

IMPROVING HYDROPHILICITY AND PROTEIN ANTIFOULING OF ELECTROSPUN POLY(VINYLIDENEFLUORIDE-HEXAFLUOROPROPYLENE) NANOFIBER MEMBRANES*

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Abstract Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) nanofiber membranes with improved hydrophilicity and protein fouling resistance *via* surface graft copolymerization of hydrophilic monomers were prepared. The surface modification involves atmospheric pressure glow discharge plasma (APGDP) pretreatment followed by graft copolymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA). The success of the graft modification with PEGMA on the PVDF-HFP fibrous membrane is ascertained by X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance Fourier transform infrared measurements (ATR-FTIR). The hydrophilic property of the nanofiber membranes is assessed by water contact angle measurements. The results show that the PEGMA grafted PVDF-HFP nanofiber membrane has a water contact angle of 0° compared with the pristine value of 132°. The protein adsorption was effectively reduced after PEGMA grafting on the PVDF-HFP nanofiber membrane surface. The PEGMA polymer grafting density on the PVDF-HFP membrane surface is measured by the gravimetric method, and the filtration performance is characterized by the measurement of water flux. The results indicate that the water flux of the grafted PVDF-HFP fibrous membrane increases significantly with the increase of the PEGMA grafting density.

Keywords: Poly(vinylidene fluoride-hexafluoropropylene); Nanofiber membrane; Graft polymerization; Hydrophilic property; Protein fouling resistance.

INTRODUCTION

The ultrafiltration (UF) membranes have numerous applications, such as in food and dairy processing^[1], biopharmaceutical recovery^[2], wastewater treatment^[3] and reverse osmosis pretreatment^[4], but they are adversely impacted by membrane fouling from proteins, other biomolecules and organic matter due to their hydrophobic nature. In general, the biofouling of membranes prepared from hydrophobic materials will lead to a change in biomolecular structure selectively decreasing the permeate flux with time, especially in the filtration of protein, platelet or cell-containing solutions. The membrane fouling results in substantial flux decline that necessitates frequent membrane cleaning and replacement. It also modifies the retention characteristics of UF membranes, precluding their widespread adoption for protein fractionations. Antifouling of UF membranes attracted much attention in the past decades. It is found that the increase of hydrophilic moieties on a hydrophobic material surface can effectively reduce its membrane fouling as a consequence of the hydrophobic interactions between the biomolecules and the hydrophobic surface. To obtain a hydrophilic surface with anti-fouling property, several approaches have been investigated for surface modification of membranes such as

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surface grafting polymerization^[5], coating^[6] and blending^[7].

Electrospinning is a simple and versatile method for producing microporous membranes that are composed of nanofibers with diameter in the range of several micrometers to tens of nanometers^[8, 9]. The electrospun nanofiber membranes can be used as filter media such as UF membranes, nanofiltration (NF) membranes due to their highly effective porosity and large surface area to volume ratio^[10–12]. Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) is a heat resistant, chemically inert and mechanically strong polymer. It has been commonly used for the development of micro-filtration membranes and protective coating by taking advantage of its outstanding properties. PVDF-HFP can be electrospun to generate nanofiber membranes which has potential applications in the areas, such as polymer electrolytes or separators, filtration membranes^[13–16]. However, in the application involving protein solution, the protein adsorption on the PVDF-HFP membrane surface may cause serious membrane fouling due to the inherent hydrophobic nature. Therefore, there is a need to modify the surface of PVDF-HFP membranes with good hydrophilic property in order to improve their protein fouling resistance.

Plasma treatment is a convenient method for the improvement of hydrophilic property of polymer surface^[17]. However, one of the major drawbacks of plasma treatment is that the surface property can be time dependent and exhibit hydrophobic recovery^[18]. The plasma-induced graft copolymerization of hydrophilic monomers, is an efficient and versatile way of introducing a selective hydrophilic polymeric layer on the surface of a hydrophobic membrane^[19]. Plasma-induced graft copolymerization treatment is limited only to the surface and hence, the bulk properties of the membranes are still maintained. Kaur *et al.*^[20] reported the plasma-induced graft copolymerization of poly(methacrylic acid) onto electrospun poly(vinylidene fluoride) nanofiber membranes and obtained high flux performance membrane material.

Poly(ethylene glycol) (PEG) is a well-known hydrophilic polymer and has been confirmed to have significant biocompatibility such as reducing protein absorption^[21–23], inhibiting platelet adhesion^[24–26] and suppressing cell/bacteria attachment^[27–29]. The improvement of biocompatibility by immobilizing of PEG on polymer surface can be attributed to hydrophilic modification. Chang *et al.*^[30] reported the biofouling resistance of PTFE membranes by plasma induced graft copolymerization of PEGMA. Zou *et al.*^[31] used the argon plasma-induced graft polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA) on poly(tetrafluoroethylene) (PTFE) films to render the PTFE surfaces hydrophilic and protein-repellent.

The aim of this paper is to develop electrospun PVDF-HFP fibrous membranes with hydrophilic properties in order to improve their protein fouling resistance. The surface modification of the electrospun PVDF-HFP fibrous membrane is conducted by atmospheric pressure glow discharge plasma (APGDP) induced PEGMA grafting. The surface structure is characterized by XPS. The hydrophilicity of PEG grafted PVDF-HFP fibrous membranes is evaluated by water contact angle measurements. Protein fouling resistance of PEG grafted PVDF-HFP fibrous membranes is evaluated by Bovine serum albumin (BSA) deposition assay.

EXPERIMENTAL

Materials

Poly(vinylidene fluoride-hexafluoropropylene) PVDF-HFP (Flex2501) was provided by Elf Atochem. Poly(ethylene glycol) methyl ether methacrylate (PEGMA) ($M_n = 1000$) was supplied by Taijie Chemicals. *N,N*-dimethylformamide (DMF) and acetone were purchased from Shanghai Chemicals.

Electrospinning of PVDF-HFP Fibrous Membranes

Electrospun fibrous PVDF-HFP membranes were prepared using a conventional electrospinning setup. PVDF-HFP solution with the concentration of 300 g/L in the mixture of DMF and acetone (8/2, *V/V*) as a solvent was used for the electrospinning. The delivery rate of the solution was 6 mL/h. After a high voltage of +15 kV was applied to the spinneret, PVDF-HFP nanofibers were generated and deposited on the collector with a distance of 15 cm from the spinneret tip. The electrospun PVDF-HFP nanofiber membranes were dried under vacuum at room temperature.

Graft Polymerization of PEGMA on PVDF-HFP Fibrous Membranes

The as-prepared PVDF-HFP nanofibrous membrane was cut into strips (2 cm × 2 cm) and placed in a quartz vessel in a glow discharge plasma system. The plasma system was equipped with two parallel electrode plates in a distance of 6 mm and the quartz vessel was sandwiched by the electrode plates. Helium with a flow rate of 5 L/min was used as the medium of glow discharge plasma. Both surfaces of the membrane were exposed to plasma with the power of 60 W for 30 s followed by exposure to air for approximately 10 min to facilitate the formation of oxide and peroxide groups^[32] on the membrane surface.

The treated membranes were then placed in glass tubes containing 5 mL aqueous solution of PEGMA with the concentration of 2%, 5%, 10%, 20% (*W/W*), respectively and sealed with a silicone rubber stopper. Then, the tubes were placed in a water bath at 75°C for 24 h to conduct the graft polymerization. The membranes were washed with pure water repeatedly to remove any adsorbed homopolymer and unreacted monomer. The surface modified PVDF-HFP fibrous membranes were dried under vacuum.

Characterization

The morphology of the PVDF-HFP fibrous membranes was observed by SEM (Mirero AIS2100) after being coated with gold.

The surface composition of the membranes was analyzed using a highly sensitive X-ray photoelectron spectroscopy (EscaLab 210, UK). To compensate for surface charging effect, all binding energies (BEs) were referenced to the C 1s hydrocarbon peak at 284.6 eV.

The chemical composition of surface-modified PVDF-HFP fibrous membranes was characterized using a single bounce horizontal attenuated total reflectance Fourier transform infrared (ATR-FTIR, Thermo Nicolet Avatar 360, USA) spectrometer. Each spectrum was obtained by accumulating 64 scans at a resolution of 4 cm⁻¹.

The grafting density of PEGMA on the PVDF-HFP fibrous membrane was determined by the extent of weight increase compared to the pristine PVDF-HFP fibrous membrane. Prior to the weight measurements, the membranes were dried overnight in a vacuum oven at 50°C. Weight measurements were performed using three independent samples for each modified membrane, and the average value was reported.

Static water contact angles were measured at room temperature with a sessile drop method (Model JC2000C1, Shanghai zhongchen technology company). Redistilled water was used for the measurement. All measurements were triplicated for each sample.

Tensile tests of electrospun PVDF-HFP fibrous membranes were performed using a Series IX Automated Materials Testing System (Instron corporation, UK) with a 10 N load cell in a constant relative humidity (60%) room at 25°C. The thickness of these samples was measured with a digital micrometer having a precision of 1 μm. A cross-head speed of 10 mm/min was used and at least three samples were tested for each fibrous membrane.

Protein adsorption experiments were carried out by bicinchoninic acid assay (BCA Assay Kit K3000, Shanghai Biocolor BioScience & Technology Company) using bovine serum albumin (BSA) as a model^[33]. The PVDF-HFP fibrous membranes (2 cm × 2 cm) were immersed in 3 mL of BSA solution with concentration 5.08 mg/mL in phosphate-buffered saline (pH 7.4) for 24 h at room temperature. The membranes were rinsed 3 times (10 min each) in PBS to remove loosely bound protein. The sample was then transferred into a glass tube containing 3 mL of 1 wt% aqueous solution of sodium dodecyl sulfate (SDS) and shaken for 4 h at room temperature to release protein adsorbed on the membrane surface. The amount of adsorbed protein was calculated from the concentration of proteins in the SDS solution read at 562 nm and a calibration curve prepared from a pure sample measured by a Microplate Reader (Bio-Rad 680, USA). Three repeats were measured and the average value was taken.

A dead-end cell filtration system was designed to characterize the filtration performance of the membranes. A dried membrane with thickness of 150 μm was placed in the filtration cell which was then filled with 50 mL of deionized water. The pressure was gradually increased and the pressure at which the first water droplet was

observed at the permeate side was determined. This was defined as the liquid entry pressure of water (LEP_w). The membrane was then removed from the cell, wetted with 50% ethanol, and then immersed in deionized water for 30 min to ensure that the membrane was completely wet. The wetted membrane was then placed back in the cell for water flux study. The pure water flux (J_w) of the pristine or modified membranes was calculated by following equation:

$$J_w = V/(A \cdot \Delta t)$$

where, parameters V , A , and Δt were permeated water volume (L), membrane area (m²) and permeation time (h).

RESULTS AND DISCUSSION

XPS and ATR-FTIR Analyses

The surface composition of the PVDF-HFP fibrous membranes was analyzed by XPS spectroscopy as shown in Fig. 1. Two strong peaks centered at 285 eV and 689 eV are observed for the pristine PVDF-HFP fibrous membrane as indicated in Fig. 1(a), which could be attributed to C 1s and F 1s respectively. After PEGMA grafting on the PVDF-HFP fibrous membrane, a new peak centered at 525 eV could be observed, which could be attributed to O 1s as revealed in Fig. 1(b). Meanwhile, the relative strength of the peak of C 1s increases significantly and the strength of the F 1s peak decreases (Fig. 1). The results demonstrate the success of PEGMA graft modification on the PVDF-HFP fibrous membrane surface.

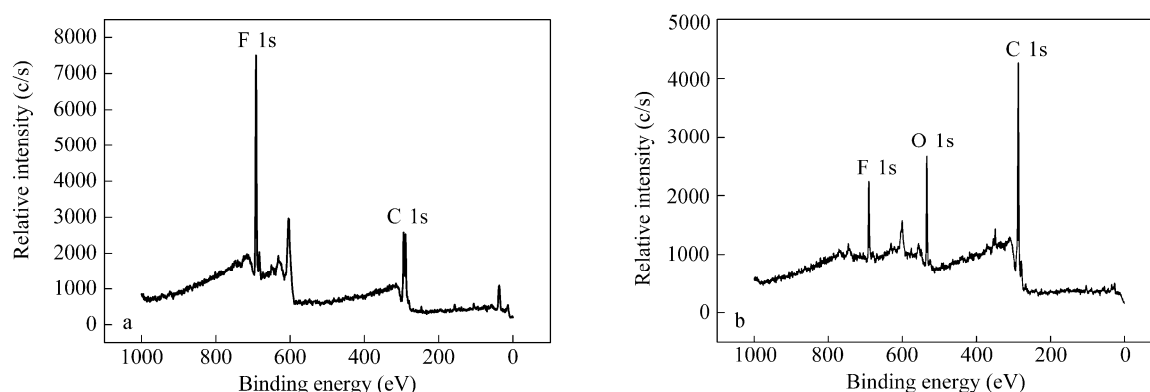


Fig. 1 Survey XPS spectra of (a) pristine and (b) PEGMA grafted PVDF-HFP fibrous membranes prepared by surface graft polymerization in 20 wt% PEGMA aqueous solution

The high resolution specific elemental core-level spectra were examined from the curve fitting spectra as shown in Fig. 2. Representative C 1s spectrum for the pristine PVDF-HFP fibrous membrane is shown in Fig. 2(a). It is found that carbon exists in three different chemical states. The 285.0 eV peak corresponds to carbon with no bonds to oxygen (C—H, hydrocarbons), the 291 eV peak is corresponding to —CF₂— and the 293 eV peak is corresponding to —CF₃. After PEGMA is grafted onto the surface of PVDF-HFP fibrous membrane, the peak of 293 eV corresponding to —CF₃ disappears, and the intensity of the peak 291 eV corresponding to —CF₂— decreases significantly as indicated in Fig. 2(b). Besides, a new peak of 287.7 eV corresponding to —C—O— is observed. Representative F 1s spectra for the pristine and the modified PVDF-HFP fibrous membrane are shown in Fig. 2(c) and Fig. 2(d), respectively. The peak of 689 eV corresponds to —CF₂— groups. After surface graft modification, a new peak at about 684 eV attributed to F[−] appears, which confirms the scission of —CF₂— group. The results further confirm that PEGMA have been introduced onto the PVDF-HFP fibrous membrane surface by the atmospheric pressure glow discharge plasma induced graft polymerization of PEGMA.

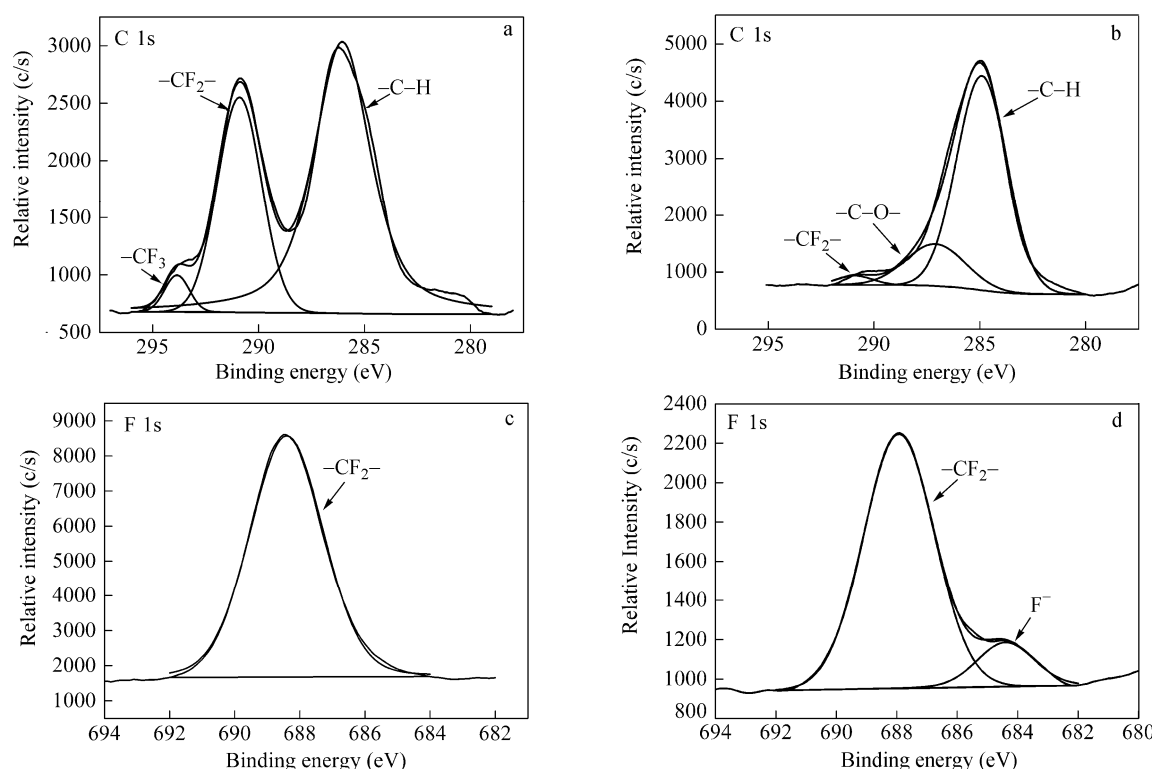


Fig. 2 High resolution C 1s and F 1s core-level spectra of (a), (c) the pristine and (b), (d) PEGMA grafted PVDF-HFP fibrous membrane prepared by surface grafting in 20 wt% PEGMA aqueous solution

The chemical composition of the PVDF-HFP fibrous membranes was further characterized by ATR-FTIR, and the typical spectra are shown in Fig. 3. For the PEGMA grafted PVDF-HFP fibrous membranes, the presence of the grafted PEGMA polymer chain can be ascertained from the band of O—C=O stretching at 1727 cm^{-1} for the ester carbonyl groups. The ratio of the intensity of the adsorption band for O—C=O at 1727 cm^{-1} to that of the adsorption band for C—F at 1400 cm^{-1} ($[\text{O—C=O}]/[\text{C—F}]$ ratio) reflects the relative graft amount of PEGMA on the PVDF-HFP fibrous membrane surface. It is found that the $[\text{O—C=O}]/[\text{C—F}]$ ratio increases upon increasing the PEGMA macromonomer content in the reaction solution. This result is in agreement with the surface grafting density (mg/cm^2) data of the PVDF-HFP fibrous membrane as shown in Fig. 4. The grafting density of the surface-modified PVDF-HFP fibrous membrane is defined as the difference in weight between the modified membrane and the pristine divided by the outer surface area of the pristine. It can be seen that the grafting density of the PEGMA polymer on the PVDF-HFP fibrous membrane increases as the PEGMA content used for surface copolymerization increases. The result indicates that the growth of the grafted PEGMA polymer is dependent on the control of the graft macromonomer concentration during the reaction.

Structure

Figure 5 shows the SEM images of PVDF-HFP fibrous membranes. The pristine PVD-HFP fibrous membrane shows a microporous structure composed of fully interconnected multi-fibrous layers and interstices between ultra-fine fibers. Average fiber diameter (AFD) of the fiber was about 800 nm. After graft polymerization of PEGMA, the surface of the PVDF-HFP fibrous membrane becomes curly and the fibers appear to swell as seen Figs. 5(b), 5(c). It may be attributed to the thermal process the membranes experienced during surface grafting^[20].

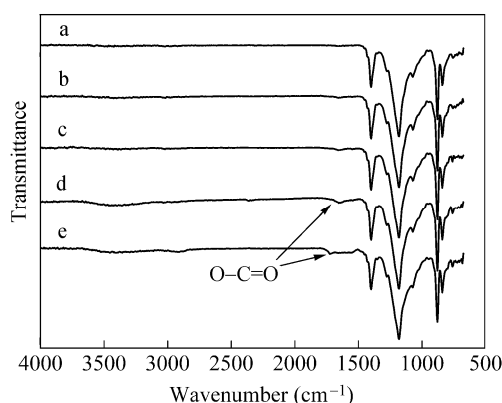


Fig. 3 ATR-FTIR spectra of PVDF-HFP fibrous membranes: (a) pristine PVDF-HFP fibrous membrane; (b), (c), (d), (e) PEGMA grafted PVDF-HFP fibrous membranes prepared by surface graft polymerization in PEGMA solutions with concentration of 2%, 5%, 10% and 20% (*W/W*), respectively

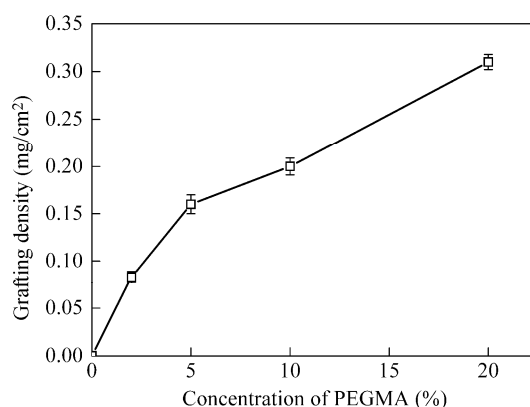


Fig. 4 Effect of PEGMA concentration in the reaction solution on the surface grafting density of the modified PVDF-HFP fibrous membrane

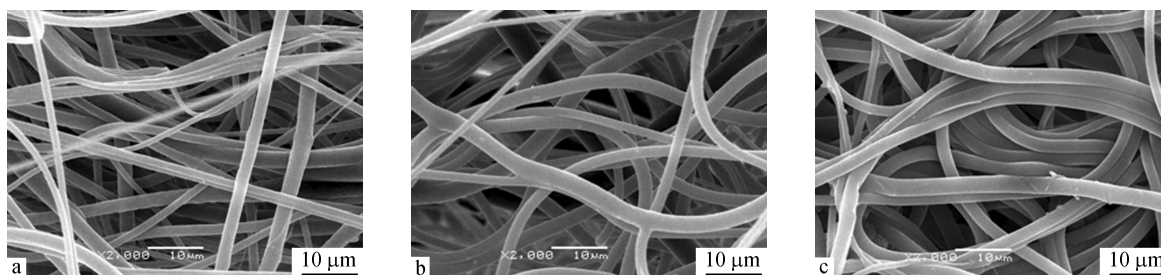


Fig. 5 SEM images of (a) pristine membrane, (b), (c) PEGMA grafted PVDF-HFP fibrous membranes prepared by surface graft polymerization in PEGMA solutions with concentration of 5% and 20% (*W/W*), respectively

Hydrophilic Properties

The water contact angle of the pristine PVDF-HFP fibrous membrane is measured to be $(132 \pm 9)^\circ$ due to inherent surface roughness and trapped air pockets as showed in Fig. 6^[20]. After plasma pretreatment with power 60 W for 30 s, water contact angle of the fibrous membrane decreases to 90° , but increases to 130° after storage in air for 4 h (Fig. 7). This is ascribed to the instability of peroxides on the surface of PVDF-HFP fibrous membrane^[18]. In comparison, the PVDF-HFP fibrous membrane without surface plasma pretreatment is immersed into PEGMA solution at concentration of 20 wt% at temperature 75°C for 24 h and washed repeatedly. It has the water contact angle of 132° , the same to that of the pristine. This indicates that the

PVDF-HFP fibrous membrane cannot be grafted with PEGMA without plasma treatment. When, the PVDF-HFP membrane was pretreated with plasma followed by graft polymerization of PEGMA, it has the contact angle of zero after contacting with water for a few seconds as indicated in Fig. 6. This is due to the inherent surface roughness of PVDF-HFP fibrous membranes. The rough surface is grafted with hydrophilic PEGMA, leading to the ultra-hydrophilic properties of the PVDF-HFP fibrous membrane.

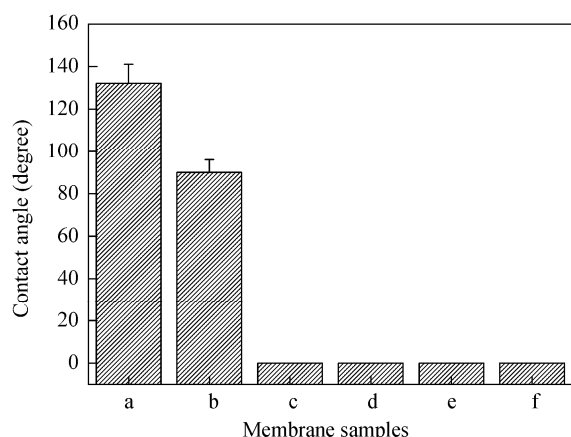


Fig. 6 Water contact angle of PVDF-HFP fibrous membranes: (a) unmodified, (b) plasma treated, (c), (d), (e) and (f) grafted in PEGMA solutions with concentration of 2%, 5%, 10% and 20%, respectively

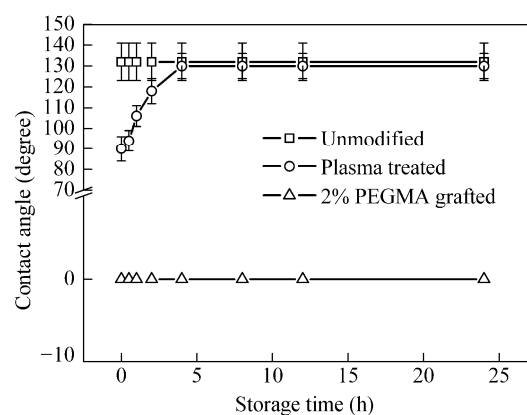


Fig. 7 Change of water contact angle of PVDF-HFP fibrous membranes after storage in air

Mechanical Properties

The mechanical properties of the PVDF-HFP fibrous membranes are listed in Table 1. The pristine PVDF-HFP fibrous membrane has tensile strength of 13.42 MPa, Young's modulus of 27.64 MPa and elongation at break of 249.63%. After APGDP induced graft polymerization of PEGMA onto surface, the PVDF-HFP fibrous membrane shows a decrease of Young's modulus and an increase of elongation at break. But the tensile strength shows no significant decrease. These results indicate that APGDP induced PEGMA graft polymerization maintains the bulk mechanical properties of electrospun PVDF-HFP fibrous membranes.

Table 1. Mechanical properties and BSA protein adsorption of PVDF-HFP fibrous membranes

Samples	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Protein absorption ($\mu\text{g}/\text{cm}^2$)
1#	13.4 ± 2.6	250 ± 45	27.6 ± 4.5	2.43 ± 0.15
2#	11.2 ± 1.1	286 ± 36	27.2 ± 1.5	1.26 ± 0.10
3#	10.9 ± 1.9	273 ± 44	25.4 ± 5.0	0.76 ± 0.11
4#	12.2 ± 1.0	261 ± 16	21.3 ± 6.8	0.20 ± 0.06
5#	14.5 ± 5.8	328 ± 10	19.7 ± 3.0	0.05 ± 0.02

1#: pristine PVDF-HFP fibrous membrane; 2#–5#: PEGMA grafted PVDF-HFP fibrous membranes prepared by surface graft polymerization in PEGMA solutions with concentration of 2%, 5%, 10% and 20% (W/W), respectively

Protein Adsorption

The protein adsorption behavior on a surface with grafted polymer chains has been extensively studied theoretically and experimentally over the past two decades. The formation of the hydration layer on a hydrophilic surface is believed to be a crucial issue to repel proteins. In this study, BSA is selected as model proteins for the testing of protein adsorption onto the surface of PVDF-HFP fibrous membranes. The protein adsorption is evaluated by immersing the membranes in 5.08 mg/mL BSA solution, and the amount of adsorbed protein is estimated by bicinchoninic acid assay as listed in Table 1. The amount of BSA protein adsorbed onto the surface of PEGMA grafted PVDF-HFP fibrous membranes is much lower than that of the pristine membrane. This is attributed to the hydrophilic property of PEGMA^[30]. Furthermore, it is found that the

reduction in protein adsorption exhibits a correlation to the concentration of PEGMA of the polymerization solution. The protein adsorption is effectively reduced with increasing the concentration of PEGMA as shown in Table 1. The results demonstrate that graft polymerization of PEGMA onto PVDF-HFP fibrous membrane surface is an effective approach for the improvement of antifouling property of the PVDF-HFP fibrous membrane.

Water Flux Performance

Water cannot penetrate inside a dry membrane unless a transmembrane hydrostatic pressure that exceeds the liquid entry pressure of water (LEP_w) was applied. The LEP_w of pristine PVDF-HFP fibrous membrane is 1.52×10^4 Pa as shown in Fig. 8. The water flux subsequently increased in an exponential manner with increasing pressure. However, the LEP_w of the PVDF-HFP fibrous membrane dropped to 0 Pa after grafting, corresponding to the rapid decrease in the water contact angle within few seconds.

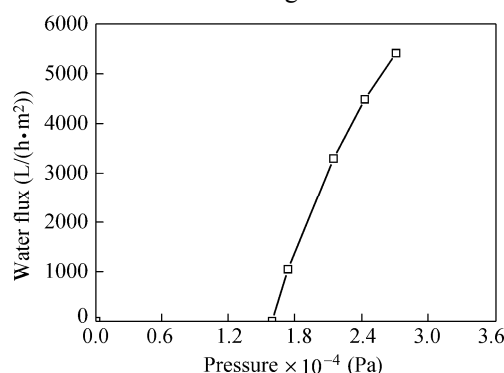


Fig. 8 Pressure-flux profile of electrospun PVDF-HFP fibrous membranes

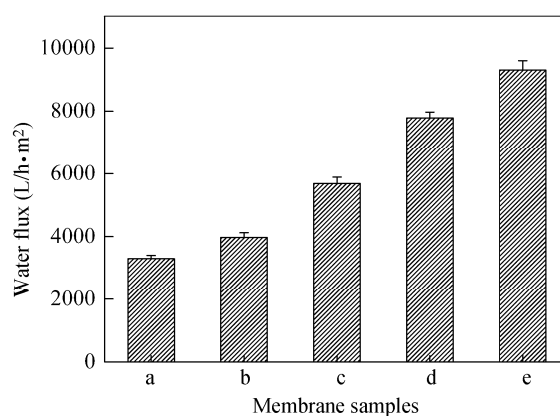


Fig. 9 Water flux of pristine and surface modified PVDF-HFP fibrous membranes: (a) pristine PVDF-HFP fibrous membrane; (b), (c), (d), (e) PEGMA grafted PVDF-HFP fibrous membranes prepared by surface graft polymerization in PEGMA solutions with concentration of 2%, 5%, 10% and 20% (W/W), respectively

The filtration performance of the prepared PVDF-HFP fibrous membrane was evaluated by deionized water filtration experiment. The measurements of water fluxes of the pristine hydrophobic PVDF-HFP fibrous membrane and PEGMA grafted PVDF-HFP fibrous membrane were carried out at pressure of 2.0×10^4 Pa. The typical results for the water fluxes of the PVDF-HFP fibrous membranes are shown in Fig. 9. It is observed that, with increase of the PEGMA grafting density, the water flux of PVDF-HFP fibrous membranes increases. Generally, pore size and surface hydrophilicity are the two parameters that affect water flux mostly^[34]. When the grafting density is low, the surface hydrophilicity is the dominant factor and the water flux enhances with the increase of grafting density accordingly. However, pore blocking becomes the leading factor at higher grafting density and causes the decline of the water flux^[35]. In this study, decline of the water flux has not been observed

yet when the PEGMA concentration is lower than 20%. The results indicate that the grafting of PEGMA onto the surface of PVDF-HFP fibrous membranes at appropriate grafting density can increase water flux efficiently.

CONCLUSIONS

In this report, the surface of electrospun PVDF-HFP fibrous membranes is successfully grafted with PEGMA by atmospheric pressure glow discharge plasma (APGDP) pretreatment and thermally induced graft copolymerization. XPS and ATR-FTIR analyses confirm the attachment of PEGMA molecules on the PVDF-HFP fibrous membrane surface. Contact angle measurement proves that the PEGMA grafted PVDF-HFP fibrous membrane shows superior hydrophilic property and protein antifouling. Moreover, with the increase of the PEGMA grafting density, the water flux of PVDF-HFP fibrous membranes increases significantly. The results reveal that the surface modified PVDF-HFP nanofibrous membranes have potential applications in the area of ultrafiltration.

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