MEMBRANES FOR GAS AND LIQUID SEPARATIONS

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ABSTRACT

Poly(phenylene oxide)s were used to prepare flat, integrally skinned self-supported asymmetric membranes by dry-wet phase separation. The intrinsic ideal gas selectivity of poly-(2,6-dimethyl-1,4-phenylene oxide) (PMPO) was retained in the membranes, and improved by a coating with silicone rubber. Polymers of the same class were coated on UF supports with a silicon rubber gutter layer, yielding composite membranes with high flux but lower selectivity.
The effect of the glutaraldehyde cross-linking of sodium alginate (SA) membranes on the mobility of water and ethanol has been studied with pfg nmr. Crosslinking reduces water self-diffusion, and does not seem to be stable on the timescale of weeks.

INTRODUCTION

Gas separation membranes made from glassy polymers are widely used in industrial processes [1]. They consist of a defect-free skin layer supported by a highly permeable substructure [2]. In this work poly(phenylene oxides) have been used for the preparation of integrally skinned self-supported membranes, and of composite membranes on UF supports.

The search for a more durable alginate membrane, able to separate effectively and for a long time water from organics in pervaporation, with no loss of performance, is gathering more and more attention from the scientific community. The effect of the glutaraldehyde crosslinking of sodium alginate (SA) on the self diffusion of water in the polymer matrix has been studied with the pulsed field gradient-nmr technique.

EXPERIMENTAL

Integrally skinned asymmetric membranes

Poly(2,6-dimethyl-1,4-phenylene oxide) (PMPO, M_w = 123 kD, T_g = 213_C), with good thermal and mechanical properties [3], was dissolved in a solution of chlorinated solvents and of 1-octanol. The knife-cast solutions on glass plates were quenched in methanol after a fixed evaporation time. The permeability of pure gases (N_2, He, O_2 and CO_2, purity $\geq$ 99.995%) at room temperature and pressure gradients of 0.05-1.0 MPa was measured with a volumetric method [4]. The asymmetric membranes were coated with silicon rubber (Sylgard 184, Dow Corning) in order to plug the residual pinholes of the skin layer.

Composite membranes with a PDMS gutter layer [5, 6].

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 = 7] were used. A PDMS precursor solution (Sylgard 184) was cast over a PSf ultrafiltration support (cut-off 300 kD) which had been 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.

Sodium alginate pervaporation membranes

Membrane Preparation

Sodium alginate (SA, Grade M-1, Kimitsu Chemical Industries Ltd., lot 40808) was dissolved in water (2.7 %), the solution was cast on a glass plate and left drying in a clean environment for two days. The SA film (20 μm thick) was peeled off the glass surface and part of it transferred to a glutaraldehyde (GA) crosslinking solution [7] of the following composition: GA 25% (Sigma): 10 vol %; HCl 36%: 0.0482 vol %; acetone: the rest. The membrane was kept in the GA solution for 48 h at 40_C, then thoroughly rinsed and soaked with methanol, and dried. The equilibrium amount of water absorbed at 25_C in air with 100% relative humidity was 84.6% of the mass of the dry polymer.

Pfg nmr experiments

The water self-diffusion measurements were performed on a Bruker AM300 nmr spectrometer - 300 MHz on proton - using a pulsed field gradient experiment in the Fourier Transform mode. They were determined using the PFGLED sequence [8] due to the short transverse relaxation time of the signal. Details on the experimental conditions can be found elsewhere [9]. Strips of the SA samples in 5 mm glass nmr tubes were added with water (25-125 wt % of the dry membrane) and water/ethanol solutions (5:1 and 2:1), the tubes were frozen and sealed under nitrogen.

RESULTS AND DISCUSSION

Integrally skinned asymmetric PMPO membranes

The ternary phase diagram PMPO/trichloroethylene (TCE)/1-octanol (1-OcOH) reported by Wijmans et al. [10] was used as a starting point for the preparation of the polymeric solutions. 1-OcOH was used to reduce the solubility of the polymer and accelerate the phase separation process. More volatile solvents (CH_2Cl_2 and $CHCl_3$) substituted part of TCE in order to ease the evaporation of solvent prior to quenching, and to promote the formation of a thin skin layer. The best results were obtained with the following composition of the casting solution: 14.2% PMPO, 10.3% OcOH, 36.3% $CHCl_3$, 39.2% TCE (ASY-E) , and 14.2% PMPO, 10.8% OcOH, 25.1% $CHCl_3$, 49.9% TCE (ASY-F). The ASY-E membrane (Figure 1) showed a sponge-like porous substructure under a thin dense top layer (0.25 μm) with no evident superficial defects; the ASY-F membrane had a similar structure, with a thicker skin layer though (1.3 μm), probably due to a slower phase separation of the casting solution with respect to membrane ASY-E. When increasing the PMPO content in the casting dope (20% PMPO, 5.1% OcOH, 18.5% $CHCl_3$, 56.4% TCE), a closed-cell structure with a very thick skin layer was obtained, and the polymer crystallized yielding spherulitic aggregates. The N_2 permeance of the ASY-E and ASY-F membranes at 18_C and Δp=0.5 MPa was 1.11 and 0.18 GPU [1 GPU = 10^{-6} $cm^3(STP)/(cm^2*cmHg*s)$], respectively, and the O_2/N_2, CO_2/N_2 and He/N_2, selectivity was 3.5, 15 and 23 (ASY-E), and 6.1, 23 and 36 (ASY-F).
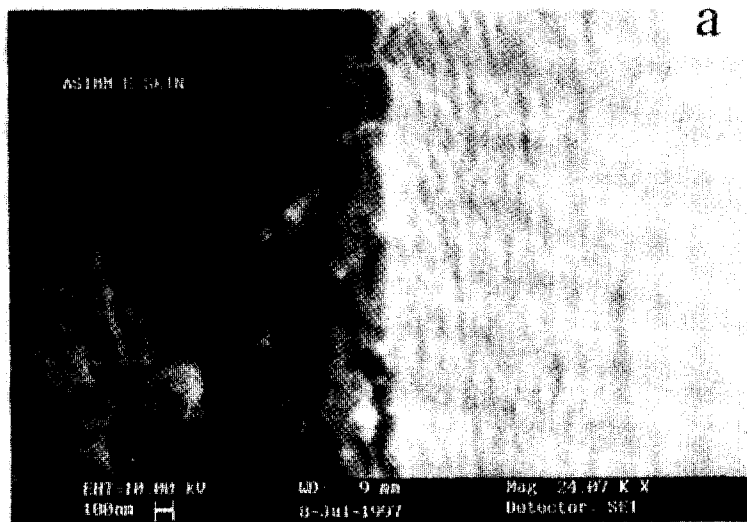
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Figure 1. ASY-E membrane [14.2% PMPO, 10.3% OcOH, 36.3% CHCl$_3$, 39.2% TCE; quenched in MeOH], with a sponge-like porous substructure under a very thin dense top layer (0.25 μm), and no evident superficial defects

The selectivity of these membranes were close to the intrinsic value of PMPO [3, 11], but could be improved by a PDMS coating in order to plug the residual pinholes of the skin layer: the CO$_2$/N$_2$ and He/N$_2$ separation factors increased to 33 and 48 in the case of membrane ASY-F (30_C, Δp = 1 MPa). The decrease of the He/N$_2$ selectivity of membrane ASY-E after the PDMS coating suggested that the solvent of the silicon rubber can spoil very thin dense layers. In fact, the use of solvents for PDMS with lower surface tension than cyclohexane (hexane, pentane) resulted in better performances of the membranes.

Composite PPO membranes with a PDMS gutter layer

The PDMS coated PSf support showed the same selectivity values of PDMS [1], and a CO$_2$ flux of about 250 GPU. 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. The composite membranes obtained by coating PPPO (contact of the support with the polymer in CCl$_4$) were not very satisfactory: although the morphology of the surface was perfectly smooth, selectivity values intermediate between the ones of PDMS and those of PPPO [3] were found. In particular, the permeability of He was lower than the one of CO$_2$.
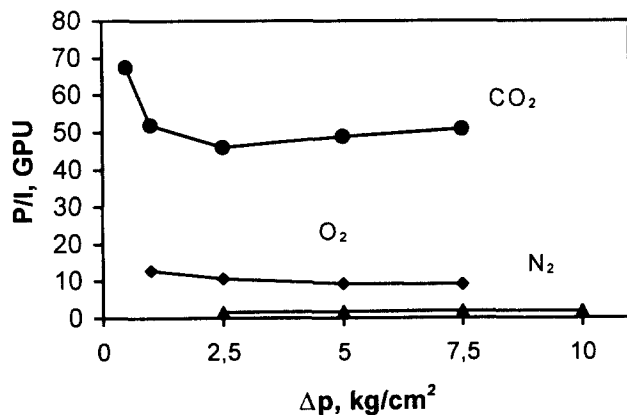

Figure 2. Gas permeances at 20_C through the CPAMPO composite membrane

2,2-dimethoxy-2-phenylacetophenone (4 wt % of the polymer) was added to the CPAMPO

coating solution. 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. Membranes with smooth surfaces and satisfactory transport properties resulted, even though the results were not completely reproducible. 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. 2).

Sodium alginate membranes

The water self-diffusion coefficients in virgin SA membranes showed a biexponential dependence, indicating the presence of two different populations of water molecules. Upon increasing the water percentage in the membrane/penetrant system at 70_C, the self-diffusion coefficient trend indicated possible structural modifications of the membranes. The presence of ethanol in mixture with water increased water mobility.

GA cross-linking reduced the amount of water that can be sorbed by the polymer, but only to a small extent its mobility. By increasing water uptakes, the penetrant mobility increased too steadily. Unexpectedly, however, water mobility reduced sensibly after one month. The reasons for this behaviour are currently investigated.

CONCLUSIONS

PMPO was used to prepare flat asymmetric gas separation membranes with high selectivity and flux via dry-wet phase inversion, by adding a non-solvent and a volatile solvent to the polymeric solution. High flux composite membranes were obtained on a PSf support caulked with silicon rubber by repeatedly coating a phenylene oxide polymer containing allyl groups and crosslinking with UV light. Two water populations with different mobility were evidenced in SA membranes by pfg nmr experiments. Ethanol increased water mobility, whereas glutaraldehyde cross-linking reduced it.

ACKNOWLEDGEMENTS

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