Transport diffusion of CO₂ in mixed matrix membranes

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Over the last few decades there have been significant research efforts aimed at developing energy-efficient Mixed Matrix Membranes (MMMs) which have great potential for gas separation processes by overcoming the limitation of pure polymeric membranes, namely, the trade-off between permeability and selectivity. Considering the progress on MMM fabrication techniques and enhanced characteristics of new MMM generations, however, there have been relatively few studies carried out on understanding fundamental diffusion phenomena in MMMs. In other words, it is hardly understood how differently the guest molecules, such as CO_2, H_2 and methane, penetrate the two distinctive spaces, i.e. polymer and filler regions, within the MMMs.

With Infrared microscopy (IRM) [1], we have recently investigated the diffusion mechanism of CO_2 molecules in pure 6FDA-DAM polymer sheet. By varying the thickness of the polymer from 25 μm to 320 μm, it was found that the diffusional time constant, τ, was linearly proportional to the thickness of the polymer, as shown in Fig. 1. This linear relationship, in turn, means that the CO_2 adsorption in the polymer is strongly limited by the surface barrier instead of the diffusion inside, according the Eq. (1):

$$\tau = \tau_{barrier} + \tau_{diffusion} = \frac{L}{\alpha} + \frac{L^2}{3D_T} \tag{1}$$

where, $2L$ is thickness, α is surface permeability, and D_T is transport diffusivity. Further research is required to elucidate whether the insertion of fillers alters the limiting step of the CO_2 uptake process in MMMs.

In addition, our IR microimaging technique enabled us to record CO_2 concentration profiles over a MMM consisting of 6FDA-DAM polymer and big ZIF-8 crystals (>70 µm size) during transient adsorption. From this we can directly observe how fast and how much the guest molecules diffusion into and adsorb on to the two different regions in the MMM.
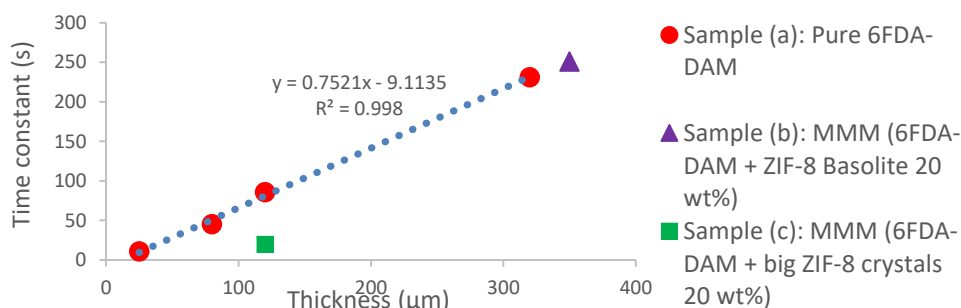

Figure 1: Relationship between diffusional time constant and thickness of polymer

Reference

[1] J. Kärger, et al.: *Microimaging of transient guest profiles to monitor mass transfer in nanoporous materials*. Nature Materials **13**, 333-343 (2014).