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Properties of Polymer Solutions Intended for Formation of Hollow Fibers Membranes by Inversion Phases Process

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Abstract:
The gas separation process by asymmetric polymeric membranes has received much attention during the last decades because of its more energy efficiency than other conventional separation processes. Hollow fibers are the most favored membrane geometry owing to their high surface area per unit volume of membrane module. One of the key elements determining the potential and applications of asymmetric hollow-fiber membranes are the structural properties mainly including pore size, pore distribution, selective layer thickness, molecular orientation and defectiveness. These elements can generally vary depending on conditions during dry-jet wet-spinning process. Flow conditions in spinneret during extrusion are known to affect the dense-layer of hollow fibers and possibly to enhance separation performance of hollow fibers. The aim of this study was to determine flow conditions of polyetherimide/N-Methyl-2-pyrrolidone solvent/ethanol non-solvent spinning solutions flowing through concentric annulus of spinneret during hollow fiber spinning process. The rotational rheometer was used to characterize rheological properties of spinning solutions. Newtonian behavior of the spinning solutions with arbitrary composition was shown. The effect of spinning solution and spinneret dimension on flow profile in spinneret was investigated. The Newtonian character of the spinning solutions caused constant velocity profile resp. shear rate profile regardless of dope composition when flowing through a spinneret with some flowrate. It has been shown the spinneret dimensions and geometry play a crucial role in controlling the shear flow in spinneret. The phase behavior of the PEI/NMP/EtOH dope system at a temperature of the hollow fiber spinning process (40 °C) was studied.

Key words:
Hollow fiber spinning, flow profile, spinneret, phase separation, binodal curve, cloud point

1 INTRODUCTION

The gas separation process by asymmetric polymeric membranes has received much attention during the last decades because it is more energy efficient than other conventional separation processes. The membrane gas separation processes can be used in a wide range of applications, including hydrogen recovery from ammonia purge gas, enrichment of O_2 and N_2 from air and the removal of CO_2 from natural gas. Hollow fibers are the most favored membrane geometry owing to their high surface area per unit volume of membrane module. Two key elements determine the potential and applications of asymmetric hollow-fiber membranes: firstly, inherent properties of the membrane material; secondly, membrane structural properties mainly including pore size, pore distribution, selective layer thickness, molecular orientation and freedom from defects. The second key elements can generally vary depending on conditions during fabrication of fibers. Actual gas separation process occurs in dense skin layer, therefore its thickness and structure is crucial for gas separation and plays an important role in fiber separation performance. The selective layer thickness determines the membrane flux [1] and the molecular structure affects selectivity. For an asymmetric membrane fibers to be useful in separating gases, its active layer thickness must be within 10-1000 nm and have as few defects as possible [2].

It is not a trivial task to fabricate defect-free hollow fiber membranes with an ultra-thin dense-selective layer. Phase inversion is a common method to form hollow-fiber asymmetric membranes. The resulting membranes have a dense skin layer that is generally bonded in series with a thick porous substructure. Fibers are produced by the dry-jet wet-spinning process. This involves the extrusion of a more or less concentrated polymer dope solution through a spinneret annulus in

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3.3 PHASE DIAGRAM FOR PEI/NMP/ETOH SYSTEM

The phase behavior of the ternary system PEI/NMP/EtOH was determined by four cloud point measurements at a temperature of 40 °C. The compositions of the cloud points refer to the position of the binodal curve (Figure 7). From obtained cloud points the appropriate linear cloud point correlation (LCP) in Equation 9 describing the binodal curve was generated using least square fit. The LCP parameters for this ternary system at room temperature were also reported [15].

$$ln\frac{w(EtOH)}{w(PEI)} = a\,ln\frac{w(NMP)}{w(PEI)} + b \tag{9}$$

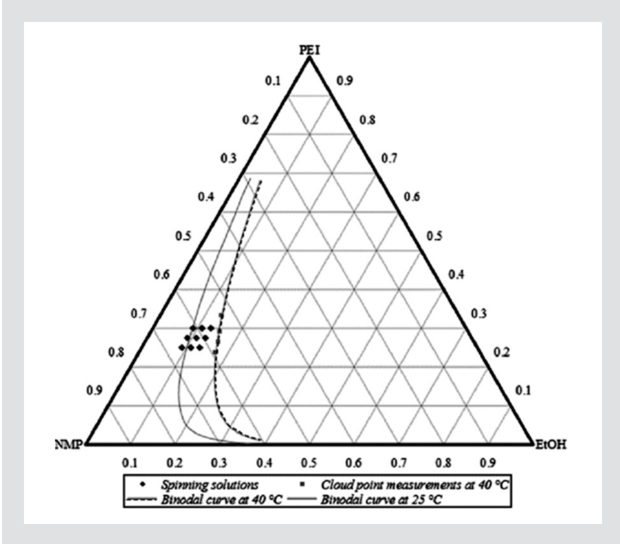

Figure 7: The binodal curves for PEI/NMP/EtOH system. Binodal curve for 25 °C (Data from [15]).

4 CONCLUSIONS

In order to develop asymmetric PEI hollow fiber membranes with high performance for gas separation, the influence of dope composition on rheology was studied for PEI/NMP/EtOH dope system. The effect of spinning solution and spinneret dimension on flow profile in spinneret was investigated. The phase behavior of the PEI/NMP/EtOH dope system was examined. Newtonian behavior of the spinning solutions with composition in range 25 – 30 wt% of polyetherimide and 9 – 13 wt% of ethanol in N-methylpyrrolidone was shown. The viscosity of the dope solutions increases non-linearly with polymer mass fraction. The Newtonian character of the spinning solutions causes constant linear velocity profile and shear rate profile regardless of its composition when flowing through a spinneret with some flowrate. The spinneret dimensions and geometry play a crucial role in controlling the shear flow in a spinneret. For considered spinnerets the shear rates on the wall significantly differ during flow of the same flowrates (for example from 500 1/s in big spinneret to 14000 1/s in small spinneret with flowrate of 1 ml/min). The Newtonian character of the spinning solutions causes linear relation between the shear rate respective shear stress and the distance from the axis of rotation (the radius) in a concentric annulus of spinneret. The phase behavior of the dope system at a temperature of the hollow fiber spinning process (40 °C) has shown there is some more “space” for the solution composition to get closer to the relevant binodal curve. Obtain data will be used to optimize in production of hollow fibers membrane for gas separation.

	Temperature /°C	
	25	40
a	1.3113	1.2559
b	−2.1619	-1.4661
R^2	0.9991	0.9958

Table 4: The LCP parameters for PEI/NMP/EtOH system.

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REFERENCES

[1] Chung TSN: Fabrication of Hollow-Fiber Membranes by Phase Inversion, Advanced Membrane Technology and Applications (2008) 821 – 839.
[2] Sharpe ID, Ismail AF, Shilton SJ: A study of extrusion shear and forced convection residence time in the spinning of polysulfone hollow fiber membranes for gas separation, Separat. Purificat. Technol. 17 (1999) 101 – 109.
[3] Ekiner OM, Vassilatos G: Polyaramide hollow fibers for hydrogen/methane separation – spinning and properties, J. Membrane Sci. 53 (1990) 259 – 273.
[4] Aptel P, Abidine N, Ivaldi F, Lafaille JP: Polysulfone hollow fibers – Effect of spinning conditions on ultrafiltration properties, J. Membrane Sci. 22 (1985) 199 – 215.
[5] Shilton SJ, Bell G, Ferguson J: The rheology of fibre spinning and the properties of hollow-fibre membranes for gas separation, Polymer 35 (1994) 5327 – 5335.
[6] Ren J, Chung TS, Li D, Wang R, Liu Y: Development of asymmetric 6FDA-2,6 DAT hollow fiber membranes for CO_2/CH_4 separation. 1. The influence of dope composition and rheology on membrane morphology and separation performance, J. Membrane Sci. 207 (2002) 227 – 240.

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[7] Chung TS, Lin WH, Vora RH: The effect of shear rates on gas separation performance of 6FDA-durene polyimide hollow fibers, J. Membrane Sci. 167 (2000) 55 – 66.
[8] Ismail AF, Shilton SJ, Dunkin IR, Gallivan SL: Direct measurement of rheologically induced molecular orientation in gas separation hollow fibre membranes and effects on selectivity, Journal of Membrane Science 126 (1997) 133 – 137.
[9] Shilton SJ, Ismail AF, Gough PJ, Dunkin IR, Gallivan SL: Molecular orientation and the performance of synthetic polymeric membranes for gas separation, Polymer 38 (1997) 2215 – 2220.
[10] Peng N, Chung TS, Lai JY: The rheology of Torlon® solutions and its role in the formation of ultra-thin defect-free Torlon® hollow fiber membranes for gas separation, J. Membrane Sci. 326 (2009) 608 – 617.
[11] Ding X, Cao Y, Zhao H, Wang L, Yuan Q: Fabrication of high performance Matrimid/polysulfone dual-layer hollow fiber membranes for O_2/N_2 separation, J. Membrane Sci. 323 (2008) 352 – 361.
[12] Shilton SJ: Flow profile induced in spinneret during hollow fiber membrane spinning, J. Appl. Polymer Sci. 65 (1997) 1359 – 1362.
[13] Holeček O: Chemicko-inženýrské tabulky, VŠCHT Praha (2013) 118.
[14] Langan JR, Arthur Salmon G: Physical properties of N-methylpyrrolidinone as functions of temperature, J. Chem. Eng. Data 32 (1987) 420 – 422.
[15] Bakeri Gh, Asmail AF, Rahimnejad M, Matsuura T: Analysis of Polyetherimide/N-Methyl-2-Pyrrolidone/nonsolvent phase separation behavior, J. Polymer Res. 21 (2014) 386.

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