Thermoregulated gas transport through electrospun nanofiber membranes

CrossMark

Sangil Han [a,b,*], Gregory C. Rutledge [a]

[a] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[b] Department of Chemical Engineering, Changwon National University, Changwon 641–773, South Korea

HIGHLIGHTS

- The developed membranes showed the flux decrease with temperature increase.
- Three-layered electrospun membranes were developed by electrospinning and hot pressing techniques.
- Transition temperature of flux decrease was controlled by blending of polystyrene and polysulfone.
- Modeling of transport was performed to estimate the impact of the morphological properties of the membranes.

ARTICLE INFO

ABSTRACT

Thermoregulation of gas transport using electrospun fiber membranes is demonstrated experimentally for the first time. The fiber membranes comprise three layers: a middle layer of electrospun polystyrene sandwiched between two outer layers of electrospun cellulose acetate mat as supports, bonded together by hot pressing. The electrospun polystyrene layer serves as a phase change material that blocks transport of gases though the membrane when the fibers de-vitrify. The membrane exhibited a reduction in oxygen flux at temperatures in excess of 140 °C. Using a blend of polysulfone and polystyrene resulted in an upward shift of the transition temperature to 250 °C. Modeling of transport was performed to estimate the impact of the morphological properties of the membranes such as tortuosity, fiber diameter, and porosity.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Electrospinning (Ramakrishna et al., 2005; Rutledge and Fridrikh, 2007) is a technology for the production of submicrometer diameter polymer fibers from polymer solutions or melts using electrostatic forces. Fine polymer jets are ejected from a spinneret or free surface at high voltage and stretched by the action of a "whipping" instability. Solid fibers are collected on a grounded target, resulting in nonwoven fiber mats with remarkable characteristics such as high porosity and large surface area (Pai et al., 2009). Such fiber mats have a variety of potential applications including filtration, tissue scaffolds and medical prostheses (Huang et al., 2003).

Due to their large surface areas and interconnected pore structures, functionalized nonwoven electrospun fiber mats can provide good resistance to hazardous chemicals such as volatile organic compounds and aerosols, while allowing water vapor and other inert gases to pass through, offering breathable protective fabrics and membranes (Gibson et al., 1999). Although there are now thousands of studies of electrospun membranes, only a few of these works discuss gas transport properties (Chen et al., 2010; Gibson et al., 1999, 2001; Soukup et al., 2010). It is known that the Darcy permeability of fiber membranes, including electrospun membranes, decreases as the square of the fiber diameter for membranes of comparable porosity, as predicted by the analysis of Happel (Happel, 1959).

There are prior research efforts on thermoresponsive membranes for liquid phase transport, with potential applications in biomedical engineering, drug delivery, and tissue engineering. Thermoresponsive polymers such as poly(N-isopropylacrylamide) (PNIPAM) have been used to control the mean pore size of a membrane by swelling and de-swelling as the polymer switches between hydrophilic and hydrophobic behavior around 32 °C (Ward and Georgiou, 2011). Ionizable polymers with pK_a's between 3 and 10 have been shown to exhibit pH-responsive behaviors (Ward and Georgiou, 2011). In response to a change in pH, acidic groups such as carboxylic or phosphoric acids, or basic groups such as amines, change their ionization state, resulting in polymer swelling in an aqueous phase (Schmaljohann, 2006).

---

* Corresponding author at: Department of Chemical Engineering, Changwon National University, Changwon 641–773, South Korea.
Tel.: +82 55 213 3757; fax: +82 55 283 6465.
E-mail address: sangilh@changwon.ac.kr (S. Han).

In this work, we demonstrate thermoresponsive behavior for gas phase transport using a three-layered electrospun membrane where a phase change in the middle layer (actually, a de-vitrification) permits it to swell into and block the pores of the outer layers. The novel three-layered membranes exhibit a significant reduction in gas flux with increasing temperature. Such composite membranes, composed of a thermoresponsive porous middle layer and thermostable porous outer layers, have potential for application in combustion control, sensors, and controlled gas transport in high temperature applications.

2. Experimental

2.1. Preparation of polymer solutions

Cellulose acetate (CA, $M_n=30,000$ g/mol), polystyrene (PS, $M_w=280,000$ g/mol), and polysulfone (PSU, $M_n=22,000$ g/mol) were purchased from Sigma Aldrich. Reagent grade acetone, dimethylacetamide (DMAC), dimethylformamide (DMF) and ethanol were used as received. In a typical solution, 1 g of CA was dissolved in a mixture of 3.8 g acetone and 1.9 g DMAC by stirring overnight to prepare a 15 wt% solution. Similarly, 1 g of PS or a mixture of 0.7 g PS and 0.3 g PSU were dissolved in 4 g of DMF by stirring at 50 °C overnight to produce a 20 wt% solution of PS or PS:PSU, respectively.

2.2. Electrospinning of membranes

Nonwoven fiber membranes were fabricated by electrospinning using a home-built apparatus as described previously (Shin et al., 2001). The polymer solutions were placed in a 10 ml syringe with a capillary needle of 0.05 cm diameter. A positive potential was applied to the polymer solutions by connecting an electrode of a high voltage power supply (ES30P-5 W/SDPM, Gamma High Voltage Research, Inc.) to the metal capillary needle. A grounded electrode was connected to a metal collector wrapped by aluminum foil. The applied voltages were 25 kV for the CA solution and 30 kV for the PS and PS:PSU solutions. The feed rate was controlled at 0.015 ml/min for the CA solution and 0.02 ml/min for the PS and PS:PSU solutions using a syringe pump (Infusion PHD 2000, Harvard Apparatus). The metal collector was placed 19 cm or 26 cm below the capillary needle for the CA solution or for the PS and PS:PSU solutions, respectively. After the fabrication, the electrospun mats were dried in a vacuum oven at 80 °C for 2 h.

2.3. Three-layered membrane preparation

To form thee-layered composite membranes, a nonwoven electrospun PS or PS:PSU mat was sandwiched between two electrospun nonwoven CA mats and hot-pressing at 80 °C under 4,000 lbs load for 5 min, as described elsewhere (Mannarino and Rutledge, 2012). Disks (3.7 cm in diameter) were cut from the three-layered membranes and sandwiched between two pieces of aluminum tape (Han and Martin, 2009) having circular openings to expose an effective membrane area of 0.95 cm². Silicone glue (RTV Silicone Gasket Maker, Ultra Copper, Permatex®) was used to seal the three-layered membrane where it contacts the aluminum tape, so that gas transport takes place only through the three-layered membrane itself. The thickness of the three-layered membrane was estimated 0.00014 m $\pm$ 25% ($n=9$) using a micrometer equipped with a ratchet thimble (Mitutoyo Co., Japan).

2.4. Oxygen permeation experiments

Two types of permeation experiments were performed. In the first type of experiment, a gas mixture was fed to the membrane at 1 atm and zero trans-membrane pressure differential. Components of the feed gas diffused across the membrane and were picked up by a sweep gas of helium, and their concentrations measured by gas chromatography. The resulting transport coefficient determined in this experiment is the binary diffusion coefficient. In the second type of experiment, a gas mixture was fed to the membrane at an elevated pressure with respect to the permeate side of the membrane. In this experiment, components of the feed gas permeate the membrane by a combination of diffusion and viscous flow (convection).

For the diffusion experiments, a mixture of oxygen (7 ml/min) and nitrogen (16 ml/min) (30:70) was used as a feed stream that flows continuously across the membrane during the experiments, as illustrated in Fig. 1. A stainless steel porous support with 20 μm pore size and 1.6×10^{-3} m thickness (McMaster Carr Co.) was used to support the membrane. The membrane was sealed in place with silicone O-rings (McMaster Carr Co.). Gas compositions in the permeate stream were measured using a gas chromatograph (GC) (Shimadzu GC-2014 with TCD detector and Restek Molecular Sieve 5 A column) with helium carrier gas. The GC was operated at 35 °C column temperature, 50 °C detector temperature, and 15 ml/min helium carrier gas flow. The entire membrane apparatus was placed in an oven (Blue M Box Furnace, Lindberg), where temperature was controlled to an accuracy of $\pm$ 0.3%. The inlet gas was preheated by passing through a 3 m coil of 3.2×10^{-3} m diameter stainless steel tubing within the furnace, before entering the membrane holder. A thermocouple (42515-T Type K, Extech) with a contact to the surface of the membrane holder was used to measure accurately the temperature of the membrane. A heating rate of 1.3 °C/min was used from 20 °C up to the transition temperature (approximately 140 °C for CA/PS/CA membrane, and 250 °C for CA/PS/PSU/CA membrane), and then a higher heating rate of 7.6 °C/min was applied, up to
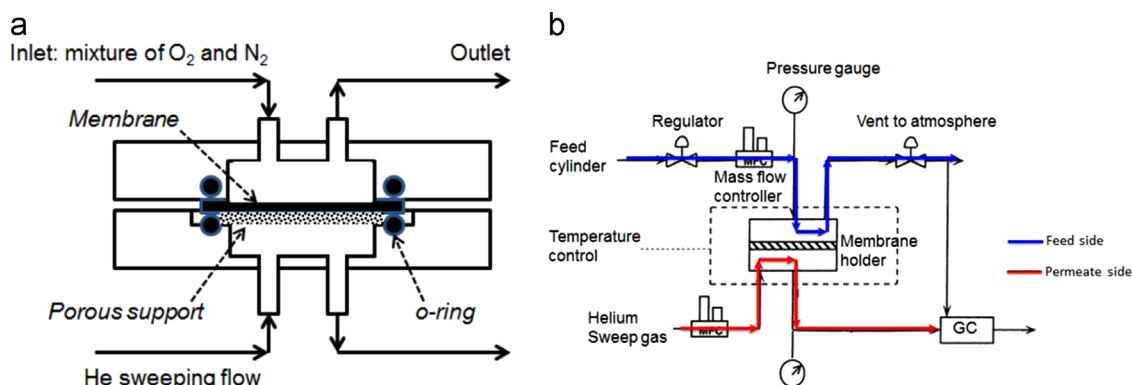

Fig. 1. (a) Schematic of a membrane holder with feed side flow and a permeate side flow. (b) Mixed gas permeability apparatus for gas permeability measurements, adapted from ref. 16.