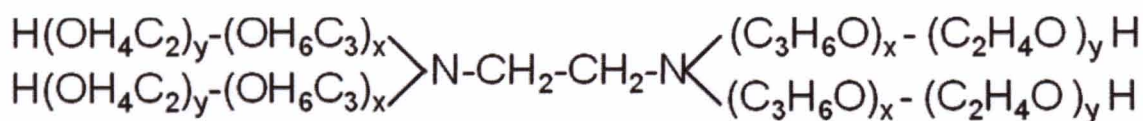


Fig. II.1. Structure of cellulose acetate.



(a) Tetronic 1307



(b) Pluronic F127

Fig. II.2. Chemical structures of surfactants.

II.2.2 Phase diagram

The cloud point of the CAB/triethylene glycol system was investigated. Homogeneous polymer and diluent samples were prepared by a mixer with a twin-blade (Imoto Co., IMC-119D). Thirty grams of a homogeneous solution was obtained by mixing at 50 rpm for 14 min at 180 °C. A milk-colored solid sample was then obtained by dropping the uniform solution on a dish. At that time, the CAB concentration in the solution was fixed at 20 wt% and that of the additive was varied.



Fig. II.3. Mixer with a twin blade for cloud point sample.

The solid sample was placed between a pair of cover slips and set onto a hot stage slotted into an upright microscope (Olympus, BX50). The sample was heated to 10 °C higher than the expected cloud point. Subsequently, the sample was cooled at a rate of 1 °C/min. The cloud point was determined to be the temperature at which drops of phase separation appeared.

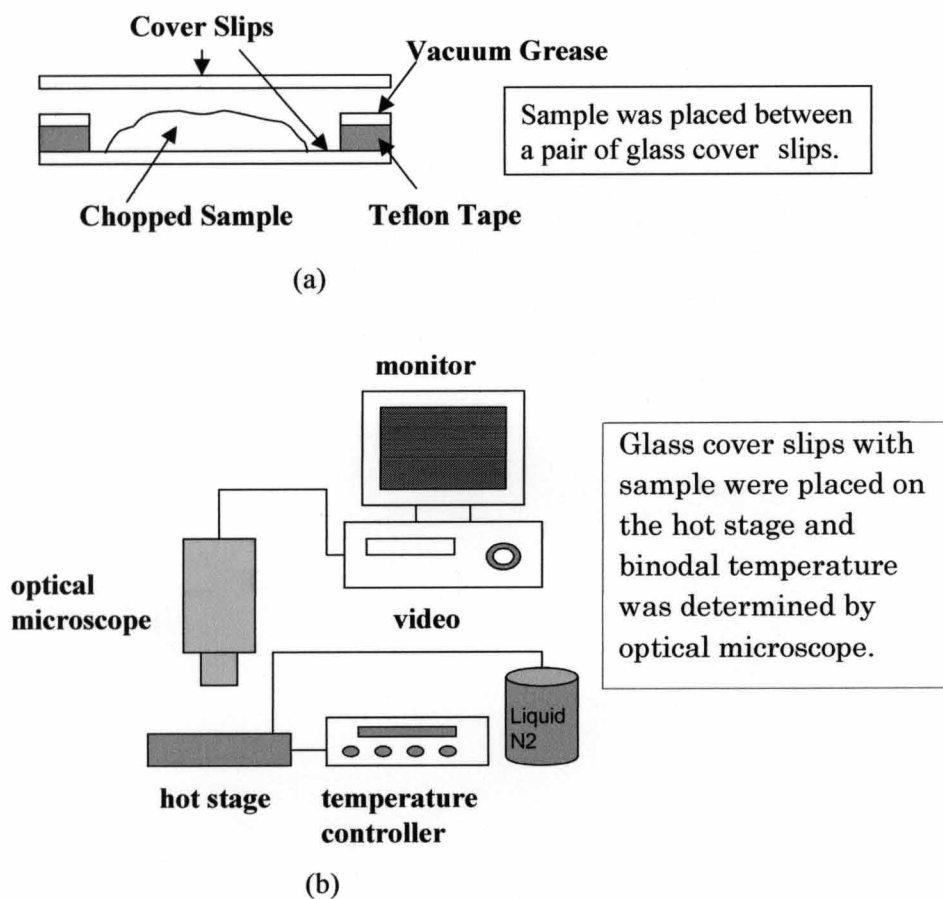


Fig. II.4. (a) Sample assembly with a pair of cover slips; (b) Apparatus for measuring binodal temperature.

II.2.3 Hollow fiber membrane preparation

The method of manufacturing hollow fiber membranes is outlined in Fig. II.5. To prepare homogeneous solution, CAB and an additive were mixed in advance with

triethylene glycol (polymer concentration, 20 wt%; additive concentration, 5 wt%) as a slurry. Subsequently, the mixture was placed into the mixing site of the membrane manufacturing apparatus and heated until it melted completely at 180 °C. After 2 hr standing to remove bubbles, it was injected into water (40 °C) by nitrogen gas pressure through hollow spinneret at a speed of 0.20 m/s with triethylene glycol as the bore fluid at a speed of 0.16 m/s. During the membrane preparation, the air gap between the spinneret and the quench bath was set at 0 or 5 mm.

The polymer solution was solidified during immersion into the low-temperature quench bath and was taken up at a speed of 0.26 m/s. The solvent in the hollow fiber membrane was then extracted and removed by immersion in water. The hollow fiber membrane was stored in water until it was used for experiments.

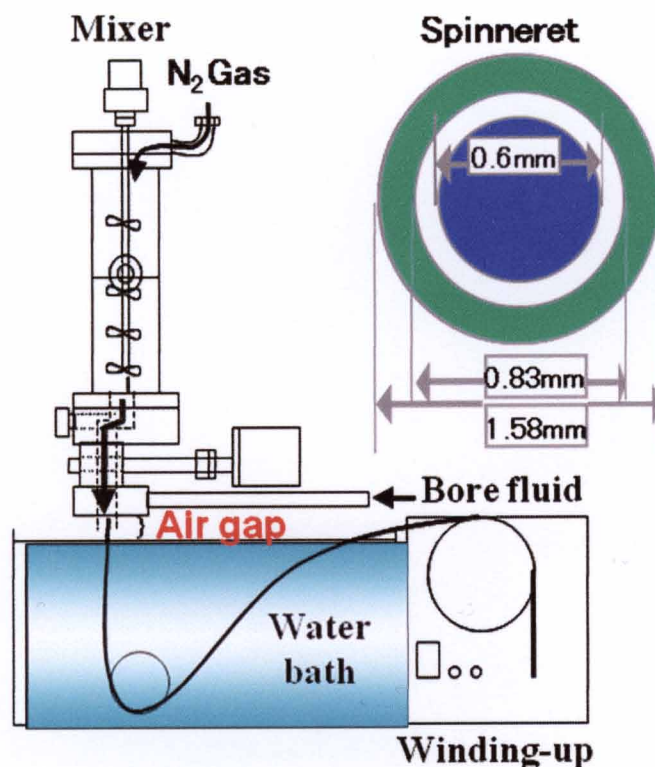


Fig. II.5 Hollow fiber membrane fabrication equipment

II.2.4 SEM and AFM observation

Hollow fiber membranes were freeze-dried and imaged by scanning electron microscopy (Japan Electron Optics Laboratory Co., Ltd., JSM-5610) with an accelerating voltage of 15 kV. The morphology of the outer surface of the hollow fiber membrane was also observed using atomic force microscope (AFM; Seiko Instruments Inc., SPI3800N/SPA-400).

II.2.5 Water permeability and mechanical strength

To assess the capability of the hollow fiber membrane, the water permeability and the membrane strength were measured. The water permeability experiment was performed by the internal pressure method to measure the quantity of deionized water that permeated through the membrane using the apparatus shown in Fig. II.6. A tensile test was carried out to measure the stress and the elongation at failure at a tensile speed of 50 mm/min using an Autograph (Shimadzu Corporation, AGS-J).

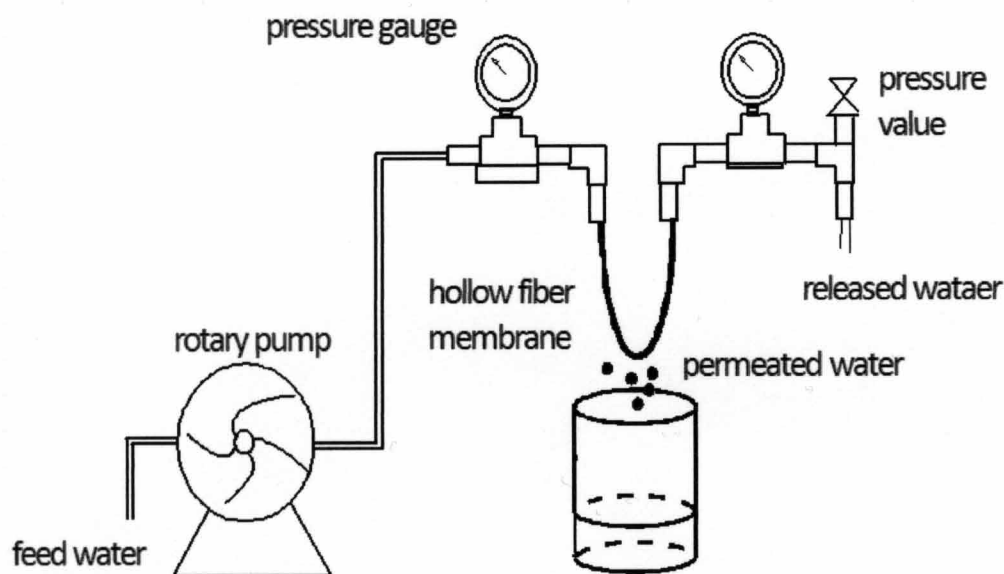


Fig. II.6. Apparatus for water permeation equipment.

II.3 Results and discussion

Cellulose acetate was developed in 1964 [7] as an asymmetric reverse osmotic membrane to desalinate seawater and is still in use even today. However, cellulose acetate itself has defects as a material in that it has a tendency to decompose when used in water long term because it has a high biodegradability [8]. Thus, in this study, CAB was used instead of CA, which is made by partially modifying CA by butyryl groups [9] and is expected to have high resistance against decomposition.

II.3.1 Phase diagram

First, the cloud point temperature of 20 wt% CAB solution with 10 wt% additive was examined. As shown in Fig. II.7, PEG addition to the dope solution slightly increased the cloud point temperature. In contrast, adding surfactants such as Tetronic 1307 and Pluronic F127 lowered the cloud point temperature. Consequently, it seems that adding PEG to CAB lowered the affinity of the system, while adding the surfactants enhanced the affinity.

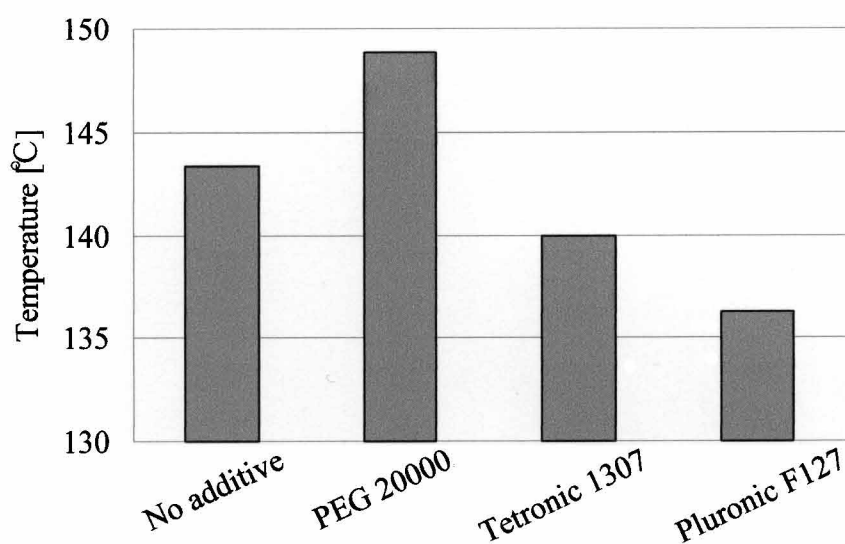


Fig. II.7. Effect of additives on the cloud point temperature.

II.3.2 SEM observation

The effect of the air gap on the structure of the hollow fiber membrane surface was investigated in the absence of additives. The SEM images of the hollow fiber membranes are shown in Fig. II.8. The outer surface of the hollow fiber membrane

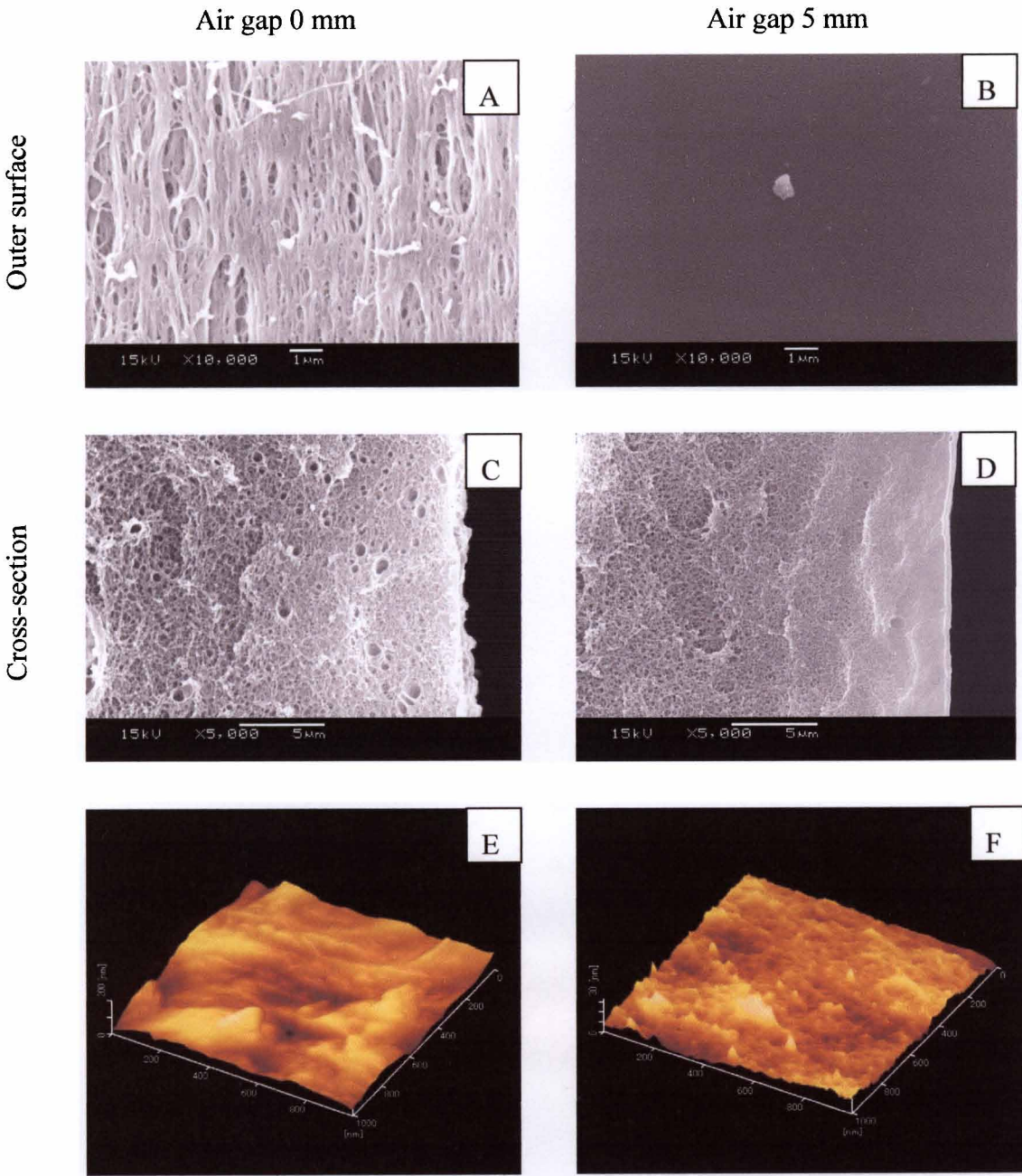


Fig. II.8. SEM (A-D) and AFM (E-F) images of hollow fiber membranes.

prepared with an air gap of 0 mm showed a fibrous structure and pores were observed. A cross-section adjacent to the outer surface also showed a porous structure. These structures seem to be formed when the dope solution is injected into the quench bath, followed by an immediate phase separation. On the other hand, hollow fiber membranes prepared with an air gap of 5 mm had no porous structure on the outer surface, as shown in Fig. II.8 (B). The cross-section adjacent to the outer surface showed the structure of a compact polymer skin layer. When the air gap was 5 mm, the solvent was extensively evaporated near the outer surface until the solution reached the quench bath and the polymer concentration of the solution on the outer surface significantly increased, resulting in the compact skin layer. The AFM images of the hollow fiber membrane outer surface structure are shown in Fig. II.8e, f. When the air gap was 0 mm, a rough phase-separation structure was obtained, as shown in Fig. II.8e. When the air gap was 5 mm, a small nodule structure was observed. The surface morphology (average surface roughness, R_a) was dependent on the setting of the air gap. For example, R_a was 21.3 nm and 1.7 nm in the cases where the air gap was 0 and 5 mm, respectively. When the air gap was 0 mm, a porous structure was maintained on the outer surface because almost no solvent was evaporated. When the air gap was 5 mm, however, a more dense structure was formed because the solvent adjacent to the outer surface evaporated and the polymer concentration increased. Consequently, polymer (CAB) was deposited with lower porosity and then a nodule structure seems to have been formed.

The effect of additives on membrane structure was then examined. SEM images of the outer surface and a cross-section of the hollow fiber membranes prepared with an air gap of 0 mm are shown in Fig. II.9. For any additive, the outer surface of the membranes had porous structures. In particular, addition of PEG led to a increase in

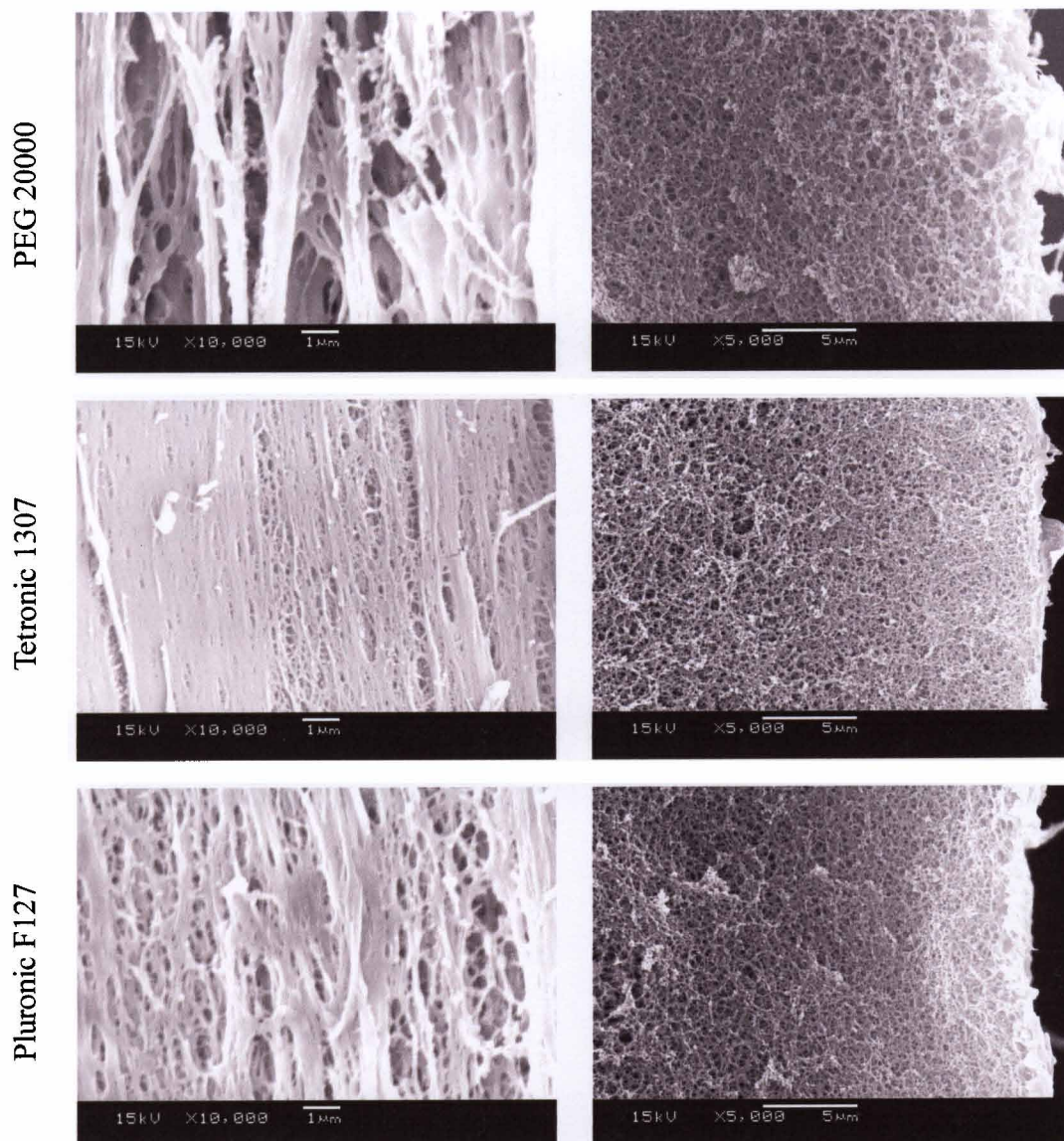


Fig. II.9 SEM images of hollow fiber structure (surfactant additive-air gap, 0 mm)

porosity of the outer surface. On the other hand, polymeric surfactants (Tetronic[®] 1307, Pluronic[®] F127) decreased the porosity on the outer surface. It was assumed that PEG is highly hydrophilic and dissolved out into the water and played a role in pore formation. Similar pore-forming effects were reported in membranes via NIPS [10,11]. Because surfactants such as Tetronic 1307 and Pluronic F127 have high molecular weight and relatively long hydrophobic chains, they remained in the membranes after preparation.

Therefore, in comparison with PEG, the pores ratio was decreased. Residual ratios of additives in the membranes after washing were measured by elemental analysis. PEG 20000 and Tetronic® 1307 remained at levels of 23 and 87% in the membranes, respectively. Addition of polymeric surfactants reduced the pore size of the membranes. Two reasons are possible for this phenomenon. First, the phase separation temperature decreased through the addition of surfactants (Fig. II.7) and the difference between phase separation temperature and crystallization temperature became small, and consequently the coarsening time of the porous structure would be shorter [12].

Another reason is that the existence of surfactants led to formation of a smaller emulsion structure after phase separation. As a result, the pore size became smaller after the membrane matrix was solidified. SEM images of the outer surface and a cross-section of the hollow fiber membranes with an air gap of 5 mm are shown in Fig. II.10. The membranes formed dense skin layers and no pores were observed on the outer surface. Evaporation of the diluent from the outer surface of the dope solution

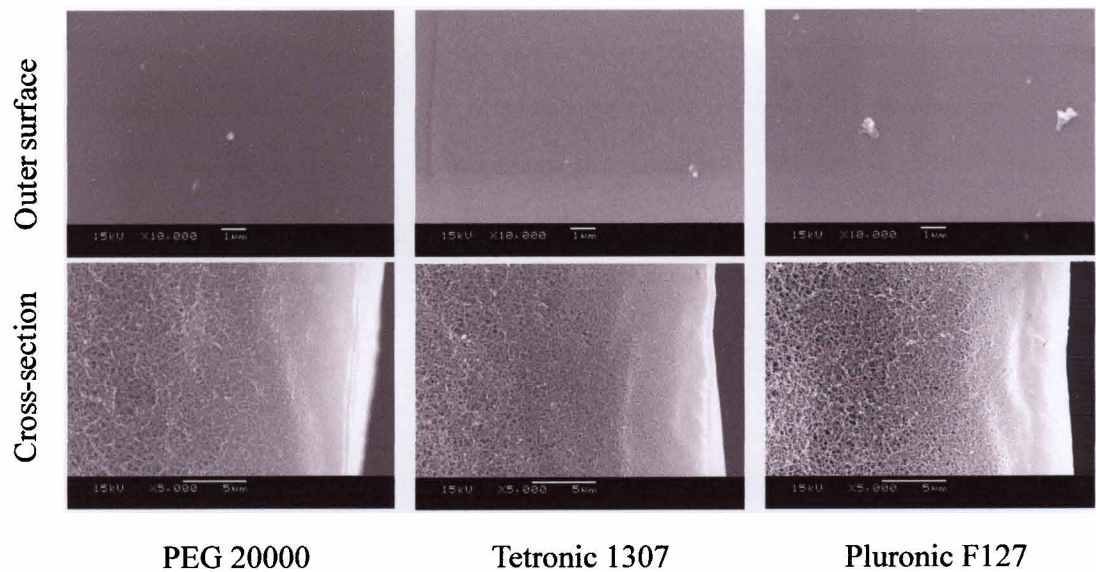


Fig. II.10. SEM of hollow fiber structure (surfactant additive-air gap, 5 mm).

frequently occurred during the brief time before the high temperature dope solution was immersed into the cold water bath during the TIPS process. The evaporation resulted in a remarkable increase in the polymer concentration. Consequently, dense skin layers were formed on the outer surface.

II.3.3 Water permeability

Water permeability measurements were carried out for membranes prepared with air gaps of 0 and 5 mm. As shown in Fig. II.11, the membranes with an air gap of 0 mm had a much higher water permeability than with a 5 mm gap because no pores were observed on the outer surface of the latter. In contrast, the membrane formed with a 0 mm gap had a porous structure on the outer surface, so the water permeability was dramatically elevated. With an air gap of 0 mm, the water permeability increased with the addition of PEG. On the other hand, addition of polymeric surfactants depressed the water permeability. These results corresponded to the porosity of outer surface shown in

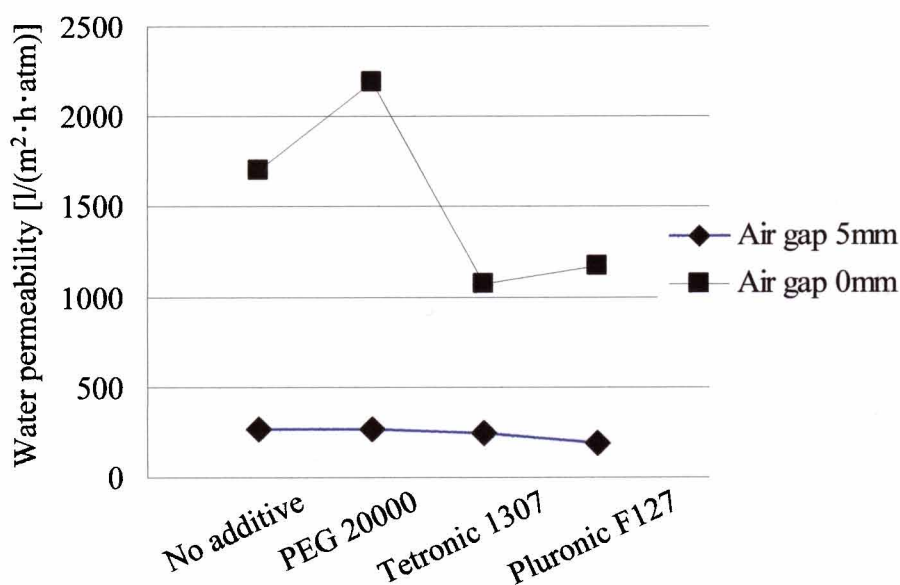


Fig. II.11. Effect of additives on water permeability of hollow fiber membranes.

Table II.1. Water contact angles for CAB flat membranes with additives, prepared by TIPS.

Additive	Contact angle(°)
No additive	81.8
PEG 20000	75.8
Tetronic 1307	65.1
Pluronic F127	69.1

Fig. II.9. With a 5 mm air gap, additive effects on water permeability were insignificant. This is because a dense polymeric skin layer existed on the outer surface, as shown in Fig. II.10 [13]. The hydrophilicity of the membrane surface is an important factor in aqueous membrane processes in terms of fouling [14,15]. Flat membranes were prepared using the same CAB and additives via TIPS. The membrane was soaked in deionized water for 6 h to remove the diluent.

Water contact angle results are listed in Table II.1. Addition of Tetronic 1307 and Pluronic F127 depressed the contact angle by 10 degrees and enhanced the hydrophilicity compared with the control, in agreement with reports of surfactants enhancing hydrophilicity by other groups [13,16]. Addition of PEG had little effect on contact angle, indicating that PEG was eluted from the membranes, whereas polymeric surfactants remained in the membranes.

II.3.4 Mechanical strength

The mechanical properties of the hollow fiber membranes were measured. The results of tensile stress and elongation at failure were shown in Figs. II.12 and II.13,

respectively. The tensile stress and elongation of membranes made with an air gap of 5 mm were much larger than that made with 0 mm. With a 5 mm air gap, dense skin layers were formed near the outer surface so polymeric connectivity was tight and led to an increase in the mechanical strength.

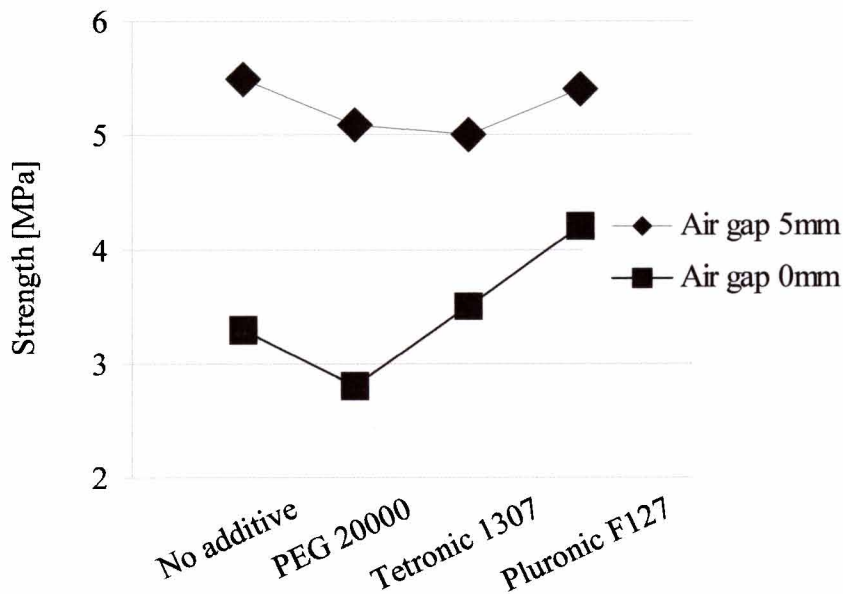


Fig. II.12. Effect of air gap and additives on tensile stress of hollow fiber membranes.

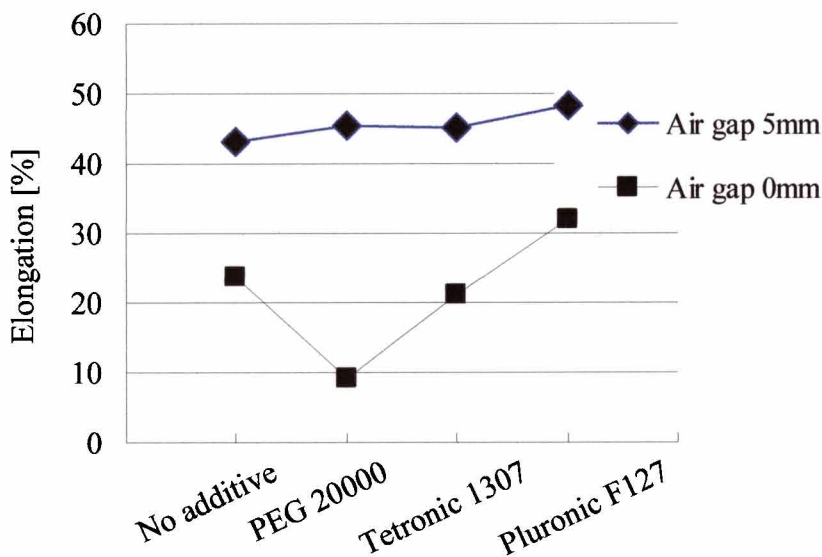


Fig. II.13. Effect of air gap and additives on elongation of hollow fiber membranes.

Moreover, dense skin layers were formed on the outer surface, independent of additive at a 5 mm air gap. Therefore, the effects of additives on the stress and elongation were not significant. On the other hand, at a 0 mm air gap, effects of additives were marked. Addition of PEG 20000 slightly decreased stress and elongation of the obtained membrane, while Tetronic 1307 and Pluronic F127 increased the stress and elongation of the membranes. This is because PEG was eluted in water during membrane preparation and storage, the porosity was increased and consequently stress declined. In contrast, Tetronic 1307 and Pluronic F127 have relatively longer hydrophobic chains, which helped the surfactants to remain in the membranes. The porosity of the membrane was low and stress and elongation were consequently enhanced.

II.4 Conclusions

In this study, hollow fiber membranes were prepared using CAB as a membrane material via the thermally induced phase separation (TIPS) method. It was confirmed that the air gap used during preparation, which is peculiar to TIPS, has an important effect on structures and properties of the membranes. The characteristics of membranes prepared with the addition of PEG and polymeric surfactants were examined. As a result, it became clear that PEG worked as a pore forming agent and polymeric surfactants were effective in improving hydrophilicity on membranes surfaces and membrane strength.

References

- [1] S. S. Madaeni, The application of membrane technology for water disinfection, *Water Res.*, **33** (1999) 301–308.
- [2] D. Jermann, W. Pronk, S. Meylan, M. Boller, Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water production, *Water Res.*, **41** (2007) 1713–1722.
- [3] M. Cheryan, Ultrafiltration and Microfiltration Handbook, *Technomic Publishing, Lancaster, PA* (1998).
- [4] K. E. Kinzer, D. R. Lloyd, Thermally induced phase separation mechanisms for microporous membrane formation, polymer asymmetric membranes through the thermally induced phase separation process, *Polym. Mater. Sci. Eng.*, **61** (1989) 794–798.
- [5] D. R. Lloyd, K. E. Kinzer, H. S. Tseng, Microporous membrane formation via thermally induced phase separation. I. Solid-liquid phase separation, *J. Membr. Sci.* **52** (1990) 239–261.
- [6] F. J. Tsai, J. M. Torkelson, On studying the formation of PMMA asymmetric membranes through the thermally induced phase separation process, *Polym. Mater. Sci. Eng.*, **61** (1989) 789–793.
- [7] S. Loeb, S. Sourirajan, D. E. Weaver, Porous membranes for separating water from saline, US Patent 3133137 (1964)
- [8] T. Ishigaki, W. Sugano, M. Ike, Y. Kawagoshi, I. Fukunaga, M. Fujita, Abundance of polymers degrading microorganisms in a sea-based solid waste disposal site, *J. Basic Microbial.*, **40** (2000) 177–186.
- [9] T. Wang, G. Cheng, S. Ma, Z. Cai, L. Zhang, Crystallization behavior, mechanical

- properties and environmental biodegradability of poly(β -hydroxybutyrate)/cellulose acetate butyrate blends, *J. Appl. Polym. Sci.*, **89** (2003) 2116–2122.
- [10] J. H. Kim, K. H. Lee, Effect of PEG additive on membrane formation by phase inversion, *J. Membr. Sci.*, **138** (1998) 153–163.
- [11] W. L. Chou, D. Yu, M. C. Yang, C. H. Jou, Effect of molecular weight and concentration of PEG additives on morphology and permeation of cellulose acetate hollow fiber, *Sep. Purif. Technol.*, **57** (2007) 209–219.
- [12] M. Shang, H. Matsuyama, T. Maki, M. Teramoto, D. R. Lloyd, Preparation and characterization of poly(ethylene-co-vinyl alcohol) membranes via thermally induced liquid-liquid phase separation, *J. Appl. Polym. Sci.*, **87** (2003) 853–860.
- [13] Y. R. Qiu, N. A. Rahman, H. Matsuyama, Preparation of hydrophilic poly(vinyl butyral)/PluronicF127 blend hollow fiber membrane via thermally induced phase separation, *Sep. Purif. Technol.*, **61** (2007) 1–8.
- [14] T. Maruyama, S. Katoh, M. Nakajima, H. Nabetani, T. P. Abbott, A. Shono, K. Satoh, FT-IR analysis of BSA fouled on ultrafiltration and microfiltration membranes, *J. Membr. Sci.*, **192** (2001) 201–207.
- [15] L. J. Zewan, A. L. Zydney, Microfiltration and ultrafiltration: principles and applications, Marcel Dekker Inc., New York (1996)
- [16] Y.-Q. Wang, Y.-L. Su, X.-L. Ma, Q. Sun, Z.-Y. Jiang, Pluronic polymers and polyethersulfone blend membranes with improved fouling-resistant ability and ultrafiltration performance, *J. Membr. Sci.*, **283** (2006) 440–447.

Chapter III

Membrane fouling properties of hollow fiber membranes prepared from cellulose acetate derivatives

III.1. Introduction

Recently, various types of membranes have been produced for applications in water purification processes. For example, poly(vinylidene fluoride) (PVDF) membranes attract attention for membrane separation applications because of their excellent mechanical strength and chemical resistance [1]. However, membranes comprising hydrophobic materials, such as PVDF, polysulfone and polyolefins, tend to suffer severe decreases in water flux during operation caused by solute adsorption, pore blocking and cake formation. Membrane fouling is an especially serious problem in the case of protein separation because hydrophobic interactions between proteins and the membrane surface induces a non-selective and irreversible adsorption. Easily fouled membranes need frequent chemical cleaning and replacement of the membrane module, giving a short lifetime, which leads to high utility costs [2–5]. In some cases, hydrophobic membranes provide higher productivity in specific apparatus [6,7]. Hollow fiber membrane adsorber, which uses a bundle of hollow fiber UF/MF filter as a particle-collecting device, shows higher performance in the case of hydrophobic membrane due to nonuniform particle deposition inside a bundle of hollow fibers.

Membrane properties such as hydrophilicity, surface roughness, zeta potential, water permeability, and solute rejection affect membrane fouling and the latter is quite complex. In general, it is claimed that membranes with a hydrophilic surface are able to moderate the impact of fouling through reducing hydrophobic interactions. Several

studies have been aimed at improving the hydrophilicity of membranes by coating [8,9], adsorption [10], and surface graft polymerization [11–14]. Another study used hydrophilic chemical modification of bulk membrane materials [15]. Hester et al. prepared amphiphilic comb copolymer derivatives of PVDF having poly(methacrylic acid) side chains (PVDF-g-PMAA) and poly(oxyethylene methacrylate) side chains (PVDF-g-POEM) via atom transfer radical polymerization (ATRP). A PVDF/5 wt% PVDF-g-POEM membrane displayed substantial resistance to BSA fouling compared with pure PVDF. Wang et al. [14] grafted PEG polymer onto PVDF microporous membrane surfaces by argon plasma treatment of a PEG-precoated PVDF membrane. The PEG-precoated PVDF membrane exhibited good antifouling properties during experiments on protein adsorption and water permeability.

However, modifications that create hydrophilic membrane surfaces usually bring about other changes in membrane properties such as water permeability, solute rejection and surface morphology. For example, Fu et al. [16] fabricated hollow fiber membranes from cellulose acetate butyrate with several types of surface morphology to investigate the effect of surface morphology on the fouling properties. They revealed that a membrane with lower porosity at the outer surface suffered more serious membrane fouling with an external pressure module. Solute rejection was also a key factor in improving the fouling properties. Vrijenhoek et al. [4] focused on the effect of membrane surface roughness and reported that more particles were deposited on rough than on smooth membranes. Thus, the effect of hydrophilicity alone on membrane fouling has rarely been reported to date. Although the hydrophilicity is vaguely believed to have an important effect on fouling behavior, it is not clarified in actual experiment. To clarify the effect of varying membrane hydrophilicity in isolation, the other factors

must be kept constant. The novelty of this work is to examine a definite membrane fouling behavior considering the effect of hydrophilicity without effects of any other parameters.

In this work, we prepared hollow fiber membranes with almost constant membrane properties, including water permeability, surface roughness and zeta potential, so as to focus on the effect of hydrophilicity itself on the fouling properties. Cellulose acetate (CA), cellulose acetate butyrate (CAB), and cellulose acetate propionate (CAP) were used as membrane materials. Water flux decline and the effect of backwashing were compared for these three types of membrane.

III.2 Experimental

III.2.1 Materials

CA ($M_w = 110,000$), CAB ($M_w = 65,000$), and CAP ($M_w = 75,000$) were used as membrane materials for thermally induced phase separation (TIPS) membrane preparation. The chemical structure and details of the polymers are shown in Fig. III.1 and Table III.1. Triethylene glycol (TEG), used as a diluent in preparing hollow fiber membranes, and acetone, used in preparing flat membranes for zeta potential

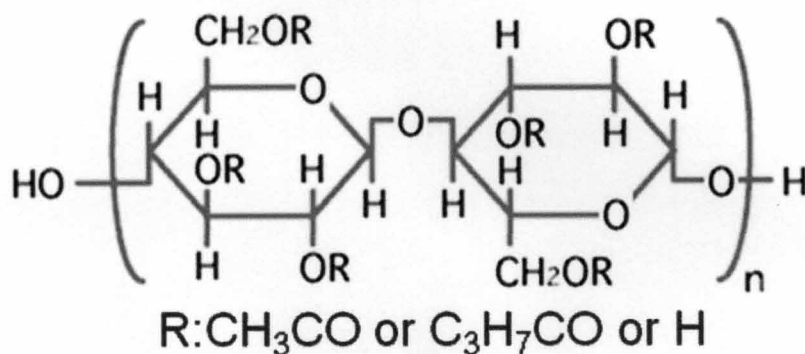


Fig. III.1 Chemical structure of cellulose acetate derivatives.

measurement, were purchased from Wako Pure Chemical Industries (Japan). Filtration solutions were prepared by dissolving humic acid from Aldrich Chemical Co. (Milwaukee, WI) and bovine serum albumin (BSA) from Wako Pure Chemical Industries in deionized (DI) water. All chemicals were used without further purification.

Table III.1 Characteristics of polymers used in this study.

	Mw	Substitution ratio		
		R: CH ₃ CO	R: C ₂ H ₅ CO	R: C ₃ H ₇ CO
CA	110,000	2.38	-	-
CAB	65,000	2.04	-	0.71
CAP	75,000	0.18	2.5	-

III.2.2 Phase diagram

Homogeneous polymer-diluent samples were prepared using a mixer with a twin-blade (Imoto Co., IMC-119D) by the method reported by Shang et al. [17]. A total of 30 g of polymer and diluents were weighed into the vessel, heated to a desired temperature and then mixed for 7 min at a rotating speed of 50 rpm. A sample of the prepared homogeneous solution was placed between cover glasses separated by a 100 μm -thick Teflon[®] sheet spacer. The sample was heated on a hot stage (Linkam, LK-600 PH) at 180 °C for 1 min and cooled to 25 °C at a rate of 10 °C min⁻¹. The cloud point temperature T_{could} was observed visually by noting the appearance of turbidity under an optical microscope (Olympus, BX50).

III.2.3 Preparation of hollow fiber membranes

Hollow fiber membranes were prepared using a batch-type extruder (Imoto Co., BA-0) [17,18]. A total of 300 g of a polymer and TEG were fed into the vessel and then mixed for 60 min at a temperature 20 °C higher than T_{cloud} . After maintaining that temperature without stirring for 2 h, the homogeneous solution was fed into a spinneret by a gear pump under nitrogen pressure. The spinneret consisted of outer and inner tubes, of diameter 1.58 and 0.83 mm, respectively. The diluent was introduced through the inner orifice to form the lumen of the hollow fiber. The hollow fiber was extruded from the spinneret and wound on a take-up winder after passing into a water bath. The extrusion rate of the polymer solution, the flow rate of the diluent in the inner tube of the spinneret and take-up speed were fixed at 0.18, 0.14 and 0.21 m s⁻¹, respectively. The diluent remaining in the hollow fiber membrane was extracted by immersing the membrane in water.

The objective of this study was to investigate the sole effect of hydrophilicity on the fouling properties of hollow fiber membranes. Thus, the other membrane characteristics should ideally be kept constant. However, it is not possible to prepare membranes with identical water permeabilities from different polymers under the same preparation conditions. Therefore, as described below, the polymer concentrations in the dope solutions and the air gap distance, i.e. the distance from the spinneret to the water surface, were changed accordingly for CA, CAB and CAP membrane preparation.

III.2.4 Characterization of the hollow fiber membrane

III.2.4.1 SEM and AFM observation

To obtain dry membranes for surface observation by scanning electron microscope

(SEM), the hollow fiber membranes were freeze-dried with a freeze dryer (EYELA, FD-1000). The dry hollow fiber membranes were fractured in liquid nitrogen and treated with Au/Pd sputtering. The cross-sections and the surfaces of the hollow fiber membranes were observed by SEM (Hitachi Co., JSM-5610LVS) with an accelerating voltage of 15 kV.

Surface morphologies of the dried hollow fiber membranes were observed using an atomic force microscope (AFM, SII Co., SPI3800N/SPA400) in dynamic force mode (DFM) with a 20 μm scanner and a SI-DF40 cantilever (spring constant = 42 N m^{-1}). Hollow fiber membranes were cut to a length of 1 cm and located on the top of the scanner tube by carbon tape. Mean roughness (R_a) was used to describe surface roughness.

III.2.4.2 Zeta potential measurement

The zeta potential of the membrane surface was determined by electrophoretic mobility with an electrophoretic measurement apparatus (Otsuka Electronics, ELS-6000) using a plate sample cell. A 1000 μm -thick flat membrane was prepared by casting polymer solution in acetone at 50 $^{\circ}\text{C}$ followed by drying under low humidity for 24 h. Polystyrene latex particles (Otsuka Electronics, diameter 520 nm) coated with hydroxypropyl cellulose (HPC, Scientific Polymer Products, $M_w = 300,000$) were used as mobility-monitoring particles. These particles were dispersed in a 10 mM NaCl solution to prevent interactions with the quartz cell surface during measurement. Zeta potential measurements were conducted with membrane samples in a background solution of 10 mM NaCl at pH 7 [19].

III.2.4.3 Contact angle measurement

A contact angle meter (Kyowa Interface Science Co., Drop Master 300) was used to measure the contact angle of water on the outer surface of hollow fiber membranes at room temperature. 0.5 μl of water was dropped on the outer surface of the membranes using a syringe and the contact angle was measured automatically. The average of 20 measurements was used as the contact angle for each membrane.

III.2.4.4 Water permeability and fouling test

Water permeability through the hollow fiber membrane was measured by a method similar to that described by Rahman et al. [20]. Pure water was forced to permeate from the inside to the outside of the hollow fiber membrane under a transmembrane pressure of 0.05 MPa. The water permeability was calculated on the basis of the inner surface area of the hollow fiber membrane.

The filtration experiment was performed using a 50 ppm humic acid solution in a 0.5 mM NaHCO_3 buffer at pH 8.4 in a single hollow fiber module as shown in Fig. III.2. A feed solution of 1000 ppm BSA in a 0.1 M phosphate buffer at pH 7.0 was also used for the filtration experiment. The zeta potentials of humic acid and BSA were -22.2 and -10.5 mV, respectively [21,22]. The membrane in the module had a length of 140 mm and the transmembrane pressure was 0.05 MPa. The feed solution was forced to permeate from the outside to the inside of the hollow fiber membrane. The feed flow rate was set at 15.8 ml min^{-1} . For each filtration, DI water was passed through the membrane until water permeability became constant and the pure water permeability J_0 was then measured. Subsequently, the humic acid or BSA solution was passed through the membrane and the time

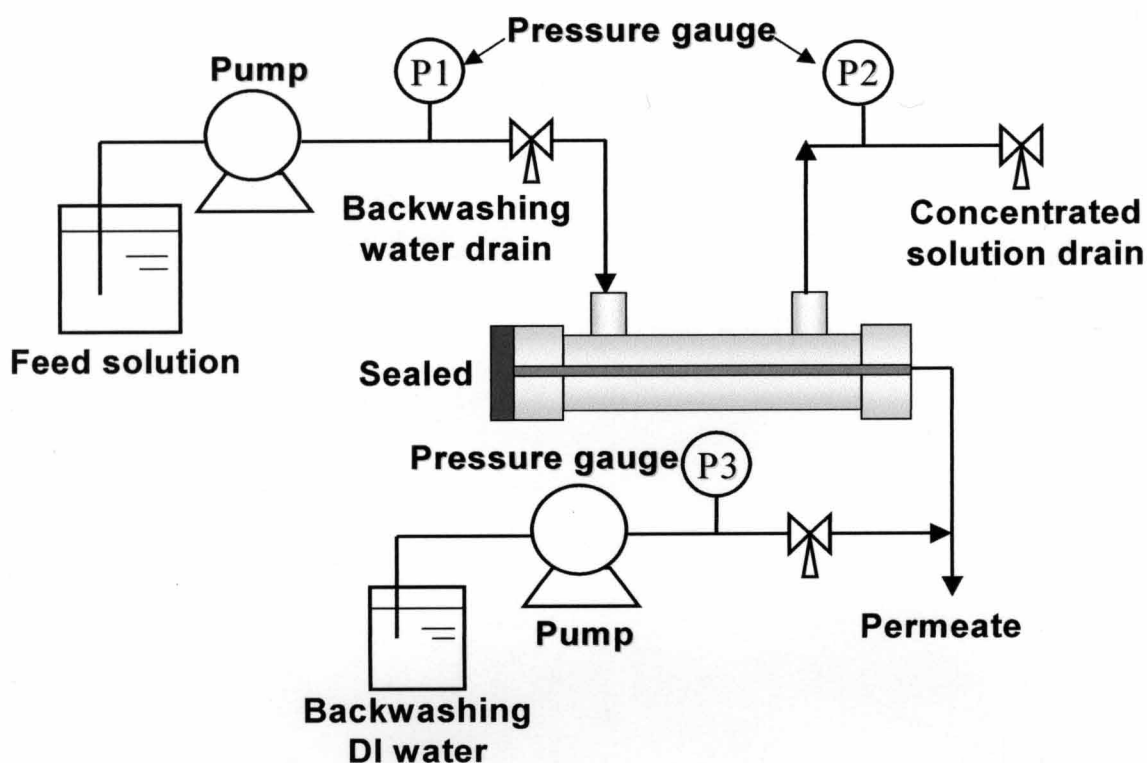


Fig. III.2 Diagram of the module with a single hollow fiber membrane used in filtration and backwashing experiments.

course of permeability, J , was measured. At the same time, the rejection, R , for humic acid and BSA were measured by absorbance using an UV spectrophotometer (Hitachi Co., U-200) at wavelengths of 254 and 280 nm, respectively.

III.3. Results and discussion

III.3.1 Phase diagram

Phase diagrams of polymer-diluent systems were investigated to determine the temperatures for hollow fiber membrane preparation. Fig. III.3 shows the correlation between cloud points and polymer concentrations. No clear phase separation was observed when more than 30 wt% of CA was dissolved in TEG. This figure indicates

that the phase separation temperatures of polymer-TEG systems increased in the order $CA < CAB < CAP$. This result can be explained in terms of the compatibility between the polymer and the diluent. The solubility parameters of polymers and TEG are summarized in Table III.2. The differences in the solubility parameters of polymers and that of TEG were in the order $CAP > CAB > CA$ and thus, the compatibility between polymers and TEG was in the reverse order. Because less compatibility between

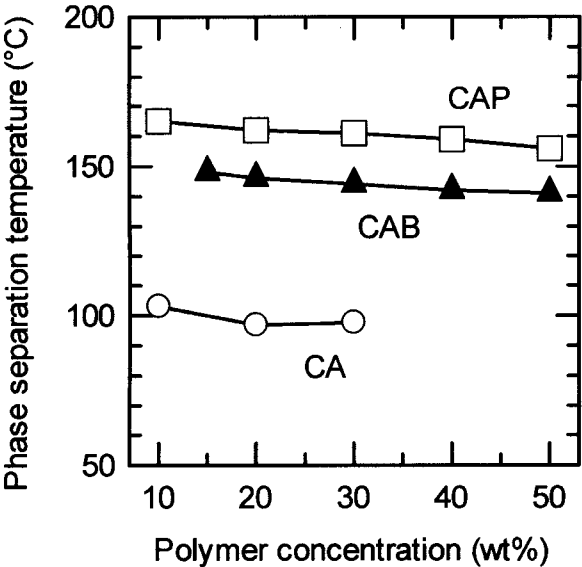


Fig. III.3 Phase diagram of the three polymer/triethylene glycol systems.

Table III.2. Solubility parameters of the materials.

Solubility parameter [MPa ^{1/2}]	
CA ^a	21.6
CAB ^a	20.3
CAP ^a	19.9
TEG ^b	27.5

^a Estimated using the group contribution method of Hoy [23]

^b Cited from reference [24]

polymer and diluent leads to higher temperatures at which phase separation takes place, the phase separation temperature decreased in the order CAP > CAB > CA system, as shown in Fig. III. 3.

III.3.2 Membrane structure and characterization

III.3.2.1. Water permeability

To prepare hollow fiber membranes with similar pure water permeabilities, the membrane preparation conditions were altered accordingly. The polymer concentrations were 19, 20 and 19 wt% and the air gaps were 5, 5 and 2 mm in the CA, CAB and CAP systems, respectively. The water permeabilities of the hollow fiber membranes obtained are listed in Table III.3. The differences between the water permeabilities of the membranes were so small that they had little influence on the fouling property of each membrane.

Table III.3. Water permeabilities, surface roughnesses and contact angles of fabricated membranes.

Hollow fiber membrane	Water permeability [L/(m ² h atm)]	R _a [nm]	Contact angle [°]
CA	316	2.5	66
CAB	406	2.4	76
CAP	355	2.0	79

III.3.2.2. Membrane morphology

Fig. III.4 shows SEM images of the series of hollow fiber membranes. No pores were

observed on the outer surfaces of the membranes, which indicates dense skin layers were formed during the preparation of membranes through the evaporation of TEG in the air gap. In contrast, porous structures were observed on the inner surfaces of all the membranes. Thus, the membranes had asymmetric structures. The porosities of the membranes also affect membrane performance in filtration studies. Judging from SEM images of outer surface of membranes, the three membranes have similar porosities on both outer surface and cross-section. Dense skin layers on the outer surfaces mainly determine the water permeabilities and the solute rejections in an externally pressurized

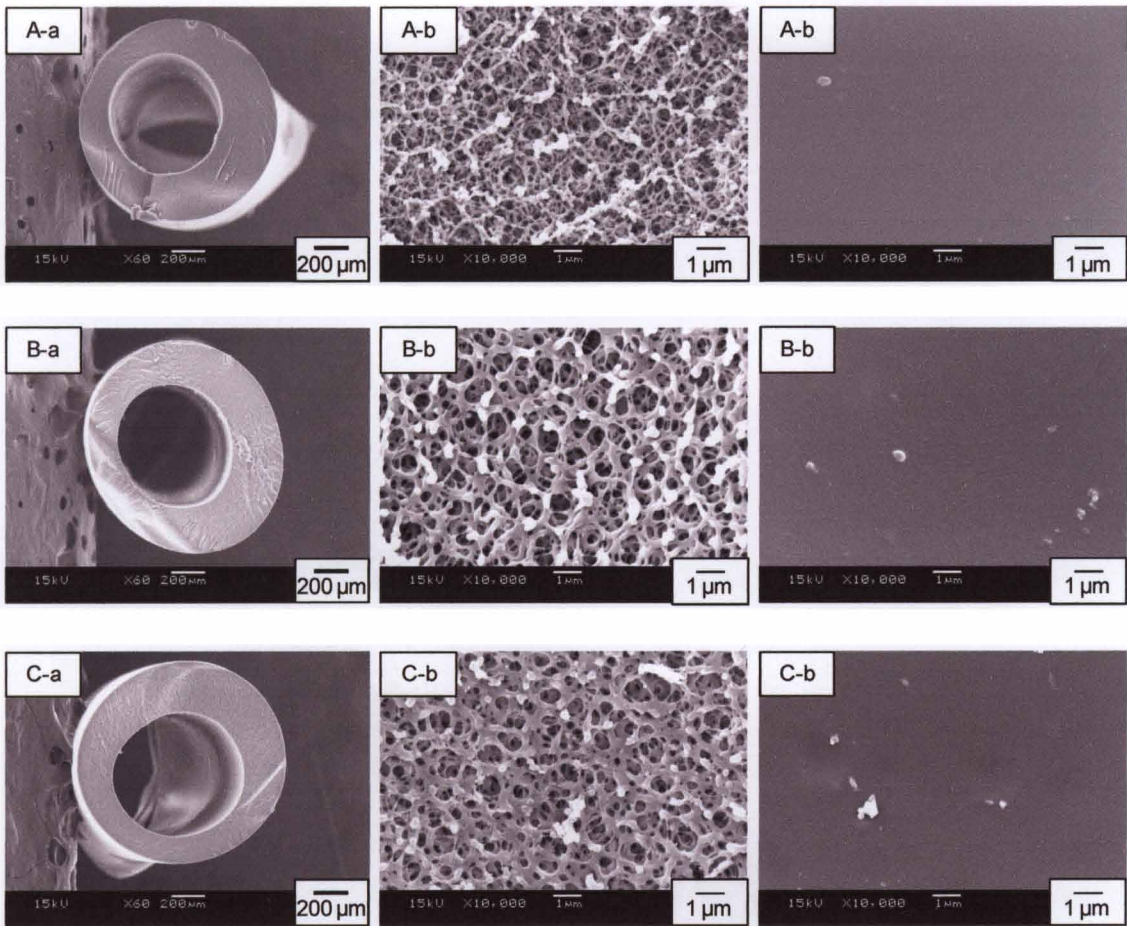


Fig. III. 4 SEM images of fabricated hollow fiber membranes. A: CA; B: CAB; C: CAP. a: cross-section; b: inner surface; c: outer surface.

fouling test. In addition, the outer diameters of all membranes, which may affect the fouling properties, were nearly 1.3 mm.

AFM measurements of the outer surface of the hollow fiber membranes were carried out. As shown in Fig. III.5, all the membranes had granular nodule structures. R_a values calculated for each membrane are listed in Table III.3. The mean roughness R_a of CA, CAB, and CAP hollow fiber membranes was approximately 2 nm and the differences between them were negligible. From this result, it was confirmed that the surface roughnesses of the membranes were almost the same and had no influence on the fouling properties.

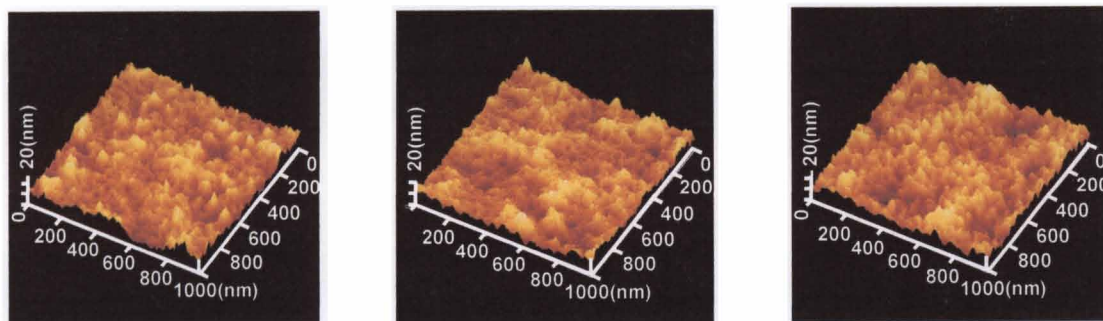


Fig. III.5 AFM images of fabricated hollow fiber membranes: (a) CA; (b) CAB; (c) CAP.

III.3.2.3. Zeta potential

Zeta potential measurements on the series of the hollow fiber membranes were carried out. As shown in Fig. III.6, all the membranes were negatively charged at between -10 and -18 mV at pH 5.5. This range may be due to the kind and degree of substituent on each polymer. The pK_a values of humic acid and BSA are 4.3 [25] and 5.5 [26], respectively. These molecules have negative charge at experimental condition of pH 7.0–8.4. Therefore, there is some electrostatic repulsion with foulant molecules

and membranes because the membranes also have negative zeta potential. If the zeta potential changes from positive to negative, the force between BSA and membrane changes from attractive to repulsive, which will largely affect fouling result. However, the effect of zeta potential of membranes is not significant as far as they are in the same negative charge and have similar value. Previous study investigated the effect of hydrophilic macromolecular additives to PES and prepared membranes with zeta potential ranging from -3 to -11 mV [27]. It was noted that the order of zeta potential on each membrane showed no correlation with that of impact of fouling. As the variation of zeta potential in the paper is similar to that in our study, the differences in the zeta potential among these membranes are small when considering the effect of zeta potential on interaction between foulants and membranes. However, the differences in the zeta potential among these membranes is assumed to be small when considering the effect of zeta potential on interaction between foulants and membranes.

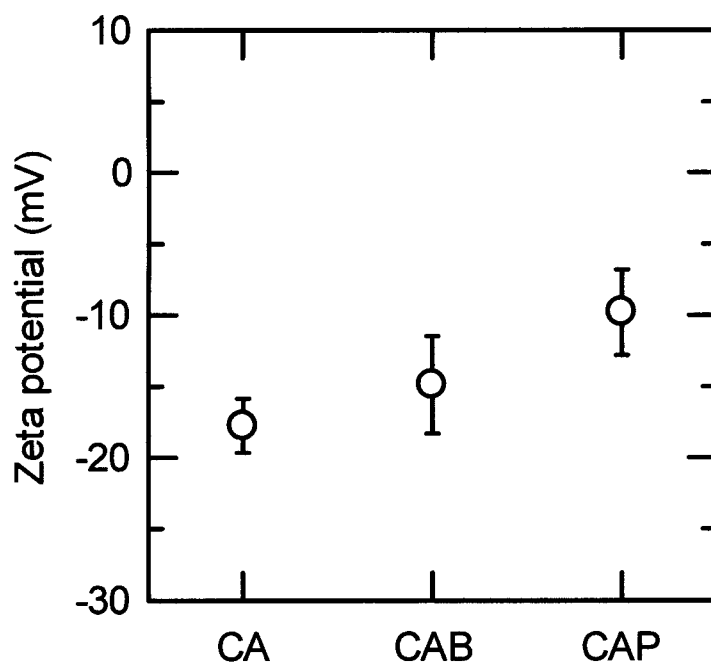


Fig. III.6 Zeta potential on outer surfaces of fabricated hollow fiber membranes.

III 3.2.4 Contact angle

Table III.3 also lists the contact angles of the series of hollow fiber membranes. The contact angle of the CA hollow fiber membrane was more than 10° lower than that of the other membranes. It is known that the surface morphology of a substance affects its contact angle. However, as it was confirmed by AFM that the surface morphology of the three hollow fiber membranes were almost identical, differences in the contact angles are dependent only on the chemical characteristics of membrane materials themselves. Previous works elucidated that surface modification of the membrane within 10° of contact angle difference affected fouling and backwashing behavior [28,12]. Therefore, the difference in the contact angles of these three membranes seems enough to affect fouling behavior.

III 3.3 Fouling experiment using membranes with similar water permeabilities

As discussed above, all membrane characteristics of the hollow fiber membranes except hydrophilicity that might affect fouling behavior were kept similar to one another. The effect of hydrophilicity alone on fouling behavior was examined by using these hollow fiber membranes.

Fig. III.7(a) shows the relative water permeability, J/J_0 , during membrane fouling measurements with the humic acid solution. Water permeability of each membrane decreased with increasing total permeate volume of the humic acid solution, indicating that the membranes were fouled by humic acid. The reduction in the relative water permeability increased in the order $CA > CAB > CAP$. Permeability of CAP membrane decreased to about 50% of the original value after 3 h, while that of CA membrane maintained 70% of the original permeability. The contact angle of the CA membrane

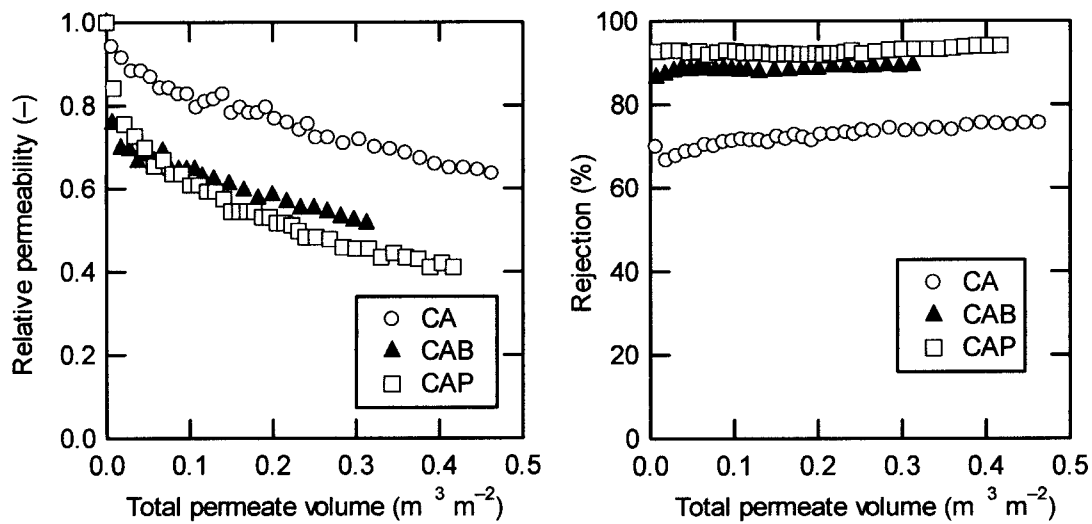


Fig. III.7 Result of fouling experiment performed with a 50ppm humic acid solution.

(a): relative permeability; (b): rejection.

was more than 10° lower than that of the other membranes. The higher hydrophilicity of the CA membrane resulted in a higher antifouling property, due to the reduction of hydrophobic interactions between humic acid and the membrane. Because the contact angle of CAB is slightly lower than that of CAP, as shown in Table III.1, CAB was more hydrophilic and a slightly higher J/J_0 was obtained for the CAB membrane. Thus, good correlation between the membrane hydrophilicity and the antifouling property was confirmed. Fig. 7(b) shows the humic acid rejection of the hollow fiber membranes used in the fouling experiments. Cake layer formation may be the dominant fouling mechanism in the case of all the membranes because the rejections are almost constant and slightly increase with permeate volume. The formation of cake layer during fouling experiment was also confirmed by SEM and optical observation. The membranes fabricated from CAB and CAP had initial rejections of 90%, while the CA membrane had a rejection of 70%. The slightly lower rejection of the CA membrane is explained as follows. As the phase separation temperature of the

CA solution was the lowest among the polymers used, membrane fabrication was performed at the lowest temperature. Therefore, evaporation of the diluents was suppressed due to the lower temperature compared with that of the other membranes. As a result of SEM observation near the membrane outer surfaces, it was confirmed that the dense skin layer thickness of CA membrane was 1 μm while those of both CAB and CAP membranes are 2 μm . Thus, the difference in the diluent evaporation led to a difference in the thickness of the dense skin layer for each membrane, which comprises a resistance to solute penetration. Moreover, pore size of membrane may affect the rejection profile during the fouling experiment. A detailed discussion is given in the following sections.

Fouling behavior for a 1000 ppm BSA solution was examined as well as the humic acid solution. Fig. III.8(a) shows that the water permeability of membranes decreased with an increase in the total permeate volume of the BSA solution. Rapid decreases in the water permeabilities were observed at the beginning of the filtration measurement. This is in contrast to the gradual decrease observed in the case of humic acid in Fig. III.7(a). Fig. III.8(b) shows the rejection of BSA during the fouling experiments. CAB and CAP membranes had more than 90% initial rejection of BSA, while the CA membrane had an initial rejection of less than 20%. This different profile may imply that the pore size of CA membrane is larger than that of the other membranes. The correlation between membrane surface morphology and fouling property was investigated previously [16]. Lower foulant rejection resulted in more significant flux decline, because more foulant penetrated through the membrane and could adsorb and/or deposit onto membrane pore surface. In the case of CA membrane, however, CA membrane showed lower fouling property in spite of the lower rejection. This low

fouling property is caused by the higher hydrophilicity of CA membrane. Regarding the rejection profile, the rejections of CAB and CAP membranes first declined while the rejection of CA increased. This difference implies the fouling mechanisms of these membranes may be different. Further study is necessary to clarify this mechanism. When backwashing was applied to the CA membrane, BSA on the membrane surface was partly removed and the BSA rejection decreased. In contrast, the solute rejections of CAB and CAP membranes were virtually unaffected by backwashing, due to the strong adsorption of BSA.

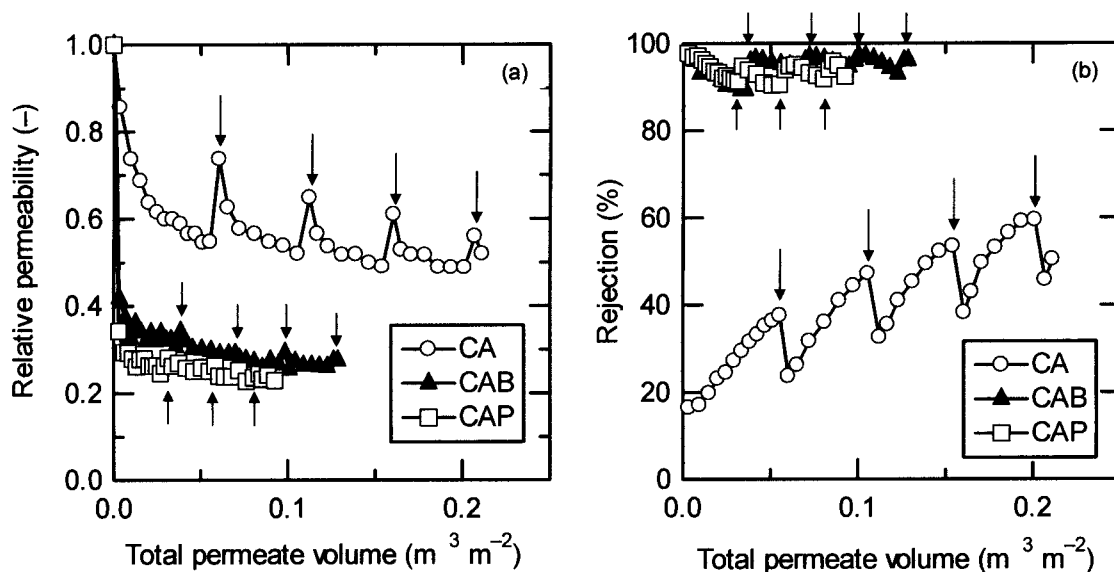


Fig. III.8 Result of fouling experiment with backwashing performed using a 1000ppm BSA solution. (a): relative permeability; (b): rejection

The hollow fiber membranes were backwashed using DI water every hour during the fouling experiment to investigate the effect of backwashing. Arrows in Fig. III.8 denote the backwashing process. The permeabilities of each membrane were partly recovered by backwashing. However, these recoveries were insufficient due to irreversible fouling. To investigate the effect of backwashing quantitatively, a normalized reversible flux

(nRF) was introduced. The total flux decline was defined as the sum of reversible flux (RF) decline and irreversible flux (IF) decline, as follows:

$$RF = \frac{J_a - J_b}{J_0} \quad (1)$$

$$TF = \frac{J_0 - J_b}{J_0} \quad (2)$$

where a and b indicate fluxes after and before backwashing, respectively. The normalized reversible flux (nRF) decline can then be calculated by the following equation:

$$nRF = \frac{RF}{TF} = \frac{J_a - J_b}{J_0 - J_b} \quad (3)$$

Because nRF represents the degree of reversible fouling, a larger nRF value means easier removal of the foulant from the membrane.

The nRF values for the hollow fiber membranes during the backwashing are plotted

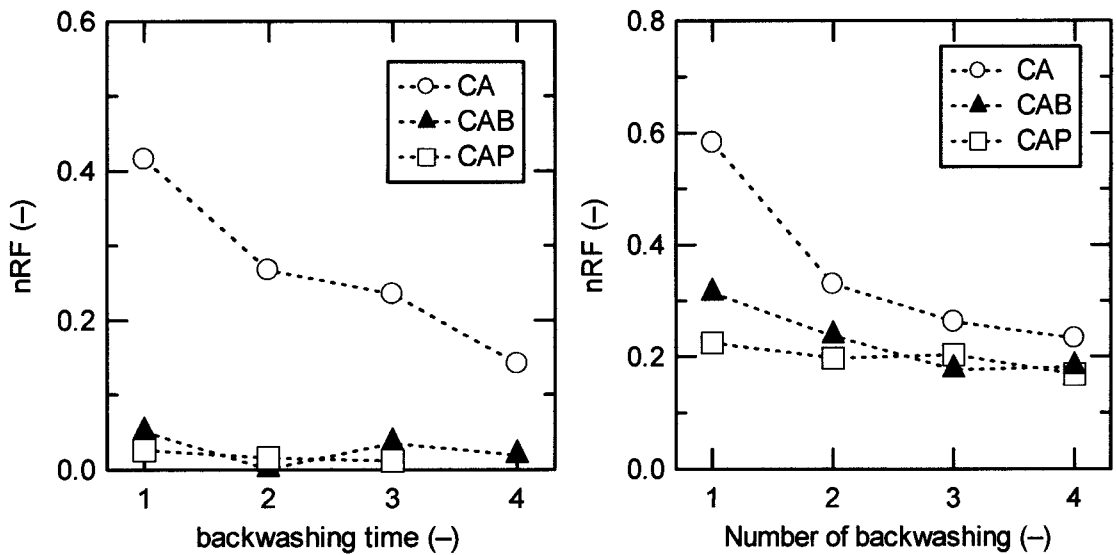


Fig. III.9. Effect of back washing in the experiment with BSA solution.

as a function of backwashing time in Fig. III.9, showing a decrease with backwashing time. The nRF of the CA membrane after the first backwashing was more than five times higher than that of the CAB or CAP membranes and it remained higher than that of the other membranes during four backwash cycles. The higher hydrophilicity of the CA membrane led to easier removal of BSA from the membrane surface compared with the other membranes. Thus, membrane hydrophilicity is quite important for achieving useful backwashing as well as a lower decrease in water permeability during filtration.

III.4 Conclusion

In this study, hollow fiber membranes were fabricated from CA, CAB, and CAP to investigate the effect of hydrophilicity on the fouling behaviors of membranes for water purification. A series of analyses, including SEM, AFM, zeta potential, contact angle measurement and water permeability measurement, confirmed that the hollow fiber membranes were successfully fabricated from each polymer with similar membrane properties except for hydrophilicity. Fouling measurements using humic acid and BSA revealed that the CA membrane, with higher hydrophilicity, exhibited a lower decrease in water permeability and had a higher backwashing effect. Thus, the usefulness of a hydrophilic membrane surface was clearly confirmed by keeping other factors virtually constant.

References

- [1] J.E. Dohany, L.E. Robb, Polyvinylidene fluoride, in: Kirk-Othmer *Encyclopedia of Chemical Technology*, vol. 11, 3rd ed., Wiley, New York, NY, 1980, pp. 64–74.

- [2] M. Pontie, A. Thekkedath, K. Kecili, H. Habarou, H. Suty, J.P. Crou, Membrane autopsy as a sustainable management of fouling phenomena occurring in MF, UF and NF processes, *Desalination*, **204** (2007) 155–169.
- [3] A.W. Zularisam, A.F. Ismail, M.R. Salim, M. Sakinah, H. Ozaki, The effects of natural organic matter (NOM) fractions on fouling characteristics and flux recovery of ultrafiltration membranes, *Desalination*, **212** (2007) 191–208.
- [4] E.M. Vrijenhoek, S. Hong, M. Elimelech, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes, *J. Membr. Sci.*, **188** (2001) 115–128.
- [5] Q. Shi, Y. Su, S. Zhu, C. Li, Y. Zhao, Z. Jiang, A facile method for synthesis of pegylated polyethersulfone and its application in fabrication of antifouling ultrafiltration membrane, *J. Membr. Sci.*, **303** (2007) 204–212.
- [6] Y. Polyakov, Membrane Fouling at the Service of UF/MF: Hollow Fiber Membrane Adsorber, *Membrane Quarterly* **20** (2005) 7–11.
- [7] Y. S. Polyakov, Particle deposition in outside-in hollow fiber filters and its effect on their performance, *J. Membr. Sci.*, **278** (2006) 190–198.
- [8] F. F. Stengaard, Preparation of asymmetric microfiltration membranes and modification of their properties by chemical treatment, *J. Membr. Sci.*, **36** (1988) 257–275.
- [9] J. M. Dickson, R. F. Childs, B. E. McCarry, D. R. Gagnon, Development of a coating technique for the internal structure of polypropylene microfiltration membranes, *J. Membr. Sci.*, **148** (1998) 25–36.
- [10] L.E.S. Brink, S.J.G. Elbers, T. Robbertsen, P. Both, The anti-fouling action of polymers preadsorbed on ultrafiltration and microfiltration membranes, *J. Membr.*

Sci., **76** (1993) 281–291.

- [11] M. Ulbricht, H. Matuschewski, A. Oechel, H. G. Hicke, Photo-induced graft polymerization surface modifications for the preparation of hydrophilic and low-protein-adsorbing ultrafiltration membranes, *J. Membr. Sci.*, **115** (1996) 31–240.
- [12] J. Pieracci, J. V. Crivello, G. Belfort, Photochemical modification of 10kDa polyethersulfone ultrafiltration membranes for reduction of biofouling, *J. Membr. Sci.*, **156** (1999) 223–240.
- [13] H. Yamagishi, J. V. Crivello, G. Belfort, Development of a novel photochemical technique for modifying poly (arylsulfone) ultrafiltration membranes, *J. Membr. Sci.*, **105** (1995) 237–247.
- [14] P. Wang, K.L. Tan, E. T. Kang, K. G. Neoh, Plasma-induced immobilization of poly (ethylene glycol) onto poly (vinylidene fluoride) microporous membrane, *J. Membr. Sci.*, **195** (2002) 103–114.
- [15] J. F. Hester, P. Banerjee, Y. Y. Won, A. Akthakul, M. H. Acar, A.M. Mayes, ATRP of amphiphilic graft copolymers based on PVDF and their use as membrane additives, *Macromolecules*, **35** (2002) 7652–7661.
- [16] X. Fu, T. Maruyama, T. Sotani, H. Matsuyama, Effect of surface morphology on membrane fouling by humic acid with the use of cellulose acetate butyrate hollow fiber membranes, *J. Membr. Sci.*, **320** (2008) 483–491.
- [17] M. Shang, H. Matsuyama, M. Teramoto, D. R. Lloyd, N. Kubota, Preparation and membrane performance of poly (ethylene-co-vinyl alcohol) hollow fiber membrane via thermally induced phase separation, *Polymer*, **44** (2003) 7441–7447.

- [18] H. Matsuyama, H. Okafuji, T. Maki, M. Teramoto, N. Kubota, Preparation of polyethylene hollow fiber membrane via thermally induced phase separation, *J. Membr. Sci.*, **223** (2003) 119–126.
- [19] C. Bellona, J. E. Drewes, The role of membrane surface charge and solute physico-chemical properties in the rejection of organic acids by NF membranes, *J. Membr. Sci.*, **249** (2005) 227–234.
- [20] N. A. Rahman, T. Sotani, H. Matsuyama, Effect of the addition of the surfactant tetronic 1307 on poly(ether sulfone) porous hollow-fiber membrane formation, *J. Appl. Polym. Sci.*, **108** (2008) 3411–3418.
- [21] A. Sharma, P. K. Agarwal, S. Deep, Characterization of different conformations of bovine serum albumin and their propensity to aggregate in the presence of *N*-cetyl-*N,N,N*-trimethyl ammonium bromide, *J. Membr. Sci.*, **343** (2010) 454–462.
- [22] J. C. Cowan, Humic substances with enhanced surface charge, U.S. Patent 4,599,181.
- [23] J. R. Fried, Polymer science and technology, Prentice-Hall, NJ (1995).
- [24] A. F. M. Barton, Handbook of solubility parameters and other cohesion parameters, 2nd ed., CRC Press, Boca Raton, FL, (1991).
- [25] H. S. Shin, J. M. Monsallier, G. R. Choppin, Spectroscopic and chemical characterizations of molecular size fractionated humic acid, *Talanta*, **50** (1999) 641–647.
- [26] M. Chiku, T. A. Ivandini, A. Kamiya, A. Fujishima, Y. Einaga, Direct electrochemical oxidation of proteins at conductive diamond electrodes, *J. Electroanal. Chem.*, **612** (2008) 201–207.

- [27] H. Susanto, M. Ulbricht, Characteristics, performance and stability of polyethersulfone ultrafiltration membranes prepared by phase separation method using different macromolecular additives, *J. Membr. Sci.*, **327** (2009) 125–135.
- [28] Z. W. dai, L. S. Wan, Z. K. Xu, Surface glycosylation of polyacrylonitrile ultrafiltration membrane to improve its anti-fouling performance, *J. Membr. Sci.*, **325** (2008) 479–485.

Chapter IV

Preparation and characterization of several types of polyvinyl butyral hollow fiber membranes by thermally induced phase separation

IV.1 Introduction

Recently, water shortages have become a severe problem worldwide because of population growth and an increase in the demand for high quality water. A possible solution to this problem is water purification by membrane technology, and this technique has attracted attention for wastewater treatment and production of drinking water. Many polymers have been investigated as membrane materials, including polyethylene, polypropylene, polyethersulfone, polysulfone (PSf), cellulose acetate, and polyvinylidene fluoride. Because each polymer is unique in terms of permeability, hydrophilicity, chemical resistance, mechanical strength, and fouling properties, membrane materials can be selected according to the application.

The main fabrication method for porous polymer membranes is phase separation. The thermally induced phase separation (TIPS) process is particularly attractive because of the high reproducibility it offers, and the fact it can be used with a variety of polymers. Novel polymers and various additives to improve membrane functionality have been adopted for the TIPS process. The polymers used in the TIPS process include polyethylene [1,2], polypropylene [3,4], cellulose acetate [5], poly(ethylene-co-vinyl alcohol) (EVOH) [6,7], poly(vinyl butyral) (PVB) [8,9], polylactic acid [10,11], polyvinylidene fluoride/polymethyl methacrylate [12,13], PVB/EVOH [14], polyethersulfone/polymeric surfactant [15] and PVB/TiO₂ [16].

Membranes for domestic water purification need to completely exclude bacteria and

have high antifouling properties. Although PSf is often used in domestic water purification, hydrophilic additives are usually required in the membrane preparation process to improve its hydrophilicity. Polyvinyl acetal is a potential candidate for membrane preparation that will not suffer from this disadvantage of PSf membranes. Polyvinyl acetal is obtained by partial saponification and subsequent acetalization of inexpensive polyvinyl acetate. The polymer has high resistance against acid and base, and high mechanical strength. A representative polyvinyl acetal is PVB, and this has been studied as an ultrafiltration flat membrane [17] and a microfiltration hollow fiber membrane. It has been reported that PVB is more hydrophilic than other polymers because of the vinyl alcohol group in its molecular structure [8]. In other studies, polymer blending with EVOH [14], blending with surfactants [9], and hydrophilization of the PVB membrane by HCl treatment [17] have been attempted.

In this study, hollow fiber membranes for water treatment were prepared from three types of PVB and their mixture. The molecular structures of the PVB polymers were investigated for suitability for the membrane in terms of membrane performance and wettability.

IV.2 Experimental

IV.2.1 Materials

Polyvinyl butyral (6000C and 6000AS) and polyvinyl acetal (067) were obtained from Denki Kagaku Kogyo (Tokyo, Japan). The polymers of 6000C, 6000AS and 067 are abbreviated as PVB-1, PVB-2 and PVB-3, respectively. Their structures are shown in Fig. IV.1 and their chemical compositions are summarized in Table IV.1. PEG 200 and PEG 600 were purchased from Wako Pure Chemical Industries. Polystyrene (PS)

latex beads with diameters of 20, 50, 100 and 300 nm were purchased from Duke Scientific Co. (Palo Alto, CA). All the chemicals were used without further purification.

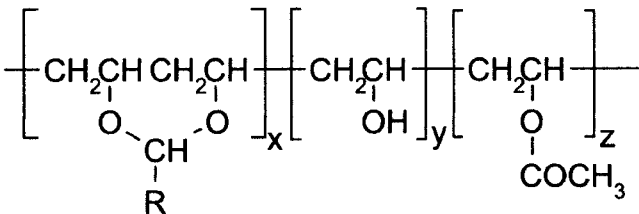


Fig. IV.1 Molecular structure of polyvinyl acetal.

Table IV.1 Copolymer composition, molecular weight and water contact angle of the three types of PVB polymers

Polymer	Composition			Mw	Water contact angle (°)	
	x	y	z			
PVB-1	83	16	1	CH ₃ : C ₃ H ₇ =1.1	288,000	76
PVB-2	87	12	1	CH ₃	190,000	71
PVB-3	85.4	13.5	1.1	CH ₃	188,000	69

IV.2.2 Phase diagram

Homogeneous polymer-diluent samples were prepared by mixing 3 g of polymer+PEG 200 at 170 °C for 10 min using a twin-blade mixer (IMC-119D, Imoto Co.). A sample of the prepared homogeneous solution was placed between two coverglasses separated by a 100 μm thick Teflon® sheet spacer. The sample was heated at 180 °C for 2 min on a hot stage (HFS91, LINKAM) and then cooled at 10 °C min⁻¹. The cloud point temperatures during cooling were observed using a microscope (BX50, Olympus). The measurements were repeated at least four times.

IV.2.3 Hollow fiber membrane fabrication

Hollow fiber membranes were prepared using a batch-type extruder (Imoto Co., BA-0) [1, 6]. Measured amounts of the polymer and PEG 200 were fed into the vessel with mass fraction of 20% the polymer, and then mixed for 60 min at 170 °C. The sample was maintained at 170 °C for 120 min, and then the homogeneous solution was fed to a spinneret by a gear pump under nitrogen pressure. The spinneret consisted of outer and inner tubes with diameters of 1.25 and 0.62 mm, respectively. PEG 600 was introduced into the inner tube to make a hollow fiber. The hollow fiber was extruded from the spinneret with an air gap of 0 mm and wound onto a take-up winder after entering a water bath at 10 °C. The extrusion rate of the polymer solution and the flow rate of PEG 600 in the inner tube of the spinneret were fixed at 0.10 and 0.27 m s⁻¹, respectively. The diluent remaining in the hollow fiber membrane was extracted by immersing the fibers in water.

IV.2.4 SEM observation

To obtain dry hollow fiber membranes, the prepared membranes were freeze-dried (FD-1000, Tokyo Rikakikai Co., Ltd.). The dry hollow fiber membranes were fractured in liquid nitrogen and sputtered with Pt/Pd. The cross-sections and the surfaces of the hollow fiber membranes were examined using a scanning electron microscope (JSM-5610LVS, Hitachi Co.) with an accelerating voltage of 15 kV.

IV.2.5 Water permeability

Pure water was forced to permeate from the outside to the inside of hollow fiber membranes. A transmembrane pressure (range 0.05–0.1 MPa) was applied by adjusting

a pressure valve on the release side, and the pressure was averaged from the readings of the two pressure gauges. The water permeability was calculated based on the inner surface area of the hollow fiber membrane. Each datum of water permeability was the average of three measurements.

IV.2.6 Mechanical strength

The tensile stress of the hollow fiber membranes was measured using a tensile apparatus (AGS-J, Shimadzu Co.). The membrane was fixed vertically between two pairs of tweezers separated by a gap of 50 mm, and extended at a constant elongation rate of 50 mm/min until it broke. Each datum of the tensile stress at the breaking point was the average of five measurements.

IV.2.7 Exclusion of PS beads and bacteria

Filtration experiments were carried out using the same apparatus as that used in the water permeability test. The solutes used were monodisperse PS latex beads with diameters of 20, 50, 100 and 300 nm. The feed solutions were prepared by dispersing the PS latex beads in an aqueous nonionic surfactant solution (0.1% (mass fraction) Triton X-100). The solute concentrations in the filtrate and feed solution were measured with an ultraviolet-visible spectrophotometer (U-200, Hitachi Co.) at 380 nm.

A bacteria exclusion test was conducted for the membranes using a suspension of *Brevundimonas diminuta* NBRC14213 (4×10^6 CFU/mL). The bacterial suspension was permeated through the PVB membranes, and the number of bacteria in the permeate were counted according to the Japanese Industrial Standard (JIS K3835).

IV.3. Results and discussion

3.1 Phase diagram

The cloud point temperatures of the solutions with a PVB mass fraction of 10–25% were measured (Fig. IV.2 (a)). The temperatures were in the order of PVB-1>PVB-2>PVB-3, which indicated the chemical compositions of the PVB polymers affected the phase separation temperatures. The solubility parameters of the polymers and PEG 200 are shown in Table IV.2. The difference between the solubility parameters of PEG 200 and PVB-1 was larger than those among PEG 200 and other PVB polymers. This meant that the cloud point temperature of the PVB-1 solution was highest, because it had the lowest compatibility between the polymer and the diluent. By contrast, the solubility parameter of PVB-3 was closest to that of PEG 200, and this solution had the highest compatibility. Thus, the cloud point temperature in this system was lowest.

The cloud point temperatures of polymer blend solutions containing PVB-1 and PVB-2 were also examined. The temperature decreased with an increase in the PVB-2

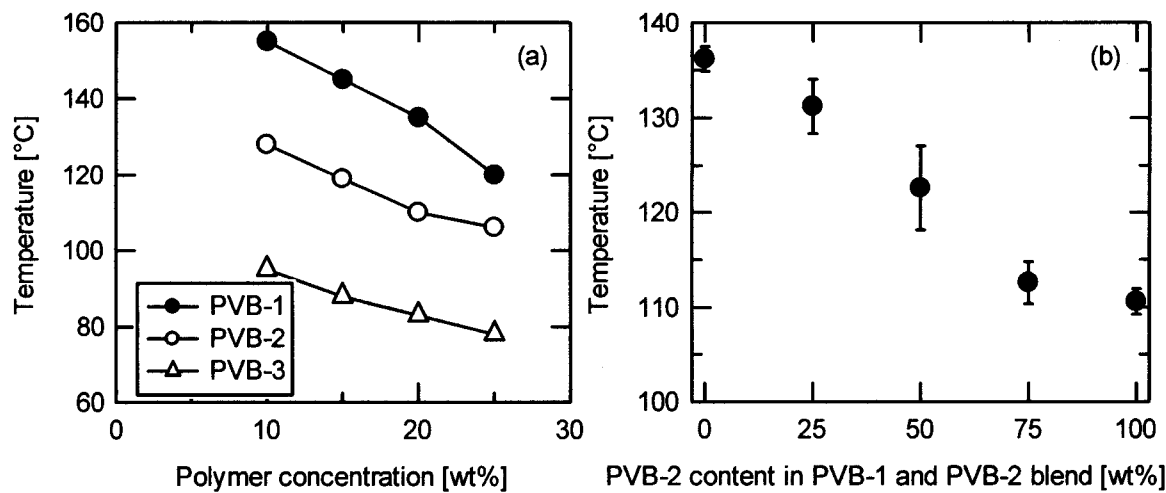


Fig. IV.2 Phase separation temperatures of the PVB solutions. (a) PVB solution; (b) polymer blend solution of PVB-1 and PVB-2.

content (Fig. IV.2 (b)), because PVB-2 had higher compatibility with PEG 200. Because PVB-1 and PVB-2 are compatible with each other, the cloud point temperatures of the polymer blend solution gradually changed with its composition, and two cloud point temperatures were not observed [14].

Table IV.2 Solubility parameters of the three types of PVB polymers and the diluent.

Solubility parameter	
[MPa ^{1/2}]	
PVB-1 ^a	22.6
PVB-2 ^a	22.9
PVB-3 ^a	23.3
PEG 200 ^b	24.3

a: Estimated using Fedor method [18]

b: Cited from Ref. [19].

3.2 SEM observation

SEM observation of prepared membranes was carried out. Fig. IV. 3 shows the cross-section, outer surface, and inner surface of the hollow fiber membranes prepared from the three PVB polymers. The outer surfaces of all the membranes had obvious pores and their sizes were in the order of PVB-1>PVB-2>PVB-3. PVB-3 had a small porous structure on the outer surface, while PVB-1 and PVB-2 had rough outer surfaces. The inner surfaces of all the polymers had submicron size pores, and the sizes of these pores were in the same order as the pores on the outer surface. These tendencies can be explained in terms of the phase separation temperatures of the PVB solutions shown in Fig. IV.2(a). The high cloud point temperature for PVB-1 resulted in a long coarsening time for the structure and large pore size, while the short coarsening time for PVB-3 resulted in small pores.

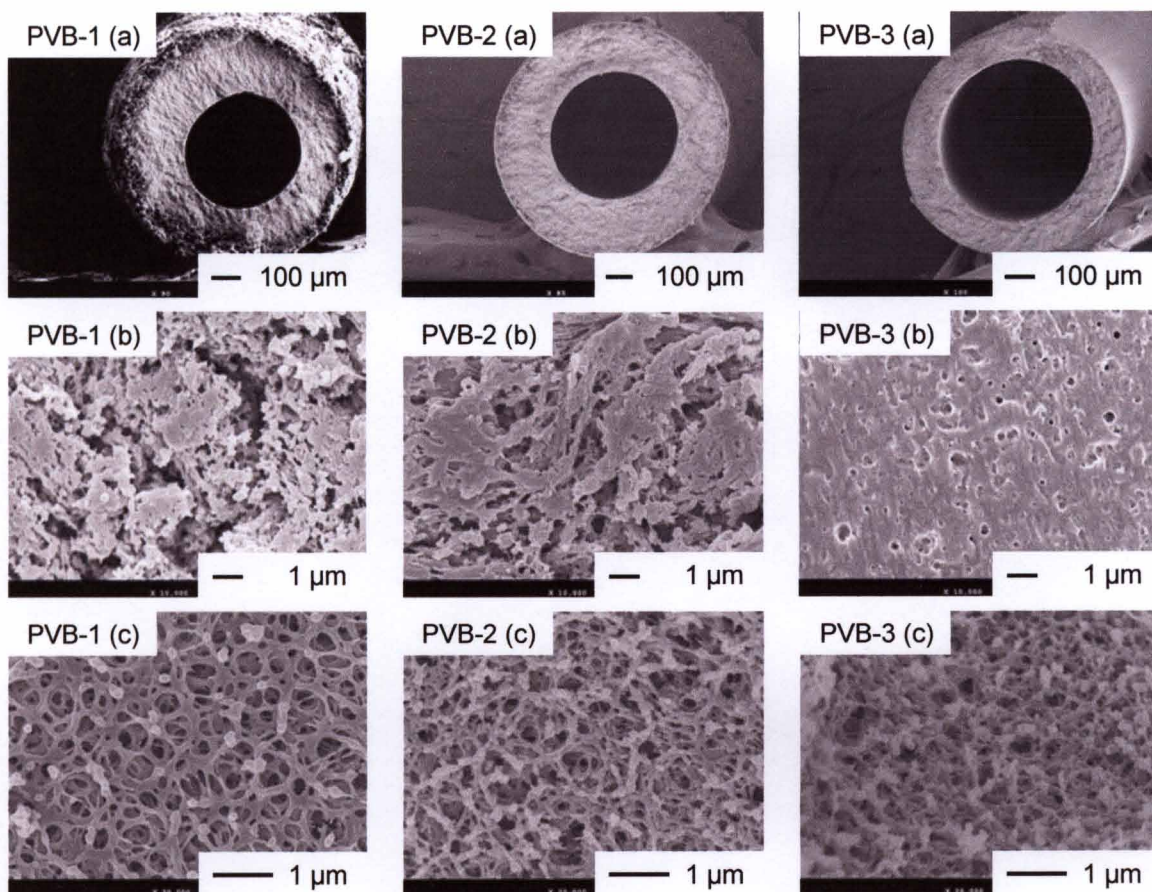


Fig. IV.3 SEM images of the hollow fiber membranes. (a) cross-section; (b) outer surface; (c) inner surface.

Fig. IV.4 shows the SEM images of the outer surfaces and cross-sections of the hollow fiber membranes prepared from the polymer blend of PVB-1 and PVB-2. The membrane structure became smaller as the content of PVB-2 increased, which corresponded to the lower cloud point temperature shown in Fig. IV.2 (b).

All the membranes prepared from the individual PVB polymers and the PVB blend had rough structure on the outer surface and small pores on the cross-section. Thus, the membranes prepared in the TIPS process had asymmetric structures. A skin did not form on the outer surface, because the air gap was 0 mm in the membrane preparation process. When the air gap is large, the solvent evaporates from the outer surface, which

leads to formation of a skin on the outer surface [6]

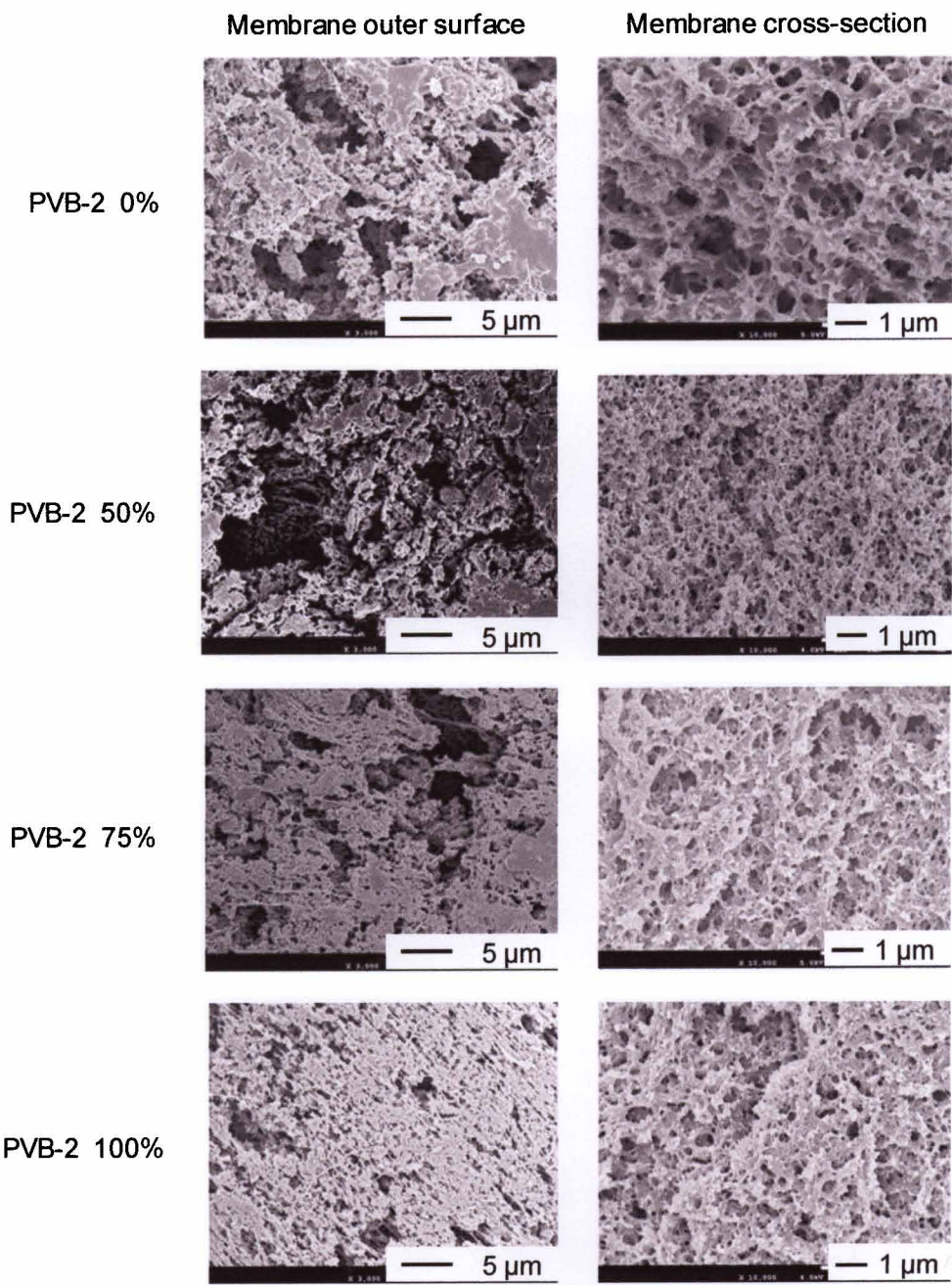


Fig. IV.4 SEM images of the polymer blend membranes.

3.3 Water permeability

Water permeability of the prepared membranes was investigated with wet membranes.

Fig. IV.5 (a) shows that the water permeability was in the order of PVB-1>PVB-2>PVB-3 for the wet membranes. As was confirmed by SEM observation, PVB-1 had the largest pores and PVB-3 had the smallest. Thus, the water permeability trend can be explained by the difference in the pore sizes. The water permeability was also measured after the membranes had been dried at 40 °C for 24 h in vacuo. The dried PVB-2 membrane had a similar water permeability to the wet membrane, while the dried PVB-1 and PVB-3 membranes had negligible water permeability (Fig. IV.5(a)). SEM observation confirmed that the pore size of the PVB membranes did not change after the drying process, and the same trend in pore size was maintained for the three polymers. Surface tension determines the pressure needed to make water penetrate membrane pores. The pressure difference Δp can be expressed as follows:

$$\Delta p = 2\gamma/r \quad (1)$$

where γ is the surface tension, and r is the pore radius. Thus, the pore size and the hydrophilicity on the pore surface affect the water permeability of the dried membrane.

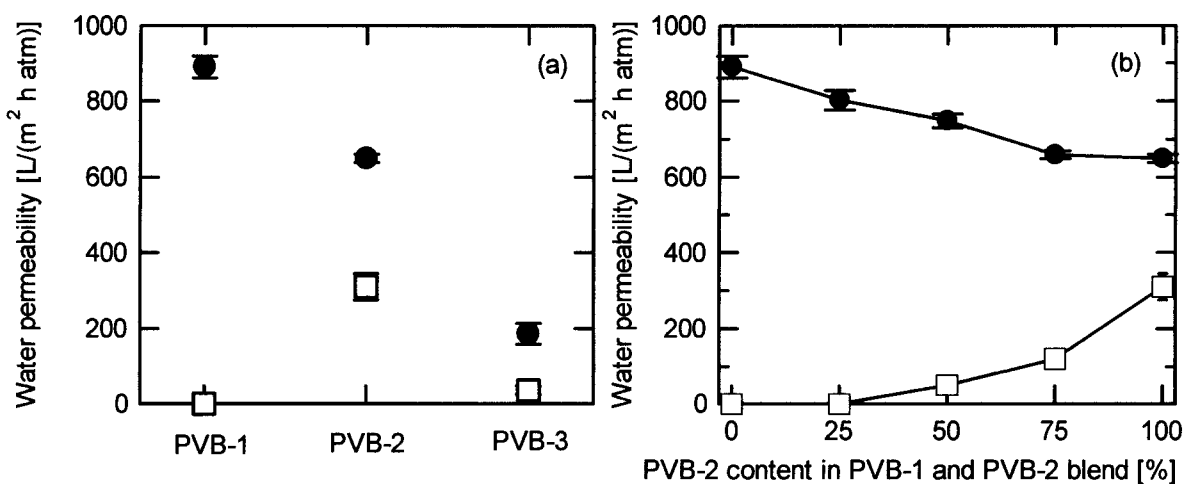


Fig. IV.5 Water permeability of the prepared membranes. (a) PVB membrane; (b) polymer blend membranes. Solid circles, wet membranes; open squares, dry membranes (40 °C, 24 h).

Judging from the SEM image of the membrane, the PVB-3 membrane had much smaller pores on the outer surface than the other two membranes. Therefore, the dried PVB-3 membrane showed no water permeability, even though it had higher hydrophilicity. By contrast, the PVB-1 and PVB-2 membranes had large pores in the SEM observation, and the difference in the water contact angle was only 5° (Table IV.1). This indicates that the difference in the membrane hydrophilicity between PVB-1 and PVB-2 is not large. Because the dried PVB-1 membrane was not water permeable, a permeability test using aqueous isopropanol solutions was carried out to investigate the effect of surface tension and hydrophilicity. Aqueous solutions containing an isopropanol mass fraction of 2 and 5% gave permeabilities of 258 and 371 L/(m² h atm), respectively. Thus, the dried PVB-1 membrane showed high permeability with lower surface tension. This result implies that the difference in the hydrophilicity between the dried PVB-1 and PVB-2 membranes resulted in the difference in the water permeability of the two membranes, even though the difference in the hydrophilicity was not large.

Some dried membranes made with hydrophobic polymers are known to have low water permeability because of their low wettability. To give high wettability on the inner pore surface, it should usually be coated with a nonvolatile hydrophilic material before producing the membrane module. Thus, the high wettability of the PVB-2 membrane is a significant advantage over other hydrophobic membranes, because this coating process can be skipped.

Water permeability was also measured for the PVB-1 and PVB-2 polymer blend membrane. The water permeability of the wet membrane decreased with an increase in the PVB-2 content of the polymer blend (Fig. IV.5(b)). However, for the dried membrane, membranes with a PVB-2 mass fraction <50% had little water permeability.

The dried membrane had higher water permeability when the PVB-2 content of the membrane was higher. Thus, the water permeability of dried membranes increased as the hydrophilic PVB-2 content increased.

3.4 PS bead and bacteria exclusion

Exclusion of PS beads was measured to investigate the pore size. The particle exclusion R is defined as follows:

$$R = 1 - C_f / C_0 \tag{1}$$

where C_0 and C_f are the particle concentrations in the feed and the filtrate, respectively. The effect of the PVB species on the exclusion is shown in Fig. IV.6. All the PVB membranes showed 100% exclusion of the PS beads with a 300 nm diameter and almost no exclusion for the beads with a 20 nm diameter. PVB-3 showed almost 100% rejection for the beads with diameters of 50 and 100 nm, while PVB-1 showed lower exclusion for these particles than PVB-3. These results are in good agreement with the SEM observations (Fig. IV.3), which showed that PVB-1 had large pores compared with the other membranes.

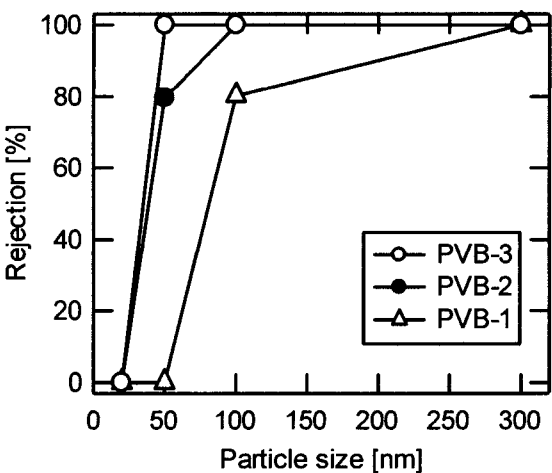


Fig. IV.6 Polystyrene bead rejection by the PVB membranes.

Particle exclusion measurements were also carried out for the PVB-1 and PVB-2 polymer blend membrane. As shown in Fig. IV.7, exclusion of the PS beads increased with the PVB-2 content in the polymer blend. Exclusion of the 50 nm diameter beads was >80% for polymer blend membranes with a PVB-2 mass fraction >75%.

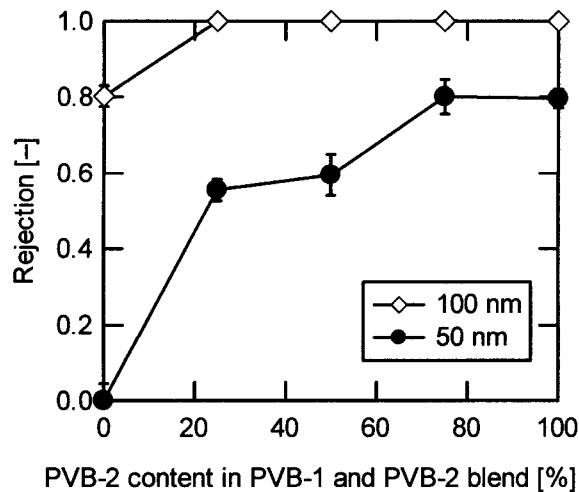


Fig. IV.7 Effect of polymer blend composition of the PVB-1/PVB-2 membrane on polystyrene bead rejection.

A bacterial exclusion test was also conducted for these membranes because the complete exclusion of bacteria is important for membrane water purification. Membranes with PVB-2 mass fractions of 75% and 100% completely excluded *B. diminuta* (Table IV.3). This result indicates that these membranes are suitable for drinking water treatment.

Table IV.3 Number of bacteria in the filtrate after the bacterial exclusion test.

PVB-2 content	[wt%]	0	25	50	75	100
Number of bacteria	[CFU/ml]	n.d.	n.d.	4.0×10 ⁵	0	0

n.d.: not determined

Initial bacteria number: 1.7 × 10⁶ CFU/ml

3.5 Mechanical strength

Fig. IV. 8 (a) shows the tensile stress at breaking point of the wet PVB hollow fiber membranes. PVB-1 showed significantly higher tensile stress than the other membranes, while its elongation was the lowest. Because the three PVB polymers have similar chemical structures, the higher tensile stress of PVB-1 is probably because of its molecular weight (Table IV.1). A high polymer molecular weight results in high tensile stress of membrane.

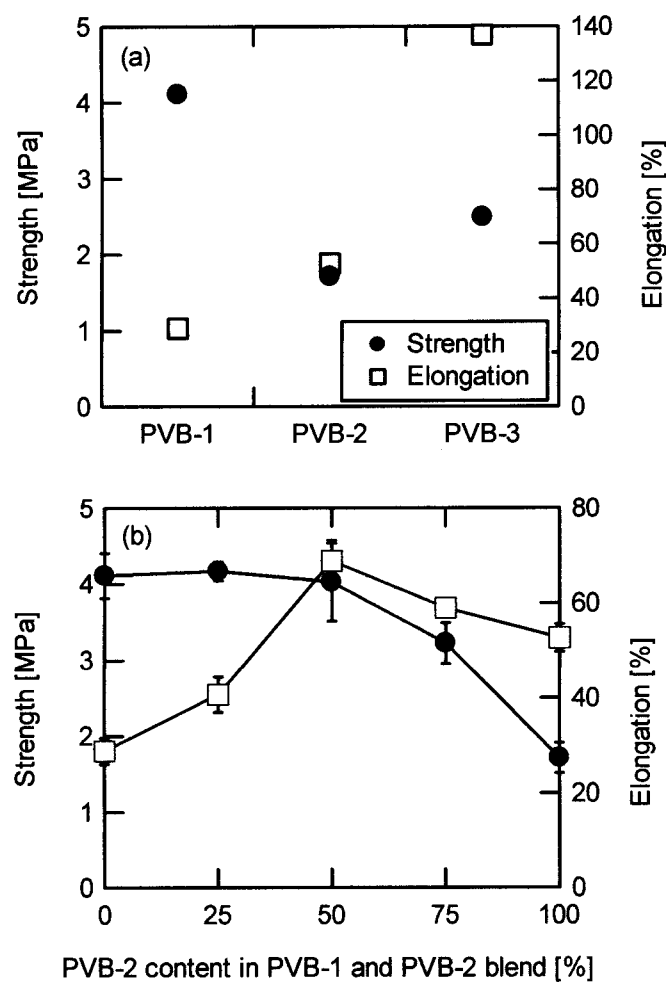


Fig. IV.8 Mechanical strength of the prepared membranes. (a) PVB membrane; (b) polymer blend membranes.

Tensile stress was also measured for the polymer blend membrane. Fig. IV. 8 (b) shows that the membranes with a PVB-2 mass fraction of up to 50% had high tensile stress (>4 MPa), which gradually decreased with higher PVB-2 mass fractions. By contrast, elongation of the obtained membranes increased with PVB-2 mass fractions up to 50%, and slightly decreased with higher PVB-2 mass fractions.

IV.4. Conclusion

Several hollow fiber membranes were prepared via the TIPS process from three types of PVB polymers and a polymer blend of two of these polymers. These PVB polymers have similar chemical structures, but different compositions.

The cloud point temperatures were measured in all three PVB systems, and the trends could be explained by the compatibility between the PVB polymer and diluent. The PVB system with a high cloud point temperature had a long structure growth period, which resulted in large pores in the membrane. The water permeability trend for the wet membranes corresponded to the trend for the cloud point temperatures of the PVB solutions. By contrast, the water permeability of dried membranes was independent of the pore size. For example, permeability of the dry PVB-2 membrane was half that of the wet membrane, while the PVB-1 membrane had a large pore when dry and almost no permeability. The permeability in the dry state could be explained by the membrane wettability, which was related to both the porous structure and hydrophilicity of the membranes. Furthermore, the effect of blending the two polymers on the membrane structures and performance was investigated. The membrane performance was easily controlled by changing the blend ratio. The membrane containing 75% (mass fraction) PVB-2 had high membrane wettability and high strength.

References

- [1] H. Matsuyama, H. Okafuji, T. Maki, M. Teramoto, N. Kubota, Preparation of polyethylene hollow fiber membrane via TIPS, *J. Membr. Sci.*, **223** (2003) 119–126.
- [2] M. Y. Jeon, C. K. Kim, Phase behavior of polymer/diluent/diluent mixtures and their application to control microporous membrane structure, *J. Membr. Sci.*, **300** (2007) 172–181.
- [3] J. M. Dickson, R. F. Childs, B. E. McCarry, D. R. Gagnon, Development of a coating technique for the internal structure of polypropylene microfiltration membranes, *J. Membr. Sci.*, **148** (1998) 25–36.
- [4] W. Yave, R. Quijada, D. Serafini, D. R. Lloyd, Effect of the polypropylene type on polymer–diluent phase diagrams and membrane structure in membranes formed via the TIPS process: Part I. Metallocene and Ziegler–Natta polypropylenes, *J. Membr. Sci.*, **263** (2005) 146–153.
- [5] H. Matsuyama, K. Ohga, T. Maki, M. Teramoto, S. Nakatsuka, Porous cellulose acetate membrane prepared by thermally induced phase separation, *J. Appl. Polym. Sci.*, **89** (2003) 3951–3955.
- [6] M. Shang, H. Matsuyama, M. Teramoto, D. R. Lloyd, N. Kubota, Preparation and membrane performance of poly(ethylene-co-vinyl alcohol) hollow fiber membrane via thermally induced phase separation, *Polymer*, **44** (2003) 7441–7447.
- [7] R. Lv, J. Zhou, Q. G. Du, H. T. Wang, W. Zhong, Effect of posttreatment on morphology and properties of poly(ethylene-co-vinyl alcohol) microporous hollow fiber via thermally induced phase separation, *J. Appl. Polym. Sci.*, **104** (2007)

4106–4112.

- [8] X. Fu, H. Matsuyama, M. Teramoto, H. Nagai, Preparation of hydrophilic poly(vinyl butyral) hollow fiber membrane via thermally induced phase separation, *Sep. Purif. Technol.*, **45** (2005) 200–207.
- [9] Y.-R. Qiu, N. A. Rahman, H. Matsuyama, Preparation of hydrophilic poly(vinyl butyral)/Pluronic F127 blend hollow fiber membrane via thermally induced phase separation, *Sep. Purif. Technol.*, **61** (2008) 1–8.
- [10] A. Moriya, T. Maruyama, Y. Ohmukai, T. Sotani, H. Matsuyama, Preparation of poly(lactic acid) hollow fiber membranes via phase separation methods, *J. Membr. Sci.*, **342** (2009) 307–312.
- [11] Y. X. Huang, J. Ren, C. Chen, T. B. Ren, X. Y. Zhou, Preparation and Properties of Poly(lactide-co-glycolide) (PLGA)/ Nano-Hydroxyapatite (NHA) Scaffolds by Thermally Induced Phase Separation and Rabbit MSCs Culture on Scaffolds, *J. Biomater. Appl.*, **22** (2008) 409–432.
- [12] S. Rajabzadeh, T. Maruyama, Y. Ohmukai, T. Sotani, H. Matsuyama, Preparation of PVDF/PMMA blend hollow fiber membrane via thermally induced phase separation (TIPS) method, *Sep. Purif. Technol.*, **66** (2009) 76–83.
- [13] Z. Y. Cui, Preparation of Poly(vinylidene fluoride)/Poly(methyl methacrylate) Blend Microporous Membranes via the Thermally Induced Phase Separation Process, *J. Macromol. Sci. Part B Phys.*, **49** (2010) 301–318.
- [14] X. Fu, H. Matsuyama, M. Teramoto, H. Nagai, Preparation of polymer blend hollow fiber membrane via thermally induced phase separation, *Sep. Purif. Technol.*, **52** (2006) 363–371.
- [15] N. A. Rahman, T. Maruyama, H. Matsuyama, Performance of

- polyethersulfone/Tetronic 1307 hollow fiber membrane for drinking water production, *J. Appl. Sci. Environ. Sanit.*, **3** (2008) 1–7.
- [16] X. Fu, H. Matsuyama, H. Nagai, Structure control of asymmetric poly(vinyl butyral)-TiO₂ composite membrane prepared by nonsolvent induced phase separation, *J. Appl. Polym. Sci.*, **108** (2008) 713–723.
- [17] X. Ma, Q. Sun, Y. Su, Y. Wang, Z. Jiang, Antifouling property improvement of poly(vinyl butyral) ultrafiltration membranes through acid treatment, *Sep. Purif. Technol.*, **54** (2007) 220–226.
- [18] R. F. Fedors, A method for estimating both the solubility parameters and molar volumes of liquids, *Polym. Eng. Sci.*, **14** (1974) 147–153.
- [19] B. Liu, Q. G. Du, Y. L. Yang, The phase diagrams of mixtures of EVAL and PEG in relation to membrane formation, *J. Membr. Sci.*, **180** (2000) 81–92.

Chapter V

General Conclusion

Water is essential to all living things and said to be the origin of lives. Especially, it weighs approximately 65 percent of human body and is metabolized about 2500 mL per day. Therefore, as well as the air, it cannot be lacked at any time. Although water is abundant on the Earth, only small amount of water is available for drinking or industrial use. This is the reason why the needs for the technique that can efficiently filter impurities from water at low cost are increasing. Filtration membranes such as RO, NF, UF and MF membranes are practically used for several purposes. However, there are still many problems to be solved for efficient membrane separation.

In order to prepare a separation membrane having low manufacturing cost, high durability and high antifouling property, many studies has been carried out. However, these investigations are not sufficient because it has been only a generation since study about membrane separation started.

The most important problem in water treatment membrane is fouling, which is a very complex phenomenon because it depends on chemical, physical, electric, structural element of the membrane and the characteristics of the fouling material. Up to now, many reports about the relationships between physical property, structure, and electrical property of the membrane and fouling behavior, the problem of biofouling and the development of antifouling membranes. These reports show that many attentions are given to fouling, but there are still a lot of problems.

In the field of polymeric porous membrane, phase separation method is one of the main preparation methods. A polymer solution is converted into solid state during the method. By

using the phase separation method, structure of the membrane obtained is easily controlled because the process of phase transition and formation of micro pores can be controlled. Although there are several ways to induce phase transition, thermally induced phase separation (TIPS) method is an outstanding method because TIPS method has advantages such as high reproducibility, no macrovoid formation and low total cost for the preparation. Although many studies on membrane developing are done using TIPS method, there is no report about the property of membranes prepared under various TIPS method conditions.

As membrane material, there are many excellent matters such as high mechanical and chemical resistance of PVDF. They are already practically used or being studied.

Since many of foulants are hydrophobic, membrane material should be hydrophilic to reduce hydrophobic interaction and prevent fouling. As the means to give hydrophilicity on the membrane, graft polymerization of hydrophilic polymer and blending of hydrophilic polymer or surfactant are reported. However, except for chemical modification, blending of a hydrophilic additive often results in the leaching out of the additive from the membrane and the decline in the improvement of hydrophilicity. This is due to the low compatibility of the hydrophilic additive with the main polymer, whereas there is no report about the way to avoid this phenomenon.

This paper consists of five chapters, mainly about the themes written in above.

Chapter 1 General Introduction

The background of this study and related previous studies were shown. The objective of this study was also mentioned.

Chapter 2 Effect of amphiphilic additives on properties of cellulose acetate butyrate hollow fiber membranes prepared by thermally induced phase separation

The effect of the membrane preparing condition in TIPS method on the membrane

property and the effect of hydrophilic additives on the membrane characteristics was examined using cellulose acetate butyrate as membrane material. As a result, it was found that air gap greatly affected the surface morphology, water permeability, and mechanical strength of the membrane. It was also certified that PEG 20000 contributed to the improvement of water permeability because the additive was leached out during the membrane preparation and the storage, whereas polymer surfactant did not affect the water permeability due to its high residual ratio in the membrane.

Chapter 3 Membrane fouling properties of hollow fiber membranes prepared from cellulose acetate derivatives

Although it is often said that hydrophilic membrane has high antifouling property, there has been no study that investigated only about hydrophilicity. To demonstrate it, we prepared three membranes from cellulose acetate derivatives with similar characteristics except for the contact angles, and examined the effect of hydrophilicity on the fouling behavior. The prepared membranes had similar properties on water permeability, surface roughness and zeta-potential. As a result of fouling experiment, membrane with high hydrophilicity obviously showed high antifouling property.

Chapter 4 Preparation and characterization of hollow fiber membranes from polyvinyl butyral

Membrane materials with different hydrophilicity are easily obtained from polymer blend of polyvinyl acetal by controlling acetalization agent and acetalization ratio. This is the desirable characteristics of polyvinyl acetal, and the polymer blend with a polymer of similar structure has high compatibility of these polymers. The high compatibility leads to no leach out of the added polymer. Since the phase separation temperature of PVB solution was dependent on the structure and the acetalization ratio, the membrane pore size changed

according to the PVB structure. For these features, we chose and blended the two types of PVBs. The characteristics of obtained membrane were favorable; having high water permeability even in the dried state, high mechanical strength, and complete rejection of bacteria.

Chapter 5 General Conclusion

Conclusion of this study was made in this chapter.

List of Publications

Chapter II 熱誘起相分離法により作製されたセルロースアセテート誘導体中

空糸膜の膜特性に及ぼす両親媒性添加剤効果、渋谷崇、丸山達生、北浦敏彦、付珣瑶、Nasrul Arahman、曾谷知弘、中塚修志、綿部智一、松山秀人、*化学工学論文集*, **35** (2009) 117–121.

Chapter III Membrane fouling properties of hollow fiber membranes prepared

from cellulose acetate derivatives, T. Shibutani, T. Kitauro, Y. Ohmukai, T. Maruyama, S. Nakatsuka, T. Watabe, H. Matsuyama, *J. Membr. Sci.*, **376** (2011) 102–109.

Chapter IV Preparation and characterization of several types of polyvinyl butyral

hollow fiber membranes by thermally induced phase separation, T. Kitauro, W. N. Fadzlina, Y. Ohmukai, T. Maruyama, H. Matsuyama, submitted to *J. Appl. Polym. Sci.*