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Toward microvascular network-embedded self-healing membranes

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ABSTRACT

A membrane that can autonomously self-heal from physical damage was fabricated by embedding a network of fluorinated ethylene propylene capillary tubes that contain a reactive healing agent, methylene diphenyl diisocyanate, inside the membrane. Upon membrane damage, the healing agent is released from the tubes and undergoes water-induced phase separation that increases its viscosity. The viscous healing agent further reacts with water, forming an expanded polyurethane/polyurea matrix that fills and plugs the damage area. After self-healing of the damage, the microvascular membrane's rejection was restored back to 82% of its original value without a need to stop filtration. Scanning electron microscopic and confocal laser scanning microscopic images confirmed the formation of a solid structure that blocks the damaged area. The results of this study suggest that microvascular networks provide a new architecture for the fabrication of self-healing membranes with significant improvement over microcapsule-embedded self-healing membrane design.

1. Introduction

A smart membrane with self-healing capability can significantly enhance the resiliency of membrane filtration processes, since membrane damages induced during installation and long term operation are a widespread problem without readily available technical solutions [1,2]. Membranes' active rejection layers are typically made of very thin, porous polymers and therefore vulnerable to damages due to, for example, material degradation by cleaning chemicals [3,4], welding sparks during installation [5], uneven airflow rates during backwashing [6,7], and objects untreated in pretreatment steps [7,8]. These damages can result in detrimental loss of water quality, which is a significant challenge in especially water treatment and reuse scenarios where a nearly complete rejection of contaminants such as viruses is often pursued. For example, in a pilot-scale reverse osmosis membrane test, even a small pinhole damage (300–500 μm) was found to significantly decrease the removal of viruses from > 6.3 (99.9999%) to 2.9 log (99.9%) [9]. Another study reported that pinhole damages with 90 μm diameter decreased the rejection of viruses from > 99% to 90.3–97.4% and the rejection of similarly-sized particles from > 99% to 87.1–93.8%, respectively [10].

We recently reported the first self-healing membrane fabricated by embedding polyurethane microcapsules that contain isophorone diisocyanate (IPDI) healing agent as a core [2]. This design inherited the concept from self-healing materials developed for other applications such as structural materials and coatings [11–21], where small vessels (typically microcapsules) containing a healing agent are embedded within the material and, when the material is damaged, release the healing agent that rapidly reacts with surrounding medium to fill the damaged area. Similarly, the IPDI-based healing agent used in our previous self-healing membrane reacts with surrounding water once microcapsules are broken to form a polyurea mass that plugs the damage. Proof-of-concept experiments showed that after being physically damaged, this microcapsule-embedded self-healing membrane could restore its performance to nearly its original value with respect to particle rejection and water flux [2].

We herein present another self-healing membrane architecture with a microvascular tube network that encapsulates a similar healing agent (Fig. 1), based on an analogous design developed using structures such as hollow glass fibers [22,23], microtubes [24], and 3D-printed micro channels [19–21]. This design is known to overcome a couple of limitations present in the microcapsule-based design [20,25], which were also identified in our past study [2]. First, by using pre-manufactured encapsulating vessel, i.e., microvascular tubes, a more reactive healing agent such as methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) can be employed, which is not possible with microcapsules due to the difficulty of synthesizing core-shell structure when the healing agent is too reactive [12,25]. Second, the capillary tubes made of chemically-resistant, water-impermeable materials such as fluorinated ethylene propylene (FEP) polymer [26,27] obviate the concern regarding gradual loss of healant due to reaction with water. In contrast, the relatively thin polyurethane shells used in the microcapsule approach allowed diffusion of water into the core, resulting in hardening of the water-reactive healant [12]. In this study,

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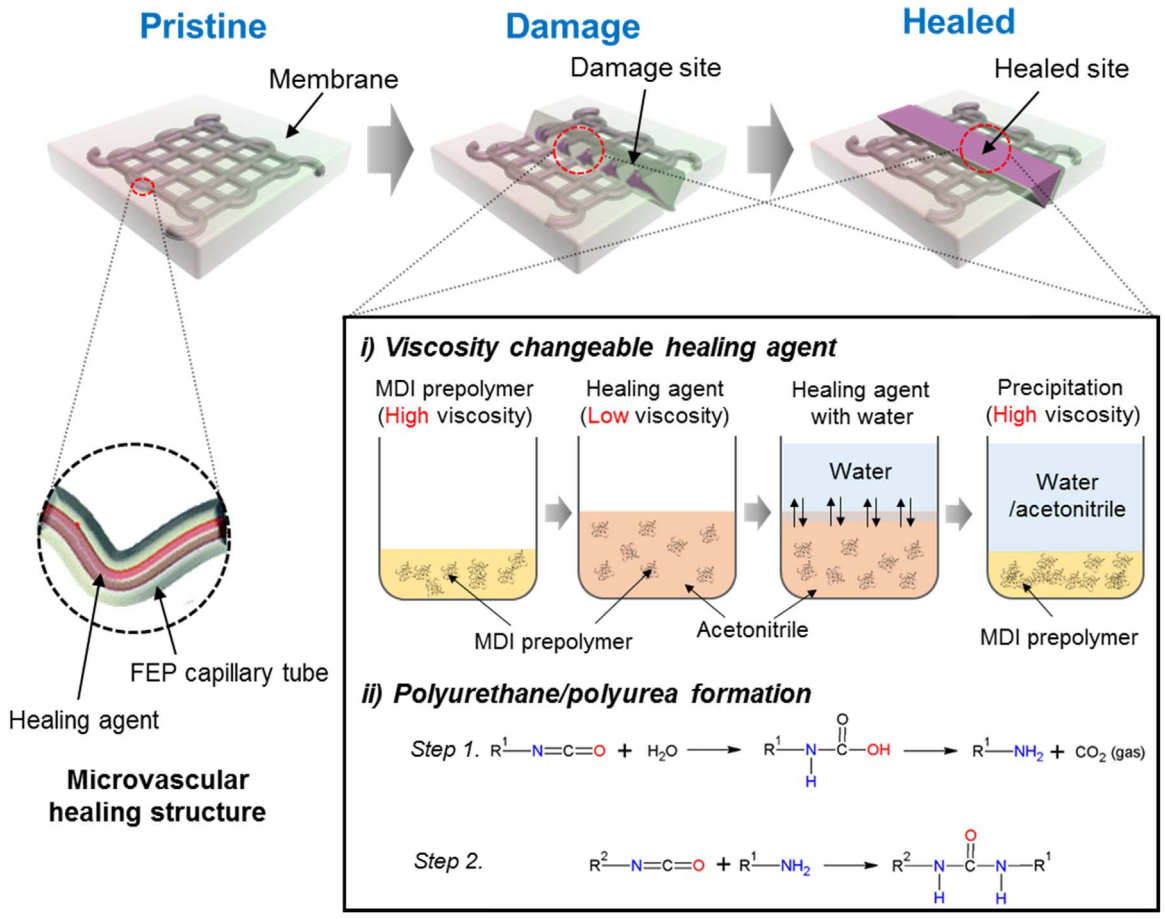

Fig. 1. Structure of a microvascular network-embedded self-healing membrane and schematic illustration of the healing mechanism. When the membrane structure is physically damaged, the microvascular network releases a reactive healing agent. Upon contact with water, the healing agent precipitates into a viscous prepolymer that further rapidly reacts with water to form a polyurethane/polyurea matrix that fills the damaged site.

we present a novel approach to fabricate a self-healing membrane by embedding a healant-delivering microvascular network and demonstrate its self-healing performance when a physical damage is artificially induced.

2. Experimental

2.1. Materials

Polyether-modified MDI prepolymer (Suprasec® 2445) and TDI prepolymer (Desmodur® L75) were obtained from Huntsman (MI, USA) and Bayer MaterialScience (PA, USA), respectively. Hexamethylene diisocyanate (HDI) prepolymer, dibutyltin diacetate (technical grade), acetonitrile (anhydrous, 99.8%), chlorobenzene (anhydrous, 99.8%), hydrochloric acid (ACS reagent, 37%), sodium hydroxide solution (0.1 N), n-dibutylamine (> 99.5%), bromophenol blue (ACS reagent), tetrahydrofuran (THF, anhydrous, > 99.9%), ethanol (absolute, > 99.8%), and *N,N*-dimethylacetamide (DMAc, anhydrous, 99.8%) were purchased from Sigma-Aldrich. All chemicals in this study were used without further purification unless otherwise specified. FEP capillary tubes with an inner diameter of 80 (± 10%) μm and an outer diameter of 90 (± 10%) μm were obtained from Paradigm Optics, Inc. (WA, USA). The FEP tube was produced from Teflon™ FEP (DuPont, USA) fluoroplastic resin which is a copolymer of hexafluoropropylene and tetrafluoroethylene.

2.2. Determination of healing agent reactivity

The healing agent was prepared by mixing equivalent weights of diisocyanate prepolymer (MDI, TDI, or HDI) and acetonitrile. The reactivity of the healing agent with water was measured by monitoring the residual free isocyanate (NCO) content using a modified version of the standard method, ASTM D 5155 [28–30]. Briefly, 1 g of the healing agent was reacted with 1 g of water and sampled periodically for 90 min. Excess 0.2 N *n*-dibutylamine in anhydrous THF (25 mL) was added to each sample in an air-tight glass bottle at room temperature (Fig. S1a). The amount of residual *n*-dibutylamine was quantified by colorimetric titration; 0.5 mL of 1 wt% bromophenol blue indicator in 0.1 N sodium hydroxide solution was added and titrated using 0.5 N hydrochloric acid aqueous solution up to the yellow-green endpoint (Fig. S1b). The color change was confirmed by monitoring the wavelength change (> 420 nm) with a spectrophotometer (Fig. S1c). Simultaneously, a control experiment, without diisocyanate prepolymer sample, was carried out. The content of isocyanate groups in each prepolymer was calculated using the following equation.

$$\%\mathrm{NCO} = \frac{4202 \times N_{HCl} \times (V_{Blank} - V_{Sample})}{W_{sample} \times 1000}$$

where N_{HCl} is the normality of the hydrochloric acid in mEq/mL, V_{blank} and V_{sample} are the volumes of the blank and sample titers in mL, respectively, and W_{blank} is weight of the sample in mg. Average values of the results from three separate experiments were reported.

2.3. Fabrication of microvascular membrane

A method to fill the FEP capillary tube with the healing agent was newly developed using a glass capillary microfluidic device. The setup consisted of a series of capillary tubes, the end of which is attached to a