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WATER-RESPONSIVE SELF-HEALING MEMBRANE MODIFIED WITH POLYETHYLENEIMINE (PEI)/POLY (ACRYLIC ACID) (PAA)

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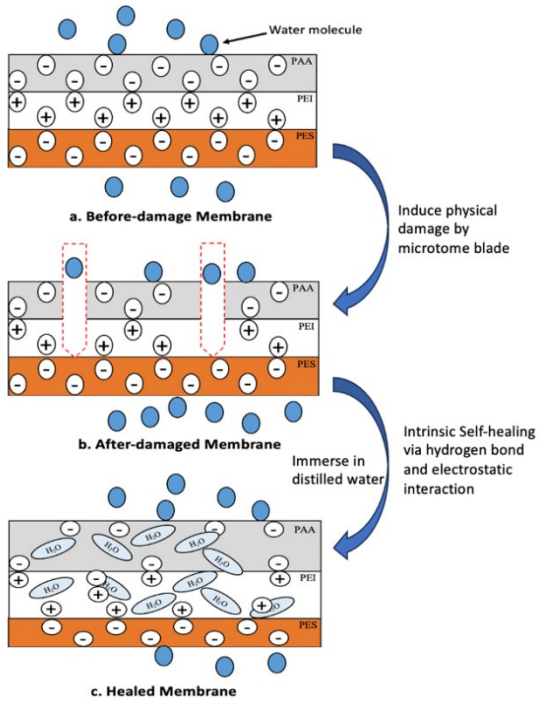
Graphical abstract



Abstract

The self-healing membrane has received substantial research attention in recent years due to its ability to overcome the difficulty in detecting the exact damage location of the membrane at a microscopic level. The healing effect of a self-healable membrane often requires the help of an external stimulus. This study reported the fabrication of a water-responsive self-healing membrane using polyethyleneimine (PEI)/poly(acrylic acid) (PAA) coated on polyethersulfone (PES) membrane via layer-by-layer (LbL) method. Fourier transform infrared spectroscopy (FTIR) and energy dispersive X-ray (EDX) were performed to observe the successful attachment of PEI and PAA onto the PES surface. The topographical analysis was performed using scanning electron microscopy (SEM) to visualize the healing performance. Apart from the instrumental analysis, pure water flux (PWF) was conducted to quantify the healing efficiency of the membrane. The best self-healing performance of the fabricated PEI/PAA self-healing membrane at 5.0 mg/mL concentration of PEI and PAA solutions displayed a healing efficiency of 70 % after being immersed into distilled water for 24 hours, compared to the concentrations of 1.0 mg/mL (19.8 %) and 3.0 mg/mL (34.3 %). This could be attributed to the higher amounts of PAA to form hydrogen bonds with surrounding water molecules, and subsequently promotes healing performance as hydrogen bonds are the basis for the self-healing process. This study proposes a newly develop water-stimulus PEI/PAA self-repairing membrane which contributes to the energy-efficient membrane filtration process.

Keywords: Intrinsic mechanism, water-responsive, self-healing, hydrogen bond, polyelectrolyte

1.0 INTRODUCTION

The accessibility and availability of clean water have been challenging due to development and population growth. The greatest issues facing humanity continue to be severe water contamination and poor water quality. Researchers are therefore looking for practical technology to meet the growing global need for clean water [1].

Membrane filtration process is widely used in water and wastewater treatment for numerous sectors because of its low operating cost and energy efficiency. However, membrane brittleness, fouling effect, and physical damage are the disadvantages of this process [2,3]. Physical damage of the

membrane often led to a severe loss in membrane performance. In the study of Huang et al. (2017) [4], membrane performance dropped drastically when the membrane was broken. The permeate flux increased by 52% as more water molecules diffused through the damaged site without proper filtration. Consequently, the rejection efficiency dropped and affected the water quality in the permeate. The identification of the exact damage location of the membrane, at a microscopic level, is challenging and usually results in the disposal of the damaged membrane [5]. Therefore, the concept of self-healing has emerged as the solution to solve the issue. For membrane filtration systems, this self-healable membrane is a type of modified membrane that restores parts or full of its original properties after being damaged and provides high flexibility and longer service life [6].

Over the decade, the self-healing membrane has been studied and reported with two main mechanisms: extrinsic and intrinsic. The former mechanism involves a microcapsule-based healing agent fixed within the matrix while the latter focuses on either physical or chemical bonding and involves no encapsulation [7–9]. Physical interactions such as hydrogen bonding are possible to be the basis for self-healing due to their reversible ability and reformation of bonds after being broken [10]. Additionally, self-healing capabilities can be designed either autonomously or non-autonomously. The non-autonomic self-healing initiates the healing process with an external stimulation like light, heat, or pH while autonomically self-healing does not need an external stimulus to repair the damage. These stimuli-responsive membranes directly increase the operating cost, making it unfavorable in long-term operation. A hydrogel pore-filled membrane with self-healing ability was developed by Getachew et al. (2017) via in-situ graft polymerization [10]. The rejection performance of the membrane before and after damage was evaluated by damaging them with a tapered needle of 450 µm diameter to understand the self-healing ability. The membrane has successfully restored the rejection autonomously from 30 % after damage to almost 99 % after healing. The self-healing property was further visualized through topographic analysis of the membrane using scanning electron microscopy (SEM) and confocal laser scanning microscope (CLSM). The study showed that the damaged area decreased after being immersed in distilled water which indicated the membrane had successfully healed. The hydrogen bonding and molecular interdiffusion cause the healing process by the enlargement of the damaged site of the hydrogel membrane.

For a water-stimulus self-healing membrane, surface modification is performed to introduce hydrophilic groups to increase the hydrophilicity of the membrane [11]. The healing agent polyelectrolytes such as polyethyleneimine (PEI) and poly(acrylic acid) (PAA) have superhydrophilicity and great water solubility. The oppositely charged polyelectrolytes interact with each other and swell in contact with water to initiate the healing process by hydrogen bonding and electrostatic interaction. A self-healing PEI/PAA film was fabricated in Chen et al. (2020) using the Layer-by-Layer (LbL) method in the field of sensing [12]. The damaged film was healed within 10 minutes after being exposed to water through the hydrophilic hydrogel swelling, diffusion of polyelectrolyte into the damage site, and subsequently filled the damage site.

This study aims to provide a preliminary view on the development and fabrication of water-responsive self-healing polymeric membranes using suitable hydrophilic monomers. In this study, PEI and PAA were used as the hydrophilic healing agents while polyethersulfone (PES) was used as the membrane support. The fabricated membranes were subjected to surface characterization and the membrane performances were evaluated in terms of pure water flux and healing efficiency.

2.0 METHODOLOGY

2.1 Materials

In this study, PES membrane support was purchased from RisingSun Membrane Technology (Beijing) Co., Ltd. while branched polyethyleneimine (PEI, average Mw = 25000) and poly(acrylic acid) (PAA, average Mw = 450000) were obtained from Sigma-Aldrich. All chemicals were used as received without further purification.

2.2 Fabrication of PEI-PAA Membrane

The PES membrane support was first immersed and rinsed with distilled water. The PES membrane was then air-dried to eliminate water droplets. Next, PEI and PAA solutions with a concentration of 1.0 mg/mL were prepared by mixing 100 mg of PEI and PAA into 100 mL distilled water separately. The prepared 1.0 mg/mL PEI solution was poured onto the cleaned PES membrane, followed by the 1.0 mg/mL PAA solution. Each deposition procedure lasted for 15 minutes and rinsed off, resulting in one PEI/PAA bilayer. The fabricated membrane was then placed in an oven at temperature of 60 ^{o}C for 30 minutes to dry and stabilize the polyelectrolyte layer. After the drying process, the membrane was taken out and ready for subsequent studies. The experiment was repeated for different concentrations of 3.0 mg/mL and 5.0 mg/mL for both the PEI and PAA solutions.

2.3 Pure Water Flux and Healing Performance

The prepared membrane was first placed in a lab-scale dead-end filtration cell, for 20 minutes of compaction, followed by a PWF test (namely PWF before damage). After that, the membrane was subjected to a damage using microtome blade with a constant load. The damaged membrane was immediately subjected to the PWF test and indicated as PWF after damaged. After the filtration test, the membrane was immersed in distilled water for a day to initiate the healing effect. On the next day, the PWF test was performed on the wetted membrane again and labelled as PWF after healed. The PWF test for all three phases was conducted for 30 minutes and was calculated using Equation (1) as follows:

$$J_w = \frac{V}{A\Delta t} \quad (1)$$

where, J_w = Pure water flux (L/m^2.h)
V = Volume of permeate (L)
A = Effective membrane area (m^2)
Δt = Permeation time (h)

To quantify the healing performance, the self-healing efficiency of the membrane was computed using Equation (2) below:

$$\text{Healing Efficiency } (\%) = \frac{\Delta f \text{ healed}}{\Delta f \text{ native}} \text{ x } 100\% \qquad (2)$$

where, $\Delta f\ healed$ = PWF after damaged – PWF after healed (L/m^2.h)
$\Delta f\ native$ = PWF after damaged – PWF before damage (L/m^2.h)

2.4 Membrane Characterization

Fourier Transform Infrared analysis (FTIR, Nicolet IR10, USA) was used to examine the surface functional groups present of the prepared membrane, scanning from 400 to 4000 cm^{-1}. Scanning electron microscopy with Energy Dispersive X-ray (SEM-EDX, S-3400, Hitachi, Japan) was used to examine the surface morphology of the membrane. For EDX analysis, the membrane was analysed for its elemental composition and its corresponding percentage.

3.0 RESULTS AND DISCUSSION

3.1 Membrane Characterization

The surface functional groups of pristine PES membrane, pure PEI, pure PAA, and PEI/PAA membrane were identified using FT-IR as shown in Figure 1. Characteristic peaks, indicated with red arrows, of 3300 cm^{-1} (N-H stretching), 2931 – 2810 cm^{-1} (C-H stretching), 1573 cm^{-1} (N-H bending), 1460 cm^{-1} (C-H bending) were observed in the PEI spectra. The carboxylic group of PAA was found in spectra of wavenumber around 1701 cm^{-1} (C=O stretching), indicated with a purple arrow [13]. The functional group of PES was confirmed by the presence of aromatic stretching peaks at 1575 cm^{-1} and 1484 cm^{-1}. For PEI/PAA spectrum, the C-H stretching at 2931 – 2810 cm^{-1} that originated from the PEI spectrum was detected. The carboxylic group of PAA was noticed as well at the fabricated membrane. These findings suggested the successful deposition of PEI and PAA onto the PES membrane.

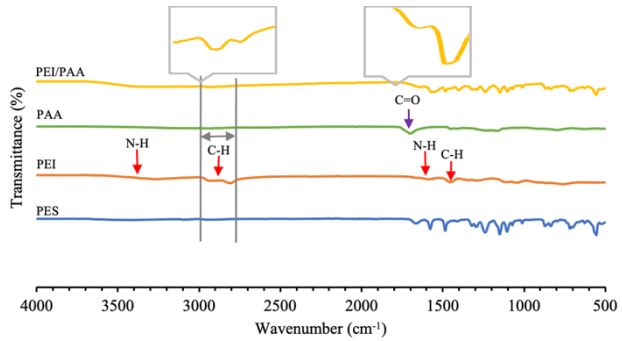


Figure 1 FT-IR spectra of pure PES membrane, pure PEI, pure PAA, and PEI/PAA membrane.

Table 1 tabulates the elemental analysis of the membranes via EDX analysis. The PES membrane consisted of carbon (71.86 %), oxygen (17.19 %), sulfur (9.46 %), and nitrogen (1.49 %). The fabricated PEI/PAA membrane showed an increase in atomic percentage in the nitrogen element (2.56 %), which corresponded to the presence of the amine group in the PEI. Despite that, it was noticed that there was an increment in the atomic percentage of carbon element (73.98 %) and oxygen element (18.24 %) suggesting the presence of PAA in the membrane [14].

Table 1 Elemental composition of PES and fabricated PEI/PAA membrane.

Sample	Atomic Percentage (At%)			
	C	O	S	N
Pristine PES	71.86	17.19	9.46	1.49
PEI/PAA	73.98	18.24	5.22	2.56

3.2 PWF and Self-Healing Performance

The healing performance of the fabricated PEI/PAA membrane at different polyelectrolyte concentrations was evaluated using PWF of three phases respectively. As depicted in Figure 2, the PWF of prepared PEI/PAA membrane at 1.0 mg/mL concentration is the highest (~ 31.2 L/m2.h), followed by the 5.0 mg/mL (~ 17.4 L/m2.h) and 3.0 mg/mL (~ 10.3 L/m2.h). At low polyelectrolyte concentration, the membrane has a loose structure with some voids which affected the PWF as more water molecules diffused through the membrane pores. In contrast, a denser structure of membrane was formed at a higher polyelectrolyte concentration which correlated to the lower PWF analysis [15].

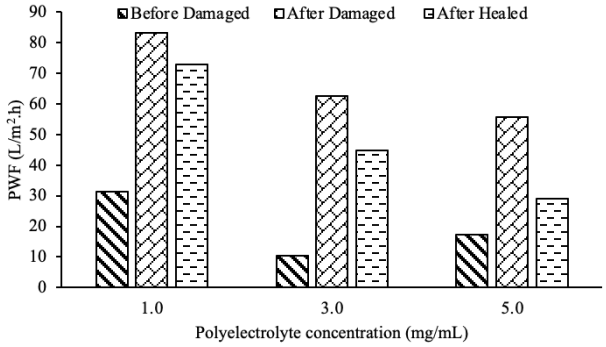


Figure 2 PWF of three membrane conditions at different polyelectrolyte concentrations.

The PWF increased drastically after the membrane was damaged, and decreased after the membrane was healed in distilled water as presented in Figure 2 For 1.0 mg/mL, the PWF increased by about 63 % from 31.2 L/m^2.h to 83.2 L/m^2.h when the membrane was damaged and decreased to 72.9 L/m^2.h after healing, leading to a healing efficiency of 19.8 %. The healing efficiency of the PEI/PAA membrane at different polyelectrolyte concentrations was illustrated in Figure 3. Similar observations of PWF trend were noticed for 3.0 mg/mL and 5.0 mg/mL, resulting in the healing efficiency of 34.3 % and 70 % respectively.

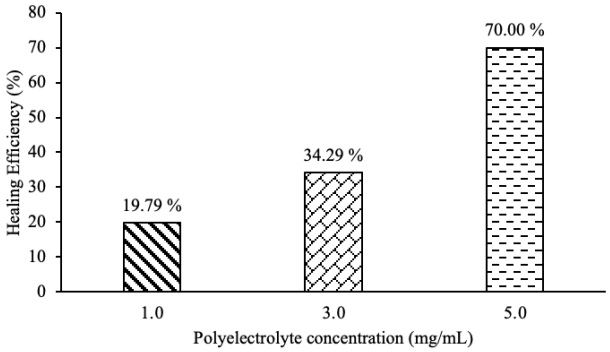


Figure 3 Healing efficiency of PEI/PAA membrane at different polyelectrolyte concentrations.

The healing phenomenon can be explained through the intrinsic self-healing mechanism. The formation of the polyelectrolyte layer of PEI and PAA is primarily through the electrostatic interaction while reversible hydrogen bonds can be the basis for self-healing due to their readily reform property after being broken [10]. When the membrane was damaged, the bonding at the damaged area was disconnected. A large amount of water molecules was able to permeate through the damaged site and subsequently increased the water flux. Upon being immersed in distilled water, or exposed to moisture, the carboxylic groups in the PAA have a stronger polar effect and led to the formation of hydrogen bonds with water molecules [16]. The water stimulus causes the swelling effect, resulting in the mobility of polymer chains to diffuse into the damaged area, and further filled the damaged area. It has been also reported that the PAA is mainly responsible for the self-healing ability due to the nature of the last deposited layer [16]. Figure 4 shows the SEM analysis of the PEI/PAA membrane at a polyelectrolyte concentration of 5.0 mg/mL. The scratch (Figure 4a) on the membrane was nearly recovered and filled up after 24 hours of immersing in distilled water (Figure 4b), suggesting that the damaged membrane was healed when contacted with water.

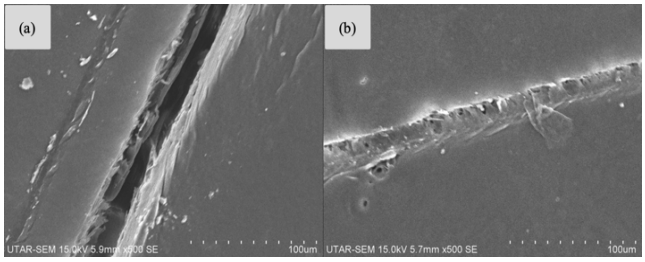


Figure 4 Top view of (a) damaged membrane; (b) healed membrane.

4.0 CONCLUSION

The water-responsive self-healing membrane was successfully fabricated using PEI and PAA through the LbL method. In this study, a polyelectrolyte concentration of 5.0 mg/mL was found to be the best self-healing performance which achieved a promising healing efficiency of 70 % after being immersed in distilled water for 24 hours. In conclusion, PEI and PAA showed their significant superhydrophilicity property and healing ability.

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