Journal of Industrial and Engineering Chemistry xxx (xxxx) xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

# Fabrication of self-repairing and low-swelling polymer network via dynamic boronic ester bonds for enhanced membranes longevity and stability

Gahee Im [a,1], Dowon Ahn [b], Bhupen Adhikari [a], Uk Sim [c], Sungbaek Seo [d], Duck Hyun Lee [e,*], Gibum Kwon [a,*]

[a] Department of Mechanical Engineering, University of Kansas, Lawrence, KS 66045, USA
[b] Center for Specialty Chemicals, Korea Research Institute of Chemical Technology (KRICT), Ulsan 44412, Republic of Korea
[c] Department of Energy Engineering, Korea Institute of Energy Technology (KENTECH), Naju, Jeollanam-do 58330, Republic of Korea
[d] Department of Biomaterials Science (BK21 FOUR Program), College of Natural Resources and Life Science/Life and Industry Convergence Research Institute, Pusan National University, Miryang, Gyeongsangnam-do 50463, Republic of Korea
[e] School of Advanced Materials & Electrical Engineering, Industrial Technology Center for Environment-Friendly Materials, Andong National University, Andong, Gyeongsangbuk-do 36729, Republic of Korea

ARTICLE INFO

*Keywords:*
Self-repairing filter
Boronic ester bonds
Low swelling
Poly(dopamine acrylamide-co-butyl acrylate)

ABSTRACT

Membrane technology has become a promising solution for a wide range of separation processes, including wastewater treatment, solvent recovery, and oil–water separation, due to its low energy consumption, cost-effectiveness, and minimal space needs. However, membrane damage caused by suspended pollutants or improper handling remains a challenge, often leading to decreased filtration capability and the need for replacement of membrane modules. Self-repairing membranes have emerged as a new solution, with various materials demonstrating autonomous healing properties through dynamic bonds such as hydrogen bonds or boronic ester bonds. However, many of these self-repairing membranes suffer from excessive swelling in water, compromising their mechanical stability. Herein, we report a self-repairing and low-swelling polymer network based on dopamine acrylamide (DA) and n-butyl acrylate (BA), crosslinked with p-phenylenediboronic acid (PDBA). The boronic ester bond formation between catechol and boronic acid groups confers self-healing properties to the polymer, while the hydrophobic nature of BA minimizes swelling in water. The polymer exhibits a low swelling ratio of 2.1% after 7 days of submersion in water. A cellulose-based filter paper coated with the polymer demonstrated that it can recover its water flux up to 91% after repairing damage. Lastly, an ultrafiltration polyethersulfone (PES)-based filter coated with the polymer demonstrated that it recovers its solute rejection capability after repairing damage.

## Introduction

Membrane technology excels over traditional filtration methods across various separation processes, including wastewater treatment, solvent recovery, and oil–water separations [1]. As the core of filtration systems, membranes have attracted significant attentions as a promising solution [2,3], primarily due to their low energy consumption, cost-effectiveness, and minimal space requirements [4]. For example, ultrafiltration (UF) membranes are highly effective in removing organic matter, suspended particulates, and solids from water [5,6]. However, these pollutants dissolved or suspended in liquids can easily contaminate or damage the membranes [7] during operation [7,8]. Consequently, chemical cleaning and backflushing are often required, which can degrade membrane integrity and lead to further damage. Since most filtration membranes are made from polymeric materials such as polysulfone, polyethersulfone (PES), and cellulose acetate because of their tunable properties, ease of processing, and affordability. However, these polymers are also more prone to damage [9]. Additionally, improper handling during the setup, commissioning, or maintenance can further impair membrane performance [10].

* Corresponding authors.
*E-mail address:* gbkwon@ku.edu (G. Kwon).
[1] Equal contributions.

https://doi.org/10.1016/j.jiec.2025.05.013
Received 3 March 2025; Received in revised form 24 April 2025; Accepted 7 May 2025
Available online 15 May 2025

Damaged membranes often lead to a sudden increase in permeability, resulting in a decline in filtration performance. Thus, it is critical to detecting and reporting any damage to a membrane system promptly, both before and during operation [11]. Several membrane integrity monitoring technologies have been developed based on permeate parameters, such as particle count, turbidity, and conductivity [12]. However, these methods typically struggle to accurately pinpoint damage during operation. Moreover, these methods are often performed offline and suffer from extended detection times [13]. Given that membrane systems generally with modules containing multiple membranes, replacing individual damaged membranes is often not feasible. Instead, replacing the entire module is usually a more practical solution, despite the high costs and the need for suspending the process [1].

Developing membranes with autonomous self-repairing capabilities has been a major research focus in recent years. For example, Getachew et al. [14], reported a microporous PES membrane grafted with 2-acrylamido-2-methyl-1-propanesulfonic acid. This membrane demonstrated the ability to restore its particle rejection efficiency up to 99 %, from levels as low as 30 % after physical damage. The recovery was attributed to the swelling of a pore-filling hydrogel into the damage site, supported by strong hydrogen bonding and molecular interdiffusion. Similarly, Lim et al. [1], developed a PES membrane coated with polyvinyl alcohol (PVA) and polyacrylic acid (PAA), capable of forming a self-repairing supramolecular system. When submerged in water, the membrane undergoes self-healing due to the reversible hydrogen bonds. Jiang et al. [15], fabricated an UF membrane using cucurbit [8]uril (CB [8]) hydrogel to fill pores. The membrane's self-healing performance was attributed to the swelling of the CB[8] hydrogel, molecular interdiffusion of the chains, and strong hydrogen bonding with guest molecules. Wang et al. [10], designed a boronic acid-containing PES UF membrane composited with PVA hydrogel. The membrane demonstrated self-healing through hydrogen bonding and reversible boronic ester formation. Li et al. [16], reported hyper-crosslinked metal–organic polyhedral (HCMOPs) membranes, covalently crosslinked with boronic acid-modified Zr-based MOPs and PVA. It exhibited reversible dynamic boronic bonds when exposed to water vapor.

Most previously reported self-repairing membranes have utilized hydrogels or hydrophilic polymers, as water-induced swelling enhances polymer chain mobility, increasing the likelihood of dynamic bond reformation and successful healing at cracked interfaces [17]. However, this swelling also leads to severe structural deformation [18] and changes in mechanical properties [19], making these materials prone to failure during underwater use. While hydrophobic polymers are expected to retain their intrinsic properties in water without swelling, the formation of a water boundary layer at cracked surfaces significantly weakens van der Waals interactions, disrupting the reformation of dynamic bonds [20]. Therefore, designing a polymer with balanced hydrophobicity and water-triggered dynamic bonds is essential for developing underwater self-healing elastomers with high stability [21,22].

Herein, we report a self-repairing, low-swelling polymer network by copolymerizing dopamine acrylamide (DA) and n-butyl acrylate (BA) followed by crosslinking with p-phenylenediboronic acid (PDBA). The boronic acid and catechol groups in PDBA and p(DA-co-BA) form boronic ester bonds through esterification. The resulting p(DA-co-BA) + PDBA exhibits a very low swelling ratio of 2.1 % after being submerged in water for 7 days. This low swelling is attributed to the hydrophobic nature of BA, which suppresses water uptake and stabilizes the polymer network in water. It is demonstrated that the concentrations of PDBA in the polymer network affects the swelling ratio, with lower concentrations of PDBA leading to higher swelling. This can be attributed to unreacted free catechol groups which can attract water and undergo hydrolysis. Furthermore, p(DA-co-BA) + PDBA demonstrates self-repairing capabilities when submerged in water. This is attributed to the re-formation of boronic ester bonds between free catechol and boronic acid groups on the cut surfaces when they come into contact. Utilizing p(DA-co-BA) + PDBA, a cellulose-based filter paper was dip-coated. The filter demonstrates that it can recover up to 91 % of its inherent water flux after repair. Lastly, an UF filter coated with p(DA-co-BA) + PDBA demonstrates that it recovers its solute rejection capability after repairing damage.

## Experimental

### *Materials*

p-phenylenediboronic acid (PDBA, $M_w$ = 165.75 g/mol), dopamine hydrochloride ($M_w$ = 189.64 g/mol), acrylic anhydride ($M_w$ = 126.11 g/mol), n-butyl acrylate (BA, $M_w$ = 128.17 g/mol), triethylamine (TEA), 2,2′-azobis(isobutyronitrile) (AIBN), humic acid (technical grade), pyridine (anhydrous), ethanol (dehydrated), tetrahydrofuran (THF, anhydrous), acetone, chloroform (anhydrous), ethyl acetate, n-hexane, hydrochloric acid (HCl, 37 % ACS reagent), were obtained from Sigma-Aldrich. A cellulose Whatman filter paper (Grade 4) and a flat sheet polyether sulfone (PES) ultrafiltration membrane were obtained from Sigma Aldrich and Snyder Filtration, respectively.

### *Synthesis of poly(dopamine acrylamide-co-n-butyl acrylate)(p(DA-co-BA)*

In a round-bottom flask, the desired amount of DA and BA were added. For this study, polymers with DA:BA molar ratios of 9.9:0.1, 9.5:0.5, and 9.0:1.0 were synthesized. Anhydrous ethanol was then added to adjust the overall concentration to 5.0 wt%. Then, AIBN was added as an initiator at concentration of 0.5 wt% relative to the total monomer content. The solution was heated to 75 °C under stirring for about 24 h while nitrogen ($N_2$) gas purging to maintain an inert atmosphere. The solution was cooled to room temperature and poured into an excess amount of n-hexane to precipitate the polymer. The precipitated polymer was then filtered and dried under vacuum.

### *Preparation of a solution for p(DA-co-BA) crosslinked with PDBA*

The resulting p(DA-co-BA) and PDBA were mixed in desired compositions. 2.7 g of p(DA-co-BA) containing 2.00 mmol of catechol groups was mixed with 165 mg, 124 mg and 82.5 mg of PDBA in 100 ml of chloroform. This resulted in 100 %, 75 % and 50 % of the catechol groups available for boronic ester bonding, respectively. Finally, 202 mg of TEA (equiv. 2.00 mmol) was added to the solution followed by stirring for 24 h at room temperature. TEA was added to form a coordinate covalent bond (i.e., dative bond) between boron (B) and nitrogen (N), which serves as dynamic crosslinks within the polymer network [23,24]. We denote p(DA-co-BA) mixed with 165 mg, 124 mg, and 82.5 mg of PDBA as p(DA-co-BA) + 5.8 wt% PDBA, p(DA-co-BA) + 4.4 wt% PDBA, and p(DA-co-BA) + 3.0 wt% PDBA, respectively.

### *Coating a filter with p(DA-co-BA) + PDBA*

The p(DA-co-BA) + PDBA solution was applied to the surface of a filter. Note that we used Whatman cellulose-based filter paper (Grade 4) and a flat sheet PES-based UF filter as substrates. Subsequently, the coated filter was heated at 50 °C for 24 h to facilitate the crosslinking process.

### *Measurements of water flux*

Water flux through the filter was measured using a custom-made dead-end and gravity-driven filtration apparatus. Approximately 100 ml of deionized (DI) water was poured into a container with the filter attached at the bottom. Prior to the water flux measurements, the filter weas pre-swollen for 4 days to eliminate the effects of absorption and swelling on flux. The water flux measurement was conducted over a period of 10 min. All tests were repeated three times unless otherwise

specified. The water flux was calculated using the equation: $J_w = V/(A\Delta t)$, where $J_w$ (L/m$^2$-h) is the water flux, $A$ is the area of the filter, and $\Delta t$ is the permeation time.

*Calculation of self-repairing efficiency*

Damage was engraved on the filter surface using a razor blade, creating a hash mark (#) with dimensions of approximately 1 cm long, 10 μm wide, and 2.0 μm deep. The water flux of the damaged filter was measured for an initial 10 s to minimize the effects of ongoing repair on the flux. The self-repairing efficiency, $\eta$ (%), was calculated using the following equation:

$$\eta(\%) = (\Delta f_{repaired}/\Delta f_{inherent}) \times 100 \quad (1)$$

where $\Delta f_{repaired}$ = ($J_w$ of damaged filter) – ($J_w$ of repaired filter) and $\Delta f_{inherent}$ = ($J_w$ of damaged filter) – ($J_w$ of inherent filter).

*Humic acid rejection*

A 60 ppm aqueous solution of humic acid was prepared for the rejection experiments. A flat sheet PES UF filter was coated with p(DA-co-BA) + PDBA as described above. The humic acid rejection experiments were conducted at 2 bar using a dead-end filtration cell (Sterlitech, HP4750). The concentration of humic acid in the permeate solutions was measured using UV–Vis Spectrophotometer (Thermo Evolution 600, UV–Vis Spectrophotometer, Thermo Fisher Scientific). The rejection $R$ (%) was calculated by:

$$R(\%) = \left(1 - C_p/C_f\right) \times 100 \quad (2)$$

where $C_p$ and $C_f$ are the concentrations of humic acid in the permeate and feed solutions, respectively.

## Results and discussion

To fabricate a self-repairing polymer with minimal swelling in water, we chose dopamine acrylamide (DA) and n-butyl acrylate (BA) as monomers. DA was chosen for its low glass transition temperature ($T_g$) of −50 °C, which enhances chain mobility at room temperature and results in self-repairing capability [21]. BA was selected for its hydrophobicity which contributes to its stability in water and prevents significant swelling [25]. Using a free radical polymerization method [21,22], we fabricated poly(dopamine acrylamide-co-n-butyl acrylate, p(DA-co-BA)) (Fig. 1). A detailed description of the polymerization procedure and polymer properties are provided in **Supporting Information (SI) Section 1**. A crosslinked p(DA-co-BA) network was fabricated using PDBA. The catechol moieties in the polymer and boronic acid groups in PDBA undergo esterification reaction, forming non-ionic boronic ester bonds [26]. The formation of these bonds between p(DA-co-BA) and PDBA was confirmed through the Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy (**SI Section 2**).

The swelling ratio of p(DA-co-BA) crosslinked with PDBA was determined by measuring the weight of the polymer film in its dry state and after being fully soaked in water. The swelling ratio (%) was calculated by:

$$Swelling\ ratio(\%) = \left(W_{final} - W_{initial}\right)/W_{initial} \times 100 \quad (3)$$

where $W_{final}$ and $W_{initial}$ are the fully soaked and initial (dry) weight of the polymer film, respectively. Fig. 2**a** displays the measured swelling ratio values for p(DA-co-BA) crosslinked with various concentrations of PDBA. The molar ratio of DA to BA in the polymer was maintained at 9.0:1.0. The results indicate higher concentrations of PDBA lead to lower swelling ratios. For example, p(DA-co-BA) crosslinked with 5.8 wt% PDBA (denoted as p(DA-co-BA) + 5.8 wt% PDBA) exhibits a swelling ratio of 2.1 % after 7 days submerged in water, whereas p(DA-co-BA) + 3.0 wt% PDBA exhibits a significantly higher swelling ratio of 15.3 %. This difference can be attributed to the higher PDBA concentration allowing all the catechol groups in DA to coordinate with boronic acid groups, whereas 3.0 wt% PDBA results in unreacted catechol groups. Note that 3.0 wt% PDBA provides only enough boronic acids groups to coordinate with about half of the catechol groups, leaving hydrophilic catechol moieties and resulting in a looser polymer network. Consequently, p(DA-co-BA) crosslinked with lower PDBA concentrations exhibit higher water uptake [27]. The calculated crosslinking density for p(DA-co-BA) + 3.0 wt% PDBA, p(DA-co-BA) + 4.4 wt% PDBA, and p(DA-co-BA) + 5.8 wt% PDBA are 251.3 kg/mol, 311.8 kg/mol, and 406.5 kg/mol, respectively (**SI Section 3**).

Another key feature is the stability of the polymer network in water for up to 7 days. This can be attributed to the hydrophobicity of BA which can maintain the network structure and suppress water absorption. Conversely, p(DA-co-BA) with a lower BA molar ratio (e.g., 9.5:0.5 and 9.9:0.1) starts disintegrating after 2 days in water (**SI Section 4**).

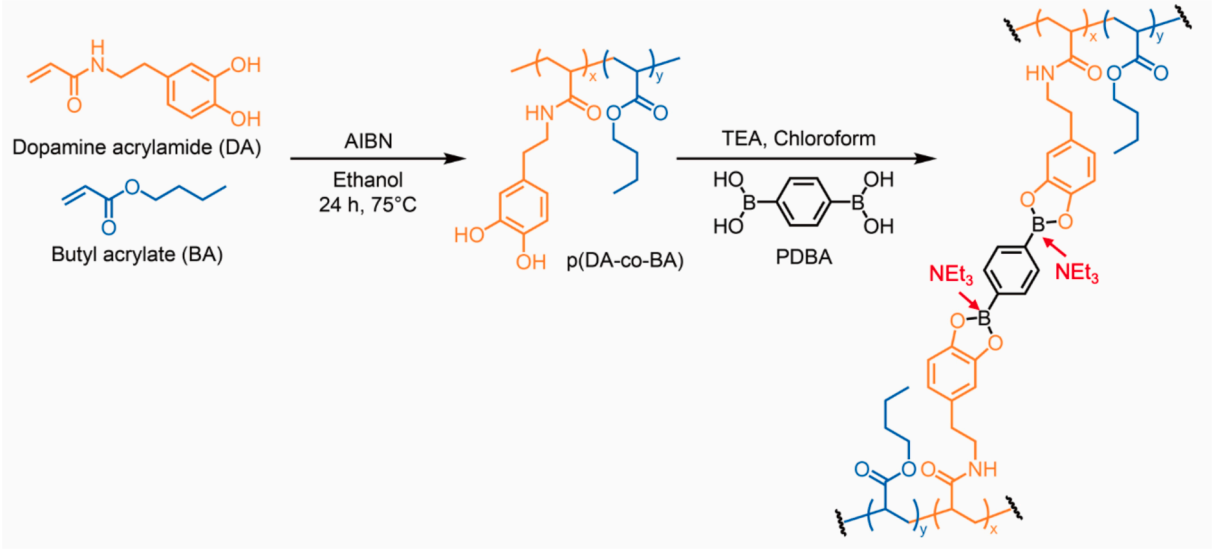


**Fig. 1.** Schematic illustrating the overall synthesis process of p(DA-co-BA) through the copolymerization of DA and BA via free radical polymerization. The resulting p(DA-co-BA) is subsequently crosslinked with PDBA. The detailed synthesis process for DA is provided in SI Section 1.

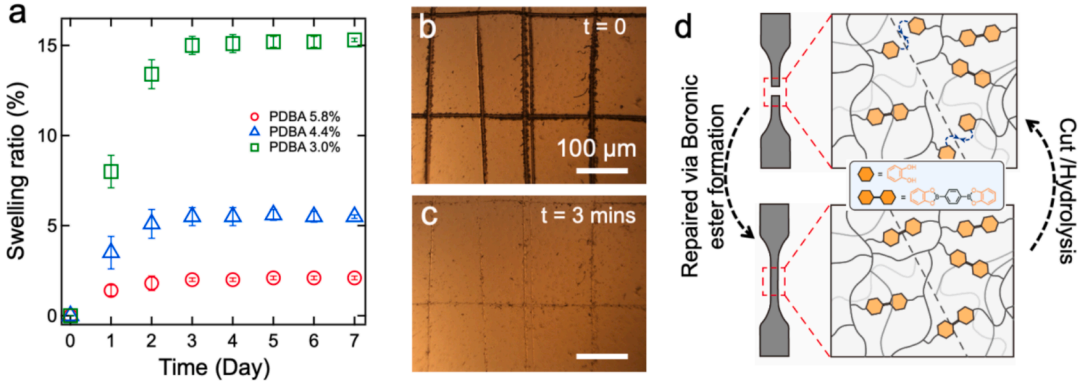


**Fig. 2.** (a) Swelling ratio of p(DA-co-BA) crosslinked with various PDBA concentrations submerged in water. (b-c) Optical microscopy images of a p(DA-co-BA) + 5.8 wt% PDBA film showing multiple breaches (b) and after undergoing self-repair process (c). (d) Schematic illustrating the proposed self-repairing mechanism.

This can be attributed to the partial loss of TEA through diffusion in water, which may weaken the boronic ester linkages.

The self-repairing capability of p(DA-co-BA) + PDBA was demonstrated by creating several breaches on the polymer surface using a sharp tip scriber (Fig. 2**b**). The breaches ranged from approximately 3 to 10 μm in width (**SI Section 5**). Upon immediate submersion in water, the breaches on the surface began to disappear. Within 3 min, most of the breaches were repaired (Fig. 2**c**). A movie demonstrating the self-repairing process of p(DA-co-BA) + 5.8 wt% PDBA is provided as **Supporting Movie S1**.

Fig. 2**d** illustrates the proposed mechanism for the self-repairing process of the polymer. When the polymer network is cut, the cut surface tends to have higher polymer chain mobility due to the rupture of crosslinkers, which leaves dynamic bonds more accessible [28]. Upon contacting water, the equilibrium of the reaction between catechol and boronic acid groups shifts slightly towards hydrolysis. This shift leads to the exposure of more catechol and boronic acid groups at the cut surface. At the same time, water absorption causes the polymer to swell, bringing the two cut surfaces into closer contact. This proximity allows the boronic ester bonds to re-form through esterification, effectively reconstructing the network structure and closing the breach [21]. This dynamic bond reformation is key to the self-repairing behavior observed in p(DA-co-BA) + PDBA.

The self-repairing capability and minimal swelling of p(DA-co-BA) + PDBA make it suitable for applications in wet conditions, such as membranes. To explore this, we coated a cellulose-based filter paper (nominal pore size = 20 – 25 μm) with p(DA-co-BA) using DA:BA molar ratio of 9.0:1.0 followed by crosslinking with PDBA (details in **Experimental**). We measured the water flux through the coated filters using a custom-made dead-end filtration apparatus. All water flux measurements were conducted at an applied pressure of approximately 400 Pa, indicating a gravity-driven process (**SI Section 6**). The results demonstrate that uncoated filter exhibits a water flux ($J_w$) of 96.0 ± 5.4 L/m$^2$-h, whereas the coated filters show significantly lower flux values. For example, a filter coated with p(DA-co-BA) + 3.0 wt% PDBA exhibits $J_w$ = 38.4 ± 9.1 L/m$^2$-h, while that coated with p(DA-co-BA) + 5.8 wt% PDBA shows $J_w$ = 76.8 ± 6.3 L/m$^2$-h. (Fig. 3**a**) Notably, filters with lower PDBA concentrations show lower water flux values. This can be attributed to a higher number of free catechol groups in the polymer network crosslinked with lower PDBA concentrations, which interact with water and reduce the permeability. Additionally, to ensure accurate flux measurement, all filters were pre-swollen in water for four days before testing to eliminate the water uptake effect (see **Experimental**).

To evaluate the self-repairing capability of p(DA-co-BA) + PDBA coated filter, we measured and compared water flux values through damaged and subsequently repaired filters. Four deep scratches in the shape of a hash sign (#), each approximately 1 cm long, 10 μm wide, and 2.0 μm deep were engraved onto the surface using a razor blade. The p(DA-co-BA) + PDBA forms a film of ≈2.5 ± 0.3 μm on the filter surface, so the underlying filter remained undamaged. It is demonstrated that the water flux increased after damaging the filter. For example, the water flux values for damaged filters coated with p(DA-co-BA) + 3.0 wt% PDBA, p(DA-co-BA) + 4.4 wt% PDBA, and p(DA-co-BA) + 5.8 wt% PDBA were $J_w$ = 75.6 ± 10.3 L/m$^2$-h, $J_w$ = 89.2 ± 14.4 L/m$^2$-h, and $J_w$ = 104.2 ± 12.8 L/m$^2$-h, respectively (Fig. 3**b**). After submerging the damaged filters in water for 7 days, allowing for complete repair, the repaired filters exhibit lower $J_w$ values of 51.6 ± 5.5 L/m$^2$-h, 65.3 ± 14.3 L/m$^2$-h, and 79.2 ± 9.7 L/m$^2$-h, respectively, for filters coated with

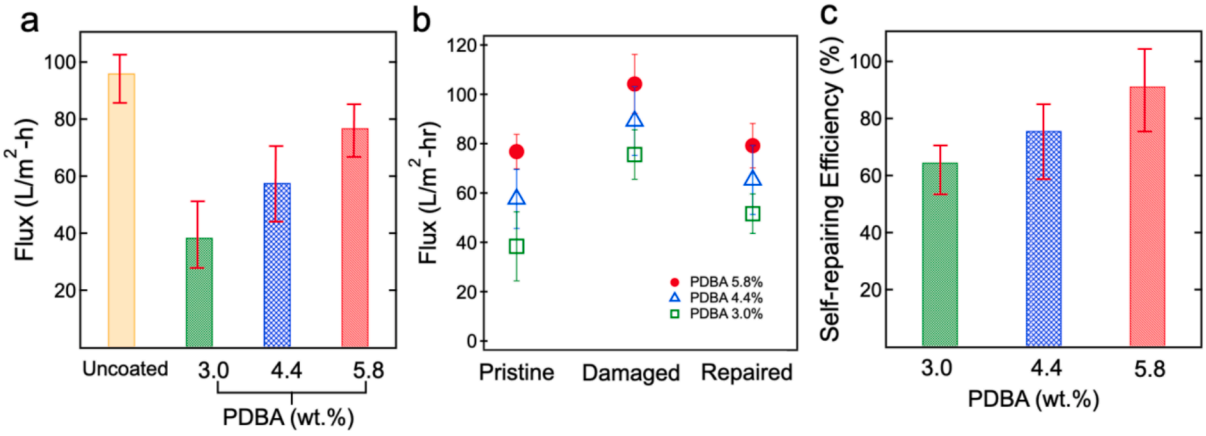


**Fig. 3.** (a) Measured water flux values through coated filters. For comparison, the water flux value through an uncoated filter is also shown. (b) Measured water flux values through damaged and repaired filters. (c) Self-repairing efficiency ($\eta$ (%)) of the filters calculated using Eq. (1).

3.0 wt%, 4.4 wt%, and 5.8 wt% PDBA.

The self-repairing efficiency, $\eta$ (%) of each filter was calculated using Eq. (1). The results indicate that filters with higher PDBA concentrations show greater $\eta$ values (Fig. 3**c**). This can be attributed to the reconstruction of boronic ester bonds, as higher PDBA concentrations provide more boronic acid groups for the re-esterification process. A movie demonstrating the water flux changes due to damage and subsequent repair is provided as **Supporting Movie S2**.

We conducted a long-term stability test of the damaged p(DA-co-BA) + 5.8 wt% PDBA-coated filter under running water conditions for 7 days. After 7 days, we measured its flux. The results are shown in Fig. 4. The results show that our p(DA-co-BA) + 5.8 wt% PDBA-coated filter recovers its inherent water flux after being submerged in running water for 7 days. This indicates that our p(DA-co-BA) + 5.8 wt% PDBA-coated filter can maintain its filtration performance in practical applications where it is continuously exposed to running water.

Lastly, we applied p(DA-co-BA) + PDBA an UF filter to impart self-repairing capabilities. A flat sheet PES UF filter was coated and cross-linked following the same procedure as described in **Experimental**. To evaluate the performance, we conducted solute rejection experiments using humic acid as a model solute. The concentration of humic acid in the permeate through both the damaged and repaired filters were measured using a UV–Vis spectrophotometer (**SI Section 7**). The rejection, $R$(%) was calculated using Eq. (2). The results show that a damaged filter coated with p(DA-co-BA) + 5.8 wt% PDBA exhibits the $R$ value of 30.5 ± 5.5 %, while the repaired filter shows 44.2 ± 4.3 %. This is comparable to the pristine filter's rejection value of 46.1 ± 6.0 % (Fig. 5). This highlights the effective restoration of filtration functionality post-repair. For comparison, an uncoated filter shows negligible change in rejection between the damaged ($R$ = 26.5 ± 5.1 %) and repaired ($R$ = 26.3 ± 6.5 %) states. These results demonstrate the practical utility of the coating in ultrafiltration applications, maintaining solute rejection performance even after damage and subsequent repair.

## Conclusion

In this work, we synthesize a self-repairing and non-swelling polymer network by copolymerizing DA and BA followed by crosslinking with PDBA. The catechol groups p(DA-co-BA) and boronic acid groups in

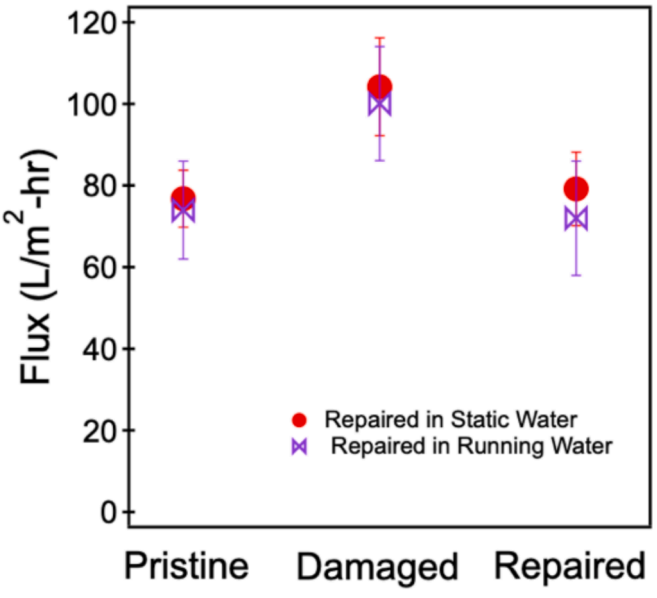


**Fig. 4.** Measured water flux values through both damaged and repaired filters. Filters were repaired by submerging them in static water or running water for 7 days.

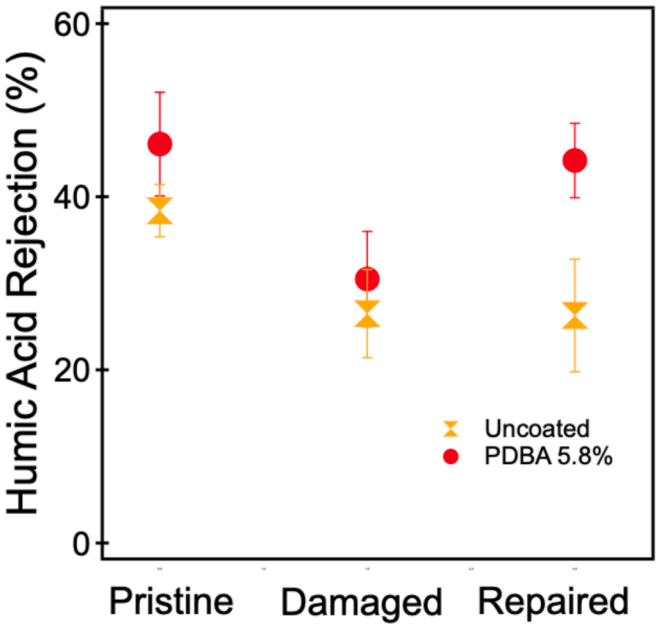


**Fig. 5.** Plots illustrating humic acid rejection ($R$(%)) for a PES-based UF filter coated with p(DA-co-BA) + 5.8 wt% PDBA, before and after damage and repair calculated using Eq. (2). For comparison, the humic acid rejection value of an uncoated filters also provided.

PDBA form boronic ester bonds through an esterification reaction, which was verified by ATR-FTIR measurements. The resulting polymer network exhibited a very low swelling ratio, as low as 2.1 % indicating its excellent stability in water. It was also demonstrated that a lower PDBA concentration in the polymer network resulted in a higher swelling ratio due to unreacted catechol groups, which can facilitate water uptake. However, even after 7 days of submersion in water, the polymer network remained stable making it ideal for underwater applications. The polymer also exhibited self-repairing capability in water. When damaged, the boronic ester bonds between free catechol and boronic acid groups at the cut surfaces can reconstruct allowing them to repair itself upon contact. Utilizing p(DA-co-BA) + PDBA, a cellulose-based filter paper was dip-coated. The coated filter demonstrated self-repairing capability. After damage, the coated filter recovered up to 91 % of its inherent water flux while the uncoated filter showed no change in water flux post-damage or after repair. Furthermore, an UF PES-based filter coated with p(DA-co-BA) + PDBA also recovered its solute rejection capability after repair. We envision that our polymer network can offer a promising solution for enhancing the longevity and durability of membrane systems.

## Author contribution statement

G.I. performed experiments and analyzed data. D.A. analyzed data and wrote an original draft. B.A. performed experiments and analyzed data. U.S. wrote and reviewed a manuscript. S.S. wrote and reviewed the manuscript. D.H.L designed the experiments and wrote the final manuscript. G.K. conceived the project and designed the experiments, wrote and reviewed the manuscript.

## CRediT authorship contribution statement

**Gahee Im:** Writing – original draft, Investigation. **Dowon Ahn:** Writing – original draft, Investigation. **Bhupen Adhikari:** Visualization, Investigation. **Uk Sim:** Writing – original draft, Investigation, Data curation. **Sungbaek Seo:** Writing – original draft, Investigation. **Duck Hyun Lee:** Writing – original draft, Funding acquisition. **Gibum Kwon:** Writing – original draft, Supervision, Funding acquisition,

Conceptualization.

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Gibum Kwon reports financial support was provided by The University of Kansas. Gibum Kwon reports financial support was provided by National Science Foundation. Duck Hyun Lee reports financial support was provided by Korea Ministry of SMEs and Startups and Energy. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgement

This research was supported by National Science Foundation (NSF) (Grant Number: 1944314), University of Kansas School of Engineering ASCEND Funding Program, and General Research Fund (2234802-FY2025). Also, Lee thanks the financial support from Andong National University and the Korea Ministry of SMEs and Startups (Grant Number: 00510369).

*Data availability*

Data will be made available on request.

## Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jiec.2025.05.013.

## References

[1] Y.H. Lim, E.C. Wong, W.C. Chong, A.W. Mohammad, C.H. Koo, W.J. Lau, Introducing self-healing properties to polyethersulfone (PES) membrane via poly (vinyl alcohol)/polyacrylic acid (PVA/PAA) surface coating, *Chemosphere* 349 (2024) 140772, https://doi.org/10.1016/j.chemosphere.2023.140772.

[2] N.M. Mahmoodi, M. Oveisi, M. Bakhtiari, B. Hayati, A.A. Shekarchi, A. Bagheri, S. Rahimi, Environmentally friendly ultrasound-assisted synthesis of magnetic zeolitic imidazolate framework - graphene oxide nanocomposites and pollutant removal from water, *J. Mol. Liq.* 282 (2019) 115–130, https://doi.org/10.1016/j.molliq.2019.02.139.

[3] S.R. Mousavi, M. Asghari, N.M. Mahmoodi, Chitosan-wrapped multiwalled carbon nanotube as filler within PEBA thin film nanocomposite (TFN) membrane to improve dye removal, *Carbohydr. Polym.* 237 (2020) 116128, https://doi.org/10.1016/j.carbpol.2020.116128.

[4] X. Li, L. Jiang, H. Li, Application of ultrafiltration technology in water treatment, *IOP Conf. Ser. Earth Environ. Sci.* 186 (2018) 012009, https://doi.org/10.1088/1755-1315/186/3/012009.

[5] C.M. Chew, M.K. Aroua, M.A. Hussain, W.M.Z.W. Ismail, Evaluation of ultrafiltration and conventional water treatment systems for sustainable development: an industrial scale case study, *J. Clean. Prod.* 112 (2016) 3152–3163, https://doi.org/10.1016/j.jclepro.2015.10.037.

[6] C.D. Peters, T. Rantissi, V. Gitis, N.P. Hankins, Retention of natural organic matter by ultrafiltration and the mitigation of membrane fouling through pre-treatment, membrane enhancement, and cleaning - A review, *J. Water Process Eng.* 44 (2021) 102374, https://doi.org/10.1016/j.jwpe.2021.102374.

[7] G. Peng, W. Yaoqin, S. Changmei, J. Chunnuan, Z. Ying, Q. Rongjun, W. Ying, Preparation and properties of PVC-based ultrafiltration membrane reinforced by in-situ synthesized p-aramid nanoparticles, *J. Membr. Sci.* 642 (2022) 119993, https://doi.org/10.1016/j.memsci.2021.119993.

[8] G. Fan, C. Chen, X. Chen, Z. Li, S. Bao, J. Luo, D. Tang, Z. Yan, Enhancing the antifouling and rejection properties of PVDF membrane by $Ag_3PO_4$-GO Modification, *Sci. Total Environ.* 801 (2021) 149611, https://doi.org/10.1016/j.scitotenv.2021.149611.

[9] I. Ibrar, S. Yadav, N. Ganbat, A.K. Samal, A. Altaee, J.L. Zhou, T.V. Nguyen, Feasibility of $H_2O_2$ cleaning for forward osmosis membrane treating landfill leachate, *J. Environ. Manag.* 294 (2021) 113024, https://doi.org/10.1016/j.jenvman.2021.113024.

[10] C. Wang, Z. Guo, C. Wang, W. Liu, X. Yang, H. Huo, Y. Cai, Z. Geng, Z. Su, High-performance self-healing composite ultrafiltration membrane based on multiple molecular dynamic interactions, *J. Membr. Sci.* 671 (2023) 121395, https://doi.org/10.1016/j.memsci.2023.121395.

[11] Q. Wang, C. Dou, C. Xin, X. Li, J. Wang, R. Zhang, X. Duan, Z. Guo, M. Sun, J. Wang, Monitoring of membrane integrity based on electrical measurement and deep learning, *IEEE Sens. J.* 21 (6) (2021) 8020–8029, https://doi.org/10.1109/JSEN.2020.3047445.

[12] C. Xin, Z. Cheng, Z. You, H. Bai, J. Wang, Using EEM fluorescence to characterize the membrane integrity of membrane bioreactor (MBR), *J. Membr. Sci.* 610 (2020) 118356, https://doi.org/10.1016/j.memsci.2020.118356.

[13] E.R. Ostarcevic, J. Jacangelo, S.R. Gray, M.J. Cran, Current and emerging techniques for high-pressure membrane integrity testing, *Membranes* 8 (3) (2018) 60, https://doi.org/10.3390/membranes8030060.

[14] B.A. Getachew, S.-R. Kim, J.-H. Kim, Self-healing hydrogel pore-filled water filtration membranes, *Environ. Sci. Technol.* 51 (2) (2017) 905–913, https://doi.org/10.1021/acs.est.6b04574.

[15] H. Jiang, S. Liu, Construction of self-healing polyethersulfone ultrafiltration membrane by cucurbit[8]uril hydrogel via RTIPS method and host-guest chemistry, *Chemosphere* 311 (2023) 137079, https://doi.org/10.1016/j.chemosphere.2022.137079.

[16] J. Li, Z. Liu, J. Liu, X. Liu, Y. Luo, J. Liang, Z. Zhang, Humidity-induced self-oscillating and self-healing hypercrosslinked metal–organic polyhedra membranes, *Adv. Sci.* 11 (20) (2024) 2307376, https://doi.org/10.1002/advs.202307376.

[17] M. Ezazi, B. Shrestha, A. Maharjan, G. Kwon, Water-responsive self-repairing superomniphobic surfaces via regeneration of hierarchical topography, *ACS Mater. Au* 2 (1) (2022) 55–62, https://doi.org/10.1021/acsmaterialsau.1c00036.

[18] H. Kamata, K. Kushiro, M. Takai, U. Chung, T. Sakai, Non-osmotic hydrogels: a rational strategy for safely degradable hydrogels, *Angew. Chem. Int. Ed.* 55 (32) (2016) 9282–9286, https://doi.org/10.1002/anie.201602610.

[19] K.-L.-G. Ho, A.L. Pometto Iii, P.N. Hinz, Effects of temperature and relative humidity on polylactic acid plastic degradation, *J. Polym. Environ.* 7 (2) (1999) 83–92, https://doi.org/10.1023/A:1021808317416.

[20] J.H. Waite, Nature's underwater adhesive specialist, *Int. J. Adhes. Adhes.* 7 (1) (1987) 9–14, https://doi.org/10.1016/0143-7496(87)90048-0.

[21] C. Kim, H. Ejima, N. Yoshie, Non-swellable self-healing polymer with long-term stability under seawater, *RSC Adv.* 7 (31) (2017) 19288–19295, https://doi.org/10.1039/C7RA01778B.

[22] J. Li, H. Ejima, N. Yoshie, Seawater-assisted self-healing of catechol polymers via hydrogen bonding and coordination interactions, *ACS Appl. Mater. Interfaces* 8 (29) (2016) 19047–19053, https://doi.org/10.1021/acsami.6b04075.

[23] C.C. Deng, W.L.A. Brooks, K.A. Abboud, B.S. Sumerlin, Boronic acid-based hydrogels undergo self-healing at neutral and acidic pH, *ACS Macro Lett.* 4 (2) (2015) 220–224, https://doi.org/10.1021/acsmacrolett.5b00018.

[24] A.R. Narkar, B. Barker, M. Clisch, J. Jiang, B.P. Lee, pH responsive and oxidation resistant wet adhesive based on reversible catechol–boronate complexation, *Chem. Mater.* 28 (15) (2016) 5432–5439, https://doi.org/10.1021/acs.chemmater.6b01851.

[25] W. Zhao, L. Duan, B. Zhang, X. Ren, G.H. Gao, Tough and ultrastretchable hydrogels reinforced by poly(butyl acrylate-co-acrylonitrile) latex microspheres as crosslinking centers for hydrophobic association, *Polymer* 112 (2017) 333–341, https://doi.org/10.1016/j.polymer.2017.02.032.

[26] R. Nishiyabu, Y. Kubo, T.D. James, J.S. Fossey, Boronic acid building blocks: tools for self assembly, *Chem. Commun.* 47 (4) (2011) 1124–1150, https://doi.org/10.1039/C0CC02921A.

[27] J. Cui, J. Iturri, J. Paez, Z. Shafiq, C. Serrano, M. d'Ischia, A. Del Campo, Dopamine-based coatings and hydrogels: toward substitution-related structure–property relationships, *Macromol. Chem. Phys.* 215 (24) (2014) 2403–2413, https://doi.org/10.1002/macp.201400366.

[28] C. Kim, H. Ejima, N. Yoshie, Polymers with autonomous self-healing ability and remarkable reprocessability under ambient humidity conditions, *J. Mater. Chem. A* 6 (40) (2018) 19643–19652, https://doi.org/10.1039/C8TA04769C.