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Preparation of hollow fiber poly(ether block amide)/polysulfone composite membranes for separation of carbon dioxide from nitrogen

Li Liu, Amit Chakma, Xianshe Feng*

Department of Chemical Engineering, University of Waterloo, Waterloo, Ont., Canada N2L 3G1

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Abstract

The separation of carbon dioxide from nitrogen is relevant to flue gas treatment for greenhouse gas emission control. This study deals with the preparation of hollow fiber poly(ether block amide) (PEBA)/polysulfone (PSf) composite membranes for CO_2/N_2 separation. PEBA 2533 copolymer was shown to be a good permselective membrane material for CO_2/N_2 separation. At 25 °C and 100 psig, a CO_2 permeability of about 260 Barrer and a CO_2/N_2 selectivity of 32 were obtained. The thin-film hollow fiber PEBA/PSf composite membrane comprising of a thin PEBA skin layer (<5 μm) and a porous polysulfone hollow fiber substrate was prepared by the dip-coating technique. The polysulfone hollow fiber substrate was formed by the solution extrusion/phase inversion process. The effects of parameters involved in the procedure of polysulfone hollow fiber spinning and PEBA layer deposition on the permselectivity of the resulting composite membranes were investigated. Defect-free PEBA/PSf composite membranes with an inside and an outside diameters of 350 and 600 μm, respectively, have been obtained which showed a CO_2 permeance of 61 GPU and a CO_2/N_2 selectivity close to the intrinsic selectivity of the PEBA dense membrane. It was shown that the N_2 permeability is essentially independent of the pressure, whereas CO_2 permeability tends to increase with an increase in gas pressure, presumably due to plasticization of the membrane caused by the relatively high solubility of CO_2 in the membrane.

Keywords: Poly(ether block amide); Composite membrane; Hollow fiber; Gas separation; Flue gas

1. Introduction

The emission of carbon dioxide from combustion flue gas is a major contributor to global warming. The capture/separation of carbon dioxide from flue gas is an important step for greenhouse gas emission control. There are primarily four approaches to CO_2 separation, namely, absorption by liquids, adsorption on solids, low temperature distillation, and membrane separation. Compared to others, the membrane process does not involve phase change, nor does it require the use of sorbent materials that need periodic regeneration. Generally speaking, the membrane process is very efficient for bulk separation where a very high purity is not required. This makes membrane process particularly attractive for flue gas separation. The CO_2 removed from flue gas can be used for enhanced oil recovery and coalbed methane recovery, where the coalbed and the depleted oil reservoirs are natural geosphere sinks for CO_2. In addition, the CO_2 captured can also be stored in deep aquifers and biosphere sinks (e.g. forest, soil and ocean ecosystems) [1].

Gas separation by membranes is a pressure-driven process, where a pressure difference across the membrane should be maintained to provide the driving force necessary for permeation. For practical applications, the quantity of flue gas to be treated is very large. Increasing the operating pressure will increase the membrane productivity, but this is at the expenses of increased compression costs. Considering the cost of compressing the flue gas from a combustion chamber, which is generally at a relatively low pressure, membranes with a high permeance and a reasonable selectivity are needed in order to make the separation process economical.

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* Corresponding author. Tel.: +1 519 888 4567; fax: +1 519 746 4979.
E-mail address: xfeng@uwaterloo.ca (X. Feng).

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Poly(ether block amide) (PEBA) is a family of copolymers, consisting of polyamide hard segments and polyether soft segments in the polymer chains [2]. Because of their micro-biphasic structure, the copolymers offer many properties that are not readily available in either constituent polymer. PEBA not only has favorable membrane-forming properties but also good chemical resistance to acid, basic and organic solvents and high thermal and mechanical stabilities [3]. There have been some studies on gas permeation through PEBA membranes. Kim et al. [4] investigated the effect of the chemical composition of PEBA copolymers on the permeation behavior of polar and nonpolar gas pairs such as CO_2/N_2 and SO_2/N_2. For small and nonpolar gases, the permeability was shown to decrease with an increase in the size of the gas permeant. For polar gases, however, a high permeability was observed because of their strong affinity to the polyether block in the PEBA copolymers. It has been shown that the sorption isotherm is convex to the pressure axis for more soluble penetrants (such as CO_2) and linear for the less soluble gases (such as N_2) [5], resulting in high solubility selectivity for carbon dioxide/nitrogen, which is attributed to the strong affinity of the polar ether linkages for CO_2. The PEBA polymers were found to compare very favorably with traditional rubbery and glassy polymers in terms of CO_2 permeability and CO_2/N_2 permeability ratio [6]. This means PEBA polymers are potential candidate materials for making membranes to separate CO_2 from flue gas. PEBA appears to be a versatile material. While the traditional techniques (such as solvent casting and dip coating) can be used to prepare PEBA membranes, we have recently developed a new method of making ultrathin (as thin as 0.3 μm) defect-free membranes from certain PEBA polymers based on spontaneous spreading and precipitation of polymer solution on liquid surface [7]. The use of PEBA membranes for separation of organic compounds from aqueous solutions by pervaporation has also been reported [8–10].

Membrane gas permeation is a rate-controlled process, and a high permeation rate can be achieved by using thin membranes. Structurally asymmetric and/or composite membranes consisting of a thin separation layer and a microporous substrate support are used in almost all industrially important gas separations. Integrally skinned asymmetric membranes with sufficient mechanical strength can hardly be formed from rubbery polymers, and in this case the thin-film composite membranes are preferred. The latter can be prepared by dip coating a suitable substrate with a thin layer of the polymer that will function as the separation layer.

The present study deals with the development of hollow fiber thin-film composite PEBA membranes for CO_2 separation from nitrogen, which is relevant to CO_2 capture from flue gas. Compared to flat membranes, hollow fiber membranes have the advantages of self-supporting and large membrane area per unit module volume, a feature favorable for practical applications. Most industrially important membranes for gas separations are hollow fiber membranes. It may be pointed out that PEBA is a general name of a series of block copolymers, and the properties of the materials vary with the nature and the content of the polyamide and polyether segments. PEBA 2533 was selected in this work because of its favorable permselectivity and good film forming properties. Among the PEBA family of polymers, PEBA 2533 exhibited a high permeability and a fairly good CO_2/N_2 selectivity. Membrane separation is a rate-controlled process, and the industrial success of membrane gas separations is to a large extent attributed to the engineering approach of reducing the effective thickness of the membranes thereby increasing the membrane productivity. In spite of the earlier work on the permeability of several gases through dense homogeneous flat PEBA films prepared by melt extrusion [6,11] or solvent casting [4], to our knowledge no study has been reported in the literature on the development of hollow fiber composite PEBA membranes. In the present study, thin-film hollow fiber composite membranes comprising of a thin PEBA 2533 layer supported on a microporous polysulfone substrate were developed in an attempt to increase the membrane permeance. The effects of parameters involved in the procedure of polysulfone hollow fiber spinning and PEBA coating application on the permselectivity of the resulting composite membranes were investigated. It should be pointed out that the gas permeability data of PEBA dense membranes reported are quite different [4,6,11], presumably due to the different thermal and process histories (e.g. melt extrusion versus solution casting) that the membrane samples underwent, which will be discussed later. Therefore, in order to evaluate how close is the selectivity of the hollow fiber PEBA/polysulfone composite membranes to the intrinsic permselectivity of the PEBA 2533 membranes for CO_2 and N_2 permeation, flat dense PEBA membranes with the same thermal history (i.e. drying conditions) during membrane formation were also prepared in this study to determine its intrinsic permselectivity.

2. Experimental

2.1. Materials

Poly(ether block amide) (PEBAX® 2533) was supplied by Atofina Canada Inc. (Oakville, Ontario). It comprises of 20 wt.% nylon 12 as the amide segments and 80 wt.% poly(tetramethylene oxide) as the ether segments. *n*-Butanol from Fisher Scientific was used as the solvent to dissolve PEBA during membrane preparation. Microporous hollow fiber substrate membranes were prepared from polysulfone (PSf) (Udel® P1700), which was purchased from Amoco Performance Products (Marietta, OH), using *N*-methyl-2-pyrrolidone (NMP) and polyethylene glycol (PEG) (average molecular weight 1000) as the solvent and additive, respectively. The latter two chemicals were obtained from Aldrich Chemical and were used as received without further purification. Nitrogen and carbon dioxide (research grade, 99.8% to 99.999% pure) supplied by Praxair Specialty Gases and Equipment were used in the permeation experiments.

2.2. Membrane preparation

2.2.1. Dense homogeneous flat membranes

PEBA 2533 was dissolved in *n*-butanol at 80 °C under vigorous agitation to form a homogenous solution containing 5 wt.% of the polymer. The polymer solution was then kept at room temperature without disturbance for 1 day to remove the fine air bubbles entrapped in the solution. Dense membranes were prepared by casting the polymer solution onto a clean glass plate, which was then placed in an oven at 70 °C for 24 h to evaporate the solvent. Then the membrane was peeled off from the glass plate, followed by complete drying at 50 °C under vacuum for 2 days to remove any residual solvent. The thickness of the resulting dry membrane was measured to be ∼55 μm. The dense membrane was used to determine the intrinsic permeability of the PEBA 2533 material.

2.2.2. Hollow fiber composite membranes

Hollow fiber composite membranes were prepared by dip coating a microporous polysulfone hollow fiber substrate with a PEBA solution. The substrate hollow fibers were spun from homogenous solutions of polysulfone dissolved in NMP, with and without PEG additive, using the phase inversion technique. After degassing under vacuum, the dope solutions were extruded through a tube-in-orifice spinneret with nominal inside and outside diameters of 0.5 and 1.0 mm, respectively. The external coagulation bath was filled with de-ionized water and maintained at room temperature, and de-ionized water was used as the bore fluid. The as-spun hollow fibers were kept in water at room temperature for 2 days to ensure complete solvent–nonsolvent exchange followed by thorough rinsing with water. The hollow fibers so prepared had an inside and outside diameters of 350 and 600 μm, respectively.

To prepare the hollow fiber composite membranes, the water–wet polysulfone hollow fiber substrates were dip-coated with a PEBA solution at a given temperature. The coating solution was prepared by the same method mentioned before, and the PEBA concentration in the coating solution ranged from 0.5 to 5 wt.%. After coating, the hollow fiber membranes were dried at the same temperature for 20 min, and the resulting PEBA/PSf hollow fiber composite membranes were further dried at 70 °C in an oven with forced air circulation for 12 h to remove any residual solvent.

2.2.3. Gas permeation experiment

The flat dense PEBA membrane was used to determine the intrinsic permselectivity of the membrane. The membrane sample was cut into circular coupons and mounted in a permeation cell comprising of two detachable parts, which have been described elsewhere [12]. The effective area of the membrane for permeation was 13.85 cm^2. The feed gas at a given pressure was admitted to the feed side of membrane, and the permeate side was kept at atmospheric pressure. The permeation rate was measured using a bubble flow meter, and the gas permeance through the membrane was calculated by

$$J = \frac{Q}{A\Delta p} \tag{1}$$

where J is the gas permeance through the membrane, which is expressed customarily in GPU (1 GPU = 10^{-6} cm^3 (STP)/cm^2 s cmHg); Q the gas permeation rate (cm^3 (STP)/s); A the effective membrane area for permeation (cm^2); and Δp the pressure difference across the membrane (cmHg). The selectivity of the membrane to the permeation of a pair of gases is characterized in terms of their permeance ratio. The gas permeability coefficient, which is equal to the permeance multiplied by the membrane thickness, is expressed in terms of the unit Barrer (1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg).

To test the permselectivity of the PEBA/PSf hollow fiber composite membranes, a miniature hollow fiber membrane module was assembled using a bundle of four hollow fibers encased in a 1/4 in. copper tubing. One end of the fiber bundle was sealed with an epoxy resin, whereas the other end was potted with epoxy to form a gas-tight tube sheet. The tube sheet was carefully cut to make the fiber bores fully open. The feed gas at a predetermined pressure entered the shell side of the module, and the permeate gas exited at atmospheric pressure from the open end of the fiber bores. The effective length of each hollow fiber was 15 cm, which corresponds to a total permeation area of 11.3 cm^2 in the membrane module. The permeate pressure buildup inside the hollow fibers was found to be negligibly small, and the gas permeance through the hollow fibers was evaluated from the permeation rate measurements using the same method as that used for determining the flat membrane permeability.

3. Results and discussion

3.1. Gas permeation through dense flat membranes

The permeation of pure carbon dioxide and nitrogen through a dense PEBA 2533 membrane at different operating pressures and temperatures were investigated to obtain the intrinsic permselectivity of the PEBA membranes. The effect of feed pressure on the gas permeability at various operating temperatures is shown in Fig. 1. The permeability of nitrogen is shown not to be affected significantly by the feed pressure. At a high temperature (i.e. 60 °C), the nitrogen permeability tends to decrease slightly as the pressure increases, primarily due to compaction of the membrane. When the diffusivity and solubility coefficients of nitrogen in the membrane are constant and if the membrane compaction is insignificant, the membrane permeability will be independent of the gas pressure. This is normally the case for permeation of non-condensable gas molecules in rubbery membranes. However, the permeability of carbon dioxide through the PEBA membrane increases slightly with an increase in the feed pressure, especially when the temperature is relatively low. The latter observation is believed to be the result of membrane plas-

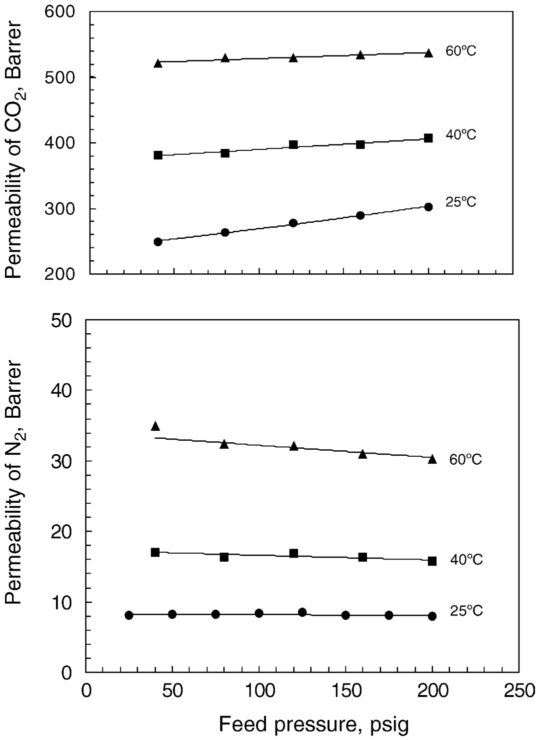

Fig. 1. Permeability of carbon dioxide and nitrogen through the dense PEBA membrane as a function of feed pressure at different temperatures.

ticization by the permeant. There exists a strong interaction between carbon dioxide and the polymer material, as reflected by the strong sorption of carbon dioxide in the polymer [5]. When a sufficiently large amount of CO_2 is sorbed into the membrane, the polymer is swollen and the free volume of the membrane increases, leading to an increase in the gas permeability. The plasticization effect is generally reflected by the dependence of the effective diffusivity coefficient and/or permeability coefficient on the penetrant concentration in the polymer. It needs to be pointed out that in practical membrane gas separations where a gas mixture is involved, the membrane swelling by a penetrant will affect the permeation of all components in the mixture, and the membrane selectivity is generally lower than that would be obtained on the basis of pure gas permeability.

It should be pointed out that the intrinsic CO_2 permeabilities of PEBA 2533 dense membranes reported in the literature are quite different. Kim et al. [4] measured the CO_2 permeability to be 142 Barrer at 25 °C, while Bondar et al. [6] and Wilks and Rezac [11] reported a CO_2 permeability of 222 and 350 Barrer, respectively, at 35 °C. Based on the experimental data of Wilks and Rezac [11], the CO_2 permeability at 25 °C can be estimated to be 320 Barrer. In this study, the CO_2 permeability at 25 °C was determined to be 260 Barrer, a value that falls within the range of permeabilities reported in the literature. The difference in the permeability, which apparently cannot be attributed only to the different measurement conditions, is due to the fact that PEBA is a block copolymer comprising of soft ether segments and hard amide segments. Hatfield et al. [13] characterized the structure and morphology of the PEBA polymers using X-ray diffraction, differential scanning calorimetry and solid state nuclear magnetic resonance, and found that the polymer exhibited microphase separated morphology. A recent study on the morphological solid state structure of a series of PEBA polymers verified that the microphase separated morphology existed over a broad temperature range [14], and it was also found that the complex morphology was strongly affected by the sample's thermal and process history. As one expects, the membrane morphology affects the gas permeability. This explains the discrepancy in the permeability coefficients reported. This is why instead of using the literature values, the intrinsic permeability was actually measured here in order to evaluate how well the hollow fiber composite membranes compare with a dense membrane in terms of permselectivity for CO_2/N_2 separation. It may be mentioned that similar observations can also be made on gas permeability through PEBA 3533, a polymer having the same constituent blocks as PEBA 2533 but with a higher content of amide blocks; for example, Kim et al. [4] determined that at 25 °C and 4 atm the CO_2 and H_2 permeabilities through PEBA 3533 were 132 and 20 Barrer, respectively, which are significantly different from the data reported by Wilks and Rezac [11] (230 and 46 Barrer, respectively, at 35 °C and 10 atm).

Previous studies [15–18] have shown that gas sorption in glassy polymers can be characterized by the dual-mode sorption model and as such the permeability tends to decrease with an increase in the feed pressure when the pressure is relatively low due to competitive nature of Langmuir sorption. However, when the feed pressure is sufficiently high, the permeability tends to increase with a further increase in the feed gas pressure because membrane plasticization is increasingly important [19,20]. For rubbery polymer membranes that have no Langmuir "sorption sites", the membrane permeability tends to increase as the feed pressure increases because of membrane swelling. PEBA 2533 is a copolymer comprising of 20 wt.% glassy polyamide segments and 80 wt.% rubbery polyether segments. Apparently, the above-observed pressure dependence of CO_2 permeability in the PEBA membrane is due to the combined effects of Langmuir sorption on polyamide segments and the swelling of polyether segments.

The experimental data in Fig. 1 show that at 25 °C an increase in gas pressure from 40 to 200 psig will increase the permeability of carbon dioxide by about 21%, while at 60 °C the same pressure change results in only 3% increase in the membrane permeability. Clearly this indicates that the plasticization and swelling of the membrane is less significant at higher temperatures. This is in agreement with physical reasoning that the solubility of carbon dioxide in the polymer decreases at higher temperatures, rendering membrane plasticization/swelling by the permeant less significant. Okamoto et al. [21], who studied CO_2 permeation through glassy polyimide membranes, also found that the plasticization of the membrane became less significant as the operating temperature increased.

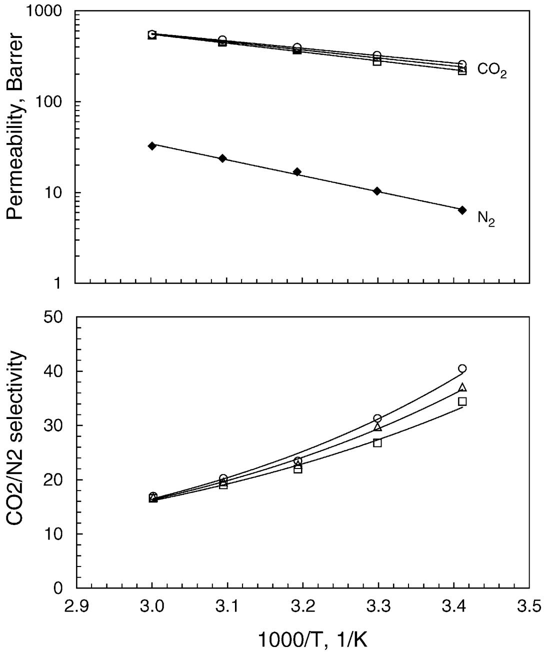

Fig. 2. Temperature dependence of CO_2/N_2 permselectivity through the dense PEBA membrane. Feed pressure: (□) 50 psig; (△) 100 psig; (○) 150 psig; (◆) 20–150 psig.

Fig. 2 shows the effect of operating temperature on the membrane permeability for permeation of carbon dioxide and nitrogen through the dense PEBA membrane in a temperature range of 25–60 °C. Note that as shown previously, the feed gas pressure has little effect on nitrogen permeability, and the nitrogen permeability data in the figure were obtained at a feed pressure of 20–150 psig. The selectivity of the membrane for CO_2/N_2 expressed in terms of pure gas permeability ratio is also shown in Fig. 2. It is shown that the temperature dependence of permeability follows the Arrhenius relation for both N_2 and CO_2 permeation. The activation energy for permeation, which is determined from the slope of the Arrhenius plot, is presented in Table 1. Unlike nitrogen permeability, which is essentially independent of pressure, the permeability of CO_2 is affected by pressure, and so is the activation energy for carbon dioxide permeation. The activation energy for permeation can be approximated as the sum of activation energy for diffusion and the heat of sorption. The activation energy for diffusion may be considered as the minimum energy that molecules must possess to achieve molecular jumps. In general, small molecules tend to have a high diffusivity coefficient and low activation energy for diffusion, whereas condensable gases tend to have a higher solubility and stronger sorption heat effect (which is often exothermic) than noncondensable gases. The activation energy of diffusion for N_2 and CO_2 should be similar considering their similar kinetic diameters (which are 0.36 and 0.33 nm for N_2 and CO_2, respectively [22]), and as such the relative magnitude of the activation energy for permeation of CO_2 and N_2 would be mainly determined by their relative sorption heat. Therefore, it is not surprising that the activation energy for N_2 permeation is greater than that for CO_2 permeation considering the fact that CO_2 molecules are more condensable than N_2. As a result, the selectivity of carbon dioxide over nitrogen decreases with an increase in the operating temperature. As the feed pressure increases, the activation energy for carbon dioxide permeation decreases, which may be attributed to the increased swelling of the membrane caused by the increased quantity of CO_2 dissolved in the membrane.

Table 1
Activation energy of permeation

Gas	Pressure (psig)	E_p (kJ/mol)
Nitrogen	20–150	33.6
Carbon dioxide	50	18.6
	100	17.0
	150	15.6

At 25 °C and 100 psig, the dense PEBA membrane exhibited a CO_2 permeability of about 260 Barrer and a CO_2/N_2 permeability ratio of about 30–35, which can be considered to be the intrinsic properties of the membrane in subsequent studies of hollow fiber PEBA/PSf composite membranes.

3.2. PEBA/PSf hollow fiber composite membranes

It is well known that the permselectivity of a composite membrane is generally affected by the parameters involved in the formation of both the membrane substrate and the skin layer. The appropriate conditions for preparing PSf hollow fiber substrate and PEBA coating were thus investigated. In preliminary studies, the dope composition for PSf fiber spinning, the PEBA concentration in coating solution and the coating temperature were found to influence the performance of the resulting composite membranes significantly. These parameters were specifically studied on the basis of the “one variable at a time” method.

3.2.1. Effect of dope composition on PSf hollow fiber spinning

Two representative polymer dope solutions containing PSf/NMP/PEG (wt.%) 19/79.4/2.6 and 23/77/0, designated as dope I and dope II, respectively, were used to produce microporous PSf hollow fibers for use as a substrate to the composite PEBA membranes. De-ionized water was used as the bore fluid. The air gap between the spinneret and the coagulation bath was 5 cm. The detailed operating conditions for hollow fiber spinning are summarized in Table 2. The hollow fibers were coated at 50 °C with PEBA solutions containing

Table 2
Hollow fiber substrate spinning conditions

Spinning pressure	30–60 kPa gauge
Spinning temperature	23 °C
Air gap	5 cm
Bore fluid	Water
Bore fluid flow rate	1.2–2.0 ml/min
External coagulant	Water
Coagulation temperature	23 °C
Fiber take-up speed	7 m/min

Table 3
The gas permeation performance of CO_2/N_2 through PEBA/PSf composite membranes

Dope composition for PSf hollow fiber spinning (wt.%) (PSf/NMP/PEG)	PEBA wt.% in coating solution	Number of coating times	Permeance (GPU)		CO_2/N_2 selectivity
			CO_2	N_2	
Dope I: 19/79.4/2.6	1.5	3	17.0	0.88	19.3
	1.5	4	40.5	1.93	21.0
	3.0	2	27.7	1.14	24.2
	3.0	2	22.1	1.29	17.1
Dope II: 23/74/0	1.5	2	17.0	0.58	30.2
	3.0	1	35.7	1.18	29.1

PEBA coating temperature: 50 °C. Gas permeation test temperature and pressure: 25 °C and 50 psig.

1.5 or 3 wt.% PEBA to form composite membranes. It was found to be difficult to achieve a composite membrane with a selectivity reasonably close to the intrinsic selectivity of PEBA 2533 when the PSf hollow fibers prepared from dope I were used as the substrate, even with repeated coating of PEBA layer for several times.

The typical results of membrane permselectivity achieved under different membrane preparation conditions were presented in Table 3. However, when the PSf substrate prepared from dope II was used, only one or two PEBA coatings, depending on PEBA content in the coating solution, were sufficient to obtain PEBA/PSf membranes with a CO_2/N_2 selectivity of about 30. This is understandable because both the presence of PEG additive and the relatively small content of PSf in dope I contribute to the formation of large pores in the hollow fiber membrane matrix during the phase inversion process. If the pore size is too large, the PEBA coating solution would penetrate into the pores of the PSf substrate; upon evaporation of the solvent in the PEBA solution, the thin layer of PEBA formed over the pore that is designed to bridge the “gap” may collapse, rendering the membrane surface defective. On the other hand, the penetration of PEBA coating solution in the substrate pores will increase the resistance of the substrate to gas permeation. Consequently, the membrane permeability decreases while the selectivity does not improve significantly. Because of the relatively low polymer content in the PEBA coating solution, even the use of multiple coatings cannot guarantee that the membrane defects will be repaired because of the possible re-dissolution of the prior thin coating layer by the solvent in the coating solution. This explains why increasing the number of coating times does not always reduce the membrane permeability.

From a membrane manufacturing point of view, a single coating process is preferred, though this sometimes requires the use of relatively high polymer concentration in the coating solution. The data in Table 3 show the two composite membranes prepared using dope II have essentially the same selectivity, but the membrane prepared by single coating of a 3 wt.% PEBA solution is about twice as permeable as the membrane prepared by double coatings of a 1.5 wt.% PEBA solution. The gas permeance through a composite membrane is determined by the resistance of both the coating layer and the microporous substrate, while the membrane selectivity to a pair of gases is determined by their relative permeance. When the coating layer dominates the overall resistance to gas permeation, the membrane selectivity will approach the intrinsic selectivity of the coating material. The above results indicate that by coating the polysulfone substrate with 3 wt.% PEBA once or with 1.5 wt.% PEBA twice, all the pores on the substrate have essentially been bridged to form a defect-free PEBA layer. Ideally, a thin layer of PEBA layer would form on the surface of the polysulfone substrate, and the PEBA layer is responsible for selective permeation whereas the substrate functions only as a mechanical support. However, because of the relatively low viscosity of the 1.5 wt.% PEBA solution, the coating solution is more likely to “leak” into the pores of the substrate, and the pore blocking will decrease the permeance of the composite membrane. Consequently, the selectivity of the membranes will be the same and close to the intrinsic selectivity as long as the PEBA layer dominates the permeation, and the permeance of the composite membrane will be smaller when a low concentration of coating solution is used. An evaluation of the resistance components in the composite membranes on the basis of the resistance model [23], which is not pursued here, could be used to provide a quantitative explanation. In subsequent studies, only PSf substrates prepared from dope II were used to prepare composite membranes, and the membrane performance was evaluated at 25 °C and 50 psig, unless specified otherwise.

3.2.2. *Effect of PEBA coating conditions*

The effect of PEBA concentration in coating solution on the permselectivity of the resulting composite membrane is shown in Fig. 3. A single coating was applied in all cases. Without PEBA coating, the PSf substrate membrane was highly permeable (about 3000 GPU) but of little selectivity. The CO_2/N_2 permeance ratio was only 0.88, which is just slightly higher than the reciprocal square root of their molecular weight ratio (i.e. 0.80), indicating that Knudsen diffusion dominated the gas permeation through the membrane substrate and there were no large defects that would allow for significant viscous flow. After coating with 0.5 wt.% PEBA solution, the membrane permeance for both gases decreased substantially but the permeance ratio was still too low (only 1.2). Apparently, at a low concentration of coating solution, a defect-free PEBA coating layer cannot be formed on the PSf

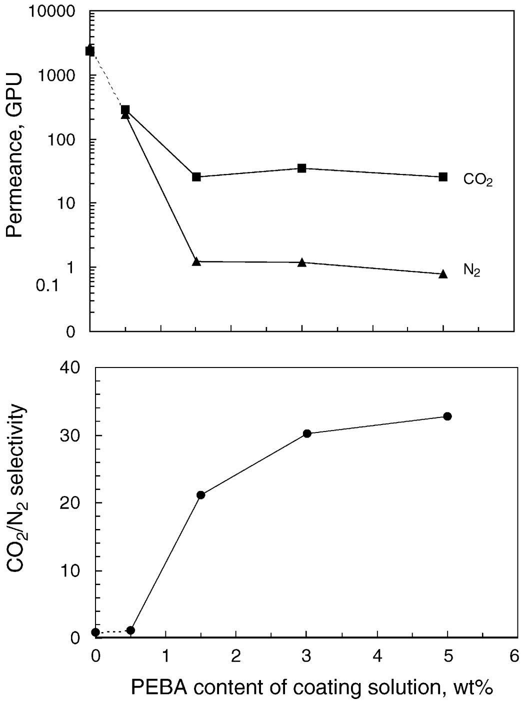

Fig. 3. Effect of PEBA concentration in coating solution on the performance of PEBA/PSf hollow fiber composite membranes (PEBA coating once, coating temperature 50 °C, permeation test at 50 psig, 25 °C).

substrate. When the PEBA content in the coating solution was increased to 1.5 wt.%, the membrane permeability continued to decrease but the decrease is more discriminative in favor of CO_2 permeation, and as a result the membrane began to exhibit significant selectivity for CO_2/N_2. A further increase in the PEBA coating concentration to 3 or 5 wt.% resulted in a CO_2/N_2 selectivity of 30–32, which matches the intrinsic selectivity of PEBA polymer, as shown previously. This suggests that the composite membrane is defect-free and that the PEBA skin layer dominates the permeation.

The effect of coating temperature on the membrane performance is shown in Fig. 4. The temperature of the coating solution was maintained the same as the coating temperature so that there would be no temperature change during the coating process. The coating temperature influences the viscosity of the coating solution and the rate of solvent evaporation, and both aspects affect the resultant membrane. At a low temperature, the viscosity of the coating solution is high, which help prevent the coating solution from penetrating into the pores of substrate. This, however, is compromised by the slow evaporation of solvent in the coating solution. A reduced solvent evaporation rate means a longer contact time between the coating solution and the substrate membrane, which is undesirable because the prolonged contact favors penetration of the coating solution into the substrate pores. The data in Fig. 4 show that as the coating temperature increases, both CO_2 and N_2 permeabilities decrease. The selectivity, expressed in terms of CO_2/N_2 permeance ratio, follows a similar trend in spite of the scatter data points. It should be pointed out that the temperature also influences the solubility of PEBA in the solvent, and the temperature of the coating solution should not be too low in order to retain a well-stretched structure of polymer chains in the coating solution. Using 3 wt.% PEBA coating solution and at a coating temperature of 50 °C, the PEBA/PSf composite membrane exhibited a CO_2 permeance of 61 GPU and a CO_2/N_2 selectivity of 30.

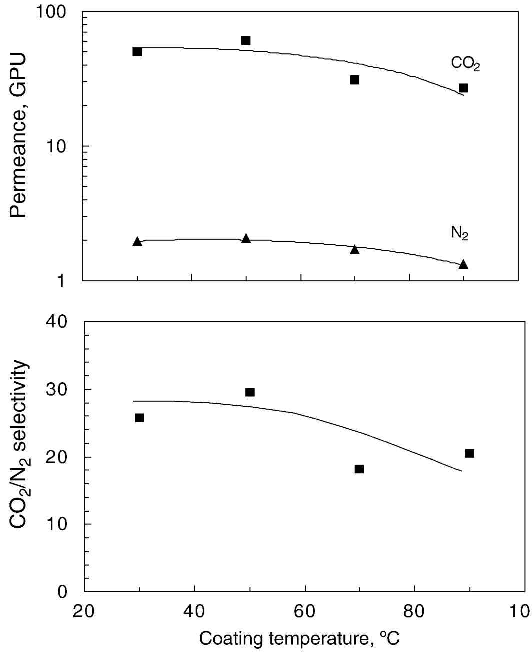

Fig. 4. Effect of PEBA coating temperature on the performance of PEBA/PSf hollow fiber composite membranes (PEBA concentration in coating solution, 3 wt.%, PEBA coating once, permeation test at 50 psig, 25 °C).

3.2.3. Effects of operating conditions on the performance of the composite membranes

Fig. 5 shows the effects of feed pressure on the permeance of carbon dioxide and nitrogen through PEBA/PSf hollow fiber composite membranes at various temperatures. The permeance of carbon dioxide shows a slight increase with an increase in the gas pressure while that of nitrogen is essentially independent of pressure. This trend is consistent with results obtained with dense PEBA film. The permeance of carbon dioxide increases by about 10% when the feed pressure was increased from 10 to 50 psig at all three temperatures investigated. This demonstrates that the effect of plasticization of carbon dioxide in the composite membrane is stronger than in the dense PEBA film, in which remarkable plasticization was only observed at relatively low temperatures. Assuming that the PEBA skin layer in the composite membrane dominates the gas permeation, then on the basis of intrinsic permeability the thickness of the PEBA layer in the composite membrane can be estimated to be less than 5 μm, which is much smaller than the thickness of the dense film (about 55 μm). Wessling et al. [24] also observed that the significance of plasticization

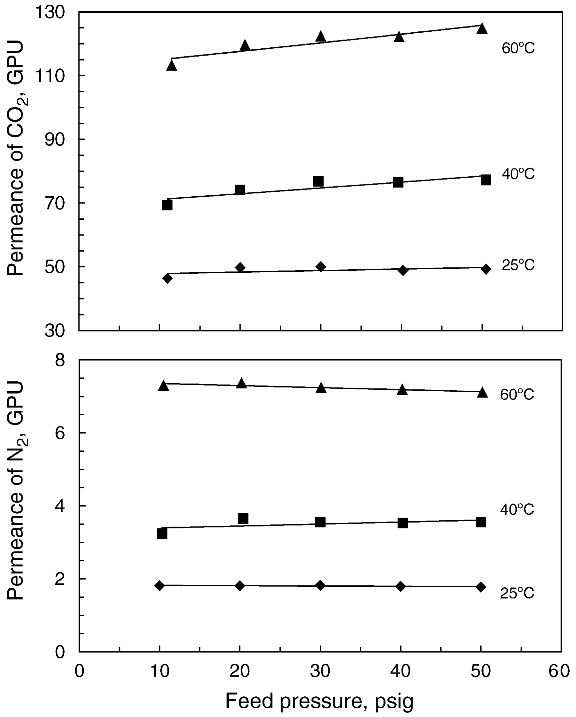

Fig. 5. Permeance of carbon dioxide and nitrogen through PEBA/PSf hollow fiber composite membrane at various pressures and temperatures.

of carbon dioxide in glassy polyimide membranes depends on whether the membrane is a dense film or a thin layer in a composite membrane. A thin layer of polyimide (1.5–4 μm thick) in a composite membrane was found to be plasticized more significantly than a thick (20–50 μm) dense film membrane.

Plasticization of the membrane by a permeant (which is often the fast permeating component) tends to increase the permeability of other components when a gas mixture is involved in actual separations, rendering the membrane less selective. Further studies with permeation of gas mixtures will be needed to determine how the membrane plasticization affects the actual separation performance. However, for the applications of interest (that is, CO_2 capture from flue gas), the desired operating pressure is relatively low because of the costs associated with gas compression and the feed CO_2 concentration is moderate, and thus the membrane plasticization may not be very significant especially for bulk separation of CO_2 from flue gas.

Fig. 6 shows the effect of temperature on the permselectivity of the composite membrane for carbon dioxide and nitrogen permeation. As one may expect, the temperature dependence of membrane permeance follows the Arrhenius type of equation, which is consistent with the results observed earlier with the dense PEBA film. The selectivity of CO_2/N_2 is shown to decrease with an increase in the temperature. This result further confirms that the composite membrane is defect-free and gas permeation through the membrane is by solution–diffusion mechanism.

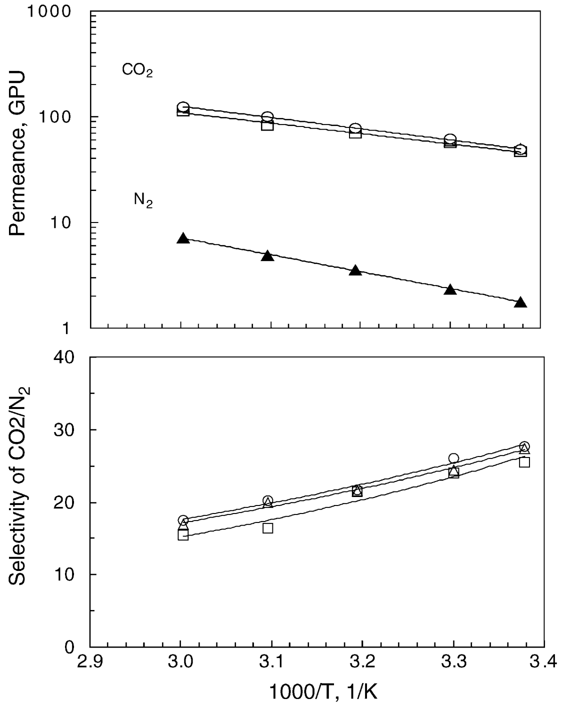

Fig. 6. Effect of temperature on the permeance and selectivity of carbon dioxide and nitrogen through the PEBA/PSf hollow fiber composite membrane. Feed pressure: (□) 10 psig; (△) 30 psig; (○) 50 psig; (▲) 10–50 psig.

4. Conclusions

The permeation of carbon dioxide and nitrogen through poly(ether block amide) (PEBA 2533) dense homogeneous membranes was tested. The polymer showed a good permselectivity for CO_2/N_2 separation; at 25 °C and 100 psig, a carbon dioxide permeability of about 260 Barrer and a CO_2/N_2 selectivity of 32 were obtained. While the permeability of nitrogen is essentially independent of the gas pressure, the permeability of carbon dioxide tends to increase when the gas pressure increases presumably due to plasticization of the membrane by CO_2. This is typical of rubbery polymer membranes. As temperature increases, the effect of plasticization becomes less significant.

In order to increase the membrane permeance, thin-film composite membranes comprising of a thin PEBA skin layer supported on a microporous polysulfone hollow fiber substrate was prepared. The effects of parameters involved in the procedure of polysulfone hollow fiber spinning and PEBA coating on the permselectivity of the resulting composite membranes were investigated. Composite membranes having a CO_2 permeance of 61 GPU and a CO_2/N_2 selectivity of 30 have been obtained. That the selectivity of the composite membrane is very close to the intrinsic selectivity of PEBA dense membrane implies that the composite membrane is defect-free and the PEBA skin layer dominates the permeation.

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