

Surface Modification of PVDF Hollow Fiber Membrane to Enhance Hydrophobicity Using Organosilanes

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ABSTRACT: This work investigates the membrane modification to enhance hydrophobicity aiming for applications as membrane contactors. The PVDF membranes were activated by NaOH and by plasma activation followed by grafting using three organosilanes. For the NaOH, the contact angle of original membranes (68°) was decreased from 44° to 31° with increasing NaOH concentration from 2.5M to 7.5M at 60°C for 3 h. The contact angle of NaOH treated membranes was increased to 100° after modification with 0.01M FAS-C8 for 24 h. A needle-like structure was observed on the membrane surface while there was no significant change in pore size and pore size distribution. Moreover, FTIR and XPS data showed Si peak and composition. The mechanical strength was improved. The surface modified membranes under helium plasma activation followed by grafting with 0.01M FAS-C8 for 24 h showed higher contact angle, mechanical strength and surface roughness than that obtained by NaOH activation method while other physical properties did not change. The long-term performance test for 15 days of operation was conducted. The modified membranes exhibited good stability and durability for CO₂ absorption. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 610–621, 2013

KEYWORDS: alkaline treatment; hydrophobicity; organosilanes; plasma activation; PVDF hollow fiber membrane; surface modification

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INTRODUCTION

Membrane contactor is a device that allows two fluid phases to come into direct contact with each other for the purpose of mass transfer between the phases, without dispersing one phase into the other. The potential membrane contacting processes are membrane distillation (MD), osmotic distillation (OD), and gas–liquid absorption and stripping processes.¹ The membranes applied in membrane contactors are typically fabricated from hydrophobic polymers to reduce the membrane wetting. Even though the membranes are highly hydrophobic, the membrane wetting can occur leading to the reduction in the performance. Membrane wetting depends on the structural characteristics of the porous material and hydrophobicity. The common hydrophobic membrane materials are polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE). Based on the contact angle data, the hydrophobicity of the mem-

branes is in the order of PTFE > PE > PP > PVDF.^{2,3} However, PTFE is much more expensive than PVDF due to the use of thermal method for fabrication. On the contrary, PVDF has received much attention as a membrane material due to its high mechanical strength, thermal stability and chemical resistance.⁴ Fabrication of PVDF membrane by phase inversion method is also much more simpler.

Recently, several studies have shown success in ceramic membrane modification to improve hydrophobicity since ceramic membranes are hydrophilic. The ceramic membranes had been successfully grafted by fluoroalkylsilanes (FAS).^{5–12} FAS are the group of compounds, which can be efficiently used to create the hydrophobicity. Grafting process, leading to the increase of the hydrophobic properties, can be performed by the reaction between OH groups of the ceramic membrane and ethoxy groups (O-Et) presented in organosilane compounds.

Table I. Specifications of the PVDF Hollow Fiber Membrane

Fiber o.d. (mm)	1.16
Fiber i.d. (mm)	0.8
Membrane pore size (μm)	0.16
Membrane porosity	70%

The methods used for modification of ceramic membranes can be applied to modified PVDF membranes. However, PVDF membranes have no hydroxyl groups. Therefore, hydroxyl groups must be introduced on the membrane surface. There are several methods to produce OH groups on the PVDF membrane surface. Examples are the chemical method (alkaline treatment), plasma treatment, and radiation. Basically, the alkaline treatment is a simple method that has been investigated to introduce OH groups on the membranes. Zheng et al.¹³ successfully prepared a superhydrophobic PVDF film by alkaline treatment enhancing chemical bath deposition method. The treated membrane using NaOH showed the lowest contact angle of 27° under 30% of NaOH at 60°C for 3 h. The contact angle of original membrane was 88°. In contrast, the contact angle of the treated membrane was increased to 157° after grafting with the mixture of dimethyldichlorosilane (DDS)/methyltrichlorosilane (MTS). Yang et al.¹⁴ conducted surface modification of PVDF membrane using LiOH solution followed by cross-linking with a perfluoro compound of perfluoropolyether containing ethoxysilane terminal groups. The contact angle was increased from 88° to 115° after modification. Wongchitphimon et al.¹⁵ studied the surface modification of polyvinylidene fluoride-*co*-hexafluoropropylene (PVDF-HFP) using 10% of NaOH followed by the mixture solution of Fluorolink®S 10 (FS10) and tetraethoxysilane (TEOS) as hydrophobic modifying agents. The contact angle of original membrane was 95.5°, whereas the contact angle of the modified membrane was 127.8°.

However, it was reported in the literature that the properties of PVDF membrane were destroyed by NaOH solution because NaOH had chemically attacked PVDF membrane and caused the dehydrofluorination in the polymer chain^{16,17}. For example, the mechanical strength and crystallinity of PVDF membranes were decreased even at 4wt% NaOH solution at 70°C within 24h or in 10wt% NaOH solution within 8h¹⁶. The reduction in mechanical strength of membrane treated by NaOH was due to the degradation of membrane as a result of the chemical reaction between PVDF membrane and NaOH. Liu et al.¹⁷ also reported the hydrophilic PVDF membrane modification by alkaline treatment. The results showed that the alkaline treatment changed the membrane surface structure based on the results of pore size distribution.

Plasma treatments can alter the surface energy of membranes and change the surface polarity which is the less damaging method of membrane modification. Plasma treatment of membranes was used in order to increase hydrophilicity by the reaction between hydrophilic monomers and membrane.^{18–20} During the plasma treatment, the membranes were exposed to a reactive environment of excited atomic, ionic, and free radical

species by hydrogen abstraction and radical formation, which resulted in modification of only the top-most nanometers of the membrane structure being altered.^{18,21} Therefore, the surface can be selectively modified for a specific application while the bulk properties of membrane are unaffected.^{21,22} Surface modification of membrane by plasma treatment is mainly achieved by using different gases including oxygen, nitrogen, argon, helium, water vapor and air.^{21–25} The use of plasma to activate the surface to generate oxide or hydroxide groups can be used in surface modification.²⁰

As mentioned above, plasma treatment can be used to activate the PVDF membrane surface in order to have the reaction with modifying agent which can replace the alkaline treatment. There is no work reported on the surface modification of PVDF membrane using plasma activation, followed by grafting with organosilane. Yang et al.¹⁴ conducted surface modification of PVDF membrane using plasma treatment followed by in situ polymerization of 1H, 1H, 2H, 2H-perfluorodecyl acrylate as hydrophobic monomer. The contact angle of modified membrane increased from 88° to 105°.

This work aimed to modify PVDF hollow fiber membranes to increase hydrophobicity using two different activation methods, alkaline treatment and plasma activation, followed by grafting with organosilanes. Three organosilanes, i.e., hexadecyltrimethoxysilane, 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane and 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane, were selected for the study. To the best of our knowledge, these organosilanes have not been used to modify PVDF membranes. Effects of NaOH concentration and grafting time were investigated. The chemical and physical changes of original and modified membranes were investigated. The stability of the modified membranes was examined by testing the CO₂ absorption flux by 2M Taurine sodium for 15 days. The modified membranes were expected to be the potential membranes for membrane contactor applications.

EXPERIMENTAL

Materials

PVDF hollow fiber membrane was supplied by Altrateck (China). The specifications of the membrane were reported by the manufacturer as listed in Table I. Aqueous sodium hydroxide (NaOH) solutions were prepared from NaOH pellets (Carlo Erba, 97%). The different organosilanes used in this study are listed in Table II. Hexane [AR® (ACS), 98.5%] was used as a solvent and deionized water was used in aqueous solution.

Methods

In order to increase hydrophobicity of PVDF hollow fiber membranes, two surface modification methods were applied to modify the original PVDF hollow fiber membrane as follows.

Chemical Modification

The chemical modification involves the hydroxylation of the PVDF membrane, namely alkaline treatment, by an aqueous NaOH solution followed by immersing in organosilane solution. First, the PVDF hollow fiber membranes were immersed in NaOH aqueous solution (2–7.5M) under magnetic stirring for 3–12 h, then the membranes were rinsed with deionized (DI)

Table II. Description of Organosilanes Used

Name	Formula	Code	Supplier
Hexadecyltrimethoxysilane	$C_{16}H_{33}Si(OCH_3)_3$	AS-C16	(Sigma-Aldrich, 85%)
1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane	$C_6F_{13}C_2H_4Si(OCH_2CH_3)_3$	FAS-C6	(Sigma-Aldrich, 98%)
1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane	$C_8F_{17}C_2H_4Si(OCH_2CH_3)_3$	FAS-C8	(Sigma-Aldrich, 97%)

water for five times in order to stop reaction. After rinsing, the membranes were immersed in an organosilane solution at fixed concentration using hexane as solvent for 6–24 h. Then, the grafted membranes were rinsed with pure hexane for five times to remove any unreacted chemicals from the membranes and were dried at 100°C in an oven for 2 h. Finally, the membranes were kept at room temperature (25°C) before characterization.

Plasma-Activated Modification

Plasma activation of the original PVDF hollow fiber membranes was conducted using a Plasma Enhancement machine (Model HD-1B) from Chang Zhou Zhongke Changtai Plasma Technology. Power was inductively supplied at a power of 80 W and the sample chamber (30 cm × 30 cm × 30 cm) was kept under vacuum. Plasma was sustained by a radio frequency (13.56 MHz) generator and was induced to the sample chamber. The plasma modification involved two steps: (1) the membranes were exposed for surface activation by plasma wave with helium gas for 180 seconds and working pressure at 10 Pa and (2) the membranes were immersed in organosilane solution with the same method as chemical modification.

Membrane Characterizations

Dynamic contact angle was measured using a tensiometer (DCAT11 Dataphysics, Germany). A lumen of fiber was glued by epoxy to measure only the outer surface contact angle. The sample was immersed into Milli-Q water and the contact angle was calculated from the wetting force based on the Wilhelmy method. The membrane morphology was observed by scanning electron microscopy (SEM) (ZEISS EVO 50). The surface infrared spectra were recorded between 650 cm^{-1} and 4000 cm^{-1} on an IR Prestige-21 Fourier transform infrared (FTIR) spectrophotometer (SHIMADZU). All spectra were required by signal averaging 50 scans at a resolution of 4 cm^{-1} in attenuated total reflection (ATR) mode.

The chemical composition of sample surface was investigated by X-ray photoelectron spectrometer (XPS; AXIS ULTRA^{DLD}, Kratos analytical, Manchester UK.). The base pressure in the XPS analysis chamber was about 5×10^{-9} torr. The samples were excited with X-ray hybrid mode 700 × 300 μm spot area with a monochromatic Al K_{α} 1,2 radiation at 1.4 keV. X-ray anode was run at 15 kV 10 mA 150 W. The photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45° with respect to the normal to the sample surface. The mean pore size and pore size distribution of the fibers were measured using a capillary flow porometer (Porous Materials, model CFP-1500A). The pores of the samples were filled with the Galwick® solution as the wetting liquid. The surface tension of Galwick® solution is 16 mJ/m².

The mechanical strength of the fibers was measured using a Zwick/Roell BT1-FR0.5TN.D14 testing machine at a constant elongation under room temperature. The surface roughness of the membrane was recorded by atomic force microscopy (AFM, SPA 400, SEIKO instrument) operated in tapping mode. Silicon nitride tips coated with Al on the reflective side, resonance frequency of 200–400 kHz and a spring constant of 25–75 N/m were used. The rate of 2 $\mu m \times 2 \mu m$ images was 1 Hz.

Long-Term Stability Study of Modified PVDF Membranes for CO₂ Absorption

To examine the stability of the modified membranes, long-term performance test for 15 days of operation was conducted. The membrane modules were made to test the CO₂ flux. The module consisted of four fibers with an effective length of 20 cm and inner diameter of 7.4 mm. The liquid absorbent, 2M Taurine sodium, flowed on the shell side and CO₂ in the lumen side of the hollow fiber membrane under counter current mode at room temperature. The feed gas flow rate was adjusted by mass flow controllers (Cole-Parmer) and measured by digital bubble meters (Bios Dender 510L). A digital peristaltic pump (MasterFlex) was used to control the liquid flow and pumped the liquid into the shell side of the hollow fibers from a 10 L container. The CO₂ flux was calculated by the difference of CO₂ flow rate before and after the membrane module. Experimental data were recorded after the contactor system was stabilized. The experimental setup of CO₂ absorption in the membrane contactor over 15 days is presented in Figure 1.

RESULTS AND DISCUSSION

Effect of NaOH Concentrations and Organosilanes

Contact Angle. The contact angle of the original membrane was 68.91°. By increasing the concentration of NaOH from

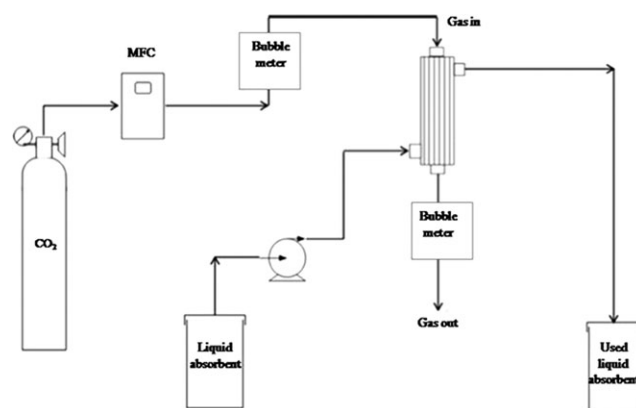


Figure 1. Experimental setup of CO₂ absorption in a membrane contactor.

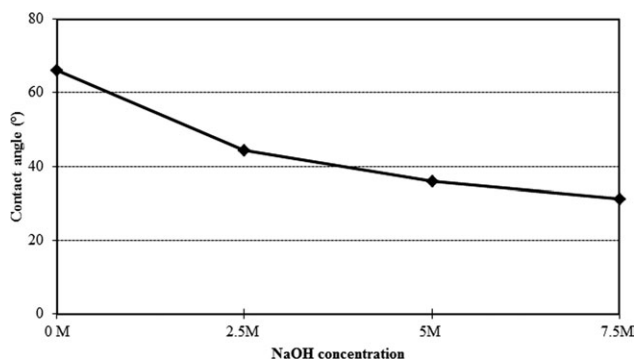


Figure 2. Contact angle of treated membrane by NaOH under 60°C for 3 h.

2.5M to 7.5M, the contact angle of membranes was decreased from 44.23° to 31.27°, respectively, as shown in Figure 2. Zheng et al.¹³ reported that with the concentration of 7.5M NaOH and treatment time for 3 h, the contact angle gradually decreased with more hydroxide and carbonyl groups found on the membrane. Dehydrofluorination mechanisms of PVDF occur by the reactions of defluorination and oxygenation, formation of hydroxide and carbonyl groups as shown in Figure 3.^{26,27}

After membrane modification by organosilanes, the results showed that the modified membranes had higher contact angles than original membrane because organosilane with three inorganic reactive groups on silicon (ethoxy) reacted with OH groups on the membrane surface. Increasing the concentration of NaOH, the contact angles of membranes were increased as shown in Figure 4(a). This was because more OH groups were generated on PVDF membrane surface. Therefore, more organosilane molecules reacted with OH groups. As the results, the modified membranes showed higher hydrophobicity. The contact angles of the modified membrane by FAS-C8 were higher than 90 (increasing hydrophobicity) compared to AS-C16 and FAS-C6 because the FAS-C8 has higher molecular weight, carbon and fluorine atoms than AS-C16 and FAS-C6. The C-F bonds of FAS-C8 act as the hydrophobic part of the molecule and the Si-(OR)₃ act as anchor at the membrane. In contrast, the element compositions of AS-C16 have no F atoms. Picard et al.⁵ found that the contact angle should increase with increasing length of fluorinated chains. However, the contact angles of

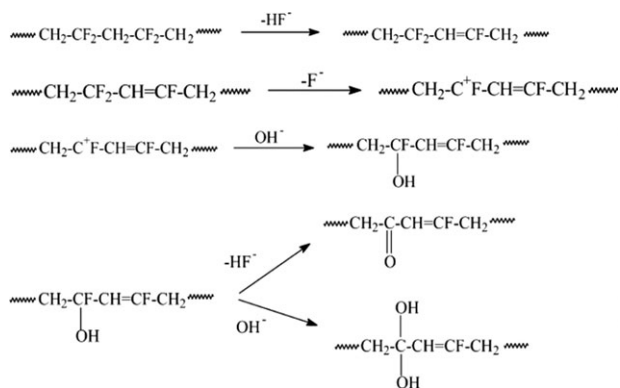


Figure 3. Dehydrofluorination mechanisms of PVDF membrane.

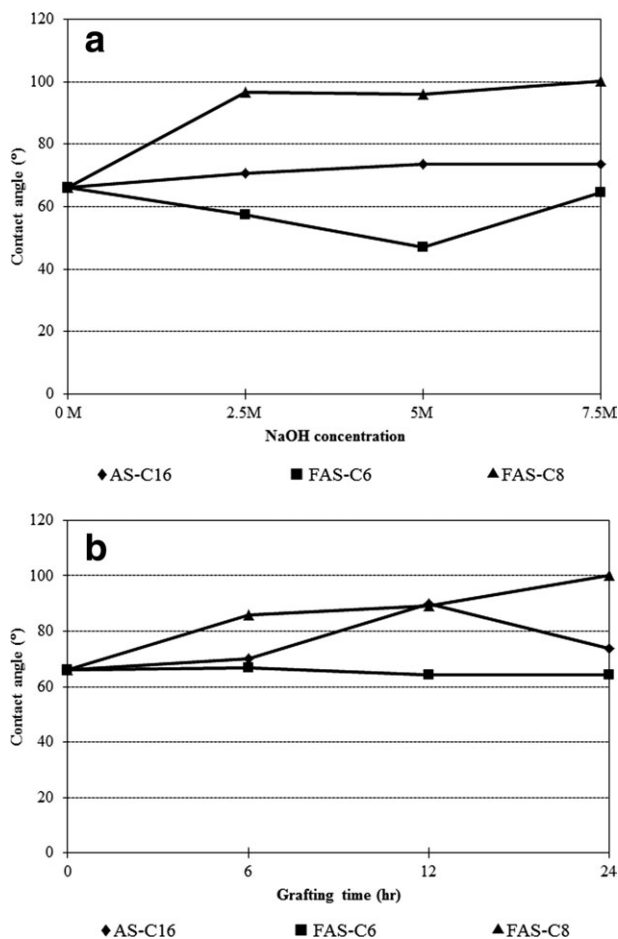


Figure 4. (a) Influence of NaOH concentration (60°C for 3 h) in 0.01M of organosilane modification for 24 h; (b) Influence of grafting time and organosilane under 7.5M NaOH (60°C for 3 h).

FAS-C6 modified membranes were decreased. This is likely due to the unsuccessful FAS-C6 grafting by a self assembly of FAS-C6 molecules. Therefore, FAS-C6 molecules were not grafted with the OH groups on the treated membrane, resulting in the reduction of contact angles.

In addition, it was observed that increasing the grafting time of organosilane, the contact angles were increased as shown in Figure 4(b). Lu et al.⁸ reported that after increasing multiplicity of grafting time, the contact angles were also increased. Zhang et al.²⁸ reported that the contact angles of the modified PAI membrane by 3-aminopropyltrimethoxysilane (APTMS) were increased from 108° to 118° with the increase in grafting time from 30 to 120 min. The highest contact angle of modified membrane in this study was 100.2° under the condition of 7.5M NaOH at 60°C for 3 h, followed by grafting 0.01M FAS-C8 for 24 h. The contact angles from this study were lower than those of Zheng et al.,¹³ Yang et al.,¹⁴ and Wongchitpimon et al.,¹⁵ which were in range of 110°–135°. Zheng et al.¹³ used mixed organosilanes (DDS and MTS) which were more hydrophobic. Yang et al.¹⁴ performed the alkaline treatment at lower NaOH concentration (2M). Wongchitpimon et al.¹⁵ used mixed solution of cross-linking agent and organosilane which was also more hydrophobic.

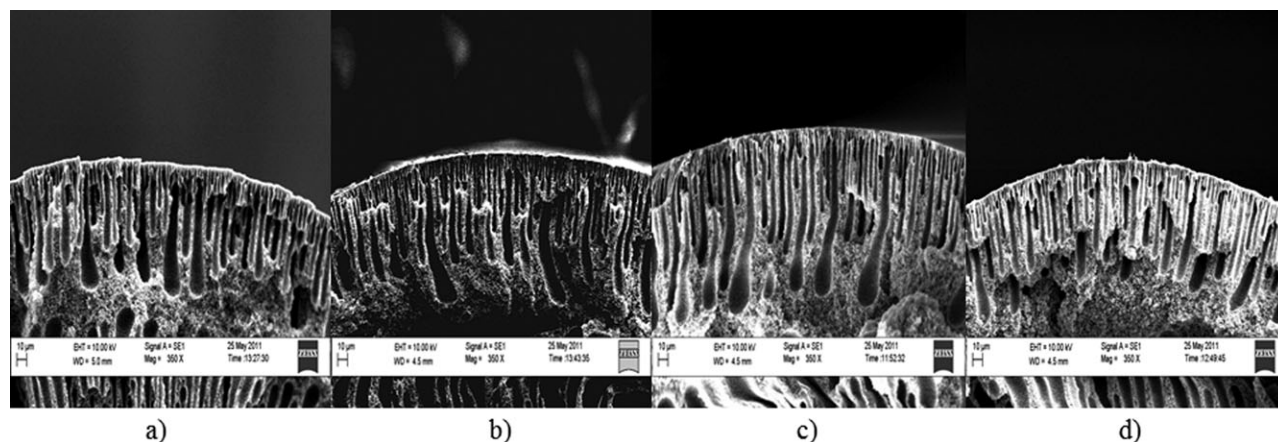


Figure 5. Cross section morphology of PVDF membrane: (a) original membrane; (b) AS-C16 modified membrane; (c) FAS-C6 modified membrane; (d) FAS-C8 modified membrane.

SEM Images. The SEM images of the cross section and outer surface of the original and modified membranes are as shown in Figures 5 and 6. The needle-like structures were formed on the modified membrane surface by 7.5M NaOH treatment, followed by grafting with 0.01M FAS-C8 for 24 h, which are randomly arranged and intertwined together as shown in Figures 5 and 6. It is known that a needle-like structure is one of the ideal surfaces for hydrophobicity.⁸ Additionally, the surface of AS-C16 modified membrane was the same as original membrane. In contrast, there were some needle-like structure on AS-C16 but they were very small compared to FAS-C8 because AS-C16 molecules have no F atoms, leading to a lower hydrophobicity. FAS molecules were hydrolyzed to a silanol, which can react with OH groups on the PVDF membrane, resulting in the formation of a self-assembled needle-like structures on the membrane. It was reported in the literature that FAS molecules are covalently attached and the nanometer-scale aggregates are generated through the further polymerization⁸ and the FAS-C8 molecular axis is predominantly oriented perpendicular to the membrane surface (needle-like structure) and partly oriented parallel on the surface. Zheng et al.¹³ also reported that the frosts or needle-like structure were also found on the modified membrane by DDS/MTS.

Meanwhile the vertical polymerization to form grafted polysiloxane could be induced on the surface. Lu et al.⁸ reported that for the membrane surface modified with FAS many needle-like structures were formed that is responsible of the superhydrophobicity of the surface.

Pore Size and Pore Size Distribution. The membrane pore size and pore size distributions of modified membrane were analyzed. Compared to the original membrane which had a maximum pore size of 0.282 μm and mean pore size of 0.1305 μm , the mean pore size and maximum pore size of modified membranes were in the range of 0.136–0.147 μm and 0.283–0.3 μm , respectively. In other words, no significant change was observed.

FTIR. The FTIR spectra of the modified PVDF membrane with organosilanes compared to the spectrum of the original membrane were given in Figures 7 and 8. There were three new peaks detected in the spectra of Figure 7. The 1634 cm^{-1} was assigned to the Si—O—Si bending. This was due to the difunctional or trifunctional silanes forming a polymerized chain on the OH groups of membrane surface^{6,29}. The 2890–2970 cm^{-1} broad band of medium intensity was CH_2 asymmetric stretching. The 3480 cm^{-1} was OH group. However, there were OH groups on the modified membrane surface indicating that all

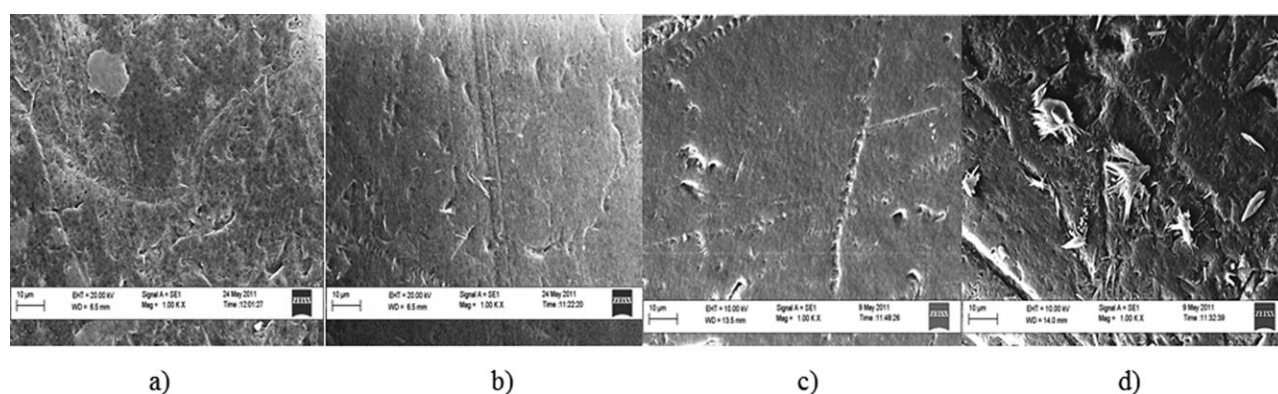


Figure 6. Outer surface morphology of PVDF membrane: (a) original membrane; (b) AS-C16 modified membrane; (c) FAS-C6 modified membrane; (d) FAS-C8 modified membrane.

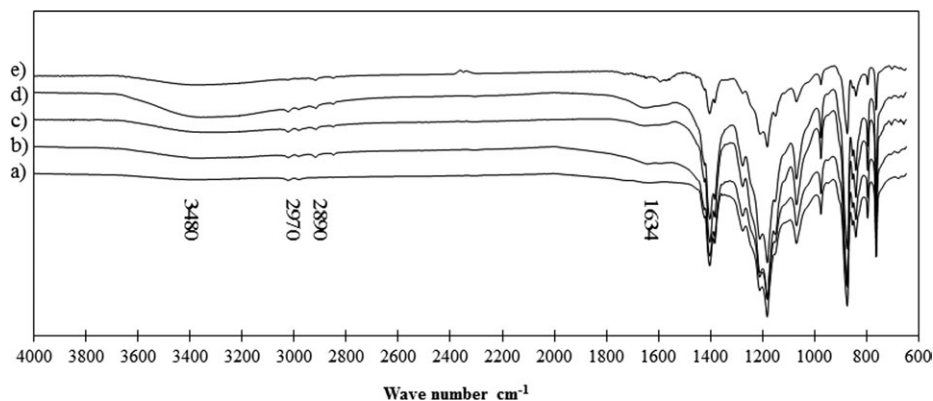


Figure 7. FTIR spectra of PVDF membrane: (a) original membrane; (b) 2.5M NaOH, 0.01M FAS-C8 for 24 h; (c) 5M NaOH, 0.01M FAS-C8 for 24 h; (d) 7.5M NaOH, 0.01M FAS-C8 for 24 h; (e) 7.5M NaOH, 0.02M FAS-C8 for 24 h.

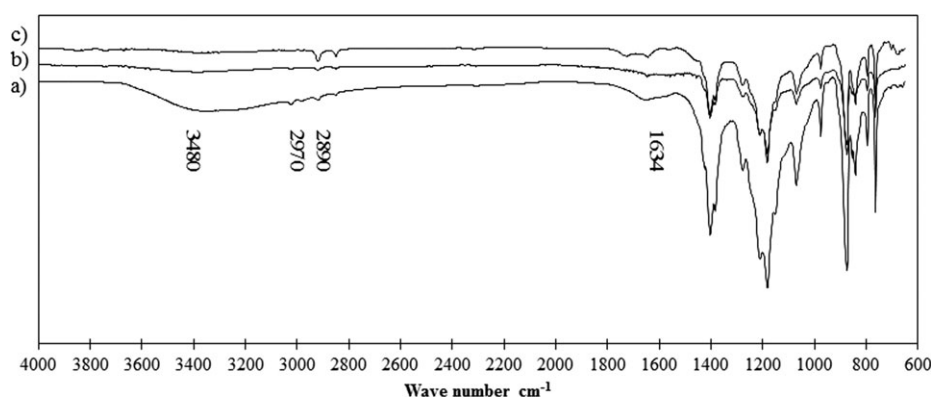


Figure 8. FTIR spectra of modified PVDF membrane by 7.5M NaOH: (a) 0.01M FAS-C8 for 24 h; (b) 0.01M FAS-C6 for 24 h; (c) 0.01M AS-C16 for 24 h.

OH may not react with the silanols in the FAS molecules. The OH peak was smaller under the higher FAS concentration because the more FAS-C8 molecules were able to react and graft with OH groups more completely. The presence of Si and CH₂ implied that there were FAS molecules and the grafting was successful. From Figure 8, the peak of Si—O—Si and CH₂ were

found on the modified membranes by three organosilanes modification. The CH₂ peaks of AS-C16 modification were stronger than FAS-C6 and FAS-C8 modifications due to the composition of AS-C16 which is consisted of CH₂ groups on its structure. Organosilanes with three reactive groups on silicon (usually methoxy, ethoxy or acetoxy) bond well to the hydroxyl groups

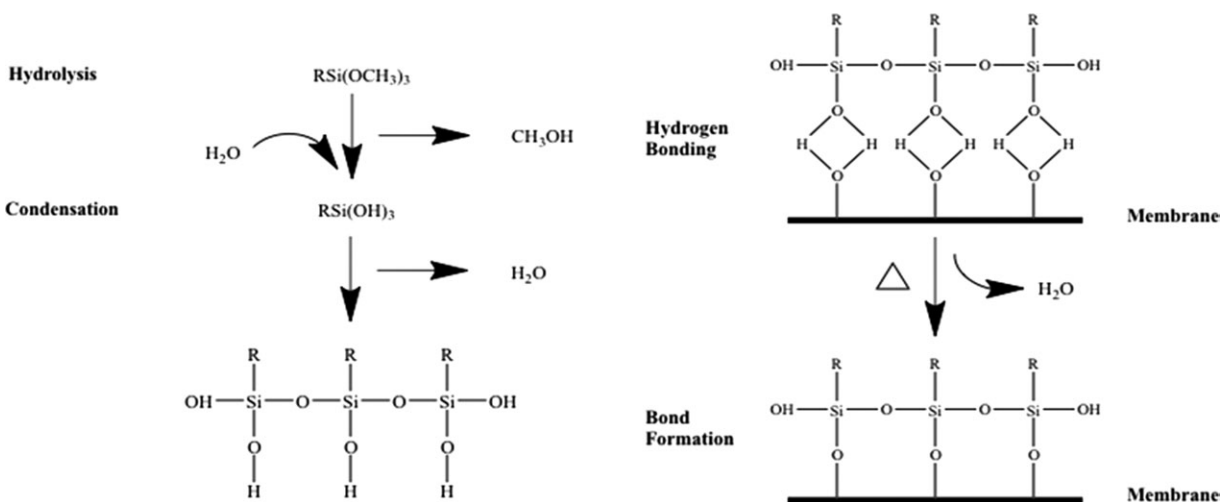


Figure 9. The hydrolysis reaction of the organosilane and the addition of the silanol groups onto the PVDF membrane surface.

Table III. Changes of the Chemical Structure of Membrane Surface

Surface	Atomic concentration (%)			
	C	F	O	Si
Original	52.5	38.9	7.1	-
Alkaline treatment: 7.5M NaOH at 60°C for 3 h				
0.01M AS-C16 for 24 h	58	7.3	27.6	1.3
0.01M FAS-C6 for 24 h	48.1	29.9	14.6	2.0
0.01M FAS-C8 for 24 h	48.7	32.9	14.6	1.9
0.02M FAS-C8 for 24 h	36.4	49.8	8.5	3.8

on the treated membrane. The alkoxy groups on silicon were hydrolyzed to silanols, either through the addition of water or from residual water. Then, the silanols coordinate with hydroxyl groups on the membrane surface to form an oxane bond and eliminate water as shown in Figure 9.

XPS. The presence of FAS on the membrane was confirmed by XPS analysis as shown in Table III. The fluorine (F) content on the surface of modified PVDF membranes decreased compared to the original membranes, except for 0.02M of FAS-C8. This is caused by the elimination of H-F during the alkaline treatment. In case of AS-C16 modification, F content was lowest because it has no F atom on its structure. In addition, oxygen (O) content of modified membranes was found because of the silanols formed. On the other hand, the amount of silicon (Si) was also found on the modified membranes. The XPS results implied that there were organosilane molecules and the grafting was successful even after rinsing with hexane for five times.

Mechanical Strength. The mechanical properties of the original and modified PVDF hollow fiber membranes are summarized in Table IV. The results showed that the tensile modulus and tensile stress of modified membranes were increased by 11–18% and 0.4–7%, respectively, in contrast, the strain at break of modified membranes was decreased by 4–17%. This implied that the rigidity of modified membranes was increased, whereas, the elasticity of modified membranes was decreased. In addition, the tensile modulus and tensile stress of modified membranes were higher than those reported by Yang et al.¹⁴ and Wongchitphimol et al.¹⁵

Comparison of Chemical Modification and Plasma-Activation Modification

The grafting conditions, 0.01M FAS-C8 for 24 h, were selected to modify PVDF hollow fiber membrane in order to increase

Table IV. Mechanical Properties of Original and Modified PVDF Membranes

Membrane	Tensile modulus (MPa)	Tensile stress (MPa)	Strain at break (%)
Original PVDF	50.5 ± 2.1	2.81 ± 0.05	219.4 ± 10.2
Alkaline treatment: 7.5M NaOH at 60°C for 3 h			
0.01M AS-C16 for 24 h	56.5 ± 3.2	2.84 ± 0.05	188.6 ± 9.8
0.01M FAS-C6 for 24 h	59.6 ± 0.9	2.89 ± 0.06	191.9 ± 10.1
0.01M FAS-C8 for 24 h	58.8 ± 5.8	3.01 ± 0.07	180.6 ± 8.5
0.02M FAS-C8 for 24 h	56.3 ± 2.3	2.82 ± 0.06	208 ± 11.2

Table V. Contact Angle and Surface Roughness of the Original and the Modified Membranes by 0.01M FAS-C8 (24 h) after Chemical and Plasma Activation

Membrane modification	Contact angle (°)	R_{rms} (nm)
Original membrane	68.91 ± 0.89	31.13
2M NaOH at room temperature for 12 h (CM(2))	119.46 ± 1.64	49.67
7.5M NaOH at 60°C for 3 h (CM(7.5))	100.20 ± 2.97	48.77
Plasma-activated modification	145.61 ± 3.11	53.65

hydrophobicity. The two chemical modifications, which were 2M NaOH under room temperature for 12 h and 7.5M NaOH at 60°C for 3 h, namely CM(2) and CM(7.5), respectively, were selected to compare with original membrane and plasma-activation modification (PAM).

Contact Angle. The contact angles of modified membrane treated by CM and PAM are summarized in Table V. Overall, the contact angles of the modified membranes were increased. Both conditions of chemical modification [CM(2) and CM(7.5)] resulted increased the contact angle but the CM(2) showed higher contact angle than CM(7.5). The contact angles of the modified by CM(2) and PAM were 119.46° and 145.61°, respectively. Wongchitphimon et al.¹⁵ found that the contact angle of modified membranes at 2.5M NaOH concentration was higher than 7.5M NaOH.

Additionally, Yang et al.¹⁴ reported that the contact angles of the modified membrane using chemical and plasma modifications, compared to the original membranes were increased by 20 and 30%, respectively. The contact angles of modified membrane by CM(2) and PAM in this study were higher than the study of Yang et al.,¹⁴ which were 105° and 115° by plasma modification and chemical modification, respectively. The membranes of Yang et al.¹⁴ were modified by plasma polymerization that the monomers were added in the plasma enhancement machine for 21 ms; while the membranes in this study were immersed in FAS-C8 for 24 h.

Hashim et al.¹⁶ reported that the PVDF membrane was attacked by NaOH solution which led to the decrease in the melting temperature, melting enthalpy and crystallinity. Additionally, the decrease was accelerated by either a high temperature, or a

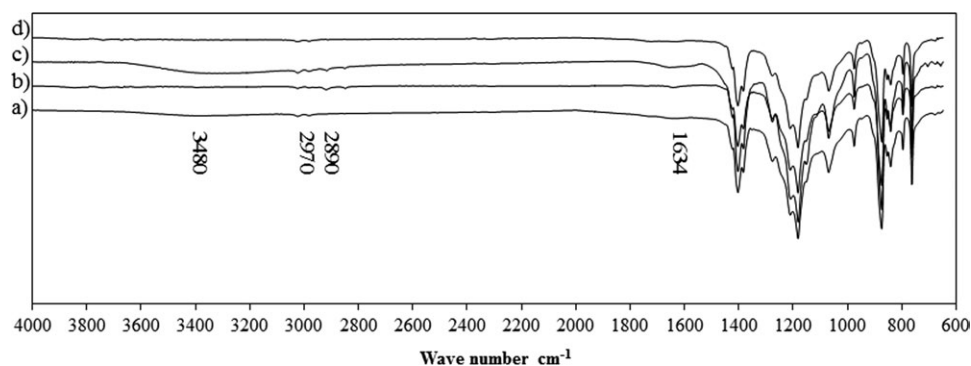


Figure 10. FTIR spectra of the PVDF membrane: (a) original membrane; (b) CM(2); (c) CM(7.5); (d) PAM.

concentrated NaOH solution. The degree of crystallinity of PVDF membranes was reduced after the NaOH treatment. In contrast, plasma activated modification showed the highest contact angle. PAM is the less damaging method of membrane modification compared to the alkaline treatment. Plasma only activates the surface of membrane to generate oxide or hydroxide groups without membrane destruction.

FTIR. In Figure 10, the FTIR spectra of the original membrane and the modified membrane with organosilanes by CM and PAM are compared. There were three new peaks detected in the spectrum of Figure 10. The 1634 cm^{-1} was assigned to the Si—O—Si bending. The $2890\text{--}2970\text{ cm}^{-1}$ broad band of medium intensity was CH_2 asymmetric stretching. The 3480 cm^{-1} was OH^- group. For the CM(7.5), there were OH groups on the membrane surface since all OH groups may not react with silanol of the FAS molecules. Under the PAM, membrane surfaces were activated by helium plasma activation, which followed by grafting with FAS-C8. Polar functional groups can be introduced on membrane surface after breaking C—C and C—H bonds²³. The OH peak was undetected due to the complete chemical reaction between OH and silanol forms. As a result, the contact angles of membrane modified by PAM were higher than by CM.

XPS. The XPS analytical results were shown in Table VI. The fluorine (F) content on the surface of modified PVDF membranes increased compared with that of the original membranes, except the CM(7.5). This is caused by the elimination of H-F during the alkaline treatment due to high NaOH concentration in which F atoms were released from the PVDF membrane.

Table VI. Changes of the Chemical Structure of Membrane Surface

Membrane modification	Atomic concentration (%)			
	C	F	O	Si
Original membrane	52.5	38.9	7.1	-
CM(2)	43.99	48.98	4.85	1.07
CM(7.5)	48.7	32.9	14.6	1.9
PAM	39.44	46.96	10.21	2.7

*The membranes were modified in 0.01M FAS-C8 for 24 h.

In case of PAM, Si content was higher and the XPS results implied that there were organosilane molecules and the grafting was successful. The exposure of the He plasma treated membrane to atmosphere caused the attachment of oxygen molecules on the PVDF membranes resulting in the OH groups on the membrane surface. Wavhal and Fisher¹⁹ and Liu et al.⁴ reported that when the membrane was exposed to argon plasma, and then to air, there were the formations of oxide and peroxide. Figure 11 shows XPS spectra obtained from the PVDF membrane surface grafted with FAS-C8 solution. Three elemental compositions (Si 2s at 153 eV, Si 2p at 102.4–102.7 eV, C 1s at 284.8 eV and O 1s at 531.71–533.12eV) were clearly observed. The Si 2p, Si 2s, C 1s, and O 1s components originated from the Si— CH_3 , Si—O, CH_3 —Si, and O—Si groups, respectively. The Si 2p and Si 2s were from FAS-C8. Zheng et al.¹³ reported that the Si— CH_3 , Si—O, CH_3 —Si, and O—Si groups were found on the membrane surface modified by polydimethylsiloxane and polymethylsiloxane solution. Additionally, Na was found on the membrane surface as shown in Figure 11(d) due to the residue of NaOH in the cleaning step which due to high concentration of NaOH. The O 1s spectra in Figure 11(b) showed that the membranes were activated by helium plasma, and then were attacked by the oxygen in the atmosphere followed by the reaction with the silanol of FAS-C8, which is indicated by a stronger increase of the corresponding peak at 531.71 eV than the original membrane. In contrast, there was a significant increase in the intensity of O 1s in 7.5M NaOH treated membrane as shown in Figure 11(d). This may be the results of oxygen in the ether group at 533.12 eV.¹⁹

Pore Size and Pore Size Distribution. The membrane pore size and pore size distributions were illustrated in Figure 12. Compared with the original membrane which had a maximum pore size of $0.282\text{ }\mu\text{m}$ and mean pore size of $0.1305\text{ }\mu\text{m}$, the pore size and pore size distribution after modification were in the range of $0.136\text{--}0.1396\text{ }\mu\text{m}$ and $0.2361\text{--}0.3\text{ }\mu\text{m}$, respectively.

SEM Images. Figure 13 displays the morphology observations of the outer surface of the original and modified membranes. The outer surfaces of the modified membrane from both CM and PAM were not significantly different.

AFM Images. The effect of modification on surface roughness was shown in Figure 14 at a scan size $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$. The root-mean-squared roughness (R_{rms}) was used to report the data in

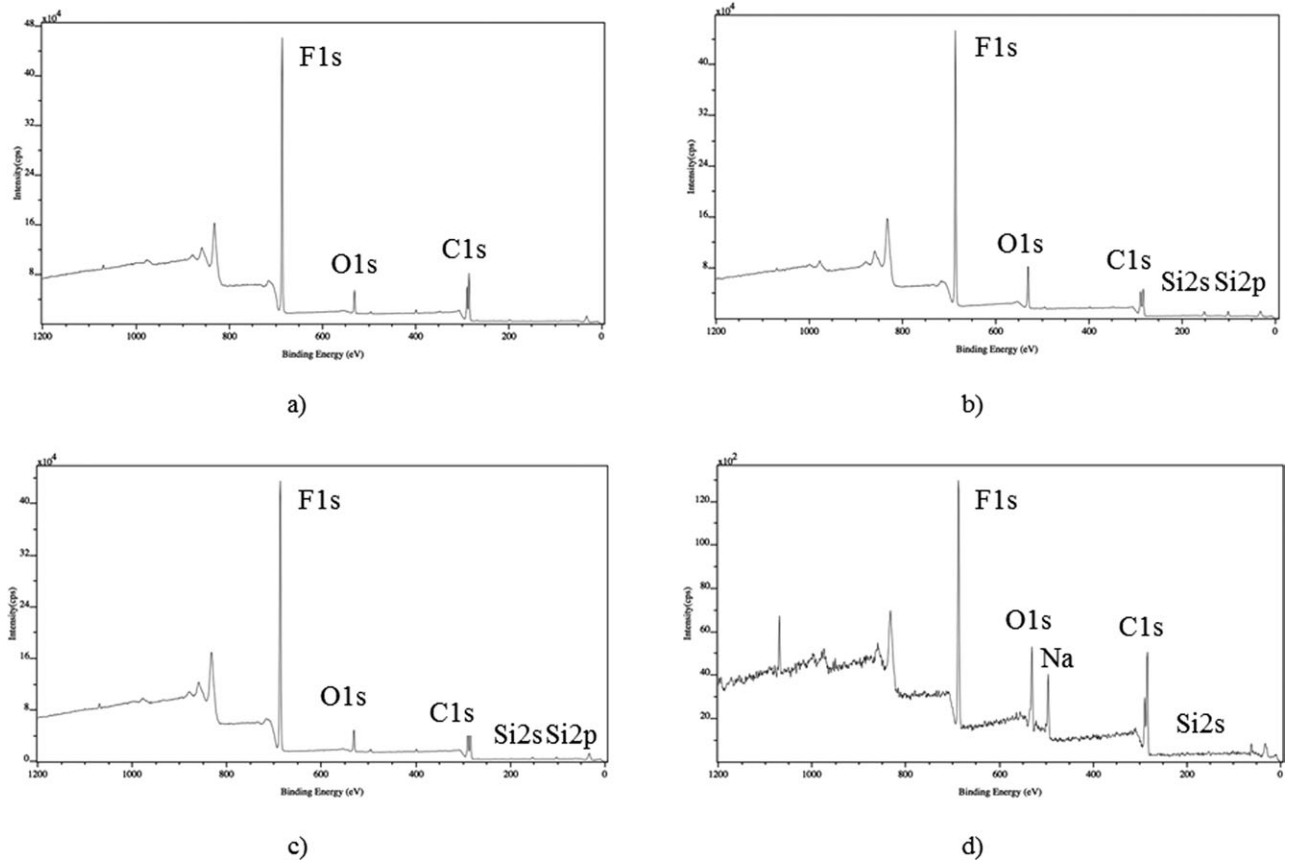


Figure 11. XPS spectra: (a) original membrane; (b) PAM; (c) CM(2); (d) CM(7.5).

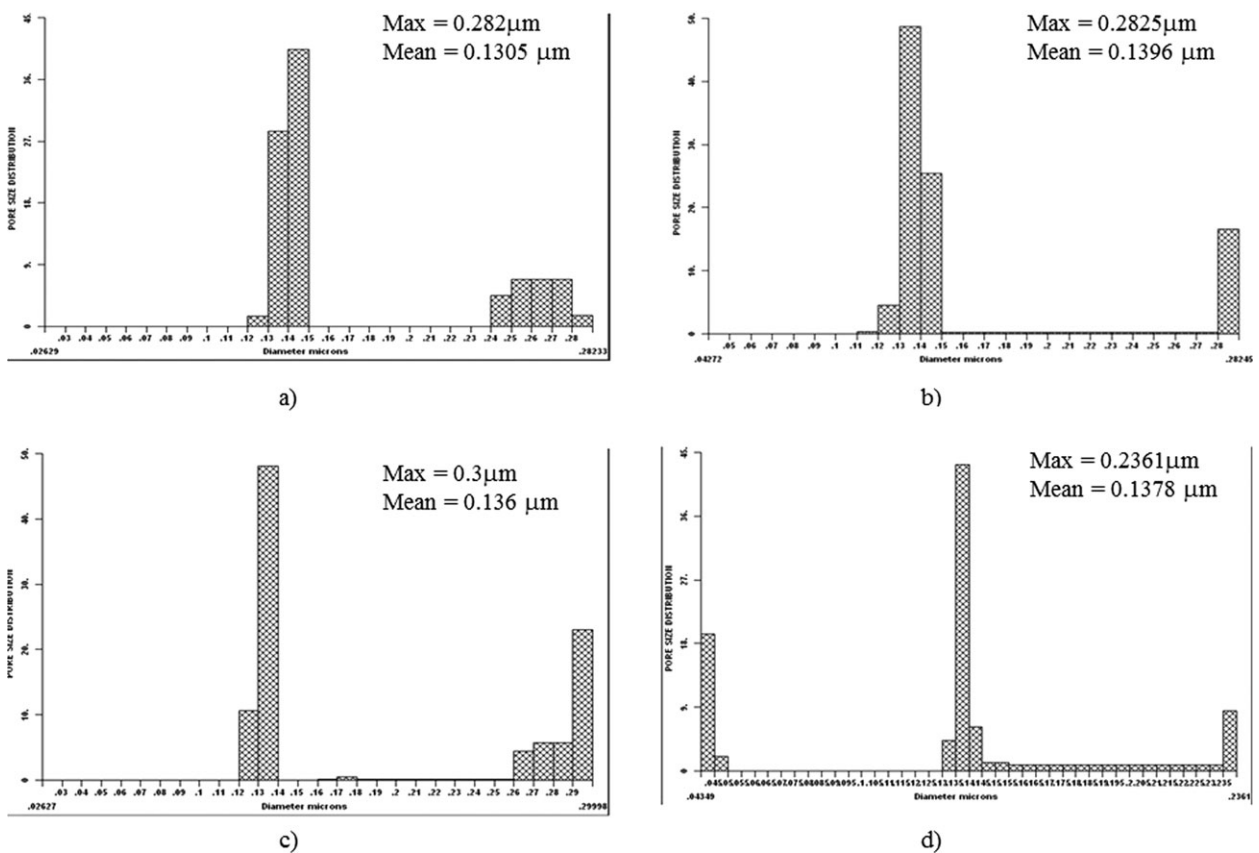


Figure 12. Pore size and pore size distribution of the original and modified membranes: (a) original membrane; (b), PAM; (c) CM(2); (d) (CM)7.5.

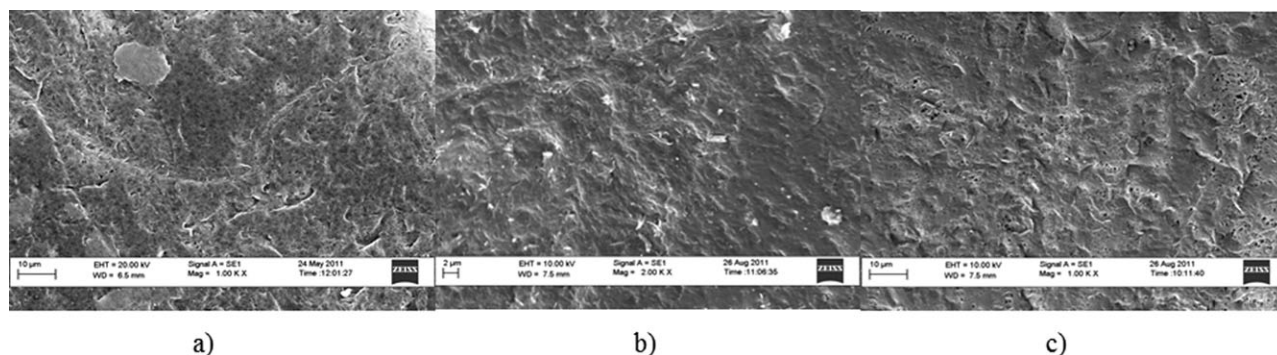


Figure 13. SEM images of the original membrane and modified membrane: (a) original membrane; (b) CM(2); (d) PAM.

Table V. The 3D images indicated that the surface modifications increased the surface roughness of membrane. The R_{rms} of membrane was increased from 31.13 nm for original membrane to 53.65 nm for modified membranes. The modified membrane surfaces were covered by many small peaks. The modified surfaces became rougher and revealed numerous bumps. The increase of surface roughness after modification can confirm the grafting of organosilane on the surface that also led to the increase in the contact angles. The roughness of the membrane surfaces increases with contact angles leading to high membrane hydrophobicity.³⁰

Table VII shows the comparison of modified membrane's properties with reported ones by different groups in the literature. The contact angle of modified membrane by the condition of CM(7.5) was 100.2°, which was lower than those of Zheng et al.¹³ and Yang et al.,¹⁴ which were in range of 105°–135°. Zheng et al.¹³ used mixed organosilanes (DDS and MTS) which were more hydrophobic. Yang et al.¹⁴ performed the alkaline treatment at lower NaOH concentration (2M), while Rahbari-Sisakht et al.³¹ used surface modifying macromolecule which was also more hydrophobic.

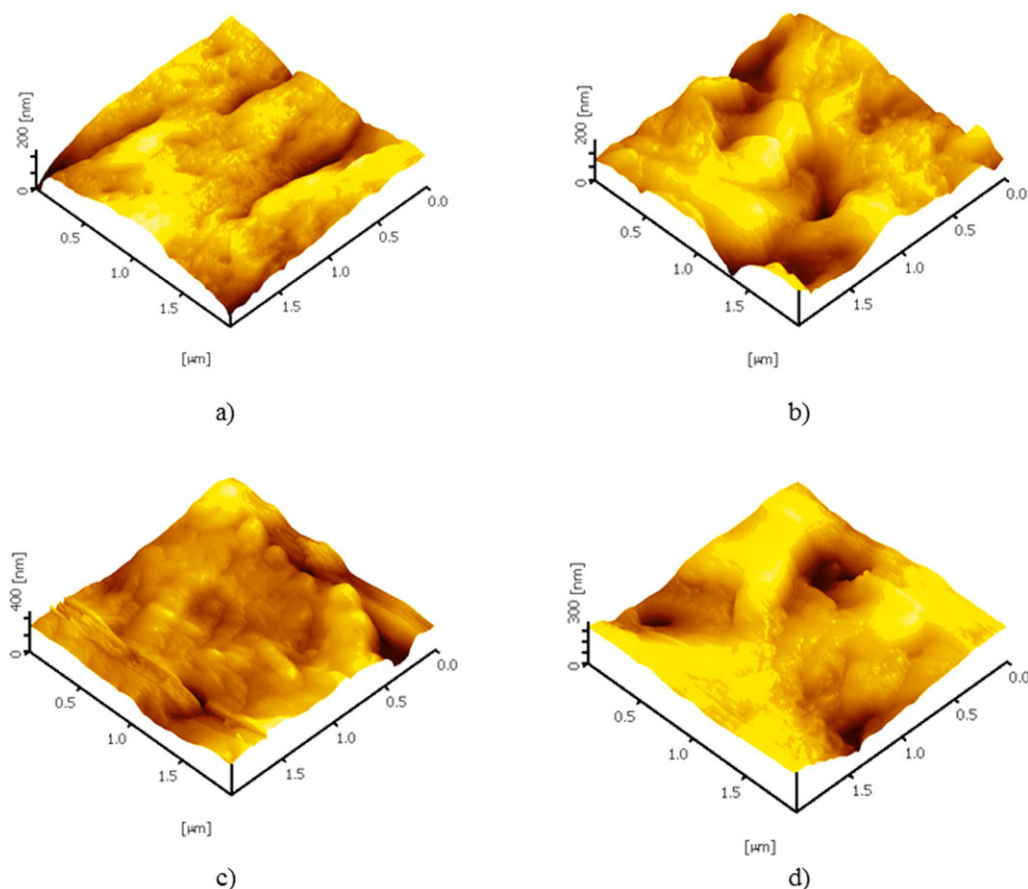


Figure 14. AFM 3D images of membranes: (a) original membrane; (b) CM(2); (c) CM(7.5); (d) PAM [all modified by 0.01M FAS-C8 (24 h)]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VII. Comparison of Various PVDF Hydrophobic Membrane Modifications

Reference	Membrane	Treatment condition	Contact angle (°)	Mechanical properties			
				Tensile Modulus	Tensile stress	Strain at break	Mean pore size
13	PVDF film	7.5M NaOH at 60°C for 3 h, 20%DDS/MTS for 30 min	157	-	-	-	-
14	PVDF hollow fiber	(1) 1-2M NaOH for 12 h, grafting with perfluoropolyether with ethoxysilane	115	Increase	-	Increase	Bigger
		(2) polymerization with 1H, 1H, 2H, 2H-perfluorodecyl acrylate	105	Decrease	-	Increase	Bigger
31	PVDF hollow fiber	Surface modifying macromolecule	92 ± 1.25	-	-	-	Bigger
Current work	PVDF hollow fiber	(1) 7.5M NaOH for 3 h at 60°C, 0.01M FAS-C8 for 24 h (CM(7.5))	100.2 ± 2.97	Increase	Increase	Decrease	No significant change
		(2) 2M NaOH for 12 h, 0.01M FAS-C8 for 24 h (CM(2))	119.46 ± 1.64	Increase	Increase	Decrease	No significant change
		(3) Helium plasma activation, 0.01M FAS-C8 for 24 h (PAM)	145.61 ± 3.11	Increase	Increase	Decrease	No significant change

However, both conditions of CM(2) and PAM in the current work resulted in an increased contact angle higher than CM(7.5). The contact angles of the modified by CM(2) and PAM were 119.46° and 145.61°, respectively which were higher than those of Zheng et al.¹³ and Yang et al.¹⁴

Moreover, the modified membranes in this study presented good performance of mechanical strength in term of tensile modulus and tensile strength which are similar to the study of

Zheng et al.¹³. However, the strain at break of membrane in this study was decreased while the modified membranes of Yang et al.¹⁴ were increased. It is worthy to mention that the mean pore sizes of modified membranes in this study show an insignificant change, whereas the modified membrane of Yang et al.¹⁴ and Rahbari-Sisakht et al.³¹ became bigger, which may play an adverse impact on the membrane performance.

Stability Test of Modified PVDF Membranes for CO₂ Absorption

The modified membranes were applied to study that used as membrane contactor for CO₂ absorption. The CO₂ absorption flux of original and modified membranes is shown in Figure 15. The CO₂ flux of the original membranes decreased from 7.7×10^{-3} to 3.1×10^{-3} mol/m².s, which is 40.3% of the initial value, during the 15 days operation. In the case of modified membrane by PAM and CM(2), the CO₂ fluxes were stable during 15 days operation. The CO₂ flux of PAM was higher than CM(2). This is because the modified membranes were more hydrophobic than the original membranes in term of contact angle; the modified membranes can reduce the membrane wetting. Therefore, the grafted hydrophobic layer (the chain side of organosilane) can resist the water penetration to the membrane. According to the results, the membrane showed a stable performance for 15 days, suggesting that the reactions between membrane and organosilane were relatively stable within this period of time.

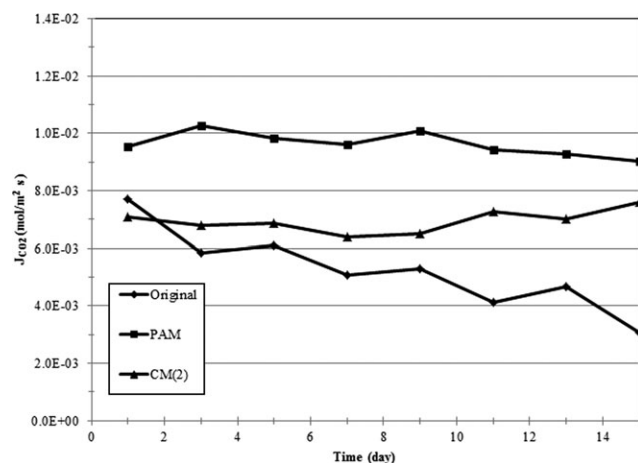


Figure 15. Membrane performance for CO₂ absorption over 15 days of operation.

CONCLUSIONS

The modification conditions of this study by chemical and plasma-activated modifications were investigated by varying the modification parameters including NaOH and organosilane concentrations, types of organosilanes and grafting time. The original and modified membranes were characterized for FTIR, XPS, contact angle, SEM and AFM images, pore size and pore size distribution, and mechanical strength. The results showed that the contact angle of original membrane (68.91°) were decreased after alkaline treatment from 44° to 31° with increasing NaOH concentration from 2.5M to 7.5M at 60°C for 3 h. For the chemical modification, the contact angle of NaOH treated membranes was increased to 100.2° after modification with 0.01M FAS-C8 for 24 h. Additionally, the contact angles increased with grafting time and number of functional groups of organosilanes. A needle-like structure was observed on membrane surface after modification while there was no significant change in pore size and pore size distribution. Moreover, FTIR and XPS data showed the peak and chemical composition of Si. The mechanical strength of membranes was also improved after modification. In contrast, the contact angle of the modified membrane was increased to 119.46° after decreasing NaOH concentration from 7.5M to 2M and immersing the membrane for 12 h under room condition, followed by grafting of 0.01M of FAS-C8 for 24 h.

The comparison between chemical modification and helium plasma activation followed by grafting 0.01M FAS-C8 for 24 h showed that the contact angle of modified membrane under helium plasma activation followed by grafting 0.01M FAS-C8 for 24 h (145.61°) was higher than the 2M NaOH followed by grafting 0.01M FAS-C8 for 24 h (119.46°). The mechanical strength and surface roughness of modified membranes were also enhanced while other physical properties did not change.

In the long-term performance, the modified PVDF membranes exhibited more stable and durable than the original PVDF membranes. This result clearly indicated the feasibility of improving the membrane performance in membrane contactor by surface modification.

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