Journal of Membrane Science 467 (2014) 175–187

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Gas-permeable composite hollow-fiber membrane with a three-layered structure

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ARTICLE INFO

Article history:
Received 20 January 2014
Received in revised form
19 April 2014
Accepted 24 April 2014
Available online 20 May 2014

Keywords:
Thin layer
Composite hollow-fiber membrane
Polymer blend
Gas permeance
Molecular mobility

ABSTRACT

Gas-permeable composite hollow-fiber membrane with a three-layered structure composed of a high-density polyethylene (HDPE) porous layer, a MK-2F thin dense layer, and a HDPE porous layer has been successfully developed by melt-spinning and cold/hot stretching. The MK-2F thin dense layer was composed of a poly(ethylenebutylene)-block–polystyrene triblock copolymer (SEBS) phase and a (poly (ethylene-co-ethylacrylate) (EEA)+poly(ethylene-co-propylene) (EPP)) phase. When the stretching ratio was increased, oxygen permeance, f_{O_2}, and nitrogen permeance, f_{N_2}, were linearly increased, while the f_{O_2}/f_{N_2} was almost constant at 2.95–3.0. The thickness of a no-pinhole thin layer was 2–5 μm and its f_{O_2} was 4.0–8.5 × 10^{-6} cm^3 (25 °C) cm^{-2} s^{-1} $cmHg^{-1}$. Structural analysis of the thin layer indicated that the SEBS and the (EEA+EPP) formed a 3D-network structure, which restricted elastic recovery of the SEBS matrix and led to the thin thickness. In a pervaporation experiment, the H_2O vapor permeation rate of the MK-2F thin layer was about 1/4 that of polydimethyl silicone (PDMS), and the IPA vapor permeation rate was about 1/12 that of PDMS even though the gas permeance of the MK-2F thin layer was almost the same as that of PDMS.

1. Introduction

The removal of dissolved oxygen or nitrogen gas in chemical liquids (e.g., isopropyl alcohol (IPA), photoresistant polymer solution, or developer solution) is very important in the semiconductor manufacturing industry. When the chemical liquid is transported to a point-of-use device from a reservoir tank with a pressure of 3–5 kg cm^{-2} and extruded from a nozzle into an atmospheric pressure situation, the excessive gas of an over-saturated state in the liquid cannot be dissolved, and it becomes small bubbles. These small bubbles lead to the formation of defects.

Many researchers [1–10] have studied the removal of dissolved oxygen from ultrapure water by using gas-permeable membranes. Most researchers [1–8] have used hydrophobic micro-porous membranes. However, the porous membranes are not available for the degassing of chemical liquids, because the liquid leaks from the pores. Ito et al. [9] have reported that the dissolved oxygen (20–22 °C, 6.0 mg L^{-1}) in ultrapure water can be removed to a level of 1.0 mg L^{-1} through the use of a non-porous cross-linked polydimethyl silicone (PDMS) microtube (oxygen permeability P_{O_2} = 299 × 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} $(cmHg)^{-1}$, thickness 60 μm). The oxygen permeance of the tube was 5.0 × 10^{-6} cm^3 (25 °C) cm^{-2} s^{-1} $cmHg^{-1}$. Yasuda et al. [10] have reported the degassing of dissolved oxygen from water via the use of a silicone rubber sheet.

However, only a few studies have reported the removal of dissolved oxygen from the chemical liquids by using a non-porous membrane [11–13]. In those studies, a poly(tetrafluoroethylene) (PTFE) tube memrane was used. The gas permeance of the PTFE membrane was 3.6 × 10^{-8} cm^3 (25 °C) cm^{-2} s^{-1} $cmHg^{-1}$, which was lower than that of the PDMS tube, due to its low level of gas permeability (P_{O_2} = 4 × 10^{-10} cm^3 (25 °C) cm cm^{-2} s^{-1} $cmHg^{-1}$) and a substantial thickness of 110 μm.

To prepare the thin dense membrane, a melt extrusion and stretching process is preferable since solvent evaporation methods tend to lead to contamination by residual solvents in the

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http://dx.doi.org/10.1016/j.memsci.2014.04.042
0376-7388/

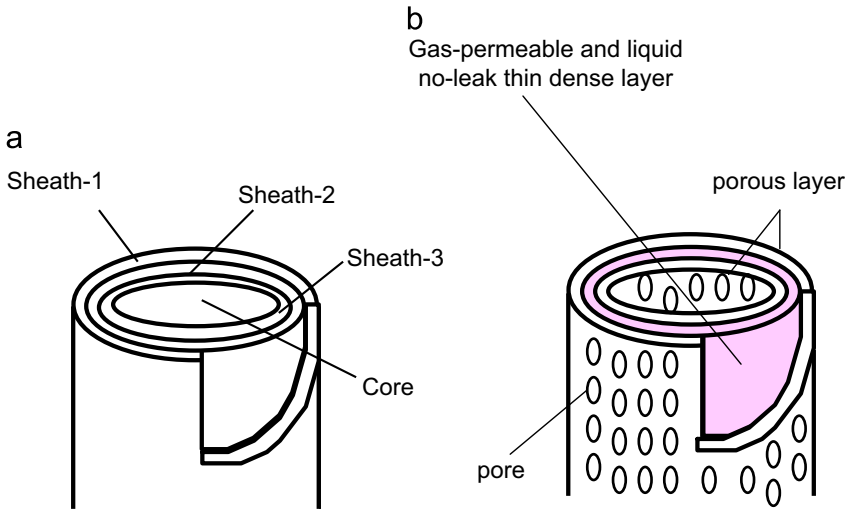

Fig. 1. Structure of a multi-layered fiber: (a) multi-layered fiber structure composed of multi-sheath layers and a core and (b) multi-layered hollow-fiber membrane structure.

membrane [14]. PDMS cannot be melt-extruded because of its cross-linked polymer.

PTFE polymer is highly resistant to chemical liquids, but it has a high melting point of about 327–330 °C and a very high melt viscosity of about 10^{11} poise even at high temperatures (e.g. 380 °C), whereas a general polymer has a melt viscosity of about 10^3–10^4 poise [15]. This makes it difficult to accomplish a melt-extrusion of PTFE and to stretch the thin membrane.

In melt-spinning technology, it is well known that a fiber with a multi-layered structure composed of multi-sheath layers and a core can be prepared via the melt-extrusion of the polymer from a conjugate type nozzle followed by spinning of the fiber [16]. The structure of the fiber is shown in Fig. 1(a). As an application of this fiber technology, Kamo et al. [17] developed hollow-fiber membranes with three-layered structures that were gas-permeable with no liquid leaks. These were composed of a thin dense layer sandwiched between two porous support layers, as shown in Fig. 1(b). In these multi-layered hollow-fiber membrane (MHF membrane) structures, the thickness of the dense layer was sufficiently thin to allow a high degree of gas permeation. The two porous layers mechanically supported the thin dense layer against applied pressure from the driving force of gas transport. The gas permeation resistance of the two porous layers is much lower than that of the thin dense layer, and therefore, the overall permeation resistance of the MHF membrane mainly depends on that of the thin dense layer.

A MK-2F polymer (Dainippon Plastics Co., Ltd., Tokyo, Japan), which is melt-processable, consists of three constituents: polystyrene-block–poly(ethylene butylene)-block–polystyrene triblock copolymer (SEBS; 50 wt%), poly(ethylene-co-ethylacrylate) (EEA; 30 wt%), and poly(ethylene-co-propylene) (EPP; 20 wt%). This polymer blend has sufficient toughness for deformation at temperatures ranging from −50 to 40 °C and also has high chemical resistance to the liquids (acids, alkali, alcohols, ester etc.) used in the semiconductor manufacturing process [18]. Both the P_{O_2} ($10–11 \times 10^{-10}$ cm^3 (25 °C) cm cm^{-2} s^{-1} $cmHg^{-1}$) and nitrogen permeability, P_{N_2} ($3–4 \times 10^{-10}$ cm^3 (25 °C) cm cm^{-2} s^{-1} $cmHg^{-1}$) of this polymer are higher than that of PTFE [18]. Therefore, the MK-2F polymer is a good material for the thin dense layer to be used in the degassing of chemical liquids.

In the present study, the MK-2F thin layer was developed through MHF membrane technology, where the three-layered structure of a porous HDPE layer, a non-porous MK-2F thin layer, and a porous HDPE layer was fabricated via a process that involved melt-spinning and stretching. After the stretching, the gas permeance of the MK-2F thin layer was measured. The obtained thickness of the MK-2F thin layer ranged from 2 to 5 μm, the oxygen permeance, f_{O_2}, was $4.0–8.5 \times 10^{-6}$ cm^3 (25 °C) cm^{-2} s^{-1} $cmHg^{-1}$, and the ratio of oxygen permeance to nitrogen permeance, f_{O_2}/f_{N_2}, was 3.0–3.2. This gas permeance of the thin layer was more than one order of magnitude higher than that of MK-2F films (thickness 27–52 μm). The phase separation structure of the MK-2F thin layer was observed by Transmission Electron Microscope (TEM) and the relationship between gas permeance and the phase separation structure was also studied. In a pervaporation experiment, the H_2O and IPA vapor permeation rates of the MK-2F thin layer were measured and the results were compared with those found in the PDMS literature data.

2. Experimental

2.1. Polymer material

HDPE and MK-2F polymers were used for the porous layer and the thin dense layer of the composite hollow-fiber membrane, respectively. The density, the melt flow rate at 190 °C under a load of 2.16 kg, and the melting point of HDPE were 0.965 g cm^{-3}, 0.90 g/10 min, and 137 °C, respectively.

The chemical structure and thermal characteristics of each constituent in the MK-2F layer are described in the previous papers [18,19].

The melt flow rate of MK-2F was 0.71 g/10 min at 190 °C under a load of 2.16 kg. TEM micrographs [18] of a MK-2F pellet indicated that the polymer had a phase-separated structure with a SEBS matrix phase and a dispersed phase comprised of a mixture of EEA and EPP with a fibril-like or droplet shape. The cylindrical polystyrene domains (diameter 200 Å) in the SEBS matrix were oriented along the MD, i.e., the extrusion direction of the MK-2F polymer pellet. The EB chains existed in narrow regions (50–100 Å wide) between the neighboring polystyrene domains.

2.2. Preparation of composite hollow-fiber membranes with a three-layered structure

A scheme for the preparation of a composite hollow-fiber membrane and a diagram of the duplex tube-type nozzle are shown in Figs. 2 and 3, respectively. MK-2F pellet and HDPE pellets were melted at 190 °C and extruded into a duplex tube-type nozzle by two extruders; one was for MK-2F and the other was