PULSED LOW ENERGY POSITRON SYSTEM (PLEPS):

A promising tool to investigate dispersion in mixed matrix membrane

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Abstract

The methodology of mixed matrix membranes (MMMs) was introduced years ago to boost the performance of polymeric membranes by passing the so called upper bound of Robeson's plot [1-3]. MMMs are composite in nature, comprising one continuous phase (i.e. polymers) and a discontinuous phase (i.e. fillers) which is dispersed in continuous matrix. Many fillers have been studied such as zeolites, silica, carbon molecular sieves, carbon nanotubes (CNT), nano particles, metal organic frame work (MOFs), etc [4-5]. The dispersion of the fillers plays a vital role in performance and properties of MMMs. An ideal MMM is one in which fillers are homogenously distributed over the polymer matrix with good adhesion. In gas separation MMMs, the defects are very critical because gas can easily pass through even very small voids without any selectivity [6-8]. Mostly in literature, researchers investigate these defects by using x-ray diffraction, scanning electron microscopy and other conventional techniques. But these characterization techniques don't tell anything about size and distribution of defects and free volume in MMMs [4-5].

Positron lifetime spectroscopy (PALS) is a valuable non-destructive technique which gives information about free volume in membranes [9]. To detect, characterize, and depth-profile free volume in thin membrane layers with PALS, monochromatic positron beams of variable energy are necessary. By varying the positron implantation energy, the mean implantation depth of the positrons can be controlled. The pulsed low energy positron system (PLEPS) at the high energy positron source NEPOMUC at the MLZ in Garching is a unique tool for detecting, characterizing and depth profiling of free volume in membranes and thin membrane layers with PALS from the surface down to some microns below the surface with a depth resolution in the nm-range[10-13].

In this work, polyimide based (Matrimid®, 6FDA-DABA) MMMs were fabricated using self-synthesized and functionalized UiO-66 based MOFs particles. These MMMs are characterized by FTIR/ATR, WAXD, and SEM. Effects of MOF functionality and loading on gas separation performance are studied for CO2/CH4 gas mixture. In addition, correlation of MOF dispersion and distribution in the polymer matrix with gas separation behavior is studied by depth profiling with different positron implantation

energy (1KeV to 16KeV) using PLEPS. Increase or decrease in the gas selectivities and permeabilities of different MMMs could easily be understood using PLEPS. Results suggested that PLEPS is a promising characterization tool to get insight in free volume distributions starting from the membrane surface to deep inside the membrane matrix.



Figure: (a) Ideal dispersion of filler in polymer matrix,
(b) Polymer rich phase on surface and filler rich phase under the surface,
(c) Filler is not homogenously dispersed.

Key words: Mixed Matrix Membranes, Pulsed low energy positron system, Gas separation

References:

[1] L.M. Robeson, J. Membr. Sci. 62 (1991) 165–185.
[2] I.F.J. Vankelecom, E. Merckx, M. Luts, J.B. Uytterhoeven, J. Phys. Chem. 99 (1995) 13187–13192
[3] C.M. Zimmerman, A. Singh, W.J. Koros, J. Membr. Sci. 137 (1997) 145–154
[4] R.D. Noble, J. Membr. Sci. 378 (2011) 393– 397
[5] J. Mater. Chem. A, 2013, 1, 10058-10077
[6] M. Moaddeb, W.J. Koros, Journal of Membrane Science 125 (1997) 143
[7] T. S. Chung, L. Y. Jiang, Y. Li, S. Kulprathipanja, *Prog. Polym. Sci*. **32** (2007) 483–507
[8] M.J.C. Ordoñez, K.J. Balkus, J.P. Ferraris, I.H. Musselman, J. Membr. Sci. 361 (2010) 28–37
[9] G. Consolati, I. Genco, M. Pegoraro, L. Zanderighi, J. Polym. Sci. B Polym. Phys. 34 (1996) 357–367
[10] W. Egger, Positron sources and positron beams. In Physics with many positrons: Proceedings of the International School of Physics "Enrico Fermi" Course CLXXIV, R. Brusa, A. Dupasquier, A. P. Mills Jr, Eds.; IOS Press: Amsterdam (2010) p 419.
[11] J. Algers,P. Sperr, W. Egger, G. Kogel, FHJ. Maurer, Phys. Rev. B 67 (2003) 125404
[12] C. Hugenschmidt, H. Ceeh, T. Gigl, F. Lippert, C. Piochacz, M. Reiner, K. Schreckenbach, S. Vohburger, J. Weber, and S. Zimnik, J. Phys. Conf. Ser. 505 (2014) 012029
[13] T. Koschine, K. Rätzke, F. Faupel, M. M. Khan,T. Emmler,V. Filiz, V. Abetz, L. Ravelli, W. Egger, (2015), J. Polym. Sci. B Polym. Phys. 53 (2015) 213–217