RESEARCH ARTICLE

Morphology and performance of polyvinyl chloride membrane modified with Pluronic F127 [version 1; referees: 1 approved, 1 approved with reservations]

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Abstract

**Background:** Attempts to modify the morphology of membrane for application in industrial separation are being undertaken by many researchers. The present study discusses the morphological modification of polyvinyl chloride (PVC) membrane by combining the hydrophilic surfactant Pluronic F127 (PF127) in a polymer solution to improve the performance of the membrane.

**Method:** The membrane is formed using the non-solvent induced-phase separation (NIPS) method. PF127 is added to the membrane solution as a membrane modifying agent. The effects of the surfactant concentration in the dope solution on the permeability of pure water, solute rejection, hydrophilic characteristics, and membrane morphology are investigated.

**Results:** Higher concentrations of PF127 had a significant effect on the permeability of pure water. The highest membrane permeation was 45.65 l/m² hr.atm with the addition of 7% PF127 additive.

**Conclusion:** PF127 is successfully proposed as a membrane pore-forming agent in this work; the blending of this additive in appropriate amounts in the polymer solution is adequate to improve the performance of the PVC membrane.

**Keywords**
polyvinyl chloride (PVC), Pluronic F127, pore forming agent

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Comments (0)
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Author roles: Arahman N: Conceptualization, Formal Analysis, Investigation, Methodology, Project Administration, Writing – Original Draft Preparation, Writing – Review & Editing; Fahrina A: Investigation, Methodology; Wahab MY: Data Curation, Investigation, Methodology; Fathanah U: Resources

Competing interests: No competing interests were disclosed.


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Introduction

Nowadays, separation of contaminant elements from drinking water using membrane technology is developing rapidly. Membrane separation technology has been adopted in many industries, owing to its numerous advantages compared with other common methods. One of the most widely applicable membrane separation technologies in industry is the use of a group of ultrafiltration (UF) membranes, particularly for the process of water purification. In view of the requirements for application in the water treatment industry, the modification of UF membrane to generate high flux, improve the resistance to fouling and chemical substances, and provide good mechanical properties is being continuously improved.

Polyvinyl chloride (PVC), with the molecular formula shown in Figure 1, is a relatively cheap polymer with suitable chemical characteristics for use as a membrane material. Hydrophobic PVC polymers cause fouling of the membrane pores due to the adherence of organic molecules to the surface of the membrane. Numerous methods have been developed to improve fouling resistance. The most common method is improving the hydrophilicity of the membrane material to minimize the attachment of foulant molecules.

The hydrophilic polymers that are frequently used as an additive are polyvinylpyrrolidone, polyethylene glycol, Brij, Tetronic, and Pluronic. Of these, Pluronic is used as a surface modifying agent for many hydrophobic polymers. Raslan and Mohammad added Pluronic F127 to a polysulfone membrane. The resulting membrane is resistant to fouling and possesses good pore distribution. Pluronic has also been used to improve the anti-fouling of cellulose acetate (CA) membranes. The combination of CA polymer and Pluronic surfactant results in a membrane that is more resistant to fouling and has a more stable filtration profile.

In this study, pluronic was developed to improve the performance of PVC membranes. PF127 is a copolymer with two segments—hydrophilic and hydrophobic (Figure 2). The polyethylene oxide (PEO) segment of PF127 improves the hydrophilic characteristics of the membrane’s surface, while polypropylene oxide, which is hydrophobic, attaches closely to the matrix of the membrane. The hydrophilic-hydrophobe balance value of PF127 ranges from 18 to 23. In this study, PF127 is used as an additive to improve the performance of a PVC membrane.

Membrane preparation

The wet inversion technique was adopted to prepare the membrane using water as a non-solvent coagulation media. PVC with a concentration of 15 wt% was dissolved in DMAc until it was homogeneous. The solution was stirred with a magnetic stirrer at 200 rpm. The homogeneous membrane solution was left for 24 hours at room temperature to completely discharge the air bubbles. The solution was then framed on a glass plate using an automatically adjustable applicator (YBA-3, Yoshimitsu, Japan) at a thickness of 0.450 µm. The glass plate containing membrane was dipped in a coagulation bath of distilled water. The de-mixing process between the DMAc solvent and non-solvent distilled water solidified the membrane and separated it from the glass plate. To improve the performance of the membrane, PF127 was added at concentrations of 1, 3, 5 and 7 wt%.

Membrane morphology

Membrane morphology was observed using scanning electron microscopy (SEM) (Hitachi Co, S-800) with an accelerating voltage of 15 kV. To obtain a clean and dry sample, about 1 cm² of the membrane sample was freeze-dried (Eyela FD-1000, Japan) for 24 hours. To ensure that the structure of the membrane was not damaged, the membrane sample was ruptured in liquid nitrogen. Next, the membrane sample was mounted on the metal module, followed by the coating process with Pt/Pd sputtering. The coated sample was inserted into the SEM apparatus, and the photo was captured at 5.0 kV. Three images was collected for each. Three images each were collected for PVC membranes containing 0, 3, 5 and 7% P127.

Permeation experiment

The permeability of water and solute rejection were tested with the module of dead-end filtration (Advantec, UHP-43K, Japan). The transmembrane pressure was regulated at a pressure of...
0.5 atm. The effective membrane surface area that passed by water was 0.023 m$^2$. The testing of water permeability was conducted four times, and the average values was taken to determine the final permeability. The permeability coefficient of pure water was counted using Equation 1.

$$L_p = \frac{V}{A \times t \times \Delta p}$$  \hspace{1cm} (1)

Where $L_p$ = permeability coefficient (L/m$^2$.jam.atm); $V$ = permeate volume (L); $A$ = membrane surface area (m$^2$); and $\Delta p$ = pressure change (atm).

A dextran solution of 100 p.p.m. was prepared to analyze the rejection efficiency. Equation 2 was used to calculate the rejection value of the fabricated membrane.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100$$  \hspace{1cm} (2)

Where $R$ = rejection coefficient; $C_p$ = permeate concentration; and $C_f$ = concentration of feed.

**Membrane hydrophilicity**

The hydrophilicity of the surface of the membrane was measured using a water contact angle meter (Kyowa Kaiwenkagaku, Saitama, Japan, CA-A). The contact angle is the angle formed between the surface of the test material and the pure water dropped onto the surface of the membrane$^{12}$. Each sample was measured 10 times, and the average value of the measurement was the value of the water contact angle of the membrane sample.

**Membrane shrinkage**

To study the effect of the blending of pluronic additives on the toughness of the PVC/ PF127 membrane, a membrane shrinkage test was performed. Three pieces of membrane at each PF127 concentration were slashed in wet conditions with a length and width of 5 and 1 cm, respectively. The membrane was dried in the oven for 24 hours at 80°C. The shrinkage of the membrane was calculated using Equation (3).

$$\text{Membrane shrink} (%) = \frac{L_0 - L_1}{L_0} \times 100$$  \hspace{1cm} (3)

Where $L_0$ = length of wet membrane (cm) and $L_1$ = length of dried membrane (cm).

**Results and discussion**

**Membrane morphology**

The results of the SEM analysis of the cross-sections of all the membranes are shown in Figure 3. The transverse part of the original PVC membrane has an asymmetric structure consisting of a thick, dense structure in the top layer and a finger-like structure in the center path of the cross-sectional area. The formation of a membrane structure fabricated using the wet inversion technique happens during coagulation, in which the DMAc solvent is leached out of the matrix of the membrane. Each image is representative of n=3 scanning electron microscopy images.

![Figure 3](image.png)

**Figure 3.** Morphology structure of PVC membrane on transverse part at PF127 concentrations of 0% (a); 3% (b); 5% (c); and 7% (d). Each image is representative of n=3 scanning electron microscopy images.
dope solution and water as a non-solvent diffuses into the membrane. This phenomenon causes the formation of membrane pores and a finger-like macrovoid structure\(^\text{13}\). The structure of the PVC membrane changes after the addition of PF127 as the additive in forming the membrane pores\(^\text{9}\).

As shown in Figure 3a, the original PVC membrane has an upper layer that is thicker than the upper layer structure after the addition of PF127. The exchange of solvent from the polymer solution to the coagulation bath occur slowly in the case of the original PVC membrane, and contribute to the formation of a thick upper layer that is larger than in the other systems\(^\text{14}\). After the addition of PF127, the membrane surface becomes more hydrophilic and the affinity between the casting solution and water increases, so the polymer solution will attract more water and the diffusion process of water into the polymer matrix will be faster\(^\text{15}\). As a consequence of this mechanism, large macrovoids and a thin upper layer are formed. In other words, the increase in the PF127 concentration results in larger pores and a thinner upper layer of the membrane.

**Membrane hydrophilicity**

The measurement of the water contact angle is the simplest way to identify the degree of hydrophilicity and hydrophobicity of the membrane\(^\text{14}\). The hydrophilicity of the membrane, as measured by the water contact angle meter, is shown in Figure 4. The addition of PF127 is proven to improve the hydrophilicity of the membrane, as indicated by the decrease in the water contact angle. The existing PEO segment contained in the PF127 on the membrane surface contributed to the improvement in the membrane hydrophilicity. A number of studies on the mechanism of the decreased water contact angle of various membrane modifications with Pluronic have been reported by researchers\(^\text{16–19}\). The most hydrophilic membrane surface obtained in this study was found in the PVC membrane with the addition of 7% additive, with a contact angle of 67.2°.

**Filtration performance**

The water permeability and rejection profile of the original PVC and PVC blend membrane are shown in Figure 5. The original PVC membrane has a water permeability of about 0.616 l/m\(^2\).h.atm. After the addition of 1 wt% of PF127 to the dope solution additive, the water permeability increases significantly. The PEO chain in PF127 increases the pore size of membrane. Therefore, the amount of water that passes through the membrane is higher than that of the membrane without the polymeric additive. The change in the bottom layer structure of the PVC blend membrane is also evidence of the increased water permeability (Figure 3). As reported by many authors, the addition of an appropriate amount of hydrophilic polymer to the dope solution might enhance the membrane pores\(^\text{7,14,20,21}\), and, consequently, high permeation would be obtained. In this work, the highest water permeability reached 45.618 l/m\(^2\).h.atm, which was obtained in the case of the blend membrane with the PF127 concentration of 7%.

Figure 5 also shows the rejection efficiency of the dextran solution. The original PVC membrane is able to reject the dextran molecules by up to 100%. The addition of PF127 at a high concentration causes a decline in the rejection efficiency. The solution sample for the rejection experiment was prepared by dissolving a low molecular weight of dextran (i.e., 10.000 Da). This may be the reason for the reduction of rejection efficiency at high concentration of additive in this work.
achieve the best performance for permeation and selectivity, the optimization of the polymer solution could be designed by changing the relative composition of the PVC and the PF127.

Membrane shrinkage
In reference to the separation industry, membranes are expected to sustain in a wide range of temperature conditions. To determine the resistance of PVC/PF127 membranes in high-temperature conditions, a shrinkage test was performed by drying the membranes at 80°C; the results are shown in Table 1. The original PVC membrane did not suffer significant shrinkage after exposure to a temperature of 80°C, nor did the blending of PF127 into a polymer solution contribute seriously to the shrinkage of the PVC membrane. As shown in Table 1, an increase in the additive concentration of up to 7 wt% only has a small impact on the decrease in membrane size. PVC is one of the most widely used polymers in UF membranes, owing to its excellent physical and chemical properties. PVC polymer has a melting point of 212°C, and material fabricated from this polymer can only be degraded at high temperature.22

Table 1. Shrinkage observation of PVC membrane (n=3 per PF127 concentration).

<table>
<thead>
<tr>
<th>PF127 in PVC membrane (wt%)</th>
<th>Shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.67</td>
</tr>
<tr>
<td>1</td>
<td>2.07</td>
</tr>
<tr>
<td>3</td>
<td>3.33</td>
</tr>
<tr>
<td>5</td>
<td>5.00</td>
</tr>
<tr>
<td>7</td>
<td>9.33</td>
</tr>
</tbody>
</table>

Dataset 3. Raw data for membrane shrinkage test
http://dx.doi.org/10.5256/f1000research.15077.d206403

Conclusion
The fabrication of PVC membrane with PF127 as an additive has been performed in this work. The characteristics and performance of the membrane have been analyzed in terms of the morphology, hydrophilic or hydrophobic properties, water permeability, and solute rejection, as well as membrane shrinkage. Morphological analysis using SEM shows the increase in the membrane porosity after addition of PF127. A considerable change in the number and length of the macrovoid structure in the center section of the membrane increased the water permeability from 0.61 to 45.61 l/m².hr.atm. Regarding the water contact angle observation, it is found that the...
hydrophilicity of the membrane improves as the proportion of PF127 is increased. On the basis of the results of the shrinkage test, it can be concluded that the PVC membrane obtained in this research is able to withstand extreme temperature conditions of up to 80°C. Regarding the experimental results, it can be concluded that PF127 succeeded in improving hydrophilic properties, filtration performance, and maintaining the stability of the membrane. Thus, the PVC-FP127 is useful to be applied in the water treatment industry.

Data availability
Dataset 1. Raw data for water permeability and solute rejection. DOI: 10.5256/f1000research.15077.d206401.

Dataset 2. Raw data for water contact angle. DOI: 10.5256/f1000research.15077.d206402.


Competing interests
No competing interests were disclosed.

Grant information
The authors declare that no grants were involved in supporting this work.

References


Open Peer Review

Current Referee Status:  

Heba Abdallah  
Chemical Engineering and Pilot Plant Department, National Research Centre, Giza, Egypt

The article studied the effect of addition of pluronic F127 on the PVC membrane morphology and performance.

The article needs Minor Revision.

Introduction

The authors should do a comparison between this work and other previous work in terms of different surfactant additions, rejection % and permeability.

In section membrane preparation

- I think this is wrong - thickness in micrometer (0.450 µm too thin) the wet thickness using most knifes or applicators can reach to 0.45 mm or 450 micrometer

- Explain where PF127 is added - is it added in polymeric solution or in coagulation bath?

SEM section

SEM section need more discussion, explain why the addition of 3% PF127 in fig 2b indicates the biggest finger like formation compared to 5 and 7%?

Membrane hydrophilicity

Explain how the PEO effects the membrane, with a reference?

Membrane Shrinkage

The method of measuring shrinkage is not correct, it depends on the length of wet membrane, which means the blend membrane will absorb more water due to hydrophilicity, so I think that can affect the wet length of the membrane.

See this reference and repeat your shrinkage experiment:
Bilad M *et al,* 2015

**Conclusion**

Re-write the conclusion in points to indicate your results clearly.

**References**


**Is the work clearly and accurately presented and does it cite the current literature?**

Yes

**Is the study design appropriate and is the work technically sound?**

Partly

**Are sufficient details of methods and analysis provided to allow replication by others?**

Yes

**If applicable, is the statistical analysis and its interpretation appropriate?**

Yes

**Are all the source data underlying the results available to ensure full reproducibility?**

Yes

**Are the conclusions drawn adequately supported by the results?**

No

**Competing Interests:** No competing interests were disclosed.

**Referee Expertise:** Membrane technology, Production of polymeric membranes

I have read this submission. I believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

**Author Response 02 Jul 2018**

Nasrul Arahman, Syiah Kuala University, Indonesia

1. Heba Abdallah, Chemical Engineering and Pilot Plant Department, National Research Centre, Giza, Egypt

**Comment 1**

The authors should do a comparison between this work and other previous work in terms of different surfactant additions, rejection % and permeability.
Response

The comparison between previous works has been added to Introduction at third paragraph. The manuscript is written as follows:

The hydrophilic polymers that are frequently used as an additive are polyvinylpyrrolidone, polyethylene glycol, Brij, Tetronic, and Pluronic \(^7,8\). Of these, Pluronic is used as a surface modifying agent for many hydrophobic polymers. Raslan and Mohammad \(^9\) added Pluronic F127 to a polysulfone membrane. The resulting membrane is resistant to fouling and possesses good pore distribution \(^9\). The highest flux reached up to around 800 L/m\(^2\).h at 4.5 bar with 4.8 g addition of PF127. Pluronic has also been used to improve the anti-fouling of cellulose acetate (CA) membranes \(^10\). The combination of CA polymer and Pluronic surfactant results in a membrane that is more resistant to fouling and has a more stable filtration profile. Hydrophilic surfactant Tween20 and Tween80 has been used to enhance the permeation and antifouling properties of PVC membrane. The surfactants were added as 0; 1; 3; 5; and 7 % to dope membrane. The result showed that higher concentration of the both surfactant resulting higher water flux. The highest water flux is 328.6 L/m2.h with 7% Tween20 addition. Contrary to the rejection performance of BSA, the result showed decreasing rejection value in higher surfactant addition. The BSA rejection by PVC original membrane is about 97%, after addition of surfactant additives the rejection value decreased up to around 86-87.5% at 7% Tween20 and Tween80.

Comment 2

- I think this is wrong - thickness in micrometer (0.450 µm too thin) the wet thickness using most knifes or applicators can reach to 0.45 mm or 450 micrometer

Response

F There was a typo and it has been revised in membrane preparation section as follows: The solution was then framed on a glass plate using an automatically adjustable applicator (YBA-3, Yoshimitsu, Japan) at a thickness of 450 µm.

Comment 3

- Explain where PF127 is added - is it added in polymeric solution or in coagulation bath?

Response

F we have rewrite the script in membrane preparation section

To improve the performance of the membrane, PF127 was added at concentrations of 1, 3, 5 and 7 wt% to polymeric solutions and dissolve until homogene.

Comment 4

SEM section need more discussion, explain why the addition of 3% PF127 in fig 2b indicates the biggest finger like formation compared to 5 and 7%?

Response

F The more discussion of finger like formation has been added in the second paragraph of
membrane morphology discussion. The finger-like structure forms at PVC membrane with 3wt% of PF127 is dominate a half of the cross-section area of the membrane. While, in case of the addition of 5 and 7wt% of PF127, the finger-like structure formed in all cross-section area of the membrane.

Comment 5
Explain how the PEO effects the membrane, with a reference?

Response
The more discussion of PEO effects has been written in membrane hydrophilicity section.

the hydrophilic nature of PEO chain in Pluronic increased the diffusion rate of non-solvent during membrane formation. The increasing of nonsolvent in-diffusion rate promoted instantaneous demixing, which enhanced macrovoid formation. It has been reported that a rapid precipitation caused by the hydrophilicity of the additive results in higher surface porosity and more porous sublayer, leading to a higher water permeation.


Comment 6
The method of measuring shrinkage is not correct, it depends on the length of wet membrane, which means the blend membrane will absorb more water due to hydrophilicity, so I think that can affect the wet length of the membrane.

See this reference and repeat your shrinkage experiment:

Bilad M et al, 2015

Response
Thank you for your correction, we agree with your idea that the length of wet membrane has an effect on membrane shrinkage. We, therefore, calculated the membrane shrinkage by measuring the length of the wet cast and the dried membrane. Research group of Bilad (Bilad et al. 2015) designed the shrinkage calculation by measuring of the width of wet cast and the dried membrane. We revised the manuscript as follow:

To study the effect of the blending of pluronic additives on the toughness of the PVC/ PF127 membrane, a membrane shrinkage test was performed. The wet cast of membrane at each PF127 concentration was dried in the oven for 24 hours at 80°C. The shrinkage of the membrane was calculated using Equation (3).

Membrane shrink (%) = \((L_0-L_1)/L_0\) x 100

Where \(L_0\) = length of wet membrane (cm) and \(L_1\) = length of dried membrane (cm).

Comment 7
Re-write the conclusion in points to indicate your results clearly.

Response
The fabrication of PVC membrane with PF127 as an additive has been performed in this work. The characteristics and performance of the membrane have been analyzed in terms of the morphology, hydrophilic or hydrophobic properties, water permeability, and solute rejection, as well as...
membrane shrinkage. From this recent study, it can be concluded as follows:

1. Morphological analysis using SEM shows the increasing the membrane porosity after addition of PF127.
2. The water permeability of PVC membrane increases from 0.61 to 45.61 l/m2.hr.atm after addition of 7% PF127. However, the optimum filtration result, water permeability and rejection are found on the membrane with 3% addition PF127. It reach 20.2 L/m2.h for permeability and 68.66% for solute rejection.
3. The number and length of the macrovoid structure in the center section of the membrane increased and change after the presence of PF127.
4. Regarding the water contact angle observation, it is found that the hydrophilicity of the membrane improves as the proportion of PF127 is increased.
5. On the basis of the results of the shrinkage test, it can be concluded that the PVC membrane obtained in this research is able to withstand extreme temperature conditions of up to 80°C.
6. Regarding the experimental results, it can be concluded that PF127 succeeded in improving hydrophilic properties, filtration performance, and maintaining the stability of the membrane. Thus, the PVC-FP127 is useful to be applied in the water treatment industry.

**Competing Interests:** No competing interests were disclosed.
Are sufficient details of methods and analysis provided to allow replication by others?
Yes

If applicable, is the statistical analysis and its interpretation appropriate?
No

Are all the source data underlying the results available to ensure full reproducibility?
Yes

Are the conclusions drawn adequately supported by the results?
Partly

Competing Interests: No competing interests were disclosed.

I have read this submission. I believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Author Response 02 Jul 2018

Nasrul Arahman, Syiah Kuala University, Indonesia

Comment 1
It is, however, not clear why the addition is only until 7%. Is there any reason for this? Looking at the results, better performance could be obtain for higher concentration of PF127. In this sense, we cannot conclude the way it is concluded now.

Response
Fin this experiment, the best membrane is the membrane which has good both of permeability and selectivity. In other words, it has optimum filtration performance. As we know, permeability of membrane has opposite relation to its selectivity. Higher water permeability leads lower selectivity, therefore the optimum value of permeability and selectivity is the best performance of membrane. In this study, the addition of 7% PF127 produced highest water permeability, but it has the lowest rejection. In previous study, Lv (2007) investigated the addition of Pluronic F127 to CA membrane with the concentration 0; 4; 8; 12; 16; and 20 %. The result showed that the addition of PF127 higher than 8% enhance membrane porosity and decrease solute rejection. So that, in this study the use of PF127 is maximum 7%.
The source of previous study: https://doi.org/10.1016/j.memsci.2007.02.011

Comment 2
The same goes with the shrinkage test, where it is only tested at 80 degC. Hence, the respective conclusion is not correct. At 7%, the shrinkage is about 10%, is it not already significant shrinkage?

Response
F Thank you for the comment. In this experiment, the shrinkage test is designed at 80 degC, and the shrinkage impact is not so significant.

Comment 3
For the permeability test, it will be clearer if all various additives are put on the same graph, with the x-axis as the time and y-axis as the permeability. Then, we can see and compare the performance
better.
Response
Fin this experiment, the all of permeability test were conducted in certain setting time. So, For that condition, the graph will be better if consist of the value of permeability and additives concentration.

Comment 4
All in all, the analysis of the data and the conclusion need to be revisited.

Response
F the analysis and the conclusion in points has been re-written.

Competing Interests: No competing interests were disclosed.

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