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Investigations on the Effect of Silica Nanoparticles on Polyamide Coated PVDF Hollow FiberMembranes

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Abstract
Hollow fiber membranes (HFMs) find extensive applications in numerous separation fields for water desalination and treatment and recently for gas separation. It is mandatory to explore optional modification modalities to come up with desirable membrane characteristics. Within this context, nanoparticles (NPs)are incorporated in HFMs membrane matrix either in the dope or as surface addition on coating by interfacial polymerization (IP) technique. In this study, silica NPs (20 nm) at different concentrations (0.05%, 0.075% and 0.1%) have been incorporated during polyamide film formation on Polyvinylidine fluoride/Polyacrylonitrile (PVDF/PAN) HFMs.The observed characteristics included surface morphology, surface hydrophilicity, surface roughness, porosity.Further, mechanical investigations centered on break stress, break strain and Young's modulus. Results revealed dimensional stability of the fabricated thin-film composite (TFC) and thin-film nanocomposite (TFN) HFMs with varying changes of the surface roughness average (Ra) with maximum increase of 60% for 0.05% silica NPs TFN HFM. Assessment of relevant mechanical properties indicated noticeable effect on mechanical propertieswhere thin-film coatedHFM without silica NPs incorporation showed maximum increase in Young's modulus and break stressof 39% and 15.8%, respectively. Interestingly, incorporation of silica NPs decreased contact anglefor all coated samples, with a maximum decrease of 30% for 0.075% silica NPs TFN HFM, consequently increasing TFC and TFN HFMs hydrophilicity. Also, a maximum of 5% alterations of porosity (between 75.7%and80.2%) have been observed.

Keywords
Hollow fiber membranes, thin film nanocomposite, silica nanoparticles, PAN, PVDF

1. Introduction

Polymeric hollow fiber membranes (HFMs) have been studied extensively and gained interest since 1960 due to their various advantages such as high packing density[1], high flux production, self supporting structure[2],as well as, possibility of hydraulic cleaning to mitigate membrane fouling[3]. These properties allow their usage in a wide spectrum of applications, ranging from water desalination[4], water treatment[5] to food industry, gas permeation[6], oil treatment[7], hemodialysis[8][9], as well as, pharmaceutical applications.

Several polymers have been used to produce HFMs, including Polyvinylidine fluoride (PVDF) which is hydrophobic in nature[5] and exhibits superior properties due to its semi-crystalline structure giving the membrane thermal stability as well as flexibility[10][11]. Also, PVDF has excellent chemical resistance in addition to ease of dissolving in organic solvents which makes it a favorable polymer for membrane fabrication.

Dope blendingwith additives or other polymers is a popular route to modify or enhance the membrane properties[12]. Several authors studied the effect ofblending Polyacrylonitrile (PAN) with PVDF membranes owing to PAN polymer‘s low cost, good biocomptability, hydrophilicity as well as good age resisting property[13].

Nanotechnology played a critical role in upscaling membrane modifications, where nanoparticles (NPs) are incorporated into the dope matrix or the selective thin coating layer to produce mixed matrix membranes (MMMs) or thin-film nanocomposite membranes (TFN), imparting further enhancement to membrane properties [14–16]. Different types (organic and inorganic NPs) such as Zinc Oxide[17, 18], CuO [19, 20], TiO_2[21], CNTs[22], Graphene and GO[23, 24] as well as different shapes (1 dimensional (D), 2D and 3D) NPs have been used [25].

Abba et al.[26, 27] studied the effect of incorporating different loadings (0.05-2 wt%) of TiO_2 NPs inside the dope to fabricate mixed matrix PVDF/PVP HFMs composites for copper and boron removal and concluded that 1 wt% TiO_2 NPs yielded maximum membrane hydrophilicity as well as maximum flux and copper and boron rejection. Kamaludin et al. [28] incorporated ZnO NPs in PVDF HFMs at different NPs concentrations (2.5-7.5 wt%) as an antimicrobial agent for water treatment applications. Results showed enhanced membrane hydrophilicity, flux and average pore size as well as decreased microbial fouling. Fan et al. [29] blended GO NPs as well as Ag/GO NPs of varying loadings (0.5-1.25 wt%) in PVDF HFMs dopes. Results confirmed NPs incorporation in the dope enhanced the mixed matrix nanocomposite membrane hydrophilicity and tensile strength while emparting the membrane with biofouling capabilities. Asadi et al. [30] added multiwalled carbon nanotubes/Ag (MWCNTs) to PVDF membranes (0.1-1 wt%) and results confirmed that NPs blending, specially 0.7 wt% MWCNT/Ag, improved membrane hydrophilicity, flux, antibacterial activity as well as antifouling.

Silica NPs are spherical inorganic NPs which are characterized by their high mechanical strength[31], outstanding hydrophilicity[32] as well as good thermal stability[6], which made them a popular choice in membrane modifications[33].

Gong et al. [34] fabricated superhydrophobic PVDF/SiO_2 HFMs via incorporating SiO_2 NPs inside the dope at different loadings (0.5-3 wt%). They concluded that PVDF HFMs incoporated with 1.5 wt% SiO_2 NPs showed increased contact angle indicating the successful formation of a hydrophobic surface with the highest CO_2 absorption was exhibited at 1.5 wt% SiO_2 NPs loading. On the other hand, Xu et al.[35]incorporated hydrophilic SiO_2NPs (0.53-1.6 wt%) inside PVDF flat sheet membranes for oil/water purification utilizing a special fabrication process. Their results showed an increased antifouling capability in addition to enhanced membrane hydrophilicity. Emamirad et al. [36] incorporated hydrophilic SiO_2 NPs in PVDF flat-sheet membrane for membrane distillation application at different concentrations (3-6 wt%). Results indicated increased membrane porosity, break stress as well as noticeably increased flux.

Another modifying technique is interfacial polymerization (IP), which is usually carried out on membranes to form a thin-film composite membranes (TFC) to improve their surface properties and performance.

Mostafa et al.[37] synthesized TFN PVDF HFMs via incorporating silica NPs during IP. Results demonstrated increased hydrophilicity and surface roughness, while mechanical properties decreased. Safarina et al. [38], Abolfazli et al. [32], Abadikhah et al. [39]reported similar results for PVDF/Polydopamine flat sheet membrane, Polysulfone (PS) HFMs and Polyether sulfone (PES) membranes, respectively,upon incorporation of Silica NPs to produce TFN membrane. On the other hand, increased hydrophobicity was detected as well as significant increase in surface roughness and contact angle values for in-situ produced Silica NPs via sol-gel during PAN TFN flat sheet membrane production [40].

Membrane structural characteristics, such as roughness and porosity, and parameters defining the interaction of membranes with solutes in feed solutions, such as wettabilitymay be used to categorise factors affectingthe membrane's performance[41].

Previous investigations have studied thoroughly the effect of NPs incorporation on TFN membranes properties and performance; however there is no reported study on their effect on PVDF/PAN TFN HFMs properties. The overall goal of this research is to fill this knowledge gap throughincorporating different ratios of silica NPs to produce PVDF/PAN TFN HFMs to study the effect on membrane morphology, surface roughness, mechanical properties, porosity and membrane's hydrophilicity.

2. Experimental Investigations

2.1 Materials

Polyvinylidene fluoride (PVDF) andPolyacrylonitrile (PAN)were used as base polymers, supplied from Alfa Aesarand Sigma Aldrich, respectively. Solventused in this study, namely, Dimethyl formamide (DMF) waspurchased from Carl-Roth.Distilled water (DW) was used as the bore fluid and in coagulation, washing baths and for preservation. Isopropyl alcohol used for membrane activation was supplied from TEDIA. Silicon (IV) oxide, nano powder (20 nm), used for TFN fabrication, was purchased from Alfa Aesar. Trimesoyl chloride (TMC), m-phenylene diamine (MPD) and Piperazine (PIP),which were used to prepare Polyamide active layer,were purchased from Siga-Aldrich and Fine Chemicals.Adipoyl chloride and Triethylamine (TEA) were supplied from ACROS and Fisher Chemicals, respectively. Cyclohexane, purchased from El Nasr Pharmaceutical Chemicals Co., was used as the organic solvent. Magnesium chloride ($MgCl_2$) used to preserve as spun and coated PVDF/PAN fiber, was purchased from El Nasr Pharmaceutical chemicals. For membrane porosity measurements, Kerosene oil was purchased from Misr Petroleum Co.

2.2 Dope Preparation

PVDF/PAN/DMF HFMs of dope composition (18/1/81 wt%) were spun by dry-wet phase inversion techniqueusing a single orifice spinneret, according to the method used by Mostafa et al.[37]. After spinning, the as-spun HFMs were soaked and rinsed with DW for 24 hours to ensure complete phase inversion as well as removing excess solvent. Then, samples were soaked in three consecutive isopropanol solutions of different concentrations (2%, 4%, and 0.5%) for 40 minutes each, for surface activation. Isopropanol supports rapid removal of residual solvent and additives andminimizes possibilities of pore dimensional changes. Fibers were washed with DW before any characterization or coating took place.

2.3 Thin-film Nanocomposite Preparation

SpunPVDF/PANHFMs were thin-film dip-coated horizontally in a rectangular dish. Fibers were washed very well with DW before starting the coating process to guarantee a clean surface. HFMs of 30 cm length were fixed separately on a wooden frame to ensure the formation of an intact coating on the fibers. The coating procedure was described in details previously in Mostafa et al. work [37]. **Figure 1** summarizes the coating procedure. Two coating solutions were prepared for IP, aqueous Amine solution (using MPD, PIP and TEA) and organic phase (using Cyclohexane, TMC and Adipoyl chloride). Different concentrations of silica NPs were added separately to the Amine solution (0.05, 0.075 and 0.1 wt%) and sonicated for an additional 40 minutes to prevent agglomeration of NPs and to ensure homogeneous solution formation.Finally, fibers were stored in 1% $MgCl_2$ solution until further investigations.

Sample codes of as spun, TFC and TFN PVDF/PAN HFMs are presented in

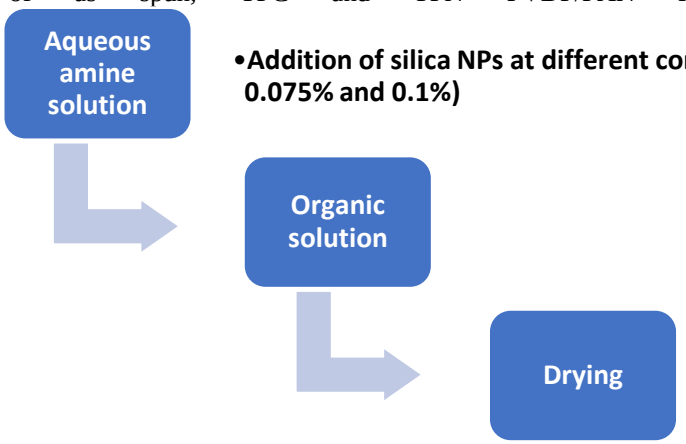


Figure 1: Coating procedure of PVDF/PAN HFMs

Table 1.

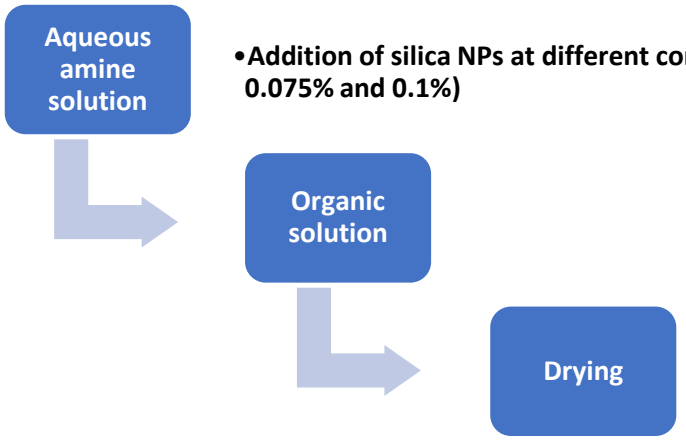


Figure 1: Coating procedure of PVDF/PAN HFMs

Table 1: Sample codes of PVDF/PAN HFMs at different conditions

Sample code	Membrane description
P	As-spun fiber
TFC	Thin film coated P sample
TFN 0.05	0.05% Silica NPs thin film nanocomposite P sample
TFN 0.075	0.075% Silica NPs thin film nanocomposite P sample
TFN 0.1	0.1% Silica NPs thin film nanocomposite P sample

2.4. Characterization

2.4.1. Membrane Morphology

Morphological characteristics of the fibers were studied using bench-top scanning electron microscope (SEM) model JEOL JCM-6000 Neoscope apparatus. SEM images were acquired at high voltage of 15 kV and standard probe current. Fibers were washed thoroughly and dried before testing, then cut with a sharp razor, set on sample holder using carbon double face tape followed by gold sputtering for 1 minute to enhance sample conductivity.

2.4.2. Surface Roughness

Fibers surface topography was measured using "TT-AFM workshop" atomic force microscope device (AFM) having 1.5 µm resolution, attached to a 400X optical microscope. Fibers were thoroughly washed, dried and 1 cm lengths were cut and set on a double face tapefixed on a magnetic coin. Testing conditions were set on vibrating mode with a scan area of 5µm×5µm. Roughness parameters as well as 3D topography images were acquired from the AFM images using "Gwidyyon" software. An average of five samples was calculated for each condition.

2.4.3. Mechanical Properties

Mechanical properties of fibers were measured using H5kS Tinius Olsen bench-top universal tensile testing machine, equipped with small sample holder and a 5N load cell. Testing conditions were set at 50 mm/min test speed and 100 mm gauge length. An average of five sample repetitionswas calculated for each condition.

2.4.4. Water Contact Angle (CA)

The OCA 15EC Contact angle model, made by the company of Data Physics Instrument GmbH, was used to measure HFMs contact angles while altering the morphology of water droplets on the samples. For each HFM condition, five fibers were assessed, and the average values were computed.

2.4.5. Membrane Porosity

Gravimetric method was used to measure HFMs porosity [5]. HFMs were dried in an oven at 60°C for one hour then weighed, followed by soaking in Kerosene oil for 24 hours, drained and wiped with filter paper to ensure removal of excess oil and finally they were weighed. Membrane porosity was calculated according to the following equation (1)

$$\varepsilon = \frac{\frac{w1-w2}{\rho k}}{\frac{w1-w2}{\rho k}+\frac{w2}{\rho p}} \times 100 \quad (1)$$

Where,

w_1: weight of wet membrane (g)

w_2: weight of dry membrane (g)

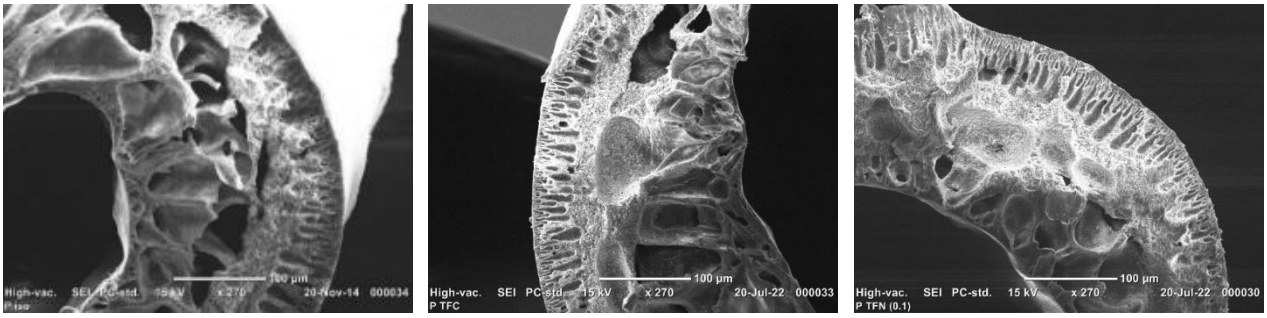
ρ_k: density of kerosene (g/cm^3)

ρ_p: density of polymer (g/cm^3)

3. Results and Discussions

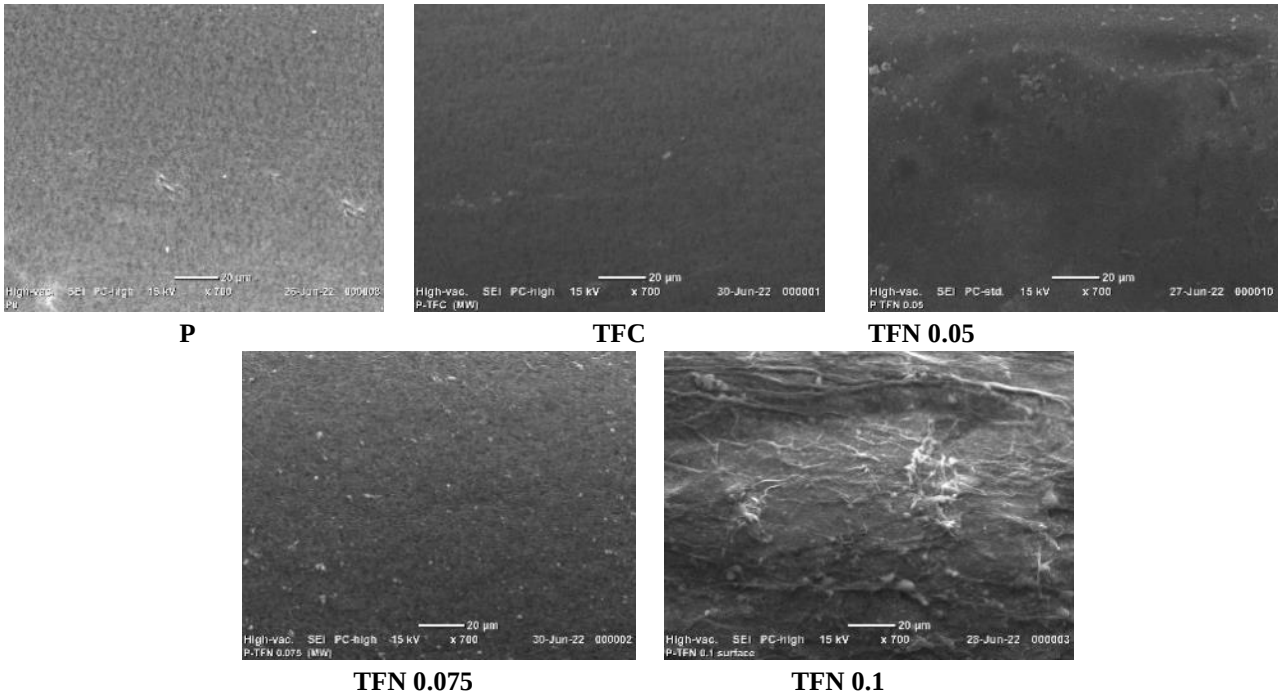
3.1. Scanning Electron Microscopy (SEM)

Cross-sectional and surface images of some PVDF/PAN HFMs are shown in **Figure 2** and **Figure 3**. Cross-sectional images present a typical asymmetricstructure exhibiting inner and outer finger-like structures, due to penetration of bore and coagulation non-solvents causing phase inversion process during spinning, with a dense spongy layer in between and a dense outer layer, agreeing with Preaneeth et al.[42] findings.SEM cross-sectional images confirm intact morphological characteristics not affected by thin film coating. **Figure 3** shows the surface morphology of HFMs, where all images demonstrate a fine porous surface. Surface pores are noticeably tighter upon coating, as shown in TFC sample, while their smoothness was slightly affected upon adding Silica NPs to the coating to form TFN. The formation of a highly rough surface upon increasing the Silica NPs content, reaching a maximum at 0.1 Silica NPs loading, is apparent, which could be attributed to Silica NPs agglomoration on the membrane surface at higher ratios.



P **TFC** **TFN 0.1**

Figure 2: Cross-sectional SEM images of P, TFC and TFN 0.1 PVDF/PAN HFMs samples



P **TFC** **TFN 0.05**

TFN 0.075 **TFN 0.1**

Figure 3: Surface SEM images of P, TFC and TFN PVDF/PAN HFMs

3.2. Mechanical Properties

Table 2 shows break stress, break strain and Young's modulus of as spun, TFC, TFN PVDF/PAN HFMs. All break stress values decreased slightly after silica NPs incorporation to form TFN membranes, whilebreak stressincreased significantly by 15.8% for TFC sample, coating without silica NPs incorporation, which could be due to NPs acting as stress concentrations in the TFN surface leading to overall strength decrease. A similar decreasing trend was depicted for break strain, where it decreased after coating with and without silica NPs, which is expected as composites usually sacrifice the membrane's strain as a result of combined strain of membrane and the coating layer[37][43]. On the other hand, coating with and without silica NPs enhanced Young's Modulus with a maximum increase for TFC sample, coated membranes without silica NPs.

Table 2: Mechanical properties of as spun, TFC and TFN PVDF/PAN

Sample	Break stress (MPa)	Break strain (%)	Young's modulus (MPa)

P	2.84	42.2	71.3
TFC	3.29	33	99.1
TFN 0.05	2.85	36	79.5
TFN 0.075	2.5	39.3	70.2
TFN 0.1	2.79	37.3	96.2

3.3. Surface Roughness

Figure 4shows topographical 3D images of some PVDF/PAN HFMs where they exhibit characteristic peaks and valleys of the membrane surface, becoming rougher or smoother according to the condition to which they were subjected.**Figure 5**shows average surface roughness (Ra) values of HFMs in this study, where all roughness Ra values increased upon coating, whether thin film coating or after incorporating silica NPs in the thin film coating, with the highest value of 52.3 nm for TFN 0.05 silica NPs loading.These findings are in accordance with Mostafa et al. [37], Guzman et al. [40] and Abadikhah et al. [39] where surface roughness values increased for PVDF-TFN HFMs, PAN-TFN FS membranes and PES-TFN FS membranes, respectively, after coating. This increase in surface roughness Ra was attributed to the nature and shape of the coating layer, having a leaf like structure.

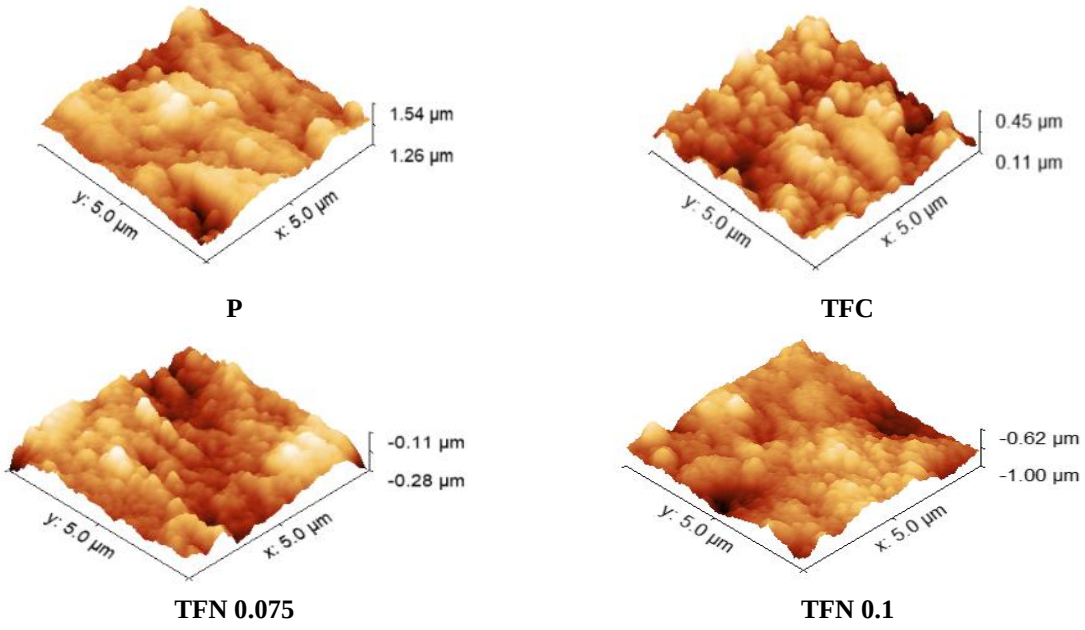


Figure 4: Surface roughness Ra 3D images of P, TFC, TFN 0.075 and TFN 0.1 PVDF/PAN HFMs samples

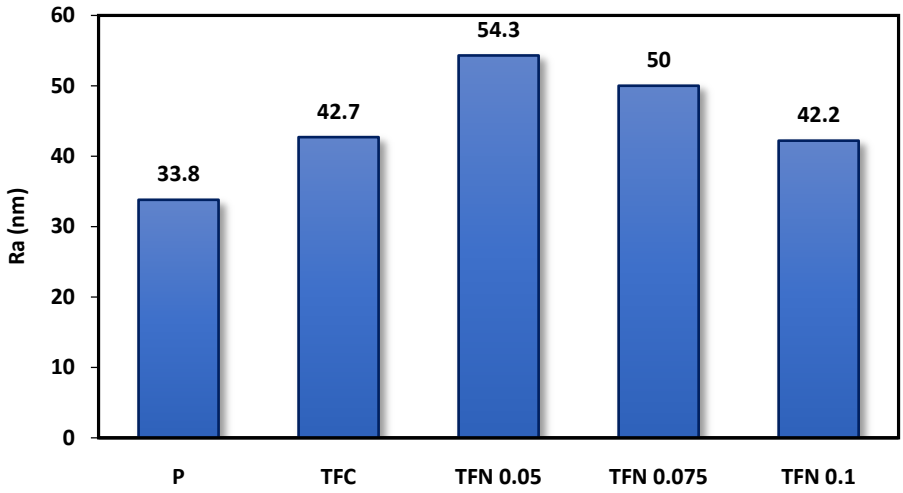


Figure 5: Average surface roughness (Ra)values of P, TFC and TFN PVDF/PAN HFMs

3.4. Water Contact Angle

Table 3 shows contact angle (CA) values of as spun, TFC, TFN PVDF/PAN HFMs. All CA values decreased after coating whether with TFC or after incorporating silica NPs indicating increased membrane hydrophilicity. Results agree with most published research on silica NPs incorporation to fabricate thin film nanocomposite membranes[32][37][39][44].TFN 0.075 sample showed a maximum decrease of 31.4%, while, TFN 0.05 sample showed minimum decrease of 9.55%, which agrees with its increased roughness value.

Table 3: Water contact anglesand membrane porosity values of as spun, TFC and TFN PVDF/PAN HFMs

Sample	Contact Angle (°)	Porosity (%)
P	89	80.26
TFC	72	78.27
TFN 0.05	80.5	78.42
TFN 0.075	61.9	75.71
TFN 0.1	75.4	79.78

3.5. Membrane Porosity

As shown in **Table 3**, it is apparent that porosity of HFMs decreased after coating, where TFN 0.075 sample, having 0.075% Silica NPs,showed lowest porosity. As expected, interfacial polymerization manifested moderate decrease of porosity due to intrinsic self-healing property of coating process.

4. Conclusions

In this study, the effects of incorporating silica NPs on morphological and mechanical characteristics of thin-film PVDF/PAN HFMs have been investigated. Silica NPs were incorporated during the interfacial polymerization stage with concentration ranging from 0.05 to 0.1%. The effects of different silica NPs concentrations on membranes characteristics were evaluated including morphological characteristics through SEM, contact angle, total porosity, surface roughness (Ra), break stress, break strain and Young's modulus. Results showed that the process has good capacity to regulate PVDF/PAN HFMs contact angle through a range from 61.9° to 89° and to regulate its total

porosity through a range from 75.7% to 80.2%. Also, results showed that the process has the capacity to regulate PVDF/PAN HFMs mechanical properties. Accordingly, the process presented in this study would facilitate preparation of TFC and TFN PVDF/PAN HFMs that have tailored properties, which would enable it to properly cope with a wider range of intended applications while minimizing potential fouling.

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