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Preparation and assessment of polyvinylidene fluoride hollow fiber membrane for desalination by membrane distillation

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ABSTRACT

Membrane distillation is an emerging thermally driven separation processes in which vapors pass through a hydrophobic microporous membrane due to temperature difference. This work is concerned with the fabrication and characterization of polyvinylidene fluoride (PVDF) hollow fiber membrane fabricated on a pilot scale spinning system using different spinnerets (D_o/D_i mm: 1.2/0.5, 1.12/0.36, 0.96/0.28, 1.25/0.36) to provide fibers of different thicknesses. Several batches have been prepared using N-methyl pyrrolidone or dimethyl formamide as solvents. Further, the effect of different additives on characteristics including polyvinylpyrrolidone (PVP 40K), polyethylene glycol, polyvinylidene fluoride-*co*-hexafluropropylene (PVDF-*co*-HFP) and nano-silica has been explored. Prepared fibers have been post treated before drying. The fibers have been characterized using scanning electron microscopy, energy-dispersive X-ray spectroscopy, atomic force microscopy (AFM), porosity and contact angle to determine internal structure, composition, morphology and surface properties. AFM results indicated average surface roughness for the raw sample ranging between 34 and 38 nm, water contact angle about 85–95° and porosity about 85%–95% Further, mechanical properties have been investigated to determine tensile properties including break force, stress, strain and Young's modulus. The later varied widely between 30 and 60 MPa. The article has been terminated with conclusions and recommendations regarding further work.

Keywords: Hollow fiber; Polyvinylidene fluoride; Additives; Characterization; Atomic force microscopy; Scanning electron microscopy; Membrane distillation; Performance evaluation

1. Introduction

Membrane distillation (MD) has gained great interest in many industrial applications, as well as, water treatment for desalination of seawater and brackish water and brine treatment [1–3]. Commercial MD plants are still in its infancy. However some demonstration and pilot plants have been reported [4]. The separation process mainly depends on the temperature gradient between feed and permeate solutions creating vapor pressure difference over the membrane surface at low operating temperature and pressure [3,5]. The main applied MD configurations comprise direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweeping gas membrane distillation (SGMD), and vacuum membrane distillation (VMD) [6]. Hollow fiber (HF) membranes has been recently studied for MD due to their favored properties including low boundary layer resistance, high surface area and high packing density [7,8]. Many polymers have been studied to prepare membranes used for MD including polypropylene (PP), polyvinylidene fluoride (PVDF),

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and polytetrafluoroethylene (PTFE) [9–11]. Recently, PVDF HF membranes have gained great attention in separations process. The main features of these membranes include distinguished hydrophobic nature, high porosity, low tortuosity, good mechanical and thermal stabilities, high liquid entry pressure, low surface energy, very high rejection and high water permeability [1,3]. PVDF shows good chemical resistance and several studies have been conducted to fabricate PVDF MD membranes with improved properties and characteristics [12].

Several organic additives have been investigated to enhance the hydrophobicity, mechanical properties, thermal stability and performance of such membranes, for example, polyethylene glycol (PEG) [13,14], polyvinylpyrrolidone (PVP) [15,16] in addition to using co-polymers such as polyvinylidene fluoride-*co*-hexafluropropylene (HFP) [17–19]. Moreover, inorganic nanomaterials have been also widely explored as additives to tune membrane structure and physicochemical properties [20,21]. Silica nanoparticles enhanced the membrane flux [22,23]. Sorour et al. [24] prepared hydrophobic PVDF hollow fiber membranes by adding LiCl and PEG and applied it to VMD of seawater. Very recently, Tibi et al. [25] improved the performance of PVDF hollow fiber membranes by adding TiO_2 and silane in addition to optimization of preparation conditions by adoption of response surface methodology for MD application. It is worth mentioning that despite the principle objective of formulating MD fibers, these fibers could be tailored via interfacial polymerization to fabricate the vital nanofiltration (NF) or ultrafiltration modules which may also be used for desalination purposes [26,27].

In this work, different additives including polyvinylpyrrolidone (PVP 40K), polyethylene glycol (PVDF-*co*-HFP) and silica nanoparticles have been added to PVDF to fabricate HF membranes for membrane distillation. The effect of these additives on membrane structure, morphology, porosity, hydrophobicity and mechanical properties have been compared and assessed. Interfacial polymerization was also undertaken and tested for selected fibers. This unique feature permits cost effective scaling-up for production of both MD and NF modules using stand-alone HF processing facility where the product of the first stage could be directed either to MD fabrication or to coating lines to develop NF modules.

2. Experimental

2.1. Materials

PVDF and silicon(IV) oxide amorphous nanopowders 99.9% (metal basis) 20 nm have been purchased from Alfa Aesar and PEG 35000, molecular weight which is used as a non-solvent additive, and PVDF-*co*-HFP have been bought from Sigma-Aldrich. NMP and DMF solvents have been supplied by Merck and Carl Roth respectively. PVP 40,000 mol wt. Additive has been supplied from Fine Chemical Industries (India). All chemicals are laboratory grade and used as received piperazine (PIP), SDFCL Sd Fine Chem Limited), m-phenylenediamine (MPD; Acros), trimesoyl chloride (TMC, Sigma-Aldrich), isophthaloyl chloride (IPC, Acros) were used for the preparation of polyamide active layer on the hollow fiber substrate. Triethylamine (TEA) and malic acid anhydride (MA) were purchased from Fisher Chemicals and SDFCL Sd Fine Chem Limited, respectively. Hexane bought from El Nasr Pharmaceutical Chemicals Company was used as organic solvent for the interfacial polymerization. All process water produced by a reverse osmosis (RO) unit treating tap water has been used.

2.2. Methods

2.2.1. HF spinning experimental set-up

HF are prepared on a semi-pilot scale unit. The system adopted is schematically represented in Fig. 1 and described elsewhere [28]. A photo of the spinning system is depicted in Fig. 2.

2.2.2. Dope and bore fluid preparation and viscosity measurements

The solvent is first added to the stirred tank jacketed vessel and the temperature is adjusted to about 70°C. For each sample the PVDF is gradually added and the RPM adjusted until complete dissolution. The additive is then added while stirring. The dope is left at set temperature and stirring conditions under nitrogen overnight for 5–6 h until complete homogenization.

For all samples, the bore fluid used has been double distilled water which is added to the dedicated jacketed vessel. The bore fluid temperature has been adjusted using a circulating water bath at 35°C–40°C. The viscosity of the polymer solution is measured after complete homogenization using Brookfield Model LVDV-II+Programmable Viscometer temperature controlled using circulating water bath.

2.2.3. HF spinning

A spin block with a single spinneret has been adopted for all experiments. Four spinneret sizes have been used viz., D_o/D_i 1,200/500, 1,120/360, 960/280 and 1,250/360 μm. PVDF spinning conditions are summarized in Table 1.

Table 1: Summary of composition and spinning condition of PVDF HF membranes.

The spin block temperature has been adjusted at 35°C–40°C using a circulating bath for all experiments. Spinning has been conducted using dry/wet phase inversion process. The dope has been pumped using a metering pump (Oerlikon Barmag). Flow rate has been adjusted using frequency inverter. Bore fluid is fed through nitrogen pressure and flow rate adjusted by ABB flowmeter.

The dope polymer mix and the bore fluid are extruded through the spinneret and the as-spun fiber exits the spinneret to fall into a coagulation bath through a preset air gap (11–15 cm). The coagulation bath is continuously fed with fresh RO water to avoid building up of solvent. Raw fibers are drawn manually to first take-up roller at adjustable tension. The fibers then pass through two consecutive washing baths with take-up rollers then collected on a reel winder. At the end of the experiment the reel winder is immersed in RO water until the next day.

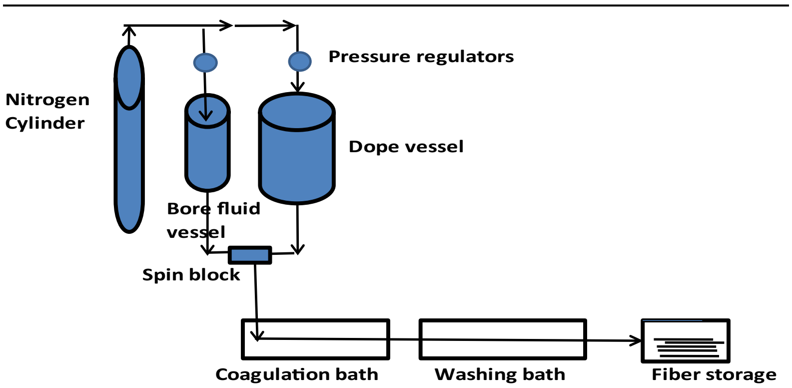


Fig. 1. Schematic diagram of spinning system.

Fig. 2. Photo of adopted pilot-scale spinning system.

Table 1a
Dope composition and viscosity

Item/code	NF/MD base 1*	NF/MD base 2*	NF/MD base 3*	NF/MD base 4*
Polymers	PVDF 17.6%	PVDF 14.9%	PVDF 14.6% PVDF-*co*-HFP 2.9%	PVDF 17.3% PVDF-*co*-HFP 1.4%
Solvent	DMF 75.2%	DMF 84.4%	NMP 80.5%	DMF 74.2%
Additives	PVP (K40) 7.2%	PEG 0.34% LiBr 0.43%	Nano-silica 1% PVP 40K 2.9%	PVP (K40) 7.1%
μ(cp)@T(°C)	3,875@40°C	3,500@40°C	5,975@40°C	3,875@40°C

Samples* codes in brackets have been the earlier ones for Samples 1, 2, 3, 4 as appearing in some SEM figures.

Table 1b
Spinning conditions

Item code	NF/MD base 1	NF/MD base 2	NF/MD base 3	NF/MD base 4
Reactor temperature (°C)	65–70	70	70	65–70
Bore fluid temperature (°C)	40	40	40	40
Flow rate mL/min (bore fluid/dope)	1	0.7	2.8:9	8:12
Spin block Temperature (°C)	45:50:00	45	45:50:00	45:50:00
Spinneret (D_o/D_i) μm	1,200/500	1,120/0.36	960/280	1,250/360
No. of spinnerets	1			
Air gap distance (cm)	11	12	15	15

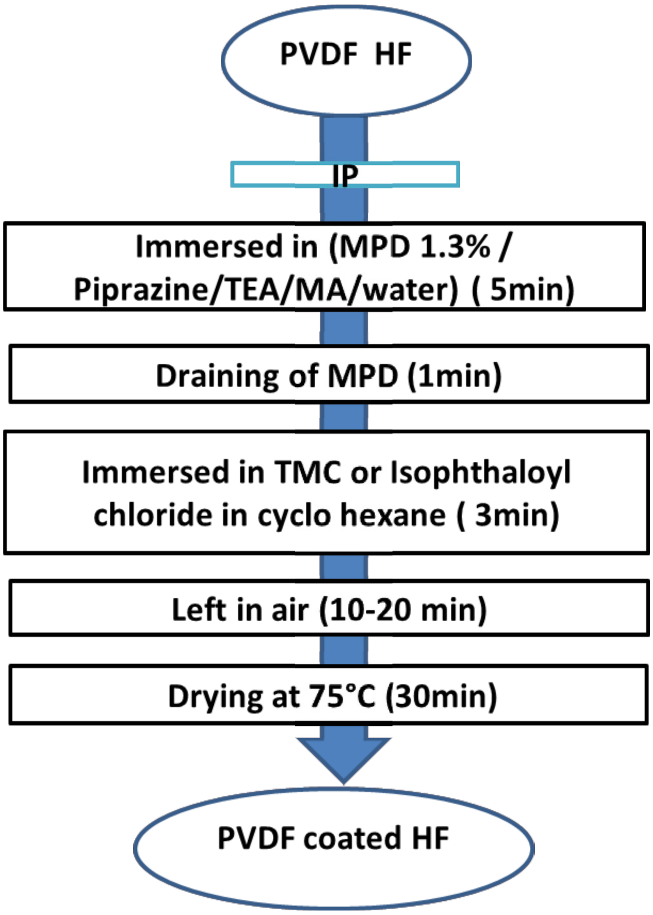


Fig. 3. Process flowsheet of interfacial polymerization of HF.

2.2.4. HF interfacial polymerization

Typical approach for formation of polyamide layer by interfacial polymerization on raw or previously coated to form a second layer is depicted in Fig. 3.

Symbols of coated samples are denoted as follows:

Treatment	Symbol
Metaphenylene diamine (MPD) + trimesoyl chloride (TMC)	MT
MPD + piperazine (PIP) + isophthaloyl chloride (IPC)	MPI

3. HF characterization

PVDF HF are characterized using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), water contact angle, porosity and mechanical properties as follows:

3.1. Scanning electron microscopy and energy-dispersive X-ray spectroscopy

Morphology and cross-section are characterized using SEM imaging scanning microscopes JEOL SEM 6000 Neoscope desktop. Fiber cross-sections have been prepared by freezing fractions in liquid nitrogen. For SEM observation, samples have been covered with a thin layer of gold using a gold-sputter. The elemental analyses of the produced PVDF hollow fibers has been evaluated by EDS.

3.2. Surface roughness

Surface roughness is measured by 1.5 micron resolution TT-AFM workshop, equipped with a video optical microscope with up to 400X zoom. A one cm long fiber sample is fixed using a double face tape on the magnetic plate of the AFM apparatus. Vibrating scan mode is used for testing a scan area of 15 µm × 15 µm. Average roughness parameters of 5 fibers have been calculated for each sample using "Gwidyyon" software.

3.3. Water contact angle

Contact angle (CA) is used to determine the hydrophobicity of each sample. The CA of the PVDF HF samples have been measured on an attention theta optical contact angle instrument (KSV Instruments Ltd.) through a digital video image of the water drop of 5 µL volume on the dried surface of the hollow fiber at 25°C. For each sample CA has been measured at five different positions and the results are presented as average of the measured values.

3.4. Porosity

The porosity of the fibers has been measured using the gravimetric method according to the reported procedure [29] by measuring the weight of the liquid entrapped within the membrane pores. The overall porosity has been estimated according to the following formula:

$$\varepsilon(\%) = \frac{\dfrac{(w_1 - w_2)}{D_k}}{\dfrac{(w_1 - w_2)}{D_k} + \dfrac{w_2}{D_{\text{pol}}}} \times 100 \qquad (1)$$

where w_1 is the weight of the wet membrane, w_2 is the weight of the dry membrane, D_k the density of kerosene (0.82 g/cm^3), D_{pol} is the density of PVDF (1.78 g/cm^3) [29]. For each sample, five measurements have been carried out and average values are presented.

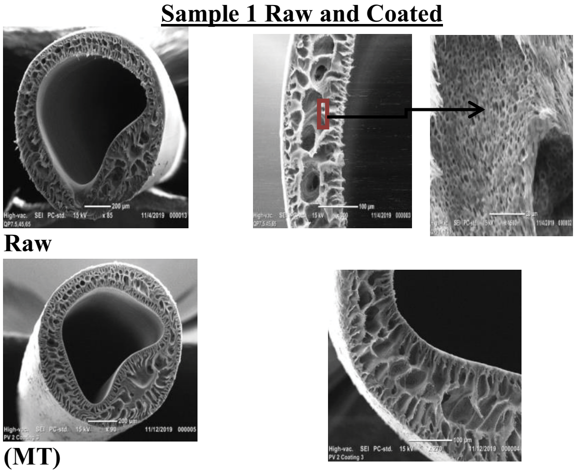
3.5. Mechanical properties

Mechanical properties of PVDF HF samples have been measured using a benchtop tensile testing machine (Tinius Olsen H5kS) provided with a 5N load cell. Testing has been conducted at 50 mm/min speed and a gauge length of 100 mm. Tensile stress, strain, elongation at break, have been measured and fibers Young's modulus has been determined.

4. Performance evaluation

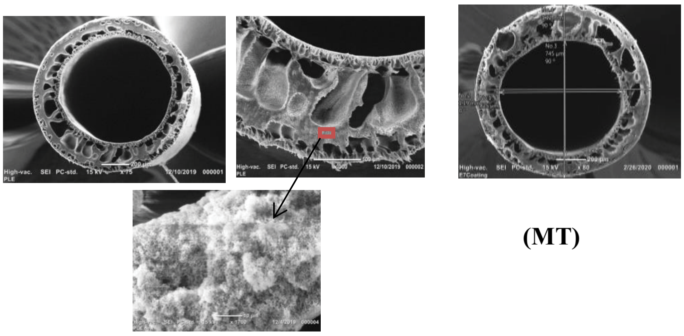
The performance of the prepared fibers has been assessed by permeability measurements of prepared samples. For each sample, about 10 fibers have been potted in a suitable connection using epoxy resin to form

Sample 1 Raw and Coated


Raw

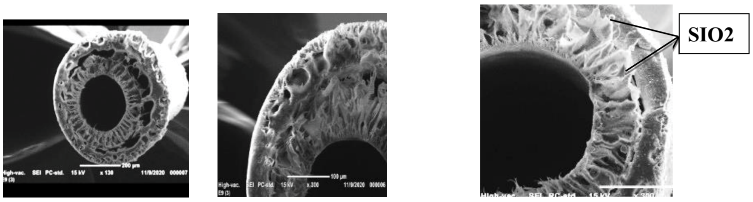
(MT)

Sample 2 Raw and coated

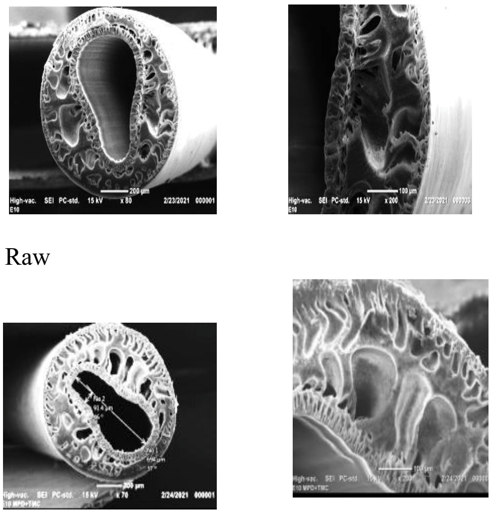

(MT)

Raw

Sample:3 Raw



Sample:4 Raw and Coated


Raw

(MT)

Fig. 4. SEM cross-section images of Samples 1, 2, 3, 4 HF raw and/or typical coated membrane samples.

min-modules. The pure water flux and permeability have been measured using a permeability tests set up provided by "Philos Membrane".

5. Results and discussion

5.1. Characterization results

5.1.1. Scanning electron microscopy

The morphologies of the hollow fibers are depicted in SEM images showing cross-section, wall thickness and sponge layer. It can be seen that fibers show finger-like and sponge-like structures, with some macrovoids on the surfaces as shown in the images presented in Fig. 4. In Sample 1, by adding PVP as the pore former to the PVDF dope solution, it is observed that macrovoids and cavities are formed near the inner layer. These cavities have increased the surface porosity of Sample 1. As reported by Simone et al. [30], macrovoids decrease with increase of PVP concentration to 15%.

The SEM images of Sample 2 in Fig. 4 shows that the prepared hollow fiber membrane has an asymmetric structure with finger like macrovoids in inner and sponge-like structure in outer surfaces. This is attributed to the presence of PEG as non-solvent additive which tends to form finger-like structure with large cavities in the membrane. Similar results are reported by Hou et al. [31] and Huang et al. [32] who also showed a similar finger and sponge-like structures for PVDF with PEG as additives.

The cross-section and wall thickness of Sample 3 as presented in Fig. 4 reveals the appearance of small particles on the membrane pores. These particles could be nano-silica which is added to the dope solution of this sample.

Sample 4 depicts larger finger-like macrovoids as compared to Sample 1. This is attributed to the presence of PVDF-*co*-HFP in the dope solution which affects demixing process and macrovoids formation. This is agreement with Wu et al. [33] who reported that the thin layer of the outer and inner membrane skin have finger-like macrovoids due to blending of PVDF and PVDF-*co*-HFP polymers.

Images of coated Samples 1, 2, 4 are depicted in Fig. 4 for Sample 4, the surface of coated PVDF membrane displays the typical rough surface of polyamide, which was confirmed by AFM where roughness increased by formation of polyamide (PA) layer [26]. Average fiber dimensions are summarized in Table 2 for Samples 1, 2, 3 and 4.

5.1.2. Atomic force microscopy

AFM results are shown in Fig. 5.

It is noted that the AFM roughness parameters of PVDF raw samples have almost the same order of magnitude. However these parameters increase with coating as reported earlier [34,35].

5.1.3. Energy-dispersive X-ray spectroscopy

EDS results of raw and coated PVDF samples are summarized in Table 3 and Fig. 6 as typical for Sample 3. EDS spectra of all PVDF hollow fiber membrane samples are analyzed to confirm the presence of nanoparticles in HF membrane. Carbon/fluoride ratio is almost constant for all raw fibers. However, Sample 3 shows the characteristic peak of nano Si with average value of about 1.5 mass%. This is attributed to the presence of SiO_2 on surface of PVDF polymer [35]. After interfacial polymerization rich Nitrogen atoms are observed on the surface of coated Samples (4MT, 4MPI), which confirm the formation of PA layer on the surface of membrane.

Table 2
Average fiber dimensions and thickness of raw and coated samples

Sample	SEM		
	D_o (µm)	D_i (µm)	Thickness (µm)
1	901	394	198.6
1 (MT)	937.5	422	203
2	1,106	777	179
2 (MT)	1,153	778	186
3	596	225	188
4	1,010	420	281
4 (MT)	1,014	432	292

Table 3
Composition as obtained by EDS for PVDF raw and coated samples

Sample code	C	N	O	F	Si	Cl
1	37.2	12.1	3.7	52.0	–	0.2
1 (MT)	37.3	18.0	12.0	32.6	–	0.1
2	30.6	12.6	3.2	53.3	–	0.2
2 (MT)	41.6	28.3	29.4		–	0.2
3	31.6	12.3	5.8	48.8	1.5	–
4	33.00	16.70	6.20	44.00	–	–
4 (MT)	34.11	19.40	21.40	25.00	–	–
4 (MPI)	36.35	22.70	19.12	21.70	–	–

5.1.4. Water contact angle

Water contact angle for a typical sample and average values for raw samples are summarized in Fig. 7a and b respectively.

Sample 1 had the highest contact angle exceeding 93%. This is in good agreement with the work of Simone et al. [30] who reported contact angles ranging between 82° ± 1° and 91° ± 1° for varying dopes rather similar composition to Sample 1 regarding PVDF and PVP but including water as non-solvent and different bore fluid composition. As for Sample 2 which essentially comprises PVDF and PEG, the contact angle has been slightly lower than Sample 1 to be about 90°. This value is rather higher than the contact angle reported by Kusuma et al. [27] who used a much higher PEG content. Contact angle for Sample 4 is much lower than Sample 3 with nano SiO_2 which improves the wetting resistance of the membrane [36].

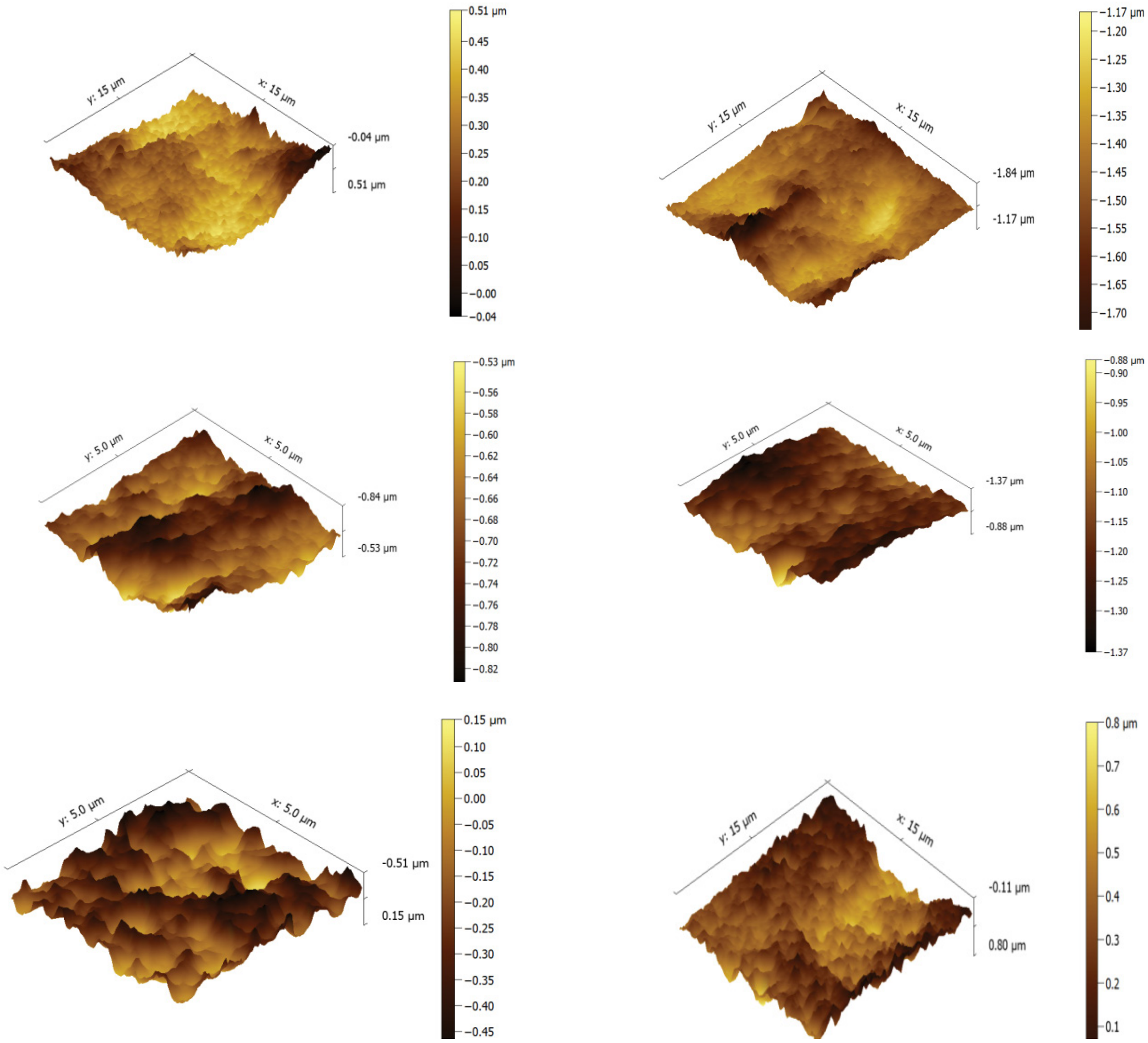
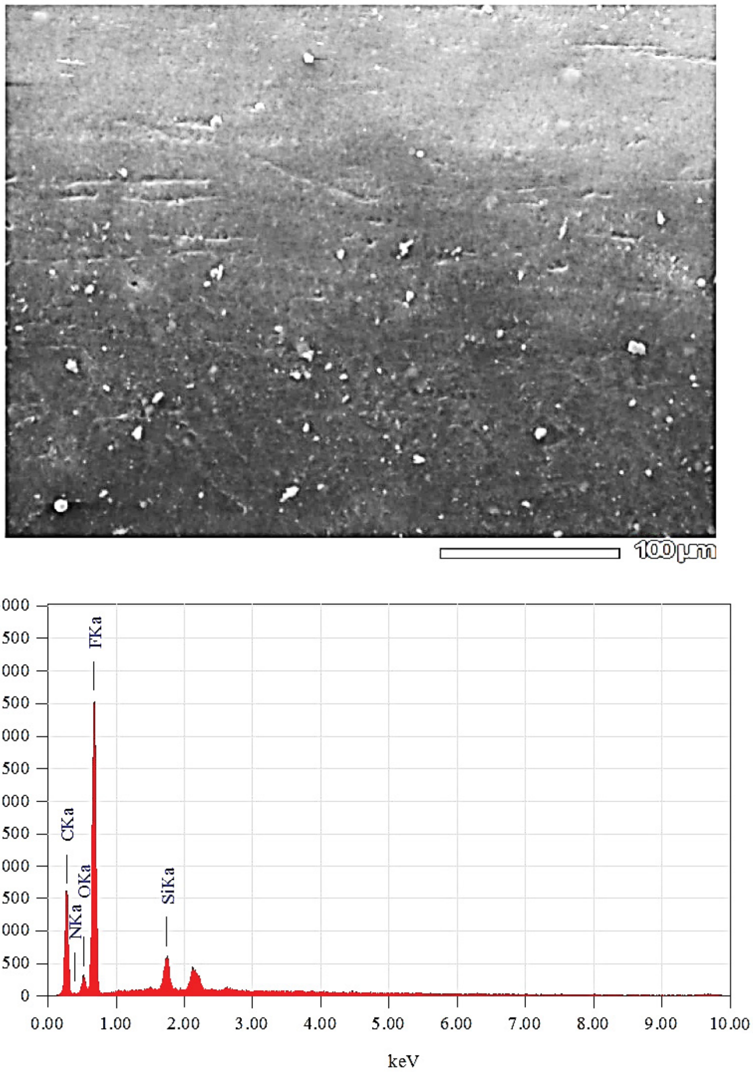


Fig. 5. AFM images and roughness parameters of raw and coated samples.

Table 4
Mechanical properties of PVDF raw and coated samples

Sample	Tensile			
	Break force (N)	Break stress (MPa)	Break strain (%)	Young's modulus (MPa)
1	0.7	1.5	93.1	30.3
2	1.1	2.2	57.3	47.8
3	0.34	1.41	35.1	40.9
4	1.26	1.86	62.1	60.5
4 (MT)	1.27	1.92	58.7	47.9
4 (MPI)	1.26	1.89	59.1	50



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Instrument     : JCM-6000
Volt           : 15.00 kV
Mag.           : x 300
Date           : 2020/11/14
Pixel          : 512 x 384
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Acquisition Parameter
Instrument     : JCM-6000
Acc. Voltage : 15.0 kV
Probe Current: 7.47500 nA
PHA mode       : T3
Real Time      : 60.98 sec
Live Time      : 60.00 sec
Dead Time      : 1 %
Counting Rate: 1662 cps
Energy Range :   0 - 20 ke\
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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1057
Element          (keV)    Mass%    Sigma    Atom%  Compound    Mass%  Cation          K
 C K             0.277    32.11     0.12    41.16                               13.0382
 N K*            0.392    11.63     0.23    12.78                                7.2234
 O K             0.525     5.56     0.11     5.35                                3.2938
 F K             0.677    49.21     0.22    39.88                               74.2490
Si K             1.739     1.50     0.03     0.82                                2.1956
Total                    100.00            100.00
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Fig. 6. EDS for Sample 3.

5.1.5. Porosity

The porosities of the raw and coated samples are presented in Fig. 8. Minor variations in porosities are observed among the raw samples. Porosities of coated samples are slightly reduced as compared to raw samples which may be attributed to the formation of the PA layer.

5.1.6. Mechanical properties

The mechanical properties of raw and coated PVDF samples are summarized in Table 4. Typical chart for Sample 4 is presented in Fig. 9.

It is noted that the maximum break strain percent exceeding 85.5% is observed for Sample 1 with PVP as additive. Sample 4 had almost the same PVDF, PVP and solvent content but a second polymer, namely PVDF-*co*-HFP has been added. It has been noticed that the break strain hardly exceeded 62% despite larger thickness. The break strain was lower for Sample 3 in presence of nano-silica where NMP, not DMF was the main solvent. The order of magnitude of Young's modulus of 40 MPa for Sample 3 is in agreement with the work of Zhou et al. [37] for nano-silica on PVDF-*co*-HFP. However, for Sample 1 where the additive in the current work is PVP 40K, the obtained Young's modulus is much lower than the findings

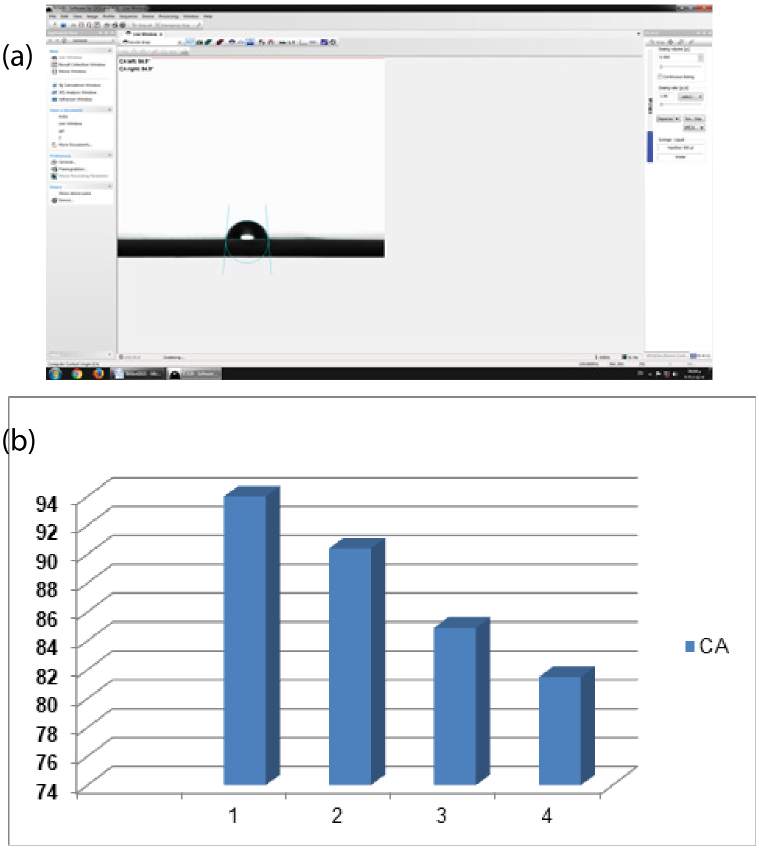


Fig. 7. Water contact angle of PVDF HF membranes.

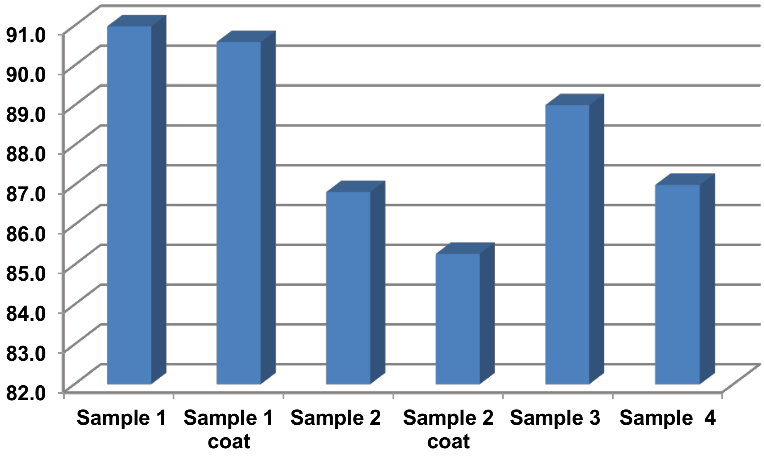
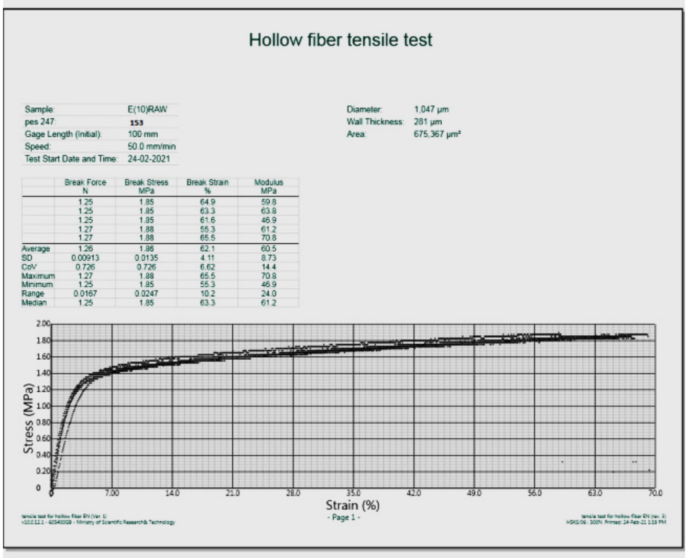


Fig. 8. Porosities of PVDF HF samples raw and coated.

of Simone et al. [30], which could be attributed to the smaller molecular weight of the added PVDF in the reference which is 17 K in addition to the presence of water as a non-solvent. It is also noticed from the results of the current work that coated samples have much lower Young's modulus than raw ones as demonstrated by comparing Samples 4 raw and coated, respectively in Table 4.

5.2. Performance evaluation

Performance evaluation has been conducted for most of the samples. However results as typical for PVDF base samples are presented for Sample 3 as shown in Fig. 10 for flux and permeability of RO water and RO water + dye, respectively. The dye used is Remazol brilliant R of molecular weight 626.5 g/mol. These results have same order of



Hollow fiber tensile test

Sample:	E(10)RAW
pes 247:	153
Gage Length (Initial):	100 mm
Speed:	50.0 mm/min
Test Start Date and Time:	24-02-2021

Diameter: 1,047 µm
Wall Thickness: 281 µm
Area: 675,367 µm²

	Break Force N	Break Stress MPa	Break Strain %	Modulus MPa
	1.25	1.85	64.9	59.8
	1.25	1.85	63.3	63.8
	1.25	1.85	61.6	46.9
	1.27	1.88	55.3	61.2
	1.27	1.88	65.5	70.8
Average	1.26	1.86	62.1	60.5
SD	0.00913	0.0135	4.11	8.73
CoV	0.726	0.726	6.62	14.4
Maximum	1.27	1.88	65.5	70.8
Minimum	1.25	1.85	55.3	46.9
Range	0.0167	0.0247	10.2	24.0
Median	1.25	1.85	63.3	61.2

Fig. 9. Mechanical properties of Sample 4.

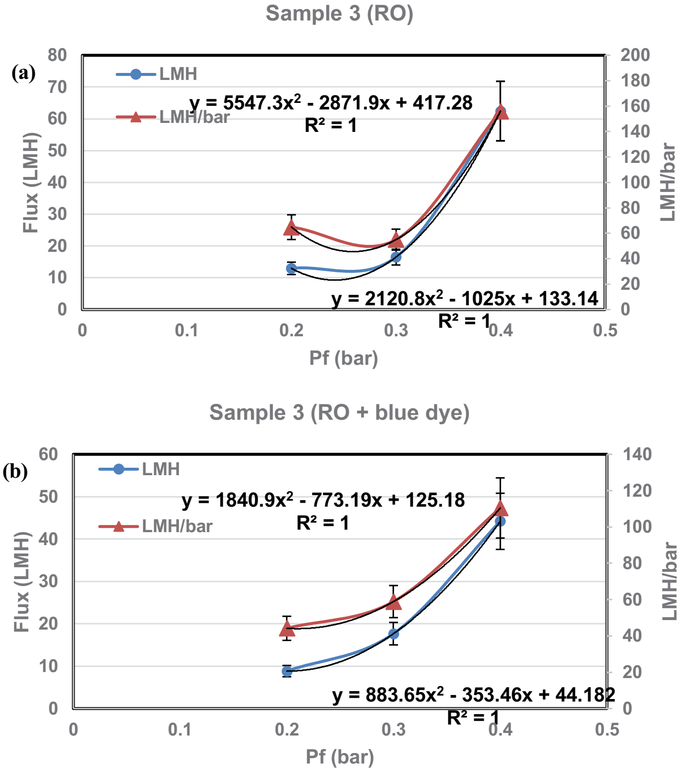


Fig. 10. Performance evaluation for Sample 3.

magnitude for PVDF-*co*-HFP polymer but with different additives [38].

6. Conclusions

PVDF base fibers with different polymers and additives have been thoroughly investigated to explore the suitability of this base polymer not only for MD but, also for NF when subjected to interfacial polymerization to form PA layer. Fibers have been prepared by HF spinning on a pilot scale unit. Extensive characterization studies have been conducted using SEM, AFM, EDS, water contact angle, porosity and mechanical properties. Results are presented to compare the effects of varying additives on dope and produced fibers. Performance has been assessed for a typical sample and results are compared with previous work. These results confirm the suitability of this base fibers with different additives for MD, and, when coated, for NF respectively, as depicted by its characteristics. Further work on performance evaluation of PVDF different MD or coated for NF application is recommended for scaling up purposes.

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