Phase Inversion and Performance Evaluation of a Silica incorporated PVDF Membrane for Water Based Filtration.*

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ABSTRACT

Membrane technology has long been applied in the wastewater industry due to its numerous advantages. However the chemistry behind the formation of a membrane via phase inversion still has to be explored upon. In this study, a novel PVDF-DMF membrane is developed with silica nanoparticles (surface modified with dimethyldichlorosilane) as additives. This paper focuses on the polymerisation reaction that occurs in the membrane by studying the change in the viscosity of the dope solution, the reaction of additive during the phase inversion process and its effect on the structural properties of the membrane. An increase in the viscosity of the dope with addition of water proves polymerization reaction of dimethyldichlorosilane mechanism of silica to form polydimethylsilohexanediol, as also supported by FTIR results. SEM images prove the increase in the number of pores on the membranes with a higher silica loadings and demonstrate its effect in lowering the surface pore size. Filterability tests show a much higher purity water performance, in which, notably the 3% silica loading increased the performance by 4 times more than the pristine membrane. Overall, it can be concluded silica plays a huge role in the phase inverter by enhancing the viscosity of the dope to produce a more porous and highly permeable membrane which is expected to be more resistant to fouling.

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1. Introduction

One in nine people in the world today lacks access to clean water, which makes water scarcity as one of the most prevalent issues of the 21st century [1]. Implementing membrane technology in water and wastewater treatments has been an established solution. Nevertheless, it still requires further developments to improve its effectiveness and efficiency in providing the ultimate solution to tackle this issue [1-3]. The phase inversion process has remained as a complex process that requires deep

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understanding in order to further improve the membrane properties. This is due to the complex polymer-solvent-nonsolvent interactions, polymer chain arrangement and entanglement that occurs simultaneously when in contacts with non solvent. (Beygi, Karimi, Farazi, & Ebrahimi, 2016).

The properties of the membrane often enhanced by incorporating an additive (Han & Nam, 2002; Kim & Lee, 1998; Lee, Seo, Nam, & Han, 2003; Ng, Mohammad, Leo, & Hilal, 2013).Understanding the roles of additives in membrane formation is vital for better understanding of the phase inversion process. This leads to the formation of a structurally strong membrane with high resistance to fouling, which later massively propels the advances in membrane technology.

This study investigates the activity of phase inversion with the presence of inorganic additive to facilitate porous formations by using silica as the additive into PVDF membrane. The effect of a silica loading on membrane formation and its water permeability was also observed. The proposed hypothesis is that the silica will increase the viscosity of the dope solution which would promote the formation of a higher number of pores on the membrane surface. This in turn will improve its performance in water treatment strategies.

2. Materials and Methods

2.1. Materials

The main materials used to synthesise the membrane were poly (polyvinylidene fluoride) (PVDF, Sigma-Aldrich, molecular weight of 534 kDa by GPC), dimethylformamide (DMF, Sigma-Aldrich) and DI water as polymer, solvent and non-solvent respectively. The additive was fumed silica (CAB-O-SIL of TS-610, CABOT EMEA Switzerland) surface modified with dimethyldichlorosilane. All chemicals were used as received without prior treatment or purification.

2.2. Dope Solution Preparation

Fumed silica was added into DMF and stirred at 150 RPM to ensure good dispersion of silica. Later, 10% of the total polymer (PVDF) was added slowly to facilitate priming. Priming is a process to reduce the surface tension of the solution for easier silica loading. The remaining polymer was then added slowly in 10wt% intervals after every 30 minutes in the solvent-silica solution until it was completely dissolved. The solution was further sonicated for 1-2 h to remove trapped air bubbles and ensure optimum mixing before it was used for casting.

2.3. Membrane Fabrication

The dope solution was cast using a doctor blade at a net casting thickness of 220 µm at room temperature & humidity atop a non-woven support (Noratexx 2471, Freudenberg-Filter, Germany). The cast film was then immediately immersed in a water bath where precipitation takes place due to the solvent and non-solvent exchange. Five PVDF membranes with different fumed silica loading were prepared. Table 1 shows the amount of silica loadings that were applied.

Table 1: Amount of Silica Loading for PVDF Membrane

Sample	Silica loading (wt%)	PVDF (wt%)
M-0	0	15
M-1	1	14
M-1.5	1.5	13.5

| M-2 | 2 | 13 |
| M-3 | 3 | 12 |

2.4. Membrane Characterisation

Scanning Electron Microscopy (SEM) was used to study the topography and microstructure of the membranes. The chemical bonds in the membrane matrix were characterized using Fourier-transform infrared spectroscopy (FTIR, Nicolet, Thermo Fisher Scientific). The viscosity of the dope solutions was measured using a Brookfield CAP 2000 Viscometer using Spindle 6 and 9 at 900 RPM for a hold time period of 20 seconds.

2.5. Filtration Tests

The filterability performance of different parameters was assessed in constant-pressure submerged filtration system as shown in Figure 1. In order to keep the trans-membrane pressure (ΔP) constant at -0.1 bar, an air pump was used to create a vacuum and the pressure was controlled by regulating the valve. The pumping system was equipped with a manometer, connected with the permeate collection system. The aeration rate was fixed at a rate of 1.80 l min-1, a value corresponds to the specific aeration demand with respect to the membrane area of 0.23 m3 m-2 h-1 in a simulated full-scale panel. The value falls within the lower range of most commercial modules as reported in our earlier study (Eliseus, Bilad, Nordin, Putra, & Wirzal). Chemical cleaning was performed after each test by soaking the membrane into a 1% sodium hypochlorite (Cloroc®) solution in DI water at 60 °C for at least 2 h to ensure the permanence recoveries were >95% of the pristine value.
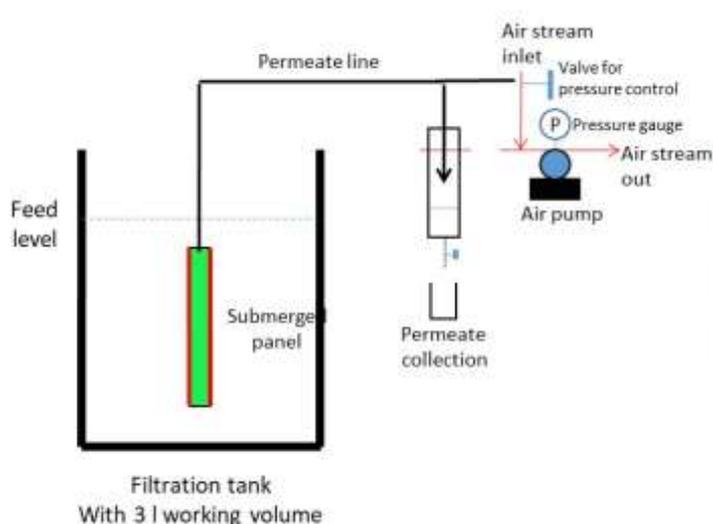

Figure 1 Illustration of experimental set-up for filterability

The permeance (L) of the membrane was calculated as:

$$L = \frac{V}{A\,t\,ThMP}\left(\frac{L}{m^2 bar}\right)(1)$$

Where V is permeate volume (L), A is the effective filtration area (m2), t is time (h) and ΔP is trans-membrane pressure (bar). The tests were run for an hour at a period when a steady state permeance were observed. Steady state flux, a value that only had a slight change as a function of time was observed after 1 h of filtration.

3. Results and Discussion

3.1 Effect of Water and Silica on Phase Inversion

One of the basic parameters that greatly affects the performance of the membrane is the viscosity of the dope solution. It affects the diffusional rate of solvent and non-solvent during the phase inversion process. Figure 2 shows the effect of addition of water on the viscosity of the PVDF-DMF solution and the PVDF-DMF-Silica solution. The role of water in inducing polymerization is studied though the change in viscosity of both solutions. The influence of silica polymerization reaction with water during phase inversion is evaluated by observing the changes into the viscosity of the solution.(Han & Nam, 2002; Lee et al., 2003) Logically, the polydimethylsilohexanediol which is formed by the addition of water will lead to an increase in solution viscosity.

The role of water in the polymerization of a pure PVDF solution is first studied upon. The viscosity of the solution increases with the addition of water because of the entanglement of the PVDF polymer with water. Even without the presence of an additive, PVDF alone can function to initiate polymerization. This reaction becomes the primary cause for the phase inversion that occurs in this membrane (Han & Nam, 2002; Kim & Lee, 1998).

The role of silica in the polymer solution is evaluated through the graph of PVDF-Silica solution. 3wt% dope solution is used in this study because it will have a maximum reaction with water compared to the dope solutions with smaller silica loading. The graph shows that the viscosity of the polymer solution increase dramatically from 251.3 cP to 519.75 cP (Figure 2). The addition of silica into the dope radically increases the viscosity which later will have a great impact on the pore formation and the performance of the membrane. There is an increasing trend in the viscosity however we note a rapid increase occurring between 1-2 wt% of water added. This could be due to the rapid polymerization reaction that occurs. The viscosity reaches a plateau at 3wt% of water added. This is because all the silica in the dope has already reacted. A further increase in water addition will only cause the solution to become too dilute and it will not be able to undergo phase inversion to form a solid membrane. We hypothesise that the increase in viscosity of the dope solution is due to the presence of PDMS, which causes massive entanglement with the PVDF polymer chains. This reaction
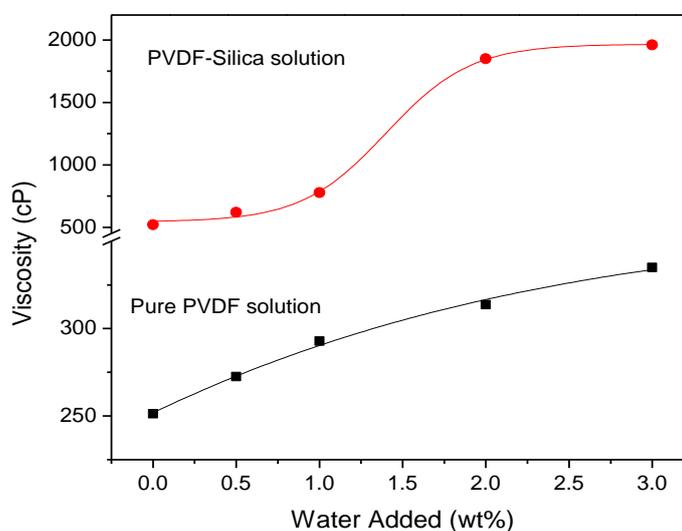
this increases the overall viscosity of the solution.

Figure 2 The effect of water on phase inversion

3.2 Proving the Formation Mechanism of PDMS during Phase Inversion

According to the postulated reaction mechanism (Figure 3), the DCMS (silica) reacts with water to form dimethylsilanediol and the by-product of this reaction of HCl. This reaction was proven by analyzing the pH of a 3wt% Silica- DMF dispersion with different inputs of water (Figure 4). DMF acts as a solvent and does not form any reaction with silica or with water. A decreasing trend was observed in the pH, which means the solution turns more acidic, most likely due to the presence of HCl (formed from the reaction) in the solution. Figure 4 also shows a reciprocate reaction in which the viscosity increases and pH decreases, which proves the theory of formation of

Dicholomethylsilane
(DCMS)

Dimethylsilanediol

Dimethylsilanediol

Polydimethylsilohexanediol
(PDMS)
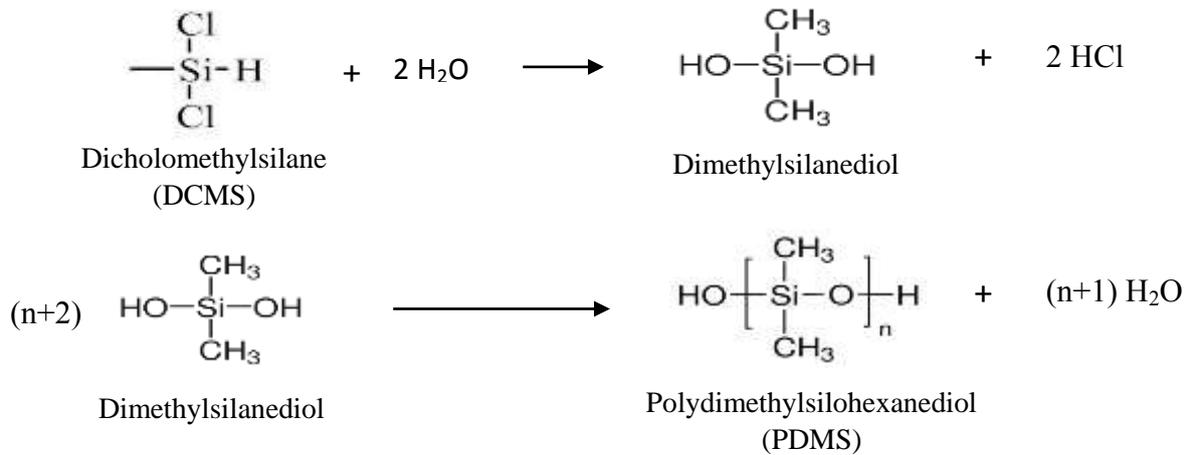
Polydimethylsilohexanediol (PDMS) (as also depicted in Figure 3).

Figure 3 Postulated reaction mechanism for formation of Polydimethylsilohexanediol
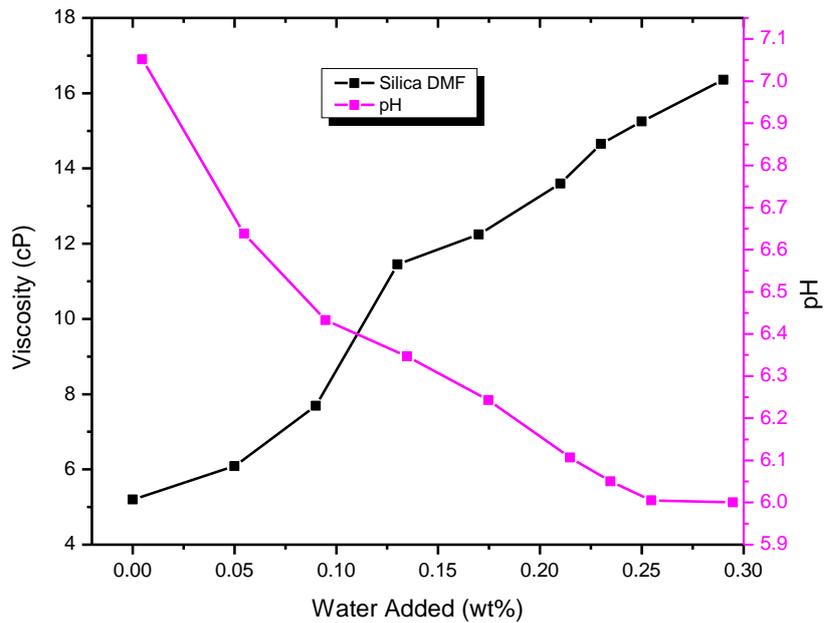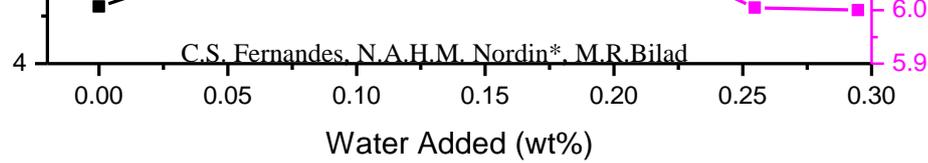
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Figure 4 Effect of water on pH and viscosity of dope

To further justify our hypothesis, the prepared membrane with different silica content undergoes FTIR analysis. Figure 5 shows the FTIR spectra for membranes with different silica additives. The small peak at 1018cm-1 for all the membranes except M-0 proves the presence of a Si-0-Si bond in the membrane. A very small peak at 950 cm-1 shows the asymmetrical stretching of unhydrolysed groups of Si-O-C2H5.(Kunst et al., 2014). The presence of dimethyl Si-O2 can be proven by the band in 2853 cm-1 and 2923 cm-1 showing vibrations of CH3 groups. At 1470 cm-1 bending of Si-CH3 is observed. (Lin, Chen, Ji, & Zhang, 2012). The peaks between 700 and 1100 cm-1 shows the vibration of Si-O-Si. Si-Cl is bending occurs at 850 cm-1 and Si-C stretching occurs at 1405 cm-1. The symmetric and asymmetric vibrations of C-H forms the peaks from 2808 cm-1 to 3148 cm-1. All these bonding energies not only proves the presence of silica but also highly supports the presence of PDMS (Beygi et al., 2016; Pakizeh, Moghadam, Omidkhah, & Namvar-Mahboub, 2013).
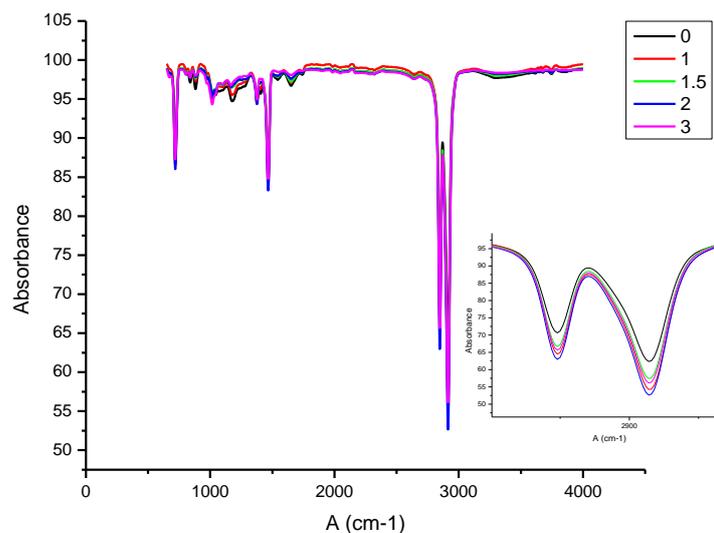
Figure 5 FTIR analysis of membranes

3.3 Effect of silica on pore formation and its effect on membrane permeance

The SEM images in Figure 6 show that a combination of fumed silica loading and decreasing PVDF concentration have mixed results. The surface pore size of M-0 is larger than M-1 and M-1.5, but pore size of M-2 and M-3 are larger than M-0. These findings can be explained in-term of competing effect of viscosity on the dope solution during the phase inversion as reported earlier (Beygi et al., 2016; Kim & Lee, 1998). The decrease in pore size of M-1 and M 1.5 can be ascribed by the dominant effect of viscosity as results of fumed silica loading (in enhancing dope solution viscosity) despite lowering the polymer concentration. It is worth noting that, lower polymer concentration (without loading silica) would increase of pore size because higher polymer concentration leads to an increased polymer volume fraction at the film interface (Eliseus et al.). As fumed silica loading further increased coupling with a decrease in PVDF concentration, the pore size enlarges prompted by a decrease in the polymer PVDF fraction at the film interface. This effect overshadowed the viscosity effect due to higher fumed silica loading
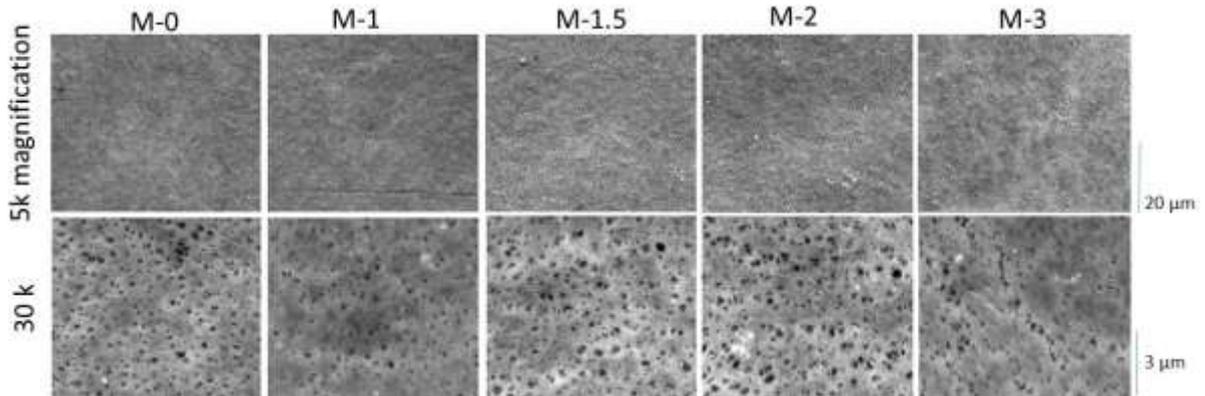
Figure 6 SEM Images of Membranes

Figure 7 shows that the membrane with higher silica content shows the highest permeance. Overall, the permeance of the membranes, increased with the increasing silica contents. In addition, the increase in permeance from M-2 to M-3 is due to the increase in pore size, thus reduced the mass transport resistance across the membrane (Zinadini, Zinatizadeh, Rahimi, Vatanpour, & Zangeneh, 2014).
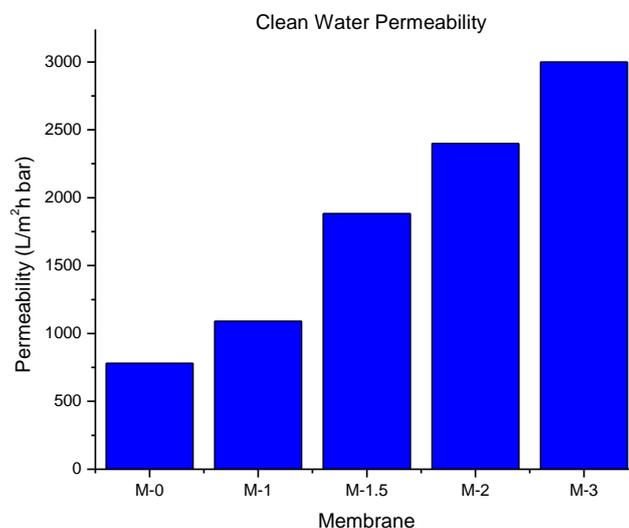

Figure 7 Clean Water Permeance of Membranes

As the PVDF replacement with fumed silica progresses, the clean water permeance increases as shown in Figure 7. It begs the question of how such smaller pores in M-1 and M-1.5 outperform the larger pores (M-0) in term of clean water permeance. Here, we propose an explanation that fumed silica improve the number of pores despite has an important role in decreasing the pore size. This proposition can be illustrated using M-1 and M-1.5. M-1 and M-1.5 have almost similar pore size, but

the latter has significantly higher CWP (780 vs 3000 m-2 h-1 bar-1) because it has a significantly larger number of pores.

A significant advantage of M-2 and M-3 is thus can be attributed to both the enlargement of pore and increase in pore population. The fumed silica here can thus be considered as a pore forming agent during PVDF membrane formation. The same explanation was proposed by another report that having the similar finding with us (conflicting trend between permeance and pore size)(Baghbanzadeh, Rana, Lan, & Matsuura, 2015; Efome, Baghbanzadeh, Rana, Matsuura, & Q. Lan, 2015). Unfortunately, no demonstrative proof can be provided (i.e., representative SEM images) in our result to support this proposition, mostly because of large deviation in surface morphology of membrane sheet and small coverage of SEM imaging at high magnifications. A trade-off between pore size and surface pore population can indeed be combined in term of surface porosity as discussed elsewhere(AlMarzooqi, Bilad, Mansoor, & Arafat, 2016), with a help of image processing software if high-quality SEM images are available.

This finding unravels the important role of fumed silica as an attractive addition to improve structural membrane properties. This finding is quite significant since a membrane with high surface pore and pore population would offer a lower local flux and thus specific hydraulic load of pore during filtration and will help to prolong the filtration period before it gets fouled. However, it's worth to mention that its effect on surface chemistry is less so because of its hydrophobic properties, like the PVDF. Additional treatment to render surface chemistry is thus required to further enhance membrane fouling resistant of the membranes. Further exchange of PVDF polymer with fumed silica by lowering PVDF concentration and increasing of fumed silica loading is also limited since high loading of silica largely enhance dope solution viscosity turning the condition close to the gel point.

4. Conclusion

The phase inversion of PVDF-DMF membrane with silica nanoparticles as an additive to improve the pore structure was studied upon in this paper. An increase in the viscosity of the dope with the addition of water proves the reaction mechanism of silica to form PDMS. The FTIR results closely supports this theory too. SEM images prove the increase in the number of pores on the membranes with a higher silica loadings. Filterability test also shows a much higher purity water permeance whereby 3% silica content increased the permeance by 4 times more than the pristine membrane. Overall, it can be concluded silica can play a huge role in the phase inverter by enhancing the viscosity of the dope to produce a more abundant pores and highly permeable membrane which is more resistant to fouling.

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