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Fabrication of integrally skinned asymmetric membranes based on nanocomposite polyethersulfone by supercritical CO_2 for gas separation

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ABSTRACT

Integrally skinned asymmetric membranes based on nanocomposite polyethersulfone were prepared by the phase separation process using the supercritical CO_2 as a nonsolvent for the polymer solution. All the membranes have been prepared from originally dense nanocomposite films inducing asymmetry by the formation of the porous layer adding N,N-dimethylacetamide as solvent and supercritical CO_2 (SC-CO_2) to one side of the dense films, and then allowing the supercritical CO_2 expansion to occur. The effect of pressure, temperature and nanoparticles on the permeability of CH_4 and CO_2 and also selectivity performance of membranes has been investigated. The results showed that the membranes formation pressures which varied from 100 to 120 bar have significant effect on the pore sizes and thickness of obtained dense and porous layers. Also, the effect of the temperature which varied from 45 to 55 °C has been evaluated and it was concluded that by changing the temperature, it is possible to induce a very-controlled asymmetry in a dense film and pore sizes and thus increasing in CO_2 permeability and selectivity performance of membranes. Finally, the permeability of CH_4 and CO_2 measured at the constant temperatures of 30, 40 and 50 °C and at the pressures of 8, 10 and 12 bar and the effects of temperature and nanoparticle on selectivity performance and permeability of gases has been investigated.

1. Introduction

Supercritical carbon dioxide (SC-CO_2), is well known in the fields of solid and liquid extraction which has been successfully employed in industrial applications [1–4]. Properties like low cost, non-flammability, non-toxicity pressure-dependent solubility of various substances are reasons, why supercritical CO_2 is gradually replacing organic solvents in various technologies Furthermore, its moderate critical conditions (T_c = 31.1 °C, P_c = 73.8 bar) can be easily achieved [5].

The use of SC-CO_2 to produce porous polymeric membranes that may be useful in micro, ultra and nano filtration has been extensively investigated with different polymers such as polysulfone [6], poly(vinyl alcohol) [7], polylactide acid [8], nylon [9], polystyrene [10], cellulose acetate [11,12], poly(methyl methacrylate) [13] and modified poly(ether ether ketone) [14], but it has not been widely employed to fabricate integrally skinned asymmetric membranes for gas separation processes. Due to optimum combinations of gas permeance and gas separation selectivity in an integrally skinned asymmetric membrane, it is generally used for gas separation processes. A typical process to produce such membrane is dry/wet phase inversion [15–20] that is based upon fabricating a dense skin layer of the polymer membrane by first allowing the evaporation of the solvent in a cast membrane and then creating the porous support by solvent/non-solvent exchange during a quench step [21]. The aim of this work is to investigate the potential of supercritical CO_2 as the non-solvent to obtain integrally skinned asymmetric nanocomposite membranes based on polyethersulfone (PES). In this process, the advantage of SC-CO_2 is that can dry the polymer membrane rapidly without collapsing the structure and primal morphology of the membrane. On the other hand, the solvent can be easily recycled to form gaseous CO_2 after the pressure is diminished. To the best of our knowledge, it has not yet been widely used to produce integrally skinned asymmetric membranes for the gas separation processes.

Studies on gas permeation properties of polyethersulfone (PES) membranes have been shown that PES exhibits better selectivity for the commercially important gas pairs like CO_2/CH_4, He/CH_4, H_2/N_2, O_2/N_2 compared to polysulfone and cellulose acetate and some other polymers [22–27]. To this, polyethersulfone

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and its nanocomposites are widely used for the preparation of gas separation membranes [28,29]. Furthermore some favorable characteristics of this polymer made it applicable for separation processes. Few characteristics to mention are wide temperature limits, wide pH tolerances, easy to fabricate membranes in a wide variety of configurations and modules, wide range of pore sizes from 10 Å to 0.2 μm used for ultra and micro filtration applications, good chemical resistance to aliphatic hydrocarbons, alcohols and acids and capability to load with different nanoparticles [28–31]. In the field of CO_2/CH_4 separation, Saedi et al. showed that the asymmetric membranes of PES which were coated by polydimethyl siloxane (PDMS) had the permselectivity of 25 for CO_2/CH_4 with CO_2 permeance of 9 GPU (GPU = 1×10^{-6} cm^3 (STP)/cm^2 s cmHg) [32]. Cusworo et al. fabricated asymmetric membranes of neat PES and polyethersulfone-functionalized multi-walled carbon nanotubes which CO_2/CH_4 selectivities of 5.46 and 23.89 were achieved for the membranes, respectively [33].

It should be noted that much of previous work that has been published focused on influence of polymer concentration, experimental temperature, quench medium, solvent evaporation time and incorporation of nanoparticles on the structure and gas permeation properties of integrally skinned PES membranes which were produced by dry/wet phase inversion [32–34].

The main goal of this study is to investigate how SC-CO_2 as a non-solvent influences the structure and permeation properties of integrally skinned asymmetric membranes of PES/silica for gas separation application. This approach consists of forming the sponge-like structure layer using an already formed nanocomposite dense layer, by contacting one face of the membrane with solvent and SC-CO_2 for a specific period of time, and then allowing the extraction of solvent/SC-CO_2 by depressurizing the membrane formation cell. The CO_2 pressure and temperature in forming the membranes, the presence of nanoparticle as well as pressure and temperature of the feed gas (CH_4 and/or CO_2) in permeation tests are the variables in this work.

2. Experimental

2.1. Materials

Polyethersulfone E6020P (M_w = 51,000 g/mol) with the structure shown in Fig. 1 was obtained from BASF (Germany), N,N-dimethylacetamide (DMAc) was used as solvent provided by Merck (Germany), Silica modified by octylsilane (PL-SiOF-OS) with average size of 14 nm, density of 2.2 g cm^{-3} and specific area of 150 m^2 g^{-1} was purchased from Plasma Chem Co. (Germany), CO_2 gas (purity 99.99%) was purchased from Aboughadare (Shiraz, Iran) and CH_4 (purity 99.9%) was acquired from Air Products Co.

2.2. Dense nanocomposite layer preparation

Dense polyethersulfone membranes were prepared using casting solutions containing PES and octylsilane modified nanosilica (silica-OS) in DMAc as solvent. First of all, silica nanoparticles were dispersed in DMAc by stirring for 1 h and sonicated for 45 min at 50 °C in order to obtain a homogenous 5 wt% solution before the addition of the polymer solution. Thereafter, a 10 wt% solution of polyethersulfone in DMAc which was stirred for 1 h and was heated

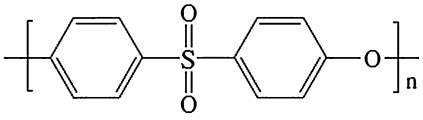

Fig. 1. The chemical structure of PES.

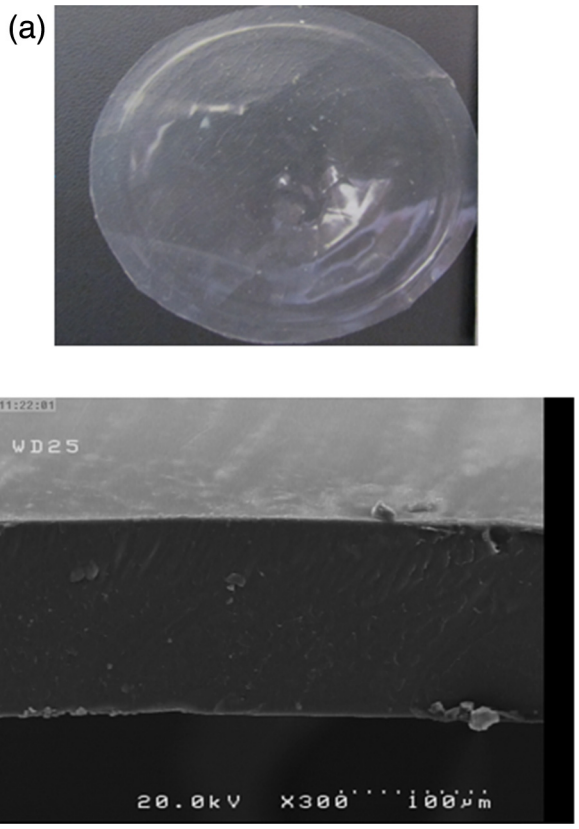

Fig. 2. The dense nanocomposite PES: (a) top surface and (b) cross section.

at 50 °C separately, was blended with prepared nanoparticle solution. The resultant polymer solution was stirred again for 15 min and then sonicated for a short period of time to allow a complete release of air bubbles and homogenous solution. The blend solution was then casted on a glass plate and dried in an oven for 24 h at 80 °C. After that, the polymer film was located in vacuum oven at 80 °C for another 8 h for complete removal of the remaining solvent. Also, it must be mentioned that all membranes were treated according to the same procedure and their thicknesses, measured with a Mitutoyo caliper, varied from 100 to 150 μm. The image of nanocomposite polyethersulfone dense layer is depicted in Fig. 2.

2.3. Asymmetric membrane preparation

As indicated in Fig. 3, a typical procedure to produce a polyethersulfone porous layer on a dense film membrane without applying any additional porous layer, consists of delivering a predetermined amount of DMAc as solvent (controlled as the DMAc/polyethersulfone mass ratio) in a well-defined film area which the dense film is fixed into a clean glass support [6]. Then, the glass with the membrane was immediately transferred into a high-pressure vessel and CO_2 was introduced into it until the desired pressure was reached. The system was maintained the pressure at a constant value for 60 min in order to form a ternary mixture of polymer/solvent/nonsolvent. Then, the system was slowly depressurized for about 45 min at the experimental temperature and a dried polyethersulfone integrally skinned asymmetric membrane was obtained as indicated in Fig. 4. All experiments were conducted at constant temperature in a high-pressure stainless steel (160 cm^3) vessel where the CO_2 is charged by a high-pressure syringe pump (DB-80, Beijing Satellite Manufacturing Factory, Beijing). A pressure gauge consisting of a transducer (model 93, IC Sensors Co.) and an indicator (XS/A-1, Beijing Tianchen Automatic Instrument