ORIGINAL ARTICLE

Elaboration of porous poly(ether-imide) membrane using vapor induced phase separation

Lanoizelée Elodie[1], Deratani Andrée[2], Menut Paul[3], Pochat-Bohatier Céline[4], and Dupuy Claude[5]

Abstract

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Polymeric films were prepared from poly (ether-imide)/N-methyl-2-pyrrolidinone solutions using vapor induced phase separation process at 40 °C. The influence of such operating conditions as relative humidity and polymer concentration on the final morphology was investigated in order to consider potential future membrane applications with the objective of elaborating presupposed quality porous materials. In our experiments, the water vapor concentration in the atmosphere used during the film forming process was the predominant parameter governing the microstructure. Polymeric films with a cellular morphology were produced for a processing relative humidity (RH) higher than 30% whereas dense homogeneous films were obtained below this value. The influence of the polymer concentration was studied at 40 % RH. The results were discussed with respect to the cell and pore size and to the occurrence of macro-void defects.

Key words : vapor induced phase separation, poly (ether-imide), porous membrane, morphology

[1] **Graduate student in Material Chem.,** [2] **Ph.D. (Material Chem.), Senior Scientist, Institut Européen des Membranes, Université Montpellier II, cc47, 34095 Montpellier cedex 5, France,** [3] **Ph.D. student in Chem. Eng.,** [4] **Ph.D. (Chem. Eng.), Assoc. Prof.,** [5] **Ph.D. (Chem. Eng.), Prof., Lab. de Genie des Procedes, Universite Montpellier II, cc05, 34095 Montpellier cedex 5, France**
Corresponding e-mail : dupuyc@univ-montp2.fr
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Industrial applications of polymeric membranes depend both on their intrinsic properties related on the chemical nature, and on their morphology. Previous works have shown that the membrane microstructure can be controlled by the elaboration process (Mulder, 1996; Van de Witte *et al*., 1996; Han *et al*., 1995). Different procedures to prepare membrane materials start by casting a homogeneous polymer solution. When the solvent is evaporated under anhydrous conditions, a dense film is obtained. At the opposite, the immersion of the cast film into a coagulation bath leads to the formation of an asymmetric membrane with a greater or lesser porous structure. The diffusion of non-solvent inside the polymer solution induces a phase separation yielding the formation of pores. An intermediate process consists in supplying the non-solvent from the vapor phase, so-called "non-solvent vapor induced phase separation (VIPS)". The milder conditions of the phase inversion process taking place in this technique result in an easier possibility of understanding how the microstructure is formed, which can further afford a better control on the properties of the membranes obtained.

We have recently reported on the preparation of poly (ether-imide) (PEI) films using VIPS (Ripoche *et al*., 2002; Menut *et al*., 2002). The phase inversion was initiated from 16 wt-% PEI/ 1-methyl-2-pyrrolidinone (NMP) solutions using water vapor as the non-solvent. The penetration of water into the film forming system induced a phase separation, via nucleation and growth of a polymer-lean phase dispersed in a polymer-rich phase. The polymer-poor phase droplets slowly grew and coalesced until the polymer rich-phase formed the foam wall structure when the gelation concentration was reached. The membrane materials presented a cellular structure without macrovoids. We clearly showed that the concentration of water vapor in the air used to dry the dope solution was the predominant parameter, which determine the dense or cellular structure of the obtained membrane (Caquineau *et al*., 2003).

The aim of this study was to examine the role played by the relative humidity (RH) and the polymer concentration in the dope solution on the membrane morphology regarding the cell and pore size distribution using scanning electron microscopy (SEM) and mercury intrusion porosimetry as analysis techniques.

Materials and Methods

Materials

PEI (Aldrich) was dried for 24 hours at 170°C under vacuum before use. Anhydrous NMP (Aldrich) was taken under a nitrogen atmosphere without any further purification. The dope solutions (10, 12, 14, 16, 18 and 20 wt-%) were prepared at room temperature by stirring PEI in NMP during 5 days under nitrogen. The obtained solutions were used within a week.

Film preparation

The PEI solution was cast on a glass plate in a glove box at 25°C under an atmosphere with a RH value less than 7%. The initial thickness of the film was 250 μm. The plate was then rapidly introduced in the drying bench (40°C ± 0.5°C) and brought into contact with a constant laminar air flow. RH in the drying bench was adjusted to the desired value (30, 40, 50, and 70 % with an error range of ± 2 %) by bubbling air through a water column at a controlled temperature. The solvent evaporation process was completed for the mass transfer measurements. Otherwise, films were immersed after 30 min into two successive water baths at 40°C and 70°C for 30 min and 2h, respectively, to quench the process.

Mass transfer analysis

In-situ mass measurements were carried out by weighting the forming film every 10 seconds until such time as no significant variation was observed meaning that the evaporating process was completed. Error on mass measurements was lesser than 0.005 g, for a sample weight of about 0.4 g. Each experiment was conducted at last twice to verify the repeatability of the method.

Film characterization

The micrographs obtained by SEM (Hitachi S-4500) were analyzed using the software Image Tool™. Mercury intrusion porosimetry (Micrometrics – Autopore II 9213) was used to determine the pore size distribution and the porosity volume.

Results and Discussion

Influence of the atmosphere relative humidity on the film morphology

Reproducible structure and properties of PEI membranes can be obtained from a given PEI/NMP solution only if the water vapor concentration in air, i.e. RH, is strictly controlled. In this way, we carried out the experiments in a glove box equipped with an atmosphere conditioner suitable to produce air containing a controlled humidity within a RH variation range going from 0 to 80 %. The drying bench was equipped with a balance allowing in-situ mass variation measurements of the membrane forming system during the elaboration process. The air flow used to evaporate the solvent of the polymer solution, was adjusted to a constant value, with a low speed, in order to be close to static operating conditions.

Figure 1 shows the mass variation for a starting 16 wt-% PEI liquid film, dried under RH ranged from 0 to 70 %. The data were expressed by the percentage ratio between the mass of the film at a given time and the initial mass. When a dry atmosphere was applied, we observed the expected mass decrease of the film traducing the solvent evaporation until the weight remained constant indicating the end of the process. A different behavior was observed under a humid atmosphere. The film mass variation was first positive followed by a decrease after having passed beyond a maximum similar as that observed when the film underwent the evaporation under a dry air flow. This clear positive mass increase of the film forming system observed at the beginning of the process can be accounted for an intake of water from the atmosphere, which was at that time higher than the outflow of solvent. As seen on Figure 1, the maximum of the mass variation curve increases with the RH value. From these findings, it can be concluded that the main driving force governing the water mass transfer from the gaseous phase to the liquid polymer film was the water chemical potential in the gaseous phase (i.e. RH) indicative of a rapid diffusion in the entire film. After the maximum was passed, the overall mass of the film decreased until to reach approximately the same mass variation value whatever RH. During this period, the two volatile components (water and NMP) evaporated from the film.

Figure 2 exhibits the influence of RH on the thickness and on the membrane morphology

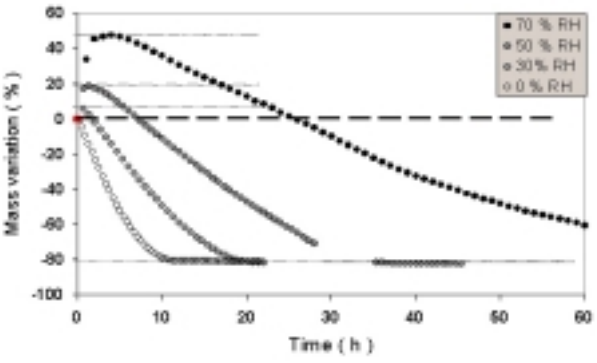

Figure 1. Influence of RH on membrane mass variation (%) versus time, during the elaboration process.

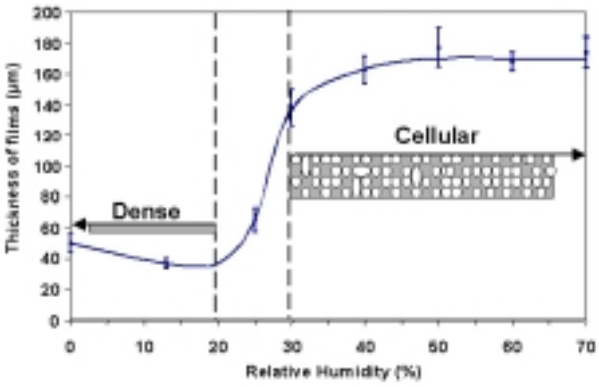

Figure 2. Influence of RH on the morphology of the membranes.

observed using SEM. When RH was lower than 20 %, the microstructure was dense and only thin and transparent materials were obtained from a 16 wt-% PEI dope solution within this domain. By contrast, the membranes were white, thicker and porous for RH values higher than 30 %. The RH values located between these two well-defined domains, gave rise to an intermediate morphology made of mixed transparent and dense parts resulting from local small fluctuations. The transition is featured by a strong rising of the film thickness, the porous membranes being three times thicker than dense membranes for the same starting liquid film thickness. As showed by the micrographs, the porous membranes displayed an anisotrope cellular microstructure. The cross-section morphology is characterized by a top layer consisting in large cells, and by a gradient of decreasing cell size from the air/film interface to the film/support interface.

The number of cells per unit area (100 μm^2) was determined using an image processing software on SEM cross-section micrographs of membranes obtained for different RH values (RH > 30 %). By plotting these data as function of RH on Figure 3, it appears that the number of cells per unit increased as the RH value was enhanced indicating that the mean cell diameter decreased. As stressed above, the amount of water penetrating into the film is proportional to RH. Therefore, it can be assumed that a high RH value induced the formation of a greater number of the polymer-lean phase nuclei. The growth of these nuclei by coalescence produced then a greater number of cells per volume unit than for a lower RH value. This observation was also reported by Park *et al*, (1999) for the preparation of polysulfone membranes by VIPS.

The cells are interconnected by holes in their wall formed during the growth of nuclei. The mercury intrusion measurements can bring information on the porosity volume accessible (open cells) and on the distribution of pore diameter. The results plotted on Figure 4, indicate that RH as soon as its value is higher than 30 %, had little influence on the porosity volume though a trend to the decrease was observed when RH going from 30 to 70 %. The decrease of the interconnecting mean pore diameter with RH was more significant showing that material with a desired pore size can be obtained by controlling the water chemical potential of the gaseous phase in which the film is evaporating. Further developments in the elaboration process of the PEI porous membrane could now be done in the direction of a higher porosity volume. We chose to study the influence of the polymer concentration of the dope solution using a RH value of 40 %.

The observation of the phase separation using an optic microscope for a 16 wt-% PEI liquid film under 40 % RH showed that the polymer-poor phase droplets stopped their apparent evolution after ca. 15 min of coarsening. We assumed that after this short period, the cell wall

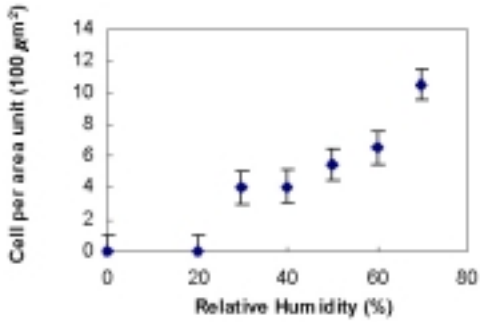

Figure 3. Influence of RH on the number of cells counted in the membrane core.

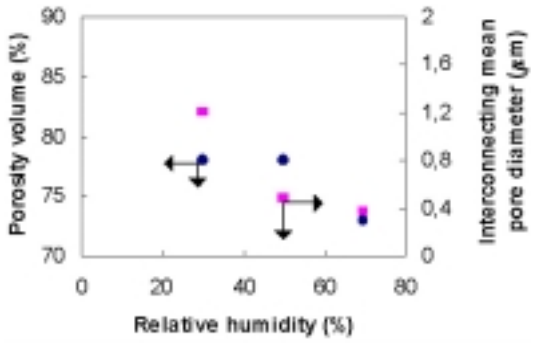

Figure 4. Influence of RH on the porosity volume (%) and on the interconnecting mean pore diameter (µm).

constituted by the polymer rich-phase reached the glassy state, stopping by this way the process of cell development. These findings extrapolated to the preparation of membrane using VIPS imply that the final morphology was determined in a large part after a very short period compared to the entire evaporation process time-scale.

To confirm this assumption, the film forming system was quenched by immersion into a water bath at different stages of the evaporation process as described on Figure 5. In the case of a quenching before the film whitening, an asymmetric structure was obtained with finger-like macro-voids, as often observed in that case. It can be concluded that before the occurrence of the demixing, the composition variation generated by the solvent and non-solvent exchange between the liquid film and the gas phase cannot alter enough the nature of the final morphology: it plays only a role in the formation of the top layer. The other experiments consisted in the immersion after evaporating the polymer solution under a humid atmosphere until the phase separation occurred. As expected, cellular structures were produced in this case (periods II-III). No major difference was observed (on microphotographs) between these structures and those obtained after the complete evaporation process. As a conclusion, we can say that the film cellular morphology can be produced using a shorter process composed of 1) a water absorption step from the gaseous phase until the solidification of the polymer rich-phase in the glassy state takes place and 2) a quenching of the biphasic polymer forming film in a strong non-solvent bath. On the basis of these results, the liquid films were quenched after 30 min of the evaporation process in the second part of this study.

Influence of the polymer concentration of dope solutions on the film morphology

The polymer concentration of the dope solution was varied from 10 to 20 wt-%. In these experiments the other operating conditions (T = 40 °C, RH 40 %) were kept constant. The membranes were porous whatever the starting polymer concentration, indicating that this parameter is not predominant in the range studied for the

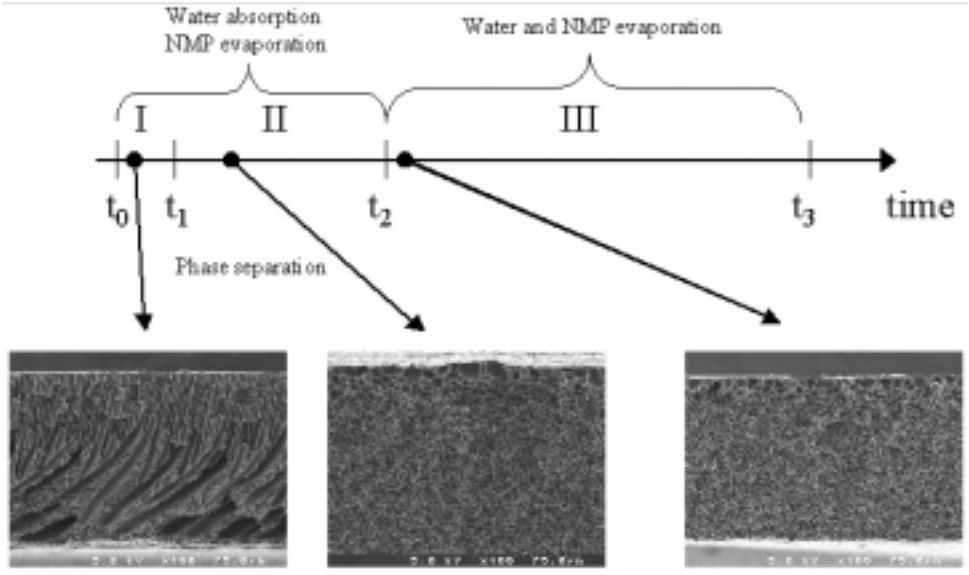

Figure 5. Quenching of the film forming system at different stages of the elaboration process, (t_0 introduction of the liquid film in the drying bench, t_1 : beginning of the phase separation, t_2 : maximum of the membrane mass variation, t_3 : end of the elaboration process).

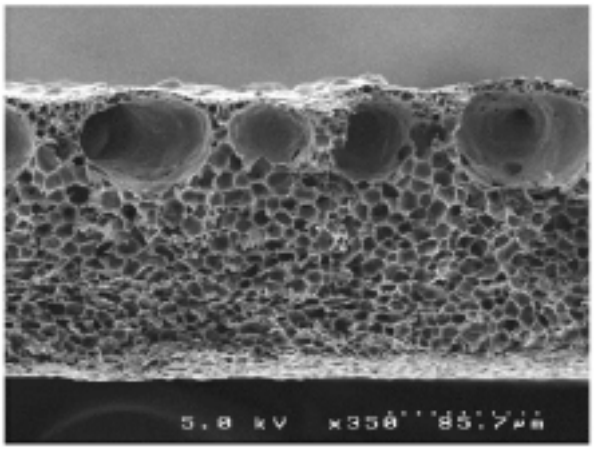

Figure 6. Cross-section micrograph of membrane made from 12 wt-% polymer concentration.

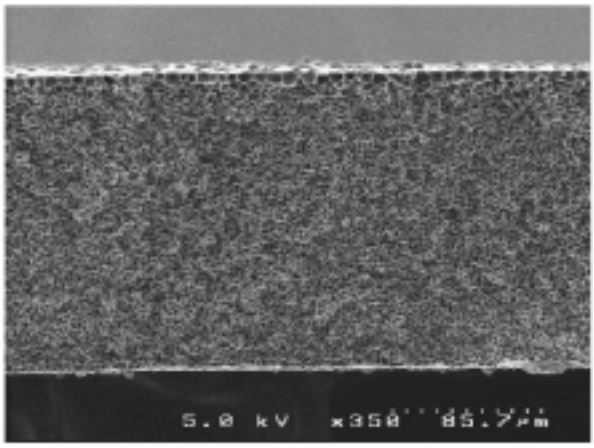

Figure 7. Cross-section micrograph of membrane made from 20 wt-% polymer concentration.

nature of the membrane morphology. The main differences in morphology, which can be observed in SEM micrographs, were related to the cell size and to the presence of macro-voids (Figure 6 and 7). When the polymer concentration was lower than 16 wt-%, macro-voids were observed near the air/film interface. This can be considered as defaults as macro-voids reduce the mechanical strength of membranes. Indeed,

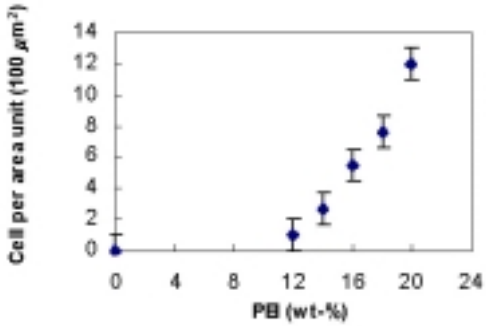

Figure 8. Influence of polymer (PEI) concentration on the number of cells counted in the membrane core.

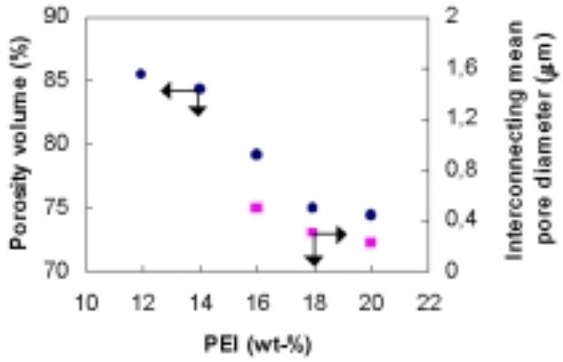

Figure 9. Influence of polymer (PEI) concentration on the porosity volume (%) and on the interconnecting mean pore diameter (µm).

the membranes made from a 10 wt-% polymer concentration could not actually be analyzed by mercury intrusion porosimetry due to their weakness. The membranes elaborated with a 20 wt-% PEI solution presented a quite homogeneous microstructure (Figure 7), with an average cell diameter of about 3.2 µm. The existence of a mono top layer consisting of larger cells (6 µm diameter) has to be noticed. The density of this material was determined to be ca 0.3.

The number of cells per unit area increased meaning that the average cell size became smaller, with a rising of the starting polymer concentration (Figure 8). This phenomenon can be explained by the increase of viscosity related

to higher polymer concentrations involving a slowing down of the droplet coarsening. The vitrification of the polymer rich phase takes place earlier leading to the formation of smaller cells.

Mercury intrusion porosimetry data (Figure 9) showed that rising the polymer concentration led to lower porosity volumes while the interconnecting mean pore size remained almost constant. The porosity volume of the membrane ranged between 74 and 85 % for 20 and 12 wt-% PEI solutions, respectively. It can be seen that the polymer concentration of the dope solution has a stronger influence on the porosity volume than RH. It was assumed that it is due to the occurrence of macro-voids in the case of the less concentrated dope solutions used. The variation of porosity volume shows an inflection point for the PEI concentration value of 16 wt-%. It is interesting to note that this value is the limit beyond which a cellular morphology without macro-voids can be produced.

Conclusion

The present study has shown the influence of two processing parameters (RH and the polymer concentration in the dope solution) on the morphology of poly (ether-imide) membrane produced by VIPS process at 40 $^{\circ}$C. During the elaboration process, the RH of the air used to evaporate the solvent was shown to be the predominant parameter to monitor the nature of the morphology. For porous membrane preparation, RH needed to be controlled to a set value higher than 30 %. When RH was adjusted to 40 %, the influence of the polymer concentration in the dope solution on such morphological parameters as the cell size, the porosity volume and the interconnecting mean pore diameter was clearly presented. These results let us supposed that the choice of the polymer concentration combined with a RH set to a defined value superior to 30 % would allow a better control of the final membrane morphology. This confirms the interest of this approach in membrane elaboration for industrial applications. Others processing parameters are now to be studied, as the temperature of the elaborating chamber, and the air flow rate used to evaporate the solvent.

References

Caquineau, H., Menut, P., Deratani, A. and Dupuy, C. 2003. Influence of the relative humidity on film formation by vapor induced phase separation, Polym. Engin. and Sci., (in press).

Han, M.-J. and Bhattacharyya, D. 1995. Changes in morphology and transport characteristics of polysulfone membranes prepared by different demixing conditions, J. Memb. Sci., 98: 191-200.

Mulder, M. 1996. Basic Principles of Membrane Technology, 2nd edition, Kluwer Academic Publisher, Dordecht, 89.

Menut, P., Pochat-Bohatier, C, Deratani, A., Dupuy, C. and Guilbert, S. 2002. Structure formation of poly(ether imide) films using non-solvent vapor induced phase separation : Relationship between mass transfer and relative humidity, Desalination, 145 :11-16.

Park, H. C., Kim, Y. P., Kim, H. Y and Kang, Y. S. 1999. Membrane formation by water vapor induced phase inversion, J. Memb. Sci., 156 : 169-178.

Ripoche, A., Menut, P., Dupuy, C., Caquineau, H. and Deratani, A. 2002. Poly(etherimide) membrane formation by water vapour induced phase inversion, Macromol. Symp., 188: 37-48.

Van de Witte, P., Dijkstra, P.J., Van den Berg, J.W.A. and Feijen, J. 1996. Phase separation process in polymer solutions in relation to membrane formation, J. of Memb. Sci., 117 :1-31.