



## MINIMIZING MORPHOLOGICAL DEFECTS OF PEI HOLLOW FIBRE MEMBRANE BY OPTIMIZING THE DOPE VISCOSITY

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### ABSTRACT

Phase inversion processes have been used to fabricate hollow fibre membranes but these processes often lead to morphological defects such as formation of macrovoids. Thus far, several approaches have been investigated to solve this problem, but no consensus has been achieved. In this study, the optimal dope viscosity for PEI/NMP solution was elucidated to produce improved membrane morphological structure that can enhance its gas separation performance. Five concentrations of PEI/NMP dope solutions were prepared and their viscosities were measured. The critical viscosity was found to be at approximately 25 wt. % polymer concentration at ambient conditions. SEM analysis revealed that the most uniform finger-like pores with a thin skinned upper layer was obtained at critical dope viscosity.

**Keywords:** polyetherimide, hollow fibre membrane, critical viscosity, macrovoids.

### INTRODUCTION

Since the past few decades, membrane based separation processes have been extensively studied by membrane scientists. The process parameters to control the structure and morphological mechanism of flat sheet asymmetric membranes have been carefully examined and understood but development of hollow fibre asymmetric membranes require more research. On performance basis, hollow fibre membranes are far superior than flat sheet membranes, but the former has more sensitive parameters to control morphological behavior as compared to its latter counterpart. To date, many commercially available polymers have been used for spinning hollow fibre membranes, nevertheless, polyetherimide has certain distinct features over the others like chemical/ thermal stability as well as ease in spinning hollow fibres via phase inversion technique (Wang and Li, 1998) (Wang and Teo, 2002) (Chung and Ronald, 1992). The separation performance such as permeance and selectivity are very much dependent on its morphological structure. The presence of structural defects will produce mechanical weak spots in the membrane surface and could possibly lead to membrane rupture when used for higher pressure or severe conditions. Development of defect-free membrane structure is essential to achieve high separation performance.

Surface defects or voids have been created during phase separation process using conventional membrane forming techniques. These voids ranged from a few to tens of micrometer in length and in some cases it moves parallel to membrane phase separation front (Hussain and Kros, 2009). The solvent coagulant exchange in phase inversion process produced polymer rich and polymer lean phases, as a result form unstable membrane structure. The subsequent solidification process afterwards provides stability. The exchange process between solvent and coagulant trigger the macrovoids formations which are mostly shaped as finger or sponge-like structure. The

formation of finger-like and sponge-like structure depends on the rate of phase separations. Finger-like structure formed because of instantaneous demixing whereas delay in demixing produced sponge-like macrovoids (Ren and Li, 2004). Different theories have been presented to explain the formation and suppression of macrovoids. According to Frommer, osmotic pressure between solvent and coagulation is the driving force in phase inversion technique. The membrane surface porosity or voids creation can be controlled by reducing this osmotic pressure (Frommer and Messalem, 1973). This can be achieved by the addition of salt in coagulation bath in order to limit water activity. Also, the addition of solvent in coagulation bath could reduce the concentration gradient for phase separation and porosity is controlled (Strathmann, 1978).

Along with these techniques, the macrovoid formation can be minimized by controlling spinning parameters like dope viscosity, air gap, polymer concentration, delayed demixing, addition of high viscous component, surfactant addition, high shear rate spinning, increasing coagulation bath temperature, or high elongational draw (Ren and Li, 2004) (Kosuri and Madhava, 2008) (Natalia and Chung, 2006). In all the aforementioned approaches, the easiest choice is to increase dope solution viscosity either by introducing highly viscous additive or by increasing polymer concentration. Kesting et al. claimed in his patent that a membrane with critical polymer concentration of 30 wt. % and viscosity around  $5 \times 10^4$  cp would produce macrovoid-free membrane. This was the initial attempt to quantitatively correlate dope viscosity and macrovoid-free structures (Kesting and Fritzsche, 1989). Peng et al. analysed 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 all these parameters are closely associated to each other. The critical value of aforementioned parameters are studied and



spinning of hollow fibres at critical parameters helped to eliminate macrovoids from polymer spun hollow fibre membranes (Peng and Chung, 2008).

This research work investigates the effect of polyetherimide (PEI) concentration or dope viscosity on the structure of PEI hollow fibre membrane. All other parameters such as air gap, coagulant and coagulation bath temperature, take up velocity, bore fluid flow rate were held constant.

## EXPERIMENTAL

### Materials

Polyetherimide (PEI, melt index 9g/10 min) was purchased from Sigma Aldrich and dried at 120°C overnight to remove moisture. *N*-methyl-2-pyrrolidone (NMP, 99.5 %) supplied by Merck Chemicals was used as received. Distilled water was used as internal and external coagulant.

### Dope preparation and viscosity measurement

For dope preparation, five polymer solutions of different concentration (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 two days to remove trapped air. The viscosity of the prepared dope solutions were measured using Fungilab Rotational viscometer (Model Alpha L) at 12 rpm.

### Hollow fibre membrane spinning

Lab-scale hollow fibre spinning experimental set up was used to spin the hollow fibre membranes. The spinneret with outer diameter of 0.6 mm and internal diameter of 0.3 mm was used for all dope solutions. Water was used as internal and external coagulation at room temperature. The spinning of hollow fibre membranes was carried out at ambient temperature. Table 1 summarised the conditions used for spinning the hollow fibre membranes. After spinning, the membranes were immersed in distilled water for three days for solvent exchange. The membranes were then dried at ambient conditions.

### 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.

**Table-1.** PEI/NMP hollow fibre membrane spinning parameters.

Spinning conditions	PEI/NMP solution
Temperature	25°C
Coagulant	Water
Coagulant temperature	25°C
Air gap	10 cm
Dope solution flow rate	0.8 ml/min
Bore water flow rate	1 ml/min
Take up velocity	Free falling

## RESULTS AND DISCUSSIONS

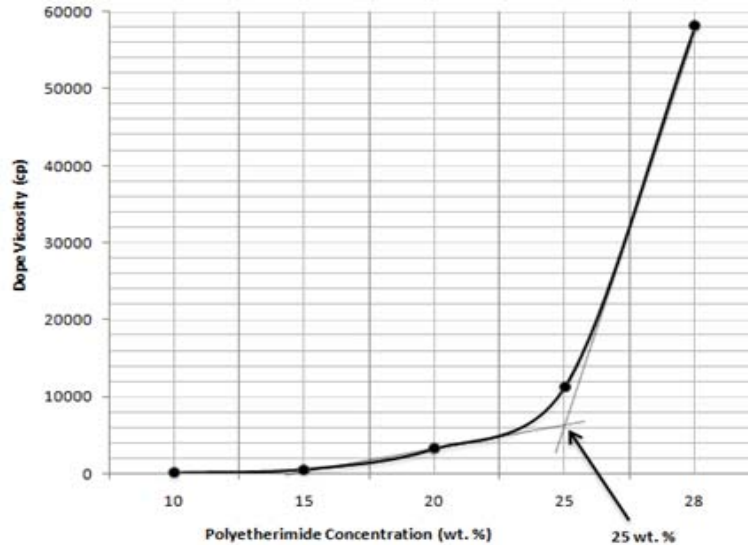
The polymer concentration in a dope solution has a significant impact on mean pore size, porosity and permeance of hollow fibre membranes. With the increase in polymer concentration, the solution viscosity and density increased, resulting in depression of void formation in the membrane microstructure (Bakeri, 2010). For an asymmetric membrane consisting of porous sublayer and thin-skinned layer, only the upper thin-skinned layer is crucial in determining the separation properties of membranes. Thus, it is essential to fabricate membranes with a defect-free thin upper layer as it would lead to enhanced membrane performance. The spinning of hollow fibre membrane from a dilute polymer solution often leads to porous membrane with improved permeability but lower selectivity. On the other hand, higher concentration of polymer in the dope solution complicates the spinning procedure and often form upper skin layer with increased thickness, resulting in low permeance but high selectivity. In order to produce hollow fibre membranes with optimum performance and defect-free morphology, it is important to obtain the critical polymer concentration and dope viscosity (Ismail and Lai, 2003). 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. In other words, the critical viscosity is the point at which a balance

is observed between the highly dense structures and porous



**Figure-1.** Critical dope viscosity for PEI/NMP solution.

structure of membranes to achieve optimum separation performance (Ismail and Lai, 2003). Figure-2 displays the SEM images of PEI hollow fibre membranes using various polymer concentrations. Figure-2a shows the morphological structure of 10 wt. % PEI in NMP. The lower concentration of PEI in dope solution leads to loosely packed structure, thereby the non-solvent water penetrated through the inner surface of hollow fibre membrane and created pores on the membrane surface. Prior to entering the water coagulation bath, the inner water diffused rapidly through the membrane structure and created pores on the surface largely due to the loosely packed polymer chains. The phase separation process was so instantaneous that it created finger-like pores that extended all the way to the outer surface. This morphology will lead to poor separation performance and low mechanical strength (Benjamin and Li, 2009). Similar morphology was found for 15 wt.% PEI/NMP dope solution (Figure-2b). This indicated that 10 and 15 wt. % PEI concentration in NMP solvent is too low to form mechanically strong membranes which may achieve good separation performance. For 20 wt. % PEI concentration, finger-like pores existed but the length and width of the pores have been greatly enhanced forming macrovoids. Also, thin-skinned layer was observed and finger-like pore structure dominated the outer skin layer. The presence of outer skinned layer ensures its ability to perform in separation applications but the presence of macrovoids in the surface morphology suggested a membrane with higher permeance but lower selectivity.

As shown in Figure-2d, for the hollow fibre membrane with 25 wt. % PEI composition, finger-like

structure was initiated from the inner skin layer which extended to the outer skin layer. For this polymer concentration, void formation was greatly reduced as compared with Figure-2c. The size and shape of finger-like structure was also uniform throughout the membrane surface. Membrane spinning at this critical PEI composition will be advantageous in terms of mechanical strength and separation performance.

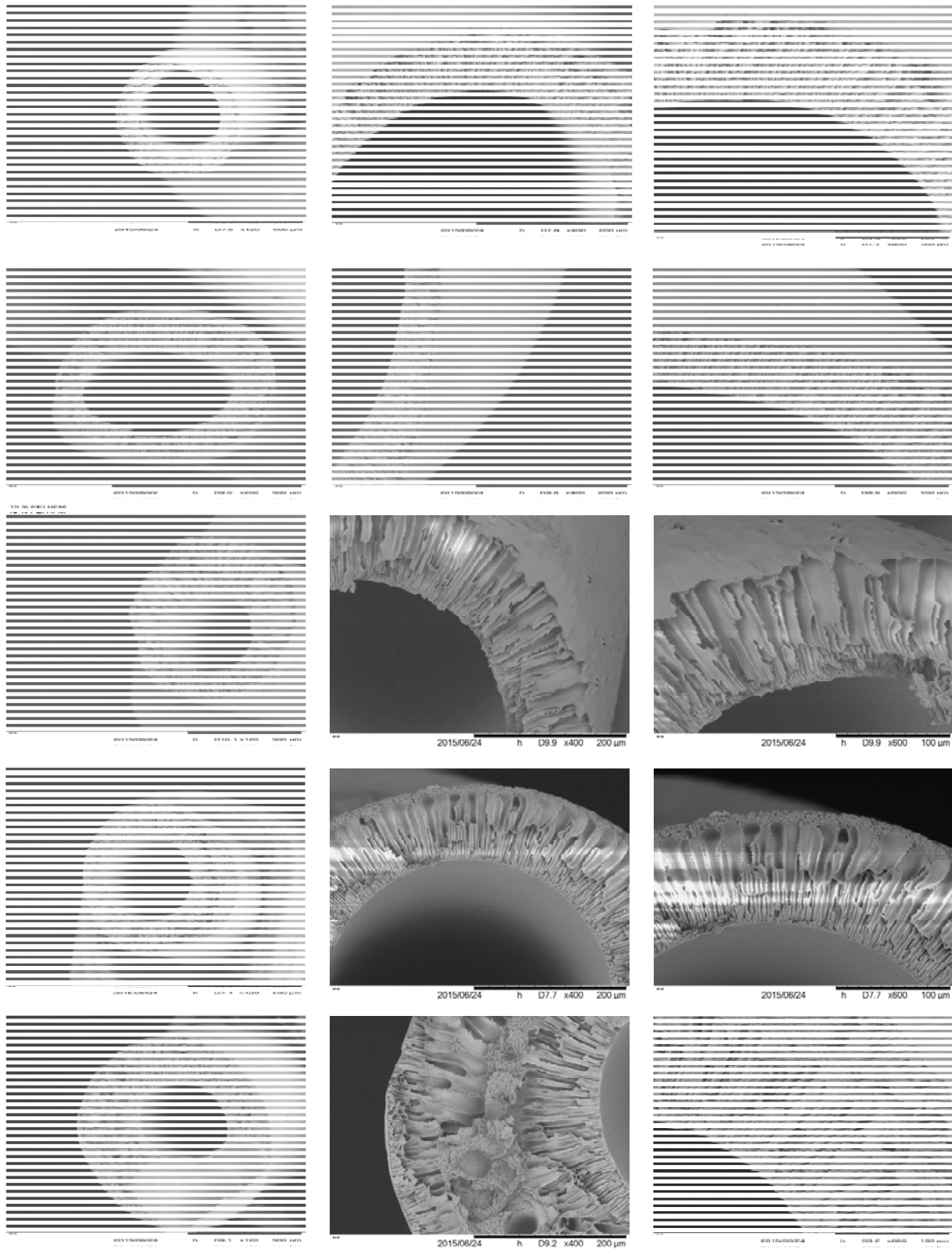
The hollow fibre membrane spinning with 30 wt. % PEI concentration was not possible because of the high viscosity value; therefore 28 wt. % PEI concentration was considered as the upper limit. Figure-2e revealed that at this polymer concentration, the pore structure was extremely distorted and nonuniform. Due to the dense and highly entangled polymer chains, the diffusion of internal solvent through the inner membrane surface was limited. Besides that, large spherical pores were also observed from the SEM images. The mechanical strength of this membrane was expected to increase; nevertheless, its gas separation performance might be reduced.

## CONCLUSIONS

Macrovoid-free PEI/NMP hollow fibre membranes can be fabricated by controlling the dope viscosity, which was known to produce defects in the structure. The critical viscosity for optimum membrane morphology was obtained at 25 wt. % PEI concentration. This was supported by SEM analysis, in which the macrovoids have reduced as compared to other PEI concentration studied.



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**Figure-2.** SEM images of dope solution with PEI concentration a) 10 wt. % b) 15 wt.% c) 20 wt. % d) 25 wt. % e) 28 wt. %.



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## ACKNOWLEDGEMENT

This research work was supported by Universiti Teknologi PETRONAS and Ministry of Higher Education (MOHE), Malaysia under URIF grant No. 0153AA-B27 and MyRA Research Grant for CO<sub>2</sub> Rich Natural Gas Value Chain Program.

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