7 A 11 SETEMBRO 2020 | FAURGS | GRAMADO | RS

COBEQ 23° CONGRESSO BRASILEIRO DE ENGENHARIA QUÍMICA

ENBEQ 18° ENCONTRO BRASILEIRO SOBRE O ENSINO DE ENGENHARIA QUÍMICA

OBTAINING DUAL-LAYER HOLLOW FIBER MEMBRANES BY QUADRUPLE SPINNING TO BE APPLIED IN CO_2 SEPARATION

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ABSTRACT – *A novel quadruple spinneret to produce dual-layer hollow fiber membranes by simultaneous spinning of two polymer solutions, using the dual precipitation bath technique, is proposed. Hollow fibers aimed at gas separation processes were prepared in spinning system specifically designed and built for this purpose. A polyurethane polymer was selected as the selective layer (outer-layer), while polyethersulfone was defined as the support (inner-layer). Activated carbon powder was added into the PU solution to further improvement of the transport properties. The hollow fibers showed good adhesion between the polymer layers and a defect-free selective layer. Representative results include a CO_2/N_2 selectivity of 34.6.*

1. INTRODUCTION

Polymeric hollow fibers have been widely used for gas separation (e.g. CO_2/CH_4, O_2/N_2, H_2/CO) allowing a high packing density per module volume, being self-supporting and providing separation systems flexible to be scaled up. Yet, obtaining fibers with a high permeability and selectivity is a permanent challenge due to the complexity of the spinning process (Peng and Chung, 2008).

Phase inversion is the most successfully applied technique to obtain hollow fibers with anisotropic dense skin that will promote gas separation through the sorption-diffusion mechanism. This technique involves a change in the composition of the polymer solution until it becomes thermodynamically unstable, resulting in two phases: a concentrated polymer phase, which will form the solid membrane structure and a lean polymer phase that will originate the pores (Baker, 2004).

For the preparation of integral anisotropic hollow fibers, the greatest challenge is to obtain a thin defect-free dense skin. Van't Hoff *et al.* (1992) were the first to report a dual-bath phase

inversion process to prepare a defect-free integral anisotropic hollow fiber for gas separation. The outer precipitation media starts the formation of a dense outer-layer and the external coagulation bath completes the polymer precipitation of the nascent fiber. This technique was used to synthetize polyethersulfone (PES) hollow fibers with high selectivities using glycerol or 1-pentanol as the first nonsolvent, and water as the second one. For a feed gas with 25 vol% of CO_2 in methane, the intrinsic selectivity of PES [α ($CO_2/CH_4 \approx 50$)] was easily obtained without the necessity of additional coating step.

Accounts reported in the scientific literature show that most studies have been focused on preparing dual-layer anisotropic hollow fiber membranes in one or two steps. The biggest challenge in developing dual-layer hollow fibers by co-extrusion is the adhesion between the layers, since this phenomenon is still not well understood (Fu *et al.*, 2013; Li *et al.*, 2004; Setiawan *et al.*, 2012; Widjojo *et al.*, 2007).

In this work, dual-layer anisotropic hollow fiber membranes are produced in one-step by co-extrusion of polyurethane (PU) and polyethersulfone (PES) solutions. The first solution generates a selective layer (outer-layer), while the second solution allows the formation of the porous support (inner-layer). To improve the transport properties of the selective layer, activated carbon (AC) was added into the PU solution. A quadruple orifice spinneret was designed and used to allow simultaneous spinning of two polymer solutions, as well as the outer precipitation media. To the best of our knowledge, this is the first dual-layer hollow fiber membrane produced through a quadruple spinneret using a dual-bath phase inversion process.

2. EXPERIMENTAL

2.1. Polymeric solutions

Polyurethane (PU) polymer, Ellastolan® PU1185A10, supplied by Basf was chosen as the outer-layer polymer solution and N, N-dimethylformamide (DMF, 99%, Sigma) was used as solvent. Activated carbon (AC) particles (400 nm average particle size), supplied by ConoccoPhillips, were added to the outer-layer solution. Polyethersulfone (PES), P3000, supplied by Solvay and polyvinylpyrrolidone (PVP), K-90, supplied by Sigma-Aldrich, were dissolved in N-methyl-2-pyrrolidone (NMP, 99%, Tedia) to prepare the inner-layer polymer solution (Duarte *et al.*, 2008). PVP is an anphiphilic polymer extensively used as macromolecular additive in membrane fabrication. All polymers were previously dried at 60 ºC for 24 hours before the preparation of polymeric solutions.

2.2. Quadruple spinning

The anisotropic dual-layer hollow fibers were produced by co-extrusion of two polymeric solutions, using the dual precipitation bath technique at room temperature through a quadruple orifice spinneret (Figure 1). The spinning set-up is shown schematically in Figure 2. In order to prepare dual-layer hollow fibers, the inner and outer polymeric solutions were kept at rest for at least 12 hours to eliminate air bubbles. A water/NMP/PVP (46.5/46.5/7 %wt.) solution was used

as bore liquid. The selected water/NMP composition in the bore fluid was suggested by previous studies with a triple extrusion of PU/PES hollow fibers, resulting in controlled and adequate morphologies (Duarte *et al.*, 2002; Duarte *et al.*, 2008). The PVP was added to increase the liquid viscosity. Anhydrous ethanol (EtOH 99.5 %, Vetec) was used as the first precipitation media in the outer annular channel of the quadruple spinneret. An extensive empirical set of experiments led to the definition of the successful values of the operational parameters. The air gap between the spinneret and the external coagulation bath was set at 30 cm (Pereira *et al.*, 2003). The fiber take up rate was adjusted in 3.8 m/min.

The hollow fibers were stored in demineralized water at 60 °C for at least 12 hours for removal of residual compounds (PVP, DMF and NMP). Subsequently, the fibers were maintained initially in ethanol (95 %, Vetec) for 2 hours and, then, in hexane (65 %, Vetec) for 2 hours. The hollow fibers were then dried at room temperature for 12 hours.

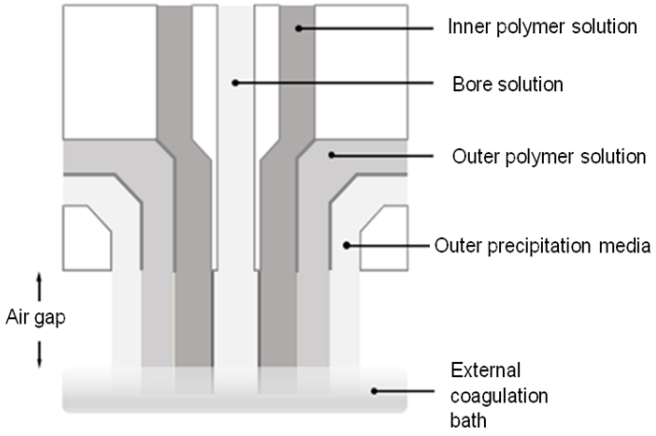


Figure 1 – Schematic cross section of the quadruple spinneret.

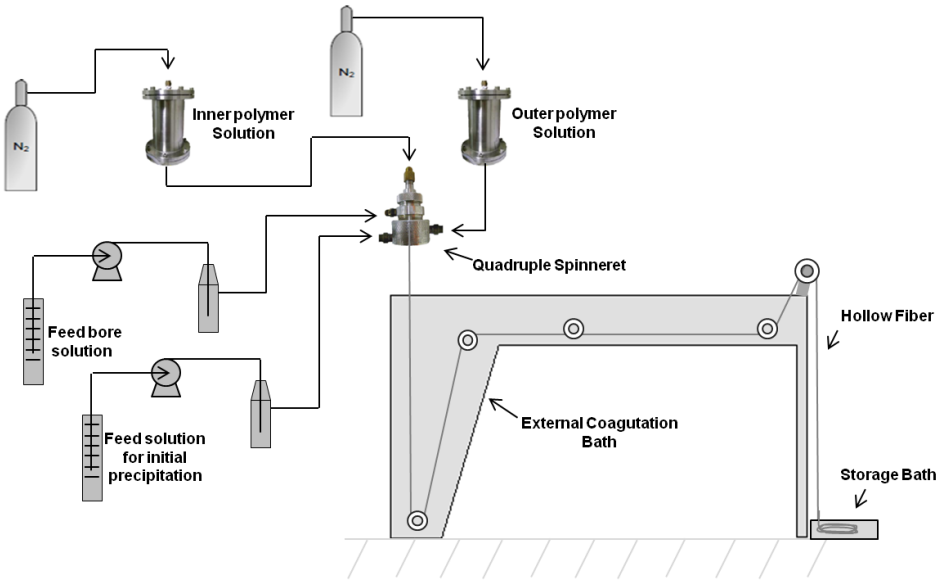


Figure 2 – Schematic of the hollow fiber spinning system.

2.3. Membrane morphology

Membranes samples were prepared by immersing the samples in liquid nitrogen in order to fracture them and to minimize deformation. The samples were metalized with gold by sputtering (Q150R ES Quorum). Morphology of the hollow fibers was observed with a scanning electron microscope (Quanta 200, Fei Company and EVO MA-1, Zeiss).

2.4. Permeance measurements

Gas permeance experiments were carried out at 25 ºC using pure CO_2 and N_2 and a hollow fiber module. In the membrane module the shell side was pressurized by the feed gas and the permeate was collected in the lumen of the fibers, which is connected to a permeate chamber containing a pressure transducer.

Gas permeance, normally expressed in GPU (1 GPU = 10^{-6} $cm^3(STP)/cm^2cmHg$) can be correlated with the pressure increase in the permeate chamber as shown in Equation 1:

$$Permeance = \frac{dp}{dt}\left(\frac{V_{chamber}}{A \cdot \Delta p}\right) \cdot \left(\frac{T_{STP}}{T \cdot P_{STP}}\right) \quad (1)$$

where (dp/dt) is a measure of the average increase of pressure with time in the permeate chamber ($V_{chamber}$), A is the hollow fiber permeation area, Δp is the gas pressure difference through the hollow fiber sides, and T , T_{STP} and P_{STP} are the test temperature, the standard temperature and the standard pressure, respectively.

3. RESULTS AND DISCUSSION

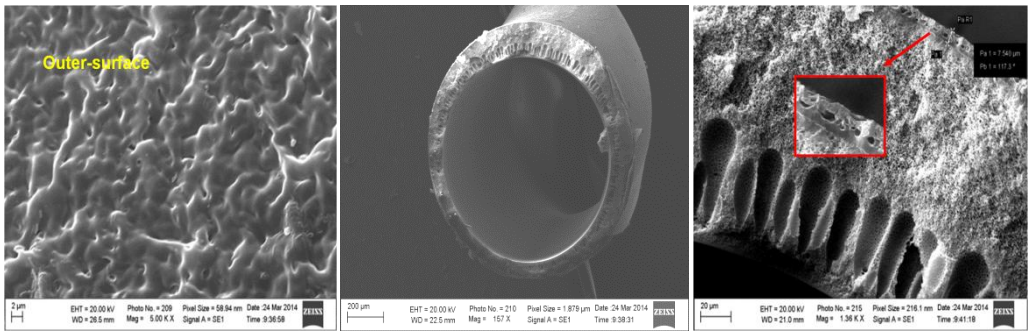
3.1. Hollow fiber spinning

Comparing with single-layer asymmetric hollow fiber membranes, delamination phenomenon is critical in the co-extrusion approach as described by several works and, in particular, by Li *et al.* (2004). This undesirable effect depends on several complex interdependent phenomena occurring during membrane formation, such as the mass transfer between polymer solutions in the early stages of the spinning process and the die-swell effect at the spinneret outlet. The authors found that the use of the same solvent for the polymeric solutions facilitated the interpenetration between the layers, resulting in a defect-free dual-layer hollow fiber with an interconnected porous structure at the interface, enhancing the mass transport kinetics through the nascent membrane. In this work aimed at obtaining defect free membranes for gas separation, anhydrous ethanol was used as the outer precipitation media. For all investigated spinning conditions NMP/water/PVP solution (46.5/46.5/7 wt%) was used in the bore liquid. The addition of NMP in the bore liquid aims to reduce the mass exchange intensity with the inner polymer solution, delaying the onset of phase separation and favoring sponge-like morphology. Addition of

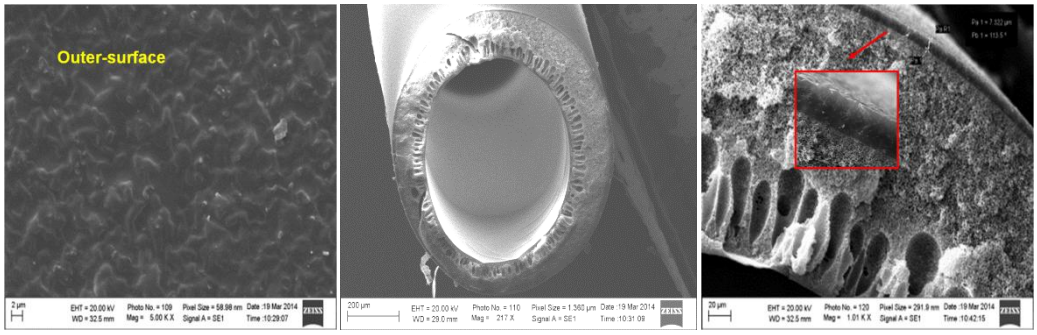
PVP in the bore liquid aims to increase its viscosity in order to avoid irregularities in the inner diameter of the hollow fiber by die-swell effects (Fu *et al.*, 2013; Zhu *et al.*, 2014)

Figure 3 shows the photomicrographs of dual-layer hollow fibers. Anhydrous ethanol as the outer precipitation media promoted adhesion between layers along the entire perimeter of the hollow fibers. Moreover, it was observed a densification of the outer surface of the fiber.

This figure also compares the fibers produced with and without AC in the outer polymer solution. When AC was added to the outer polymer solution (Figure 3(b)) an increase in the viscosity was observed, which facilitates co-extrusion spinning. The presence of this inorganic filler in the polymer solution also changes the outer-layer morphology reducing macrovoids formation, as observed by other authors (Fu *et al.*, 2013; Shi *et al.*, 2008).This effect may be related to changes in the mass transfer flow rates due to higher viscosity of the polymer solution. In addition, morphology examination of fiber samples did not reveal unequivocally presence of particles, even of the larger ones observed in the particle size distribution, but there was clearly a uniform strong darkening (black color) of the outer-layer of the hollow fiber with the addition of AC, whereas the original free AC outer-layer was completely translucent. In this figure one may notice that the bore liquid composition still promoted growth of macrovoids.



(a)



(b)

Figure 3 – Photomicrographs of hollow fibers produced with anhydrous ethanol as the outer precipitation media. Outer polymer solution: (a) PU/DMF (25/75 wt%); (b) PU/AC/DMF (22.5/2.5/75 wt%). Inner polymer solution: PES/PVP/NMP (20/7/73 wt%); Bore liquid: NMP/water/PVP (46.5/46.5/7 wt%).

3.2. Gas permeation tests

Table 1 summarizes the results of gas permeation tests of dual-layer hollow fiber membranes. The tests were undertaken maintaining the feed side at 3 bar and the permeate at atmospheric pressure. In the permeation process of dense membranes, elastomeric polymers such as PU show that permeant solubility is the limiting step. Therefore, more condensable gases such as CO_2 permeate faster (Baker, 2004). As it can be seen in Table 1, the presence of activated carbon in the polymer solution seems to improve even more the gas selectivity. As one can attribute to visco-elasticity phenomena during die- swell one of the possible cause of defects in the outer-layer, the addition of inorganic particles in the polymer solutions may have reduced this effect during the spinning process. Duarte *et al.* (2008) obtained CO_2/N_2 ideal selectivity of 49 for a composite membrane of PU/PES produced by triple spinning; however, the CO_2 gas permeance was 0.53 GPU. In the present work, the quadruple spinning promoted CO_2 gas permeance of 3.5 GPU, showing an improvement of almost 7 times.

Table 1 – CO_2 and N_2 permeance of hollow fibers spun by quadruple spinneret. Tests performed in triplicate at 25 ºC and pressure difference of 3 bar.

Fiber	Outer polymer solution (PU/DMF/AC)	Gas	Permeance GPU	Variation Coef. (%)	Selectivity CO_2/N_2
PU/PES	25/75/0	CO_2	15.7	0.8	6.9
		N_2	2.3	9.1	
AC-PU/PES	22.5/75/2.5	CO_2	3.5	1.1	34.6
		N_2	0.1	15.4	

4. CONCLUSIONS

Novel dual-layer PU/PES hollow fiber membranes have been prepared aiming at applications in gas separation. The newly developed quadruple spinneret allowed the production of dual-layer hollow fiber membranes with CO_2/N_2 selectivity of 34.6. Anhydrous ethanol was used in the outer annular channel of the quadruple spinneret as outer precipitation media to produce a defect-free outer-layer. This condition also promoted very good adhesion between the outer- and inner-layers along and over the surface of the hollow fibers. Addition of activated carbon in the outer polymer solution improved the gas separation selectivity. The results achieved in this work point out that this unique quadruple spinneret fabricating technique can provide useful insights in the science and engineering of selective polymeric membranes as well as new strategies to prepare dual-layer hollow fiber membrane useful for gas separation processes.

5. ACKNOWLEDGMENTS

CNPq and CAPES, Brazilian government agencies, are acknowledged for providing scholarships during the development of this research.

6. REFERENCES

PENG, N. AND CHUNG, T.S. The effect of spinneret dimension and hollow fiber dimension on gas separation performance of ultra-thin defect-free Torlon® hollow fiber membranes. *J. Membr. Sci.*, v. 310, p. 455-465, 2008.

BAKER, R.W. *Membrane Technology and Applications*; 2ndEd.; John Wiley & Sons Inc.: Chichester, U.K., 2004

VAN'T HOF, J.A.; REUVERS, A.J.; BOOM, R.M.; ROLEVINK, H.H.M.; SMOLD, C.A. Preparation of asymmetric gas separation membranes with high selectivity by a dual-bath coagulation method. *J. Memb. Sci.*, v. 70, p. 17-30, 1992.

LI, D.; CHUNG, T.-S.; WANG, R. Morphological aspects and structure control of dual-layer asymmetric hollow fiber membranes formed by a simultaneous co-extrusion approach. *J. Membr. Sci.*, v. 243, p. 155-175, 2004.

FU, F.-J.; ZHANG, S.; SUN, S.-P.; WANG, K.-Y; CHUNG, T.-S. POSS-containing delamination-free dual-layer hollow fiber membranes for forward osmosis and osmotic power generation. *J. Memb. Sci.*, v. 443, p. 144-155, 2013.

SETIAWAN, L.; SHI, L.; KRANTZ, W.B.; WANG, R. Explorations of delamination and irregular structure in poly(amide-imide)-polyethersulfone dual layer hollow fiber membranes. *J. Membr. Sci.*, v. 423-424, p. 73-84, 2012.

WIDJOJO, N.; CHUNG, T.-S.; KRANTZ, W.B. A morphological and structural study of Ultem/P84 copolyimide dual-layer hollow fiber membranes with delamination-free morphology. *J. Memb. Sci.*, v. 294, p. 132-146, 2007.

ZHU, W.-P.; SUN, S.-P.; GAO, J.; FU, F.-J.; CHUNG, T.-S. Dual-layer polybenzimidazole/polyethersulfone (PBI/PES) nanofiltration (NF) hollow fiber membranes for heavy metals removal form wastewater. *J. Membr. Sci.*, v. 456, p. 117-127, 2014.

DUARTE, L.T.; PEREIRA, C.C.; HABERT, A.C.; BORGES, C.P. Polyurethane/polyethersulphone composite hollow fibers produced by co-extrusion spinning of two polymer solutions. *J. Membr. Sci.*, v. 311, p. 12-22, 2008.

PEREIRA, C.C.; NOBREGA, R.; PEINEMANN, K.V.; BORGES, C.P. Hollow fiber membranes obtained by simultaneous spinning of two polymer solutions: a morphological study. *J. Memb. Sci.*, v. 226, p. 35-50, 2003.

DUARTE, L.T.; HABERT, A.C.; BORGES, C.P. Preparation and morphological characterization of polyurethane/polyethersulfone composite membranes. *Desalination*, v. 145, p. 53-59, 2002.

SHI, L.; WANG, R.; CAO, Y.; LIANG, D.T.; TAY, J.H. Effect of additives on the fabrication of poly(vinylidenefluoride-co-hexafluropropylene) (PVDF-HFP) asymmetric microporous hollow fiber membranes. *J. Membr. Sci.*, v. 315, p. 195–204, 2008.