

Enhancement of Resistance to Protein Fouling of Poly(ether imide) Membrane by Surface Grafting with PEG under Organic Solvent-free Condition

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Abstract Poly(ether imide) (PEI) membrane with enhanced antifouling property was successfully prepared in a mild and simple procedure. The virgin membrane was firstly functionalized with an aqueous solution of diamino-terminated poly(ethylene oxide) block copolymer (PEG-diamine). Glutaraldehyde was used in a second step as a linker to chemically attach additional PEG-diamine to the primary amine groups grafted on PEI membrane surface. Immobilization of PEG segments was confirmed using Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy and atomic force microscopy. Ultrafiltration experiments revealed that the enhancement of a PEG coverage on the membrane surface provided superior anti-protein-fouling property. Cycles of protein filtration also demonstrated that the antifouling surface was stable over time and excellent ultrafiltration performance could be maintained without the need of harsh cleansing operation.

Keywords Poly(ether imide); Surface modification; Anti-protein-fouling; Ultrafiltration; Poly(ethylene glycol)

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INTRODUCTION

Membrane fouling in water treatment often arises from the deposition and adsorption of natural organic matter and proteins to the surface and internal pores of polymeric membrane^[1–3]. This phenomenon is a severe problem in ultrafiltration membrane process because it leads to a reduction of permeation flux, membrane selectivity and lifetime^[4]. An increase in membrane hydrophilicity is believed to be the more efficient approach to reduce membrane fouling by biomolecules. In recent years, the development of surface modification has been reported by numerous researchers and can be divided into two main methods, *i.e.* polymer modification by either synthesis of new polymeric materials, modification of available polymer or blending with hydrophilic additives before membrane preparation (pre-modification) and surface modification or functionalization after membrane preparation (post-modification)^[5].

The former route is a way leading to an alteration of the hydrophilic nature of polymer matrix at molecular level in bulk solution. Consequently, by using this method, the increase of hydrophilicity of both the inner part and the outer

surface of membranes is obtained. However, either synthesis of new materials or modification of polymer needs a large number of starting materials that can be expensive, toxic and pollutant. Therefore, blending novel or available hydrophilic additives with hydrophobic polymer matrix is the simplest and the more common route for modifying the membrane hydrophilicity. However, it has been extensively shown that the membrane performance is deteriorated during ageing by filtration and cleaning procedure due to a low coverage of additives on membrane surface and their leaching out^[5, 6].

On the other hand, many investigations have been carried out to increase the membrane surface hydrophilicity by coating, grafting and functionalization of the membrane surface^[7, 8]. Surface coating is the simplest way for a membrane surface post-modification but it most often suffers from the same drawback as blending *i.e.* long-term instability due to weak adhesion of the coating layer to membrane surface^[9]. Stronger stable binding can be created through covalent bonds. Thus, hydrophilic membrane surfaces have been designed by chemically or radiation-induced grafting polymerization of monomer on the membrane surface, yielding the membrane resistant to fouling and to cleansing procedure^[5]. However, the method needs a pretreatment step using UV^[10], ozone^[11], plasma^[12] and γ -radiation^[13], which requires high cost operation and may lead to polymer degradation^[5, 14]. A milder approach consists of performing the chemical modification with a

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liquid reagent generating reactive functional groups without requirement of specialized equipment. Interestingly, this approach makes an easier and deeper penetration of modifying agents into the porous membrane structures than the previous routes, enabling a better coverage of the whole entire pore surface area^[15]. The PEGylation of membrane surfaces to improve their antifouling performance has been extensively studied. For instance, recent work successfully prepared PEGylated polysulfone (PSF) ultrafiltration membranes by conducting the copper(I) catalyzed azide-alkyne cycloaddition reaction to graft propargyl terminated poly(ethylene glycol) (PEG)^[16, 17]. The obtained PSF-g-PEG membrane surface provided excellent antifouling property with a 95% flux recovery after three cycles of real oily waste water emulsion filtration^[17]. For the same purpose, Ugi four-component reaction was recently exploited to graft PEG on polyamide top surface of reverse osmosis membranes in a single step under mild condition in methanol without any catalyst^[18]. On the other hand, we have reported on the fabrication of surface hydrophilyzed poly(ether imide) (PEI) membranes without using harmful solvent and reagent as it is generally done in most of the published works to date^[19, 20].

Polyimide and PEI are polymer materials with excellent film forming ability, good mechanical properties, thermal stability and chemical resistance^[21]. However, their direct use for membrane formation is limited in the case of application in water treatment due to their hydrophobic nature, which is a major drawback leading to severe membrane fouling. Fortunately, the backbone of these polymers comprises imide groups available for reaction with nucleophilic functions like amine groups^[21]. For instance, it has been demonstrated that hydrophilicity of PEI membranes can be significantly enhanced by a wet chemical treatment using aliphatic amine or poly(ethylene imine) in propanol or its mixture with water as a solvent^[21–24]. On the other hand, it was shown from our previous work that hydrophilic PEGylated PEI membrane can be successfully obtained in mild condition using a commercial amino-terminated poly(propylene oxide)/poly(ethylene oxide) copolymer in water as solvent^[19]. The modified membrane showed a strong improvement of the resistance to protein fouling with a water flux recovery ratio of more than 85%. Based on this study, it can be concluded that the antifouling property of PEI membrane depends on the surface hydrophilicity related to the PEG block density. We then assume that an enhancement of the PEG coverage should provide an even better antifouling property of the PEGylated PEI membrane.

We report herein the preparation of PEGylated PEI membranes with excellent resistance to the protein fouling by using a similar approach as previously described^[19, 20]. Our strategy is to perform the post-treatment in a two-step procedure. In that case, Jeffamine® ED-2003 based on a predominantly PEG backbone with each extremity terminated by an amino group (PEG-diamine) was used as the modifying agent. It is expected that only a part of primary amine groups reacts directly with the imide groups of PEI and the remaining amine groups can be further reacted with other functional group to enhance the coverage

of PEG chains and thereby to create a very hydrophilic layer on the membrane surface. Thus, a subsequent grafting was carried out by reacting the treated PEI membrane with glutaraldehyde (GA) as a linker and PEG-diamine. Performance of the resulting membranes for protein filtration was evaluated as a function of the post-treatment conditions. These results showed that this approach not only is simple but also enables the design of very efficient anti-protein-fouling membrane surface under mild conditions.

EXPERIMENTAL

Materials

PEI (ULTEM 1000®) was kindly supplied by NOK Precision Component (Thailand) Ltd. The modifying agent PEG-diamine (Jeffamine® ED-2003, 2 kDa) was a gift from Huntsman (USA). Anhydrous NMP, glutaraldehyde (GA, 50% content in water) and bovine serum albumin (BSA) were supplied by Aldrich. All reagents were used as received.

Membrane Preparation and Modification

Membrane preparation

Porous membranes were prepared by the conventional immersion precipitation method using water as coagulant. PEI solutions (16 wt%) were cast on a glass plate with the fixed thickness of 250 μm in atmosphere of $(50 \pm 5)\%$ relative humidity at $(29 \pm 1)^\circ\text{C}$. The cast films were then immediately immersed into a 25°C water bath for complete precipitation followed by a soaking step in a water bath at 70°C for 2 h to eliminate the residual NMP. The membranes were then stored in distilled water until use.

Membrane modification

The chemical surface modification of PEI membrane involved a two-step post-treatment (Fig. 1), with the S1 and S2 steps corresponding to the functionalization of unmodified membrane and to the enhancement of PEG coverage on membrane surface, respectively.

In the S1 step as shown in Fig. 1(a), unmodified PEI membranes (U-PEI) were firstly treated with the 10 wt% aqueous PEG-diamine modifier at 88°C for desired time spans. The resulting materials were then thoroughly washed with deionized water to remove the modifying agent in excess and named S1-PEI membrane.

In the S2 step as represented in Fig. 1(b), S1-PEI membranes were first immersed in 5 wt% aqueous GA for 30 min. Then, a certain amount of PEG-diamine was added to the solution to reach 5 wt% and the membrane was left to react for an additional 3 h. All modifications in this step were performed at room temperature. The modified membranes were then thoroughly washed with deionized water to remove the remaining unreacted reagents. The obtained S2-PEI membranes were stored in deionized water at 4°C .

The modification conditions used in this study for the surface treatment of PEI membranes are summarized in Table 1.

Membrane Characterization

A Fourier transform infrared spectrometer, with attenuated

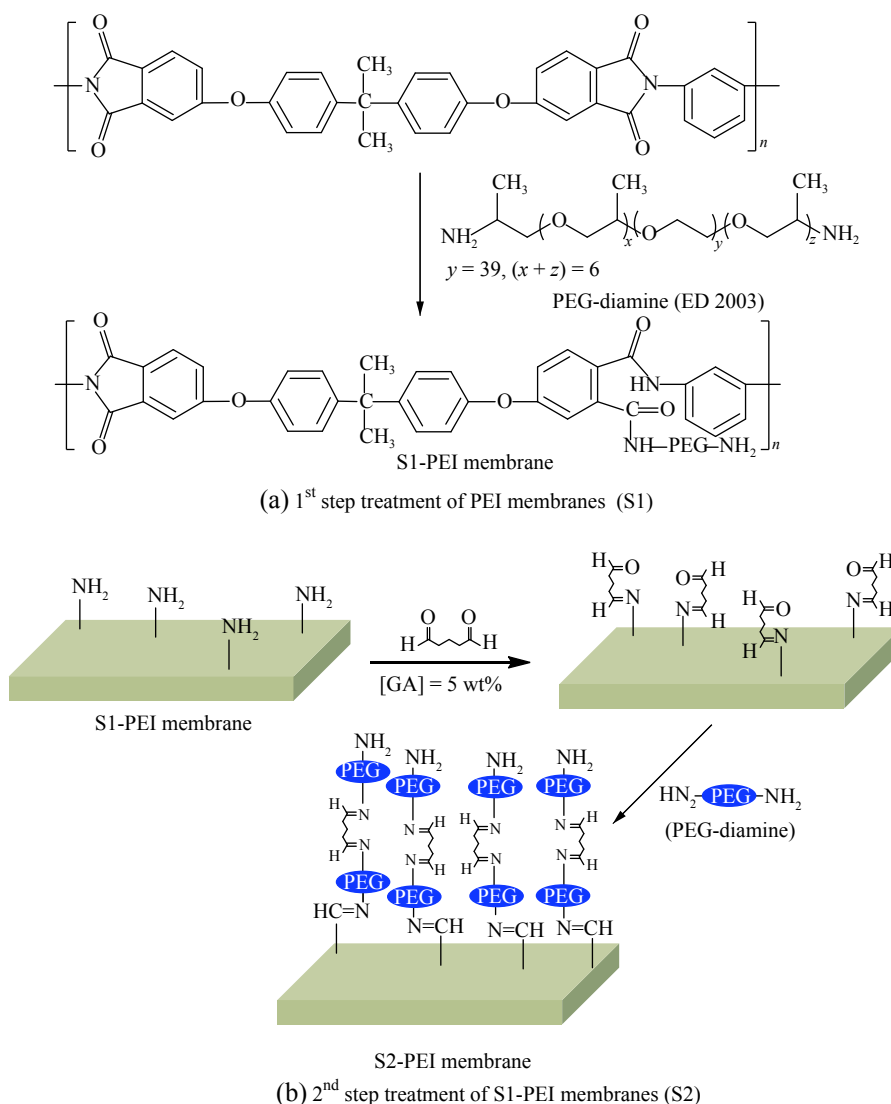


Fig. 1 The two-step procedure for preparation of PEI membrane grafted with a surface PEG layer: (a) functionalization (S1) and (b) enhancement of the PEG chain coverage on S1-PEI membrane (S2)

Table 1 Reaction conditions used for the surface modification of PEI membranes

Membrane sample	1 st step treatment (S1)		2 nd step treatment (S2)				
	[PEG-diamine] (wt%)	Reaction time (h)	[GA] (wt%)	Reaction time (min)	[PEG-diamine] (wt%)	Reaction time (h)	
U-PEI	—	—	—	—	—	—	—
S1-PEI-1	10	1	—	—	—	—	—
S1-PEI-3	10	3	—	—	—	—	—
S1-PEI-5	10	5	—	—	—	—	—
S2-PEI-1	10	1	5	30	5	3	3
S2-PEI-3	10	3	5	30	5	3	3
S2-PEI-5	10	5	5	30	5	3	3

total reflection mode (ATR-FTIR: Equinox 55, Bruker) was used to examine the functional groups present on the membrane surface. The degree of PEG grafting (DG) of S2-PEI membranes was calculated from ATR-FTIR spectra^[4, 25] by computing the ratio of the absorbance at 1142 cm⁻¹ (absorption band of ether group in PEG) to the one not affected by the modifying agent during grafting. The peak at 1500 cm⁻¹, corresponding to C—C stretching in phenyl ring, was selected as internal reference wavenumber.

The chemical composition was investigated by X-ray

photoelectron spectroscopy (XPS) with the AXIS ULTRA^{DLD}, Kratos analytical, Manchester UK. Spectra were obtained with a monochromatic Al K $\alpha_{1,2}$ radiation at 1.4 keV. X-ray anode was run at a reduced power of 150 W (15 kV and 10 mA).

The hydrophilic property of the obtained membrane surfaces was characterized by static water contact angle (WCA) and water absorbance ratio (WAR) measurements. WCA determinations were carried out using a constant volume water droplet placed on the membrane surface with

an automatic interfacial tensiometer (Data physic). WAR was investigated according to the procedure reported by Zhu et al.^[26].

A scanning electron microscope (SEM, JSM 5200) was used to analyze the surface and cross-section morphology of membranes. The membranes immersed in liquid nitrogen were broken and coated with gold before analysis. Surface morphology and roughness of the studied membranes were also characterized by using atomic force microscopy (AFM, Nanoscope IIIa, Digital Instruments/Veeco Metrology Group) operated in tapping mode. The cantilever had a spring constant of 20–100 N/m, drive frequency of 200–300 kHz and length of 125 μm . The tip radius of the probe was 5–10 nm.

Tensile properties of membrane were tested with a Universal Testing Machine (LLOYD). The measurements were carried out at room temperature using a pull rate of 5 mm/min.

Permeation and Antifouling Property Determination

A stirred dead-end filtration cell (Amicon 8050) with a volume capacity of 50 mL and an active surface area of 13.4 cm^2 was used to measure the transport and separation properties of membranes. All experiments were conducted at room temperature in the filtration set-up presented in Fig. 2.

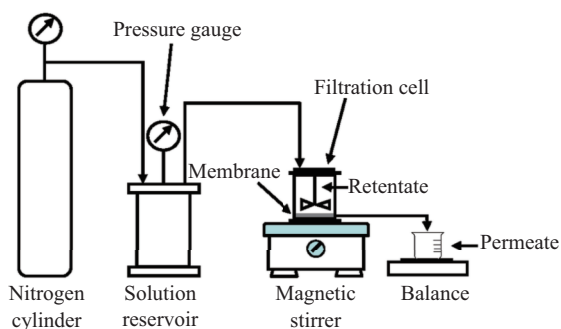


Fig. 2 Schematic of the dead-end filtration cell process

The stirred filtration cell and reservoir were filled with deionized water. The membranes were firstly pre-compacted by filtrating pure water at 0.15 MPa until the steady state flux was obtained. The pure water flux (J_{w1}) was measured using an operating pressure of 0.1 MPa and calculated using the following equation:

$$J_{w1} = \frac{Q}{\Delta t \cdot A} \quad (1)$$

where Q is the amount of water permeated, Δt the permeation time (h) and A the membrane area (m^2).

After determining the pure water flux, 500 mL of feed solution containing 1 g/L BSA in phosphate buffer saline (pH 7.4) was filled in the empty filtration cell and reservoir. BSA flux (J_p) was then measured at 0.1 MPa trans-membrane pressure for 1 h with a 300 r/min stirrer speed. Depending on the membrane flux, about 50 mL to 170 mL of permeate were collected. The protein concentrations in permeate (c_p) and retentate (c_r) were determined using spectrophotometry (UV-model Lambda 25, Perkin Elmer) at

a wavelength of 280 nm. The BSA rejection, R , was calculated according to the following equation:

$$R(\%) = \left(1 - \frac{c_p}{c_r}\right) \times 100 \quad (2)$$

To determine the anti-fouling properties, membranes were washed with deionized water in a shaking set-up for 30 min. The water flux was then re-evaluated for 30 min and defined as J_{w2} . The flux recovery ratio (FRR) was calculated according to the following equation:

$$\text{FRR}(\%) = \frac{J_{w2}}{J_{w1}} \times 100 \quad (3)$$

RESULTS AND DISCUSSION

Preparation of PEG-grafted Membranes

As mentioned above, the preparation of PEI membranes grafted with PEG chains was carried out in a two-step aqueous procedure by using PEG-diamine and GA as hydrophilic modifier and linker, respectively. Fig. 1 displays the sketch of reactions taking place at the membrane surface. The first stage (S1) is assumed to yield modified membranes having pendent primary amino groups at the surface (S1-PEI). The reaction time was varied to find the optimal conditions (Table 1). Unfortunately, titration of the amino group concentration, using an anion exchange technique with a dye (Acid Orange II)^[20, 21], was not successful probably due to the too small available content of amino groups. ATR-FTIR and XPS were then used to characterize the presence of functional groups at the membrane surface. Fig. 3(a) shows the comparison between the FTIR spectra obtained for the S1-PEI-5 membrane (reaction time 5 h) and that of U-PEI. As can be seen, the spectrum of S1-PEI-5 sample shows two new peaks at 1665 and 1547 cm^{-1} assigned to the stretching absorption amide I ($\text{C}=\text{O}$) and amide II ($\text{N}-\text{H}$), respectively. This clearly indicates that the covalent binding of PEG-diamine with PEI involved the formation of amide bounds missing in U-PEI, as reported in our previous work for a mono-aminated derivative^[19, 20]. Another proof lies in the strong absorption of CH_2 rock and $\text{C}-\text{C}$ stretch^[27], $\text{C}-\text{O}$ stretch^[19] and CH_2 symmetric stretch^[27] of grafted PEG-diamine at 945, 1142 and 2870 cm^{-1} , respectively. If there is no doubt about the grafting, the question about the presence of available primary amine groups remains open as both extremities can react with the imide rings, hindering the possibility of further reaction. Actually, their presence can be demonstrated by the broad band corresponding to the $\text{N}-\text{H}$ stretch absorption in the 2500–4000 cm^{-1} domain (Fig. 3b).

The second stage of the modification process (S2) consisted of enhancing the PEG chain coverage through the attachment of a cross-linked PEG-diamine at the membrane surface (Fig. 1b). The S2-PEI-5 FTIR spectrum, compared to that of S1-PEI-5 (Fig. 3a), exhibits a new peak at 1652 cm^{-1} , which is characteristic of the stretching absorption for $\text{C}=\text{N}$ imine group^[28] originated from the crosslinking reaction between primary amine groups and GA. On the other hand, the rise of the band located at 1050–1150 cm^{-1} assigned to ether groups confirms the expected enhancement of the

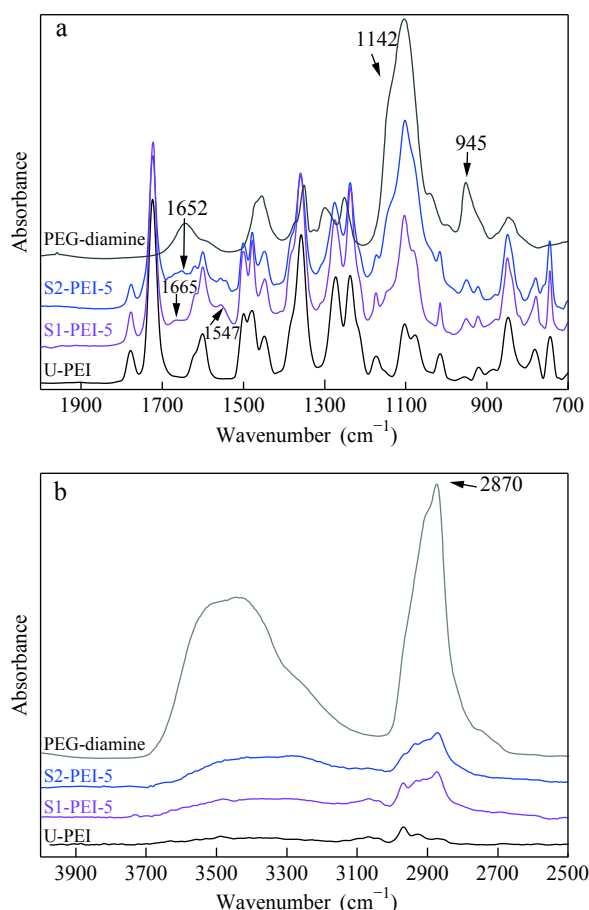


Fig. 3 ATR-FTIR spectra of PEG-diamine modifying agent, unmodified membrane (U-PEI), membrane modified with 10 wt% of PEG-diamine at 88 °C for 5 h (S1-PEI-5) and S1-PEI-5 membrane after the second modification step (S2-PEI-5): (a) 2000–700 cm^{-1} and (b) 4000–2500 cm^{-1}

membrane surface coverage by PEG chains.

Additional investigation on the chemistry of membrane surface was performed with XPS analysis. As shown in Figs. 4(a) and 4(b), it is found that introduction of PEG chains on PEI increases the intensity of C1s peak (C–O, at 286.6 eV) for S1-PEI-1. In literature, the peak C1s at 287.7 eV refers to C=O^[29], C=N^[30] and C–N^[31]. Also, the new peak appearing at 287.7 eV might be indicative of the formation of terminal amino groups during the S1 functionalization step. In Figs. 4(d) and 4(e), the strong intensity of O1s peak for S1-PEI-1 membrane at 532.7 eV (C–O) clearly indicates the appearance of PEG chains on the membrane surface. This observation is in agreement with the increase in the ether carbon atom observed in C1s spectrum (286.6 eV). For N1s spectrum (Figs. 4g and 4h), two new peaks are observed for the S1-PEI-1 membrane at 399.5 and 401.7 eV, which are assigned to NH₂ group^[32] and NHC=O group^[33], respectively. Even if of small intensity, this latter observation definitively confirms the presence of remaining available primary amine at the extremity of grafted PEG chains.

Functional groups and chemical composition of the S2-PEI membrane surfaces were also investigated by XPS. Figs. 4(c), 4(f) and 4(i) show that C1s, O1s and N1s XPS

spectra are quite similar to those of the corresponding S1-PEI membrane (Figs. 4b, 4e and 4h). This observation is expected as the composition of membrane surface did not change drastically from step 1 to step 2 except the formation of imine groups in a very small content that can be hardly evidenced from XPS spectra. On the other hand, the increase of respective ratios for bands corresponding to the ether bonds is consistent with an improvement of the PEG coverage as emphasized from the FTIR observations.

Physico-chemical Properties of the Prepared Membranes

Membrane morphology and surface structure

The surface and cross-section morphologies of U-PEI, S1-PEI, and S2-PEI membranes were examined by SEM (Fig. 5). No apparent differences can be seen after 1 h of S1 functionalization in surface (Figs. 5a and 5b) and cross-section (Figs. 5e and 5f) micrographs, while a pore opening is observed for longer reaction times from 3 h (Fig. 5c) to 5 h (Fig. 5d). At the same time, a thinning of the top layer is clearly evidenced with an almost complete disappearance after 5 h of treatment (Fig. 5h). The pore opening and decrease in top surface layer of PEI membrane can be described as proposed in our previous works^[19, 20]: the reaction between imide ring of PEI and primary amine of PEG-diamine first results in the covalent attachment of PEG. Then, the interfacial membrane hydrophilicity rapidly increases, allowing the swelling of the surface PEI chains. PEG-diamine molecules can then penetrate deeper into the swollen PEI network. At this point, further functionalization leading to the formation of water-soluble highly PEGylated PEI chains results in a superficial erosion of PEI matrix, which accounts for an enlargement of pore size (Figs. 5c and 5d) and a reduction in top layer thickness (Figs. 5g and 5h)^[19, 20]. From this layer-by-layer erosion mechanism, it can be concluded that the PEG modification takes place only at the membrane interface. On the other hand, it should be noted that the resulting S1-PEI membranes were completely soluble in NMP and chloroform, indicating that no cross-linking took place during S1-treatment in our operating conditions.

Figs. 5(i) and 5(j) show the surface of S1-PEI-3 and S1-PEI-5 after the S2-treatment. Now, the surface appears uniform, which indicates the presence of a PEG layer covering the open pores of S1-PEI-3 and S1-PEI-5. The visible cracks may be originated from the shrinkage of the highly hydrated grafted PEG surface upon drying since the water absorbance ratio (WAR) was measured going from less than 5% for the virgin PEI to about 75% for the S2-PEI membranes. On the other hand, the SEM cross-sections depicted in Figs. 5(h) and 5(l) clearly confirm the formation of a surface layer formed by the crosslinked PEG chains though it is hard to distinguish it from the PEI matrix, probably owing to a good adhesion between them related to the covalent grafting^[34]. It should be noted that no morphology change was observed for the S2-PEI-1 membrane (not shown).

The mean surface pore diameter and the surface pore size distribution for the membranes obtained after the S1 and S2 treatment were determined by processing the SEM images

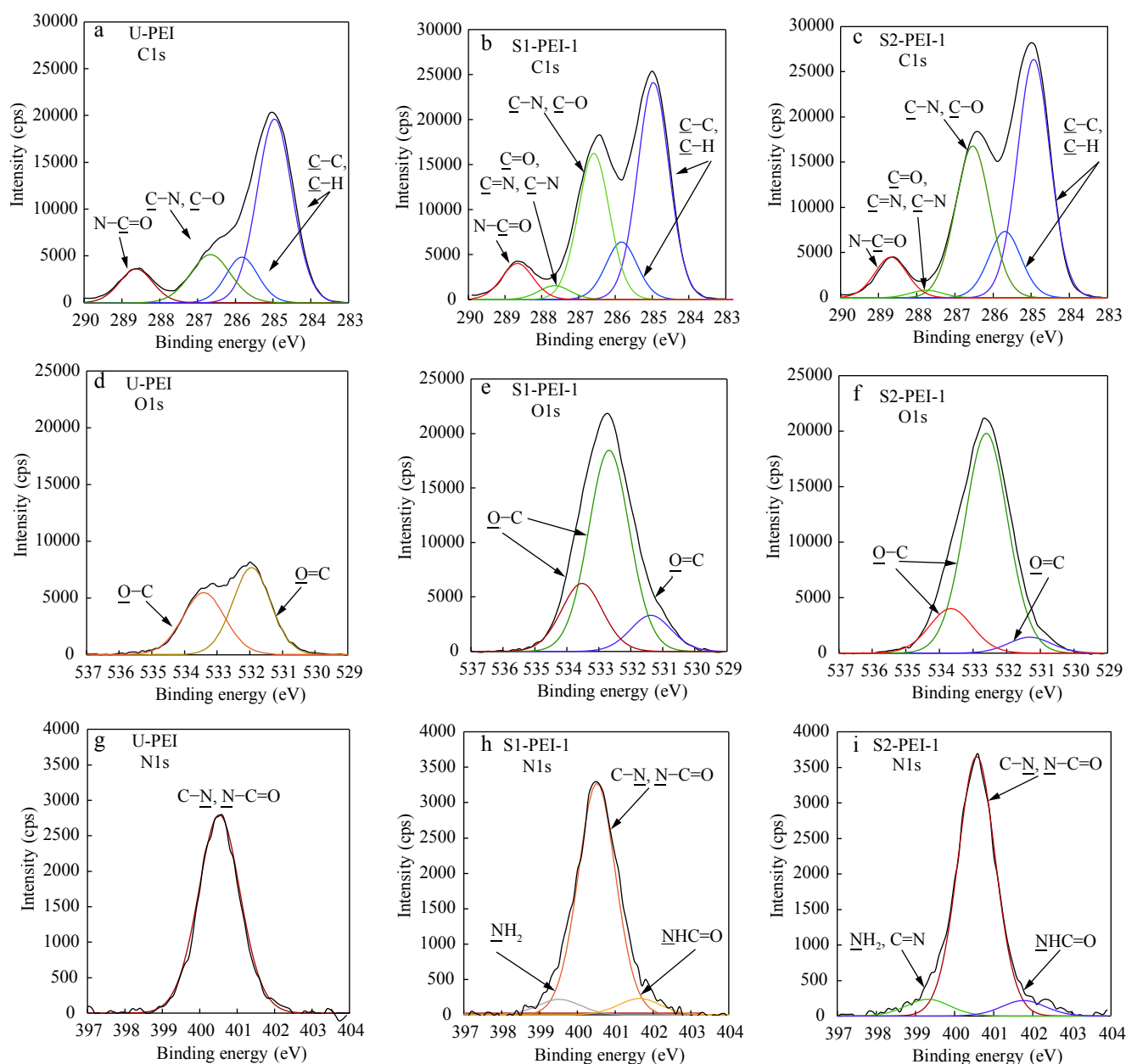


Fig. 4 XPS spectra of C1s, O1s and N1s for (a, d, g) unmodified membrane (U-PEI), (b, e, h) membrane modified with 10 wt% of PEG-diamine at 88 °C for 1h (S1-PEI-1) and (c, f, i) S1-PEI-1 membrane after the second modification step (S2-PEI-1)

obtained with a magnification of $\times 50000$ using the Image J software^[35] and the results are summarized and presented in Table 2 and Fig. 6, respectively. These data evidence the pore opening and distribution widening occurring when S1 treatment is extended to longer time. The S2-treatment induced a decrease of the surface pore size and their distribution in all cases of prepared membranes, which indicate a partial obstruction of pore by formation of the PEG layer during the S2 treatment process.

AFM observation was also conducted in order to have a deeper insight of the surface structure. As shown in Fig. 7, it can be seen that the membrane surface roughness (represented by root mean square roughness RMS, nm) increases by about 50% after S1 treatment. Similar results reported in literature after grafting on polyamide membrane

have been explained by the presence of PEG nodules at the surface^[27, 36]. Interestingly, as shown in Figs. 7(c) and 7(e), the surface roughness of S2-PEI membranes is even greater than that of S1-PEI membranes. This observation could be explained by the size increase of PEG nodules due to the chain lengthening taking place during the S2 treatment.

Hydrophilic property

The interfacial property of membrane surface was determined by using static WCA measurement and presented in Fig. 8(a). As expected, a strong enhancement of the membrane surface hydrophilicity is obviously observed since the virgin PEI membrane shows a WCA of about 85° against 60° to 50° for the S1 and S2 treated membranes. This observation confirms the functionalization of hydrophobic PEI by hydrophilic PEG chains.

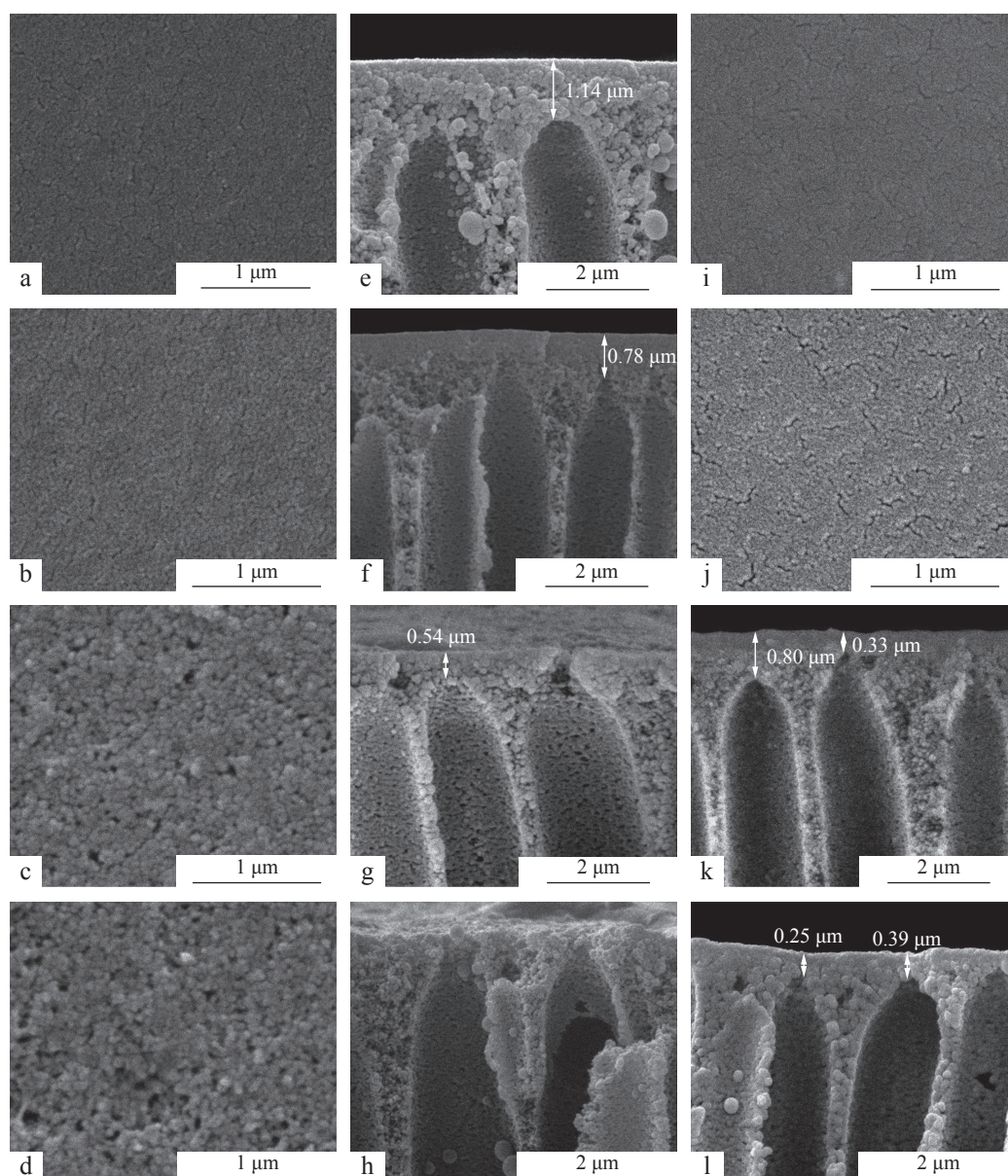


Fig. 5 Surface and cross-sectional SEM micrographs: (a, e) unmodified PEI membrane (U-PEI); membrane modified by S1-treatment (b, f) for 1 h (S1-PEI-1), (c, g) for 3 h (S1-PEI-3) and (d, h) for 5 h (S1-PEI-5); (i, k) S1-PEI-3 and (j, l) S1-PEI-5 modified by S2-treatment (S2-PEI-3 and S2-PEI-5, respectively)

Table 2 Mean surface pore diameter of modified PEI membranes

Sample	Mean pore diameter (nm)
S1-PEI-1	17
S1-PEI-3	27
S1-PEI-5	35
S2-PEI-1	15
S2-PEI-3	25
S2-PEI-5	30

Permeation Properties of the Prepared Membranes

Filtration of pure water and BSA solution as a protein model was performed under 0.1 MPa trans-membrane pressure.

Pure water permeability

In Fig. 8(b), S1-PEI-1 membrane shows a 50% enhancement of the pure water flux when compared to U-PEI owing to the increase of membrane hydrophilicity. Surprisingly, no

further increase is observed for longer S1 treatment unlike what was observed for the mono-aminated derivative^[20]. Actually, two phenomena (the pore size and the membrane porosity) affect the permeability in opposite direction: a constant pure water might mean that the pore opening observed by SEM is counter balanced by a decrease of porosity related to the top layer thinning. The reduction in thickness of the upper skin layer also diminished the membrane mechanical property (from (2.9 ± 0.5) MPa for U-PEI to (1.8 ± 0.3) MPa for S1-PEI-5), increasing the chance of compaction during filtration, which also leads to an enhancement of pure water flux lower than expected. On the other hand, the pure water flux is observed to be strongly reduced after the S2-treatment at a similar value whatever the starting material Fig. 8(b).

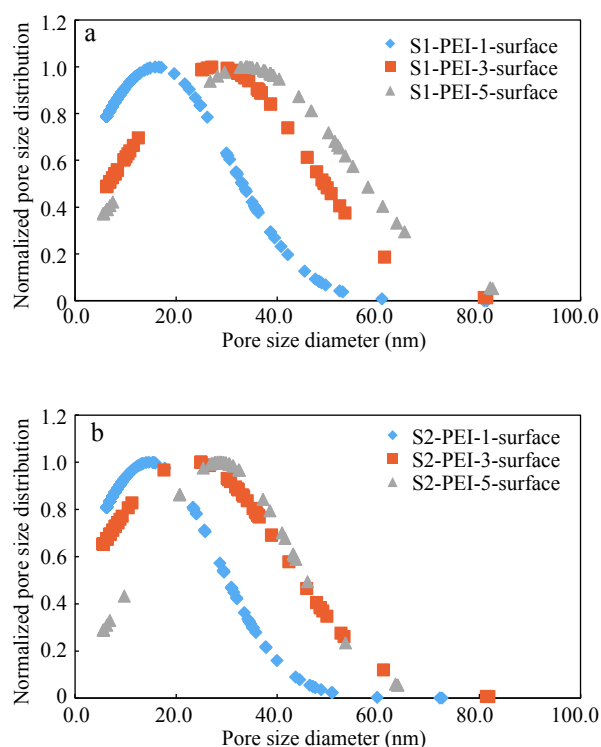


Fig. 6 Surface pore size distribution for (a) S1-modified PEI membranes and (b) S2-modified PEI membranes

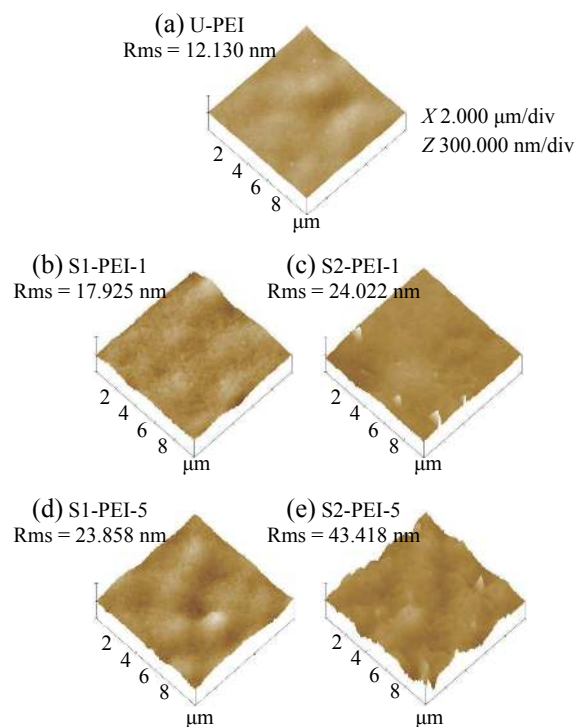


Fig. 7 AFM micrographs for (a) unmodified membrane (U-PEI), membranes modified by S1-treatment for (b) 1 h (S1-PEI-1) and (d) 5 h (S1-PEI-5), then by S2-treatment (c) S2-PEI-1 and (e) S2-PEI-5

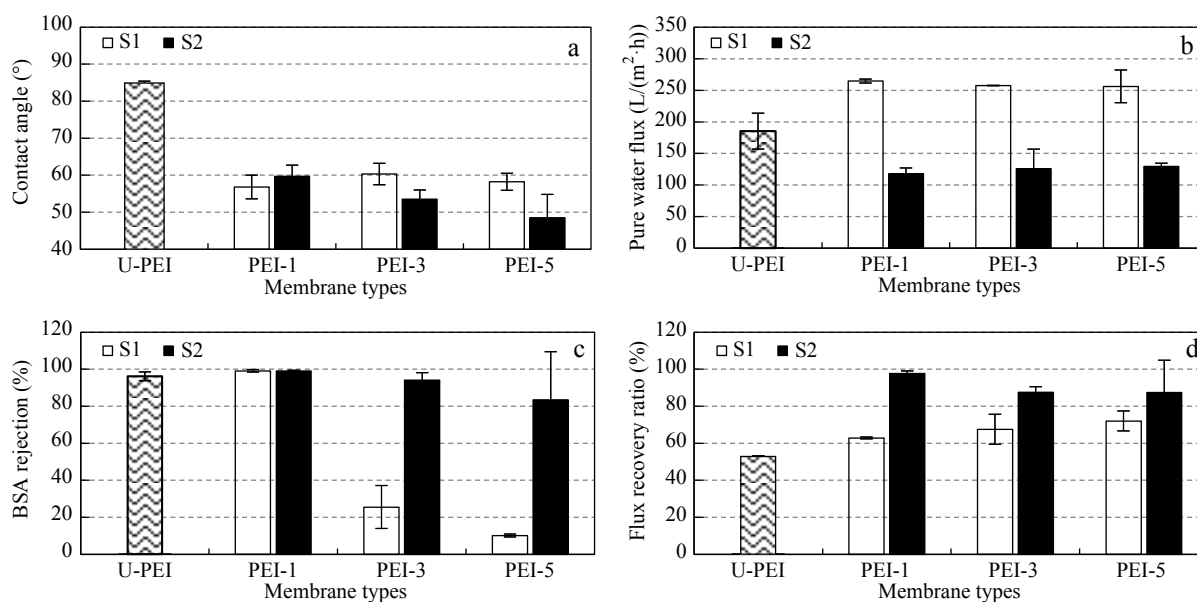


Fig. 8 (a) Water contact angle, (b) pure water flux, (c) BSA rejection, and (d) flux recovery ratio of U-PEI, S1-PEI, and S2-PEI membranes

BSA rejection

In order to reveal how the surface modification really affects the membrane pore size, rejection of BSA was studied as a function of the post-treatment conditions (Fig. 8c). It can be seen that BSA is above 95% retained by the virgin PEI. As expected, the rejection dramatically decreases for reaction time longer than 1 h due to the above-mentioned pore opening. At this point, an enlargement of the pore size and pore distribution (Table 2, Fig. 6) with a decrease of the top

layer thickness (Figs. 5g and 5h) have been observed. By comparison with U-PEI membrane, the larger pore size of S1-PEI-3 and S1-PEI-5 membrane allows the BSA molecule to easily pass across the membrane, leading to an increase of BSA concentration in permeate. By contrast, S1-PEI-1 membranes have improved BSA rejection property along with an enhancement in pure water permeability, indicating a slight decrease of the pore size (not noticeable by SEM observation) owing to the functionalization by the short

polymer chains (M_w ca. 2000 g/mol). The S2-treatment results in the recovery of a high BSA rejection value, indicating that the additional grafted PEG layer governs the filtration performance of the resulting membranes. However, the increase of S1-treatment time leads to a decrease in BSA rejection values. It is assumed that the top PEG layer is not thick and tight enough to retain the quantitative BSA rejection as demonstrated by SEM cross-section observations (Fig. 5) and pore size distribution (Fig. 6). The pore opening observed when the S1 treatment is extended for 1 h to 3 h, which probably should require a more drastic S2-treatment such as either the longer PEG grafting or an increase of modifying concentration to achieve an efficient coverage by PEG segments.

Flux recovery ratio

FRR after filtration experiment must be as close to 100% as possible to obtain membranes having high performance against the protein fouling. Fig. 8(d) displays the FRR data obtained after 1 cycle of filtration (pure water/BSA/pure water). Only one cleaning step with pure water was applied after the BSA filtration. The dead-end filtration is supposed to ensure the optimal conditions for fouling the membrane. The hydrophobic virgin U-PEI membrane exhibits the lowest FRR value due to non-specific protein adsorption. A slight rising of FRR is obtained as a function of the S1 reaction time consistent with a better coverage of the pore surface area by PEG moieties. By contrast, a strong enhancement can be observed after the S2-step as illustrated in Fig. 8(d).

Based on the pore diameter and pore size distribution in Fig. 6, it is assumed that the S2-reticulation takes place mainly at the top surface of membranes. Moreover, several reasons lead us to make the proposition of superficial layer formed during the second step of modification. First, the S2-treatment induces a strong resistance to the permeate flux as proven by the 50% pure water flux decline (Fig. 8b) with a similar variation whatever the initial membrane type. The S2-modification enables the formation of a uniform coverage of the surface for membranes obtained after S1-treatment, resulting in the strong enhancement of the BSA rejection (Fig. 8c).

The excellent anti-fouling properties of the S2-treated membranes can be accounted for the formation of a soft highly hydrated superficial layer which serves as the boundary barrier to prevent the adhesion of BSA on PEI membrane surface^[8, 9, 37]. However, it can be seen that the FRR values of S2-PEI-3 and S2-PEI-5 are lower than that of S2-PEI-1 going in the same way as the data obtained for the BSA rejection. This observation suggests an incomplete PEG coverage within the pores causing BSA adsorption or deposition. This residual fouling could not be eliminated by simple hydrodynamic cleaning and thus caused a reduction of FRR^[2].

The best increment in FRR is obtained for the S2-PEI-1 membranes with a value of $(97.7 \pm 1.3)\%$. To our knowledge, this result is the highest ever reported for a PEG membrane surface modification as the maximum FRR values found in literature generally lie in the range of 82% to 92%^[19]. In conclusion, it appears that the S2-PEI-1 mem-

branes show the best compromise in terms of pure water flux, BSA rejection and FRR (Fig. 8). Therefore, the reaction conditions for the first step corresponding to the preparation of S1-PEI-1 membranes were chosen for the optimization of the S2 step.

Optimization of the S2 Step

As demonstrated in the previous sections, the proposed two-step procedure enabled to obtain a coverage of PEI membrane surface consisting of a soft hydrated PEG layer, giving rise to the unique antiprotein-fouling property. However, it was also shown that the permeability was strongly lowered even compared to the virgin PEI membrane probably due to the thickness of the PEG layer and the partial blocking of the top surface pores. In this section, a variation of reaction parameters including contacting time with GA before adding PEG-diamine (from 30 min to 10 min), PEG-diamine concentration (from 5 wt% to 1 wt%) and reaction time (between 10 and 180 min) was investigated to optimize the formation of the PEG layer on the S1-PEI-1 membrane. As shown in Fig. 9(a), no difference is evidenced between 10 and 30 min of GA contacting time regarding the pure water permeability and the BSA rejection. This result suggests that a longer reaction time (> 10 min) is not required to achieve a hydrophilic coverage of the membrane surface since the calculated DG (Fig. 9a) is not significantly different and WCA and WAR remain constant with respective values of ca. 60° and 75%. Therefore, the GA contacting time is fixed at 10 min for the subsequent experiments. Then, the key parameter for controlling the thickness of the PEG layer seems to be related to PEG-amine.

The effects of reaction time and PEG-amine concentration on pure water flux and FRR are presented in Figs. 9(b) and 9(c), respectively, after a contacting time of 10 min with GA. In both cases, a slight increase of the permeability followed by a decrease leveling off after 30 min of reaction and 2 wt%, respectively, is observed. The increase in permeability for both cases may be due to the increase of the surface hydrophilicity of membranes. However, further increase in the PEG segment on the membrane leads to a decrease in flux due to the increased resistance of grafted layer^[37] caused by an increase of DG (Figs. 9b and 9c), while the FRR values of about 95%–98% are obtained, indicating an excellent antifouling of PEI membranes. It has to be noted that the BSA rejection remains constant ($> 98\%$) whatever the conditions of modification. This suggests that the post-treatment method does not damage the selective layer of membrane^[25].

It was concluded that the optimal reaction time and PEG-diamine concentration could be 60 min and 2 wt%, respectively. For this membrane named S2-PEI-1[2] in the next section, the FFR value of about 95% and a water permeability of about 1400 L/(h·m²·MPa) are obtained compared to about 98% and 1100 L/(h·m²·MPa) for 5 wt% (Fig. 9c).

Recycling Properties of PEG-modified Membrane

In ultrafiltration application, the polymeric membrane should offer long-term antifouling property to enable a decrease of

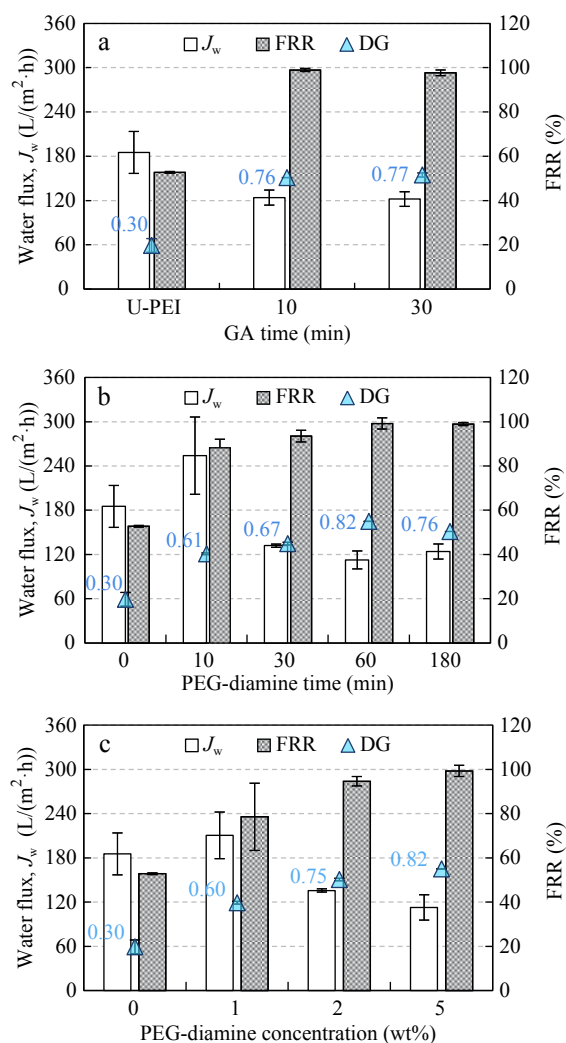


Fig. 9 Pure water flux (J_w), flux recovery ratio (FRR) and degree of PEG grafting (DG) for S2-PEI membranes versus (a) GA contacting time, (b) reaction time with PEG-amine (5 wt%) and (c) PEG-diamine concentration (reaction time 60 min)

operating cost. S2-PEI-1[1] (1 wt% PEG-amine in the S2 step), and S2-PEI-1[2] (2 wt% PEG-amine in the S2 step) were chosen to undergo a recycling test because of the high permeation flux of the first one and the high FFR for the second one. Their permeation performance through three fouling cycles is compared to that of U-PEI in Fig. 10. In the initial stage, the BSA permeation flow rate dramatically decreases for the three studied membranes due to a combination of polarization concentration, adsorption and/or deposition on the membrane surface^[38]. The same cleaning protocol by soaking the membranes in water was applied. The fact that the initial value is not reached points out an irreversible fouling even for the PEG modified membranes. However, it can be seen that, after the first cycle, the fouling is strongly hindered since excellent FFR values are obtained for S2-PEI-1[1] (88%), and S2-PEI-1[2] (96%). After three cycles, the pure water flux of U-PEI is only 71 L/(m²·h), namely 41% of the initial value, while that of S2-PEI-1[1], and S2-PEI-1[2] are 158 L/(m²·h), 83% and 118 L/(m²·h), 88%, respectively.

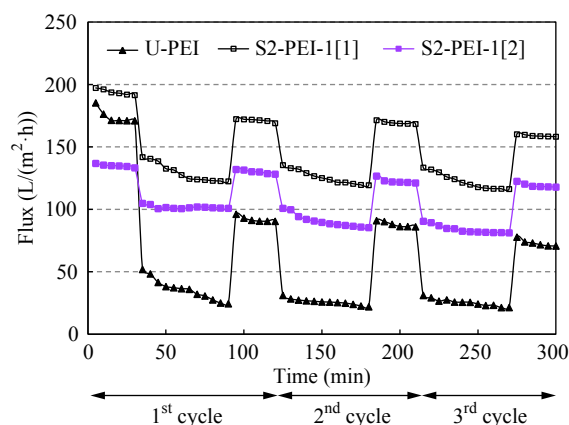


Fig. 10 Time-dependent recycling flux of U-PEI and S2-PEI prepared by grafting the S1-PEI-1 membranes with 5 wt% of GA solution (contacting time of 10 min) and PEG-diamine addition of 1 wt% (S2-PEI-1[1]), and 2 wt% (S2-PEI-1[2]) (reaction time: 60 min)

CONCLUSIONS

Highly PEGylated PEI membranes with excellent resistance to protein fouling were successfully prepared by a wet chemical two-step post-treatment with an aqueous solution of PEG-diamine. The functionalization of PEI membrane surface was carried out in the first step while the second step enabled to graft a more or less dense crosslinked PEG coating depending on the reaction conditions. Thicker PEG coverage gives better resistance to protein fouling and stability but lower permeation rate. The formed layer is supposed to cover the hydrophobic surface and acts as a hydrated layer on which proteins can bounce without non-specific adsorption. This approach proves to be promising to design PEI surface with excellent antifouling properties. A compromise between permeation flux and resistance to fouling has to be found depending on the application by varying the grafting conditions.

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