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Effect of post-treatment routes on the performance of PVDF-TEOS hollow fiber membranes

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Abstract. Membrane separation is widely used for several applications such as water treatment, membrane reactors and climate change. Cross-linked organic-inorganic hybrid polyvinylidene fluoride (PVDF) / Tetraethyl orthosilicate (TEOS) was adopted for the preparation of optimized hollow membrane (HFM) for membrane distillation or other low pressure separators for mechanical properties and permeability under varying pretreatment schemes. HFMs were prepared on semi-pilot membrane fabrication system. Novel adopted post-treatment schemes involved soaking in glycerol, magnesium sulphate ($MgSO_4$), sodium hypochlorite (NaOCl), and isopropanol for different durations. All fibers were characterized for morphology using a scanning electron microscope (SEM), surface roughness using atomic force microscope (AFM), elemental composition by examining Energy Dispersive Spectroscopy (EDS), water contact angle (CA^o) and porosity. The performance of the fibers was evaluated for pure water permeation flux (PWF). Post-treatment with $MgSO_4$ gave the highest both tensile modulus and flux. Assessment of properties and performance revealed comparable results with other organic-inorganic separators, HF or flat. In spite of few reported data on post treatment using $MgSO_4$ in presence of TEOS, this proves the potential of low cost treatment without negative impact on other membrane properties. The flux is also comparable with hypochlorite which manifests substantial precaution requirements in actual industrial use.The relatively high values of flux/bar for sample treated with TEOS, post treated with $MgSO_4$ and hypochlorite are 88 and 82 LMH/bar respectively.
Keywords: characterization; hollow fiber membranes; performance evaluation; post-treatment; PVDF; TEOS

1. Introduction

Membrane technology has served powerfully in different issues such as water shortage, water treatment, global warming, and fossil-fuel depletion (Matsuyama *et al*. 2017). Among different configurations, hollow fiber membranes offer higher productivity per unit volume and accordingly reduced foot-print modules as compared to flat-sheet membranes, thus being more beneficial for many applications (Matsuyama *et al*. 2017, Sorour *et al*. 2021). Polymeric membranes have been thoroughly investigated for numerous applications such as microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), membrane bioreactor (MBR), membrane contractors, pervaporation, and membrane distillation (MD) (Matsuyama *et al*. 2017). Tewfik *et al*. (2018) investigated the effect of spinning parameters on the morphological and the mechanical properties on the fabricated HFMs.

One of the promising polymeric materials is polyvinylidene fluoride (PVDF) due to its superior properties such as high hydrophobicity, ease of handling during fabrication, high chemical and physical resistances, high mechanical strength, and good thermal and hydrolytic stabilities (Yu *et al*. 2009, Sorour *et al*. 2021, Xu *et al*. 2021). However, membrane fouling and decrease of permeability due to its hydrophobicity are the main challenges facing its widespread application. It has been found that the penetration of coagulant (water) into the polymer dope solution is restricted during the phase inversion process (Wang *et al*. 2000). As a result, the slow coagulation rate of PVDF might cause difficulty in the preparation of highly porous membranes. Surface modification, chemical grafting, and physical blending have been used to improve the PVDF membranes performance. Blending with inorganic materials offers higher separation performances and composite membrane characteristics (Huang *et al*. 2015). Examples of inorganic particles that have been incorporated into the PVDF membrane include zirconium dioxide (ZrO_2) (Bottino *et al*. 2002), alumina (Al_2O_3) (Yan *et al*. 2009), titanium dioxide (TiO_2) (Oh *et al*. 2009) and silica (SiO_2) (Yu *et al*. 2009). Among these, Silica (SiO_2) is widely used as inorganic additive due to its mild reactivity and well-known chemical properties, as well as good compatibility with organic solvents used to prepare the PVDF solution (Bottino *et al*. 2001, Yu *et al*. 2009).

Mixing an organic polymer with a metal alkoxide, such as PVDF with Tetraethyl orthosilicate (TEOS), followed by

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a sol–gel process involving hydrolysis and poly-condensation of TEOS is considered a simple method to obtain an organic–inorganic mixture. The sol-gel technique results in improvement of the composite membrane stability and hydrophilicity keeping intact the polymer features (Yu *et al*. 2009). Zhao *et al*. (2008) have reported the preparation of PVDF membrane using a commercial amphiphilic block copolymer of poly(ethylene oxide) and poly (propylene oxide) while, Chun *et al*. (2012) prepared PVDF hollow fiber membrane with high performance (2530 $L \cdot m^{-2} \cdot h^{-1}$ MPa^{-1} , MWCO of 53000 and contact angle of 71°) using Pluronic F127 as both the pore-former and the surface modifier and LiCl as an inorganic additive. Incorporation of PTFE particles into the PVDF matrix enhanced the membrane hydrophobicity, yielding a resultant water contact angle of 103° when the PTFE loading was 50 wt% compared to other hollow fiber membrane fabrication methods (Huang *et al*. 2015).

Several studies have investigated the effect of post-treatment on membrane performance. Post-treatment was conducted to enhance membrane performance as reported by Kim (2002) and Gholami *et al*.(2003) who reduced the membrane pore size by post-treatment.Hashim *et al*. (2011) conducted post-treatment using NaOH solution and hydrofluoric acid to remove SiO_2 particles from PVDF hollow fiber membrane which showed significant improvement in pure water flux (748.4 $L/m^2/h$ and 690.7 $L/m^2/h$, respectively) without affecting the membrane tensile strength. The results of Hong and He, (2012) revealed that adding ZnO nanoparticles to PVDF composite membranes, reduced water contact angles, resulting in improved antifouling properties. Kamaludin *et al*. (2022) prepared ZnO/PVDF HFM for inhibiting bio fouling with more porous structure compared to the neat membrane due to the presence of ZnO nanoparticles.

This work is concerned with the preparation of organic-inorganic PVDF TEOS HFM membrane separator and its post-treatment using different routes. For each case, the post treated fibers have been characterized and its performance has been assessed. The ultimate aim is to identify the optimum route that provides highest mechanical properties and highest performance regarding pure water permeability (PWF). Numerous reports indicate the use of isopropanol (Khulbe 2018), hypochlorite (Saghafi 2016) and glycerol (Bildyukevich 2016) as post treatment agents for HFM. To the best of our knowledge, very scarce data are published on performance comparison with $MgSO_4$ in presence of TEOS. Further, few data are available on the dimensional change of HFM in presence of $MgSO_4$ as compared with other selected pretreatment methods which might impact the design of HFM modules.

2. Experimental investigations

2.1 Materials

Polyvinylidene fluoride (PVDF), used as the base polymer, was purchased from Alfa Aesar, Germany. Dimethylacetamide (DMAc) used as the solvent, was supplied from Carl-Roth. Polyvinyl pyrrolidone (PVP) of molecular weight (360 k) was acquired from Sigma-Aldrich and used as a pore former. TEOS was purchased from Acros, Dimethyl formamide and HCl supplied from Carl-Roth were used to prepare TEOS solution. Reverse osmosis (RO) water was used as the bore fluid and in coagulation, washing baths and, for fiber preservation. $MgSO_4$ was supplied from SD Fine Chem Limited, Formalin from Piochem, NaOCl from Research-Lab Fine Chem. Industries, Ethanol as lab grade from ALgomhoria for chemical and iso-propanol from AL Naser Pharmaceutical chemicals.

Table 1 Dope composition and operating conditions of PVDF HFMs

Parameter	S_1	S_2
Dope composition (wt%)	PVDF/DMAc/PVP (19.2/77.9/2.9)	PVDF/DMAc/PVP /TEOS (18.75/ 76.01/2.81/0.94)
Dope flow rate (ml/min)	9	
Bore fluid	Distilled water	
Bore flow rate (ml/min)	4.7	
Air gap (cm)	10	
Take-up speed (m/min)	18	

2.2 Dope preparation and spinning of PVDF HFMs

Two PVDF HFM samples were prepared, first, the control PVDF sample (S_1) and the second is the TEOS modified sample (S_2) through the incorporation of TEOS inside the dope. PVDF powders were thoroughly dried at 55°C to ensure moisture removal before dope preparation.

For S_1 dope solution, PVP 360k was only used as the pore former, while, for sample S_2, TEOS solution was prepared according to Yu *et al*. 2009, where 10 ml TEOS was added to 14 ml DMF and 1.5 ml 0.01 HCl and sonicated at 25°C for 30 minutes until the pH of the solution was 3. TEOS modified solution was then added to the prepared dope and stirred for additional 4 hours to ensure homogeneity of the dope (S_2). Two different PVDF dope compositions with and without SiO_2 (TEOS) (S_1 and S_2), respectively were prepared and stirred at 70°C for 4 days under a nitrogen blanket to ensure the formation of a homogeneous dope. Dope solutions were degassed properly before spinning using a vacuum pump.

Hollow fiber membranes were prepared by dry-wet phase inversion method through a single orifice spinneret, according to the dope and operating conditions mentioned in Table 1. Dope solution was pumped using a metering pump into a heated spin block where it was co-extruded with bore fluid, distilled water, through the spinneret. It was then passed through a specified air gap length where the dry phase-inversion took place. Then, the spun semi-formed fiber was dropped into the coagulation bath filled with RO water, where the wet phase-inversion took place. Then, the HFMs were passed through two washing baths for solvent and pore-former additives leaching from the membrane to

form the desired pore structure. Finally, the fibers were collected on a winder to be stored.

The as-spun HFMs were rinsed and soaked in RO water for 24 hours to ensure complete phase inversion as well as the removal of excess solvents and additives. The fibers were preserved in 20% glycerol to prevent pore collapse. Fibers were then washed with water before any further characterization and post-treatment, took place.

2.3 Post-treatment

Samples were post-treated as follows:

a) Soaked 2 hours in 15 to 20% glycerol (Sn G). Where n=1,2: pH= 6.8: Density= 1.26 g/l

b) Soaked 2 hours in 1% Mg SO_4: pH= 7 (Sn Mg)

c) Soaked 2 hours in 0.1%NaOCl: pH= 7.4 (Sn Cl)

d) Soaked 2 hours in (0.1% ethanol +0.1% isopropanol): pH= 6.9 (Sn Iso)

e) All samples were soaked for 2 hours, then, washed in RO water and dried before characterization.

f) All remaining fibers were stored in 0.1% formalin except those Glycerol treated.

2.4 Characterization

2.4.1 Morphological structure and composition

Morphological structures, dimensions and elemental analysis were obtained using JOEL JCM-6000 Neoscope desktop apparatus at high vacuum of 15 kV. HFMs were cut using a sharp razor, then fixed on the sample holder using carbon tape before they were gold sputtered to increase the sample conductivity to obtain better images. A minimum of 5 segments from each sample were studied and their average values were calculated to ensure the reproducibility of the results.

2.4.2 Surface roughness

Surface topography and roughness were studied using TT-AFM workshop of 1.5 micron resolution, equipped with 400X zoom video optical microscope. Samples were fixed on a magnetic plate using a double-face tape. Testing was done in the vibrating scan mode with a scan area of 5μm×5μm. "Gwidyyon" software was used to calculate roughness parameters. An average of five tested segments for each sample was obtained.

2.4.3 Mechanical properties

Mechanical properties of HFMs were tested using Tinius Olsen H5kS, a bench top tensile testing machine equipped with a 5N load cell. Testing was done at a gauge length of 100 mm and 50 mm/min jog speed. Average of 6 tested segments for each sample was obtained.

2.4.4 Water Contact angle

Hydrophobicity of the HFMs were tested through measuring their water contact angles. The contact angle was measured through manipulating of water drop shape on the samples using the OCA 15EC Contact angle model produced by the company of Data Physics Instrument Gmbh. Five different positions were tested for each HFM condition, and their average values were calculated.

2.4.5 Porosity (%)

Porosity was calculated by applying the following Eq. (1):

$$\varepsilon(\%) = \frac{\frac{(w1-w2)}{dk}}{\frac{(w1-w2)}{Dk} + \frac{w2}{Dpol}} * 100, \quad (1)$$

where w1 is the membrane wet weight, w2 is the membrane dry weight, Dk is the kerosene density and Dpol is the polymer density.For porosity calculations, three pieces of the same membrane were weighed before and after the immersion in kerosene for 24 hours. The average of the calculated triplicates was taken.

2.5 Performance evaluation

The performance of the prepared fibers has been assessed by permeability measurements of prepared samples. For each sample, about 10 fibers were potted in a suitable connection using epoxy resin to form testing modules. The pure water permeability and flux were measured using a permeability test set up provided by "Philos Membrane". The pure water flux (PWF) was calculated according to the following Eq. (2):

$$PWF = V/A/t \quad (2)$$

V is the collected volume in liters (L), A is the effective membrane area (m^2) and t is the sampling time (h) and PWF is in $L/m^2/h$.

3. Results and discussion

3.1 Characterization

3.1.1 SEM

The cross-sectional images of all the control and post treated samples have the same morphological structure, with almost regular concentric circles showing double finger-like structures where the inner finger-like structures were wider than the outer ones. Also the cross-section exhibited large macro-pores which can be attributed to TEOS addition. The slight changes in the cross-sectional dimensions are mainly due to variations during spinning process.

Yu *et al*. (2009) presented SEM cross-section of PVDF-TEOS HFM with double finger-like. However the large micro-pores were observed in the inner finger-like for TEOS 1%. The difference as compared to samples S_1 and S_2 or post treated shown in Fig. 1 may be attributed to the presence of PVP in this work. The dimensions of the pristine, with and without TEOS added to dope and post treated samples are compiled in Table 2.

Dimensional changes have been thoroughly investigated throughout the course of post treatment as presented in Table 2. Post treatment with glycerol demostrated the highest diameter increase (12%) while the highest decrease (6%) was depicted by hypochlorite treatment. The range of diameter change should be taken into consideration during

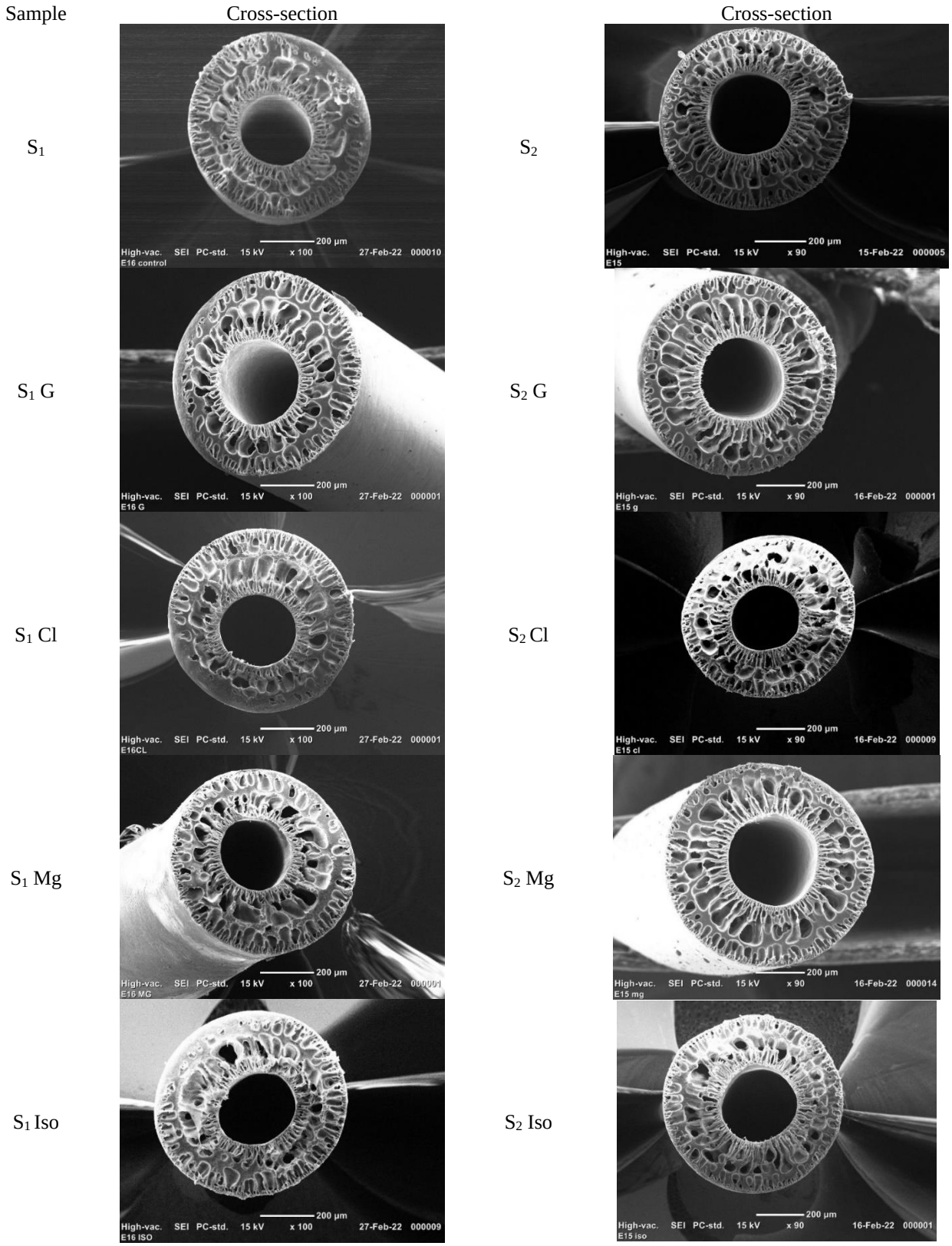


Fig 1 SEM cross-section morphology of pristine and post treated samples with and without TEOS

membrane construction to maintain the desired filling ratio. Additional research is still needed to investigate the effect of possible dimensional changes on modules efficiencies and pressure drop. Also, the mass transfer and flux indicators warrant further investigations.

3.1.2 EDS

The EDS readings, as presented in Table 3, show the elemental composition of the fibers' surfaces, where the main elements present are C (32.5 to 36.1%), N (13.5 to

Table 2 Dimensions of PVDF samples with and without TEOS, control and after post-treatment

Sample code	SEM					
	S_1			S_2		
	Do (μm)	Di (μm)	Thickness (μm)	Do (μm)	Di (μm)	Thickness (μm)
Control	699	276	220	752	335	196
G	736	315	217	824	363	235
Cl	673	269	207	633	295	200
Mg	672	263	210	706	294	208
Iso	723	286	226	727	318	202

Table 3 Composition (wt.%) of pristine and post-treated samples with and without TEOS

Sample Code	Si	Mg	Cl	F	O	N	C
S_1	0	0	0	44.98	5.49	15.62	33.91
S_1 G	0	0	0	43.68	8.6	15.19	32.53
S_1 Cl	0	0	0.36	47.4	7.38	13.5	35.76
S_1 Mg	0.11	0.22	0	40.2	8.15	16.92	34.35
S_1 Iso	0	0	0	39.78	6.87	16.59	34.72
S_2	0.17	0	0.08	41.6	6.67	16.1	34.4
S_2 G	0.22	0	0	40.1	11.9	15.1	32.5
S_2 Cl	0.14	0	0	39.4	6.65	18.5	35.3
S_2 Mg	0	0.39	0	36.3	8.35	18.7	35.9
S_2 Iso	0.17	0.17	0.07	34.8	8.54	18.1	36.1

Table 4 Mechanical properties of PVDF samples with and without TEOS pristine and after post-treatment

Sample Code	Modulus (MPa)	Break Strain (%)	Break Stress (MPa)
S_1	50.5	85.7	2.42
S_1 G	34.5	97.3	1.75
S_1 Cl	61.1	91.7	2.58
S_1 Mg	63.3	89.3	2.53
S_1 Iso	59.7	66.6	2.53
S_2			
S_2 G	51.3	76	2.2
S_2 Cl	23.0	114	1.46
S_2 Mg	72.1	85.1	2.1
S_2 Iso	54.2	89.5	2.41

18.7%), O (5.5 to 11.9%) and F (34.8 to 47.4%) indicative of the PVDF polymer, as well as Si (0.11 to 0.22%) due to TEOS addition in sample S_2, and some traces of other elements corresponding to the post-treatment regimes performed. For example, the samples post-treated with $MgSO_4$ showed up to 0.39% Mg elemental composition in sample S_2. The EDS results imply that some elements used in post-treatment remain in the fibers after soaking for prolonged times.

3.1.3 Surface roughness

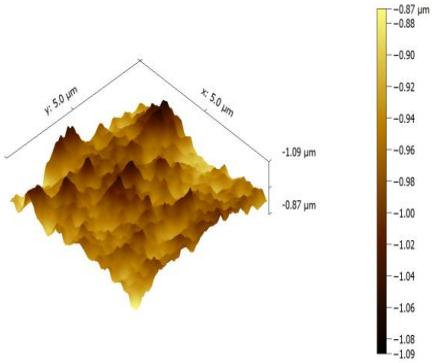
Ra is average roughness of microscopic peaks and valleys and Rms is corresponding calculated root mean square.It is observed that there has been a decrease between Ra and Rms of about (3-45%) and (15-45%) respectively for all samples with TEOS as compared to the corresponding samples without. This may be attributed to the hydrophylization effect and surface modification impact of the TEOS.

The values of Ra (nm) obtained in this work are comparable with that reported by Yu *et al*. (2009) for 3% TEOS which is 31.1nm but this was higher than the corresponding sample without TEOS which was 19.2 (nm). This difference may be attributed to the presence of PVP in this work.

3.1.4 Mechanical properties:

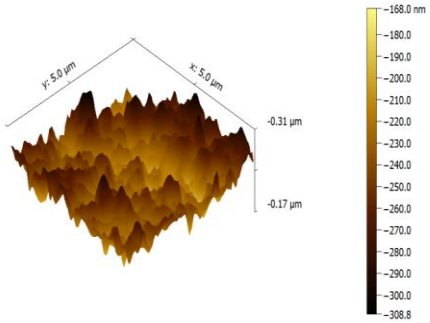
Yu *et al*. reported (2009) Modulus of 8.5 MPa which is much lower than this work. Conversely, they reported 189% elongation at break at 1% TEOS content which is higher

S_1



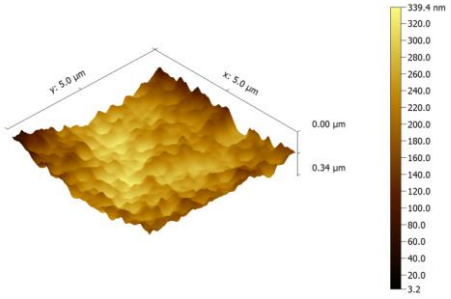
Ra=23.45nm Rms=29.85nm

S_2



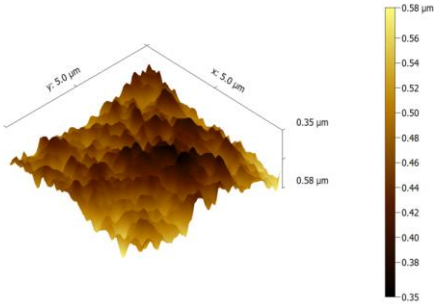
Ra=20.3nm Rms=25.8nm

S_1G



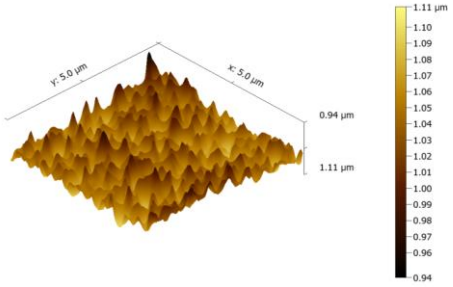
Ra=32.4nm Rms=41.16nm

S_2 G



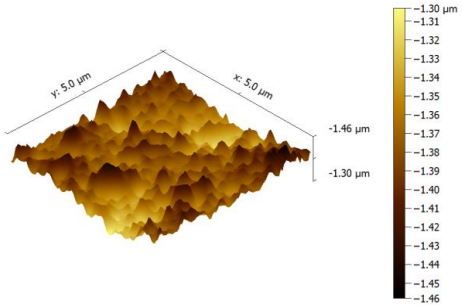
Ra=31.36nm Rms=30.5nm

S_1Cl



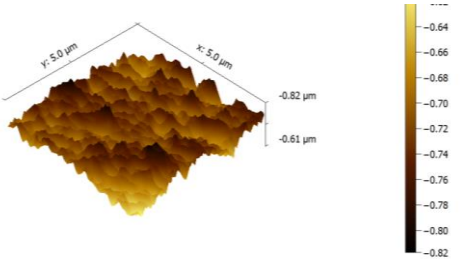
Ra= 31.74nm Rms=41.1nm

S_2 Cl



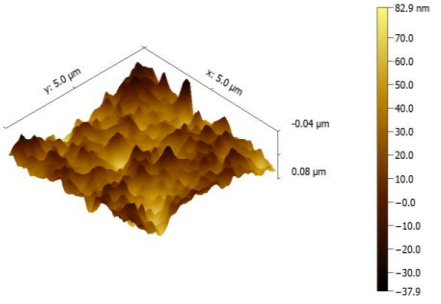
Ra=23.29nm Rms=29.24nm

S_1Mg



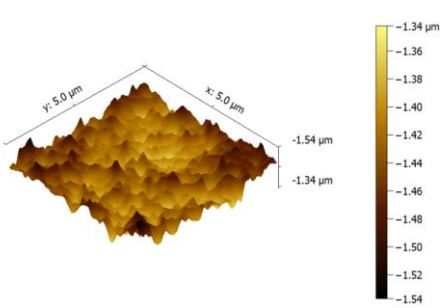
Ra=25.5nm Rms=32.1nm

S_2 Mg



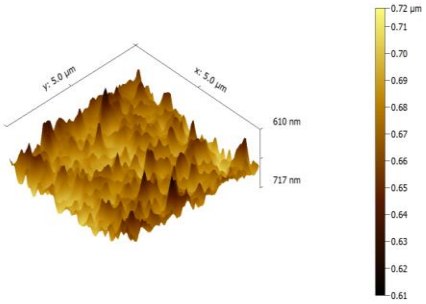
Ra=21.08nm Rms=27.28nm

S_1 Iso



Ra=25.9nm Rms=32.7nm

S_2 Iso



Ra=14.06nm Rms=17.78nm

Fig. 2 Surface Roughness: 3D images, Ra (nm) & Rms (nm) of S1, S2, control and post treated samples

Table 5 Porosity (%) of selected PVDF samples with and without TEOS after post-treatment (Iso)

Sample code	Porosity (%)
S_1	86.13
S_1Iso	86.02
S_2	88.46
S_2Iso	87.77

Table 6 Water contact angle of PVDF samples with and without TEOS and after post-treatment

Sample code	CA (^{O})
S_1	69.8
S_1G	56.4
S_1 Cl	91.8
S_1Mg	80.07
S_1Iso	72.5
S_2	74.1
S_2G	57.3
S_2Cl	69.7
S_2Mg	62.5
S_2Iso	64

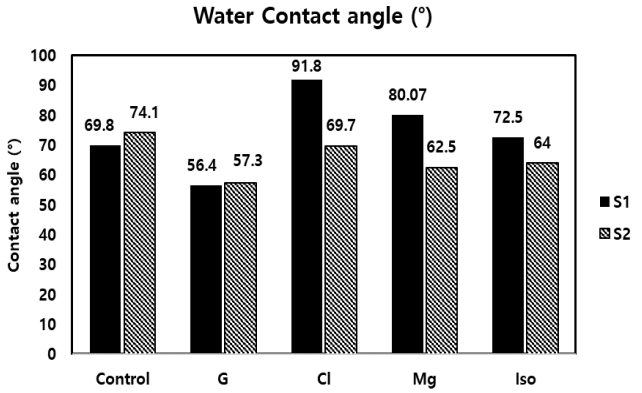


Fig. 3 Water contact angle of pristine and post treated samples with and without TEOS

than the highest value (114%) in this work, as presented in Table 4. Huang *et al*. (5) reported much lower values for all mechanical properties for PVDF TEOS flat sheet membrane at TEOS 10%.

3.1.5 Porosity(%)

Yu *et al*. (2009) reported porosity of 70% at 1% TEOS content, which is similar to the result of Huang *et al*. (2015) at 10% TEOS for flat sheet membranes. The minor increase of porosity is associated with the presence of TEOS and its changes in the final membrane matrix which also impacts dimensional changes of HFM samples.

3.1.6 Water Contact angle (^{O})

It is demonstrated as presented in Table 6 and Fig. 3 that the water contact angle ranged between as low as 56.4^o for

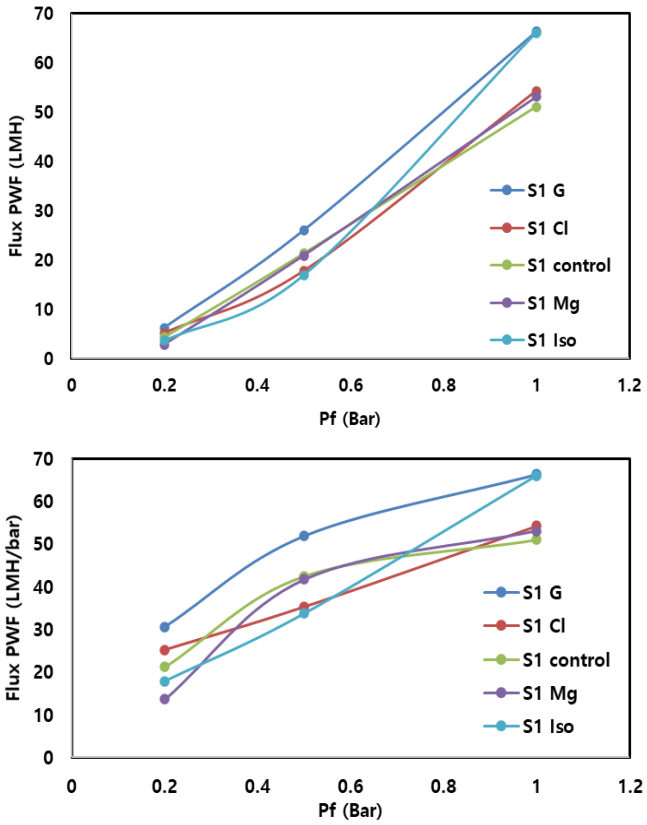


Fig. 4 PWF and PWF/bar (LMH L/m^2/h and LMH/bar) of pristine and post-treated samples without TEOS

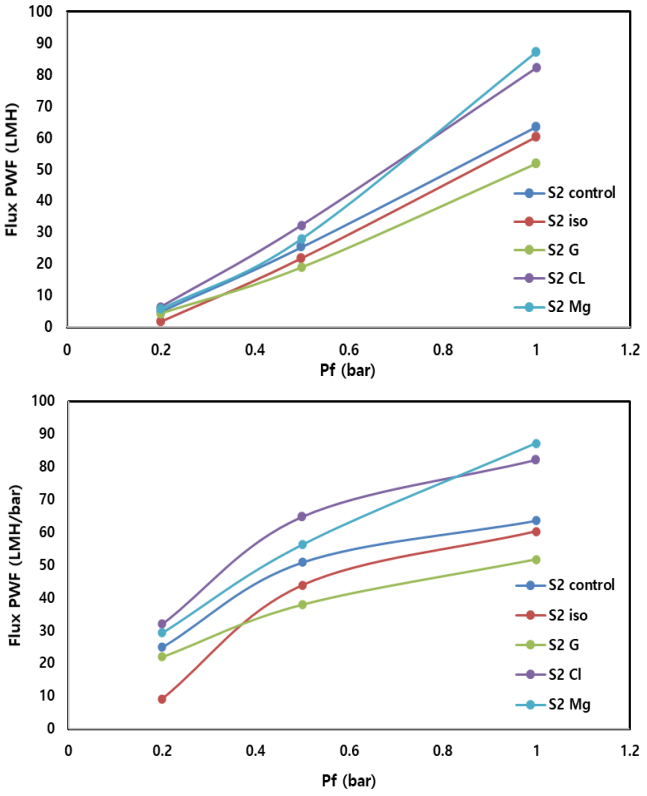


Fig. 5 PWF and PWF/bar (LMH L/m^2/h and LMH/bar) of pristine and post-treated samples with TEOS

pristine sample post-treated with glycerol and as high as 91.8° also for pristine sample post-treated with NaOCl which compares well with Yu *et al*. (2009). The impact of hypochlorite on post treated sample might be due to its moderate oxidative effect.

3.2 Performance evaluation

3.2.1 PWF – Sample 1 (S_1)

It is clearly noticed from Fig 4, that post-treatment with $MgSO_4$ and isopropanol gave significant increase of PWF which approached about 68 LMH at 1 bar while the pristine sample was about 51 LMH at the same pressure. At 0.5 bar, PWF was about 27 LMH for glycerol post treated and 20 LMH for isopropanol post treated and control respectively.

3.2.2 PWF – Sample 2 (S2)

In sample S_2 where TEOS has been added to the dope, the effect of several optional post-treatment schemes is depicted in Fig. 5. PWF on post-treatment with $MgSO_4$ and hypochlorite reached 88 and 82 LMH/bar at 1 bar for S_2 sample while the corresponding values for the pristine sample were only 51 and 52 LMH/bar respectively. These results demonstrate that significant increase has been achieved in PWF by adding TEOS to the dope and post treating the sample with $MgSO_4$.

In general it is noticed with few exceptions that the decrease of contact angle corresponds to flux increase. This is confirmed by higher flux for S_1G (contact angle 56°) and S_2Mg (contact angle 62.5°)

4. Conclusions

Fabricated PVDF/TEOS hollow fiber membranes were post treated using optional schemes including NaOCl, $MgSO_4$, glycerol and isopropanol for different durations. These membranes were characterized using SEM, AFM, water CA, porosity, and mechanical properties. Performance was evaluated through measurement of pure water permeation flux. The assessment of all samples indicated the following:

a) The cross-sectional images of all the control and post treated samples have almost the same morphological structure, with concentric circles showing double finger like structures where the inner finger-like structures were wider than the outer ones. For almost all sample S_2, dope treated with TEOS, control and post treated, the outer diameter was slightly larger than the samples untreated with TEOS, sample S_1.

b) Surface roughness of all samples S_2, pristine and post treated, where the dope was treated with TEOS, was lower than those untreated with TEOS (S_1).

c) Also, for almost all samples S_2, pristine and post treated, where the dope was treated with TEOS, the water contact angle was lower than those untreated with TEOS (S_1). However there were minor changes for the average surface porosity for both TEOS untreated and treated samples respectively.

d) The variation of mechanical properties of all membranes with TEOS addition and post treated and without TEOS is rather sporadic with no distinct pattern.

e) The HFM membranes performance indicated that for S_2 samples with TEOS addition to the dope and post treated, there has been significant increase in PWF/bar with maximum value of 88 LMH/bar attained for post-treatment with ($MgSO_4$) at 1 bar.

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