Preparation of PVDF Membrane by Thermally-Induced Phase Separation

Chi-Haeng Heo, Kyung-Mo Lee, Jin-Ho Kim, and Sung Soo Kim[†]

College of Environmental and Applied Chemistry, Kyung Hee University, Gyeonggido 447-701, Korea

Abstract: PVDF membrane formation via TIPS was performed for PVDF/DBP and PVDF/DMP systems. PVDF/DBP system showed solid-liquid phase separation behavior, while PVDF/DMP system has liquid-liquid phase separation characteristic as well as solid-liquid phase separation characteristic. PVDF contents and cooling conditions had great influence on structure, and the effects of each parameter were examined. Spherulitic structure was obtained due to the dominant PVDF crystallization. Diluent rejected to the outside of spherulite occupied the surface of the PVDF spherulites to result in the microporous spherulite formation and micro-void between spherulites. PVDF/DMP system had competitive solid-liquid and liquid-liquid phase separation depending on the cooling path.

1. Introduction

Polyvinylidene fluoride (PVDF) has several advantages over the other polymers as membrane materials such as excellent chemical and thermal resistances and mechanical strength [1-3]. Since part of hydrogen in polyolefin resins are substituted with fluorine for PVDF resin, it showed excellent resistance to acids and bases, and especially to chlorine dissolved in water [4]. Therefore, PVDF membranes are best candidates for the microfiltration and ultrafiltration of potable water which had been treated with chlorine for disinfection. PVDF membranes also have electronic applications since it has uniform electric properties [2].

PVDF membranes were commercialized in flat sheet and hollow fiber forms by several membrane manufacturing companies such as Toray, Ashai Kasei, Zenon and US Filter Co. Most of the PVDF membranes have been prepared by nonsolvent-induced phase separation process (NIPS) by dissolving the polymer in solvent followed by precipitation in nonsolvent. Ashai kasei,

US Filters and Toray produce PVDF hollow fiber microfiltration membranes for submerged type applications. Zenon devised PVDF ultratiltration tubular membranes with inner fabric support, which enabled the excellent mechanical strength. Pall Co. produced the flat sheet PVDF membranes for microfiltration of chemicals in electronic process [5-7].

In this work, preparation of PVDF membranes was attempted by thermally-induce phase separation (TIPS) process. TIPS process has several advantages over NIPS process in terms of number of affecting parameters on the phase separation mechanism. Therefore, morphology and structure control are much easier in TIPS process than NIPS process [8-11]. Proper diluents for PVDF were selected as DBP and DMP for TIPS process, and several affecting parameters were investigated on hot stage with optical microscope system.

2. Experiments

2.1. Materials

Solef 1012 of Solvay Co. was selected as PVDF, which has melt flow index of 0.5 g/10 min for fiber

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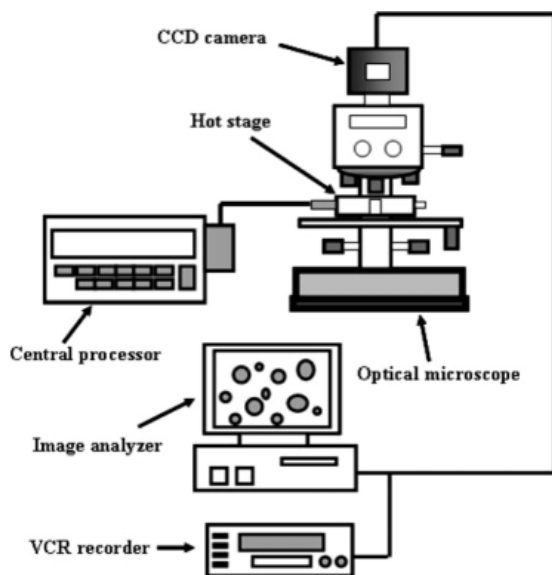 (e-mail : sungkim@khu.ac.kr)

Fig. 1. A schematic diagram of thermo-optical microscope system.

spinning grade. Diluents were selected as dimethyl phthalate (DMP) and dibutyl phthalate (DBP) from Yakuri Pure Chemical Co. For extraction of diluent after membrane fabrication HCFC-141B from Kefron Chemical Co. was selected.

2.2. Thermal and Optical Analyses

Phase diagrams of polymer-diluent systems were determined by using DSC and thermo-optical microscope (TOM) system. DSC (Q100, TA instruments) was used to determine the crystallization temperature of the sample, and TOM system was used to determine the cloud point of the sample. Polymer and diluent were melt blended at a specified composition at 200°C for 4 hr under nitrogen atmosphere. Homogeneous melt blended sample was quenched into water to be solidified without migration of diluent during solidification.

For DSC experiments, samples were heated at a scanning rate of 10°C/min to 200°C to determine the melting temperature and it was held at to 200°C for 10 min to remove the previous thermal history of the sample. The sample was then cooled at a scanning rate of 10°C/min to room temperature to determine the crystallization temperature. Isothermal crystallization

experiments were performed by quenching the sample from 200°C to specified crystallization temperature at a rate of 100°C/min.

TOM system was assembled as shown in Fig. 1 and it was composed of hot stage with a central processor (FP82HT and FP90, Mettler Co.) and a optical microscope (Jenaval, Carl Zeiss) equipped with CCD camera and VCR. Images obtained were analyzed by an image analysis system (IP win, Image Pro Co.). Solid sample was sliced and placed between two cover slips sealed with vacuum grease. It was also heated at 200°C and held there for 10 min before cooling. It was cooled at a rate of 10°C/min, and phase separation images were continuously monitored. Surface and cross sectional images of the membrane samples were obtained from Scanning Electron Microscope (SEM, Stereoscan 440, Leica).

3. Results and Discussions

3.1. Phase Diagrams

Phase diagrams of PVDF/DBP and PVDF/DMP systems were determined as shown in Figs. 2 and 3. In both cases, T_m depression phenomena were observed by addition of diluent to PVDF. DMP has lower molecular weight than DBP and showed greater T_m depression than DBP. As is the other cases, both systems have T_m curve much above the T_c curve depending on heating or cooling mode. PVDF/DBP system undergoes solid-liquid phase separation only by the crystallization of PVDF through out the composition range, and they do not show the cloud point curve at the temperature ranges shown in Fig. 2. PVDF/DMP system has cloud point curve between T_m and T_c curves, which stands for the liquid-liquid phase separation. Monotectic point is located at 28 wt% of PVDF and 75°C, it undergoes liquid-liquid phase separation below this point.

20 wt% of PVDF in DBP and DMP were quenched from 185 to 0°C, and diluents were extracted as compared in Fig. 4. PVDF/DBP sample has much greater supercooling for crystallization of PVDF than PVDF/
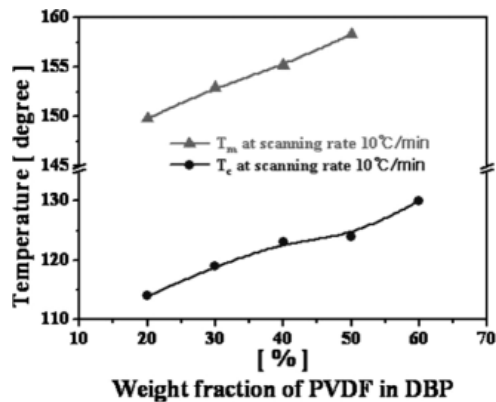
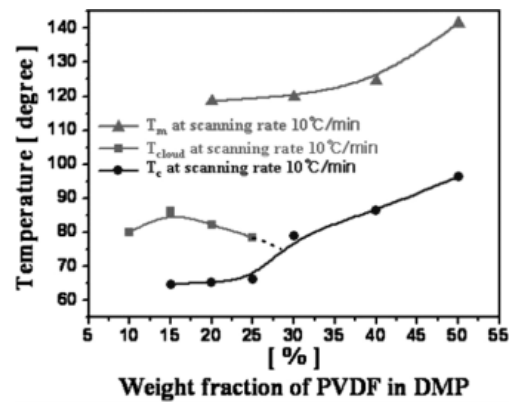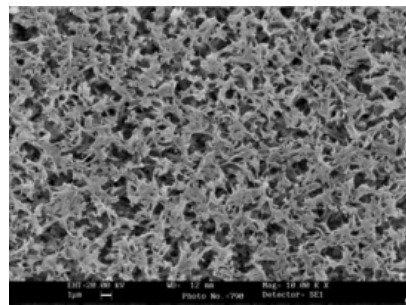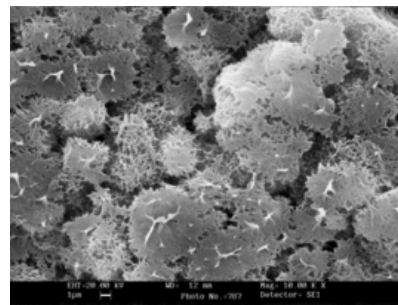**Fig. 2.** Phase diagram of PVDF/DBP system.

Fig. 3. Phase diagram of PVDF/DMP system.

(a) (b)

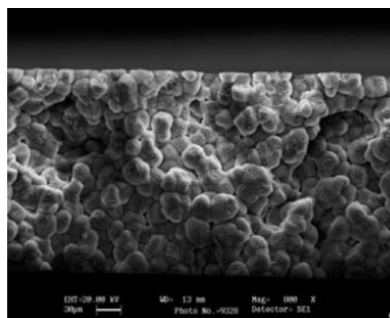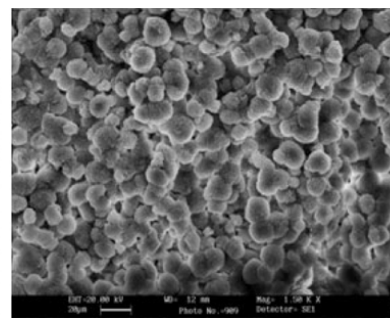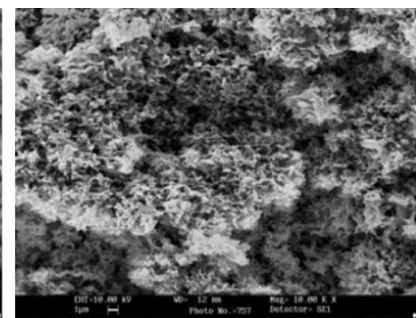**Fig. 4.** Cross sectional images of flat membranes prepared from 20 wt% PVDF in (a) DBP and (b) DMP systems quenched from 185 to 0^oC.

(a) (b) (c)

Fig. 5. Cross sectional images of flat membranes prepared from PVDF/DBP systems quenched from 185 to 25^oC at various PVDF compositions (a) 60%, (b) 25%, (c) 20%.

DMP. PVDF/DBP sample has lacy structure without any discernible spherulites due to the fast cystallization rate. PVDF/DMP sample has spherulitic structure with microporous structure at the surface and between the spherulite due to the slow crystallization rate and simultaneous liquid-liquid phase separation.

3.2. PVDF/DBP Systems

PVDF/DBP samples were prepared at various compositions: 20, 25 and 60 wt% of PVDF. Those samples were melt blended and quenched from 185 to 25^oC as shown in Fig. 5. As expected, high PVDF content sample as 60 wt% spherulictic structure, and 25 wt% sample also has the spherulictic structure. However,
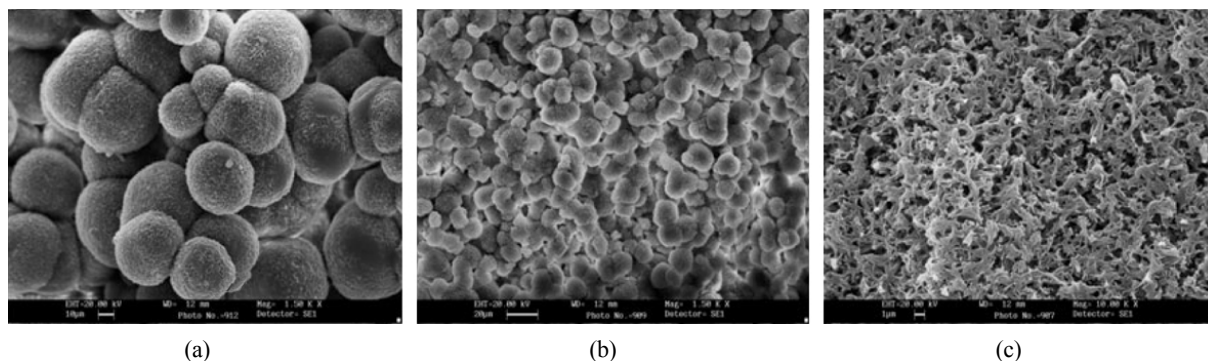
(a)   (b)   (c)

Fig. 6. Cross sectional images of flat membranes prepared from 25% PVDF in DBP systems cooled at different conditions (a) cooled at $10^{\circ}C/min$ to $25^{\circ}C$, (b) quenched from 185 to $25^{\circ}C$, (c) quenched from 185 to $0^{\circ}C$.

(a)   (b)   (c)
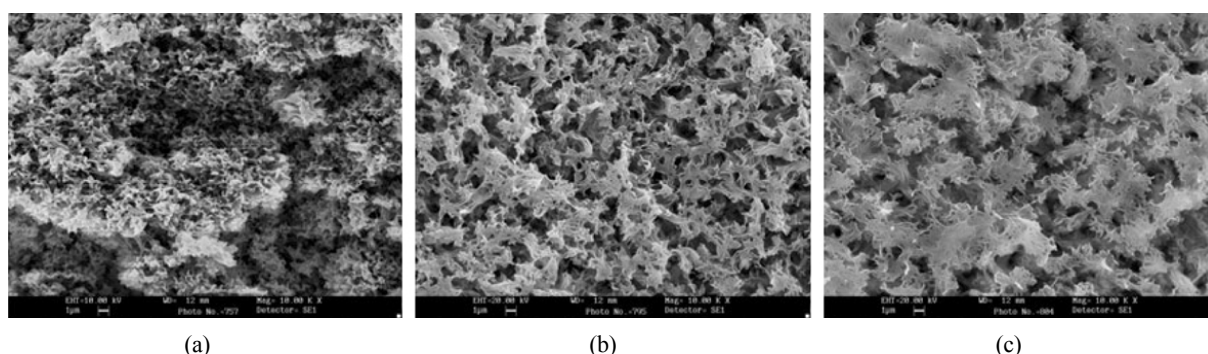
Fig. 7. Cross sectional images of flat membranes prepared from 20% PVDF in DBP systems quenched from $185^{\circ}C$ to different holding temperatures (a) $25^{\circ}C$, (b) $75^{\circ}C$, (c) $95^{\circ}C$.

spherulitic density of 60 wt% sample is much higher than that of 25 wt% sample. On the other hand 20 wt% PVDF sample has lacy structure without any spherulitic structure. There is very remarkable structure difference between 20 and 25 wt% samples.

PVDF/DBP sample with 25 wt% PVDF were cooled at several cooling conditions: (a) cooling at $10^{\circ}C/min$ to $25^{\circ}C$ and (b) quenching from 185 to $25^{\circ}C$ (c) quenching from 185 to $0^{\circ}C$, as shown in Fig. 6. The sample cooled at $10^{\circ}C/min$ has dense spherulitic structure with great size spherulite formation. The sample quenched to $25^{\circ}C$ also have the spherulitic structure, and the spherulite size was much smaller than $10^{\circ}C/min$ cooled sample. $25^{\circ}C$ quenched sample had much greater supercooling and nucleation density than $10^{\circ}C/min$ cooled sample. $0^{\circ}C$ quenched sample has no discernible spherulite structure, because it underwent too fast crystallization to form the spherulite. Instead, it showed

lacy structure with continuous matrix structure.

PVDF/DBP sample with 20 wt% PVDF were quenched from $185^{\circ}C$ to several holding temperatures between 185 and $25^{\circ}C$, and it stayed at each holding temperature for 10 min followed by quenching to $25^{\circ}C$. As shown in Fig. 7, each sample has lacy structure without discernible dense spherulites. As the sample holding temperature increased shape of spherulite was formed with tiny micropores at the surface. At high holding temperature the sample underwent low crystallization rate of PVDF to result in the spherulite formation. However, diluent rejected to the outside of spherulite occupied the surface of the PVDF spherulites to result in the microporous spherulite formation and micro void between spherulites. The sample directly quenched to $25^{\circ}C$ has no trace of spherulites with micropores througout the sample.

(a)   (b)   (c)
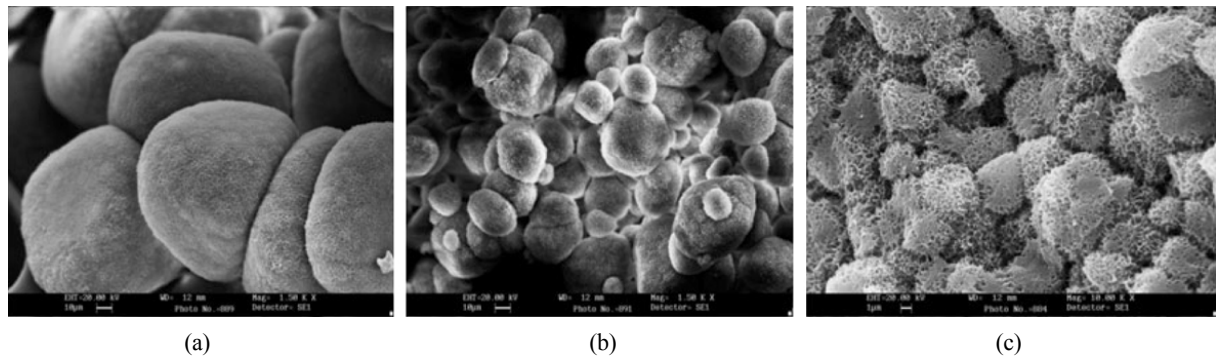
Fig. 8. Cross sectional images of flat membranes prepared from 25% PVDF in DBP systems cooled at different conditions (a) cooled at 10°C/min to 25°C, (b) quenched from 185 to 25°C, (c) quenched from 185 to 0°C.

3.3. PVDF/DMP Systems

PVDF/DMP sample with 25 wt% PVDF were cooled at several cooling conditions: (a) cooling at 10°C/min to 25°C and (b) quenching from 185 to 25°C (c) quenching from 185 to 0°C, as shown in Fig. 8. Cooling condition effects on PVDF/DMP system are quite similar to those on PVDF/DBP system as shown in Fig. 6. Spherulite sizes for PVDF/DMP system are greater than those for PVDF/DBP system. Supercooling for DMP system was smaller than that of DBP system to result in the slow crystallization with lower nucleation density. Moreover, DMB has lower molecular weight and less viscosity than DBP, spherulite growth for DMB system was easier than DBP system. The PVDF/DMP sample quenched to 0°C has the structure of spherulite with surface pores unlike the PVDF/DBP sample, because it underwent simultaneous crystallization and liquid-liquid phase separation.

PVDF/DMP system has cloud point as shown in Fig. 3, sample with 20 wt% PVDF were quenched from 185°C to several holding temperatures, 35, 55 and 75 ^{o}C, and it stayed at each holding temperature for 10 min followed by quenching to 25°C. Holding temperature of 75°C locates below cloud point and above crystallization temperature as shown (a) in Fig. 9, and the sample underwent the liquid-liquid phase separation only at this point. Holding temperature of 55°C locates below the cloud point and just below the crystallization

temperature as shown (b) in Fig. 9, and competitive simultaneous liquid-liquid and solid-liquid phase separations were expected. Holding at 35°C, as shown (c) in Fig. 9, has greater driving force for crystallization, and it underwent too fast crystallization to allow the liquid-liquid phase separation. Therefore, as shown in Fig. 10, liquid-liquid phase separation happened before crystallization for sample (a) in Fig. 10 had lacy structure without spherulite formation. Competitive simultaneous liquid-liquid and solid-liquid phase separations resulted in the lacy structure with porous spherulite as shown in (b) in Fig. 10. Fast crystallization froze the structure before liquid-liquid phase separation happened, and it made structures with many small spherulites as shown in (c) in Fig. 10.
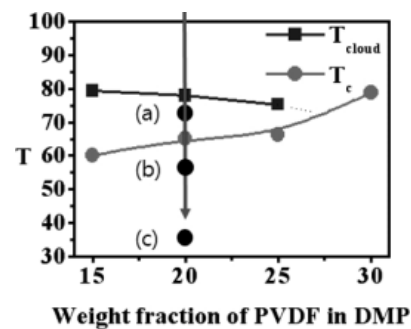

Fig. 9. Experimental scheme to examine the effects of holding temperature for 20% PVDF in DMP systems quenched from 185°C to different holding temperatures (a) 75°C, (b) 55°C, (c) 35°C.

(a)   (b)   (c)
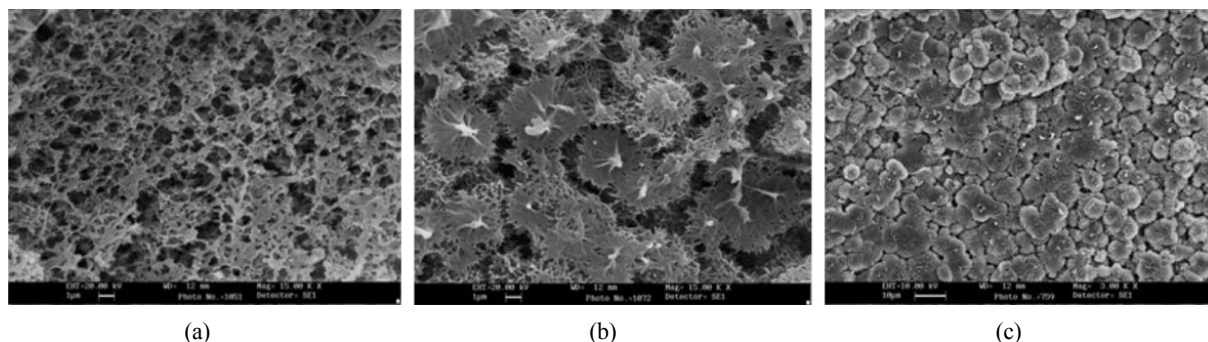
Fig. 10. Cross sectional images of flat membranes prepared from 20% PVDF in DBP systems quenched from 185°C to different holding temperatures (a) 75°C, (b) 55°C, (c) 35°C.

4. Conclusion

DBP and DMP were selected as diluents for PVDF membrane preparation via TIPS because they formed the homogeneous melt solution with PVDF. PVDF/DBP system showed solid-liquid phase separation behavior only, while PVDF/DMP system has the liquid-liquid phase separation characteristic as well as the solid-liquid phase separation characteristic. Increase of PVDF contents and slow cooling conditions resulted in the formation of spherulites. Diluent rejected to the outside of spherulite occupied the surface of the PVDF spherulites to result in the microporous spherulite formation and micro void between spherulites. PVDF/DMP system had lower supercooling than PVDF/DBP system to result in the slow crystallization with lower nucleation density, and the spherulite size was increased. Location of holding temperature determined the phase separation mechanism to interpret the structure.

Acknowledgement

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