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Procedia Engineering 44 (2012) 1230 – 1231

Procedia Engineering

www.elsevier.com/locate/procedia

Euromembrane Conference 2012

[P2.028]
Neck-size distributions of through-pores in polymer membranes

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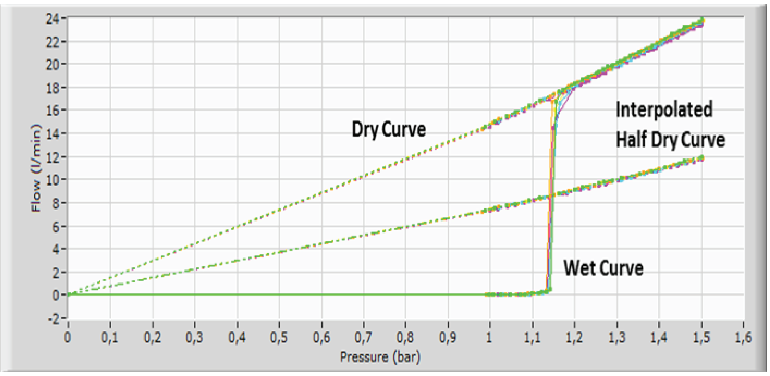
ABSTRACT. The capillary flow porometry (CFP) is generally used for measuring the bubble point pressure corresponding to largest through pore-size in the membrane. In present work, the CFP technique was used for developing a methodology for determination of the neck-size distributions in the synthetic membranes. It is important as the transport flux across the membrane is controlled by the neck size of through-pores. Therefore the average, maximum and minimum pore sizes and pore-size distribution in these membranes was determined by CFP and compared with different techniques like Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and Molecular Weight Cut-off (MWCO). For the MWCO method, the Stokes radius of solute poly(ethylene oxide) (PEO) was calculated using the method commonly used, and also confirmed by Dynamic Light Scattering (DLS).

The CFP required analysis of the plot between N_2 gas flow rate as a function of the applied pressure across the membrane in that the pores were filled with the inert wetting liquid 'Porefil'.

a) 

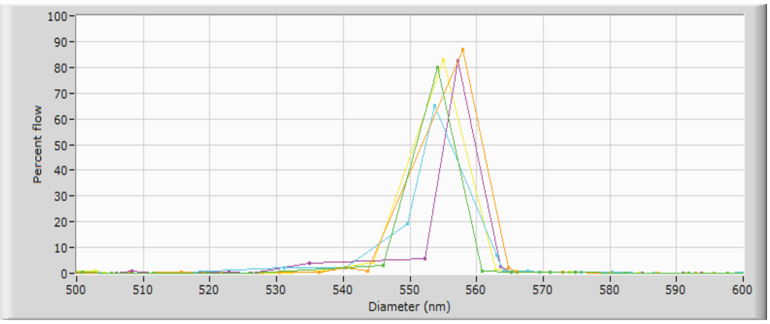
(b) 

Figure 1. The plots flow rates as function of applied pressure across dry and wet poly(ether sulphone) membrane subjected to five replicate cycles of measurements (a) and corresponding differential flow rates as a function of pore diameter (b).

doi:10.1016/j.proeng.2012.08.736

The dry run plot obtained without wetting the membrane was used as the reference. The maximum and the minimum pore sizes were determined by the bubble point (pressure at which first flow of gas across wet membrane was observed) and the point where wet and dry runs converged, respectively. Mean flow pore size was calculated from the pressure at which the wet flow was half of the dry flow. The pore-size was obtained from the applied pressure using the Washburn equation. The portions of plot of wet run from the point where first flow of gas observed upto the point where it meets the dry run plot were used for determining pore size distributions. The pore-size distribution is given by the distribution function:

$$f = -[d(f_w / f_d)100 / dD]$$

Where f_w and f_d are flow rates through wet and dry samples. The negative sign in right side of this equation indicates that increase in pore diameter (decrease in pressure) decreases flow rate.

The studies carried out in the present work clearly demonstrated that the capillary flow porometry can be used for accurate measurement of neck-size distribution of the through-pores in the membrane. The CFP is simple, non-destructive, rapid and capable of providing accurate and reproducible pore-size distribution in the membranes.

It was observed that average, minimum and maximum pore-sizes in TEM samples obtained by microscopy (AFM/SEM) were in good agreement with mean flow pore-size, smallest and bubble point pore-sizes determined by the CFP. The average pore size in TEM samples was found to be under estimated by the MWCO method indicating that the steric and the hydrodynamic interactions between the solute and pore cannot be ignored. The analytical performances of the CFP like effects of thickness, wetting liquids, tortuosity, reproducibility etc were also studied. These studies showed that (i) the CFP remained practically independent of the sample thickness, (ii) it measured the most constricted size of the pore when membrane sample having small pores was sandwiched between membrane samples having high pore-size, (iii) the maximum, minimum, and mean flow pore-sizes data were highly reproducible (±5%), and (iv) any wetting liquid can be used provided it does not dry or swell the membrane matrix. Finally, the CFP was used to obtain the mean, smallest and bubble-point pore size of commercial ultrafilteration membranes such as poly(ethersulfone), poly(vinylidene fluoride), poly(propylene) and poly(tetrafluoroethylene). The data thus obtained were corroborated with their SEM images. They indicated that CFP can be used not only to measure bubble point pore-size but also to full pore size distributions. This would help in proper pore size grading of the membrane, which is important for selecting the membrane for a particular application.

Keywords: Capillary flow porometry, Pore-size distribution