Fabrication of composite hollow fiber membranes with thin film selective layers from highly permeable polymers

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Abstract. Fabrication of highly efficient composite gas separation membranes involves selection and pretreatment of the support material. In the present work, porous support pretreatment was for the first time studied for deposition of thin selective layers made from highly permeable organosilicon polymers. Asymmetric polysulfone hollow fiber membranes with mesoporous skin layer structure were employed as supports. It was shown that preliminary impregnation of the support pores is essential for composite membranes fabrication. If poly[1-(trimethylsilyl)-1-propyne] layers from casting solution are deposited onto the polysulfone support without impregnation, the casting solution penetrates the mesoporous layer to a depth of > 1 μm, thus predominantly (>90%) contributing to the overall mass transfer resistance, as estimated by the resistance-in-series model. Such membranes provide relatively poor transport properties: carbon dioxide permeance is 0.2-0.3 m³/(m²·h·bar). Preliminary impregnation of porous support by distilled water or aqueous glycerol solution prevents casting solution penetration into porous support and results in defect-free thin polymer layer. According to SEM, the deposited selective layer thickness is less than 1 μm. Composite membranes fabricated via this technique provide permeance increase more than order of magnitude. The composite membranes with poly[1-(trimethylsilyl)-1-propyne] and polydimethylsiloxane selective layers show high transport properties in gas-liquid membrane contactors.

1. Introduction

In recent years, membranes have been frequently proposed for fixing gas-liquid interfacial areas [1]. Such types of non-dispersive gas-liquid contactors are generally termed as gas-liquid membrane contactors. In contrast to other membrane processes, in the membrane in a contactor acts as a barrier and as a means of bringing two immiscible fluid phases, such as gas and liquid, into contact with each other without dispersion [2]. The membrane contactor acts as a mass-transfer device with continuous contact, like, i.e., packed columns. However, in case of contactor, there is no need to disperse physically one phase in another or to separate the phases at the end of the process. One of the key benefits of this scheme is high specific surface area (phase contact area), making the membrane contactor different from other membrane processes. Whereas conventional packed columns have...
specific surface area ~ 20–500 m²/m³, the hollow fiber membrane contactors provide 500–5000 m²/m³ [3].

The main disadvantage of separation process in a gas-liquid membrane contactor is the fact that the membrane itself contributes significantly in the overall mass transfer resistance value. If liquid phase penetrates into the membrane (i.e., wetting phenomenon occurs), the membrane resistance increases [4,5]. For this reason, different researches proposed various approaches to prevent membrane wetting in contactors: employment of hydrophobic membranes or composite membranes with dense layer on the side of phases contact area, modification of membranes [6-9], selection of absorption liquids with suitable surface tension [10], and optimization of the process parameters. One of the solutions for gas-liquid membrane contactor configuration is employment of composite membranes constituted by a thin dense layer of polymer (selective layer) on a porous support. The dense layer is exposed to liquid phase side, thus stabilizing the membrane properties and preventing penetration of absorbent into the porous substructure. When choosing the selective layer material for composite membrane, one should consider the ratio between gas and liquid permeabilities – the higher this value, the more suitable is the polymer [11]. Furthermore, it is preferable to use the polymers possessing good hydrophobic properties.

Polysulfone (PSf) is widely used as membrane material due to its mechanical stability as well good thermal and chemical stability. Also, it is well suited for producing hollow fiber membranes with controlled pore size [12]. In the present work, the composite hollow fiber membranes with thin selective layers based on highly permeable organosilicon polymers – poly[1-(trimethylsilyl)-1-propyne] (PTMSP) and polydimethylsiloxane (PDMS) – are fabricated on asymmetric polysulfone hollow fiber supports with mesoporous structure of the skin layer. The major problem under deposition of selective layers onto porous supports is that the solution of modifying polymer penetrates into porous matrix of the support to a depth of > 1 μm, thus predominantly (> 90%) contributing the overall mass transfer resistance, as estimated by the resistance-in-series model. Such membranes provide relatively poor transport properties: carbon dioxide permeance is 0.2-0.3 m³/(m²·h·bar) [13]. To solve this problem, it is proposed to use preliminary impregnation of porous support, which results in deposition of thin selective layer on the membrane surface. The fabricated composite membranes were characterized by various techniques to study their morphological and transport properties.

2. Experimental

Asymmetric hollow fiber supports were fabricated using the dry-wet phase inversion technique in the free spinning mode in air when bore fluid was brought into liquid polymer solution orifice, resulting in the selective layer appearance on the fibers lumen side. The spinning solution included the polymer – polysulfone (Ultrason® S 6010, BASF), the solvent – N-methylpyrrolidone (NMP, Acros Organics 99% extra pure) and the pore forming agent – polyethylene glycol with average molecular weight 400 g/mol (PEG-400, Acros Organics).

For deposition of selective layer, the solutions of PTMSP (1 wt. %) in hexane and PDMS (1 wt. %) were prepared. The impregnation liquids used for fabrication of composite membranes were water or aqueous glycerol solution (20 wt. %) in case of PTMSP and ethyl or isopropyl alcohols in case of PDMS. The impregnation liquid was injected into the fibers by a syringe. After that, the excessive liquid was removed with air flush and the polymer solution was deposited on the lumen surface of the fibers. The composite membranes fabricated were rinsed with distilled water and dried at ambient conditions to constant weight.

The membranes were characterized using scanning electron microscopy (SEM) technique and measurement of gas permeance and contact angle. To obtain SEM micrographs of the membranes cross sections, we used Hitachi Table top TM 3030 Plus microscope with proprietary highly sensitive low-vacuum secondary electron detector; accelerating voltage was 15 kV. The contact angle values were measured by the conventional sessile drop technique using the VK-1 goniometer (Open Science, Russia). Measurement error was ± 2°. Gas permeance of the hollow fibers was determined via the volumetric technique using the laboratory setup described elsewhere [7]. Ideal selectivity value was determined as the ratio between individual gases permeability values (α = P₁/P₂).
3. Results and discussion
Table 1 shows gas transport properties and water contact angle values for both porous supports and composite membranes based on PTMSP and PDMS.

Table 1. Nitrogen permeance and water contact angle values of porous supports and composite membranes based on PTMSP and PDMS

| Membrane                | Impregnation liquid  | P/l (N\textsubscript{2}), m\textsuperscript{3}/m\textsuperscript{2}\cdot h\cdot bar | \(\theta (\text{H}_2\text{O}), ^\circ\) |
|-------------------------|----------------------|-------------------------------------------------|---------------------------------|
| Porous support          | –                    | 270                                             | 78                              |
| Composite (PDMS)        | Ethanol              | 2.3                                             | 147                             |
|                         | Isopropyl alcohol    | 0.4                                             | 132                             |
| Composite (PTMSP)       | Distilled water      | 3.5                                             | 98                              |
|                         | Aqueous glycerol     | 1.7                                             | 92                              |
|                         | solution             |                                                 |                                 |

As can be seen from Table 1, the type of impregnation liquid affects the properties of the composite membrane fabricated. For the membranes with PDMS selective layer, impregnation by isopropyl alcohol leads to poor gas permeance as well as membrane defects. In contrast, use of ethanol results in enhanced gas transport properties of the membranes. Furthermore, these membranes showed drastic increase in hydrophobicity: contact angle value increases from 78° to 147°.

The composite membranes with PTMSP layer also differ depending on the type of impregnation liquid. With minor difference in water contact angle values, the membranes treated by distilled water show nitrogen permeance 2 times higher than that of membranes treated by glycerol solution.

In order to prove that the selective layer of PTMSP composite membrane had no defects, we also measured the membrane gas permeance by carbon dioxide, P/l (CO\textsubscript{2}), and ideal selectivity value \(\alpha (\text{CO}_2/\text{N}_2)\), for both composite membrane specimens. The results are given in Table 2.

Table 2. Gas transport properties of PTMSP composite membranes depending on the type of impregnation liquid

| Impregnation liquid     | P/l (N\textsubscript{2}), m\textsuperscript{3}/m\textsuperscript{2}\cdot h\cdot bar | P/l (CO\textsubscript{2}), m\textsuperscript{3}/m\textsuperscript{2}\cdot h\cdot bar | \(\alpha (\text{CO}_2/\text{N}_2)\) |
|-------------------------|-------------------------------------------------|-------------------------------------------------|---------------------------------|
| Distilled water         | 3.5                                             | 4.1                                             | 1.2                             |
| Aqueous glycerol solution| 1.7                                             | 9                                               | 5.3                             |

As can be seen from Table 2, the selectivity of PTMSP-based composite membrane, fabricated with the use of distilled water, almost fully corresponds to the porous support selectivity, which indicates that the polymer coating is inhomogeneous and the selective layer has defects. At lower permeance, the composite membranes fabricated with glycerol solutions pretreatment show selectivity close to that of the dense PTMSP film (\(\alpha (\text{CO}_2/\text{N}_2) = 5.7\)). So, it can be concluded that aqueous glycerol solution is preferable for fabrication of such membranes.

Fig. 1 shows SEM micrographs of the composite PTMSP-based hollow fiber membrane which was fabricated via preliminary impregnation by aqueous glycerol solution.

As can be seen from Fig. 1 (a), the PTMSP composite membranes possess pronounced asymmetric morphology constituted by thick macroporous support, spongy transitional layer and thin selective
layer. Fig. 1 (b) shows enlarged image of the PTMSP layer. It can be seen that the coating is uniform and homogeneous. The estimated PTMSP layer selectivity is $< 1 \mu m$, which, presumably, accounts for relatively high nitrogen permeance of the membrane.

![Figure 1. SEM micrographs of the composite PTMSP membrane (cross-section): a – general view, magnification 200x; b – enlarged image of the selective layer, magnification 1000x](image)

4. Conclusion
Fabrication of composite hollow fiber membranes based on PTMSP was studied. Mesoporous polysulfone supports were pretreated via liquid impregnation. The membranes were characterized using gas permeance and contact angle measurements; SEM micrographs are provided. The PTMSP composite membranes show selectivity corresponding to that of the dense polymer film, at reasonable permeance. The PDMS composite membranes provide higher gas permeance combined with high selective layer hydrophobicity (water contact angle value $\sim 150^\circ$). Depending on the particular tasks, both types of the composite membranes fabricated are promising for employing them in gas-liquid membrane contactors.

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