

Influence of Solvent and Thickness Variation on the Performance of Poly(Vinylidene Fluoride-co-hexafluoropropylene) Polymer Membrane

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ABSTRACT: *This study involves the synthesis and characterisation of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) polymer membrane by using breath figure method. The study was performed mainly to investigate the effect of solvent (acetone to NMP ratio of 100:0, 40:60, 50:50 and 60:40) and thickness (20 μm , 25 μm , 30 μm and 40 μm) variation on the performance of PVDF-HFP membrane. The different membrane samples were fabricated and characterised by different techniques such as scanning electron microscope (SEM), Fourier transform infrared (FTIR), porosity and mechanical strength. The mechanical stability of the membranes was mainly found to be thickness dependent, whereas the solvent variation has shown significant effect on the porosity, thickness and morphology of the prepared membranes. The highest porosity of 81.6% was obtained with acetone to NMP ratio of 40:60 compared to 53.4% of pure acetone based membrane. In addition, the 30- μm thickness membrane was the second highest in mechanical strength compared to 40- μm membrane; however, its highest porosity of 70.7% has given it an added advantage and makes it a strong choice to consider as a porous membrane for various applications.*

Keywords: PVDF-HFP membrane, solvent variation, thickness variation, poly(vinylidene fluoride, polymer membrane

1. INTRODUCTION

Since their introduction, several fluoropolymers have been developed, modified and investigated, among which the poly(vinylidene fluoride co-hexafluoropropylene) (PVDF-HFP) has received much attraction; its amorphous HFP phase and crystalline VDF phase fulfils the requirement of many energy applications.¹ Furthermore, its more hydrophobic nature compared to PVDF polymer makes it a suitable choice for membrane distillation and pervaporation.^{2,3} Additionally, its crystalline nature (VDF) provides mechanical strength and the amorphous nature (HFP) helps to hold the electrolyte in polymer electrolyte membranes mainly used in lithium batteries and fuel cells.^{4,5}

The porous structure for better porosity and mechanical stability are among the most important parameters for many applications, especially in energy devices. However, these particular properties depend a lot on solvent selection, thickness and processing method. The number of techniques such as plasticiser extraction, electrospinning, breathe figure method, solvent casting and phase separation, etc. have been used for membrane preparation.⁶⁻⁹ In this work, the breathe figure method has been modified for the first time and used to synthesise and characterise the PVDF-HFP porous membrane.⁸ It will be interesting to see the effect of solvent and thickness variation on the performance of PVDF-HFP membrane. The prepared porous membrane can provide an effective alternate to several commercial membranes in energy storage applications.

2. EXPERIMENTAL

2.1 Experimental Procedure

The breathe figure method was used to fabricate the PVDF-HFP membrane.⁸ In short, 15 wt% of PVDF-HFP with acetone to NMP ratio (50:50) was cast with varying thickness such as 20 μm , 25 μm , 30 μm and 40 μm . Afterward, the obtained optimum thickness of membrane was used to investigate the effect of solvent variation. For this, the varied ratio of acetone to NMP such as 100:00, 40:60, 50:50, and 60:40 was used to dissolve PVDF-HFP polymer. After mixing, a viscous and homogenous solution was obtained and was left overnight for proper degassing. After casting, the samples dried at room temperature (about 50%–60% RH) for around 48 h. The dried membranes were peeled out and stored in a dry cabinet for further usage.

2.2 Characterisation

The structure and morphology of the prepared PVDF-HFP membranes were noticed by field emission electron microscope (FESEM, Zeiss Supra 35VP). The Fourier transform infrared (FTIR) characteristic peaks were obtained in a wavenumber range from 400–4000 cm^{-1} through Thermo Scientific Nicolet iS10 spectrometer by OMNIC software. The mechanical strength test was performed with a load cell of 10 kN by using Instron 3366 (United States). The specimen of the membrane strip was cut as per ASTM-D882-10 standard. The viscosity of the different solvent mixture solutions was determined by Brookfield DV-III Ultra Programmable Rheometer, while porosity of the different membrane samples was determined by soaking membrane samples in n-butanol for 2 h and weighing the sample weight before and after soaking. The equation used to calculate the porosity of the membrane sample is given by:

$$P = W_{\text{wet}} - W_{\text{dry}} / (\rho_b \times V_{\text{dry}})$$

where W_{wet} , W_{dry} , ρ_b and V_{dry} stand for weight of the butanol dipped membrane, weight of the dry membrane, density of butanol and volume of dry membrane, respectively.

3. RESULTS AND DISCUSSION

3.1 FTIR Analysis

Figure 1 shows the characteristic peaks obtained for the prepared PVDF-HFP membrane through FTIR analysis. The $-\text{CH}_2-$ group has been observed at around 3030 cm^{-1} , whereas, the characteristics obtained at 1401–1455 cm^{-1} are attributed to $-\text{C-F}-$ stretching. Moreover, the peak shown at 1174 cm^{-1} is assigned to $-\text{CF}_2-$ group. Likewise, the peaks obtained near 1070 cm^{-1} , 874 cm^{-1} to 975 cm^{-1} , 657 cm^{-1} and 838 cm^{-1} correspond to $-\text{C-C}-$ skeletal vibration, vinylidene group and $-\text{CH}_2-$ bonding respectively. Therefore, all the peaks including 761 cm^{-1} to 769 cm^{-1} ($-\text{CF}_3-$ stretching) confirm the successful preparation of PVDF-HFP polymer membrane. In addition, FTIR spectra of PVDF-HFP membranes with highest porosity in both tests have presented; however, both the spectra haven't shown much difference compared to spectra of pure PVDF-HFP membrane. It shows that the solvent variation cannot alter the functional groups present in the polymer membrane.

3.2 Mechanical Strength

The mechanical properties of PVDF-HFP membranes were investigated for different thickness and tabulated in Table 1. The results suggested that the increase in thickness improves the tensile strength and Young's modulus of the membrane. The highest tensile strength of 14 Pa has obtained with 40 μm membrane. On the other hand, 20- μm membrane showed only 3.6 MPa and 129 of tensile strength and Young modulus respectively. Interestingly, membrane with thickness 30 μm showed highest porosity of 70.7% which may be attributed to better porous structure at a particular thickness.

Furthermore, the better mechanical strength has attributed to higher membrane thickness. For this reason, NMP added membrane has also shown better mechanical stability compared to pure acetone membrane, as reported in Table 2. The pure acetone membrane showed tensile strength and Young modulus of 5.7 and 172 MPa respectively. Whereas, around 8.2 MPa tensile strength and 134 MPa of Young modulus has been noticed with NMP added membrane. However, more than 60% NMP hasn't found suitable for breathe figure method as higher amount of non-volatile solvent cannot evaporate effectively and results in poor morphology of membrane. Subsequently, the acetone itself has been a very good solvent for PVDF-HFP porous membranes especially when prepared by breathe figure method; however, NMP is well known for its best compatibility with nanoparticles and inorganic fillers and its right combination with the volatile solvent will make a breathe figure method more flexible for future research.

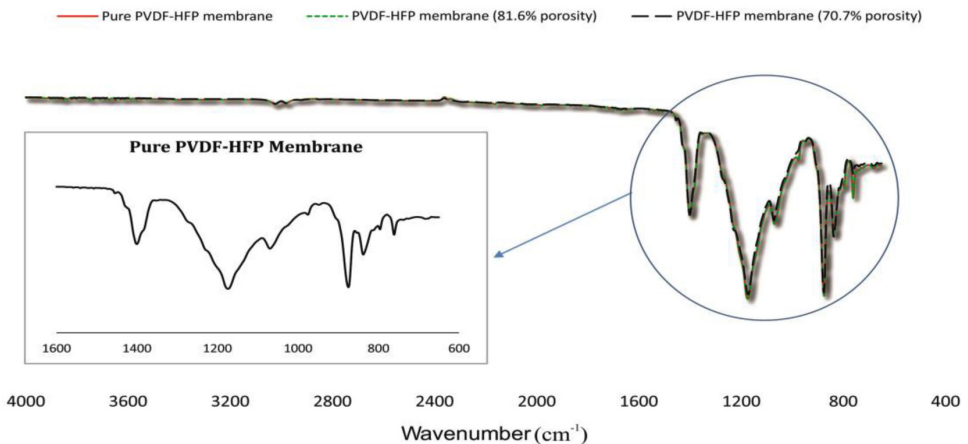


Figure 1: The FTIR characteristic peaks of different PVDF-HFP polymer membrane.

Thus, the investigation shows that the highest tensile strength has been obtained with 40 μm membrane due to higher thickness. However, almost an equal porosity was noticed with 30 μm membrane sample as well. Nonetheless, the other membrane samples have also shown respectable mechanical stability too. In addition, the NMP addition to acetone solvent have shown a significant impact on the mechanical stability of PVDF-HFP membrane when cast by proposed technique.

Table 1: Effect of thickness variation on porosity and mechanical strength of PVDF-HFP membrane.

Sr. No	Membrane samples (15 wt%) (Acetone-NMP [1:1])	Porosity (%)	Tensile strength (MPa)	Young's modulus
1.	20 μm	53.6	3.6	129
2.	25 μm	60.7	4.4	182
3.	30 μm	70.7	5.7	172
4.	40 μm	69.8	14.0	460

3.3 SEM Analysis

As shown in Figure 2, each membrane has shown a considerable difference with solvent variation. The membrane samples with acetone to NMP ratio of 60:40 (c, g) and 100:00 (i, j) show lesser pores. However, porosity of both samples are still considerable for many applications. Also, a similar pattern has been observed with 40:60 (a, e) and 50:50 (b, f) membrane samples. The cross-section images (e, f, g and j) also confirms the porous structure of all membranes.

Acetones are almost linear molecules. Hence, it leaves smaller voids on evaporation, and it also did not form a strong bonding with the host polymer due to lack of bonding groups. Therefore, the acetone molecules escape freely and leaves uniform pores upon evaporation, while NMP (a nonvolatile solvent) interacts well with the host polymer due to its amide group. The structure of the prepared membranes was also attributed to breathe figure method. When the cast membrane was allowed to dry in a natural environment with 50%–60% RH, the water droplets were generated on the surface of the membrane due to lower temperature caused by endothermic evaporation.⁸ The water droplets attract the PVDF-HFP molecules, which gathers around the droplets and assembled to provide a unique structure.

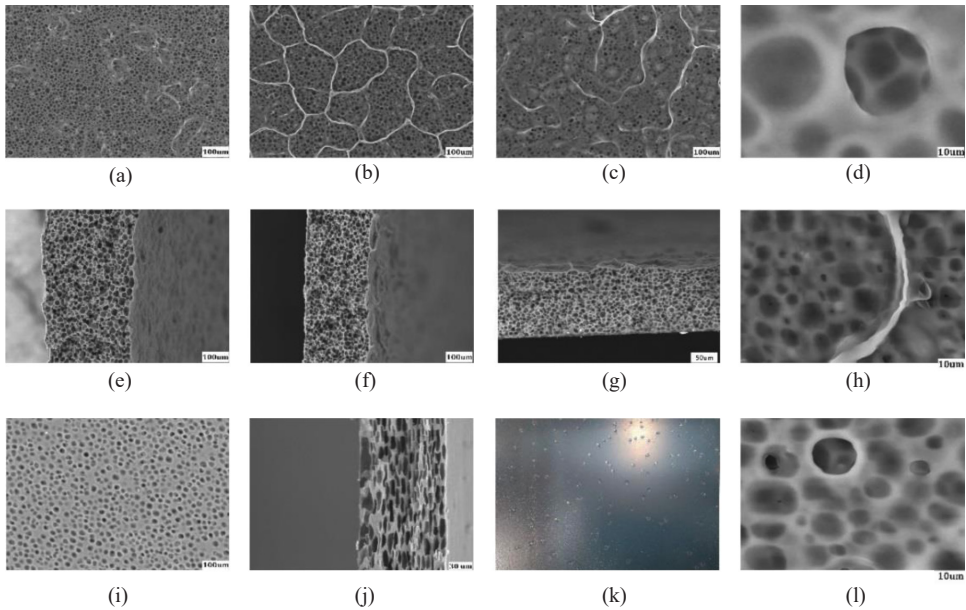


Figure 2: SEM images of PVDF-HFP membranes with different acetone to NMP solvent ratio; 40:60 (a, d and e); 50:50 (b, f and h); 60:40 (c, g); 100:00 (i, j and l); water droplets formed on surface (k).

The SEM images confirm the morphological changes due to solvent variation with the host polymer. Even though most of the prepared membranes have shown good porosity, the membrane prepared with acetone to NMP ratio of 40:60 has shown uniform pores and resulted in highest porosity of 81.6%. The highest porosity at a particular solvent mixture is attributed to the better interaction of acetone and NMP at particular ratio, which resulted in improved morphology of PVDF-HFP membrane.

Table 2: Effect of solvent variation on porosity, thickness and viscosity of PVDF-HFP membrane.

Sr. No	Membrane samples (15 wt% and 30 μm) (Acetone : NMP)	Porosity (%)	Obtained membrane thickness (μm)	Viscosity (Cp)	Tensile strength (MPa)
1.	100:00	53.4	30	75 ± 5	–
2.	40:60	81.6	65 ± 10	350 ± 5	–
3.	50:50	70.2	65	325 ± 5	5.7
4.	60:40	60.3	60 ± 5	300 ± 5	–
5.	00:100	–	75	500 ± 5	8.2

4. CONCLUSION

The porous PVDF-HFP polymer membrane has been successfully synthesised through breath figure method. The solvent and thickness variation has shown significant impact on various factors of prepared membranes. The 40 μm thickness membrane has resulted in highest tensile strength; however, the 30 μm thickness membrane was more considerable one due to an equal porosity (70.2%) of 40- μm membrane. The PVDF-HFP membrane with acetone to NMP ratio of 40:60 has resulted in highest porosity of 81.6%. In addition, NMP addition to the solvent has shown a substantial impact on the mechanical stability of membrane when prepared with the proposed technique. Therefore, the 40:60 acetone to NMP ratio has found suitable when cast with 30 μm membrane with the proposed technique. However, this solvent combination and thickness variation study has just opened a new window for breath figure method and still needs an extensive research to optimise the performance of porous membrane.

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