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Effect of the preparation conditions on the properties of polyetherimide hollow fibre membranes for gas separation

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ABSTRACT

Preparation and properties of polyetherimide (PEI) hollow fiber membrane are described in a paper. PEI hollow fibers were produced on the spinning machine by phase inversion process. Experiments were designed with the aim to optimize the process parameters for the production of asymmetric polyetherimide hollow fibers. These parameters include polymer solution flow through the nozzle, bore liquid flow, air-gap distance, and the fiber take-up speed. CO_2/CH_4 gas mixture permeation experiments were performed on produced membranes as well as the morphology studies by optical microscopy and scanning electron microscopy (SEM). The impact of the process parameters on the hollow fiber morphology and mixed gas transport and separation properties was investigated. Results show the critical influence of the bore liquid flow and the take-up speed on the fiber structure. With higher values of these parameters the membranes exhibited higher CO_2/CH_4 selectivities. Tubular aspects of the fiber were obtained without deformations when high bore liquid flows were used. Smaller fiber diameters were achieved when the fiber take-up speed was higher.

Keywords: Hollow fiber membrane; Asymetric membrane; Design of experiments; Selectivity; Polyetherimide; Permeance; Gas separation

1. Introduction

Gas separation membrane systems have been received a lot of attention thanks to their efficiency and their economic and ecological advantages [1,2]. Asymmetric hollow fiber membranes have been recognized very suitable for gas separation; they exhibit high gas fluxes due to ultrathin selective layer, high surface area that can be packed in the unit volume of the membrane module, sufficient mechanical resistance while keeping good transport and separation properties, as well as good productivity, flexibility, and easy handling.

High selectivity and permeance of the material are obviously desirable along with the mechanical properties and chemical resistance; however, the selection of the material should be carefully made in the way that the mixed gas performance is not compromised in the process conditions. Many materials exhibit outstanding performance in the laboratory, but in the real process they fail; usually due to fast physical or chemical aging, plasticization effects, etc. From this reason, only relatively few materials are applied in the industry so far [1–3].

Highly aromatic glassy polymers like polyimides, polysulfones, polyetherimides, etc. are often preferred in indus-

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trial gaseous separations, including natural gas sweetening [4,5]. A polymer with a rigid backbone generally exhibits higher mobility selectivity because it will behave more likely as molecular sieve [6–8].

Typical asymmetric hollow fiber membranes are prepared by phase inversion process using hollow fiber spinning device [9]. The process, involves the introduction of the polymer dope into the annulus of the spinning nozzle where it is co-extruded with the bore liquid in the center and both phases are spun from the nozzle to the water bath. Inside the water bath, the polymer phase coagulates, and the hollow fiber is formed. Residual solvents are washed out and, the hollow fiber membrane is collected and dried out. Often several post-treatments of the hollow fibers are performed, such as swelling in the presence of organic non-solvent or its vapor, coating with another polymer such as silicon rubber, vacuum drying, etc.

They are many parameters which more or less influence the structure, morphology and the gas separation performance of the hollow fiber. Such parameters are: polymer dope composition, an extrusion speed of the dope, bore liquid composition and its extrusion speed, coagulation bath composition, temperature of polymer dope, bore liquid and coagulation bath, washing and drying procedure, post-treatments and others [10–17]. To test all the influences on the gas transport performance require enormous amounts of variation of such conditions resulting in huge amount of samples should be analyzed.

In our work we have prepared a series of hollow fibers made from aromatic polyetherimide (PEI) ULTEM® 1000 under different spinning conditions. These conditions were carefully set up according so called 2^{4-1} one half factorial experimental design [18] to reduce the number of the necessary experiments on half. From the statistical analysis, we have identified the weight of the individual parameters which had an influence on properties of hollow fiber membrane.

2. Experimental

2.1. Materials

Polyetherimide (ULTEM 1000) was obtained from Sabic. The formula of a repeated unit of ULTEM 1000 is shown in Fig. 1. Granules were dried at 105°C for 24 h before use.

Solvent for the PEI was N-methyl-2-pyrrolidone (NMP) with purity 99.5% from producer Sigma-Aldrich. Non-solvent component of spinning solution was absolute ethanol supplied by Penta Chemicals. Precipitation bath was filled by RO water. A solvent exchange fluid includes ethanol and hexane.

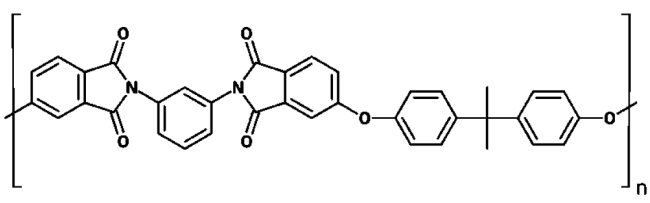

Fig. 1. Repeating unite of polyetherimide Ultem 1000.

2.2. Membrane preparation

Polymer solution was prepared by dissolution of PEI (29 wt. %) in NMP in the reactor which is direct part of the pilot-scale spinning machine from FillaTech, Germany under argon atmosphere. The dope solution was stirred at 40°C about 15 h and then non-solvent (absolute ethanol) was added (11 wt.%). The dope was stirred next 15 h, followed by vacuum degassing. Bore liquid was prepared separately by mixing NMP with RO water in the ratio of 89:15 and filled into spinning machine bore liquid container. Hollow fibers were co-extruded from dope end bore liquid through a spinneret with dimensions 1.5; 1.0; 0.7 mm (outer diameter – OD; inner diameter – ID; lumen). Four spinning conditions dope flow (D), bore liquid flow (B), take up speed (T) and air gap (A) were changed in two levels during membrane preparation. There are only two levels for each factors (k), it is assumed that the response is roughly linear over the range of the levels. Eight types of hollow fibers were prepared and tested which is according half factorial design 2^{k-1}, Table 1. Factorial design is often used in experiments involving several factors [18].

2.3. Membrane testing

2.3.1. Microstructure

Optical microscopy in reflected light was used for assessment and documentation of the membrane microstructure. Inner and outer diameter was evaluated from micrographs.

Detailed microstructure of fiber's wall was studied by scanning electron microscopy. Hollow fibers were broken in liquid nitrogen, fracture surface was stained by thin film of chromium. The membrane was mounted into holder and observed in FEI microscope in secondary electron mode.

2.3.2. Measuring of permeation and selective properties of asymmetric membranes

Laboratory modules containing 10–20 fibers of about 20 cm length were prepared. One end of fibers is closed by epoxy resin. Membranes were treated by ethanol and then annealed in hot air oven at 45°C for 24 h. Mixture of gases is fed to the outer surface of fibers and permeates leaving the center of fibers. Gas permeation experiments were carried out with CH_4/CO_2 mixture 1:1 (by volume) at 8 bar respectively to determine separation properties of asymmetric polyetherimide hollow fiber membrane. A permeate flow was measured by bubble flowmeter and composition of a permeate stream was analyzed by mass spectrometer Prima BT (Thermo Fisher Scientific). Permeance P_i [Eq. (1)] for CO_2 and CH_4 and CO_2/CH_4 mixed gas selectivity α^*_{ij} were evaluated from measured data [19,20]. Permeance P_i [Eq. (1)] is defined as volumetric flow rate per unit driving force per unit area.

$$P_i = \frac{Q_P \cdot y_i}{\left(p_F \cdot x_i - p_p \cdot y_i\right) \cdot A} \quad (1)$$

where Q_p is flow rate of permeate, y_i is the mole fraction of i gas in permeate, p is absolute pressure in the feed or perme-

Table 1
One half factorial experimental spinning design in coded variables

Membrane	Dope (D)	Bore (B)	Take up (T)	Air gap (A)		Level	
A5_1	–1	–1	1	–1		–1	1
A5_2	–1	–1	–1	1	Dope /ml·min^{-1}	2.1	3.0
A5_3	–1	1	1	1	Bore /g·min^{-1}	2.1	2.6
A5_4	–1	1	–1	–1	Take up /m·min^{-1}	9.7	12.0
A5_5	1	–1	1	1	Air gap /cm	2.0	5.0
A5_6	1	–1	–1	–1			
A5_7	1	1	1	–1			
A5_8	1	1	–1	1			

For example membrane A5_4 had dope flow 2.1 ml·min^{-1}, bore liquid flow 2.6 g·min^{-1}, take up speed of 9.7 m·min^{-1} and air gap 2 cm.

ate, x_i and y_i are molar fraction of *i* gas in feed and permeate. *A* is membrane area. The mixed gas selectivity α^*_{ij} of the *i* gas over the *j* gas is calculated as follows:

$$\alpha^*_{i/j} = \frac{P_i'}{P_j'} \tag{2}$$

Permeance unit in this work is reported in GPU – gas permeation unit, where:

$$GPU = 1\cdot 10^{-6}\cdot \frac{cm^3(STP)}{cmHg\cdot s\cdot cm^2} = 7.5\cdot 10^{-12}\, m^3(STP)\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-1} \tag{3}$$

3. Results and discussion

3.1. Microstructure

The outer diameter of hollow fibers is in the range from 530 to 640 mm. In Fig. 2 is a comparison of the microstructure of the best (Fig. 2a) and worst (Fig. 2b) hollow fiber membrane on SEM micrographs. The separation layer is on the outer surface for all samples of hollow fiber membranes without exception. All hollow fibers spun at different conditions contain finger-like macrovoids in the wall of hollow fibers. Larger finger-like voids are oriented wholly in the radial direction. The presence of macrovoids in the wall of the asymmetric membrane may substantially decrease mechanical strength under high pressure. Formation of macrovoid can be inhibited by increasing the dope solution viscosity, by increasing the solvent concentration in bore liquid and by increasing of the fiber take up speed [9,21]. Membrane A5_4 exhibited relatively thin wall, which means that there is a higher probability of the contact between the larger finger-like voids with the separation layer on the outer surface of the hollow fiber, Fig. 2a. This is in accordance with the corresponding CO_2/CH_4 selectivity value of 22.4 (Table 2) which is the lowest from the whole membrane series. Thin wall is most probably the result of the improper ratio of dope solution flow/bore liquid flow. Membrane A5_7, on the other hand, exhibited larger wall thickness and voids are therefore located deeper under outer fiber surface, Fig. 2b. Thicker wall had apparently also a positive influence on the CO_2/CH_4 selectivity which in the case of the A5_7 membrane was the highest from all samples and reached the value of 39.2.

3.2. Mixed gas transport properties

Mixture gas permeation tests were conducted to determine transport and separation properties of membranes.

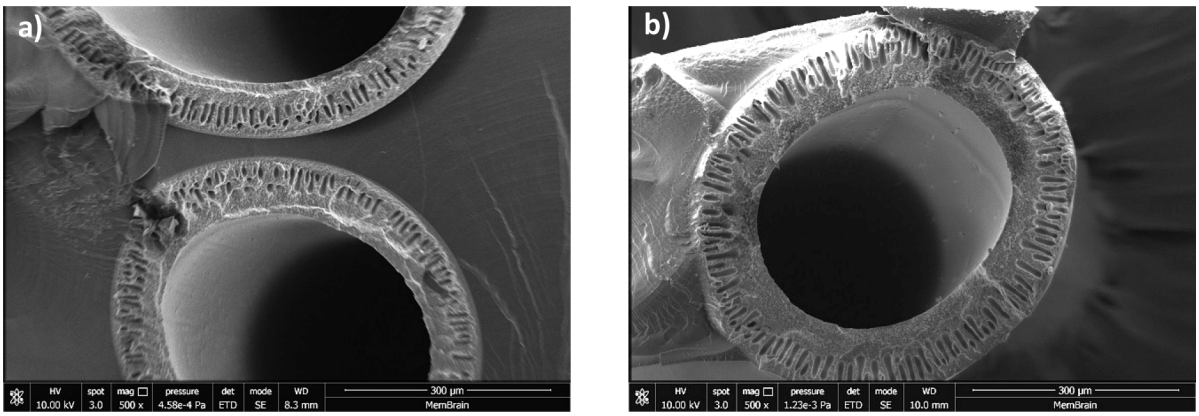

Fig. 2. Comparison of the SEM micrographs of hollow fibre membranes with the lowest (2a) and highest (2b) CO_2/CH_4 selectivity.

Before gas transport measurements, the membrane was treated by immersion into ethanol for 2 min and then annealed at 45°C for 24 h in hot air oven. Heat treatment is supposed to reduce the polymer chain mobility and suppress CO_2 plasticization of a polymer [22,23]. Six laboratory modules were tested in series, where retentate from the first module was used for the second one like feed, this setting minimizes gas consumption and saves time.

The scheme of 2^{4-1} one half factorial design and the influence of the flow rate of the polymer solution (D), the flow of bore liquid (B), take up speed (T), and the air gap (A) on the CO_2/CH_4 selectivity of hollow fiber membrane is presented in Fig. 3. Influence of the spinning process parameters on the quality of membrane was studied with the aid of statistical method for designing of experiments.

Results of permeation tests are summarized in Table 2. It can be clearly seen, that A5_1–A5_4 membranes have significantly lower OD compared to the rest of the membranes which is obviously connected to the lower polymer dope flow. The best transport properties were achieved when the flow of polymer solution, bore liquid and take up speed were on the higher level (+1) and air gap on the lower level (–1) for A5_7 with the CO_2 permeance 19.2 GPU and mixed gas CO_2/CH_4 selectivity 39.2. These values correspond with results which were obtained by Saimani [19]. CO_2 permeability through PEI membrane is given in a range of 1.0 to 1.33 Barrer [25,26]. Apparent thickness of separation layer may be calculated by dividing the permeability of the permeance. The thickness of separation layer of hollow fiber membranes of series A5 varies from 65–135 nm.

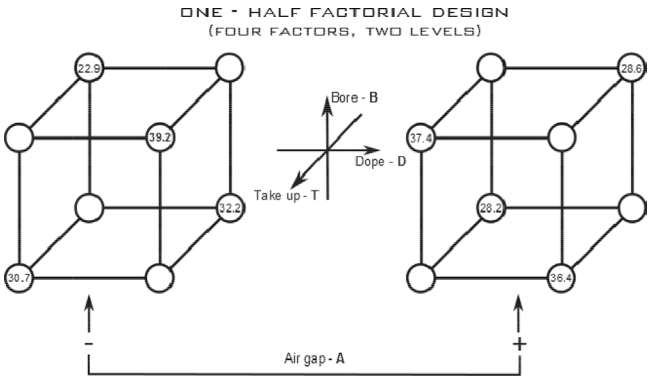

Fig. 3. 2^{4-1} one half factorial design examining effects and interactions of D, B, T and A on the CO_2/CH_4 selectivity of membrane.

Table 2
Results of A5 series hollow fiber membrane

Membrane	OD μm	ID μm	Permeance CO_2 (8 bar) GPU	Selectivity (8 bar)
A5_1	560	371	11.5	30.7
A5_2	556	367	10.3	28.2
A5_3	529	368	17.5	37.4
A5_4	578	397	20.6	22.9
A5_5	620	390	17.3	36.4
A5_6	623	395	16.5	32.2
A5_7	616	401	19.2	39.2
A5_8	640	408	12.8	28.6

DEVELVE software [24] was used to determine which factors and interactions are significant for the membrane selectivity. Main factors which influenced CO_2/CH_4 selectivities of PEI hollow fiber membranes include take up speed, flow of polymer solution and the interactions of the factors: the flow of bore liquid – take up speed. Linear regression model of selectivity for 1:1 mixture CO_2/CH_4 was created based on these calculations.

$$\alpha = 31.9 + 4.0T + 2.3BT + 2.2D \quad (4)$$

Levels of factors are filled into equation in code form (–1; 1). The highest influence of the take up speed on mixed gas selectivities can be explained by increased shear rates on the spinning solution (in the air gap area). High shear rates modify the precipitation path, retard the formation of macro-voids and could tighten the selective layer by more effective macromolecule alignment [27].

Selectivity measured and calculated according to Eq. (3) is compared in graph on Fig. 4. Correlation factor between measured and calculated selectivity is 0.988. Moreover residues between experiment and calculations follow a normal distribution, which means that linear model is adequate [18].

4. Conclusions

Basically defect free hollow fiber membranes were prepared by phase inversion process from PEI solution. One half factorial design examined the effect and interaction of four parameters on the selectivity of the asymmetric hol-

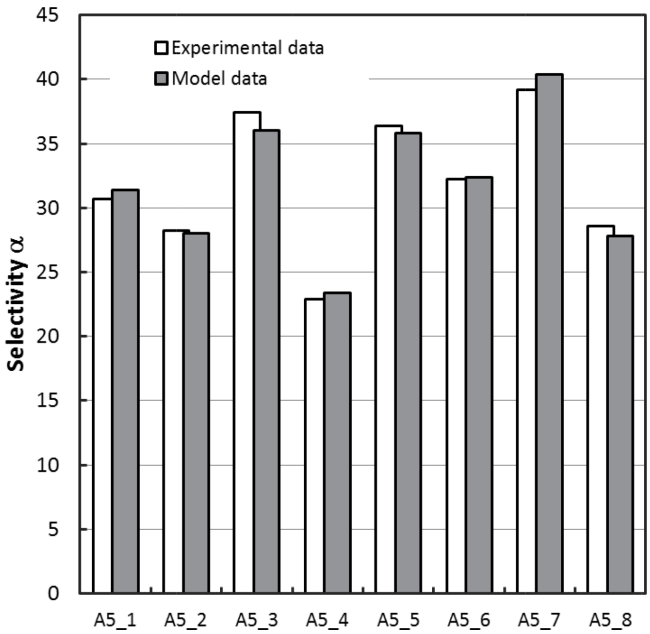

Fig. 4. Comparison of experimental and calculated selectivity of hollow fiber membrane.

low fiber membranes. The best result was achieved when the flow of polymer solution, bore liquid and take up speed were on higher level (+1) and air gap on lower level (–1), $P(CO_2)$ = 19.2 GPU and CO_2/CH_4 α = 39.2. Linear regression model for selectivity calculation was created.

Symbols

OD	—	Outer diameter
ID	—	Inner diameter
P_i'	—	Permeance of *i* component
A	—	Membrane area
p	—	Pressure
x_i	—	Molar fraction of component *i*
α	—	Membrane selectivity
GPU	—	Gas Permeation Unit, 1 GPU = 10^{-6} $cm^3/(cm^2 \cdot s \cdot cm\ Hg) = 7.5 \cdot 10^{-12}$ $m^3/(m^2 \cdot s \cdot Pa)$

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