Hybrid silica – polymer macroporous membranes with tunable surface functionality

Ana-Mariana Urmenyi[a]*, Albert P. Philipse[b], Rob Lammertink[a], Matthias Wessling[a]

[a]University of Twente, Membrane Technology Group, Faculty of Science and Technology, P.O. Box 217, 7500 AE, Enschede, The Netherlands
[b]Van't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute, Utrecht University, Padulaan 8, 3584 CH, Utrecht, The Netherlands
email: aurmenyi@nalco.com

1. Introduction

We report a generic synthetic route to prepare polymer-silica hybrid membrane with tunable porosity and surface properties. First, a macroporous polymeric membrane is prepared using immersion precipitation technique. Subsequent encapsulation of the polymer matrix with a continuous silica layer, substitutes the surface properties of the polymer by the silica layer. This enables the use of the rich spectrum of silica functionalisation techniques. Hydrophilization and hydrophobization to control wetting properties of the macroporous hybrid membrane are evaluated.

2. Results and discussion

Copolymer ethylene vinyl alcohol with an average of 27 mol% ethylene (EVAL 27) and 44%

(EVAL 44), respectively and polyethersulphone (PES) were used for membrane preparation. The membranes were characterized by scanning electron microscopy (Fig. 1), IR, pure water fluxes, contact angle measurements, pore-size distribution, density measurements, streaming potential, etc.

In the Stöber [1] silica spheres grow in a solution supersaturated with silicate species resulting from the hydrolysis and condensation of TEOS. To prepare a hybrid silica polymeric membrane, we performed the Stöber synthesis in the presence of the macroporous polymeric membrane as a polymeric template. The presence of silica on the membrane surface, independent of the chemical nature of the substrate, is confirmed by SEM (Fig. 2), IR, XPS, TGA analysis, density, contact angle measurements and streaming potential. For example, for PES membranes we find $\xi = -1.7$ mV whereas for PES-T-G the zeta potential has dropped to -4.9 mV, consistent with the presence of silica species on its surface.
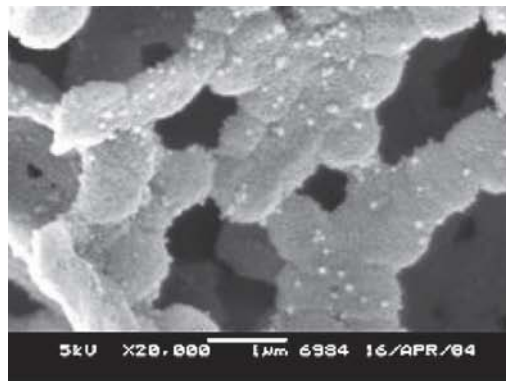
The silica on the membranes contains surface silanol groups that react easily with silylating
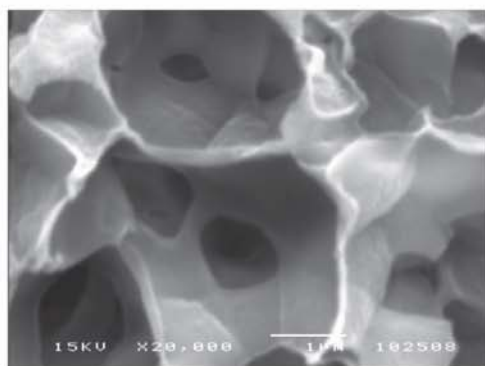
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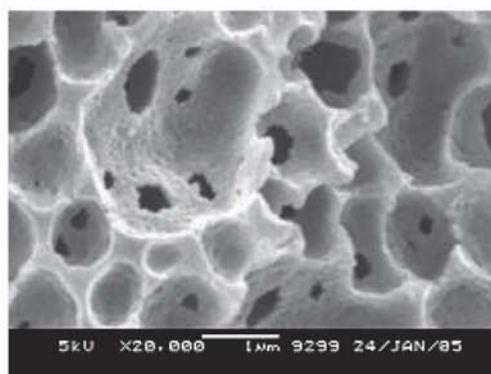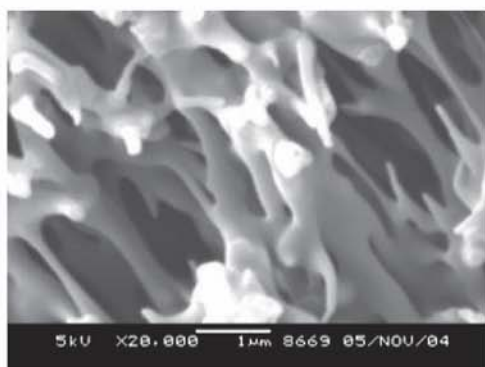 Present address: Nalco Company, Water R&D Europe, Ir. G. Tjalmaweg 1, 2342 BV, Oegstgeest, The Netherlands.
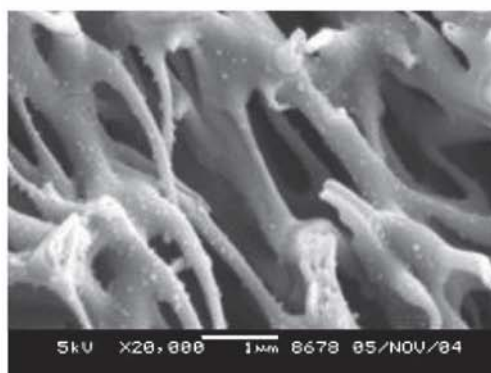
(a)

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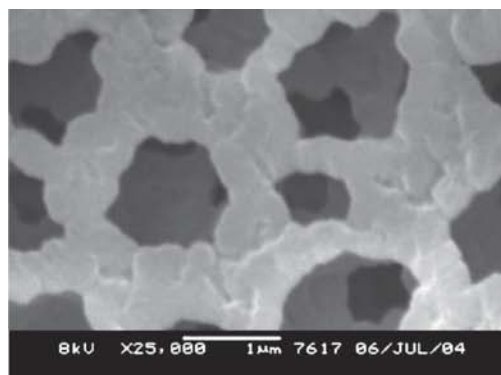
(c)

Fig. 1. SEM micrographs of membrane – before silica deposition: a – EVAL 27-T; b – EVAL 44-T; c – PES-T.

(a)

(b)

(c)

Fig. 2. SEM micrographs of membrane – after silica deposition: a – EVAL 27-T; b – EVAL 44-T; c – PES-T.

agents in the form of a silane-coupling agents (SCA). As a proof of principal, we performed several surface modifications of hybrid silica-

polymeric membranes to obtain a variety of functionalities. Hydrophobic, 1H, 1H, 2H,

2H-perfluorooctyltrichlorosilane (FTEOS) and octadecyl alcohol (C18) and hydrophilic aminated (3-aminopropyl tri-methoxysilane (APS) functionalities were introduced on the hybrid silica-polymeric membranes. The presence of the coupling agent onto the membrane surface was proven by XPS, confocal microscopy, streaming potential, contact angle measurements, etc.

3. Conclusions

We have shown that alkaline hydrolysis of tetraethoxysilane inside various polymer matrices leads to coverage of the polymer surface with an amorphous silica layer. The silica allows subsequent functionalization with hydrophobic as well as hydrophilic silane coupling agents as confirmed by a variety of characterization techniques. The properties of the thus functionalized macroporous structure are independent of the type of the starting polymeric membrane substrate that merely provides the architecture of the pore structure without affecting the substrate chemistry.

Reference

[1]   W. Stöber, A. Fink and E. Bohn, J. Colloid Interface Sci., 26 (1968) 62.