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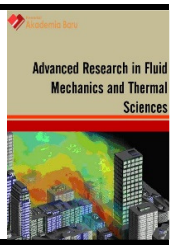

Phase Inversion and Pore Formation of PVDF Membrane with Silica as Additive

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ABSTRACT

Membrane technology is seen as an effective alternative in water treatment strategies. Additive are often used to improve the pore formation on the surface of a membrane. However, little study has been done to prove the effect of an additive on the phase inversion of a membrane. This paper focusses on the effect of silica nanoparticles (additive) on the phase inversion of a PVDF membrane. SEM images shows the increase in pore distribution and filterability tests indicate an increasing permeability with an increasing silica content. A study on the viscosity of the dope solution illustrates the theory occurring behind the phase inversion process. Overall, silica plays a huge role in altering the phase inversion process that occurs in a membrane. This in turn produces a more porous membrane which is expected to be more resistant to fouling.

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 ultimate solution to tackle this issue [1-3].

The phase inversion process is remains as complex process that requires deep 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 nonsolvent [4].

The properties of the membrane often enhanced by incorporating an additive [5-8]. Additives usually promote pore formation on the membrane surface. 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 [5].

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Pores are formed on the surface of the membrane via a two-step mechanism. Upon contact with the nonsolvent, the solvent in the casting solution will diffuse out into the coagulation bath. Meanwhile the nonsolvent diffuses into the adjacent space created by the solvent that diffused out. This process will continue till all the nonsolvent has taken the place of the solvent [9].

This study investigates the activity of phase inversion with the presence of inorganic additive 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 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 synthesis the membrane was 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

A solution of PVDF polymer and solvent together with addition of silica nanoparticles was first prepared. Silica was first added to 41 g of solvent and it was stirred well until a clear suspension was formed. The solution was sonicated for around 1 hour to remove bubbles. A little polymer about 10wt % of the total polymer weigh is then added slowly into the solution and priming occurred. Priming is a process to reduce the surface tension of the solution for easier silica loading. The remaining 7wt% of the polymer solution was then added into the solvent-silica suspension until completely dissolved. The solution was further sonicated for around 1 hour to ensure optimum mixing before used for casting. 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%)
PVDF	0	15
PVDF-1.0	1	14
PVDF-1.5	1.5	13.5
PVDF-2.0	2	13
PVDF-3.0	3	12

2.3 Fabrication of Polyvinylidene Fluoride (PVDF) Membrane

All membranes were prepared via immersion precipitation method. The prepared polymer solution was casted using a doctor blade with net casting thickness of 220 µm at room temperature & humidity atop a non-woven support (Noratexx 2471). The cast film then immediately immersed in a water bath where precipitation takes place.

2.4 Membrane Characterizations

Field Emission Scanning Electron Microscopy (FESEM) are devices used to study the topography and microscopic observation of the membrane. 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 Filterability Test

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 manometer, connected with permeate collection system. The aeration rate was fixed at a rate of 1.80 l min-1, a value corresponds to specific aeration demand with respect to 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 [10]. 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 permeance recoveries were >95% of the pristine value.

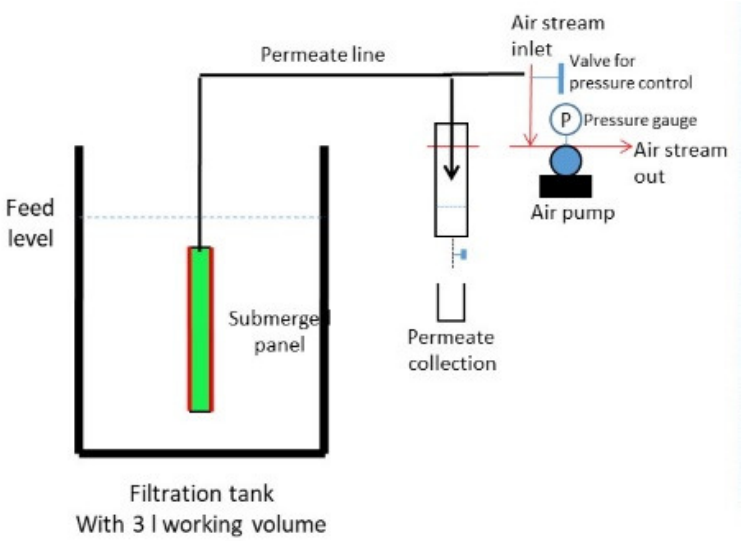

Fig. 1. Illustration of experimental set-up for filterability

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

$$L = V/(A\ t\ TMP)\ \ (L/(m2h\ bar)) \quad (1)$$

Where V is permeate volume (L), an effective filtration area (m^2), t time (h) and TMP trans-membrane pressure (bar). The volume of filtered water was collected every 10 minutes continuously for an hour. Steady state flux was observed after 1 h of filtration, as such the presented data are the one obtained after 1 h of test.

3. Results and Discussion

3.1 Effect of Silica on Membrane Morphology

The SEM images as Figure 2 show the effect of increasing the silica loading to the surface pore structure of the membranes. As the amount of silica increases, the number of pores on the surface also increases. As shown in the figure, an increasing silica content will stimulate pore formation and thus increase the number of pores formed on the membrane surface. The addition of silica improved the viscosity of the dope solution. A more viscous dope will produce a membrane with a higher number of pores. However, M-3 noticeably has fewer pores compared to M-2. This could be due to the competing effects between the increase in dope viscosity and the decrease in polymer concentration. Increasing the viscosity will promote pore formation however lowering polymer concentration restricts pore formation. It is believed that the decrease in polymer concentration overshadowed the viscosity effect [11-13].

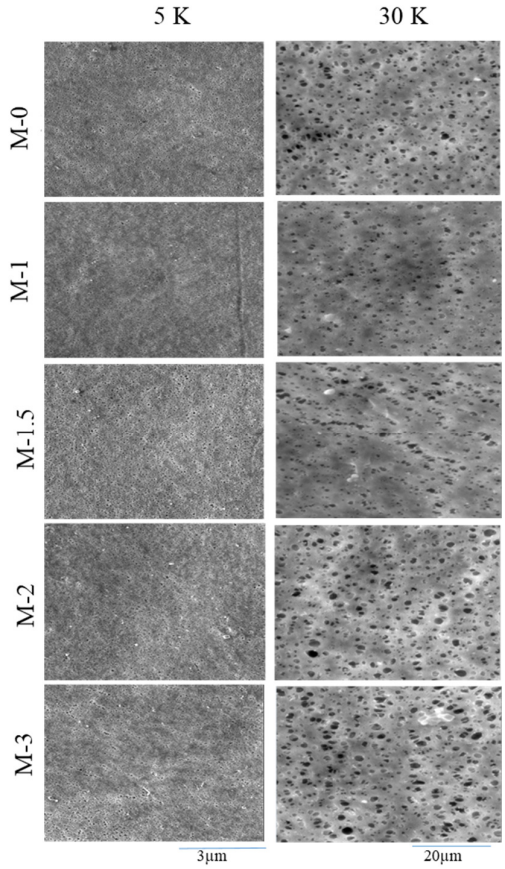

Fig. 2. SEM images of membrane surface

Figure 3 shows the clean water permeability of the membranes. As the amount of silica added to the dope solution increases, the permeability of the membrane increases as well. A higher silica content shows the highest permeance (Figure 3).

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 [14,15].

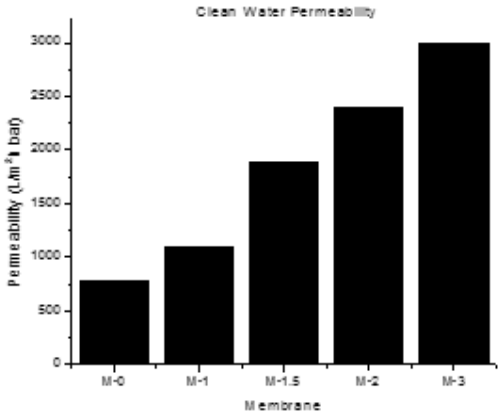

Fig. 3. Clean Water Permeability of Membranes

3.2 Effect of Silica on Phase Inversion of Membranes

One of the basic parameters that greatly affects the performance of the membrane is the viscosity of the dope solution. Figure 4 shows the effect of addition of water on the viscosity of the PVDF-DMF solution and the PVDF-DMF-Silica solution [6,8].

The effect of water addition on 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, a PVDF-DMF dope solution can form a membrane. However, a less porous membrane will be formed compared to the one with the incorporation of additives [5,6].

The effect of silica addition into the dope 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 in Figure 4 shows that the viscosity of the polymer solution increases dramatically from 251.3 cP to 519.75 cP. 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. Further research is needed to justify this occurrence. Consecutively, the viscosity reaches a plateau at 3wt% of water addition. 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.

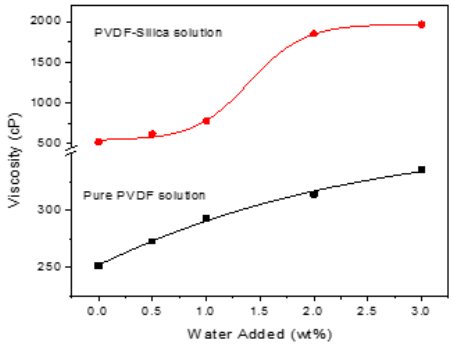

Fig. 4. The effect of water on the viscosity of the respective solutions

4. Conclusions

The phase inversion of PVDF-DMF membrane with silica nanoparticles as an additive to improve pore structure was studied upon in this paper. An increase in the viscosity of the dope with addition of water proves the reaction mechanism occurring during phase inversion. SEM images prove the increase in the number of pores on the membranes with higher silica loadings. Filterability test also shows a much higher pure 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 inversion 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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