Development and Characterization of PPO Composite Membranes for Gas Separation

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SUMMARY: Poly(phenylene oxide) (PPO) composite membranes have been prepared on a polysulfone (PSf) ultrafiltration support, which was previously coated with highly permeable polydimethylsiloxane (PDMS). The PDMS gutter layer was used in order to: plug the pores of the support; minimise the thickness of the separating PPO deposit; and reduce the tortuosity of the path of the gas molecules to the pores of the support.
Composite membranes with high fluxes and good selectivities for gas separations have been obtained with an amorphous and cross-linkable phenylene oxide co-polymer.

Introduction

Next generation's gas separation membranes must yield good performance in aggressive environments (high temperature, solvents, extreme pH values). Poly(phenylene oxide)s (PPOs) form a class of polymers of good thermal, chemical and mechanical properties with very good transport properties. In this work composite PPO membranes have been prepared by interposing a silicon rubber gutter layer in between a polysulfone UF support and the active polymer layer[1,2].

Experimental

In this work poly(2,6-diphenyl-1,4-phenylene oxide) (PPPO), and poly(2,6-dimethyl-1,4-phenylene-*co*-2-allyl-6-methyl-1,4-phenylene oxide) [CPAMPO, monomers molar ratio (dimethyl-to-allylmethyl) = 7] have been used for the preparation of composite membranes. A PDMS precursor solution (Sylgard 184, Dow Corning; base/curing agent = 10, in cycloexane) was cast over a PSf ultrafiltration support (cut-off 300 kD) which had been

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impregnated with a suitable liquid to prevent the intrusion of PDMS into the pore system. PDMS was cured at 65°C for 5 hrs. Afterwards, the supports were contacted repeatedly with PPO solutions and, only for CPAMPO, crosslinked by UV light. The procedures for all of the different steps indicated had to be optimized (solvents, materials, times, cross-linking conditions, etc.) in order to yield good results. The gas permeability of the membranes (O_2, N_2, He, CO_2, 99.995% or higher purity) has been measured by using a volumetric method[3] in the range 0.5-10 kg/cm^2 of pressure gradient at room temperature.

Results and discussion

The permeance of the PSf support is $14 \cdot 10^4$ GPU [1 GPU $\equiv 10^{-6}$ cm^3(STP)/(cm^2·cmHg·s)] with $\Delta p = 10$ kPa, with no selectivity for the gases tested. The results indicate a convective flux through the pores. The PDMS coated PSf support shows the same selectivity values of PDMS[4], and a CO_2 flux of about 250 GPU (Fig. 1).

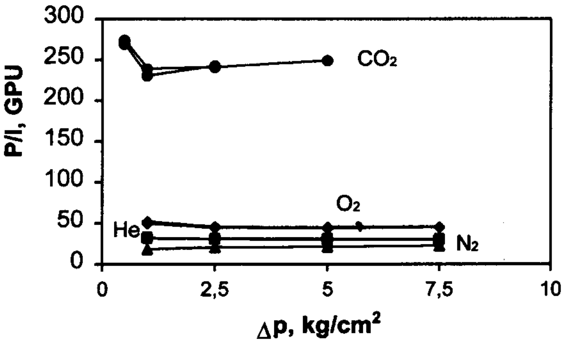

Fig. 1: Permeance at 28°C through the PDMS covered UF polysulfone support

The SEM pictures of the naked and of the coated PSf supports indicated that the penetration in the pores of PDMS and the thickness of its deposit on the surface are limited to about 100-200 nm (Figs. 2a- 2d).

The composite membranes obtained by coating PPPO (Fig. 2e) are not very satisfactory: although the morphology of the surface is perfectly smooth, selectivity values are intermediate between the ones of PDMS[4] and those of PPPO[5]. In particular, the permeability of He is lower than the one of CO_2 (Fig. 3) indicating a defective coverage of PPPO.

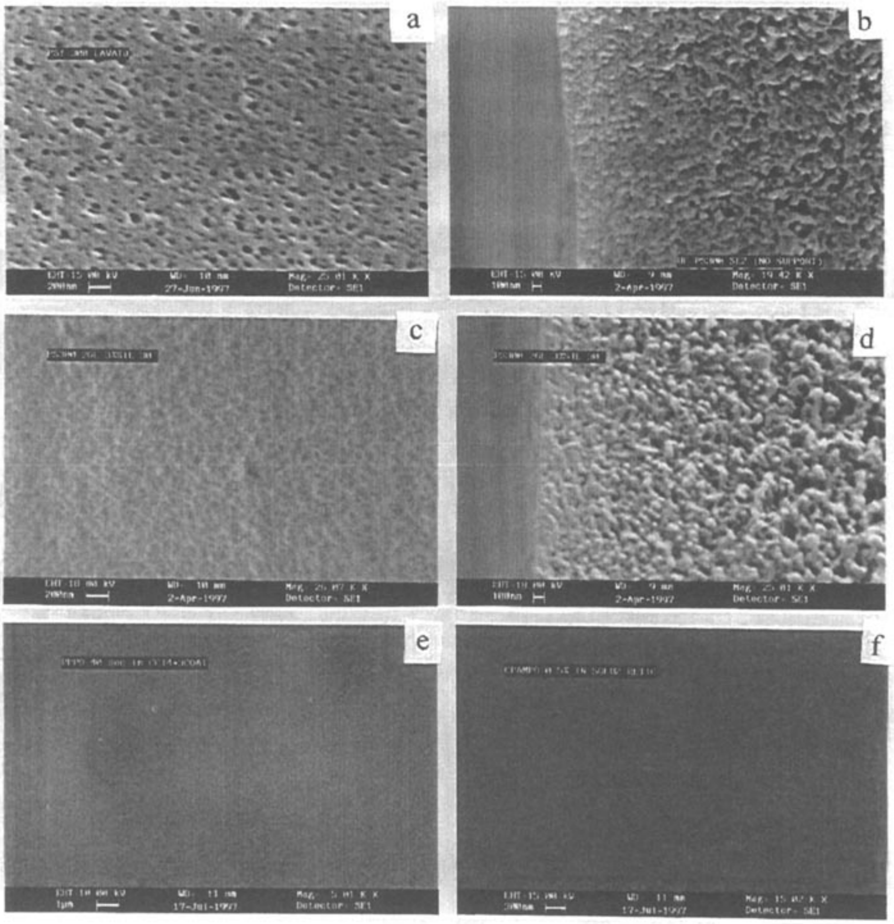

Fig.2: Top view and cross section of the UF PSf support before (a-b) and after (c-d) the coating with PDMS. Top view of the composite membranes obtained by coating 0.29 wt% PPPO solution in CCl_4 (e) and 0.5 wt% CPAMPO in CCl_4 with 0.02 wt% of a crosslinking agent (f).

2,2-dimethoxy-2-phenylacetophenone (4 wt % of the polymer) was added to the CPAMPO solution (0.5 % in CCl_4). The PDMS coated PSf supports were contacted with the CPAMPO solution and exposed to UV light before drying in vacuum at 50°C for 45 min. The morphology of the surface of the resulting membranes is smooth (Fig. 2f) and the transport properties are satisfactory, even though some samples resulted to be defective and had to be discarded. The CO_2/N_2 selectivity is about 30 and of about 5.5 for O_2/N_2, with a CO_2 flux of 50 GPU (Fig. 4). These values compare well with the performance of industrial UBE gas separation membranes[6].

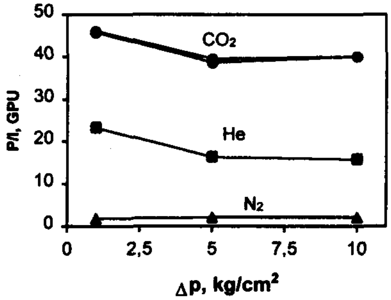

Fig.3: Permeance @ 30°C through the PPPO composite membrane

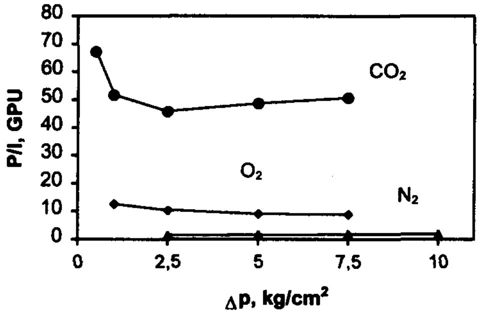

Fig.4: Permeance at 20°C through the CPAMPO composite membrane

Conclusions

PPO composite membranes have been prepared on polysulfone porous supports by interposing a PDMS gutter layer. Good selectivity and high flux were obtained by using a cross-linkable PPO co-polymer containing allyl moyeties. The use of PPPO resulted in defective membranes with poor separation properties.

Acknowledgements

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