Journal of Membrane Science 440 (2013) 88–97

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

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

A new strategy for ultralow biofouling membranes: Uniform and ultrathin hydrophilic coatings using liquid carbon dioxide

Ratna F. Susanti [a,b], Yang Soo Han [c], Jaehoon Kim [d,e,*], Young Haeng Lee [c,**], Ruben G. Carbonell [f]

[a] Clean Energy Research Center, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea
[b] Chemical Engineering Department, Industrial Technology Faculty, Parahyangan Catholic University, Ciumbuleuit 94 Bandung, West Java 40141, Indonesia
[c] Center for Water Resource Cycling, Korea Institute of Science and Technology, Republic of Korea
[d] School of Mechanical Engineering, Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 440-746, Republic of Korea
[e] SKKU Advanced Institute of Nano Technology (SAINT), 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 440-746, Republic of Korea
[f] Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606-7905, USA

ARTICLE INFO

Article history:
Received 23 December 2012
Received in revised form
27 March 2013
Accepted 30 March 2013
Available online 8 April 2013

Keywords:
Hydrophilization
Liquid carbon dioxide
Coating
Biofouling

ABSTRACT

Highly stable, uniform and ultrathin hydrophilic polymer coatings on the surface as well as in the pores of a PVDF microfiltration (MF) membrane are obtained by coating a hydrophilic monomer in liquid carbon dioxide (l-CO_2) followed by subsequent crosslinking reaction. Polyethylene glycol diacrylate (PEGDA, M_n ~258 g/mol) is used as the l-CO_2 soluble hydrophilic monomer source and azobisisobutyronitrile (AIBN) was used as a radical initiator. The extremely low surface tension and the low viscosity of l-CO_2 result in ultrathin and uniform PEG coatings on the hydrophobic polyvinylidene fluoride (PVDF) microfiltration membrane. The chemical composition, morphology, and the depth profiles of the PEG-coated membranes are characterized in detail using X-ray photoelectron spectroscopy, scanning electron microscopy, electron probe microanalysis and energy dispersive X-ray microanalysis. Long-term permeation flux test using a bovine serum albumin solution shows that the 1.0 wt% PEGDA-coated membrane using l-CO_2 exhibits 1.34 times larger BSA solution flux than that of the uncoated PVDF membrane, and 1.3 times larger flux than that of a commercial hydrophilic membrane. Fouling resistance estimation shows that the 1 wt% PEGDA-coated membrane exhibits ~30% lower internal fouling resistance than the pristine membrane, and ~24% lower internal fouling resistance than the commercial hydrophilic membrane.

1. Introduction

Water filtration membranes are used in a wide variety of applications including waste water treatment, reverse osmosis pretreatment, food/diary processing, pharmaceutical recovery, and blood contacting medical devices [1–3]. One of the major drawbacks of membrane-based filtration applications is membrane fouling. Membrane fouling causes a significant decrease in the permeation flux, resulting in substantial increases in energy demand, and operational and maintenance costs. In a typical membrane filtration plant, the membrane replacement and membrane cleaning can account for up to 80% of the total operating costs [4]. Membrane fouling can result from the adsorption and accumulation of proteins, cells, cell debris, colloidal particles and other rejected natural organic matter (NOM) on the surface of the membrane (external fouling), and from the deposition of small organic or macromolecules on the internal surface of the pores in the membrane (internal fouling). The membrane fouling should be reduced as much as possible for the efficient use of the water filtration membranes in the various areas. Hydrophilization of conventional hydrophobic membranes such as poly(vinylidene fluoride) (PVDF) and polypropylene (PP) is known to be effective in reducing membrane fouling and in improving biocompatibility [5].

An ideal membrane hydrophilization process would include the following characteristics: (1) long-term stability of the hydrophilization treatment, (2) modification of the internal surface area of the pores as well as the surface of the membrane to reduce both internal and external fouling, (3) thin or ultrathin coating of a hydrophilic layer that minimizes changes in pore diameter and retains high flux, (4) minimal impact on the chemical and mechanical properties of the base membrane, and (5) simple and efficient hydrophilization procedure. A number of different hydrophilization strategies have been investigated including chemical treatment [6], coating/adsorption of hydrophilic species [7–9], surface grafting polymerization of hydrophilic monomers

---

* Corresponding author at: School of Mechanical Engineering & SKKU Advanced Institute of Nano Technology (SAINT), 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 440-746, Republic of Korea. Tel.: +82 31 299 4843; fax: +82 31 290 5889.

** Corresponding author. Tel.: +82 2 958 5841; fax: +82 2 958 5805.

E-mail addresses: jaehoonkim@skku.edu, kjh0508@gmail.com (J. Kim), younglee@kist.re.kr (Y.H. Lee).

0376-7388/$ - see front matter Crown Copyright © 2013 Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2013.03.068

using high energy sources (such as UV [10–13], γ-ray [14], electron beam [15] and plasma [16,17] and chemical reaction [18]), blending with hydrophilic polymers [19–21], surface crosslinking reaction of hydrophilic monomers [22], composite with hydrophilic nanoparticles [23,24], surface deposition of hydrophilic molecules [25]. Although hydrophilization processes using the above methods have proven to be effective in reducing fouling to some degree, none of these methods meet all of the above-mentioned criteria. This is mainly due to pore blocking during application of the hydrophilic coating [15,22], hydrophilization only on the surface of the membrane [10], leaving internal pores still susceptible to fouling [26–28], and harsh modification conditions [29,30], resulting in deterioration of the intrinsic bulk properties of the membranes [22]. In addition, most of these common hydrophilization methods rely on the extensive use of organic solvents and monomers, which generate large quantities of organic wastes.

Herein we present the first use of liquid carbon dioxide (l-CO_2) as a coating solvent for depositing ultrathin and uniform hydrophilic coatings in the pores as well as the surface of water filtration membranes. The extremely low surface energy of l-CO_2 (from $\sim$1.95 mJ/m^2 at 15 °C) makes it an excellent wetting agent, even on very low surface energy materials such as PVDF (γ=42–47 mN/m [10]). This low surface energy leads to the formation of thin, uniform coatings of solutes. In addition, the low surface energy of l-CO_2 facilitates the permeation of coating materials into small pores of the membrane. The low viscosity of l-CO_2 (0.00074 Ns/m^2 at 15 °C) also results in faster diffusion of coating materials into a porous membrane. Higher solute diffusion rates combined with a low surface tension make l-CO_2 a particularly suitable solvent for the deposition of uniform coatings of hydrophilic species onto highly porous membranes. After the coating step using l-CO_2, there are no residual toxic organic solvents remaining in the final product, making the process particularly suitable for biomedical applications while at the same time resulting in no organic solvent emissions to the environment. In our previous works, we have shown that ultrathin films of small organic molecules and fluoropolymers with extremely low surface roughness can be coated on silicon wafer substrates using high-pressure free meniscus coating with l-CO_2 as the coating solvent [31–34].

In this paper, we demonstrate that highly stable, uniform and ultrathin hydrophilic polymer coatings on the surface as well as in the pores of a PVDF microfiltration (MF) membrane (pore size of 0.45 μm) can be obtained by coating a hydrophilic monomer in l-CO_2 followed by subsequent crosslinking reaction. The sections that follow describe the high-pressure coating apparatus and coating process, and the effect of PEGDA concentration on surface chemical composition, membrane morphology, coating thickness, porosity and pore size diameter. The performances of the coated membranes were measured using dead-end filtration cell. Based on the flux results, the total resistance (R_t) and internal fouling resistance (R_{if}) were estimated. The flux results of the coated membranes were compared with a pristine hydrophobic PVDF membrane and a commercial hydrophilic PVDF membrane.

2. Experimental

2.1. Materials

The pristine hydrophobic PVDF membrane (pore size of 0.45 μm, HVHP14250, Durapore) and the commercial hydrophilic PVDF membrane (pore size of 0.45 μm, HVLP14250) were purchased from Millipore Co. (MA, USA). Polyethylene glycol diacrylate (PEGDA, purity of ≥ 92%, MW of 258 g/mol, Aldrich, MO, USA) was purified using an inhibitor-removing column unit and azobisisobutyronitrile (AIBN, purity of > 98% Junsei, Japan) was recrystallized using methanol prior to use. PEG-based materials are well-known for their ability to reduce fouling and to increase biocompatibility [18,20,35]. High-purity CO_2 (purity of > 99.999%) and N_2 (purity of > 99.99%) were purchased from Sinyang Sanso (Seoul, Korea). Distilled and deionized water was prepared using a Milli-Q Ultrapure water purification system with a 0.22 μm filter (Billerica, MA). Bovine serum albumin (BSA) was purchased from Sigma Aldrich Chemical Co. and phosphate buffer saline (PBS) was purchased from Amresco Co. (Province, USA).

2.2. High-pressure coating apparatus

The hydrophilization experiment was carried out in a custom-built large-scale high-pressure coating apparatus. The schematic of this apparatus is shown in Fig. 1. The coating vessel (CV, Hanyang Accuracy, Seoul, Korea) is rectangular in shape with inside dimensions of 10 cm × 5 cm × 23.5 cm, giving a volume of 1175 cm^3. The solution vessel (SV, Hanyang Accuracy, Seoul, Korea) is cylindrical in shape with a 9 cm inside diameter and a 23 cm inside height, giving a volume of 1464 cm^3. Both of the coating vessel and solution vessel are equipped with 17 cm × 1 cm quartz windows for visual inspection during the coating process and measuring the liquid level inside of the vessel. Extensive mixing of l-CO_2 and the solute can be achieved using a model MG-100 magnetic agitator (A) made by Hanwoul Engineering Inc. (Kyunggido, Korea). The transfer of coating solution between the coating vessel and the solution vessel was achieved using a model series GM (5500) high-pressure gear pump (P1) manufactured by Micropump® (Vancouver, WA). The whole apparatus is housed in a temperature controllable chamber, which can maintain the temperature of the system within 15 ± 1 °C. The temperatures in the coating vessel and the solution vessel were monitored using Type K thermocouples (T) manufactured by Omega Engineering, Inc (CT, USA) and the pressures were monitored using a JUMO MIDAS HP Type 401005 (JUMO GmbH and Co. KG, Fulda, Germany) pressure transmitters (P).

The substrate temperature and the coating vessel wall temperature were controlled individually. For the control of the substrate temperature, an aluminum heating stage was used, in which a heater (electrical cartridge type) and a thermocouple (K type) were inserted. The aluminum heating stage is rectangular in shape with dimension of 17.5 cm × 9.3 cm × 1.5 cm and it has three separate holes with two holes of 0.635 cm in diameter for the insertion of the heaters and one hole of 0.3175 cm in diameter for insertion of the thermocouple. The PVDF hydrophobic membrane at each coating run was fixed to the heating stage with a

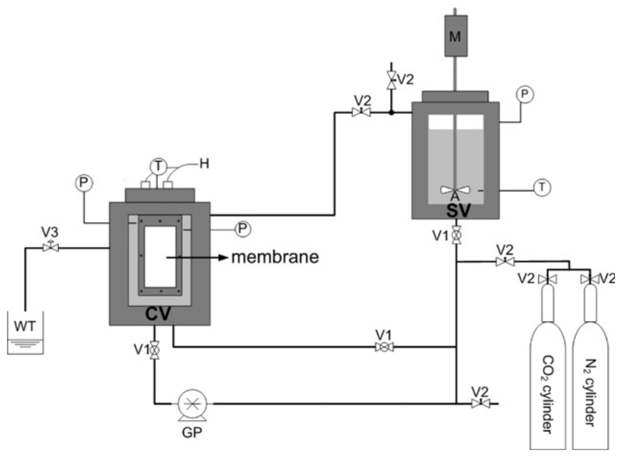

Fig. 1. Schematic of the high-pressure coating apparatus with l-CO_2 as the coating solvent. CV–coating vessel, SV–Solution vessel, V1, V2, V3–Isolation valves, GP–High-pressure gear pump, P–Pressure transducer, T–Thermocouple, M–Magnetic agitator, A–Agitator.