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Macrovoids suppression in Polyetherimide (PEI) hollow fibre membranes by optimizing the air gap

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Abstract
Asymmetric polyetherimide (PEI) hollow fibre membranes have been prepared by dry-wet phase inversion method in which N-methyl-2-pyrrolidone (NMP) was used as solvent whereas water was used as both internal and external solvent. The polymer dope solution contained 25 wt. % of PEI and was spun at different air gaps at ambient conditions. The air gap effect was analyzed based on the surface morphology of the membranes using scanning electron microscopy (SEM). At longer air gaps, due to the dominant dry processes, finger-like pores extended to the outer skin layer and larger macrovoids appeared under the skin layer which may result in poor separation performance. The wet process presided as air gap was reduced to zero, and the instant solidification created macrovoids under the outer skin layer. At 15 and 20 cm air gaps, optimum results were obtained with minimum macrovoids and uniform finger-like pores under the thin skin layer.

Keywords: Polyetherimide (PEI), Macrovoids, Hollow fibre membrane, Surface defects.

INTRODUCTION

In recent years, membrane based separation processes have found widespread applications in industrial processes due to versatility in nature, low operational and capital cost [1]. The first commercial-scale membrane gas separation system was set up in 1970 [2]. In order to further enhance its performance, every process parameter which controls membrane properties need to be optimized. In literature, the process parameters that tune membranes' morphological and structural properties have been discussed in detail for flat sheet membranes due to simplicity in processing, nevertheless, hollow fibre spinning systems which is more complex in nature need more comprehensive study. Hollow fibre membranes possess higher surface to volume ratio than other membrane configurations and exhibit higher productivity per unit volume [3]. As a consequence, the separation efficiency of hollow fibre membranes is far superior as compared to flat sheet membranes but the former requires more study in order to produce defect-free structure. Different polymers have been investigated for synthesis of gas separation membranes, however, the superior gas selectivity, chemical stability, thermal stability and ease in spinning hollow fibre membrane via phase inversion technique made polyetherimide (PEI) a very attractive choice as compared to polysulfone and polyethersulfone [4, 5]. Moreover, PEI asymmetric membranes posses superior gas selectivity in comparison to aforementioned polymers [6, 7]. At ambient temperature, PEI tends to dissolve in common solvents like NMP, methanol and ethanol, and form low intrinsic viscosity solution, which increases the demixing and form porous structure [8]. Since the performance parameters are closely associated with structural and morphological behavior of membranes, any defects on the surface will create mechanical weak spots that could lead to membrane failure at high temperature, high pressure or under vibrational operations. Therefore, in order to withstand harsh conditions, the development of defect-free membrane is essential.

Generally in membrane forming processes via phase inversion, macrovoids have been generated and appeared as large elongated pores that can grow across the membrane thickness [9]. Generally, the size of macrovoids reported ranged from a few micrometers to tens of micrometer or even appeared parallel to membrane phase separation front [10]. Using phase inversion technique, polymer-rich and polymer-lean phases have been produced during solvent exchange process, which is responsible for creating voids in the membrane surface. The shape and size of macrovoids created depend on the rate of solvent exchange; finger-like pores are generated due to instantaneous phase exchange whereas slow exchange produced sponge-like structure [11]. Finger-like pores favour gas permeance whereas sponge-like pores result in selectivity enhancement as the latter are produced due to greater molecular orientation and closely packed molecular chains [3]. A number of theories exist to explain the creation of macrovoids in membrane forming processes. According to early researchers, the macrovoids appeared by instantaneous demixing and nucleation in polymer-lean phase due to diffusion process, nevertheless some scientists believed it to be due to local instability, rupture, solvent intrusion and nucleation of droplets in polymer-lean phase. The two most accepted theories among membrane scientists are 1) diffusion driven soluto-capillary convection and 2) surface instability followed by rupture and solvent intrusion. Frommer et al. claimed that osmotic pressure between solvent and coagulant in phase inversion technique was responsible for macrovoids creation in membrane surface and surface porosity or macrovoids can be minimized by controlling the aforementioned parameter [12].

In essence, various parameters which dictate membrane morphology have been studied in literature to suppress the

formation of macrovoids such as air gap, polymer concentration, dope viscosity, delayed demixing, surfactant addition and elongation draw [13, 14]. With the rise in dope viscosity, the macrovoids formation increases then decreases and increases again; this trend provides the evidence of optimum viscosity for a certain dope solution. Peng et al. studies the effect of dope viscosity, air gap and take up speed on the morphological structure of polysulfone, p84 and cellulose acetate. According to his findings, optimum morphological structure for improved separation performance can be obtained by optimizing all the aforementioned parameters [15]. Wang et al. prepared PEI asymmetric hollow fibre membrane using a dope containing NMP as solvent and ethanol as non-solvent additive. Pre- and post-treated PEI membranes were analysed to optimise the gas separation performance. According to findings, at longer air gaps, macrovoids formation increased to a great extent, similarly a highly distorted structure was observed when air gap was greatly reduced. Dry processes are the only phenomenon that took place in the aforementioned condition whereas wet processes dominate in the latter case. It was proven that the gas separation performance can be enhanced by optimizing the air gap distance [16]. Similar results were obtained by Tsai et al for polysulfone hollow fibre membrane with variation in air gap distance [17].

In this study, critical PEI concentration is evaluated and the effect of air gap is studied at the critical PEI concentration while keeping all other parameters constant like spinning temperature, coagulation bath temperature, bore fluid flow, take up velocity, dope solution viscosity.

MATERIALS AND METHODS

A. Materials

Polyetherimide (PEI, melt index 9g/10 min) was supplied by Sigma Aldrich and dried overnight for moisture removal. N-methyl-2-pyrrolidone (NMP, 99.5 %) was purchased from Merck Chemicals and used as received. Distilled water was used as internal and external coagulant.

B. Dope solution and viscosity measurement

For dope preparation, five polymer solutions of different concentrations (10, 15, 20, 25, 28 wt.%) were prepared by dissolving PEI in NMP. The solutions were stirred for 12 hrs for uniform mixing and degassed for 2 days to remove trapped air. The viscosity of the prepared dope solutions were measured using Fungilab Rotational viscometer (Model Alpha L) at 12 rpm.

C. Fabrication of hollow fibre membrane

Hollow fibre asymmetric membrane was produced at ambient conditions by phase inversion method using lab-scale hollow fibre spinning experimental set up. The spinneret used have a 0.8-mm outer and 0.4-mm inner diameter and distilled water was used as both internal and external coagulant. The critical PEI concentration was found to be at 25 wt. % PEI, as shown in Figure 1. Subsequently, the hollow fibre membranes were spun with different air gaps (0, 5, 10, 15, 20, 25, 30, and 35 cm) at the critical polymer concentration. The spinning conditions for hollow fibre membranes formation are summarised in Table 1. After spinning, the membranes were immersed in distilled water for solvent exchange for 2 days followed by drying at ambient conditions.

Table 1: Spinning parameters for PEI/NMP hollow fibre membrane.

Spinning Conditions	PEI/NMP solution
Temperature (°C)	25
Coagulant	Water
Coagulant temperature (°C)	25
Air gap (cm)	0, 5, 10, 15, 20, 25, 30, 35
Dope solution flow rate (ml/min)	0.8
Bore water flow rate (ml/min)	1
Take up velocity	Free falling

D. Morphology study

In order to study the surface and cross-section morphology of the membranes, the fibres were fractured in liquid nitrogen and coated with platinum using Qorum Q150RS platinum coater. HITACHI TM3030 scanning electron microscopy (SEM) was used to observe the morphological structure of the fibres.

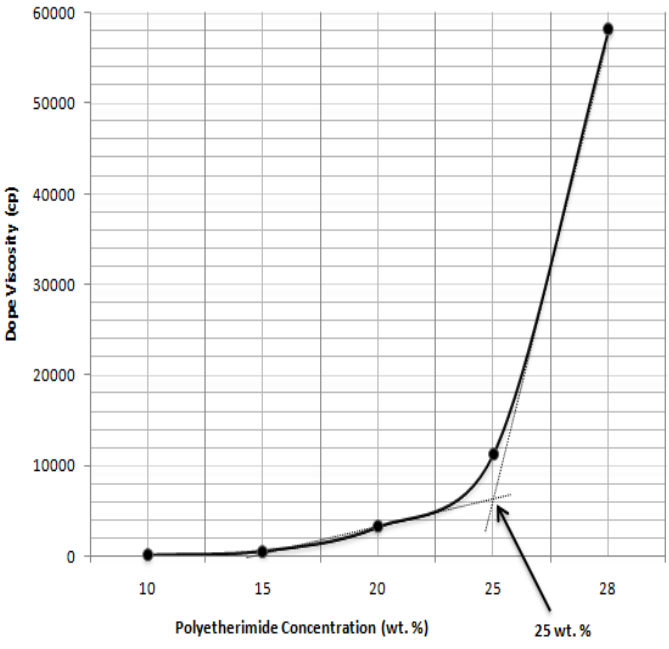

Figure 1: Critical dope viscosity for PEI/NMP solution.

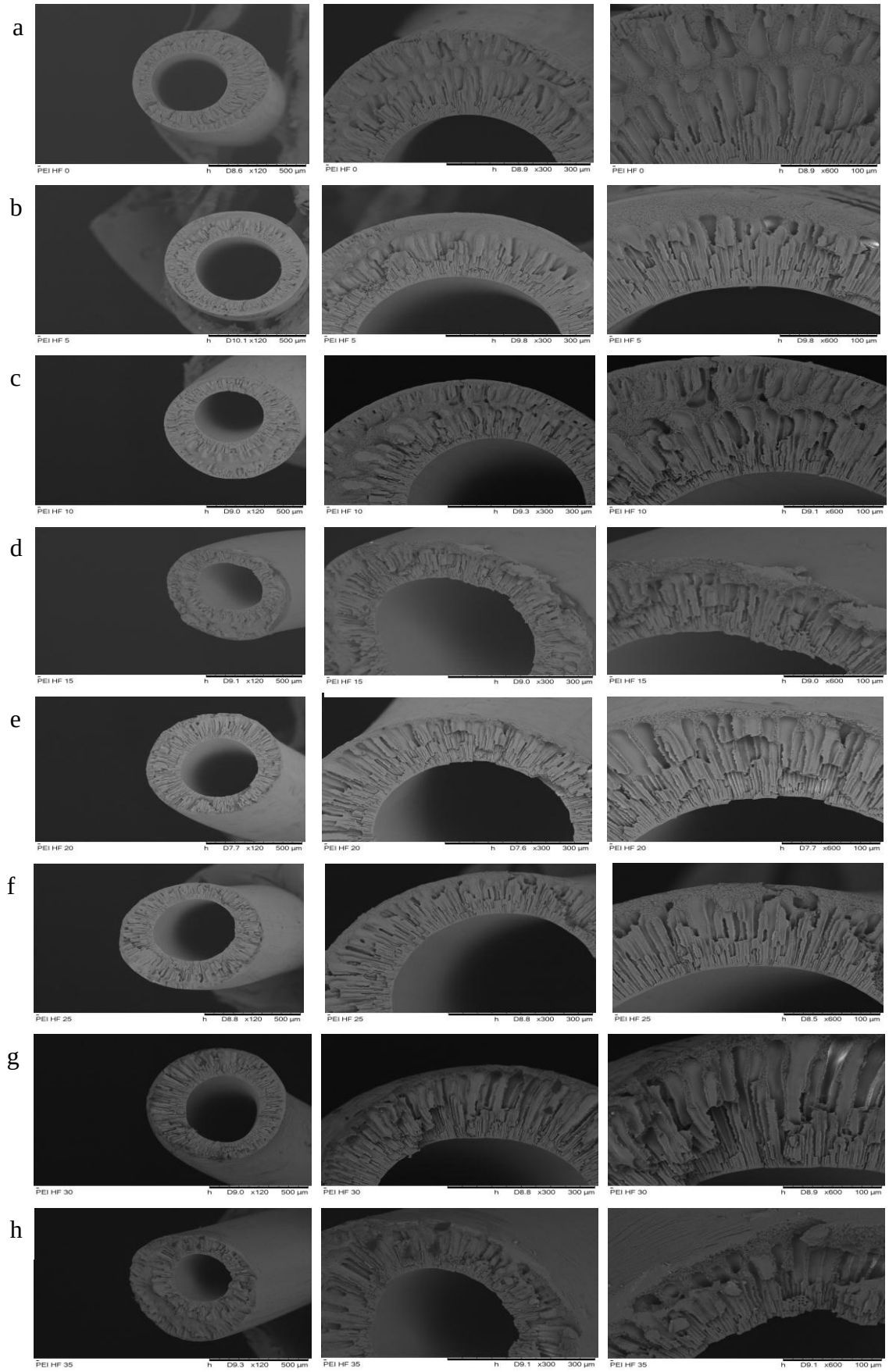

Figure 2. SEM images of PEI/NMP hollow fibre membranes (PEI, 25 wt.%), where rows a, b, c, d, e, f, g, h are representing air gaps in cm of 0, 5, 10, 15, 20, 25, 30 and 35 respectively.

RESULTS AND DISCUSSION

The polymer concentration in dope solution is a key component in determining the surface and morphological properties of spun membrane. The dope viscosity and density increases with polymer concentration by suppressing the factors responsible for void formation in membrane microstructure [18]. Figure 1 represents the viscosity curve for PEI/NMP binary dope solution.

The viscosity increased steadily with increasing polymer concentration, nevertheless, above a specific limit, the slope suddenly becomes steeper. The extrapolation of the relatively linear sections of the viscosity curve generated an interception point which represents the critical polymer concentration. This extrapolated critical viscosity curve has been used extensively and proved to be valid for synthesis of separation membranes. For PEI in NMP solvent, the critical dope viscosity was found at approximately 25 wt. % PEI concentration. This critical dope viscosity corresponds to the degree of chain entanglements for the particular polymer concentration. Above this critical point, the polymer chains exhibited significant entanglement which hinders the intrusion of non-solvent through the surface, resulting in reduced formation of macrovoids. For polymer concentration below the critical point, the chains are loosely packed thus are able to move freely, which allows the non-solvent to penetrate through diffusion mechanism to form macrovoids on the membrane surface [19].

The hollow fibre membranes were prepared with the dope solution at critical PEI concentration (25 wt.%) at various air gaps from 0 to 35 cm. Asymmetric membranes consist of porous sub-layer and thin skinned outer layer, in which the latter is the active participant in separation process whereas the former acts as support only [20]. Thus, the fabrication of defect free outer thin-skinned layer is essential to produce high performance membranes in which it is not only dependent on evaporation and coalescence in dry process but also highly dependent on the subsequent wet process and internal coagulation rate.

The hydrophilic nature of PEI and the presence of water as internal coagulant increase the polymer-coagulant interaction in solvent exchange process. As a result, for longer air gaps, the dry process dominates due to longer time in air which ultimately provides opportunity for the internal coagulant to diffuse in the outer skin layer. During dry phase inversion, the occurrence of liquid-liquid phase separation forms a distorted nascent dense skin due to coalescence and deformation of polymer aggregates [21]. The macrovoids produced as a result of longer air gaps are larger in size as shown in Figure 2 (f, g, h) for air gaps 25, 30 and 35 cm. Sometimes, for very long air gaps, the coagulation front reach the outer skin layer before it touches the external coagulant in coagulation bath. Nevertheless, for shorter air gaps, coagulation front will not have enough time to move to the outer skin layer before the nascent outer skin layer solidifies in the coagulation bath. Thus, the resulting membranes exhibit the desired defect-free structure. The membranes with air gap 15 to 20 cm exhibit the same uniform structure around the periphery of the membranes. This uniformity of microstructure brings mechanical strength and improved separation performance in hollow fibre membrane. The optimum air gap distance for PEI/NMP hollow fibre membrane is 20 cm where a very thin, defect free outer skin is observed and contained uniform finger-like pores under the outer thin skin. This pore structure favours the gas permeation through the membrane.

As the wet process dominates when air gap is reduced to zero, the inner coagulant did not have enough time to diffuse through the membrane before solidification took place in the coagulation bath. This produced larger macrovoids in the membrane surface and a highly non-uniform structure. Figure 2 (a, b, c) shows the hollow fibre membranes spun at small air gaps (0, 5, 10). It was found that solidification process took place along with water penetration from the outer layer. This created highly non-uniform and larger voids which will ultimately affect membrane separation properties.

CONCLUSION

Macrovoids in PEI/NMP hollow fibres membranes can be eliminated by optimizing the air gap which has a significant role in membrane morphology. The effect of dope viscosity on membrane structure was optimized by evaluating critical polymer concentration and was found to be at 25 wt. % PEI concentration. By varying the air gap from 0 to 35 cm, the macrovoids appeared in membrane microstructure in the order of large, small and large as analyzed by SEM. The optimum air gap for PEI/NMP hollow fibre membranes at critical PEI concentration was observed at 20 cm as compared to other air gaps studied. Hence, the hollow fibre membrane with the pore structure obtained at 20 cm air gap is capable to increase gas separation performance.

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