



## Improved stability of self-healing hydrogel pore-filled membranes with ionic cross-links



Bezawit A. Getachew, Sang-Ryoung Kim, Jae-Hong Kim\*

Department of Chemical and Environmental Engineering, Yale University, New Haven, CT 06511, USA

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### ABSTRACT

A self-healing water filtration membrane that can autonomously recover from rejection loss due to physical damage is a promising solution to deal with prevalent membrane integrity deterioration problems. While hydrogel-composite membranes fabricated using poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) hydrogel and a polyethersulfone support exhibit strong self-healing property, the stability of these membranes in high ionic strength solutions is uncertain. This study investigates the effect of changes in the ionic strength of the swelling medium due to the presence of saline and acidic solutions on PAMPS pore-filled membranes. Acidic conditions had a deleterious effect on the pore-filled membranes, resulting in loss of rejection to 50%. However, the presence of cations such as calcium and sodium ions in saline solutions improved the stability and self-healing property of PAMPS pore-filled membranes substantially. Ionically cross-linked membranes showed rejection recovery from values as low as 13%, which is a marked improvement over previous pore-filled membranes which did not show any self-healing property when the rejection fell below 30%. The results of this study suggest that ionic cross-links provide a facile approach to improve the performance of self-healing hydrogel pore-filled membranes.

### 1. Introduction

Water filtration membranes play an important role in meeting the ever-increasing global demand for clean water. Membranes provide a significant improvement to current water treatment technologies by providing a versatile tool to physically remove a wide array of pollutants, ranging from suspended particles to organic pollutants, bacteria, and viruses. Membranes' increased prevalence and future promise lie partly in their modular nature and scalability, which allow them to be used not only in compact, decentralized water treatment systems but also in large scale plants [1]. One issue that commonly arises during membrane applications in varying scales is physical damage to membranes that compromises their performance; even minimal damage to membranes' active layer is known to lead to a severe loss of rejection targets [2–7]. Unfortunately, there are currently very limited technologies available to address the issue of damaged membranes. Current research in this area is mainly focused on identifying the location of membrane damages, with no alternative other than membrane or module replacement once the location of a damage is identified [8].

One potential solution to address the issue of damaged membranes is the use of a self-healing membrane that is able to recover its original properties autonomously. While self-healing materials have been

developed for applications in various fields including structural materials, coatings, robotic actuators, and biomedical devices [9–13], they have not been explored extensively for use in membrane fabrication. Efforts to make self-healing membranes have been limited to outside the water treatment field, focusing on water-proof membranes [14], anti-fogging films [15], membranes for olefin-paraffin separation [16], and electrically-conductive membranes for applications in optoelectronic devices [17]. One notable recent development is the fabrication of self-healing membranes for oil and water separation [18]. However, these self-healing membranes aim at recovery from loss of hydrophobicity rather than the recovery of rejection from a physical damage to the membrane. Our group has been exploring several techniques to address the issue of physically damaged membranes ranging from 'in-situ' healing of compromised membranes [19,20] to microcapsule-embedded [21] and micro-vascular [22] self-healing membranes. One of these techniques employs the extensively-studied self-healing property of hydrogels [23–26] to make a self-healing hydrogel-composite membrane [27].

Hydrogel-composite membranes are a class of membranes that are fabricated by combining robust polymeric supports with hydrogels [28–39]. The hydrogel layer, whether it is attached to the top of a support layer (thin-film-composite configuration) [28,31] or grafted to

\* Corresponding author.

E-mail address: [jaehong.kim@yale.edu](mailto:jaehong.kim@yale.edu) (J.-H. Kim).

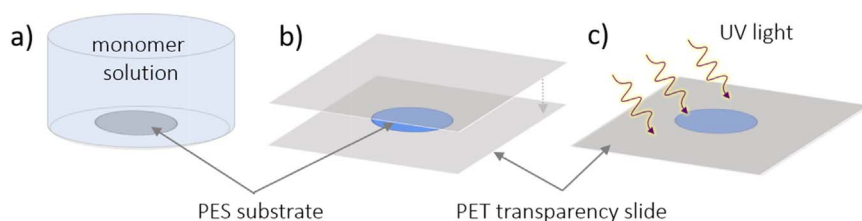
fill the pores of the support (pore-filled configuration) [40–44], acts as the sieving active layer that rejects particles and molecules that are smaller than its mesh size. By using poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS), a hydrogel known for its self-healing properties [26], we previously fabricated hydrogel pore-filled membranes with autonomous self-healing property [27]. The self-healing property of these membranes is based on three mechanisms, namely, latent swelling of the hydrogel, strong hydrogen bonding between the hydrogel chains, and molecular interdiffusion or relaxation of polymer chains across a damage [27]. The membranes showed effective, rapid rejection recovery from values as low as 30% without the need for any external stimulus.

The practical application of self-healing PAMPS pore-filled membranes requires careful investigation of their response to changes in their environment including fluctuations in ionic strength and pH. Properties of polyanionic hydrogels such as PAMPS are known to be sensitive to the presence of saline and acidic solutions but the response of PAMPS pore-filled membranes to these conditions is unknown. Given the changes in swelling ratio that PAMPS co-polymers undergo under various solution conditions [45–48], one may expect to see a drastic change in the properties of PAMPS pore-filled membranes as well. To elucidate these unknown effects, this study investigates the effect of exposure to saline and acidic solutions on PAMPS pore-filled membranes. The results of the investigation show that ionic cross-linking can improve the self-healing performance of the hydrogel pore-filled membranes, which provides a facile and cost-effective approach to improve their performance in practical applications.

## 2. Experimental

### 2.1. Bulk hydrogel and hydrogel pore-filled membrane preparation

A solution (5–50 wt%) of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS; Sigma Aldrich, St. Louis, MO) and a solution (2 wt%) of *N,N'*-methylenebis(acrylamide) (MBA, Sigma Aldrich, St. Louis, MO) were prepared by dissolving a measured amount of each monomer in DI water ( $> 18.2 \text{ M}\Omega$ ). PAMPS hydrogels were prepared by adding 40  $\mu\text{L}$  of 2 wt% MBA to 10 mL of 10 wt% AMPS solutions and heating the resultant solution at 80 °C for 2 h. PAMPS hydrogel pore-filled membranes were prepared using a previously established method [27] by soaking polyethersulfone (PES) membranes (0.8  $\mu\text{m}$  pore size, Pall Corp., Port Washington, NY) in 25 wt% AMPS solution for 12 h (Fig. 1a). The membranes were then placed between two polyethylene terephthalate transparency slides and excess monomer solution was removed by pressing the transparency slides tightly together with a roller (Fig. 1b). The sandwiched membranes were irradiated with UV-A light for 30–60 min in a chamber equipped with six 4-W black light bulbs (Philips Co., USA; intensity of 720  $\mu\text{W}/\text{cm}^2$ , membranes placed 5 cm away from bulbs) to initiate radical polymerization of the AMPS monomer (Fig. 1c). In selected experiments, the irradiated membranes were placed in 1–2 wt% solutions of MBA for 24 h, and heated to 80 °C for 2 h for cross-linking to occur. The pore-filled membranes were then placed in a DI water bath overnight followed by 2–3 cycles of washing to remove unbound monomers and oligomers.



**Fig. 1.** Fabrication of PAMPS pore-filled membranes by a) soaking them in AMPS monomer solution, b) placement of fully soaked substrates between two polyethylene terephthalate transparency slides, and UV irradiation of soaked membranes with UV-A lamps.

### 2.2. Bulk hydrogel and hydrogel pore-filled membrane characterization

Fourier transform infrared spectroscopy (FTIR; Thermo Nicolet 6700, USA) with an attenuated total reflectance (AnSe crystal plate) was used to chemically characterize the PAMPS hydrogels and the PAMPS pore-filled membranes. For each spectrum, 32 scans were taken at a resolution of 4  $\text{cm}^{-1}$ . The surface morphology of the bulk hydrogels, PES substrate and pore-filled membranes was observed by scanning electron microscopy (SEM; Hitachi SU-70, Japan) at 5–20 keV. All samples were dried at 70 °C overnight to remove any residual moisture and coated with a  $\sim 15 \text{ nm}$  layer of iridium (Cressington 208) before SEM imaging. Energy dispersive spectroscopy (EDS) spectra and maps of the pore-filled membranes were acquired with an SEM (Hitachi SU8230) equipped with a BRUKER XFlash 5060FQ detector at 6 keV.

### 2.3. Swelling ratio measurements

The swelling ratio of PAMPS hydrogels in DI water and 0.1 mM to 1 M NaCl,  $\text{CaCl}_2$ , and citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) solutions was measured gravimetrically. Pre-weighed dry hydrogel samples were immersed in 50 mL of the desired solution overnight. The weight of the dry hydrogel pieces was limited to be between 2 and 8 mg for consistency. After the overnight immersion, the swollen hydrogel was moved out of the solution, excess liquid on the surface of the hydrogel was removed, and the weight of the swollen sample was measured.

### 2.4. Permeability and rejection measurements

The permeability and rejection of pore-filled membranes was measured using an Amicon 8010 dead-end filtration cell (Millipore, USA) with a cell volume of 10 mL and an effective filtration area of 4.1  $\text{cm}^2$ , attached to a 10 L dispensing vessel and pressurized with nitrogen gas (Fig. 2). The pressure was monitored using a pressure gauge (1009 Duralife®, Ashcroft, Stratford, CT). Unless otherwise stated, experiments were conducted at 20 psi (138 kPa) with 350 rpm stirring. The permeate flow rate was measured on a weighing balance (EBTRIS2202-1S, Sartorius, Elk Grove, IL) and recorded on a computer every 10 s with a RS-232 interface. Permeability measurements were always conducted with DI water ( $> 18.2 \text{ M}\Omega$ ). Carboxylate-functionalized, fluorescent nanospheres (50 nm diameter,  $\lambda_{\text{ex}} = 441 \text{ nm}$ ,  $\lambda_{\text{em}} = 486 \text{ nm}$ ; Fluoresbrite®, Polyscience, Inc.) at a concentration of 0.25 mg/mL were used for rejection tests.

### 2.5. Hydrogel pore-filled membrane stability and self-healing test

To determine the effect of NaCl,  $\text{CaCl}_2$ , and citric acid on the hydrogel pore-filled membranes, the permeability of membranes exposed to these solutions was monitored over a period of 14 days. The permeability and rejection were first measured immediately after the fabrication of a new batch of membranes. Two membrane coupons were then immersed in each test solution (10 mL of DI water, 1 M NaCl, 1 M  $\text{CaCl}_2$ , and 0.2 M citric acid solutions) and their permeability was measured every 2–3 days. After one week, all the membrane samples were moved to a DI water bath and their permeability was measured every 2–3 days for one more week. To quantify the amount of PAMPS chains that are removed from the pore-filled membranes, pristine

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