Characterization of modified PVDF membrane by gamma irradiation for non-potable water reuse
Seung Joo Lim, Tak-Hyun Kim and In Hwan Shin

ABSTRACT
Poly(vinylidene fluoride) (PVDF) membranes were grafted by gamma-ray irradiation and were sulfonated by sodium sulfite to modify the surface of the membranes. The characteristics of the modified PVDF membranes were evaluated by the data of Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscope (FE-SEM), the contact angle of the membrane surface and the water permeability. From the results of FT-IR, XPS and FE-SEM, it was shown that the modified membranes were successfully grafted by gamma-ray irradiation and were sulfonated. The content of oxygen and sulfur increased with the monomer concentration, while the content of fluoride sharply decreased. The pore size of the modified membranes decreased after gamma-ray irradiation. The contact angle and the water permeability showed that the hydrophilicity of the modified membranes played a role in determining the membrane performance. The feasibility study of the modified PVDF membranes for using non-potable water reuse were carried out using a laboratory-scale microfiltration system. Grey wastewater was used as the influent in the filtration unit, and permeate quality satisfied non-potable water reuse guidelines in the Republic of Korea.

Key words | gamma-ray, hydrophilicity, irradiation, modification, PVDF, water reuse

INTRODUCTION
It is well-known that the physico-chemical properties of fluoropolymers including a poly(vinylidene fluoride) (PVDF) membrane are chemical and thermal stability, low dielectric constant and low surface energy. The PVDF membrane has been widely used for various separation processes such as wastewater treatment, ion-exchange membrane and bio-medical technology (Hegazy et al. 1999; Nasef et al. 2000; Mao et al. 2004). However, the PVDF membrane is subject to fouling when exposed by hydrophobic substances such as non-ionic matter and/or proteins in the aqueous phase. The surface modification of the PVDF membrane can be achieved either by chemical, by etching, or by high energy irradiation. Although the surface modification by chemicals causes environmental concerns and is difficult to control, chemical modification is the most favoured method. With respect to health and safety, chemicals offer the potential of hazards associated with reactive reagents and solvents. The method of initiated chemical vapour deposition is an all-dry free radical polymerization technique using solvents. Specifically, ultraviolet initiated graft polymerization for the surface modification of polymer membranes requires a photoinitiator, which is well known as a toxic chemical (Kang & Cao 2014; Kochkodan et al. 2014; Kochkodan & Hilal 2015). The surface modification of a membrane by high energy irradiation such as plasma, X-ray, gamma-ray and E-beam is a relatively cleaner method because it is possible to modify the surface of the membrane without generating by-products at room temperature (Dargaville et al. 2003; Liu et al. 2006; Qin et al. 2013). The membrane surface and polymer matrix can be efficiently modified by gamma-rays irradiation because the penetration of gamma-rays is very strong compared to other high energy irradiations (Zhai et al. 2008; Sehgal & Rattan 2010). Because of the water shortages in the world, many investigators have paid more attention to the requirement of experiments and technologies for water reuse (Marks 2006; Angelakis & Durham 2008; Li et al. 2009). Xiao et al. (2013) operated a pilot-scale filtration system with a PVDF microfilter membrane via a thermally induced phase separation method for water reuse. By PVDF
filtration, the chemical oxygen demand (COD) concentration decreased to 15 mg/L. Permeate quality satisfied non-potable water reuse guidelines in the Republic of Korea. Park et al. (2010) recommended some integrated membrane systems such as a coagulation–microfiltration and an ozonation–microfiltration for water reuse. For the case of using pre-treatments with coagulation or ozonation, the concentrations of COD, total nitrogen (T-N) and total phosphorus (T-P) in treated water were below 25, 10 and 5, respectively, in each integrated membrane system. The objectives of this study were to characterize the modified PVDF membranes by gamma-ray irradiation using the data of Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscope (FE-SEM), contact angle and water permeability and were to evaluate the feasibility of the modified PVDF membranes for non-potable water reuse. In this study on how to evaluate if permeate quality satisfied non-potable water reuse guidelines in the Republic of Korea, the modified PVDF membranes were applied to treat grey wastewater.

**MATERIAL AND METHODS**

**Experimental set-up for grafting and sulfonation of PVDF membrane**

PVDF membranes (average pore size: 0.2 μm) were purchased from Millipore Co. (Middlesex, UK). To investigate the grafting degree of each PVDF membrane by gamma-ray irradiation and sulfonation, the five tests were carried out at room temperature (23 °C). The experimental conditions of each PVDF membrane for grafting and sulfonation are shown in Table 1. Each test was immersed into a degassed solution (water:methanol = 1:1) in each 500 mL bottle. Glycidyl methacrylate (GMA) was used as a reactive monomer, and ethylenglycol dimethacrylate (EDMA) was used as a cross-linker monomer. The gamma-rays induced from a ⁶⁰Co source (KAERI, Daejeon, Korea) irradiated each membrane at a dose rate of 0.7 kGy/hr to a total dose of 7 kGy. After irradiation, each membrane was washed with a solution (water:methanol = 1:1), and then was washed with pure methanol. Each membrane was dried at 60 °C for 24 hours in a vacuum oven (OV-12, JEIO TECH, Seoul, Korea). The grafting degree (GD) was obtained by the following equation:

\[
GD(\%) = \frac{W_1 - W_0}{W_0} \times 100
\]

where, \( W_0 \) is the weight of the raw membrane [M], \( W_1 \) the weight of the grafted membrane [M].

The gamma-ray induced grate membranes were immersed into a solution (sodium sulfate:water:isopropanol = wt%10:75:15) at 40 °C for 24 hours in a vacuum oven to ensure the conversion of epoxy to sulfonic functional groups. The conversion from epoxy to sulfonic functional groups can be calculated by the following equation:

\[
X(\%) = \frac{W_2 - W_1}{W_1 - W_0} \times \frac{142}{103} \times 100
\]

where, \( X \) is conversion from epoxy to sulfonic functional groups, \( W_2 \) the weight of the sulfonated membrane [M], 142 the molecular weight of GMA [M], 103 the molecular weight of sodium sulfate [M].

**Characteristics of grey wastewater**

Eriksson et al. (2002) reported that ‘Grey wastewater is defined as wastewater without any input from toilets, which means that it corresponds to wastewater produced in bathtubs, showers, hand basins, laundry machines and kitchen sinks, in households, office buildings, schools, etc.’ The grey wastewater reuse schemes for non-potable water reuse were well reviewed by Li et al. (2009). According to their results, a membrane process is required to sufficiently treat grey wastewater. The characteristics of grey wastewater are usually determined by many parameters such as dilution, storage, separation, temperature and pre-processing (Li et al. 2009; Hocaoglu et al. 2013; Thirugnanasambandham et al. 2014). Among several parameters, dilution, storage and separation play a very important role in determining the characteristics of grey wastewater (Eriksson et al. 2002). The grey wastewater used in this study was collected from an office building wastewater treatment plant located at Jeongeup, Korea. The collected sample was stored at 4 °C.

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**Table 1 | Experimental conditions of each PVDF membrane for grafting and conversion**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>GMA (mL)</th>
<th>EDMA (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF-ref</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>PVDF-A</td>
<td>0.4200</td>
<td>0.0000</td>
</tr>
<tr>
<td>PVDF-B</td>
<td>0.4200</td>
<td>0.0428</td>
</tr>
<tr>
<td>PVDF-C</td>
<td>2.1039</td>
<td>0.0000</td>
</tr>
<tr>
<td>PVDF-D</td>
<td>2.1039</td>
<td>0.0428</td>
</tr>
</tbody>
</table>

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until use. The characteristics of grey wastewater used in this study are shown in Table 2.

### Water permeability measurement of each PVDF membrane

To investigate the enhanced permeability of the modified PVDF membranes, the flux test of each PVDF membrane was performed in a laboratory-scale apparatus consisting of a dead-end microfiltration system at room temperature (25 °C). Each membrane was mounted on the cell with an effective area of 40.4 cm². The membrane inside the module had a length of 11 cm. The feed pressure was controlled from 0.01 to 0.3 MPa to protect the filtration unit. The filtration unit was pre-compacted with 0.01 MPa for 10 minutes. After pre-compaction, the permeability study was carried out with grey wastewater in the dead-end microfiltration system. When the pressure approached 0.3 MPa in the test module, the test module was physically washed with water for 15 minutes. Flux was calculated by the following equation:

\[
\text{Permeability} = \left( \frac{\text{d}V}{\text{d}t} \right) \times \left( \frac{1}{A \times P} \right) = \frac{Q}{A \times P} \quad (3)
\]

where, \( V \) is permeated water volume \([L^3]\), \( t \) is permeation time \([T]\), \( Q \) is the water flow rate \([L^3/T]\), \( A \) is the mount area onto the membrane filtration unit \([L^2]\), and \( P \) is pressure \([Pa]\).

### Analytical methods

The characteristics of grey wastewater and permeate by the membrane filtration were analysed according to Standard Methods for the Examination of Water and Wastewater (APHA 1998). To investigate the change of chemical structure between unmodified and modified membranes and confirm the gamma-ray induced grafting of GMA onto PVDF, an FT-IR spectroscope (Varian, Las Vegas, NV, USA) was used. The pre-treatment of each membrane for the measurement of the FT-IR was primarily ground with (KBr:sample = 100:1) and made into pellets. The FT-IR spectra of PVDF membranes in the range of 500–4,000 cm⁻¹ were obtained using a 660-IR spectrometer (Varian, Las Vegas, NV, USA). XPS analysis was performed using a VG multilab 2000 spectrometer (ThermoVG scientific, Waltham, MA, USA) in an ultra-high vacuum. This system used an unmonochromatized Mg \( K \alpha \) (1,253.6 eV) source and a spherical section analyzer. The accuracy of the binding energy values was ±0.1 eV. For the analysis of the XPS peaks, the C 1 s peak position was set as 284.5 eV and used as internal reference to locate the other peaks. The relative surface atomic ratio was estimated from the corresponding peak areas, corrected with the tabulated sensitivity factors. To characterize surface hydrophilicity, the contact angle of each membrane surface was measured using a sessile drop method with a contact angle analyser (OCA15EC, Dataphysics, Filderstadt, Germany). Distilled water was used as a probe liquid. Each sample was preliminarily conditioned overnight at 40 °C at a relative humidity of 50%. The water drop morphologies and contact angles were analyzed by SCA 2020 software (Dataphysics, Filderstadt, Germany). The morphology of the gamma-ray induced grate membrane was investigated. The morphology of a membrane affects the filtration performance. An FE-SEM of each PVDF membrane was carried out using a JSM-7500F (JOEL, Tokyo, Japan).

### RESULTS AND DISCUSSION

#### Grafting degree and sulfonation of modified membrane

The grafting yield and sulfonation of each PVDF membrane are shown in Table 3. The grafting degree increased with the monomer concentration. In addition, sulfonation of each membrane was determined by the EDMA concentration, indicating that the epoxy functional group was formed by
the conversion grafting degree into the sulfonic functional group. These results were consistent with those of Masuelli et al. (2012). The radiation-induced grafting is one of the most effective methods for the introduction of active functional groups into the graft polymer chains in a membrane. Qin et al. (2013) showed that the grafting degree of a PVDF membrane was proportional to the monomer concentration and the absorbed dose. Gu & Jia (2013) reported that the grafting degree of a PVDF membrane by gamma-ray irradiation was highly dependent upon the monomer concentration and the absorbed dose.

**FT-IR spectra**

The modification of a PVDF membrane by gamma-ray irradiation can be qualitatively shown in FT-IR spectra. The FT-IR spectra of PVDF membranes are shown in Figure 1. The bands at 3,320 and 2,939 cm$^{-1}$ are ascribed to C-H asymmetric and symmetric stretching, respectively (Lanceros-Mendez et al. 2000). The characteristic signals of the grafted membranes prior to sulfonation are: C–O bond at 1,730 cm$^{-1}$ and C–O–C bond 1,140 cm$^{-1}$ in Figure 1(b). The predominant vibrations are C–H, C–C and C–F defections at 1,200 cm$^{-1}$. Unlike Figure 1(a), the characteristic peak for sulfite absorption can be clearly seen at 1,066 cm$^{-1}$ in Figure 1(b).

**XPS results and elemental analysis**

The elemental change of each PVDF membrane after sulfonation is shown in Figure 2. As shown in Figure 2(a), the content of oxygen increased with the monomer concentration while carbon was maintained. The content of fluorine sharply decreased, but sulfur increased in Figure 2(b). This implies that the C–C backbone in the PVDF membrane was maintained. However, the C–F chains in the unmodified PVDF membrane by gamma-ray irradiation were scissile bonds. In addition, it was identified that the epoxy functional groups increased with the monomer concentration. The ratio of sulfur to carbon and that of fluorine to carbon ultimately showed the elemental change after sulfonation in Figure 2(c) and 2(d).

**FE-SEM images**

The morphology change of the PVDF membrane after gamma-ray irradiation is shown in Figure 3. As shown in Figure 3, the pore shape was elliptical and edgeless after gamma-ray irradiation. In addition, the pore size was significantly shrunk after gamma-ray irradiation. Shim et al. (2001) reported that the morphology of a polypropylene membrane was elliptical after gamma-ray irradiation, and the pore size was sharply decreased with increase of reaction time and irradiation dose. Gu & Jia (2013) stated that the number and the size of membrane pores decreased with increasing grafting degree. Masuelli et al. (2012) concluded that the radiation-induced graft PVDF membranes have a tendency towards reduction of pore sizes.

**Contact angle of membrane surface**

The contact angle of the membrane surface has been usually used to characterize the polarity or the energy of polymers.
The contact angle of the membrane surface is an important parameter in measuring the surface hydrophilicity and is a very convenient way to estimate the hydrophilicity of the membrane. The relationship between contact angle and grafting degree of each PVDF membrane is shown in Figure 4. For the case of PVDF-ref, the contact angle of the unmodified PVDF membrane was 140°. The contact angle of each modified PVDF membrane decreased with increasing grafting degree because of the hydrophilicity of each modified PVDF membrane. The XPS result of the modified PVDF membrane supports this result. For the case of the modification test condition of PVDF-C, the lowest contact angle decreased to 30.0°. Liu et al. (2006) reported that a faster decrease of contact angle in a higher grafting degree membrane was shown.

**Water permeability of PVDF membranes**

The antifouling performance of the modified PVDF membranes was analyzed by measuring of the water permeability using grey wastewater. The water permeability of the PVDF membranes to treat grey wastewater is shown in Figure 5. After the membrane fouling by grey wastewater, the test module was physically washed with water for 15 minutes. As shown in Figure 5, the water permeability was completely recovered under the experimental conditions of PVDF-D. Although the test module was a dead-end filtration system, the permeability of PVDF-D was about 190.0 L/(m²·hr·MPa) until 180 minutes. This implies that the hydrophilicity of the modified PVDF membranes played a role in determining the water flux as well as the membrane fouling. The electrostatic charge of membranes is an especially important consideration in reducing the membrane fouling where foulants are charged, which is often the case. Usually, it is appropriate to use a membrane carrying the same electrical charge as the foulants. When the surface and foulant have similar charge, electrostatic repulsion forces between the foulants and the membrane thereby reduce the fouling. Most suspended solids in grey wastewater consist of colloidal materials, which have negative charge. In addition, a great number of micro-organisms in grey wastewater have negative charge. In this study, unmodified hydrophobic PVDF membranes were modified to hydrophilic using gamma irradiation technology. This supports the conclusion that although pore size of the modified membrane became smaller, the permeability increased.

The average water permeability of each PVDF membrane in this study is shown in Table 4. The average water permeability of modified PVDF membrane can be compared to that of unmodified PVDF membrane (PVDF-ref).
The relationship between monomer concentration and permeated time is shown in Figure 6. The permeability was proportional to the monomer concentration ($R^2 = 0.7568$). The permeated time until washing with water increased with increasing permeability (Figure 5).

**Feasibility of the modified PVDF membrane for non-potable water reuse**

Although many countries referenced the World Health Organization (WHO) guidelines for the safe use of wastewater, excreta and grey water (WHO 2006), water reuse...
guidelines and mandatory standards are very different from country to country. In the United States, water reclamation and reuse standards are the responsibility of state and local agencies – there are no federal regulations for reuse (US EPA 2012). The feasibility of the modified PVDF membranes for non-potable water reuse in this study is shown in Table 5. As shown in Table 5, the permeate by membrane filtration, except for stream augmentation and recreational guidelines, was sufficient for non-potable water reuse guidelines in the Republic of Korea. This implies that the modified PVDF membranes by gamma-ray irradiation can be widely used for non-potable water reuse after rigorous integrity tests with regard to lifetime or durability.

**CONCLUSIONS**

The PVDF membrane was successfully grafted by gamma-ray irradiation and was sulfonated by sodium sulfite. These results were confirmed by FT-IR, XPS and FE-SEM images. The contact angle of the modified PVDF membranes sharply decreased. The water permeability was enhanced when the modified PVDF membranes were used. The enhanced hydrophilicity of the PVDF membranes by gamma-ray irradiation was a very important parameter to prevent antifouling. To conclude, it is expected that the modified PVDF membranes by gamma-ray irradiation can be commercially used for non-potable water reuse after rigorous physical and chemical integrity tests.

**ACKNOWLEDGEMENTS**

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**REFERENCES**


### Table 5 | Feasibility of the modified PVDF membrane for non-potable water reuse in this study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Inf.</th>
<th>Eff.</th>
<th>Washing</th>
<th>Landscape irrigation</th>
<th>Stream augmentation</th>
<th>Recreational</th>
<th>Agricultural</th>
<th>Industrial</th>
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<tbody>
<tr>
<td>pH</td>
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<td>7.3</td>
<td>5.8–8.5</td>
<td>5.8–8.5</td>
<td>5.8–8.5</td>
<td>5.8–8.5</td>
<td>5.8–8.5</td>
<td>5.8–8.5</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>550</td>
<td>12.5</td>
<td>&lt;20</td>
<td>&lt;20</td>
<td>&lt;10</td>
<td>&lt;3</td>
<td></td>
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<tr>
<td>SS (mg/L)</td>
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<td>0</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>T-N (mg/L)</td>
<td>120</td>
<td>43.4</td>
<td></td>
<td>&lt;10</td>
<td>&lt;10</td>
<td></td>
<td></td>
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<tr>
<td>T-P (mg/L)</td>
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<td>14.0</td>
<td></td>
<td>&lt;1</td>
<td>&lt;1</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Total coliforms (CFU/100 mL)</td>
<td>2.7 × 10⁵</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>&lt;1000</td>
<td>n.d.</td>
<td>&lt;200</td>
<td>&lt;1,000</td>
</tr>
</tbody>
</table>

MOE (2005).

aAverage permeate water quality of PVDF-C and PVDF-D.

n.d.: not detectable.
US EPA 2012 Guidelines for water reuse. EPA/600/R-12/618, Washington, DC, USA.

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