Regenerable anti-fouling active PTFE membrane with thermo-reversible “peel-and-stick” hydrophilic layer

Sung Yong Park\textsuperscript{a}, Jae Woo Chung\textsuperscript{b, *}, Seung-Yeop Kwak\textsuperscript{a, **}

\textsuperscript{a} Department of Materials Science and Engineering, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151–744, Republic of Korea
\textsuperscript{b} Department of Organic Materials and Fiber Engineering, Soongsil University, 369 Sangdo-ro, Dongjak-gu, Seoul 156–743, Republic of Korea

\textbf{A R T I C L E   I N F O}

Article history:
Received 8 April 2015
Received in revised form 30 April 2015
Accepted 2 May 2015
Available online 11 May 2015

Keywords:
Anti-fouling
Dynamic bonding
Diels–Alder reaction
Peel-and-stick process
PTFE membrane

\textbf{A B S T R A C T}

We develop a regenerable anti-fouling membrane via the formation of a dynamic peel-and-stick of hydrophilic poly(ethylene glycol) (PEG) layer onto the surface of a poly(tetrafluoroethylene) (PTFE) membrane, using thermo-responsive reversible covalent bonding. In order to attach a peelable-and-stickable hydrophilic layer onto a membrane surface, a maleimide end-modified PEG layer is coupled with a furan-modified PTFE membrane by reversible Diels–Alder (DA) cycloaddition reaction. The combined results of attenuated total reflection Fourier-transform infrared (ATR FT-IR), X-ray photoelectron spectroscopy (XPS) and field-emission scanning electron microscopy (FE-SEM) measurements clearly reveal that the maleimide end-modified PEG is successfully coupled with the furan-modified PTFE membrane surface by DA reaction. In addition, the hydrophilic PEG layer is readily and repeatedly reformed on the membrane surface by a thermally driven dynamic peel-and-stick process. The PEG-coupled PTFE membrane shows effective anti-fouling performance against a highly concentrated silica colloidal aqueous solution. In particular, the anti-fouling property is remarkably recovered after regeneration of the hydrophilic layer through the peel-and-stick process.

\textcopyright 2015 Elsevier B.V. All rights reserved.

1. Introduction

In recent, water purification technology to obtain clean and affordable water supplies, has become an important global issue in order to solve the lack of clean water. Among water purification techniques, membrane separation is greatly being spotlighted as a technology to substitute for conventional water treatments such as gravity sedimentation, chemical-assisted coagulation, chlorine disinfection and microbially-mediated decomposition because the membrane process is a relatively simple and cost-effective method to successively obtain high-purified water [1, 2]. However, membrane fouling, which is defined as the deposition of contaminants (organic and inorganic materials) on the membrane surface or into membrane pores, decreases the water purification performance of the membrane and increases operating cost by gradual deterioration of membrane performance [19]. Thus, it is necessary to develop a new approach to fundamentally recover the anti-fouling property of a membrane rendered ineffective by permanently accumulated contaminants.

Of particular interest is a dynamic bond-incorporated membrane because it can selectively undergo reversible breaking and reformation of the modifier to endow the membrane surface with the desired properties. Indeed, such dynamic bonds have been extensively utilized for stimuli-responsive smart materials, such as a self-healing material [24–30], a smart adhesive [31, 32] and an actuator [33–35], the reversibility of which can be controlled by light, pH, and temperature. Among the above, Diels–Alder (DA) cycloaddition between furan and maleimide functional groups is a representative dynamic bond to form a covalently thermo-reversible cyclic coupling which can be restored to their original forms by controlling temperature [31, 36–39]. Furthermore, DA cycloadditions have been reported to have high and feasible reversible efficiencies [26, 40]. Hence, if the thermo-reversible
covalent bonding characteristics of DA reaction are applied to the membrane surface, it is expected that a regenerable anti-fouling active membrane would be developed, by changing a degraded hydrophilic layer into a fresh hydrophilic layer.

Here, we present a regenerable anti-fouling active membrane by introducing a peelable-and-stickable hydrophilic layer onto the membrane surface. This was achieved with a covalently thermo-reversible dynamic bond, i.e., DA cycloaddition, between the maleimide-modified poly(ethylene glycol) (PEG) and the furan-modified poly(tetrafluoroethylene) (PTFE) membrane surface. The hydrophobic PEG membrane was repeatedly peeled off and stuck on the surface of the PTFE membrane by adjusting temperature, and the resulting PEG-coupled PTFE membrane displayed excellent anti-fouling properties. Moreover, the fouling resistance of the PEG-coupled PTFE membrane showed a high degree of recovery after a peel-and-stick process. Our approach opens up the possibility of creating a novel platformable separating system for dynamic membranes, multi-functional membranes and smart gas separation, because desired functionalities can reversibly be assembled and combined on the membrane surface.

2. Experimental

2.1. Materials

A porous poly(tetrafluoroethylene) (PTFE) flat membrane with 47 mm diameter and 0.1 μm average pore diameter was purchased from Advantec-MFS, Inc. (Tokyo, Japan). Poly(ethylene glycol) methyl ether maleimide (M₄₀, 2000), furfuryl glycidyl ether (96%), hydrazine monohydrate (98%), and LUDOX SM-30 (30 wt% silica suspension, particle diameter about 7 nm) were purchased from Sigma-Aldrich (St Louis, MO, USA). Toluene (99.9%), tetrahydrofuran (THF, 99.9%), and sodium hydroxide (98%) were obtained from Daegung Chemical & Metals (Gyeonggi-do, Korea). All chemicals were used as received, without further purification. The aqueous solutions were prepared with deionized (DI) water having a resistivity exceeding 18.0 MΩ cm.

2.2. Preparation of furan-modified PTFE membrane

In order to provide the furan moiety onto the PTFE membrane surface, the PTFE membrane was treated with UV/hydrazine and then reacted with furfuryl glycidyl ether. The UV/hydrazine treatment is a reactive surface modification method for chemically inert PTFE membranes to introduce amine functional groups [41].

Briefly, the PTFE flat membrane was exposed to hydrazine vapor under UV light irradiation (λmax = 254 nm, 100 W) in a closed quartz cylinder, for two days. After the reaction, the surface aminated PTFE membrane was carefully removed from the cylinder and dried in a vacuum for six hours to remove unreacted hydrazine vapor. Next, the aminated PTFE membrane was treated with 1 mL of furfuryl glycidyl ether in a 60 °C pre-heated oven overnight. The furan-modified PTFE membrane was obtained after rinsing with acetone and THF several times to remove unreacted chemicals. The resulting furan-modified PTFE membrane was dried at room temperature.

2.3. Assembly of maleimide end-modified PEG to furan-modified PTFE membrane

The PEG methyl ether maleimide (PEG-maleimide) was coupled to the furan-modified PTFE membrane by Diels–Alder (DA) reaction. The furan-modified PTFE membrane was placed at the bottom of a jar and then about 1 mL of 5 wt% PEG-maleimide/toluene solution was injected. The closed jar was stored in a pre-heated oven at 60 °C for 18 h. After the DA reaction, the resulting PEG-coupled PTFE (PEG-PTFE) membrane was rinsed several times with toluene and THF and dried at room temperature.

2.4. Peel-and-stick process of the hydrophilic PEG layer

To regenerate the hydrophilic PEG layer on the membrane surface, the attached PEG layer was peeled off the membrane surface by retro DA (rDA) reaction and the fresh PEG-maleimide was then re-coupled to the membrane surface by DA reaction. As described in the previous section, the PEG-maleimide was coupled to the modified PTFE membrane at 60 °C overnight by DA reaction. To decouple furan-maleimide bonding, the rDA reaction was conducted at 150 °C overnight. Briefly, the PEG-PTFE membrane was put in a 1-neck round flask and about 100 mL of toluene was added to the flask. The solution was heated to 150 °C with reflux. After the rDA reaction, the PEG peeled membrane, denoted as rPEG-PTFE, was carefully removed from the flask and rinsed several times with toluene and THF. The peel-and-stick of the PEG layer from the furan-modified PTFE was repeated three times. The overall procedure including surface modification and dynamic coupling of the PEG layer is schematically illustrated in Fig. 1.

2.5. Characterization

The aminated PTFE membrane, the furan-modified PTFE membrane, preparation of the PEG-PTFE membrane and the repetitive regeneration of the PEG layer by dynamic peel-and-stick process were monitored by attenuated total reflection Fourier-transform infrared (ATR FT-IR, Thermo Scientific Nicolet iS5) spectroscopy with a spectral resolution of 4 cm⁻¹ with the range of 650–4000 cm⁻¹ and X-ray photoelectron spectroscopy (XPS, Kratos AXIS-HSI) using monochromatic Mg Kα X-ray source operated at 10 mA. In order to evaluate surface hydrophilicity of the resulting membranes, static pure water contact angle was analyzed at room temperature using Biolinscientific, Attention THETA LITE. The surface morphologies of the membranes were observed by field-emission scanning electron microscopy (FE-SEM, JEOL 7800F). Pt coating was carried out using Pt sputtering at 10 mA for 100 s for the FE-SEM imaging.

2.6. Evaluation of the fouling resistance

To investigate an anti-fouling behavior for the PEG-PTFE membrane, we conducted a membrane fouling test using a 500 ppm neutral silica colloidal suspension solution. The fouling test was composed of three cycles for permeation of pure water and 500 ppm silica colloidal suspension, and pure water permeation after regeneration of the hydrophilic PEG layer.

Pure water permeability (PWP) was measured using Amicon® 8010 dead-end stirred cell (Millipore Corp.) connected to a pressure vessel filled with deionized (DI) water at 0.5 bar for 30 min. The 500 ppm neutral silica colloidal aqueous suspension was then filtered over the membrane, to generate membrane fouling, for one hour. Next, to remove loosely-attached silica foulants, the membrane was backwashed at 1 bar with DI water for three minutes. These experiments were repeated three times for evaluation of fouling behavior. After three cycles of fouling, the membranes (i.e., the PEG-PTFE membrane and the neat-PTFE membrane), were treated with rDA conditions and a fresh PEG layer was attached to the PEG-PTFE membrane by DA reaction. Finally, the PWP was re-measured for the regenerated membranes. During the entire process, the water fluxes were measured continuously by collecting the permeate on an analytic mass balance.
Flux = \( \frac{Q}{t \times A} \)  

where \( Q \) is the volume of the permeate (L), \( t \) is the filtration time (in hours), and \( A \) is the effective area of the membrane (m²).

The degree of membrane fouling was verified by reversible and irreversible fouling tendencies (Eqs. 2–4) for the PEG-PTFE membrane and the neat-PTFE membrane:

\[
N = \frac{F_t}{F_i},
\]

\[
r_{rev} (%) = \left( \frac{N_{w} - N_f}{} \right) \times 100,
\]

\[
r_{ir} (%) = \left( 1 - \frac{N_{w}}{} \right) \times 100,
\]

where \( N \) is the normalized flux, \( F_i \) is the flux value and \( F_t \) is the PWP, and \( r_{rev} \) and \( r_{ir} \) are the percentages of reversible and irreversible foulings, respectively. \( N_f \) and \( N_w \) are the normalized flux values of the fouled and backwashed membranes, respectively.

3. Results and discussion

3.1. Preparation of PEG-coupled PTFE membrane by Diels–Alder reaction

PTFE and PEG were used as a membrane substance and an anti-fouling active modifier respectively, because PTFE is chemically and thermally stable compared with other polymeric membrane substances and PEG is widely used as a hydrophilic modifier in membrane applications. To reversibly couple the hydrophilic PEG to the chemically inert PTFE membrane, we first modified the PTFE membrane by the UV/hydrazine treatment to endow amine group on the membrane surface. Then, furfuryl glycidyl ether was covalently attached with the aminated PTFE membrane surface by a ring opening reaction of epoxy moiety of furfuryl glycidyl ether. FT-IR spectra (Fig. 2b–d) exhibited a broad N–H stretching IR bands corresponding to the furan group were observed at 1607 cm⁻¹ and 1558 cm⁻¹. These results revealed that the surface of the PTFE membrane was amine-functionalized and then the aminated PTFE was successfully modified by the furan moieties. In order to attach the hydrophilic PEG layer on the PTFE membrane, maleimide end-modified PEG was chemically coupled to the furan modified-PTFE membrane surface by DA reaction at 60 °C. From the FT-IR spectrum (Fig. 2e), we clearly observe the broad O–H stretch from 3600 to 3100 cm⁻¹, C–H stretch at 2945–2870 cm⁻¹ and the carbonyl stretch of the imide groups at 1702 cm⁻¹ corresponding to the maleimide end-
modified PEG, indicating the formation of a hydrophilic PEG layer on the surface of the PTFE membrane.

XPS analysis (see Fig. 3) provided more detailed information about the amine, furan, and PEG functionalization onto the surface of the PTFE membrane. In the XPS spectra of the aminated PTFE membrane, the 286.9 eV of C 1s binding energy peak corresponding to C–N species and 400.2 eV of N 1s binding energy peak corresponding to N–H species were newly developed, indicating the surface amination of PTFE membrane. After the furan-functionalization of the aminated PTFE membrane, the XPS signals corresponding to the oxygen species of the furan molecule were observed at 286.0 eV (C–O, C 1s) and 532.1 eV (O–H, O 1s). Particularly, the C 1s XPS signal for CH₂ was more developed after the modification of the furfuryl glycidyl ether compared to that of the neat PTFE membrane. This indicated that the furan moieties capable of the DA reaction with PEG-maleimide were well modified at the surface of the PTFE membrane. After the PEG-maleimide was coupled to the furan-modified PTFE membrane by the DA reaction, C 1s XPS signals at 288.1 eV, 286.0 eV and 284.5 eV (assigned as CH₂, C–O and C = O of the PEG-maleimide, respectively) were more distinct, and O 1s XPS signal at 532.1 eV was also manifested, indicating the successful formation of the PEG layer on the PTFE membrane. In addition, we found that the surface atomic concentrations of carbon increased as the surface functionalization of the membrane progressed (Table 1): 34.4 at% (for neat-PTFE), 36.5 at% (for aminated PTFE), 48.4 at% (for furan-modified PTFE), and 55.3 at% (for PEG-PTFE membrane). In contrast, the surface atomic concentrations of fluorine gradually decreased in the preparation progress of the PEG-PTFE membrane. Thus, the combined results from the FT-IR and XPS clearly showed that the hydrophilic PEG layer was chemically well coupled to the hydrophobic PTFE membrane by the DA reaction between furan-modified PTFE membrane and PEG-maleimide.

To investigate the morphological change in the membrane surface after sticking the PEG layers onto the PTFE membrane surface, we carried out the FE-SEM measurement. Fig. 4 shows the FE-SEM images for the top surface morphologies of the neat-PTFE, the aminated PTFE, the furan-modified PTFE, and the PEG-PTFE membranes. Except for the PEG-PTFE membrane, the morphologies of all the membranes were similar and showed the morphology typically observed in a stretched membrane. This indicates that the UV/hydrazine treatment and the furan modification did not significantly affect the pore structure of the PTFE membrane.

Table 1

<table>
<thead>
<tr>
<th>Sample name</th>
<th>C (atomic conc. %)</th>
<th>F (atomic conc. %)</th>
<th>O (atomic conc. %)</th>
<th>N (atomic conc. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat-PTFE membrane</td>
<td>34.44</td>
<td>65.56</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Aminated PTFE membrane</td>
<td>36.55</td>
<td>62.49</td>
<td>0.39</td>
<td>0.57</td>
</tr>
<tr>
<td>Furan-modified PTFE membrane</td>
<td>48.39</td>
<td>45.51</td>
<td>5.68</td>
<td>0.43</td>
</tr>
<tr>
<td>PEG-PTFE membrane</td>
<td>55.33</td>
<td>34.06</td>
<td>9.47</td>
<td>1.14</td>
</tr>
</tbody>
</table>

However, after the DA coupling reaction of the furan-modified PTFE membrane with the PEG-maleimide, we found that the membrane pores were partially occupied and that a dense polymeric layer was generated on the surface of the membrane. This was attributed to the formation of the hydrophilic PEG layer on the PTFE membrane surface, which was in good agreement with FT-IR and XPS results.

3.2. Reversible regeneration of the hydrophilic PEG layer through peel-and-stick process

In order to confirm whether the hydrophilic PEG layer can be regenerated on the membrane surface, we carried out repetitive peel-and-stick tests of the PEG-maleimide on the membrane surface. A furan-maleimide DA cycloaddition is typically achievable at moderate temperatures from 20 to 80 °C, and the formed furan-maleimide DA cycloaddition is reversibly decoupled through the rDA reaction at temperature above 100 °C. Meanwhile, the PTFE membrane is wetted with a few organic solvents because PTFE has an extremely low surface free energy of around 19–20 mN m⁻¹ at 20 °C [42,43] compared with other polymeric materials. Organic solvents such as acetone, ethanol, chloroform, THF and toluene, which have low liquid surface tension below 30 mN m⁻¹ at 20 °C, are able to wet a PTFE membrane. Among these wettable solvents, toluene was thought to be suitable for the rDA reaction because its boiling temperature is 110 °C, while the other wettable solvents have lower boiling points (below 80 °C). Particularly, it is known that the rDA reaction of furan-maleimide bond is more preferred at higher temperature [25,30,39]. Thus, we

![Fig. 3. XPS spectra of (a) C 1s, (b) N 1s, (c) O 1s, and (d) F 1s for neat-PTFE membrane, aminated PTFE membrane, furan-modified PTFE membrane and PEG-PTFE membrane.](image-url)
performed the peeling process of the PEG layer from the PEG-PTFE membrane at 150 °C under a reflux environment to block evaporation of the toluene for effective decoupling of the furan-maleimide bond.

FE-SEM images (see Fig. 5) show the surface morphological changes via the repetitive peel-and-stick process of the PEG layer on the membrane surface. We found that the PEG layer of the PEG-PTFE membrane disappeared from the membrane surface after the membrane was treated at 150 °C, suggesting that the PEG layer can be readily peeled from the membrane surface by adjusting thermal conditions. In addition, as can be seen from the FE-SEM image of the PEG-PTFE (2nd DA), a new PEG layer was re-formed on the membrane surface by DA coupling of fresh PEG-maleimide. In the second and third peel-and-stick processes, similar morphological changes were repeatedly observed on the membrane surface. These features revealed that the surface hydrophilic layer was readily and repeatedly regenerated through a thermally driven peel-and-stick process.

Analysis of the surface chemical structure provides more detailed information about the repetitive peel-and-stick process. Fig. 6a shows ATR FT-IR spectra signifying changes of intensity for specific IR bands, such as C–O stretch at 1100 cm\(^{-1}\), carbonyl stretch for imide at 1702 cm\(^{-1}\), and \(sp^3\) C–H stretch at 2945–2870 cm\(^{-1}\) derived from the PEG-maleimide. After peeling the PEG layer from the membrane surface by DA reaction, the intensities for these IR bands were mostly reduced. In contrast, the reduced IR bands regained their original intensities through sticking the PEG layer via DA reaction. The reversibility of the peel-and-stick process was over approximately 80% calculated from the ATR FT-IR results. XPS spectra (see Fig. 6b and c) also show similar reversibility of the PEG layers. In the XPS spectra for 1st–3rd rDA reactions, the signals at 286 eV assigned as C–O binding energy and 284 eV assigned as CH2 binding

---

Fig. 4. FE-SEM images for top surface morphologies of neat-PTFE (1st row), aminated PTFE (2nd row), furan-modified PTFE (3rd row), and PEG-PTFE membranes (4th row). (upper line) lower magnification, 3,000X, (low line) higher magnification 10,000X.

Fig. 5. (left) FE-SEM images for top surface morphologies of PEG-PTFE membrane (upper line) and re-PTFE membrane (lower line). (right) Schematic illustration of thermally driven dynamic peel-and-stick process.
energy were reduced by the peeling of the PEG layer, and the CF$_2$ signal (290.9 eV) and the C–F signal (687.8 eV) were manifested due to the appearance of the native PTFE surface. In contrast, the C–O and CH$_2$ binding energy signals originated from PEG-maleimide were recovered by the thermo-assisted sticking of the fresh PEG layer, and the XPS peaks related to CF$_2$ and C–F binding energies were reduced by shielding the native PTFE membrane surface. Fig. 7 shows the surface hydrophilicity measured by a static pure water contact angle, as well as the quantitative results for specific IR bands (i.e., C–H stretch and C–O stretch) and XPS atomic concentration (carbon and fluorine). The neat-PTFE membrane has very high hydrophobic surfaces (contact angle 147.5 ± 2.95°). Surface hydrophilicity was slightly improved by furan-modification of the PTFE membrane surface (contact angle 119.5 ± 0.92°). After sticking the hydrophilic PEG layer to the membrane surface, the pure water contact angle was significantly reduced, to 62.4 ± 2.92°, indicating that the hydrophilic PEG layer was successfully coupled with the modified membrane surface. In the re-PTFE (1st rDA) sample, the contact angle recovered to 114.9 ± 5.38°, indicating the peeling of the hydrophilic PEG layer. These tendencies were repeatedly observed during the three-cycle peel-and-stick process of the hydrophilic PEG layers. Therefore, the combined results of surface analyses disclosed that the membrane surface properties can be controlled by a thermally driven dynamic peel-and-stick process.

![Fig. 6.](image)

(a) ATR FT-IR and (b and c) XPS spectra for PEG-PTFE membrane by sticking PEG layer via Diels–Alder reaction and re-PTFE membrane by peeling of PEG layer via retro Diels–Alder reaction.

![Fig. 7.](image)

Summary of repetitive peel-and-stick of hydrophilic PEG layers on the PTFE membrane surface by intensity of ATR FT-IR spectra for carbonyl imide stretch and sp$^3$ C–H stretch (upper line), quantitative XPS analysis for carbon and fluorine (middle line) and static pure water contact angle (lower line).
3.3. Evaluation of fouling resistance

In order to investigate the fouling resistance and the recovery of the anti-fouling property of the PEG-PTFE membrane, we conducted a filtration test using 500 ppm silica aqueous colloidal solution at neutral pH condition. The neat-PTFE and the PEG-PTFE membranes were first fouled by the permeation of a highly concentrated silica suspension for one hour and the membranes were back-washed in order to eliminate the loosely-bound particles. Then, pure water permeability was recorded. After these processes were repeated three times, the PEG layer in the PEG-PTFE membrane was regenerated by a thermally driven peel-and-stick process and the pure water permeability of the regenerated membrane was measured. As a counterpart of the PEG-PTFE membrane, the neat-PTFE membrane was treated in the same manner used for the water permeability measurement of the PEG-PTFE membrane.

As can be seen in Fig. 8a, normalized fluxes for the neat-PTFE and the PEG-PTFE membranes dropped considerably after the permeation of the highly concentrated silica solution, indicating the occurrence of membrane fouling. The pure water fluxes were partially recovered by the back-washing process, and the recovered flux of the PEG-PTFE membrane was higher than that for the neat-PTFE membrane. This indicated the superior anti-fouling property of the PEG-PTFE membrane due to the surface PEG layer. These tendencies were also observed in the second and the third filtration cycles. Nevertheless, the water permeability of both the neat-PTFE and the PEG-PTFE membranes gradually decreased as the fouling and the back-washing was repeated. After three cycle filtration tests, the neat-PTFE and the PEG-PTFE membranes lost about 83.5% and 65.2% of their permeation properties, respectively (see Fig. 8b). Thus, we carried out regeneration of the PEG layer by a thermally driven peel-and-stick process to recover membrane performance. As shown in Fig. 8, the water permeability of the PEG-PTFE membrane recovered to 73.6% of its original performance after the peel and-stick process. This was attributed to the fact that the permanently fouling silica was eliminated from the membrane together with the PEG layer, and that the fresh PEG layer was reformed on the membrane surface. On the other hand, the neat-PTFE membrane is recovery of its original performance was weak (about 24.1%) owing to the absence of an eliminable layer with foulants and regenerable layer by DA and rDA reactions. These results

Fig. 8. (a) Filtration tests of neat-PTFE and PEG-PTFE membranes using 500 ppm silica colloidal aqueous suspension. (b) Calculated reversible and irreversible fouling percentages for neat-PTFE and PEG-PTFE membranes.
obviously show that the anti-fouling layer on the membrane surface can be regenerated and that membrane performance can be successfully recovered by the peel-and-stick process.

To the best of our knowledge, this is the first report showing the new paradigm membrane which has a reversible functional surface layer, achieved by applying a dynamic bond. A regenerable surface functionality will prolong the lifetime of a membrane without need of the disassembly of the membrane module and replacement of the membrane, through the reversible introduction of an anti-fouling active layer on the membrane surface. Furthermore, this can realize a novel functional separating system via a combination of desired functionalities onto the membrane surface.

4. Conclusion

We present a regenerable anti-fouling membrane platform via dynamic peel-and-stick of a hydrophilic PEG layer onto a PTFE membrane surface by thermo-responsive reversible Diels–Alder covalent bonding. The combined results of ATR FT-IR, XPS, and FE-SEM analyses showed that the maleimide end-modified PEG was successfully coupled with the furan-modified PTFE membrane surface by DA reaction between the furan and maleimide groups. As expected, the hydrophilic PEG layer was readily and repeatedly reformulated on the surface of the membrane through the peel-and-stick process, which was verified by surface chemical and morphological analyses. In addition, the evaluation of fouling resistance showed that the hydrophilic PEG layers effectively suppressed membrane fouling by repeated permeation of high concentration colloidal silica suspension. In particular, the anti-fouling property was remarkably recovered after regeneration of the anti-fouling layer, i.e., PEG, via the peel-and-stick process without membrane replacement. Our approach opens up a new paradigm membrane platform by providing reversible covalent bonding between the functional material and the membrane surface. This has various potential applications in advanced dynamic functionalized membrane processes through reversible control of surface functionality.

Acknowledgments

This work was supported by Research Institute of Advanced Materials, Department of Materials Science and Engineering in Seoul National University.

References


