Anti-fouling performance of mixed matrix PVDF membranes with mono-hydroxyl poly(dimethylsiloxane) (PDMS-OH) grafted silica nanoparticles

Muayad Al-Shaeli¹, Stefan J. D. Smith^{1,2}, Shanxue Jiang³, Huanting Wang¹, Kaisong Zhang⁴, and Bradley P. Ladewig^{3,5}✉

¹Monash University, Department of Chemical Engineering, Clayton, VIC, 3800, Australia

²CSIRO, Manufacturing, Private Bag 33, Clayton South MDC, VIC 3169, Australia

³Barrer Centre, Department of Chemical Engineering, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom

⁴Institute of Urban Environment, Chinese Academy of Sciences, No. 1799, Jimei Road, Xiamen 361021, China

⁵Institute for Micro Process Engineering (IMVT), Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

In this study, we investigate the use of surface-modified silica nanoparticles to improve the anti-fouling performance of PVDF ultrafiltration membranes. Here, fouling resistant nanoparticles were prepared by grafting monohydroxy-polydimethylsiloxane onto the surface of silica nanoparticles using Steglich esterification. The mixed matrix PVDF membranes were prepared at a range of nanoparticle concentrations (0, 1.6, 3.2, 6.3, and 11.8%) to understand how PDMS modified silica content affected membrane performance. The resulting hybrid membranes were characterised using a range of techniques including scanning electron microscopy (SEM), water contact angle (CA), porosity, and pore size measurements, in order to determine how morphological features of the nanocomposite membranes affected fouling and pure water flux. Embedding silica nanoparticles resulted in a significant reduction in membrane fouling, including lower protein adsorption and a flux recovery ratio of 9%. Although water flux was reduced by the addition of nanoparticles, the change in the porosity, mean pore size and the hydrophilicity of the membrane caused the rejection rate to be increased significantly. Together, these results are of particular benefit to the ultrafiltration industry, where improved antifouling and flux recovery can help reduce operating and maintenance costs in these membrane processes.

Membrane Fouling | Ultrafiltration Membranes | Hydrophobic Membranes | Hydrophilicity | Phase Inversion Method

Correspondence: bradley.ladewig@kit.edu

Introduction

Membrane filtration is one of the most promising technologies for applications of wastewater treatment due to the potential for low energy cost (1–3). Ultrafiltration membranes (UF) can be found in a range of industrial applications, including wastewater treatment due to their high permeability, low operating and energy costs, and simple operation (4–7). However, more widespread use of UF membranes is currently limited by unacceptable levels of membrane fouling, which can rapidly reduce performance and increase maintenance costs (8–11). Primarily, UF membrane fouling is caused by the adsorption and deposition of proteins and biomacromolecules on the membrane surfaces and within its pores,

which leads to drastic decline in water flux, shortened operating life and higher system costs (11–13).

Polyvinylidene fluoride (PVDF) is a particularly common polymer for UF membranes due to its excellent chemical and oxidation resistance, high mechanical strength, thermal stability, and resistance against corrosive media (14–18). Unfortunately, PVDF is also particularly susceptible to organic and biofouling due to the polymer's alternating CH₂ and CF₂ groups that produce a relatively hydrophobic and low energy surface (19, 20). On contact with process waters, foulants such as proteins, oils, and bacteria can easily attach to the membrane surface, causing a rapid degradation in water treatment performance (19, 20). If the membrane surface can be made to instead repel foulants and exhibit lower adhesion of biomolecules, the resulting anti-fouling properties would greatly improve the utility of PVDF UF membranes (19–21).

The capability of fouling repulsion is based on theory of interfacial surface free energy and can be achieved by increasing membrane hydrophilicity, so that water molecules are preferentially attracted to the surface. The resulting strongly bound water at the membrane surface can act as a barrier to foulants and prevent hydrophobic biomolecules and oils from adhering to the membrane surface (22–25). Polyethylene glycol (PEG) based materials (26), zwitterion-based materials (27), and hydrophilic nanoparticles (e.g., SiO₂) (28), as well as hydrophilic active groups are all common agents for hydrophilic surface treatments. The topology of membrane surfaces has also been shown to influence a membrane's fouling properties. Rough surfaces can disrupt the intermolecular forces responsible for foulant adhesion. This surface then allows hydrodynamic forces caused by the movement of water across such membrane surface, to remove weakly bound foulant species, resulting in an intrinsically fouling resistant surface (29–31). Fluorinated polymers make effective anti-fouling coating due to their low surface energy and Young's modulus, however the potential release of surface bound perfluorinated materials have become a major concern for their environmental and health effects. On the other hand, polysiloxanes such as polydimethylsiloxane (PDMS)

are effective lubricants and as coatings, exhibit low micro-roughness and favourable surface energy properties explaining their use in marine applications. PDMS' anti-fouling properties are related to its structure, with the rotational freedom of silicon-oxygen backbone, hindering foulant adsorption and reducing the difficulty of contaminants removal using shear forces during cleaning process (32, 33). While PDMS is also chemically stable and less toxic than perfluorinated polymers, achieving antifouling performance, while also preventing leaching and minimizing membrane pore blockage during coating treatments, represents a challenge (34–37). One solution to this issue is to incorporate surface grafted inorganic nanoparticles into polymer membrane during casting, dispersing the fouling resistant PDMS chains throughout the membrane instead of just the treatment exposed surface (38, 39).

In this work, PDMS grafted nanoparticles (PDMS-g-SiO₂ NPs) were prepared via Steglich esterification using short chain mono-hydroxy-polydimethylsiloxane and used to prepare asymmetric PVDF mixed matrix membranes. The anti-fouling performance, the surface chemistry, and the morphology of the resulting composite membranes were all investigated. Unlike prior works, which utilize grafting to enhance compatibility of nanoparticle additives, we found that not only did the singly bound PDMS silica nanoparticle grafting prevent leaching out of the PVDF matrix, it also encourages the formation of segregated nano-regions on the membrane surface. This paper aims to unite the anti-fouling properties of hydrophobic polymer (PDMS) and hydrophilic nanoparticles (SiO₂) to encourage surface segregation of desired moieties for mixed matrix PVDF membranes.

Experimental

Materials. Commercial SiO₂ (fumed) nanoparticles was obtained from Sigma Aldrich, Australia. It was mono-dispersed 7 nm (0.007 μ m) and had a surface area of 395 $\pm$ 25 m²/g. Polyvinylidene fluoride (PVDF Solef 6020, Mn=313 kDa) was purchased from Solvay and dried at 55 $^{\circ}$ C for 12 h before use. Lithium Chloride (LiCl, purity $\geq$ 99.99%, from Sigma Aldrich) was used as pore-forming agent and dried in oven at 90 $^{\circ}$ C for 12 h before use. N, N-dimethylacetamide (DMAC, purity $\geq$ 99%, from Sigma Aldrich), 3-(triethoxysilyl) propionitrile (TESPN, purity 97%, from Sigma Aldrich), N, N'-diisopropylcarbodiimide (DIC, purity 99%, from Sigma Aldrich), 4-dimethylaminopyridine (DMAP, purity 98%, from Fluka), polyethylene glycol (PEG, from Sigma Aldrich), sodium hydroxide pellets (NaOH, from Merck Millipore), and polydimethylsiloxane monohydroxy terminated (PDMS-OH, Mw = 4000 Da, from Sigma Aldrich) were used as received. Bovine serum albumin (BSA, 68 kDa, agarose gel electrophoresis, from Sigma Aldrich) was used as a model foulant during ultrafiltration experiments.

Synthesis of PDMS-g-SiO₂ nanoparticles. PDMS-g-SiO₂ nanoparticles were prepared by a three-step synthesis method, including silane coupling, functional group hydrolysis, and finally Steglich esterification, as described by Wu

and co-workers (40). First, 2g of fumed silica nanoparticles were functionalised with TESPN (a nitrile terminated silane coupling agent) at 57 $^{\circ}$ C. Exposed nitrile groups were then hydrolysed to carboxylic acid by presence of HCl/Milli-Q water (50:50) vol% at 72.5 $^{\circ}$ C for 12 h under gentle stirring, providing a reaction site for subsequent esterification. In the third step, 338.4 mg (i.e., 0.0828 mmol) mono-hydroxy (terminal) functionalised PDMS (PDMS-OH) was attached to 0.3 g carboxylic acid functionalised silica nanoparticles by a Steglich esterification with 10.45 mg (i.e., 0.0828 mmol) N, N'-diisopropylcarbodiimide (DIC) (coupling agent), in the presence of 5.06 mg (i.e., 0.0414 mmol) 4-dimethylaminopyridine (DMAP). The synthesis is summarised in Figure 1.

Fig. 1. Schematic illustration of grafting PDMS on the surface of SiO₂ nanoparticles.

Preparation of mixed matrix PVDF membranes. Mixed matrix PVDF UF membranes were prepared using a non-solvent induced phase separation (NIPS) method. For each membrane, casting solutions were prepared by dissolving different amounts of PDMS-g-SiO₂ (0, 1.6, 3.2, 6.3, 11.8%) in 16 mL DMAC, which was then sonicated for 20 min. To this solution, 0.426 g of LiCl was then added, followed by 3.2 g of PVDF and the mixture was stirred overnight at 200 rpm. Casting solution compositions are detailed in Table 1. After mixing, the casting solution was left covered in the fume cupboard to allow any air bubbles to settle. The casting solution was then poured onto a cleaned glass plate and cast using a casting knife (supplied by Paul Gardner CO., Inc.) with a 150 μ m air gap. Then, the membranes were immersed in a coagulation bath of deionised water until the membrane solidified. After peeling the membrane off from the glass plate, they were removed from the coagulation bath and washed three times with double deionised water (DDI) and stored in fresh DDI before use (33, 41). The resultant series of membranes were labelled PVDF+LiCl, SiO₂PDMS_xPVDF, where *x* is the mass fraction of PDMS-g-SiO₂ filler in the PVDF based membranes.

Characterization. The chemical structures of the modified membranes were characterized with Fourier Transform Infrared spectroscopy (FTIR) in the range of 4000-600 cm⁻¹

Membrane	PVDF	LiCl	DMAC	PDMS-g-SiO ₂ (in casting solution)	PDMS-g-SiO ₂ (in membrane)
PVDF+LiCl	15	2.0	83.00	0	0
SiO ₂ PDMS _{0.25%} PVDF	15	2.0	82.75	0.25	1.6
SiO ₂ PDMS _{0.5%} PVDF	15	2.0	82.50	0.5	3.2
SiO ₂ PDMS _{1.0%} PVDF	15	2.0	82.00	1.0	6.3
SiO ₂ PDMS _{2%} PVDF	15	2.0	81.00	2.0	11.8

Table 1. Composition in mass percent of the casting solution and resulting membranes

at a resolution of 4 cm⁻¹ and averaged from 64 scans. Surface and cross-sectional micrographs were taken by Scanning Electron Microscopy (Magellan SEM, FEI company, America). SEM samples were prepared by drying at room temperature and then sputter coating with a 0.5 nm layer of Iridium (208HR sputter coater, Cressington, UK). For cross-sectional morphology, the dried membrane samples were fractured in liquid nitrogen to retain the membrane structure. Elemental analysis of the membrane samples was conducted using EDX equipped Nova NanoSEM 450 (Quantax 400 X-ray analysis system, Bruker, USA). Thermal stability of the prepared membranes was measured using a TA Instruments 2950 thermogravimetric analyzer (TGA). Membrane samples were cut into small pieces and loaded into a high temperature platinum pan. The microbalance purge gas was nitrogen (flow rate: 2–2.5 cm³/min) and samples were heated at a rate of 20° C/min up to 1000 °under oxygen atmosphere (flow rate: 10 cm³/min).

Water contact angles of the membranes surface were measured using a contact angle goniometer by the sessile drop technique (PGX+, Fibro System Ab, Sweden). Membrane samples were cut of 1 cm × 6 cm and an average of 5 measurements for 2 or more membrane samples were reported. Membrane porosity was calculated by mass difference between the membrane soaked in water for 3 h and after drying in vacuum oven at 60 °C, according to Equation 1 (42, 43),

$$\epsilon = \frac{\frac{W_W - W_D}{\rho_W}}{\frac{W_W - W_D}{\rho_W} + \frac{W_D}{\rho_P}} \quad (1)$$

where W_W is the weight of the wet membrane (g) and W_D is the weight of the dry membrane (g). ρ_P and ρ_W are the densities of the polymer and water (g/cc).

Molecular weight cut-off (MWCO) and solute rejection were determined using a series of 1 g/L of polyethylene glycol (PEG) solutions, prepared by adding PEG of varying molecular weight (35, 100, 200 kDa) to deionized water. PEG rejection rates were calculated from the concentrations of PEG in the feed solution (C_f) and permeate water (C_P) using a total organic carbon analyser (TOC-LCSH, Shimadzu, Japan). The pore size of the membranes was then estimated based on the values of MWCO of the membrane according to the Equation 2 (44),

$$r = 0.262\sqrt{\text{MWCO}} - 0.3 \quad (2)$$

where r = pore size of membrane (nm), MWCO = molecular

weight cut-off (g/mol). MWCO was calculated by interpolating measured rejection rate to a rejection of 90%.

Pure water flux (PWF) of the unmodified PVDF and modified PVDF membranes were measured using dead-end cell filtration unit (HP4750 stirred cell, Sterlitech, USA) with membrane samples cut to a diameter of 49 mm to effective membrane area of 14.6 cm². The filtration cell was filled with 300 mL double deionized water (DDI) and then connected to 5 L dispensing vessel with compressed nitrogen gas used to control the feed pressure. The collected permeate was determined using an electronic balance with mass change recorded automatically with connected Labview software. During filtration tests, membrane samples are precompacted first at 150 kPa for at least 1 h to stabilise the flux, which is then recorded at a pressure of 100 kPa (J_{W1}). Reported flux values are averaged from tests using at least five membrane samples. Constant transmembrane fouling mode was used in this study to determine the fouling resistance of the membranes. The DDI water was exchanged for a BSA protein solution (1 g/L, prepared using phosphate buffer saline, pH = 7.4), pressurized to 100 kPa and operating for an hour. The flux (J_{BSA}) was recorded at the last 10 minutes of the 1 h operating. BSA concentrations in the feed and permeates side was measured spectroscopically at 280 nm using Varian Cary 100 Bio UV-VIS spectrophotometer. The protein rejection ratio of the membrane was calculated according to Equation 3,

$$\%R = (1 - (C_P/C_F)) \times 100 \quad (3)$$

where $R(\%)$ represented the rejection coefficient of the membrane, C_F and C_P (mg/mL) are the protein concentration of the feed and permeate streams and the concentration of BSA in the solution was calculated based on the calibration curve prepared in advance.

After testing, the fouled membranes were physically and chemically cleaned. For physical cleaning, the membranes in the filtration cell were rinsed twice with DDI for 20 min. For chemical cleaning, 100 mL of NaOH solution (2 g/L, pH=12) was added to the filtration cell and stirred for 20 min before being rinsed three times with DDI to wash off the NaOH solution. After each cleaning step, the membrane flux was recorded at 100 kPa (J_{W2}). To determine the performance of membranes, flux recovery ratio (FRR) of membranes was calculated by comparing the flux after each cleaning cycle to the flux before fouling according to Equation 4,

$$\text{FRR}(\%) = \frac{J_{W2}}{J_{W1}} \quad (4)$$

The amount of protein adsorbed on the membrane surface was determined using static protein adsorption experiments. Adsorption capacity of BSA macromolecules was evaluated by exposing the top surface of hybrid PVDF membranes (diameter 25 mm) to a BSA solution (1 mg. L⁻¹) in a stirring cell. The stirring cell was then incubated in a shaker (150 rpm agitation) at 30 °C for 24 h to reach the adsorption–desorption equilibrium. The amount of protein adsorbed on the top surface of membranes was calculated from the reduction concentration of BSA solution according to Equation 5,

$$Q = \frac{(C_a - C_b)V}{A} \quad (5)$$

where Q = protein adsorbed (mg/cm²), C_b = final concentration of BSA (g/L), A = area of membranes (cm²), V = volume of BSA solution (L).

The concentration of BSA was determined based on the absorbance at 280 nm using a UV spectroscope (UV mini-1240 spectrophotometer, Shimadzu, Japan). The results shown are the average of the protein adsorption on three separate samples. After static adsorption, the flux for the fouled membrane was recorded, before the resulting BSA-fouled membranes were physically and chemically cleaned and the flux was recorded again. The flux recovery ratio was calculated again by comparing the flux before and after physical and chemical cleaning.

Results and Discussion

Characterisation of PDMS grafted silica NPs. The characterisation results of silica and modified PDMS grafted silica nanoparticles are shown in Figure 2. The pristine and modified SiO₂ showed two main absorption peaks at 1060 and 800 cm⁻¹ which are ascribed to the stretching vibrations of Si-O-Si and Si-O respectively (45–48). After grafting with PDMS, a new characteristic peak is emerged. The 2960 cm⁻¹ peak assigned to the stretching vibration of methyl group (CH₃) in monohydroxy of (PDMS-OH) (48, 49) [48,49]. The IR spectra results indicated that PDMS are grafted successfully onto the surface of SiO₂ NPs via esterification process.

The results of gravimetric analysis of pristine SiO₂ NPs and PDMS-g-SiO₂ NPs are shown in Figure 3. The pure silica (red curve) exhibited two decomposition steps from 40-100 °C and from above 350 °C, attributed to the elimination of physically adsorbed water and chemically bonded water (via hydrogen bonding). At the temperature range of 700-1000 °C, a weight gain was observed, and this phenomenon could be due to the reaction of partially decomposed bridging organic groups with oxygen (50) [50]. This result is in line with the previous reported (40) [40]. After grafting SiO₂ with PDMS, the thermal decomposition of PDMS-g-SiO₂ NPs occurred between 300-700 °C with the weight loss of 10%, which is due to the decomposition of grafted PDMS segments on the surface of SiO₂ NPs at 336 °C. Based on previous reports, the thermal degradation of PDMS polymer at around 336 °C (40) [40]. The TGA analysis result confirmed the successful grafting of PDMS on the surface of SiO₂ NPs.

Fig. 2. FTIR-ATR spectra of SiO₂ nanoparticles, and PDMS-g-SiO₂ nanoparticles.

Fig. 3. Thermogravimetric analysis of SiO₂ nanoparticles, and PDMS-g-SiO₂ nanoparticles.

Characterization of hybrid membranes. In order to study the effect of PDMS-g-SiO₂ on the chemical composition of PVDF mixed matrix membranes, an IR spectrum is used, and the results are shown in Figure 4. All the PVDF mixed matrix membranes showed the characteristic absorption peaks at 1174, 1275 and 1405 cm⁻¹ which corresponded to the symmetrical and asymmetrical stretching of C–F and deformation vibration of CH₂ groups respectively (51).

Silica NPs are distributed well on the surface of membrane, as shown in Figure 5 (A). Figure 5 (B) shows the EDX elemental analysis of SiO₂PDMS_{0.25}PVDF membranes. The Si element was observed at 1.75 keV, which came from the inclusion of SiO₂ NPs in the membrane matrix. The peaks at 0.3 keV and 0.7 keV belong to carbon (C) and fluorine (F) coming from the PVDF structure. As revealed by Figure 5 (C), the silica NPs (red colour) is uniformly distributed on the PVDF membrane surface. This result confirms the presence of NPs within the membrane matrix.

Figure 6 shows the cross-section morphology of the control and modified PVDF membranes. A typical asymmetric structure was observed for all the PVDF membranes. The control

Fig. 4. FTIR-ATR spectra of control and mixed matrix PVDF membranes.

PVDF membranes showed a thin skin layer on the top of the membrane and short finger-like structures followed by large microvoids and thick layer in the bottom part of the membrane. After PDMS-g-SiO₂ was added to the PVDF membranes, the membranes showed a denser skin layer on the top and larger finger-like macrovoids extended to the bottom of the membrane and sponge-like structures in the bottom part. The formation of this cross-section structure was mainly influenced by the high mutual diffusivity of solvent (LiCl) and non-solvent (water). The presence of silica nanoparticles was confirmed by cross-sectional images. The control PVDF showed no trace of silica NPs within the membrane matrix. However, mixed matrix PVDF membranes showed the presence of silica nanoparticles within the membrane matrix, especially for membranes with 1% and 2% silica NPs, implying a higher migration rate of modified silica toward the membrane surface (see Figure S1).

The surface wettability of membrane is one of the most important aspects affecting the separation performance and anti-fouling property of ultrafiltration membranes. Generally, the hydrophilicity of PVDF membranes was evaluated by contact angle measurement and higher hydrophilicity resulted from smaller water contact angle. Table 2 shows the results of contact angle, porosity and pore size of control and modified PVDF membranes. It can be seen that mixed matrix PVDF membranes showed a slight increase in the results of contact angle (CA) in comparison with the control PVDF that showed 75.4° due to non-polarity of the dimethylsiloxane groups (52). The increase in CA value is ascribed to the difference in surface free interfacial energy between PVDF and PDMS.

The mean surface pore size of membranes reduced slightly from 22.1 nm for control PVDF to 21.1 nm for SiO₂PDMS_{2%}PVDF membrane when the contents of PDMS-g-SiO₂ increased. The decrease in mean surface pore size contributed to the lower flux of the modified membranes. However, the pure water flux was also affected by the surface porosity. The porosity of membranes also decreased from about 85% for control PVDF to 78% for

SiO₂PDMS_{2%}PVDF.

Separation performance of hybrid membranes. Separation performance of hybrid PVDF membranes was investigated and the results of pure water flux and BSA Rejection for control and modified PVDF membranes are shown in the Figure 7. The flux for control membrane is higher than the pristine PVDF membranes due to the use of LiCl as a hydrophilic modifier. After PDMS-g-SiO₂ is added, the hybrid membranes showed a gradual reduction in water flux. This was possibly because that the viscosity of the casting solution increased as a result of increasing the content of PDMS-g-SiO₂ NPs, thereby delaying the phase separation process and resulting in a lower porosity and lower pore size as confirmed in Table 2. The alteration in surface morphology of membrane resulted in reduction of water flux by increasing the thickness of skin layer.

The BSA rejection was increased when the concentrations of PDMS-g-SiO₂ increased. As said, the hydrophilicity of membranes may influence the anti-fouling ability of the membranes. It could be concluded that increased *R* values results from the reduced membrane pore size. The grafting of PDMS (hydrophobic polymer) on the surface of silica NPs (hydrophilic) has affected the water flux, thereby reducing the porosity and pore size.

Anti-fouling performance of hybrid membranes. The anti-fouling properties of the control and hybrid PVDF membranes were investigated by adsorption fouling and filtration fouling tests. BSA was used as protein model in this study. Figure 8 (A) shows the results of flux recovery ratio (% FRR) for control PVDF and mixed matrix PVDF. The mixed matrix PVDF membranes showed higher % FRR than the control membranes due to the formation of PDMS segments on the surface of SiO₂ during modification process and their hydrophobic character. The self-release property of PDMS facilitates the detachment of BSA foulant under hydrodynamic condition.

Membrane fouling can be classified into hydraulically reversible resistance and hydraulically irreversible resistance. Reversible resistance is caused by weakly attached foulants (i.e. protein) that are dislodged during physical and chemical cleaning. Irreversible fouling is caused by strong adherence to the membrane and is not removed using physical and chemical cleaning. Table 3 shows the results of reversible resistance (*R_r*), irreversible (*R_{ir}*) and total resistance (*R_t*) for the control and modified PVDF membranes. The results showed that the resistance factor (*R_r* and *R_{ir}*) for the mixed matrix PVDF membranes is lower than the control, indicating better anti-fouling property. It is noted that the total fouling resistance for the modified PVDF membranes was lower than the control PVDF membranes. The modified PVDF membranes suffered higher reversible fouling than irreversible fouling due to the fact that higher transmembrane pressure (TMP) was required during the fouling process due to the decrease the pore size of the hybrid PVDF membranes compared to the control PVDF. However, with the adding of PDMS-g-SiO₂ NPs to the casting solution

Fig. 5. (A) SEM top surface morphology of SiO₂PDMS_{0.25%} PVDF membranes. The red arrows point out the presence of NPs. (B) EDX elemental analysis of the hybrid PVDF membrane SiO₂PDMS_{0.25%} PVDF. (C) EDX mapping of the hybrid PVDF membrane SiO₂PDMS_{0.25%}.

Membrane	Porosity (%)	Contact angle (°)	MWCO (kDa)	Pore size (nm)	Thickness (μm)
PVDF+LiCl	85.3	75.4±1.2	188	22.1	45.00
SiO ₂ PDMS _{0.25%} PVDF	83.8	77.7±0.3	186	21.8	49.11
SiO ₂ PDMS _{0.5%} PVDF	80.3	78.0±0.7	182	21.7	55.39
SiO ₂ PDMS _{1.0%} PVDF	79.9	80.5±0.8	180	21.6	54.32
SiO ₂ PDMS _{2%} PVDF	78.0	82.9±1.3	178	21.1	56.35

Table 2. Porosity, contact angle, MWCO and pore size for all hybrid PVDF membranes

Membrane	R_t (%)	R_r (%)	R_{ir} (%)	R_r/R_{ir} (-)	R_{ir}/R_t (-)
Control PVDF	84.38	43.30	41.08	0.51	0.48
SiO ₂ PDMS _{0.25%} PVDF	56.01	28.75	27.26	0.51	0.48
SiO ₂ PDMS _{0.5%} PVDF	75.16	50.34	24.82	0.66	0.33
SiO ₂ PDMS _{1.0%} PVDF	84.57	61.62	22.95	0.72	0.27
SiO ₂ PDMS _{2%} PVDF	60.36	35.95	24.42	0.57	0.40

Table 3. Fouling resistance for control and hybrid PVDF membranes

Fig. 6. (A) SEM cross-section morphology of (A) control PVDF membrane. (B) SiO₂/PDMS_{0.25%} membrane. (C) SiO₂/PDMS_{0.5%} membrane. (D) SiO₂/PDMS_{1.9%} membrane. (E) SiO₂/PDMS_{2.0%} membrane.

Fig. 7. Pure water flux and BSA rejection of pristine and hybrid PVDF UF membranes. 1 g/L BSA was chosen as the feed solution and the filtration pressure was 100 kpa. The bar height is the average of five measurements and the error bars represent one standard deviation.

of PVDF membranes, the irreversible fouling was slightly decreased from 41% for control PVDF to around 24% for SiO₂/PDMS_{2%} PVDF whilst the reversible fouling increased. These results show that the modified membranes have good anti-fouling properties. In comparison with control PVDF, the ratio of (R_r/R_t) increased over the ratio of (R_{ir}/R_t) for the mixed matrix PVDF membranes, indicating that the BSA protein adsorbed onto the top surface of membranes was more easily to be washed off during the cleaning process. Therefore, better membrane performance was achieved.

To sum up, the flux recovery ratio (%FRR), irreversible fouling (R_{ir}), and reversible fouling (R_r) of the PDMS-g-SiO₂ embedded membranes were enhanced, indicating the surface properties of the membranes was modified. Static protein adsorption is one of the most factors in determining the anti-fouling properties of membranes and the reduction of protein (foulant) on the membrane surface indicates better anti-fouling property of the membranes. The results of static protein adsorption are shown in Figure 8 (B). BSA was used as model pollutant foulant. It was observed that the adsorption mass of hybrid PVDF is slashed from (5.21 $\mu\text{g}/\text{cm}^2$) for control PVDF to (1.99 $\mu\text{g}/\text{cm}^2$) for SiO₂/PDMS_{2%} PVDF when the added content of PDMS-g-SiO₂ NPs increased because the presence of SiO₂-g-PDMS in the skin layer (as confirmed

Fig. 8. (A) Flux recovery ratio (%FRR) of control and hybrid PVDF membranes. (B) Static protein adsorption and %FRR of the hybrid PVDF membranes. The bar height is the average of five measurements and the error bars represent one standard deviation.

by SEM morphology) has the capability to mitigate the adsorption of BSA pollutant due to the surface enriched of PDMS chains and self-released ability. Flux recovery ratio (%FRR) was measured again after BSA adsorption and the results are shown in Figure 8 (B). It is observed that FRR is higher for all the hybrid PVDF membranes and there is consistency between %FRR after fouling process and %FRR after static adsorption of BSA.

Conclusions

The mixed matrix PVDF membranes were prepared via traditional non-induced phase inversion method (NIPS) using PDMS-g-SiO₂ as modifier. PDMS-g-SiO₂ NPs was able to improve the anti-fouling properties of mixed matrix PVDF membranes by improving the FRR ratio. Based on the release properties of PDMS polymer, the hybrid membranes exhibited lower BSA protein adsorption on their surface during static protein adsorption test. Due to the added PDMS-g-SiO₂, the ratio of R_r/R_t increased. This indicates that the BSA molecules adsorbed onto the top surface of hybrid PVDF membranes was more easily washed off during cleaning. These results are of particular importance to the ultrafiltration industry, since improved antifouling and flux recovery can help reduce operating and maintenance costs in these membrane processes.

Supporting data. The raw experimental data from the figures, and additional images, are available from the open repository DOI:10.5281/zenodo.4139586

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Bibliography

- Xing Yin, Zhaoju Zhang, Hongyang Ma, Shyam Venkateswaran, and Benjamin S. Hsiao. Ultra-fine electrospun nanofibrous membranes for multicomponent wastewater treatment: Filtration and adsorption. *Separation and Purification Technology*, 242(January), 2020. ISSN 18733794. doi: 10.1016/j.seppur.2020.116794.
- Selina Hube, Majid Eskafi, Kolbrún Friða Hrafnkelsdóttir, Björg Bjarnadóttir, Margrét Ásta Bjarnadóttir, Snærós Axelsdóttir, and Bing Wu. Direct membrane filtration for wastewater

treatment and resource recovery: A review. *Science of the Total Environment*, 710, 2020. ISSN 18791026. doi: 10.1016/j.scitotenv.2019.136375.

- Junning Hong and Yang He. Polyvinylidene fluoride ultrafiltration membrane blended with nano-ZnO particle for photo-catalysis self-cleaning. *Desalination*, 332(1):67–75, 2014. ISSN 00119164. doi: 10.1016/j.desal.2013.10.026.
- Vadim Potapov, Roman Fediuk, and Denis Gorev. Membrane concentration of hydrothermal SiO₂ nanoparticles. *Separation and Purification Technology*, 251(March), 2020. ISSN 18733794. doi: 10.1016/j.seppur.2020.117290.
- Yifeng Huang and Xianshe Feng. Polymer-enhanced ultrafiltration: Fundamentals, applications and recent developments. *Journal of Membrane Science*, 586(March):53–83, 2019. ISSN 18733123. doi: 10.1016/j.memsci.2019.05.037.
- Tausif Ahmad, Chandan Guria, and Ajay Mandal. A review of oily wastewater treatment using ultrafiltration membrane: A parametric study to enhance the membrane performance. *Journal of Water Process Engineering*, 36(June):101289, 2020. ISSN 22147144. doi: 10.1016/j.jwpe.2020.101289.
- Polina D. Peeva, Thomas Knoche, Thorsten Pieper, and Mathias Ulbricht. Cross-flow ultrafiltration of protein solutions through unmodified and surface functionalized polyethersulfone membranes - Effect of process conditions on separation performance. In *Separation and Purification Technology*, volume 92, pages 83–92, 2012. doi: 10.1016/j.seppur.2012.03.013.
- Heru Susanto, Muhammad H. Robbani, Titik Istirokhatun, Abdullah A. Firmansyah, and Reza N. Rhamadhan. Preparation of low-fouling polyethersulfone ultrafiltration membranes by incorporating high-molecular-weight chitosan with the help of a surfactant. *South African Journal of Chemical Engineering*, 33(July):133–140, 2020. ISSN 10269185. doi: 10.1016/j.sajce.2020.07.003.
- Bin Liu, Tingting Zhu, Wenkai Liu, Rui Zhou, Shiqing Zhou, Ruoxi Wu, Lin Deng, Jing Wang, and Bart Van der Bruggen. Ultrafiltration pre-oxidation by boron-doped diamond anode for algae-laden water treatment: membrane fouling mitigation, interface characteristics and cake layer organic release. *Water Research*, 187:116435, 2020. ISSN 18792448. doi: 10.1016/j.watres.2020.116435.
- Fangshu Qu, Zhimeng Yang, Xiaoliang Li, Huarong Yu, Zhihui Pan, Gongdian Fan, Junguo He, and Hongwei Rong. Membrane fouling control by UV/persulfate in tertiary wastewater treatment with ultrafiltration: A comparison with UV/hydroperoxide and role of free radicals. *Separation and Purification Technology*, 257(August 2020):117877, 2021. ISSN 18733794. doi: 10.1016/j.seppur.2020.117877.
- Yanlei Su, Chao Li, Wei Zhao, Qing Shi, Haijing Wang, Zhongyi Jiang, and Shiping Zhu. Modification of polyethersulfone ultrafiltration membranes with phosphorylcholine copolymer can remarkably improve the antifouling and permeation properties. *Journal of Membrane Science*, 322(1):171–177, 2008. ISSN 03767388. doi: 10.1016/j.memsci.2008.05.047.
- Shanxue Jiang, Yuening Li, and Bradley P. Ladewig. A review of reverse osmosis membrane fouling and control strategies. *Science of the Total Environment*, 595:567–583, 2017. ISSN 18791026. doi: 10.1016/j.scitotenv.2017.03.235.
- Zixiao Ren, Xiaoliang Cheng, Peijie Li, Congwei Luo, Fengxun Tan, Weiwei Zhou, Wenchen Liu, Lu Zheng, and Daoji Wu. Ferrous-activated sodium percarbonate pre-oxidation for membrane fouling control during ultrafiltration of algae-laden water. *Science of the Total Environment*, 739:140030, 2020. ISSN 18791026. doi: 10.1016/j.scitotenv.2020.140030.
- Haixiang Yu, Lin Gu, Sifan Wu, Guangxia Dong, Xingbo Qiao, Kai Zhang, Xiangyu Lu, Haifeng Wen, and Daofang Zhang. Hydrothermal carbon nanospheres assisted-fabrication of PVDF ultrafiltration membranes with improved hydrophilicity and antifouling performance. *Separation and Purification Technology*, 247(January):116889, 2020. ISSN 18733794. doi: 10.1016/j.seppur.2020.116889.
- Jiayun Zhu, Shouyong Zhou, Meisheng Li, Ailian Xue, Yijiang Zhao, Wenbo Peng, and Weihong Xing. PVDF mixed matrix ultrafiltration membrane incorporated with deformed rebar-like Fe₃O₄-palygorskite nanocomposites to enhance strength and antifouling properties. *Journal of Membrane Science*, 612(July):118467, 2020. ISSN 18733123. doi: 10.1016/j.memsci.2020.118467.
- Xiujuan Chen, Gordon Huang, Yongping Li, Chunjiang An, Renfei Feng, Yinghui Wu, and Jian Shen. Functional PVDF ultrafiltration membrane for Tetrabromobisphenol-A (TBBPA) removal with high water recovery. *Water Research*, 181:115952, 2020. ISSN 18792448.

doi: 10.1016/j.watres.2020.115952.

17. Zhao Wang, Rajesh Sahadevan, Caitlin Crandall, Todd J. Menkhaus, and Hao Fong. Hot-pressed PAN/PVDF hybrid electrospun nanofiber membranes for ultrafiltration. *Journal of Membrane Science*, 611(May):118327, 2020. ISSN 18733123. doi: 10.1016/j.memsci.2020.118327.
18. Shanxue Jiang and Bradley P. Ladewig. Green synthesis of polymeric membranes: Recent advances and future prospects. *Current Opinion in Green and Sustainable Chemistry*, 21: 1–8, 2020. ISSN 24522236. doi: 10.1016/j.cogsc.2019.07.002.
19. J. F. Hester, P. Banerjee, and A. M. Mayes. Preparation of Protein-Resistant Surfaces on Poly(vinylidene fluoride) Membranes via Surface Segregation. *Macromolecules*, 32(5): 1643–1650, 1999. ISSN 00249297. doi: 10.1021/ma980707u.
20. J. F. Hester and A. M. Mayes. Design and performance of foul-resistant poly(vinylidene fluoride) membranes prepared in a single-step by surface segregation. *Journal of Membrane Science*, 202(1–2):119–135, 2002. ISSN 03767388. doi: 10.1016/S0376-7388(01)00735-9.
21. Saheli Roy, Dixit V. Bhalani, and Suresh K. Jewrajka. Surface segregation of segmented amphiphilic copolymer of poly(dimethylsiloxane) and poly(ethylene glycol) on poly(vinylidene fluoride) blend membrane for oil–water emulsion separation. *Separation and Purification Technology*, 232(March 2019):115940, 2020. ISSN 18733794. doi: 10.1016/j.seppur.2019.115940.
22. D. Rana and T. Matsuura. Surface modifications for antifouling membranes. *Chemical Reviews*, 110(4):2448–2471, 2010. ISSN 00092665. doi: 10.1021/cr800208y.
23. Motoyasu Kobayashi, Yuki Terayama, Hiroki Yamaguchi, Masami Terada, Daiki Murakami, Kazuhiko Ishihara, and Atsushi Takahara. Wettability and antifouling behavior on the surfaces of superhydrophilic polymer brushes. *Langmuir*, 28(18):7212–7222, 2012. ISSN 07437463. doi: 10.1021/la301033h.
24. Zaki G. Estephan, Philip S. Schlenoff, and Joseph B. Schlenoff. Zwitteration as an alternative to PEGylation. *Langmuir*, 27(11):6794–6800, 2011. ISSN 07437463. doi: 10.1021/la200227b.
25. Joseph B. Schlenoff. Zwitteration: Coating surfaces with zwitterionic functionality to reduce nonspecific adsorption, 2014. ISSN 15205827.
26. Yung Chang, Chao Yin Ko, Yu Ju Shih, Damien Quémener, André Deratani, Ta Chin Wei, Da Ming Wang, and Juin Yih Lai. Surface grafting control of PEGylated poly(vinylidene fluoride) antifouling membrane via surface-initiated radical graft copolymerization. *Journal of Membrane Science*, 345(1–2):160–169, 2009. ISSN 03767388. doi: 10.1016/j.memsci.2009.08.039.
27. Shengfu Chen, Jie Zheng, Lingyan Li, and Shaoyi Jiang. Strong resistance of phosphorylcholine self-assembled monolayers to protein adsorption: Insights into nonfouling properties of zwitterionic materials. *Journal of the American Chemical Society*, 127(41):14473–14478, 2005. ISSN 00027863. doi: 10.1021/ja054169u.
28. Lilin Zhou, Weizhong Yuan, Jinying Yuan, and Xiaoyin Hong. Preparation of double-responsive SiO₂-g-PDMEA nanoparticles via ATRP. *Materials Letters*, 62(8–9):1372–1375, 2008. ISSN 0167577X. doi: 10.1016/j.matlet.2007.08.057.
29. Xueting Zhao, Yanlei Su, Yafei Li, Runnan Zhang, Jiaojiao Zhao, and Zhongyi Jiang. Engineering amphiphilic membrane surfaces based on PEO and PDMS segments for improved antifouling performances. *Journal of Membrane Science*, 450:111–123, 2014. ISSN 03767388. doi: 10.1016/j.memsci.2013.08.044.
30. M. Lejars, A. Margailan, and C. Bressy. Fouling release coatings: A nontoxic alternative to biocidal antifouling coatings. *Chemical Reviews*, 112(8):4347–4390, 2012. doi: 10.1021/cr200350v.
31. Jing Zhao, Xueting Zhao, Zhongyi Jiang, Zhen Li, Xiaochen Fan, Junao Zhu, Hong Wu, Yanlei Su, Dong Yang, Fusheng Pan, and Jiafu Shi. Biomimetic and bioinspired membranes: Preparation and application. *Progress in Polymer Science*, 39(9):1668–1720, 2014. ISSN 00796700. doi: 10.1016/j.progpolymsci.2014.06.001.
32. James E. Mark. Some interesting things about polysiloxanes. *Accounts of Chemical Research*, 37(12):946–953, 2004. ISSN 00014842. doi: 10.1021/ar030279z.
33. Michael J. Owen. Low Surface Energy Inorganic Polymers. *Comments on Inorganic Chemistry*, 7(4):195–213, 1988. ISSN 15489574. doi: 10.1080/02603598808072308.
34. Harihara S. Sundaram, Youngjin Cho, Michael D. Dimitriou, John A. Finlay, Gemma Cone, Sam Williams, Dale Handlin, Joseph Gatto, Maureen E. Callow, James A. Callow, Edward J. Kramer, and Christopher K. Ober. Fluorinated amphiphilic polymers and their blends for fouling-release applications: The benefits of a triblock copolymer surface. *ACS Applied Materials and Interfaces*, 3(9):3366–3374, 2011. ISSN 19448244. doi: 10.1021/am200529u.
35. Harihara S. Sundaram, Youngjin Cho, Michael D. Dimitriou, Craig J. Weinman, John A. Finlay, Gemma Cone, Maureen E. Callow, James A. Callow, Edward J. Kramer, and Christopher K. Ober. Fluorine-free mixed amphiphilic polymers based on PDMS and PEG side chains for fouling release applications. *Biofouling*, 27(6):589–602, 2011. ISSN 08927014. doi: 10.1080/08927014.2011.587662.
36. S. S. Madaeni, S. Zinadini, and V. Vatanpour. Preparation of superhydrophobic nanofiltration membrane by embedding multiwalled carbon nanotube and polydimethylsiloxane in pores of microfiltration membrane. *Separation and Purification Technology*, 111:98–107, 2013. ISSN 13835866. doi: 10.1016/j.seppur.2013.03.033.
37. Md Saifur Rahaman, Hlose Thrien-Aubin, Moshe Ben-Sasson, Christopher Kemper Ober, Melissa Nielsen, and Menachem Elimelech. Control of biofouling on reverse osmosis polyamide membranes modified with biocidal nanoparticles and antifouling polymer brushes. *Journal of Materials Chemistry B*, 2(12):1724–1732, 2014. ISSN 20507518. doi: 10.1039/c3tb21681k.
38. Kurunthachalam Kannan, Jaana Koistinen, Kimberlee Beckmen, Thomas Evans, Jay F. Gorzelany, Kris J. Hansen, Paul D. Jones, Eero Helle, Madeleine Nyman, and John P. Giesy. Accumulation of perfluorooctane sulfonate in marine mammals. *Environmental Science and Technology*, 35(8):1593–1598, 2001. ISSN 0013936X. doi: 10.1021/es001873w.
39. Wendy D'Hollander, Luc De Bruyn, An Hagenaars, Pim de Voogt, and Lieven Bervoets. Characterisation of perfluorooctane sulfonate (PFOS) in a terrestrial ecosystem near a fluorochemical plant in Flanders, Belgium. *Environmental Science and Pollution Research*, 21(20):11856–11866, 2014. ISSN 16147499. doi: 10.1007/s11356-013-2449-4.
40. Hao Wu, Jaleh Mansouri, and Vicki Chen. Silica nanoparticles as carriers of antifouling ligands for PVDF ultrafiltration membranes. *Journal of Membrane Science*, 433:135–151, 2013. ISSN 03767388. doi: 10.1016/j.memsci.2013.01.029.
41. C. A. Smolders, A. J. Reuvers, R. M. Boom, and I. M. Wienk. Microstructures in phase-inversion membranes. Part 1. Formation of macrovoids. *Journal of Membrane Science*, 73(2–3):259–275, 1992. ISSN 03767388. doi: 10.1016/0376-7388(92)80134-6.
42. C. Feng, R. Wang, B. Shi, G. Li, and Y. Wu. Factors affecting pore structure and performance of poly(vinylidene fluoride-co-hexafluoro propylene) asymmetric porous membrane. *Journal of Membrane Science*, 277(1–2):55–64, 2006. doi: 10.1016/j.memsci.2005.10.009.
43. N. Li, C. Xiao, S. An, and X. Hu. Preparation and properties of PVDF/PVA hollow fiber membranes. *Desalination*, 250(2):530–537, 2010. doi: 10.1016/j.desal.2008.10.027.
44. C.M. Tam and A.Y. Tremblay. Membrane pore characterization-comparison between single and multicomponent solute probe techniques. *Journal of Membrane Science*, 57(2–3):271–287, 1991. doi: 10.1016/S0376-7388(00)80683-3.
45. Qing Shi, Yanlei Su, Wei Zhao, Chao Li, Yaohui Hu, Zhongyi Jiang, and Shiping Zhu. Zwitterionic polyethersulfone ultrafiltration membrane with superior antifouling property. *Journal of Membrane Science*, 319(1–2):271–278, 2008. ISSN 03767388. doi: 10.1016/j.memsci.2008.03.047.
46. E. Yuliwati, A. F. Ismail, T. Matsuura, M. A. Kassim, and M. S. Abdullah. Effect of modified pvdf hollow fiber submerged ultrafiltration membrane for refinery wastewater treatment. *Desalination*, 283:214–220, 2011. ISSN 00119164. doi: 10.1016/j.desal.2011.03.049.
47. S.P. Nunes, M.L. Sfora, and K.-V. Peinemann. Dense hydrophilic composite membranes for ultrafiltration. *Journal of Membrane Science*, 106(1–2):49–56, 1995. doi: 10.1016/0376-7388(95)00076-0.
48. J.T. Park, J.A. Seo, S.H. Ahn, J.H. Kim, and S.W. Kang. Surface modification of silica nanoparticles with hydrophilic polymers. *Journal of Industrial and Engineering Chemistry*, 16(4):517–522, 2010. doi: 10.1016/j.jiec.2010.03.030.
49. Bumsuk Jung. Preparation of hydrophilic polyacrylonitrile blend membranes for ultrafiltration. *Journal of Membrane Science*, 229(1–2):129–136, 2004. ISSN 03767388. doi: 10.1016/j.memsci.2003.10.020.
50. M.A. Wahab, Il. Kim, and C.-S. Ha. Hybrid periodic mesoporous organosilica materials prepared from 1,2-bis(triethoxysilyl)ethane and (3-cyanopropyl)triethoxysilane. *Microporous and Mesoporous Materials*, 69(1–2):19–27, 2004. doi: 10.1016/j.micromeso.2004.01.001.
51. A. Cassano, M. Marchio, and E. Drioli. Clarification of blood orange juice by ultrafiltration: analyses of operating parameters, membrane fouling and juice quality. *Desalination*, 212(1–3):15–27, 2007. ISSN 00119164. doi: 10.1016/j.desal.2006.08.013.
52. Cheryl R. Tanardi, Ana F.M. Pinheiro, Arian Nijmeijer, and Louis Winnubst. PDMS grafting of mesoporous γ -alumina membranes for nanofiltration of organic solvents. *Journal of Membrane Science*, 469:471–477, 2014. ISSN 18733123. doi: 10.1016/j.memsci.2014.07.010.