

Preparation of PVDF Hollow Fiber Membranes Using SiO_2 Particles: The Effect of Acid and Alkali Treatment on the Membrane Performances

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ABSTRACT: This work presents the preparation of PVDF hollow fiber membranes using SiO_2 particles as an additive via a conventional immersion precipitation method. The asymmetric membrane formed consists of a uniform distribution of finger-like structure near the inner layer with sponge-like structure near the outer layer. SiO_2 particles were removed from the spun membranes by a treatment using either sodium hydroxide (NaOH) solution or hydrofluoric (HF) acid. Both the NaOH solution and HF acid treatments have resulted in PVDF hollow fiber membranes with enhanced water permeability of up to $748.4 \text{ L/m}^2 \cdot \text{h}$ and $690.7 \text{ L/m}^2 \cdot \text{h}$, respectively. HF acid was found to be more efficient in dissolving SiO_2 and subsequently washing the particles out of the membrane for only 10 min compared to the treatment with NaOH solution, which took almost 1 h for complete removal. Mechanical properties of hollow fiber membrane treated with HF acid was found to be almost unaffected and showed a much better ductile behavior compared to the original one; while the one treated with NaOH solution possessed poor mechanical properties.

1. INTRODUCTION

Immersion precipitation can be said to be the most common method employed in the preparation of polymeric membranes. Most of the commercially available membranes are prepared by phase inversion via the immersion precipitation method. By preparing a homogeneous polymer solution from a suitable solvent and casting on a suitable support, membranes can be formed by immersing the casting film into a coagulation bath containing a nonsolvent. To date, phase inversion via immersion precipitation has received a great deal of attention in producing polymeric membranes from different types of polymeric membrane materials, including poly(sulfone), poly(amide), and cellulose acetate, due to its simple process.

Among these membrane-forming polymers, poly(vinylidene fluoride) or PVDF, has attracted considerable attention in industrial applications, mainly due to its excellent thermal stability, outstanding chemical resistance and good mechanical properties.^{1–3} Preparation of PVDF membranes via the phase immersion precipitation process has been extensively studied and widely employed in various membrane applications.^{4–6} Nevertheless, the semicrystalline properties of PVDF often result in the occurrence of rapid crystallization prior to liquid–liquid demixing during the membrane formation via the immersion precipitation method, which can lead to poor membrane morphology, performance, and mechanical strength. Therefore, most of the high performance PVDF membranes for microfiltration or ultrafiltration today are frequently achieved via a thermally induced phase separation (TIPS) method.^{7,8}

However, blending of inorganic materials with a polymer solution in the preparation of PVDF membranes has attracted attention among researchers. Examples of inorganic particles that have been incorporated into the PVDF membrane include titanium dioxide (TiO_2),^{9,10} zirconium dioxide (ZrO_2),¹¹ alumina

(Al_2O_3),^{12,13} and silica (SiO_2).^{14,15} Among them, silica (SiO_2) particles were found to be the most convenient and widely used because of their mild reactivity and well-known chemical properties,¹⁴ as well as good compatibility with organic solvents used to prepare the PVDF solution.¹⁶ Silica has been reported to have increased the performance of the organic–inorganic anion-exchange PVDF- SiO_2 membranes, as well as the hydrophilic properties.¹⁵ Moreover, SiO_2 particles were found to be effective in balancing the crystallization and phase inversion during the preparation of PVDF hollow fiber membrane via the TIPS method, using a large amount of SiO_2 particles as an additive.⁷ While contributing to the improvement in the flowability of the molding process at high polymer concentrations, the addition of SiO_2 particles was also believed to be advantageous since they act as nuclei for microphase separation. SiO_2 particles were then extracted and washed out using a specific solvent. This process subsequently contributes to the pore formation in membranes. This example provides an idea of which SiO_2 particles can be removed after the membrane is formed through post treatment, instead of trapped in the bulk membrane phase, thereby creating more porous membranes. By employing this principle, porous PVDF hollow fiber membranes could be fabricated through a conventional phase inversion via immersion precipitation method.

In this work, we report on the preparation of PVDF hollow fiber membranes with SiO_2 particles as an additive via a conventional immersion precipitation method. Both NaOH solution and hydrofluoric (HF) acid were employed and investigated as a membrane post-treatment solution to remove the SiO_2 particles

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from the membrane precursor. The effect of the SiO_2 particle removal on membrane performance and mechanical properties was investigated.

2. MATERIALS AND MEMBRANE PREPARATION

2.1. Materials. PVDF polymer powder Kynar 761 was purchased from Atofina Chemicals, Inc., U.S.A. Reagent grade 1-methyl-2-pyrrolidone (NMP) was obtained from Rathburn Chemicals Ltd., U.K. Colloidal silica (MEK-ST-L, 30.6 wt %, particle size: 40–50 nm, specific gravity: 1.001) in methyl ethyl ketone (MEK) was purchased from Nissan Chemical Industries, Ltd., Japan. Sodium hydroxide (NaOH, BDH AnalaR) was purchased from VWR International Ltd., U.K. Hydrofluoric acid (HF, 47–51%) was purchased from Sigma-Aldrich, U.K. In all cases, deionized water (DI) was used as the coagulation bath medium.

2.2. Preparation of PVDF Hollow Fiber Membranes with the Addition of SiO_2 . Spinning dopes for the fabrication of PVDF hollow fiber membranes were prepared by the following procedures. SiO_2 particles were obtained by drying the commercial silica through dispersion and the evaporation of MEK, followed by grinding of SiO_2 particles using a glass mortar and pestle. The desired amount of dried SiO_2 particles were then dispersed into a preweighed NMP solvent in a Duran bottle. Continuous stirring was performed until no large aggregations were observed. During this stage, an ultrasonic bath was applied for about one hour to assist the dispersion of SiO_2 particles in the solvent. Then, PVDF was added into the bottle and stirred for 24 h while keeping the solution's temperature at 60 °C to ensure the complete dissolution of the polymer. Once the polymer was completely dissolved, the solution was filtered using a fine metal mesh to remove large particles or agglomerates. After that, the solution was allowed to be degassed under vacuum at room temperature prior to use.

PVDF hollow fiber membranes were spun via a dry-jet wet spinning method from the prepared dope solution. Further treatment was applied for the removal of SiO_2 particles from the spun hollow fiber membranes using either a 20 wt % of NaOH solution at 70 °C or a HF acid at room temperature. The detailed membrane preparation, spinning, and treatment conditions are listed in Table 1.

2.3. Membrane Characterizations. **2.3.1. Membrane Morphology.** The morphology of the surface and cross-section of the PVDF membranes prepared were examined by Scanning Electron Microscope (SEM; JSM-5610LV, JEOL, Tokyo, Japan). The membranes were immersed in ethanol for 10 min, and then in liquid nitrogen for about 5–10 min. Following that, the membrane samples were fractured, and then flexed into a short sample with tweezers to maintain the original cross-sectional fracture of the membranes. These membrane samples were then positioned on a metal holder and then sputter coated with gold under vacuum for 3 min. The micrographs of the surface and cross section of the membranes were taken at various magnifications.

2.3.2. FTIR-ATR Analysis. The removal efficiency of SiO_2 particles from the membranes was analyzed using a Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer, Spectrum One equipped with an attenuated total reflection (ATR) attachment). The samples were placed on the sample holder and all spectra were recorded in the wavenumber range of 4000–500 cm^{-1} , accumulating 32 scans at a resolution of 2 cm^{-1} .

2.3.3. Pure Water Flux Measurement. Pure water flux experiments were conducted in a cross-flow membrane module filtration apparatus. For each module, ten fibers of 20-cm length were assembled into the filtration module and pure water flux

Table 1. Preparation and Treatment Conditions of PVDF Hollow Fiber Membranes

parameters	value
spinning dope:	
PVDF concentration (wt%)	18
SiO_2 concentration (wt%)	12
NMP concentration (wt%)	70
spinning conditions:	
bore liquid flow rate (DI water: mL/min)	3
extrusion rate (mL/min)	5
air gap (mm)	150
treatment using NaOH solution:	
NaOH concentration (wt%)	20
treatment temperature (°C)	70
treatment time (min.)	10–180
treatment using HF acid:	
HF acid concentration (wt%)	47–51
treatment temperature	20–22
treatment time (min.)	10–180

measurements were performed in a cross-flow mode through an outside-in configuration.

2.3.4. Mechanical Properties Measurement. Tensile strength and elongation at break of the hollow fibers were measured by Instron 4466 tensile test machine with a load cell of 1 kN, at a constant elongation velocity of 5 mm/min at room temperature (20 °C ± 2). At least five fibers with 5 mm length were tested and the average data was taken for each sample. The deviation between the sample values and the average value was less than 5%.

3. RESULTS AND DISCUSSIONS

3.1. Membrane Morphology. The SEM images of the cross-section and outer surface of the prepared hollow fiber membrane are shown in Figure 1. It can be seen from Figure 1(a) that the hollow fiber membrane spun with the addition of SiO_2 particles in the dope solution exhibits an asymmetric structure, composed of uniformly distributed finger-like structures near the inner layer and sponge-like structures near the outer layer. On the basis of the SEM images, the dimension of the hollow fiber membrane was estimated to be approximately 1.1 mm for the inner diameter and 1.7 mm for the outer diameter. The overall structure of the membranes remains unchanged after treatment either with 20 wt % NaOH solution at 70 °C or using a HF acid at room temperature.

Figure 1, parts (b) and (c), shows the SEM images of the membrane outer surface, before and after treatment with the NaOH solution, respectively. While the outer surface of the untreated membrane shows a relatively higher degree of irregularities, mainly because of the higher amount of SiO_2 particles remaining in the membrane, the treated membrane exhibits porous or moon-like (impact) crater structures. It could be observed from Figure 1(b) that the SiO_2 particles are well dispersed, with no aggregations larger than 1 μm (estimated from the scale of the SEM image). However, the removal of SiO_2 particles has left significant pores or cavities on the membrane's outer surface as seen in Figure 1(c), consequently leading to the formation of uneven membrane surfaces. The outer surface of the HF acid treated membrane exhibited almost similar structure with that

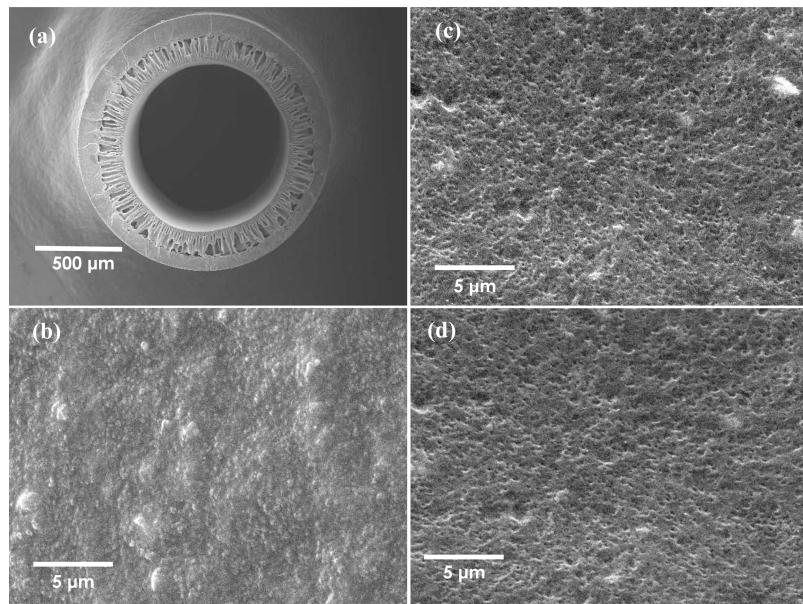


Figure 1. SEM images of the prepared PVDF hollow fiber membranes: (a) cross section, (b) outer surface before treatment, (c) outer surface after treatment with NaOH, and (d) outer surface after treatment with HF acid.

of the NaOH treated membrane, and the SEM image is shown in Figure 1(d).

3.2. Removal of SiO₂ Using NaOH Solution or HF Acid. SiO₂ particles have been used as an additive in the preparation of PVDF hollow fiber membrane in this work because it is believed that the dispersion of SiO₂ particles in the membrane solution could provide a nucleus for microphase separation. The crystal growth could be suppressed during the phase inversion process, and consequently a membrane with an interconnected porous structure may be formed. After the membranes are formed, SiO₂ particles need to be removed from the membrane in order to create a more porous membrane structure and improve water permeability.

For the purpose of removing SiO₂ from the prepared membranes, a hot NaOH solution (20 wt % NaOH at 70 °C) and a HF acid solution (47–51 wt % HF at room temperature) were chosen and compared in this study. It is worth mentioning that the color of the membranes immediately changed from white to brown upon immersion into the NaOH solution, but remained unchanged in the HF acid. Changes in membrane weight had been measured in order to determine the SiO₂ removal efficiency from the treatment, and the results are shown in Figure 2. From the compositions of spinning solution, the ultimate SiO₂ content in the resultant membrane was expected to be 40% in weight and ideally, if the SiO₂ were to be completely removed from the membrane, the final membrane weight of 60% should be retained. According to Figure 2, membrane weight gradually reduced during 30 min of treatment, and eventually stabilized at approximately 55 wt % when the NaOH solution was used for the treatment. On the contrary, when HF acid was used for the treatment, the membrane weight was reduced by approximately half of the original membrane weight in only 10 min, then stabilized in the range between 50% and 60% of the original membrane weight with a further treatment period of up to 3 h. This result shows that the SiO₂ particles dissolved much faster in the HF acid than that in the NaOH solution, indicating that HF may be a good solvent for the removal of SiO₂ compared to NaOH.

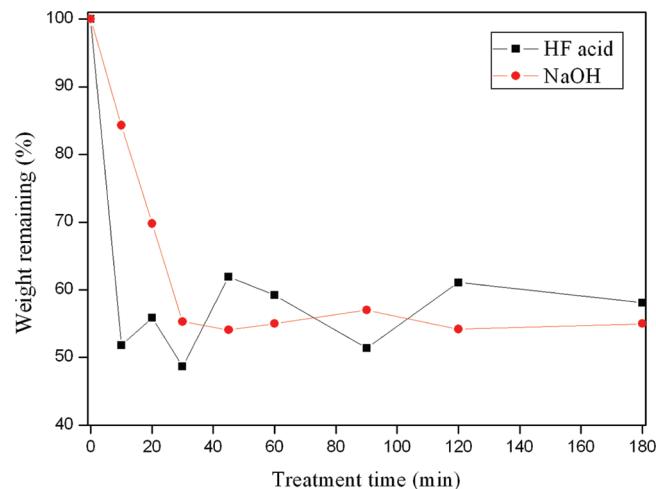
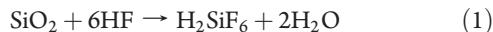


Figure 2. Weight loss measurements of PVDF hollow fiber membrane during the removal of SiO₂ particles.

During the post treatment using the HF acid, SiO₂ was attacked by HF acid to form hexafluorosilicic acid and water.¹⁷ The possible mechanism for this reaction is as follows:



Meanwhile, SiO₂ particles dissolved in hot NaOH solution during the post treatment to produce sodium silicate and water¹⁸ where the schema of this reaction is shown below:



The SiO₂ removal efficiency has been further examined by FTIR analysis. Figure 3, parts (A) and (B), shows the FTIR spectra of SiO₂ particles, the pure PVDF membrane, untreated and treated membranes with different treatment times, using the NaOH solution and HF acid, respectively. It can be seen from Figure 3(A) that the intensity of the characteristic bands at 800

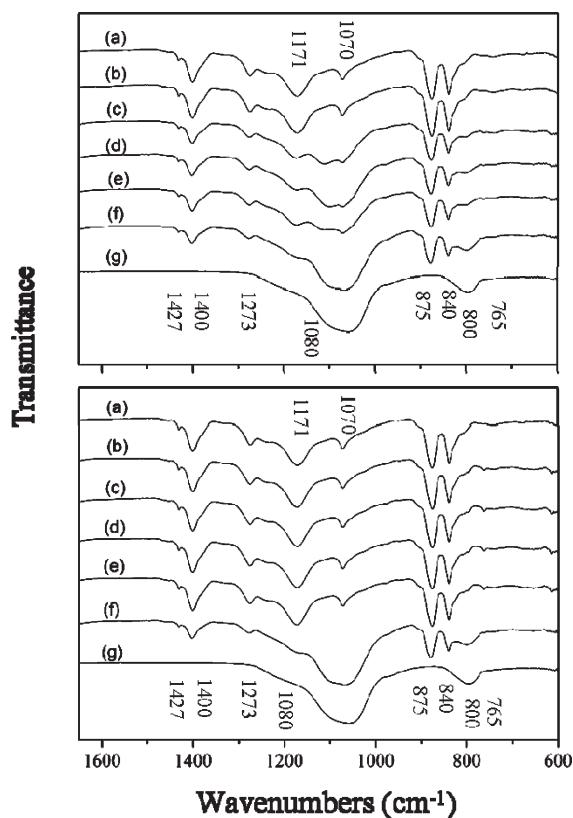


Figure 3. FTIR spectra of (a) pure PVDF membrane, and PVDF membrane containing SiO_2 particles and treated for (b) 1 h, (c) 45 min, (d) 30 min, (e) 10 min, (f) 0 min (untreated); and (g) SiO_2 powder: (A) 20 wt % NaOH solution at 70 °C and (B) HF acid at room temperature.

and 1080 cm^{-1} , attributable to the symmetric and asymmetric $\text{Si}-\text{O}-\text{Si}$ stretching¹⁴ in PVDF membranes treated with the NaOH solution, were getting smaller after 10 min of treatment. These particular bands completely disappeared after a one-hour treatment, and finally the membrane exhibits similar spectrum to that of pure PVDF membrane. Although the weight measurement results showed that SiO_2 particles might have been completely removed after 30 min, the FTIR spectra demonstrated that a relatively longer treatment time that is 1 h using NaOH solution, may be required. However, the characteristic bands at 800 and 1080 cm^{-1} in Figure 3(B) disappeared after only a 10-min treatment using HF acid, and finally showed a similar spectrum to that of the pure PVDF membrane after the 10-min treatment, demonstrating that SiO_2 could be quickly removed from the prepared membrane by HF acid. The FTIR result is observed to be in agreement with the weight measurement results, suggesting that HF acid could be more effective in removing the SiO_2 additive from membranes in comparison to the NaOH solution.

Table 2 summarizes the major FTIR peaks assigned to different functional groups and crystalline phases. As can be seen from Table 2 and Figure 3, the spun PVDF hollow fiber membrane containing SiO_2 particles may be composed of a mixture with α -form and β -form crystal structures. Nevertheless, further characterisations of the membrane such as X-ray diffraction (XRD) analysis may be required before drawing any conclusions on the type of crystal formation.

3.3. Pure Water Flux Measurement. Pure water flux measurement has been conducted on the prepared hollow fiber

Table 2. FTIR Peak Assignments for SiO_2 , PVDF Membrane, and PVDF Membrane Containing SiO_2 as Additive^{14,19–21}

wavenumbers (cm^{-1})	functional groups and crystalline forms
1427, 1070, 875, 765	α phase crystal of PVDF
1400, 1273, 1171, 840	β phase crystal of PVDF
1080	asymmetric $\text{Si}-\text{O}-\text{Si}$ stretching
800	symmetric $\text{Si}-\text{O}-\text{Si}$ stretching

Table 3. Pure Water Flux Measurement

membranes	pure water flux ($\text{L}/\text{m}^2 \cdot \text{hr} \cdot \text{bar}$)
untreated membrane	80.3 ± 1.9
NaOH treated membrane	748.4 ± 2.3
HF acid treated membrane	690.7 ± 1.5

membranes, and the results are tabulated in Table 3. It can be seen from Table 3 that the pure water flux of the untreated membrane was initially $80.3\text{ L}/\text{m}^2 \cdot \text{h}$ at 1 bar. However, the pure water flux of the hollow fibers significantly improved after treatment with NaOH and HF acid solutions. The pure water flux of the hollow fiber treated with the NaOH solution increased significantly to $748.4\text{ L}/\text{m}^2 \cdot \text{h}$, showing an approximately 9-fold increase over that of the original membrane. However, the hollow fiber membrane treated with the HF acid solution showed a slightly lower pure water flux of $690.7\text{ L}/\text{m}^2 \cdot \text{h}$ compared to that of the NaOH treated membrane. It is believed that the relatively higher pure water flux after the NaOH treatment, apart from the porous structure caused by the SiO_2 removal, may also be due to the degraded structure of PVDF membrane as a result of the strong alkaline treatment. The degradation of PVDF membranes caused by the NaOH treatment is demonstrated by weak mechanical properties, which will be further discussed in the next section. Nevertheless, the pure water flux of the HF acid treated membrane still demonstrated a remarkable improvement over that of the untreated ones.

3.4. Mechanical Strength Measurement. The mechanical properties of the PVDF hollow fiber membranes have been evaluated by tensile stress and elongation at break measurements. Figures 4 and 5 show the measurements of tensile stress at break and elongation at break, respectively. Both figures demonstrate that the mechanical strength of the PVDF hollow fiber membranes was dramatically reduced when subjected to treatment with the NaOH solution. As seen from Figure 4, the tensile strength of the hollow fiber treated with the NaOH solution decreases gradually, in line with the treatment time, and finally down to zero after a 90-min treatment. An almost similar trend could be observed on the elongation at break of the hollow fiber membranes, as demonstrated in Figure 5. By treating the membrane with NaOH solution for 20 min, the elongation was reduced to zero, indicating that the membrane had completely lost its flexibility thereafter.

However, the tensile strength of the membrane treated with the HF acid solution remained almost unchanged compared to that of the untreated one, which was around 2.23 MPa. The elongation of the HF acid treated membranes increased from approximately 38% to 90% after being subjected to a 120-min treatment time, and slightly dropped after that. It is believed that the increase in elongation was caused by the removal of SiO_2 particles from the membrane. As a result, the single PVDF polymeric phase membrane showed a better ductile behavior than the stiff composite phase membrane.

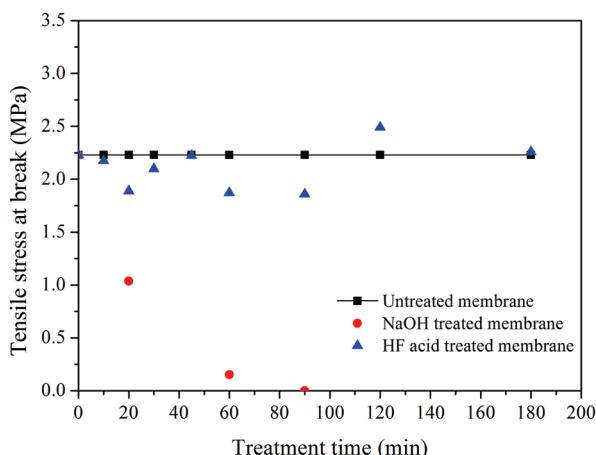


Figure 4. Tensile stress at break vs treatment time.

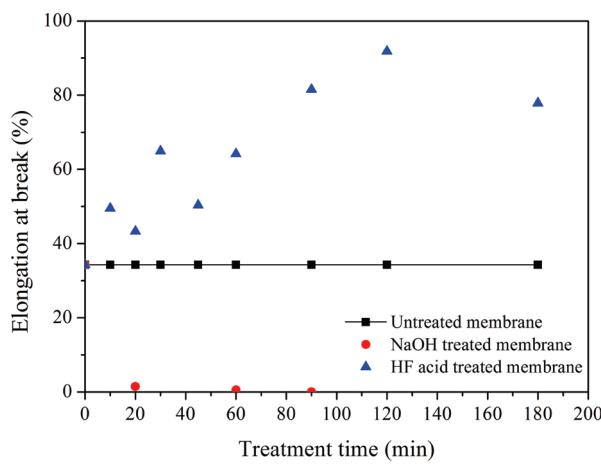
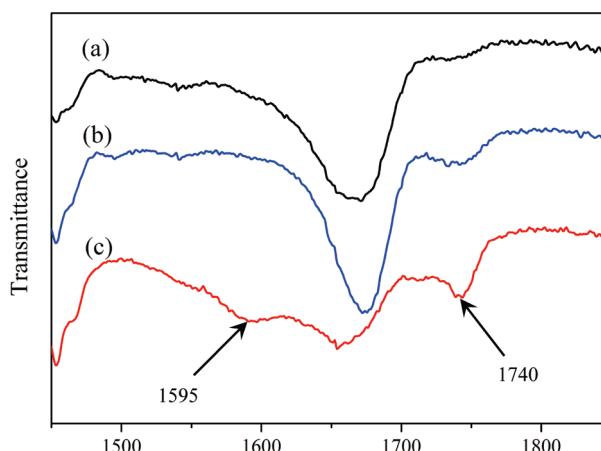


Figure 5. Elongation at break vs treatment time.

An intensive search in the FTIR spectra has been performed in order to further investigate the changes in the mechanical strength of PVDF membrane treated with the NaOH solution and the HF acid. Figure 6 demonstrates the FTIR spectra between 1450 and 1850 cm^{-1} of an untreated hollow fiber membrane, and hollow fiber membranes treated with the NaOH solution and the HF acid for 1 h. Similar spectra could be observed on the untreated hollow fiber and hollow fiber treated with HF acid. However, the spectrum of hollow fiber treated with the NaOH solution exhibited slightly different peaks. Two significant peaks appeared, which are a shoulder at around 1595 cm^{-1} and a peak at 1740 cm^{-1} attributable to the respective $-\text{C}=\text{C}-$ stretch and $-\text{C}=\text{O}-$ stretch in the FTIR spectrum of NaOH treated membrane. The presence of the former characteristic band could be due to the dehydrofluorination of PVDF, which eventually leads to the formation of carbon–carbon double bond as a result of the reaction between NaOH and PVDF.^{22,23} The presence of the latter peak at 1740 cm^{-1} that is assigned to the $-\text{C}=\text{O}-$ stretch²⁴ may also be caused by the dehydrofluorination of PVDF, where the reaction has allowed the formation of a carbonyl group between the carbon compound in PVDF and the oxygen from SiO_2 . The degradation of the PVDF hollow fiber membrane occurred after the course of NaOH treatment, and this phenomenon elucidates the cause of the reduction in membrane mechanical strength.

Figure 6. FTIR spectra between 1450 and 1850 cm^{-1} of (a) untreated membrane, (b) HF acid treated membrane, and (c) NaOH treated membrane.

4. CONCLUSIONS

In this work, PVDF hollow fiber membranes with the addition of SiO_2 particles have been fabricated via a conventional immersion precipitation method. NaOH solution and HF acid were employed and investigated as a post-treatment method in removing SiO_2 particles from PVDF hollow fiber membrane after the membrane was formed. The prepared PVDF hollow fiber membrane showed significant improvement in pure water flux after the SiO_2 particles were washed out from the membrane by using either 20 wt % NaOH solution at 70 °C or HF acid at room temperature with pure water flux of 748.4 $\text{L/m}^2 \cdot \text{h}$ and 690.7 $\text{L/m}^2 \cdot \text{h}$, respectively.

Experimental results showed that HF acid treatment was more effective in removing the SiO_2 particles from the PVDF membrane compared to the treatment with the NaOH solution. While the NaOH treatment required at least 1 h to completely remove SiO_2 particles and the resulting membrane exhibited weak mechanical properties, only 10 min of treatment with HF acid were needed to wash out all of the particles with improved ductility, yet that did not affect the membrane tensile strength. Although HF acid is categorized under corrosive/toxic materials, which require extreme care or a delicate handling procedure with particular personal protection equipment, the use of the HF acid is anticipated to be invaluable for the treatment of PVDF membranes containing SiO_2 since it is the only acid that was able to dissolve the SiO_2 particles without affecting the membrane properties.

While most of the high performance PVDF hollow fiber membranes were claimed to be prepared through a TIPS method, a conventional phase inversion immersion precipitation method still remains as a convenient and promising way to produce PVDF hollow fiber membranes from SiO_2 particles with a considerably high water permeability, without affecting the mechanical properties.

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