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Gas Separation Properties of Hollow-Fiber Membranes of Polypropylene and Polycarbonate by Melt-Spinning Method

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This work represents determination of gas separation properties of polypropylene and polycarbonate hollow fiber membranes. Hollow fibers were prepared by melt-spinning method at speed of 100-110 m/min. To improve gas separation properties of hollow fibers, silica nanoparticles were introduced into polycarbonate hollow fibers. Gas permeabilities of O_2, N_2 and CO_2 were measured to determine the gas separation properties of obtained hollow fibers. The polypropylene hollow fibers showed the selectivity of 13.25 for CO_2/N_2 and 3.75 for O_2/N_2. Adding 1 wt. % silica nanoparticles into polycarbonate hollow fibers improved the gas separation properties and increased the selectivity of CO_2/N_2 from 20.50-25.23. Higher selectivity could be achieved by proper distribution of nanoparticles into membrane structure.

Key Words: Hollow-fiber membrane, Gas separation, Permeability, Melt spinning, Nanoparticle.

INTRODUCTION

Membrane gas separation technology is worth noting as an energy-saving alternative to the cryogenic or pressure swing adsorption processes for gas separation applications. In the last decade the membrane separation processes have gained wide applications for capturing CO_2 from natural gas or producing N_2 from air. To improve the applications of membrane-based gas separation, it is necessary to develop new membrane materials which have both excellent permeability and selectivity[1,2].

Hollow-fiber membranes are the most advantageous form of membranes used in the processes of separation, since they provide high surface area-to-volume ratio, low resistance to gas flow and the ability to support high transmembrane pressure drops. Each of these properties contributes to high productivity.

Hollow-fiber membranes can be prepared by any method employed for the preparation of chemical fibers, *i.e.*, they can be spun from melt or half-melt or from a polymer solution[3,4]. The wet-spinning method (phase inversion process) was developed by Loeb and Sourirajan to produce an integrally skinned asymmetric cellulose acetate membrane[3]. Melt-spinning method is the most economic method for preparation of hollow-fiber membranes. It is also a very ecological method, since no wastewater or harmful by-products are involved. The type of membrane which perform particularly well in application to separation of gas mixtures are those membranes with an asymmetric structure[4].

This paper reports the experiments involving the preparation of hollow-fiber membranes made from polycarbonate and polypropylene by melt-spinning method. In this method polymer is extruded at high pressure through a die (a fine capillary). Generally, the polymer is extruded into ambient air that both cools the hollow fiber and exerts drag force on the hollow fibers. At some distance below the die (a meter or more), a mechanical roll provides the force that drives the extrusion process. Sub-spinneret (die) attenuation of the filament diameter occurs along the hollow fiber. The polymer exits from an annular hole.

EXPERIMENTAL

The hollow fibers were made from polycarbonate (Grade PC-175) supplied by CHIMEI-ASAHI Corporation (Taiwan) and polypropylene (Grade R60) supplied by Arak Petrochemical Complex (Iran).

Hollow fibers preparation: The hollow fibers were extruded at high pressure through a die (a fine capillary) which was designed and fabricated for this work. The polymer was extruded into cooling water that both cools the fiber and exerts a drag force on the fiber. The air was used as lumen fluid at 25 ºC and 1 atm. At some distance below the die (a meter), a mechanical roll provides the force that drives the process.

Fig. 1 shows a schematic diagram of a hollow fibers preparation apparatus. Dimensions of die (spinneret) are shown in Fig. 1.

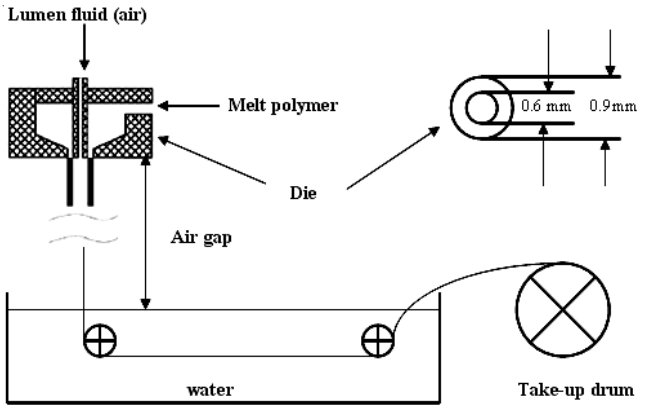

Fig. 1. Schematic drawing of melt spinning apparatus

Variables in the spinning process were: Extrusion rate: 100-110 m/min; melt temperature: 160-190 ºC; cooling conditions:water at 20 ºC.

Stretching of hollow fibers was carried out at room temperature. The dimensions of obtained hollow fibers and spinning conditions are shown in Table-1.

Membrane gas separation properties: The outer diameter, D_{out} and the inner diameter, D_{in}, of the hollow fibers were measured by the micrometer. The gas permeation and separation properties of the hollow-fiber membranes were tested on a test module, as shown in Fig. 2.

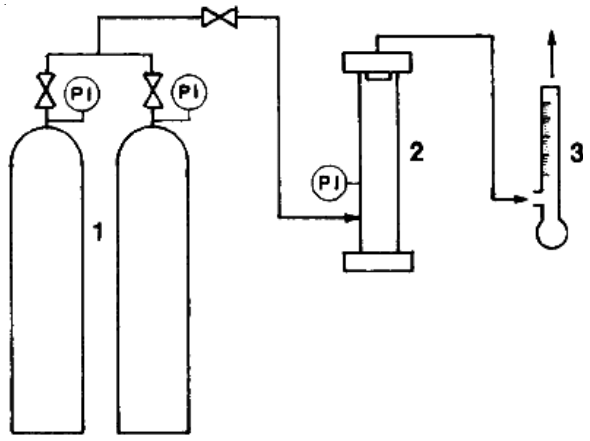

Fig. 2. Test module for measuring gas permeability of hollow-fiber membranes: (1) gas cylinders; (2) pressure vessel with test module; (3) flow-meter[4]

The experiments were carried out at constant controlled temperature condition of 25 ºC. The gases were obtained from local companies (Roham, Iran) and their purities were higher than 99.99 %. The hollow-fiber membranes of known outer and inner diameter (D_{out} and D_{in}) formed into a bunch of known length and number of elementary fibers, *i.e.*, of known area:

$$s = \frac{\pi n l (D_{out} - D_{in})}{\ln(D_{out}/D_{in})} \quad (1)$$

were inserted into a special frame to form the test module. The module was then placed in a pressure vessel. Here, the module frame separated the region of high pressure from the region of low pressure. The gas (O_2, N_2, CO_2) was supplied to the inside of the hollow fibers at a constant pressure $\Delta p = 10$ bars. The rate of permeate flux through the hollow fiber walls with a thickness $x = (D_{out} - D_{in})/2$ was measured by a film flow-meter, determining the time t_i of a soap film through a tube of precisely determined[4] volume ν. The permeability P_i was calculated from the equation:

$$P_i = \frac{\nu x}{t_i s \Delta p} \quad (2)$$

After completing the measurements of permeability (ideal permeability) for the other gas, j, the respective selectivity was calculated:

$$\alpha_j^i = \frac{P_i}{P_j} \quad (3)$$

RESULTS AND DISCUSSION

Table-1 presents the test results for gas permeation and separation properties of the hollow fibers melt-spun from polypropylene, polycarbonate and polycarbonate + 1 wt. % silica nanoparticles by extrusion through spinneret with standard cooling condition.

The results presents that hollow-fiber membranes obtained by melt extrusion from polypropylene do not separate oxygen and nitrogen and are effective in the separation of carbon dioxide and nitrogen. Strong cooling of the polymer spouts leaving the spinneret (die) is a factor leading to the formation of a highly singular type of polymer morphology described as row lamellar structure[4-6].

The results for polycarbonate hollow fibers shows selectivity of 4.33 for O_2/N_2 and 20.50 for CO_2/N_2. Gas permeation results for polycarbonate are better than polypropylene hollow fibers and polycarbonate is suitable for separation of CO_2 and N_2.

Results for polycarbonate + 1 wt. % silica nanoparticles are better than pure polycarbonate. Adding 1 wt. % nanoparticles into polycarbonate structure improved gas separation properties for separation of CO_2 and N_2. Nanoparticles increase the sorption of gases in the polymeric membrane and increase selectivity. They may decrease sorption of other gases through membrane. However, nanoparticles improve the solution-diffusion mechanism for transport of gases through the membrane. These results reveal that nanoparticles increased sorption of

TABLE-1
PERMEABILITIES AND SEPARATION PROPERTIES OF THE HOLLOW FIBER MEMBRANES MELT-SPUN FROM PP, PC AND PC + 1 wt. % FS MEASURED AT 25 ºC, FEED SIDE PRESSURE WAS 11 BARS

Hollow fiber	Spinning conditions			Permeability (Barrer)*			Selectivity	
Material	Extrusion rate (m/min)	D_{out} (μm)	D_{in} (μm)	O_2	N_2	CO_2	O_2/N_2	CO_2/N_2
Polypropylene	100	700	600	0.15	0.04	0.53	3.75	13.25
Polycarbonate	110	800	700	0.26	0.06	1.23	4.33	20.50
PC + 1 wt. % FS	110	850	800	0.17	0.04	1.01	4.25	25.23

*1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cm Hg.

CO_2 and decreased sorption for N_2 and O_2. If nanoparticles are distributed properly into polymer matrix, they show very high gas separation properties[6].

Conclusion

Hollow-fiber membranes made from polypropylene, polycarbonate and polycarbonate + silica nanoparticles were prepared in this work. Hollow fibers were prepared by melt spinning method. Gas permeation of hollow fibers was measured to determine permeability and selectivity of hollow fibers. Permeability of O_2, N_2 and CO_2 gases were measured for three types of fibers. Polypropylene hollow fibers showed selectivity of 3.75 for O_2/N_2 and 13.25 for CO_2/N_2. Silica nanoparticles were added into polycarbonate hollow fibers to improve gas separation properties of polycarbonate hollow fibers. Adding 1 wt. % silica nanoparticles into polycarbonate increased selectivity of CO_2/N_2 from 20.50-25.23.

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