ORIGINAL ARTICLE

In situ polymerization of PVDF-HEMA polymers: electrospun membranes with improved flux and antifouling properties for water filtration

Shaik Anwar Ahamed Nabeela Nasreen¹, Subramanian Sundarrajan¹, Syed Abdulrahim Syed Nizar², Ramalingam Balamurugan² and Seeram Ramakrishna^{1,2}

In situ polymerization of poly (vinylidene fluoride) (PVDF) with hydroxyethylmethacrylate (HEMA) followed by electrospinning was employed to prepare electrospun nanofibrous membranes (ENMs), referred to as PVDF-PHEMA-ENMs. Enhanced hydrophilicity of the ENMs was observed after polymerization. A decrease in the fiber thickness resulted in a decrease in the pore size and 60% improvement in the flux. The fiber mat exhibited excellent microfiltration behavior after being coated with a surface-charged chitosan (CS) polymer, compared with its non-coated counterparts. Porosity, flux and protein adsorption studies were performed for these ENMs. A comparatively less reduced flux and better recovery ratio were observed for the PVDF-PHEMA-ENMs and CS-coated PVDF-PHEMA-ENMs due to hydrophilic pendant hydroxyl groups (from PHEMA) and/or CS groups, which can prohibit irreversible protein adsorption, on the ENM surfaces.

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INTRODUCTION

Poly (vinylidene fluoride) (PVDF) polymers exhibit good stability in various solvents, good thermal behavior and very high mechanical characteristics.^{1–3} Many studies using this polymer have been performed demonstrating the vast variety of applications in the fields of science, engineering and medicine.^{4–6} However, the hydrophobic nature (that is, a contact angle of up to 130°–140°), which is much larger than conventional polymer membranes,^{7,8} is an undesirable characteristic that needs to be addressed for application in water filtration due to its contribution toward the fouling process and decreased flux. Fouling is a major concern because it decreases the efficiency of the water purification process.⁹

However, hydrophilic surfaces have very different properties that reduce the fouling and increase the flux and rejection. Many studies have been performed to examine the surface modification of polymers for water treatment applications. These modification techniques include blending,^{10–12} plasma treatment,^{13,14} chemical oxidation¹⁵ and *in situ* polymerization.¹⁶ Many research studies on blending techniques have been reported. For example, Wang *et al.*¹⁰ reported the modification of PVDF via mixing with amorphous poly[bis(benzimidazobenzisoquinolinones)] for fuel cell applications. PVDF blended with clay nanoparticles was tested for a direct contact membrane distillation application. Improved performance of the

direct contact membrane distillation was observed when the concentration of clay was increased, which influenced the crystallization process of PVDF.¹² The treatment of poly(ether sulfone) nanofibers with strong oxidants, such as ammonium persulfate, was performed, which enhanced the hydrophilicity of the resulting membrane.¹⁵ Kaur *et al.*¹² studied blending as well as the surface modification of polymers using plasma to enhance the hydrophilicity of the membrane.

Among the above-mentioned techniques, the *in situ* polymerization technique is relatively easy and results in good polymer surfaces because it does not require any additional purification of the resulting polymers. Poly(hydroxyethylmethacrylate) (PHEMA) is a hydrophobic polymer. However, a hydrophilic pendant group in the repeating unit facilitates the absorption of water. Physical and chemical changes in the structure of the polymer will change the water absorption capacity from 10 to 400% relative to the dry weight.¹⁷ The batch absorption method has been used to remove metal ions using a mixture of 2-hydroxyethylmethacrylate (HEMA) with 4-vinyl pyridine on the poly (ethylene terephthalate) (PET) surface.¹⁸

Choi *et al.*¹⁹ reported the grafting of PVDF with poly (ethylene glycol) methyl ether methacrylate (g-POEM) and found improved antifouling properties due to the surface hydrophilicity of the g-POEM membrane compared with pristine PVDF. Different

¹Department of Mechanical Engineering, National University of Singapore, Singapore, Singapore and ²Department of NUSNNI, NUS Nanoscience and Nanotechnology Institute, National University of Singapore, Singapore, Singapore

Correspondence: Dr S Sundarrajan, Department of Mechanical Engineering, National University of Singapore, Kent Ridge Crescent, 2 Engineering, Drive 3, 117584 Singapore, Singapore.

E-mail: sundarnus1@gmail.com

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foulants (namely, bovine serum albumin (BSA), alginate and *E. coli* broth) with different doping concentrations were studied using this group. Ultraviolet (UV) photografting of hydrophilic monomers (acrylic acid and HEMA as acrylic monomers and 2,4-phenylenediamine and ethylenediamine as amino monomers) on top of the PVDF membrane surface was studied by Rahimpour *et al.*²⁰ The antifouling properties and flux recovery of the PVDF membrane improved upon UV photografting of the hydrophilic monomers. The total fouling resistance of the UV photografted membranes was increased by ~20% compared with PVDF, with a 5 wt% loading of ethylenediamine, and a 3-fold increase in the total fouling resistance was observed when modified with 1 wt% HEMA + benzophenone + 5 min UV. Sui *et al.*²¹ grafted PVDF with PHEMA (PVDF-g-PHEMA) to enhance the antifouling properties of the pristine PVDF membranes. They suggested that the enhanced protein resistance was due to the hydroxyl groups present in the PHEMA chains and the net neutral charge on the membrane surfaces, which effectively reduced the quantity of adsorbing BSA. In addition, they reported that the PHEMA-based copolymers take up large quantities of free water, which builds up a stable defense layer that resists protein fouling.

Because electrospun nanofibrous membranes (ENMs) are considered as good materials for filtration,²² the present study is focused on the *in situ* polymerization of HEMA with PVDF, followed by electrospinning and surface coating with chitosan (CS). A 60% reduction in the porosity and water flux was observed for these ENMs, which allowed for the nanofiltration of heavy metals and salts. Studies of the filtration performance, porosity and morphology of the membranes were also performed.

EXPERIMENTAL PROCEDURE

Materials

PVDF (Kynar-761A) (average molecular weight (M_w) 4.41×10^5) was purchased from Arkema, Singapore, Singapore. HEMA, trimethyl phosphate, benzoyl peroxide and CS (medium M_w) were purchased from Sigma-Aldrich Pte Ltd, St Louis, MO, USA. Acetone (Chromasolv grade for high performance

liquid chromatography (HPLC), >99.9% purity, Sigma-Aldrich Company), *N,N*-dimethylacetamide (anhydrous, 99.8% purity, Aldrich Chemical Company, Inc., Milwaukee, WI, USA) and other reagents were used as purchased. PET (Hollytex 3242) was purchased from Ahlstrom, Mount Holly Springs, PA, USA and used as a backing material (BM).

Polymer synthesis

Approximately 3.5 g of PVDF was dissolved in 20 ml of trimethyl phosphate and heated at 80 °C for 6 h to obtain a clear solution. A total of 1.5 g of HEMA in 10 ml of trimethyl phosphate was mixed in a separate bottle, which was followed by the addition of benzoyl peroxide (0.012 g) as an initiator. The mixture was vigorously stirred to yield a homogenous clear solution that was transferred to the PVDF solution to initiate polymerization. The polymerization was performed at 90 °C for 4 h with continuous stirring under an inert atmosphere. A change from a clear liquid to a white liquid was observed in 1 h, and then the liquid was stirred for an additional 3 h to obtain the polymer solution containing the PVDF-HEMA polymer.

Polymer characterization

NMR analysis of the polymer. The ¹H-nuclear magnetic resonance (NMR) spectra of the PVDF and PVDF-PHEMA polymers are shown in Figure 1. The ¹H-NMR spectra were recorded on Bruker Avance AV300 (300 MHz) spectrometers (Illinois, IL, USA). The chemical shift values (δ) were characterized as follows: ¹H-NMR of PVDF (300 MHz, DMSO- d_6 , δ): 3.34 (water peak associated with DMSO- d_6), 2.89 (t, $-\text{CF}_2 \text{CH}_2-\text{CF}_2 \text{CH}_2-$, head-to-tail) and 2.25 (t, $-\text{CF}_2 \text{CH}_2-\text{CH}_2 \text{CF}_2-$, tail-to-tail). The assigned peaks are in good agreement with the reported literature.²³

¹H-NMR of PVDF-PHEMA: (300 MHz, DMSO- d_6 , δ): 4.81 (s(b) ($-\text{OH}$), 3.90 (s, broad $-\text{CH}_2$), 3.59 (s, broad $-\text{CH}_2$), 3.33 (water peak associated with DMSO- d_6), 2.89 (t, $-\text{CF}_2 \text{CH}_2-\text{CF}_2 \text{CH}_2-$, head-to-tail of PVDF), 2.25 (t, $-\text{CF}_2 \text{CH}_2-\text{CH}_2 \text{CF}_2-$, tail-to-tail of PVDF), 1.8 (s, weak $-\text{CH}_2$), 1.5 (s, broad $-\text{CH}_2$), 1.24 (s, $-\text{CH}_3$), 0.9 (s, broad $-\text{CH}$).

Gel permeation chromatography analysis of the polymer. The weight average M_w , number average M_w (M_n) and polydispersity (PDI) of PVDF and the *in situ* synthesized PVDF-HEMA polymers were determined from gel permeation chromatography using *N,N*-Dimethyl formamide (DMF) as the eluent (Figure 2). PVDF exhibited single elution curves at an M_w of

Figure 1 ¹H-NMR analysis of the PVDF and PVDF-PHEMA copolymer. A full color version of this figure is available at *Polymer Journal* online.

Figure 2 GPC curves of the PVDF and PVDF-PHEMA copolymer. A full color version of this figure is available at *Polymer Journal* online.

8048 Dalton (Da), an M_n of 3899 Da and a PDI of 2.06, whereas PVDF-HEMA exhibited two elution curves: the first curve corresponds to PVDF with an M_w of 2744 Da, an M_n of 2211 Da and a PDI of 1.24, and the second curve corresponds to an M_w of 340 Da, an M_n of 310 Da and a PDI of 1.09. The observed reduction in the M_w for PVDF from 8048 to 2744 Da could be due to the cleavage of bonds in the PVDF polymer chain or the interaction of a fluorine atom in PVDF with a hydrogen atom (from OH group) of HEMA.

Preparation of ENMs

Electrospinning was performed on a fully automated electrospinning machine (Nanon-01A electrospinning machine, manufactured and supplied by MECC CO, Ltd, Ogori-shi, Japan). The PET BM (BM-Hollytex 3242) (that is, dimensions: 60 cm (length) $\times$ 20 cm (width) $\times$ 0.013 cm (thickness)) was wrapped around the drum as the target to collect the ENMs. Then, the polymer solution was loaded into a syringe fitted to a built-in pump. The positive terminal of a high voltage DC power supply was connected to the metallic needle (22 G, B. Braun Melsungen AG, Melsungen, Germany) of the syringe. The syringe pump was set at a flow rate of 0.8 ml h^{-1} , and a high voltage (that is, 30 kV) was applied. The height of the collector with respect to the needle was set to 15 cm. Electrospinning was performed at room temperature with a rotational speed of 150 r.p.m. The humidity was maintained at 50–60%. After electrospinning, the nanofibrous support and backing layer were allowed to dry at room temperature for at least 3 h to remove any residual solvent present in the matrix. The membrane was cut into 15×15 cm pieces and was hot pressed in a thermal transfer press (Hotronix, Carmichaels, PA, USA) at 80°C for 15 min at a pressure of 0.4 MPa.

Preparation of surface-coated ENMs

All of the hot-pressed ENMs with an area of $15 \text{ cm} \times 15 \text{ cm}$ were separately pasted onto a clean dry glass container with adhesive tape (3M, USA). The procedure used for the coating was as follows. The membranes were soaked in a 2 wt% CS solution (2 g in 10 ml of acetic acid and 90 ml of de-ionized water) for 4 min. The excess solution was decanted, and the tray along with the membrane was heated in an oven at 80°C for 15 min. The coated membranes were cut into the desired sizes for further study.

Membrane characterization

The pore size distribution and bubble point measurements of the ENMs were determined using a capillary flow porometer (Porous Materials Inc., Ithaca, NY, USA). The hydrophilic or hydrophobic nature of the ENM was analyzed with a sessile drop water contact angle measurement using a VCA optima surface analysis system (AST Products, Billerica, MA, USA), where distilled water was used for drop formation. The functional groups present in the ENMs were determined using the Fourier transform infrared (FTIR) spectroscopy on an Avatar 380 (Thermo Nicolet, Waltham, MA, USA) over a range of $400\text{--}4000 \text{ cm}^{-1}$ at a resolution of 8 cm^{-1} . The surface and cross-section of the membranes were observed using field emission scanning electron microscopy (SEM, FEI-QUANTA 200F, Eindhoven, The Netherlands). For the cross-section, the samples were prepared with a sharp blade. The samples were coated with platinum in an auto fine coater (JFC-1600, JEOL, Tokyo, Japan) before recording the SEM images. The diameter of the nanofibers was determined from the field emission scanning electron microscope (FESEM) image using the Image software (<http://rsb.info.nih.gov/ij/>), and a value of $P \leq 0.05$ was considered as statistically significant. The pure water flux of the ENM layer was measured on a dead end AMICON (Millipore Corporation, Billerica, MA, USA) stirred cell (8010) unit with a capacity of 10 ml, which was attached to an 800-ml reservoir (RC800). Membranes with an effective filtration area of 4.1 cm^2 (25 mm in diameter) were placed into the stirred cell and tested. The adsorption studies were performed on a Shimadzu Spectrophotometer (Shimadzu Corporation, Kyoto, Japan). BET (Brunauer–Emmett–Teller) analyses were performed with a Nova 2200e, Quantachrome, Boynton Beach, FL, USA.

BSA adsorption studies

Protein adsorption studies (BSA studies) were performed to evaluate the fouling properties of the prepared ENMs. ENMs, which were cut to an area of $\sim 6.25 \text{ cm}^2$, were immersed in a protein solution. Various concentrations were prepared (1–4%), and the pH was maintained at 7.4 using a phosphate buffer. The solution was mixed at 30°C for 24 h using an agitator to obtain uniform adsorption and equilibrium of the BSA solution. UV adsorption spectra of the solution were recorded at 230 nm. The spectra were recorded before and after BSA adsorption.

Permeation studies

The permeability studies of the ENMs were examined with the dead end method over an active area of 2.5 cm^2 under a constant pressure of 1 bar. The pure water fluxes (J_w) were calculated by the volume of water collected per hour. A 1 g l^{-1} BSA saline solution (phosphate buffer saline) was allowed to flow through the membrane at a pressure of 1 bar per hour. The relative flux reduction (RFR) was calculated and recorded as J_p . The flux recovery ratio (FRR) of the BSA permeated membranes was calculated after washing with a 0.1 M NaOH solution for 1 h followed by washing with pure water three times (10 ml). RFR and FRR% were calculated using the following formulas:

$$\text{RFR (\%)} = 1 - (J_p/J_w) \times 100$$

$$\text{FRR (\%)} = (J_R/J_w) \times 100.$$

RESULTS AND DISCUSSION

Morphological studies

Figure 3 shows the SEM images of the ENMs. All of the ENMs were collected on the BM. To achieve good mechanical strength, it is essential to use the BM throughout the membrane structure. The average fiber size of the BM was $30 \pm 10\text{ }\mu\text{m}$, which is many orders of magnitude greater than the size of the electrospun fibers. Figure 3b shows the SEM image of PVDF spun on the BM. The average fiber diameter of PVDF was $300 \pm 25\text{ nm}$. Figure 3c represents the morphology of the surface-modified PVDF-PHEMA polymer.

After modification, major changes were observed in the PVDF properties, especially the fiber diameter and porosity, and the average

diameter was determined to be $200 \pm 25\text{ nm}$. To measure the fiber diameter of ENMs from the SEM images, $n = 40$ fibers were chosen. An SEM image of the PVDF ENM coated with a 2 wt% hydrophilic CS polymer-coated surface is shown in Figure 3d. The surface of the membrane appears to be very smooth, with a coating thickness of $\sim 2\text{ }\mu\text{m}$. The CS coating on top of the PVDF and PVDF-PHEMA reduces the pore size to enable use of the membrane for microfiltration. In addition, due to the presence of polar and ionizable groups, this membrane is very attractive for filtration studies.²⁴ This membrane exhibits an enhanced antifouling property²⁵ and also aids in binding protein species such that it functions as a good candidate for water filtration. Figure 3f shows a cross-sectional SEM image of the 2 wt% CS-coated PVDF-PHEMA polymer. Figure 3g shows a higher magnification image of the CS-coated PVDF-PHEMA-CS. The fiber diameter distribution of the PVDF ENMs and PVDF-PHEMA ENMs is given as the insert in Figure 3h and Figure 3i, respectively. The ENMs such as PVDF and PVDF-PHEMA coated with CS are referred to as PVDF-CS-ENM and PVDF-PHEMA-CS-ENM, respectively. The three tier architecture of PVDF-CS-ENM is shown in Figure 4.

Effect of polymer on pore size

The pore size and bubble point of the ENMs were studied. Table 1 summarizes the ENM porosity data, which indicate that the decrease

Figure 3 SEM images of (a) BM, (b) PVDF-ENM, (c) PVDF-PHEMA-ENM, (d) PVDF-CS-ENM, (e) PVDF-PHEMA-CS-ENM and (f) a cross-section of BM-PVDF-PHEMA-CS. (g) High magnification image of (e). The artwork represents the average fiber diameter of PVDF-PHEMA ENM (mean = 200 nm) (h) and PVDF-ENM (mean = 300 nm) (i). A full color version of this figure is available at *Polymer Journal* online.

in the fiber diameter resulted in a decrease in the pore size of the membrane. The fiber diameter of PVDF is much larger than that of the modified PVDF with HEMA, which leads to a larger pore size for

Figure 4 The three tier architecture of PVDF-CS-ENM. (a) PET (BM) (b) PVDF-PHEMA ENM (c) Chitosan coated PVDF-PHEMA ENM. A full color version of this figure is available at *Polymer Journal* online.

Table 1 Pore size distributions and fiber diameters of the different ENMs

Membrane type	Min. pore size (μm)	Ave. pore size (μm)	Bubble point (μm)
PVDF	0.8 ± 0.01	2.06 ± 0.12	3.06 ± 0.03
PVDF + CS	0.27 ± 0.03	1.11 ± 0.14	1.24 ± 0.05
PVDF-PHEMA	0.4 ± 0.01	0.43 ± 0.03	0.44 ± 0.04
PVDF-PHEMA + CS	0.26 ± 0.02	0.28 ± 0.05	0.29 ± 0.04

Abbreviations: CS, chitosan; ENMs, electrospun nanofibrous membranes; PVDF, poly (vinylidene fluoride); PHEMA, poly(hydroxyethylmethacrylate).

PVDF compared with that of the surface-modified PVDF-PHEMA. PVDF has a fiber diameter of 300 ± 25 nm, with the highest bubble point value ($3.06 \pm 0.03 \mu\text{m}$). Interestingly, the surface-modified PVDF-PHEMA exhibits a diameter of 200 ± 25 nm with a maximum bubble point value of $0.44 \pm 0.04 \mu\text{m}$ compared with PVDF. A nearly sixfold decrease in the pore size of the ENMs was observed in the PVDF-PHEMA ENMs due to a decrease in the fiber diameter, which contributed to the increase in the nanofiber density per unit area. The same trend was observed when the ENMs were coated with the CS polymer. For the PVDF-CS ENMs, the maximum bubble point observed was $1.24 \pm 0.05 \mu\text{m}$, and for the modified PVDF-PHEMA-CS, an ~ 5 -fold increase in the pore size was observed ($0.29 \pm 0.04 \mu\text{m}$). This effect may have been due to the pore-blocking nature of the CS solution.

Reaction mechanism

For reaction mechanism please see Scheme 1.

Characterization of ENMs by FTIR analysis

The structural characterization of the *in situ* polymerized polymer blends was analyzed by FTIR (Figure 5). PVDF (Figure 5a) shows a band at 712 cm^{-1} , which is assigned to a mixed mode of CF_2 bending and $-\text{C}-\text{C}-$ skeletal vibrations of PVDF.²⁶ The absorption band at 877 cm^{-1} is related to the out-of-plane bending or rocking of the CH_2 group of the PVDF α -phase, and the 780 cm^{-1} band corresponds to the vibration mode of the in-plane bending or rocking of the CH_2 group of the PVDF α -phase. The peaks at 1020, 3419, 1388 and 972 cm^{-1} can be assigned to the $-\text{C}-\text{O}-\text{C}$ group stretching, carbonyl overtone, CH_2 deformation and CH_2 group stretching, respectively, from the PET(BM).

The *in situ* polymerized PVDF-PHEMA (Figure 5c) exhibits two new bands at 3432 and 1722 cm^{-1} , which are attributed to the vibrations of the $\text{O}-\text{H}$ group and $-\text{C}=\text{O}$ stretching, respectively, in the HEMA polymer. The peaks at 836 and 884 cm^{-1} correspond to the CH_2 group in PET, and the peak at 1156 cm^{-1} corresponds to the $\text{C}-\text{O}-\text{C}$ stretching in PET. The spectra in Figures 5b and d show the FTIR spectra of PVDF-CS and PVDF-PHEMA-CS, respectively. Peaks at 3485 cm^{-1} ($-\text{OH}$ stretching), 1722 cm^{-1} ($-\text{C}=\text{O}$ stretch of PET), 1585 cm^{-1} ($-\text{N}-\text{H}$ bending) and 1405 cm^{-1} ($\text{C}-\text{C}$ stretch,

Scheme 1 Synthesis of the PVDF-PHEMA polymer by *in situ* polymerization.

Figure 5 FTIR spectra of (a) PVDF, (b) PVDF-CS, (c) PVDF-PHEMA and (d) PVDF-PHEMA-CS ENM. A full color version of this figure is available at *Polymer Journal* online.

aromatic) were observed for the PVDF-CS membrane. A stretching peak from the HEMA polymer and an NH_2 bending band, which is centered near 1579 cm^{-1} , confirms the surface-coated CS.^{27,28} The FTIR spectra clearly indicate that *in situ* polymerization and/or coating with CS onto the PVDF surface occurred in the process.

Surface contact angle measurements

The surface contact angle of pure PVDF is 132° , which is much larger than that of the other modified ENMs. Higher surface contact angles of ENMs have been previously reported for various polymers, and the increase in the surface contact angles is attributed to ENMs inherent roughness and trapped air pockets.^{29,30} The hydrophobicity decreased after coating with CS and *in situ* polymerization. This decrease is due to the hydrophilic nature of the CS and PHEMA polymers, where the pendant hydrophilic functional groups migrated to the surface during electrospinning. When PVDF is coated with CS, it becomes more hydrophilic and has a lower contact angle. The surface becomes hydrophilic due to surface charges from CS and a drop in the contact angle from 132° to 72° , which was observed after coating. However, PVDF-PHEMA exhibited an angle of 73.4° , which decreased to 65.1° after coating and became more hydrophilic than all of the ENMs.

BET adsorption studies

The ENMs were characterized using BET analysis. The surface areas of PVDF, PVDF + CS, PVDF-PHEMA and PVDF-PHEMA + CS were determined to be 12.56, 6.82, 19.59 and $8.72\text{ m}^2\text{ g}^{-1}$, respectively. The pore sizes of PVDF, PVDF + CS, PVDF-PHEMA and PVDF-PHEMA + CS were determined to be 3.4, 2.1, 3.4 and 2.7 nm, respectively. The results indicated that the surface areas and pore sizes of the PVDF and PVDF-PHEMA ENMs were reduced upon coating with CS polymer.

Pure water flux performance studies

Pure water permeation measurements were performed to characterize the permeation properties of the PVDF ENMs, PVDF-PHEMA and CS-coated ENMs, and the volume of permeated pure water flux (J_w) per hour is shown in Table 2. The observed decrease in the water flux is due to an increase in the hydrophilicity of the coated membrane as

Table 2 Water flux studies of the ENMs

ENM	J_w	J_p	J_R
PVDF Control	93.07	58.7	80.32
PVDF-CS	3.6	0.97	2.93
PVDF-PHEMA-Control	63.02	28.4	45.06
PVDF-PHEMA-CS	0.18	0.028	0.16

Abbreviations: CS, chitosan; ENMs, electrospun nanofibrous membranes; PVDF, poly(vinylidene fluoride); PHEMA, poly(hydroxyethylmethacrylate).

Table 3 Flux recovery ratio and flux reduction ratio of the ENMs

ENM	RFR %	FRR %
PVDF-Control	62	43
PVDF-CS	25.9	81.3
PVDF-PHEMA-Control	44	72.3
PVDF-PHEMA CS	14.5	88

Abbreviations: CS, chitosan; FRR, flux recovery ratio; ENMs, electrospun nanofibrous membranes; PVDF, poly(vinylidene fluoride); PHEMA, poly(hydroxyethylmethacrylate); RFR, relative flux reduction.

well as a decrease in the pore size. The pure PVDF ENM has the largest pore size compared with the coated and polymerized ENMs. The water flux was measured at 1 bar/h. The membrane appeared to be unfolded 1 h after the filtration process, thus providing additional information on the durability and stability of the ENMs.

Effect of protein adsorption–water flux studies

Various aspects of protein adsorption have been studied, and protein adsorption primarily depends on the surface chemistry of the compounds. The differences among protein studies primarily involve varying the surface electrostatic charges and the hydrophilic–hydrophobic interaction between the adsorbent and membranes. In addition, the pH and concentration of the BSA solution have an important role in flux studies. A 1 g l^{-1} BSA saline solution was permeated through the membrane at the same pressure and time, and the corresponding flux was recorded as J_p . The protein adsorption values are tabulated in Table 2. Among the ENMs, the PVDF control has the highest flux value ($58.71\text{ m}^{-2}\text{ h}^{-1}$). This high flux is primarily due to the hydrophobic interaction between BSA and PVDF. These types of interactions have been studied by Swanand *et al*³¹ in the protein adsorption of cerium nanoparticles. The surface of BSA (at pH 7.0) is negatively charged, and the surface of PVDF has more fluorine atoms compared with other membranes, which aid in the adsorption of proteins. An $\sim 52\%$ increase in the flux was observed for PVDF-PHEMA. These flux values were further increased to 98 and 99% upon coating with CS compared with the values of individual ENMs.

This result is due to electronic repulsion between the surface groups. The negative surface of the protein experienced repulsion from the CS surface as well as from the polymerized ENMs. This repulsion contributed to the increase in the flux. In addition, the permeation in the CS was caused by pore diffusion, which is dominant over solution diffusion.³² The permeation study was also performed for all of the ENMs after the NaOH treatment, and the water flux recovery values (J_R) were tabulated as J_R . The highest flux rates were observed for PVDF, and the flux rate increased based on the hydrophilicity of the ENM surfaces.

Figure 6 Water flux comparison of (a) PVDF-PHEMA-Control with PVDF-Control and (b) PVDF-PHEMA-CS with PVDF-CS-ENM. A full color version of this figure is available at *Polymer Journal* online.

Figure 7 Protein adsorption studies of the ENMs. A full color version of this figure is available at *Polymer Journal* online.

The antifouling property of the ENMs was calculated as the RFR % and FRR % values;^{33,34} the obtained values are summarized in Table 3. The maximum reduction (62%) in the flux was observed for hydrophobic PVDF ENM, which was caused by the larger amount of protein adsorption. For PVDF-PHEMA, the ~44% reduction in flux was caused by the PVDF ENMs over the polymerized sample. A smaller reduction in the flux was observed for the CS-coated ENMs. The FRR was also calculated, and more hydrophilic membranes exhibited a better recovery ratio compared with the PVDF ENMs, which suggested that the hydrophilic pendant hydroxyl groups (from PHEMA) on the ENM surfaces and/or the CS groups can prohibit irreversible protein adsorption. A graphical representation of the flux is shown in Figure 6.

Protein adsorption studies

Figure 7 shows the results from the protein adsorption studies at various concentrations for all of the ENMs. The adsorption increased for the control samples compared with that of the coated samples. A linear increase in the adsorption was observed as the concentration of the protein increased. At higher concentrations, there was a 0.8-fold decrease in the adsorption of the control membrane compared with that of its coated counterparts. This decrease was attributed to the increase in the hydrophilicity of the coated and modified polymers. Among the samples, PVDF-PHEMA-CS exhibited the lowest adsorption because it had the highest hydrophilicity (contribution from the modified polymer and CS) and fiber thickness; even though the surface of PVDF + CS is hydrophilic, the hydrophobic nature of PVDF ENM facilitated the enhancement of adsorption.

CONCLUSIONS

In this study, a PVDF polymer was successfully modified by *in situ* polymerization. The coating effect of the membranes with a more hydrophilic polymer was also investigated. The synthesized membranes exhibited high hydrophilicity and a reduction in pore size. Both the PVDF-CS and PVDF-PHEMA-CS membranes exhibited higher FRR due to their reduced pore size and the reduced thickness of the fiber morphology compared with PVDF and PVDF-PHEMA ENMs. The modification process and coating resulted in a remarkable improvement in the flux of the membranes. This method of surface modification followed by coating will enhance the property of materials intended for use in water filtration applications.

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