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Helium Permeation through Mixed Matrix Membranes Based on Polyimides and Silicalite-1

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1. Introduction

Gas separation by selective permeation through polymer membranes is one of the fastest growing branches of separation technology. The permeability of pure polymeric membranes for gases has its upper bound which can be overcome by formation of mixed matrix membranes containing as the other constituent particles of a microporous sorbent [1]. The feasibility of preparation procedures to manufacture polyimide based membranes with enhanced permeability for gases was examined in the present work using silicalite-1 crystals as the microporous constituent. The effect of silicalite-1 content on membrane permeability of self-standing composite membranes was studied using non-stationary measurement of gas permeation carried out in a quasi-steady state regime. The prevailing test penetrant used was helium.

2. Experimental and Results

Novel preparation approach was used in this study to improve interfacial adhesion of membrane constituents. It consisted in the use of coupling agent 3-aminopropyltriethoxysilane. Polyimide chains were thus first endcapped by the coupling agent and subsequently this modification enabled their reaction with silicalite-1 terminal OH groups at outer crystal surface of silicalite-1. Such improving of interfacial adhesion made possible the formation of membranes with silicalite-1 content up to 60 wt. %. The polyimide contituents of mixed matrix membranes were based on polyamic acids (PAAs) with controlled $M_n \cong 10\,000$ g.mol^{-1} which were synthesized from the following monomer combinations: (1) PMDA - ODA; (2) ODPA-ODA; (3) PMDA - BIS P; (4) ODPA - BIS P; (5) 6FDA–ODA where PMDA stands for pyromellitic dianhydride, ODA for 4,4´-oxydianiline, ODPA for 5,5´-oxybis-1,3-isobenzofurandione, BIS P for 4,4´ -(1,4 – phenylenediisopropylidene)bisaniline and 6FDA for 4,4´-(hexafluoroisopropylidene) diphtalic anhydride. Two samples of silicalite-1 crystals were used for this study (i) coffin-shaped crystals of crystal length L_c = 100 μm and (ii) boat-shaped crystals of crystal length L_c = 20 μm.

The principal membrane characteristic evaluated was the plot of relative membrane permeability P_{eff}/P_c vs. ϕ_d where P_{eff} and P_c [mol.m^{-1}.s^{-1}.Pa^{-1}] denote the effective permeability of mixed matrix membrane and that of continuous phase, respectively, and

ϕ_d stands for volumetric fraction of dispersed phase (silicalite-1). The other membrane characterization was carried out by SEM and light microscopy. The accessibility of silicalite-1 channel system for molecules of penetrants after crystal embedding into polymer was examined by iodine indicator technique [2]. The effect of interface formation on the relative permeability was examined using the nonporous inclusions which were represented by the corresponding templated crystals.

The experimental P_{eff}/P_c vs. ϕ_d plots were compared with theoretical dependences simulated using the Bruggeman model. Such a comparison is exemplified in Fig. 1. It should be noted that P_{eff}/P_c vs. ϕ_d plots were always monotonous but experimental data exhibited significant deviation from the Bruggeman model. The analysis showed that the above deviation can be explained by stratification of the composite membrane which can be considered as consisting of two or even three layers as evidenced by the SEM micrograph in Fig. 2.

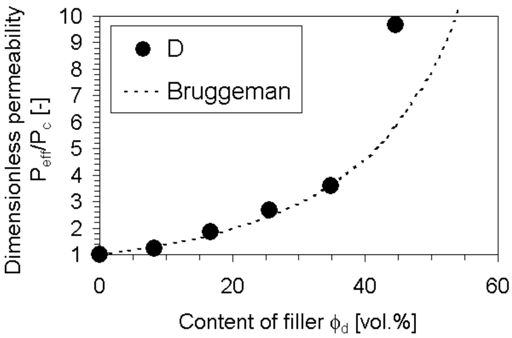

Fig. 1: The comparison of experimental P_{eff}/P_c vs. ϕ_d plot for membrane made of PI(6FDA-ODA) with theoretical dependence simulated using the model by Bruggeman.

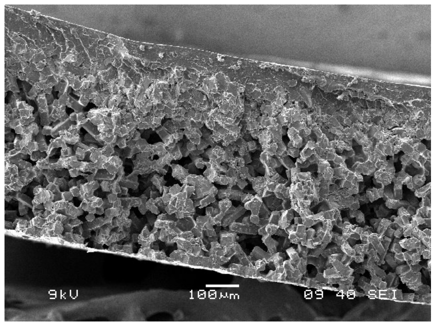

Fig. 2: The SEM image of membrane made of PI(6FDA-ODA) filled by 60 wt. % of silicalite-1.

3. Conclusion

The plots of relative He permeabilities vs. ϕ_d exhibited, for the mixed matrix membranes of the type polyimide - silicalite-1, significant deviations from dependences predicted by the Bruggeman model. The deviations could be explained by membranes stratification to the system of two or three quasi-uniform layers whereas one of the layers of the three layer system contains the continuous network of macropores.

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