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Thin-film-composite hollow-fiber membranes for water vapor separation

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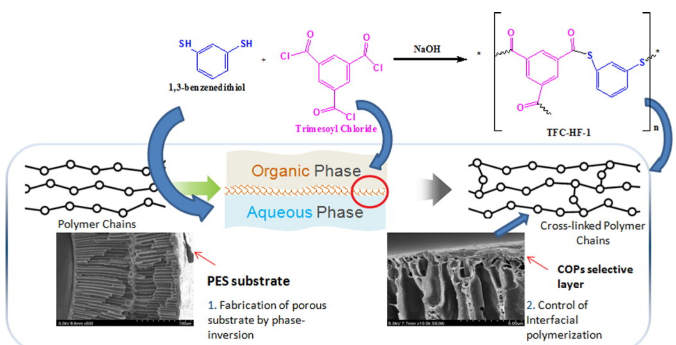
HIGHLIGHTS

- The covalent organic polymeric TFC was deposited on porous PES-HF membrane support.
- Membranes were characterized for the presence of COP thin film coating layer.
- The TFC-supported COP layer is uniform, defect-free and about 70–214 nm thick.
- The TFC-HF-1 showed improved gas separation selectivity for water vapor/N_2 of ≈119.

GRAPHICAL ABSTRACT



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ABSTRACT

Polyethersulfone (PES) hollow fiber membranes were prepared using the phase inversion technique. The surface of the PES hollow fiber membranes consisted of thin film composite polymer membranes. These membranes were prepared by interfacial polymerization using four different aqueous phase monomers: 1,3-benzenedithiol (BDT), m-phenylenediamine (MPD), 1,3,5-benzenetrithiol (BTT), and piperazine (PIP). The organic phase monomer, trimesoyl chloride (TMC), was used to produce the covalent organic polymers. Different types of aqueous monomers (with a number of reactive groups) and their structures were optimized to achieve maximum gas permeation efficiency and water vapor/N_2 selectivity. All prepared membranes were fully characterized using different analytical techniques. Among all of the prepared thin film composite (TFC) membranes the one prepared with the 1,3-benzenedithiol monomer (TFC-HF-1) exhibited superior results as water vapor permeance 2054 GPU, and the water vapor/N_2 selectivity 119. The prepared membrane substrates and TFC membranes were characterized by chemical structure, morphology and separation performance. Overall, the membranes exhibited good performance over the entire investigated range of operating conditions.

1. Introduction

Today, approximately 85% of energy is produced by fossil fuel fired power plants. These plants generate a tremendous amount of flue gas. These gases mostly consist of N_2 (~72 vol.%), water vapor (~11 vol.%) and CO_2 (~14 vol.%) [1]. A number of techniques have been applied to remove water vapor from the gas streams. These techniques include using a condenser [2,3], a desiccant drying system [4–6] or a membrane system [7–11]. However, there are several disadvantages to the first two processes. In the condensation process, the condensate is relatively dirty and corrosive. In the desiccant drying system, regeneration of the desiccant is necessary and requires a large amount of energy. Gas separation processes are generally divided into four types: absorption,

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adsorption, cryogenics and membrane technology. For the last 20–30 years, membrane processes have been applied in a wide variety of industries, such as food and beverage, water treatment and desalination, and the gas separation process. Compared to the other processes, membrane technology has low energy consumption, requires only compact spaces and has a flexible design. There are several papers that report the simultaneous permeation of water vapor and light gases [12–14].

Nowadays asymmetric thin film composite polymer membranes (either flat sheet or hollow fibers) are extensively used in industrial gas separations to achieve high water fluxes. In these fabricated asymmetric membranes, the porous substrate acts as a mechanical support and the thin skin selective layer is liable for the separation [15,16]. In particular, polyethersulfone (PES) has the advantage that it readily forms a film and, as a result, is easier to manufacture into membranes. Most importantly, PES is chemically inert, has the ability to retain mechanical strength in hot and wet environments, and is thermally stable. Therefore, PES is a reliable candidate for use in thermal power plants for the removal of water vapor from flue gas [17,18]. To improve hydrophilicity, the modification of the PES hollow fiber substrate, for different applications, has already been extensively studied by Zhao et al. [19].

The removal of water vapor from air or other gases is an important process in a wide range of industries, including chemical, electronic, electric, fossil fuel fired power plants, food and fiber. This process is also used in cooling towers. The industrial operation is important because it involves the removal of water vapor from gas streams along with the dehydration of flue gas [20] or achieving dew point for natural gas [21,22]. Covalent organic polymeric materials were used as a coating material to supply the hydrophobic membrane surface with hydrophilicity. Thin film composite membranes, which have polyamide, imide and sulfur linked polymeric functional groups (thiol ester), were formed. Interfacial polymerization (IP) is a method for manufacturing surface-modified membranes and can produce uniform and rigid micropores in a highly cross-linked selective layer [23]. A thin selective layer, comprised of repeatedly packed-on PES membrane surface structures, may serve as a good candidate to obtain high selectivity membranes for gas separation [24]. A major advantage of IP is the formation of a thin selective layer, which is hydrophilic and highly packed. More recently, membrane modifications via IP have received considerable attention. This method has been demonstrated to be versatile to modify polymer membranes with excellent hydrophilic properties [25].

In this study, the water vapor permeation method was employed for dehydrating synthetic flue gas. In principle, vapor permeation is similar to pervaporation but systematically constitutes a mixture of vapor or gases [26]. Vapor permeation takes place through the membrane by the solution-diffusion mechanism. Both molecular interactions (between the membrane and the separated species [27]) and materials are determining factors for membrane separation. Membrane performance is evaluated based on these factors. In addition, the effects of the different covalent organic polymer (COP) layer (here named as thin film composite (TFC) membrane) on water vapor and N_2 gas permeance have been studied. The synthesized cross-linked polyamide/thiol ester possible structures are shown in Fig. 1. All of these above-mentioned approaches significantly increase the efficiency and separation properties of the TFC membranes. As described here, the novel materials were tested for performance and stability, and were used for water vapor separation over a wide range of applications. Finally, the membrane performance was investigated, and the TFC membranes were analyzed by FT-IR, SEM, AFM, Brunauer-Emmett-Teller (BET) surface area, contact angle and XPS analysis.

2. Materials and methods

2.1. Membrane preparation

2.1.1. Materials and formulations

Polyethersulfone (PES, Ultrason® E 6020 P, BASF, Germany, MW = 50,000) and the solvent, *N*-methyl-2-pyrrolodone (NMP, Merck, 99.5%), were purchased and used for preparing the support layer. The membrane was modified by forming a thin film coating using the IP process. The following chemicals were purchased from Sigma-Aldrich: 1,3-

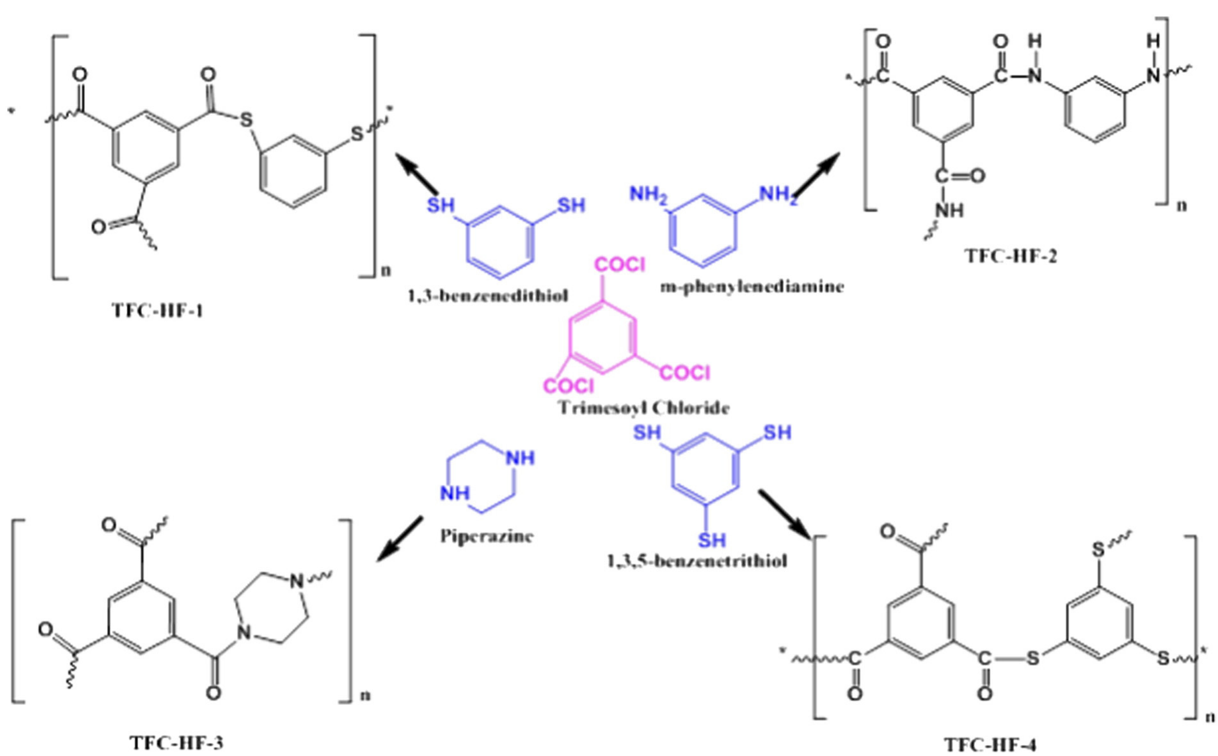

Fig. 1. Possible chemical structures of covalent organic polymers (COPs) in the form of thin film composite membrane on the surface of PES hollow fiber substrate.