THIN FILM COMPOSITE PTMSP/PAF MEMBRANES: STUDY OF PHYSICAL AGING

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Introduction

Vast majority of the membrane materials used for commercial gas separation membranes or being close to the upper bound on the Robeson diagram are amorphous, glassy polymers due to their high permeability/selectivity and ability to maintain rigid structure under processing conditions [1,2,3,4]. Meanwhile, the gas separation membrane shall meet the following criteria to be taking into account for further applications such as high gas permeability, desired level of selectivity, good mechanical and film forming properties, sufficient resistance under operation conditions, and stable performance during long-term operation. However, the polymeric materials, glassy polymers in particular, are non-equilibrium systems that are tend to relaxation of excess fractional free volume (FFV) due to macrochains rearrangements resulted in the deterioration of membrane permeability with time (so called “aging effect”).

The goal of this work was to evaluate the ability of porous aromatic framework particles (PAF-11) with the size of 150-200 nm to stabilize the performance of the thin film composite membranes with varied thickness of selective layer, based on the most permeable polymeric material PTMSP.

Experiments

PTMSP ($TaCl_5$/TIBA) and PAF-11 synthesized in [5] were used in this study. The thin top-layer of PTMSP was casted on the porous PAN-support (HZG, Germany) from 0.5 wt.% polymeric solution in chloroform by a kiss-coating technique described elsewhere [6]. In the case of loaded PTMSP layer, PAF-11 fillers were added to polymeric casting solution. It was possible to obtain TFC-membrane samples with size of 10x30 cm for further testing.

Transport characteristics of TFC membranes were monitored by the individual gas permeability (N_2, O_2, CO_2) measured by a volumetric method at room temperature, feed pressure up to 2 bar, permeate pressure was 1 bar. The active membrane surface area S was 12.6 cm^2. In all cases, the gas flux was increased linearly with the respect of trans-membrane pressure that was allowed to determine the gas permeability the graph slope. All gas flux and permeability presented in this work were recalculated to STP conditions.

All obtained membranes were analyzed by scanning electron microscopy (SEM). A high-resolution scanning electron microscope, Hitachi Tabletop Microscope TM3030Plus, was used. Beforehand the samples were immersed to *iso*-propanol to fill-up the pore structure, then fractured in liquid nitrogen and sputtered under vacuum with a thin (5 nm) layer of gold.

Results and Discussion

Figure 1 illustrates SEM visualization of the cross-section for TFC membrane sample. As might be noticed, the PAF-11 fillers are mostly well distributed within the polymer with thanks to the hydrophobic nature of porous particles, and no noticeable aggregation of these particles was observed.

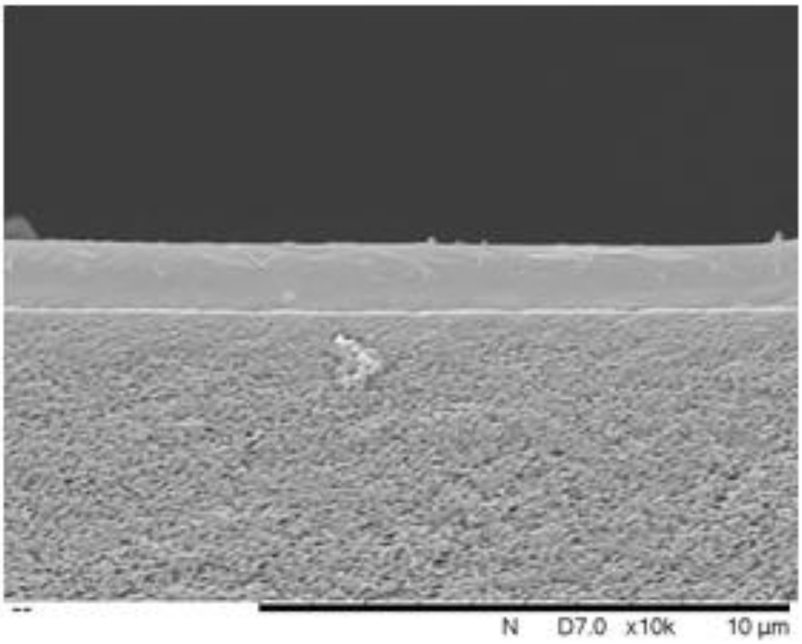

Figure 1. The Cross-Section of PAN/PTMSP TFC Membrane

In contrast to the annealing protocol used for fast aging of the dense PTMSP membranes in our recent study [5], all TFC membranes were kept at ambient temperature to monitor their physical aging preventing the possible affect of high temperature on the adhesion of top-layer and performance of PAN-support. Figure 2 presents the change in N_2, and CO_2 permeance of fabricated TFC membranes with the overall thickness of selective layer of 1.7-6.8 μm over the time of about 5000 hours; in addition, the data for TFC membrane with virgin PTMSP layer of 2.8 μm is also provided as a reference. It can be seen that the as-cast membranes showed the very promising gas permeation, but immediate decline in gas permeance occurred, which can be explained by the physical aging of glassy polymer. Worth noting that the composite membranes with loaded PTMSP layer of 1.7, 2.1 and 3.8 μm possessed more rapid decline in gas permeance in contrast to the membrane with virgin PTMSP layer of 2.8 μm. However, the steady state performance was reached within shorter time for PTMSP/PAF-11.

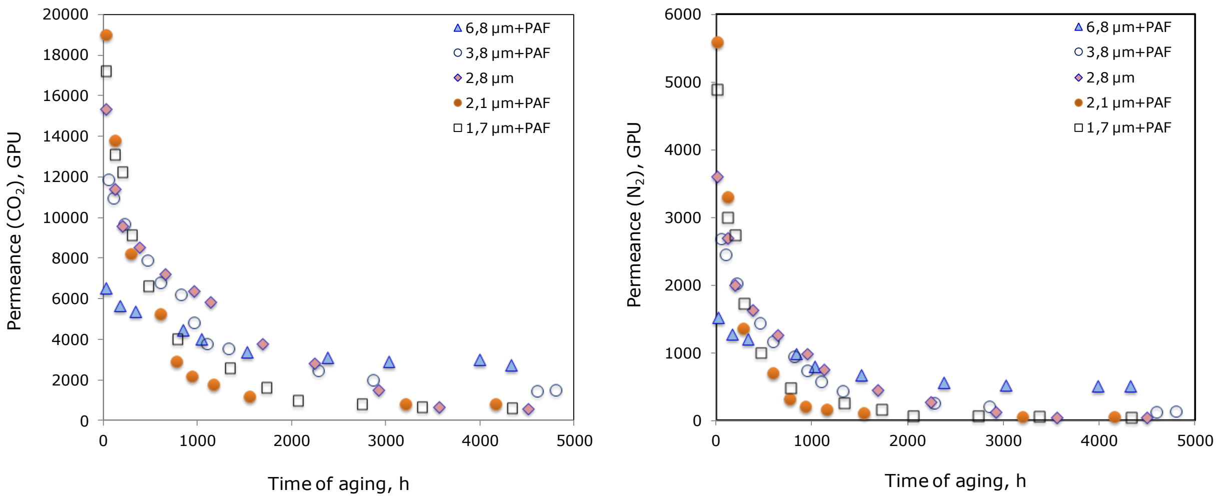

Figure 2. Gas permeance of TFC membranes with different top-layer thickness as a function of aging time.

It was found that the thickness of selective layer plays a major role in the physical aging of TFC membranes. The addition of PAF-11 (10 wt.%) resulted in achieving of faster relaxation and the increase in the resulted gas permeance in contrast with the TFC membranes with virgin PTMSP. The combination of addition of PAF-11 fillers and cross-linking of selective layer allowed to obtain the TFC membrane with N_2, O_2 and CO_2 permeance of 790, 1250 and 4450 GPU, respectively, and the ideal selectivity $\alpha(O_2/N_2)=1.6$ and $\alpha(CO_2/N_2)=5.6$. To the best of our knowledge, these are the highest gas permeance values stable in time reported in the literature for the composite membranes based on the high permeability glassy polymers.

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