

## 상전이법을 이용한 P(VDF-co-HFP) 분리막 구조제어

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### Controlling the Morphology of Polyvinylidene-co-hexafluoropropylene (PVDF-co-HFP) Membranes Via Phase Inversion Method

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**요 약:** 본 연구에서는 상전이법을 이용하여 P(VDF-co-HFP) 분리막의 구조를 조절하였다. Macrovoid 없는 구조를 얻기 위하여 다양한 조건에서 비용매유도상전이(NIPS) 공법으로 분리막을 제작하였으나 고분자의 낮은 결정화 속도로 인해 macrovoid가 생성된다는 것을 관측하였다. 이를 극복하기 위해 증발유도상전이법(EIPS)과 증기유도상전이법(VIPS)을 도입하였으며 NIPS공법과 함께 제작되었을 때 이상적인 구조를 얻을 수 있다는 것을 확인하였다.

**Abstract:** In this work, the morphology of polyvinylidene-co-hexafluoropropylene (PVDF-co-HFP) membranes were systematically investigated using phase inversion technique, to target membrane contactor applications. As the presence of macrovoids degrade the mechanical integrity of the membranes and jeopardize the long-term stability of membrane contactor processes (e.g. wetting), a wide range of dope compositions and casting conditions was studied to eliminate the undesired macrovoids. The type of solvent had significant effect on the membrane morphology, and the observed morphology were correlated to the physical properties of the solvent and solvent-polymer interactions. In addition, to fabricate macrovoid-free structure, the effects of different coagulation temperatures, inclusion of additives, and addition of nonsolvents were investigated. Due to the slow crystallization rate of P(VDF-co-HFP) polymer, it was found that obtaining porous membrane without macrovoids is difficult using only nonsolvent-induced phase separation method (NIPS). However, combined other phase inversion methods such as evaporation-induced phase separation (EIPS) and vapor-induced phase separation (VIPS), the desired membrane morphology can be obtained without any macrovoids.

**Keywords:** Phase inversion, P(VDF-co-HFP), macrovoid, vapor-induced phase separation (VIPS)

#### 1. Introduction

Since the discovery of phase inversion method by Loeb and Sourirajan[1], the field of membrane technology has expanded significantly in the past few decades, now reaching beyond 20 billion dollar annual

market[2]. The application field has mainly been in the water treatment (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis) and hence hydrophilic membranes have been preferred.

Recently, however, many interesting new membrane processes are being developed in the field of mem-

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brane contactors. Notably, membrane distillation (MD) [3], membrane crystallization (MCR)[4], membrane condensers (MC)[5], biogas upgrading[6], and artificial lung. For these emerging membrane processes, hydrophobic membranes are preferred, as the key requirement is to stay dry during operations (*i.e.* the membranes must not get wet).

Hence, instead of hydrophilization treatment, hydrophobization techniques are being actively researched nowadays to elongate the lifetime of the membranes. In addition, hydrophobic materials that were not considered before due to hydrophobicity are now being studied. A notable example is P(VDF-co-HFP) polymer. This polymer has mechanical properties comparable to that of PVDF with competitive chemical and thermal stability. Also, its hexafluoropropylene (HFP) functional group enhances the hydrophobic character of the membranes. It has been used for MD processes before with promising performances[7].

Apart from the material intrinsic properties, the overall morphology of the membranes affect the performance of membrane contactor processes. Mainly, although the presence of macrovoids are speculated to improve the membrane performances (flux), they significantly increase the membrane wettability as the liquid path from the membrane surface to the permeate side is open without much tortuosity.

Although it has been known that instantaneous demixing leads to finger-like macrovoid structures and delayed demixing leads to sponge-like membranes[8,9], there are many cases where this hypothesis does not hold true, particularly when the polymer solidification rate is slow[10]. The formation mechanism of macrovoids is still under debate, as it is a complicated process involving thermodynamic and kinetic factors such as chemical potential gradient, local interface instability, Marangoni effects, capillary convection, and osmotic pressure[11].

Expectedly, the main factor for macrovoid formation vary depending on the polymer-solvent-nonsolvent systems. However, recently reported works clearly show that macrovoid formation is due to the competi-

tion between polymer solidification rate and solvent-nonsolvent exchange rate[12,13]. In simple terms, it is a race between polymer solidification front and the solution-nonsolvent interface front. If the solidification front is faster than the nonsolvent intrusion front, no macrovoids are observed, and vice versa. Therefore, importantly, the solidification (via precipitation or crystallization) tendency of a polymer plays a significantly role for macrovoid formation. Unlike other well-known membrane amorphous polymers, semicrystalline polymers such as PVDF and P(VDF-co-HFP) behave rather differently in terms of macrovoid formation, and it is the main topic of this work.

In this work, the morphology of P(VDF-co-HFP) membranes was investigated as a function of polymer-solvent-nonsolvent dope systems as well as casting conditions. As the solidification rate of P(VDF-co-HFP) polymer is relatively slow, it was difficult to obtain porous morphology using nonsolvent-induced phase separation (NIPS) while simultaneously suppressing the macrovoid formation. However, when evaporation-induced phase separation (EIPS) and vapor-induced phase separation (VIPS) preceded NIPS, it was possible to obtain porous morphology without any macrovoids.

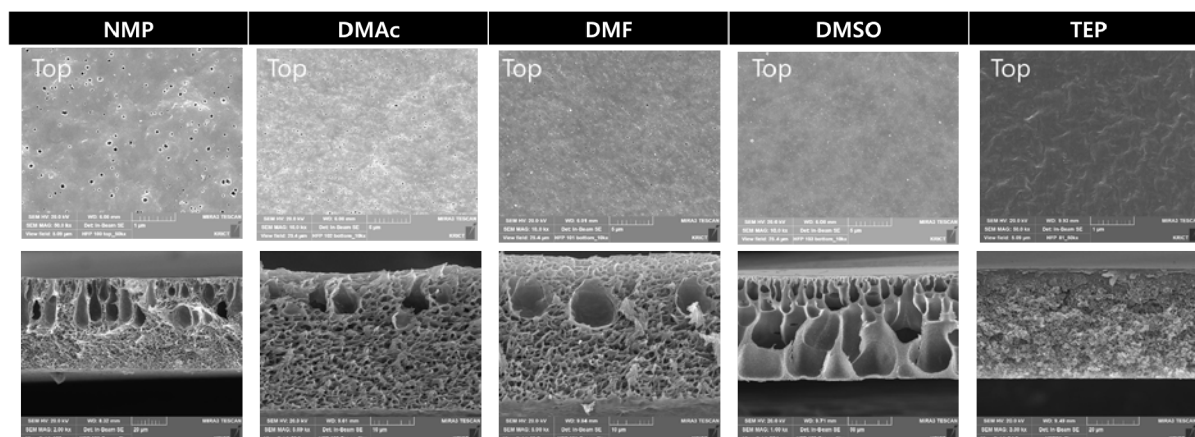
## 2. Experimental

### 2.1. Materials

P(VDF-co-HFP) polymer (5 mol% HFP content, Kynar LBG) was purchased from MNC Co. (South Korea). Triethylphosphate (TEP) and Pluronic-127, polyvinylpyrrolidone (PVP10k), and polyethylene glycol (PEG6k) were purchased from Sigma-Aldrich (South Korea). N-methylpyrrolidone (NMP), dimethylacetamide (DMAc), dimethylformamide (DMF), dimethylsulfoxide (DMSO), isopropanol (IPA), methanol, hexane were purchased from Samchun Chemicals (South Korea).

### 2.2. Membrane Fabrication and Characterization

For membrane fabrication, a homogeneous dope solution was prepared by mixing a known mass of polymer, solvent (s), and additives. The exact concen-



**Fig. 1.** Cross-sectional morphology of membranes prepared with different solvents. The polymer concentration in the dope solution was 18 wt%, cast at 30°C. The type of solvent affects the membrane morphology. Membranes with macrovoids had surface pores, whereas membranes without macrovoids (TEP) exhibited dense surface.

trations are described in the figure captions. Once a homogeneous dope solution as obtained, it was left overnight to remove air bubbles. The solution was then cast onto a glass plate using a casting knife (TQC, Netherlands) set at 200  $\mu\text{m}$  at a speed of 50 mm/s. The cast membrane was then immersed into a water-bath (nonsolvent) at a set temperature (described in the figure captions). The solidified membranes were washed in IPA to remove residual solvents and additives, then dried from hexane to avoid pore collapse. The membranes were characterized for its morphology with SEM (Scanning Electron Microscope, Hitachi, TM-3000, Japan).

### 3. Results and Discussion

The three main components in nonsolvent-induced phase inversion (NIPS) are polymer, solvent, and nonsolvent. For environmental and cost reasons, water is predominantly used as the nonsolvent. Choosing the right solvent for a given polymer is crucial, as it determines the thermodynamic stability of the dope solution, which affects the respective membrane morphology. Recently, the environmental aspect of the solvent itself has been gaining a lot of interest, and many new polar aprotic solvents have been applied for membrane fabrication [14].

Fig. 1 summarizes the surface and cross-sectional morphology of P(VDF-co-HFP) membranes fabricated using different solvents. The membranes were cast and immersed into 30°C water bath. It can be seen that the type of solvent significantly affects the cross-sectional morphology of the membranes. For instance, DMSO results in completely macrovoidic structure, whereas TEP gives the desired bicontinuous structure without any formation of macrovoids. On the other hand, macrovoids are visible for the membranes prepared using NMP, DMAc, and DMF, with honeycomb-like cellular structures. The results are very similar to the data obtained by Bottino et al.[10] for PVDF membranes.

Upon immersion of cast membranes into a nonsolvent, interfacial hydrodynamic instability nucleates macrovoids near the nonsolvent-polymer interface, which subsequently grow downwards (towards the bottom of the membrane). If the solidification of the polymer is faster than the growth rate of the macrovoids, macrovoids cannot grow and stops near the surface. Therefore, from Fig. 1 SEM images, one can deduce that the rate of solidification (or gelation) follows the order of:

$$\text{TEP} \gg \text{DMAc} > \text{DMF} > \text{NMP} \gg \text{DMSO}$$

(Order of solidification rate)

**Table 1.** Hansen Solubility Parameter Analysis of Solvent-Polymer Pairs

Solvent, Polymer	Solvent Viscosity (mPa-s)	Dope Viscosity (mPa-s)	$\delta_D$	$\delta_P$	$\delta_H$	$R_{HSP (P-S)}$
DMF	0.85	3554	17.4	13.7	11.3	3.3
DMAc	0.95	4997	16.8	11.5	10.2	2.4
NMP	1.82	11200	18	12.3	7.2	1.9
DMSO	2.19	16036	18.4	16.4	10.2	5.0
TEP	1.68	10212	16.8	11.5	9.2	1.6
P(VDF-co-HFP) 5%	--	--	17.2	12.5	8.2	--

where DMSO being the slowest to solidify. The observed data suggests that TEP should exhibit the lowest compatibility with P(VDF-co-HFP) polymer. However, the solubility parameter analysis predicts completely opposite trend (Table 1). It can be seen that the compatibility between the polymer and solvent follows the order of:

$$\text{TEP} > \text{NMP} > \text{DMAc} > \text{DMF} > \text{DMSO}$$

(Order of polymer-solvent compatibility)

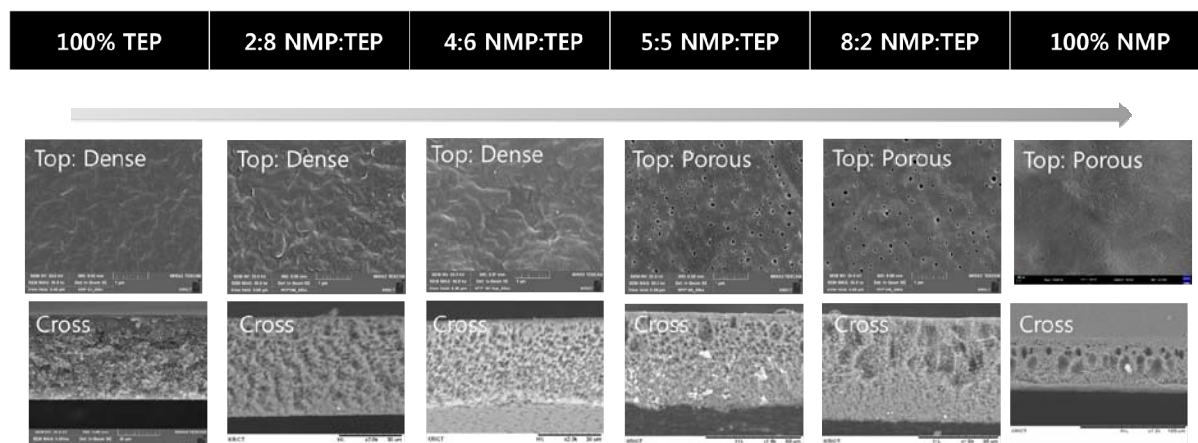
Comparing the two extreme cases, TEP and DMSO, it is clear that TEP should exhibit the best compatibility with P(VDF-co-HFP) polymer, and DMSO should exhibit low compatibility. Such data directly contradicts the observed SEM images, as TEP solidified without any macrovoids. Therefore, it can be deduced that solubility parameter approach cannot adequately describe the P(VDF-co-HFP) system, or at least the difference in thermodynamic stability is not a dominant factor. One can hypothesize that kinetic factors play more important roles in P(VDF-co-HFP) systems.

An important kinetic parameter for solvent-nonsolvent exchange rate is the dope solution viscosity. Generally, viscous dope solution results in delayed demixing which leads to sponge-like morphology without any macrovoids. From the SEM observations shown in Fig. 1, one can expect polymer-DMSO system to exhibit lowest viscosity and polymer-TEP system to exhibit the highest viscosity. However, again, Table 1 dope solution viscosity data clearly contradicts

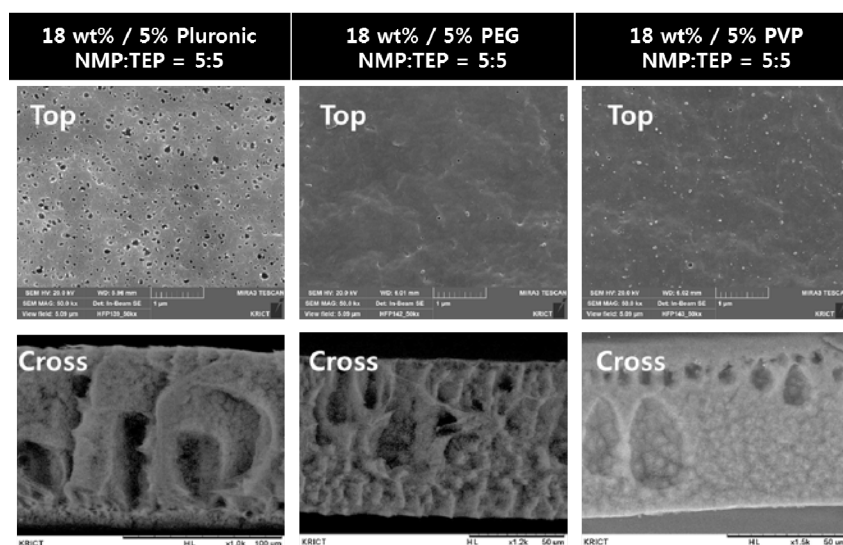
this expectation. DMSO, being the most viscous solvent among the tested solvents, also exhibit the highest dope solution viscosity. Evidently, solution viscosity data also cannot explain the observed membrane morphologies.

Therefore, other factors must be involved in terms of macrovoid formation. One likely explanation is the high rate of nonsolvent intrusion. Interestingly, the surface SEM images of the membranes show that TEP membranes are dense, whereas DMSO membranes are porous. In fact, the membranes that exhibit macrovoids were almost always porous on the surface, whereas the membranes without macrovoids did not show any surface pores. Therefore, the rate of nonsolvent intrusion rate into the cast solution must have been much faster than the rate of polymer solidification, leading to macrovoid growth. The question still remains as to why TEP forms a dense skin layer whereas DMSO does not. As for TEP membranes, the high viscosity of the solution, together with the high affinity of TEP towards water, might have vitrified the membrane surface faster than other membranes, leading to macrovoid-free morphology. Nevertheless, more studies must be carried out to correlate the observed membrane morphologies to physical characteristics of the polymer-solvent-nonsolvent systems.

Although TEP solvent suppressed the macrovoid formation of P(VDF-co-HFP) membranes, the surface was dense, which is not applicable for membrane contactor applications. Hence, a solvent mixture system was investigated using TEP and NMP, and the data are summarized in Fig. 2.



**Fig. 2.** SEM images of the membranes prepared with varying NMP : TEP ratio. The polymer concentration was fixed at 18 wt% and the membranes were cast in 30°C. With increasing NMP fraction, the membrane becomes porous and exhibit macrovoids. Although subtle, the cross-sectional morphology changes from bicontinuous to honeycomb-like cellular structure.

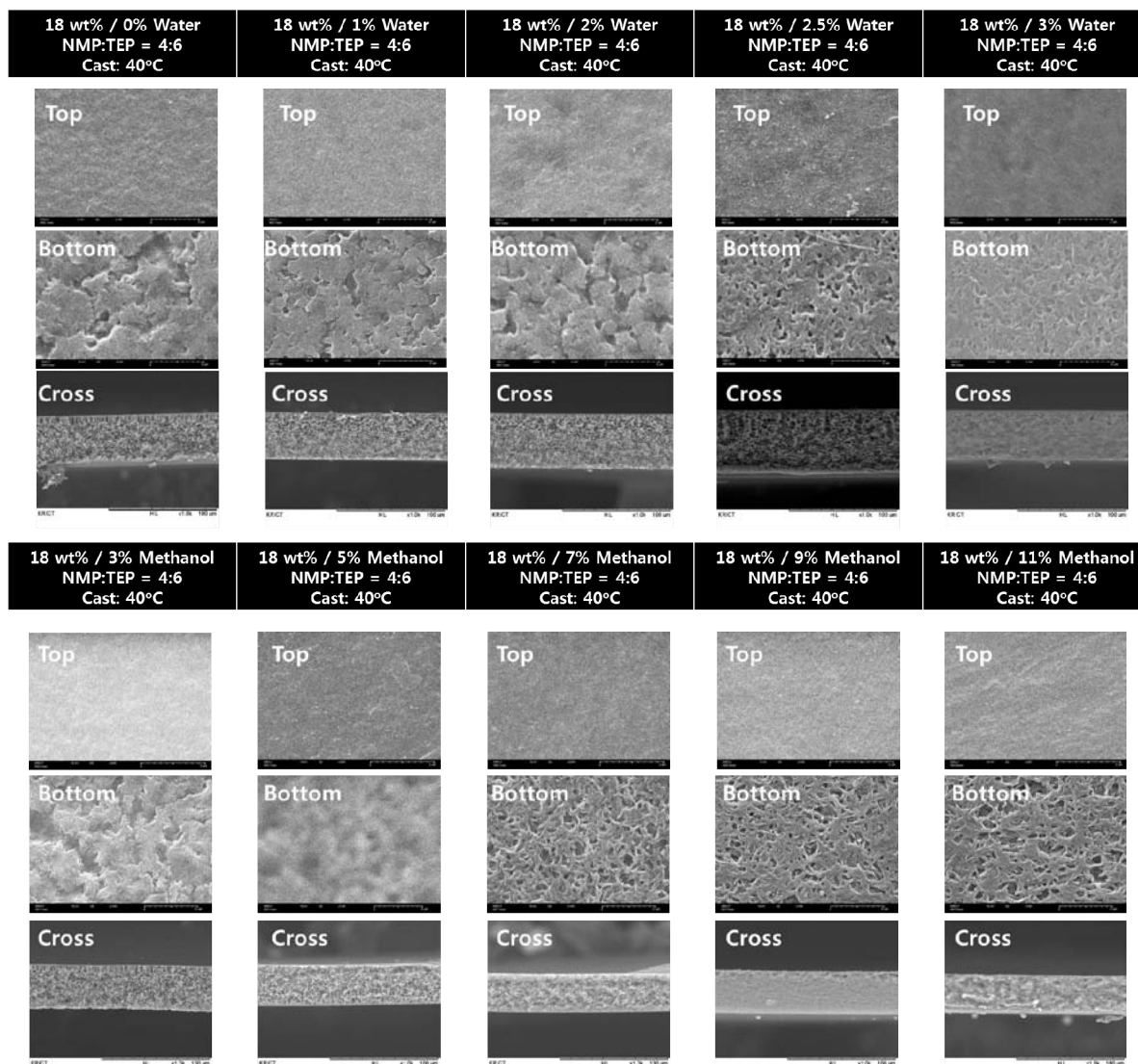


**Fig. 3.** SEM images of membranes prepared with inclusion of additives (5 wt%). The polymer concentration was fixed at 18 wt%, solvent mixture ratio was 5 : 5 (w/w NMP : TEP), and the membranes were cast in 30 oC. Including additives in dope solution induces surface pores but also the undesired macrovoids.

It can be seen in Fig. 2 that with increasing NMP fraction in the dope solution, the membrane surface becomes porous. Interestingly, macrovoids begin to appear when the membrane becomes porous. Such observation supports the hypothesis that macrovoid growth is backed by a fast nonsolvent intrusion through surface pores. It was concluded that using solvent mixture was not sufficient to prepare porous membranes without macrovoids. Therefore, hydrophilic polymeric additives were included in the dope solution

as pore-forming additives, while destabilizing the dope solution (faster solidification). The results are summarized in Fig. 3.

Fig. 3 clearly supports the hypothesis that surface pores induce macrovoids by allowing fast intrusion of nonsolvent (water). It can be seen that the well-known pore-forming additives are effective in creating surface pores, but ineffective in weakening the dope solution thermodynamic stability. An interesting finding from Fig. 4 is that Pluronic F-127 is highly effective in in-

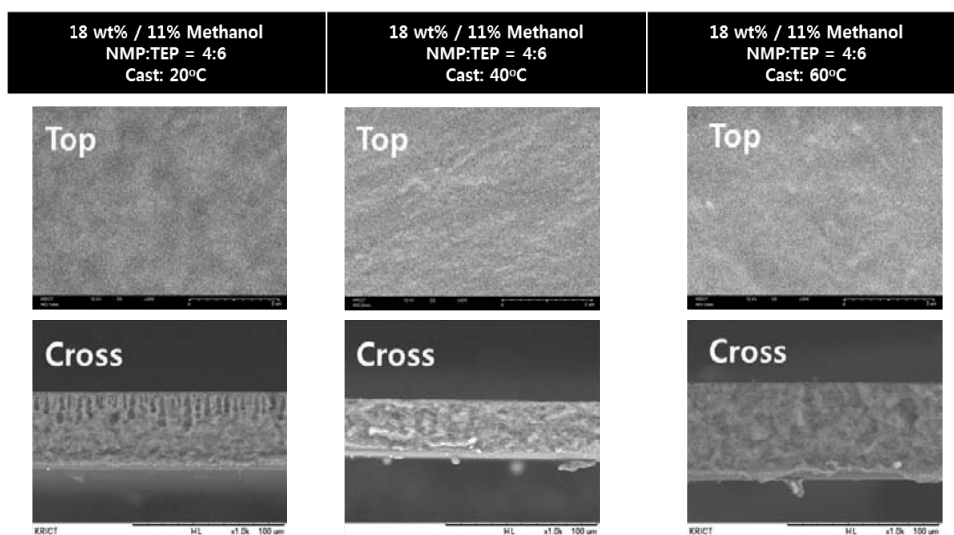


**Fig. 4.** SEM images of membranes prepared with inclusion of nonsolvents. The polymer concentration was fixed at 18 wt%, solvent mixture ratio was 4 : 6 (w/w NMP : TEP) and the membranes were cast in 40°C. With increasing water (0 à 3 wt%) or MeOH (0 à 11 wt%) content in the dope solution, the solution becomes thermodynamically unstable, and surface pores are observed without macrovoids above 2.5 wt% water.

ducing surface pores, particularly for fluoropolymers, as observed in previous works[15]. An ideal additive should destabilize the dope solution to induce fast solidification while simultaneously inducing surface pores. A soluble nucleating agent such as lithium chloride, although not included in this work, did not work either for P(VDF-co-HFP) polymer. Therefore, instead of polymeric additives, a strong nonsolvent (water) and a weak nonsolvent (MeOH) were included in the dope solution to destabilize the solution as much as possible.

The results are summarized in Fig. 4.

Including nonsolvent is an interesting method to affect the thermodynamic state of the dope solution, it was systematically investigated by Ren et al.[12] with a unique concept of approaching ratio ( $\alpha$ ). Fig. 4 suggests that the solution becomes unstable with increasing addition of nonsolvents. When water was employed as nonsolvent in the dope solution, the viscosity of the solution clearly increased, and the surface pores begin to emerge above 2.5 wt% water solution. However,

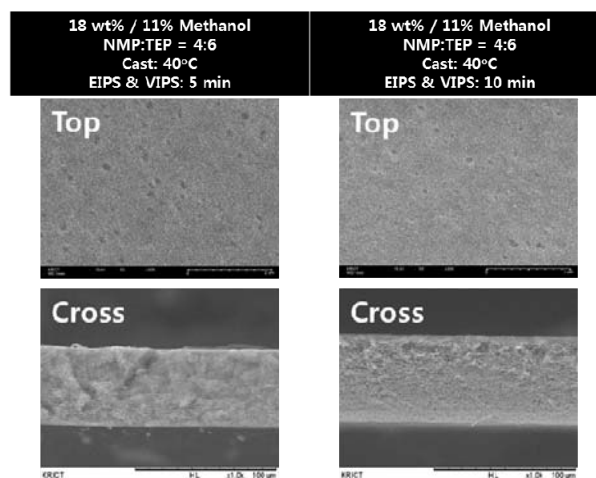


**Fig. 5.** SEM images of membranes prepared at different coagulation temperatures. The polymer concentration was fixed at 18 wt%, solvent mixture ratio was 4 : 6 (w/w NMP : TEPE), nonsolvent concentration was 11 wt% MeOH. Lowering the temperature induced macrovoids without any surface pores.

near the binodal (2.5~3 wt% water), the solution was impractical to handle and the membrane reproducibility was poor.

On the other hand, when MeOH was employed as nonsolvent additive in the dope solution, the solution became unstable above 11 wt% MeOH. SEM images clearly indicate that the solution is becoming unstable, however, unfortunately, it was not possible to induce surface pores.

Changing the coagulation temperature and thickness is also a well-known technique to control the membrane properties. In this work, the set thickness was fixed at 200 µm, as the final measured thickness was around 50 µm which was practically handle-able. Below this thickness the membrane handle-ability was low. Fig. 5 summarizes the effect of coagulation temperature on membrane morphology. As the temperature increases, the thermodynamic stability of the solution increases, while the kinetics of solvent-nonsolvent diffusion rate increases as well. The difference in mass and heat exchange rate must also be considered. Therefore, a mixed effect can be observed and the outcome varies depending on the polymer-solvent-nonsolvent system. A desired outcome is to destabilize the



**Fig. 6.** SEM images of membranes prepared with EIPS & VIPS prior to NIPS. The polymer concentration was fixed at 18 wt%, solvent mixture ratio was 4 : 6 (w/w NMP : TEPE), nonsolvent concentration was 11 wt% MeOH, ambient temperature was 21°C, and relative humidity was 45%. When the cast solution was left to evaporate (EIPS) and to absorb water (VIPS), surface pores were induced without formation of macrovoids.

dope solution as fast as possible to induce polymer solidification. It can be seen that macrovoids are induced at lower temperatures, but surface pores were not observed regardless of the coagulation temperatures.

Fig. 6 shows the desired morphology: porous mem-

branes without any macrovoids. When the cast membranes were left in ambient air prior to immersion into nonsolvent bath, two things occur simultaneously: (1) volatile solvents evaporate, increasing the surface polymer concentration (evaporation induced phase separation, or EIPS), (2) the cast solution absorbs the ambient water vapors and becomes destabilized (vapor-induced phase separation, or VIPS). Both routes destabilize the membranes while inducing surface pores, leading to the desired membrane morphologies. In practice, VIPS and EIPS are not widely employed as it is relatively slow and impractical to scale. However, for fluoropolymers that crystallizes relatively slow, it is an effective way to induce surface pores without generating any macrovoids. One can easily control the rate of VIPS and EIPS, by including volatile solvents (e.g. MeOH) for EIPS, and including hygroscopic additives (PEG, PVP, etc) for VIPS.

#### 4. Conclusion

In this work, the membrane morphology using P(VDF-co-HFP) polymer was systematically investigated, with an aim to induce surface pores without generating any macrovoids. Similar to PVDF, it was found that P(VDF-co-HFP) polymer behaves very differently compared to other well-known amorphous polymers used in membrane technology. The main reason was due to slow solidification rate (crystallization) of the polymer. The type of solvent had significant effect on the overall morphology, and the underlying cause for macrovoid is due to fast intrusion of nonsolvent through surface pores. An attempt to eliminate macrovoids using pore-forming additive, nonsolvent additive, and coagulation temperature control was ineffective. On the other hand, EIPS and VIPS method prior to NIPS were found to be highly effective to fabricate the desired membrane morphology. Therefore, for membrane contactor applications, hydrophobic materials like PVDF and P(VDF-co-HFP) should be fabricated via EIPS&VIPS-NIPS hybrid route.

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