



Material behaviour

Experimental contribution to the understanding of transport through polydimethylsiloxanenano-filtration membranes: Influence of swelling, compaction and solvent on permeation properties



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ABSTRACT

This study aims to better understand the permeation properties of polydimethylsiloxane (PDMS) membranes. The compressibility and nanofiltration fluxes were measured for swollen PDMS films using several solvents at applied pressures ranging from 5 to 50 bar. The degree of swelling varied according to the solvent and the pressure applied. To show the correlation between the behaviour of the swollen PDMS under pressure and its permeation performance, the thickness reduction of the membrane was mimicked using uniaxial compression tests. The evolution of the nanofiltration flux as a function of the transmembrane pressure proved to be non-linear. Linearization was achieved by taking into account both the swelling and the thickness reduction previously measured, confirming that these phenomena may have occurred during the nanofiltration experiments. Moreover, the solvents' viscosity and affinity for the polymer were confirmed to have a great influence on their ability to permeate the membrane. Finally, employing the most commonly used models, a study of transport through the membrane led to the conclusion that the experimental results were in agreement with the hydraulic theory of transport.

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1. Introduction

For the last few decades, solvent resistant nanofiltration (SRNF) has been an emerging topic of research because of its wide range of applications in processes involving organic solvents [1]. Among the membranes used to carry out SRNF experiments, polydimethylsiloxane (PDMS) exhibits interesting physico-chemical properties. It is a regular cross-linked rubber-like dense polymer with elastic properties and pronounced hydrophobicity [2]. Once brought into contact with an organic solvent, this polymer swells to various degrees, depending on the nature of the liquid. Solvent uptake and the consequent swelling ratio (S) of the PDMS are related to several characteristics of both

the solvent and the polymer. First, the swelling ability of a polymer is mainly attributed to its affinity for the immersion solvent, which the Hildebrand solubility parameter (HSP; δ) [3,4] tries to quantify. Secondly, the size and structure of a solvent's molecules are also factors that influence sorption into the membrane [5]. Moreover, the density of the cross-links in a polymer has a significant impact on solvent uptake; its increase leads to a stiffer polymer with reduced free volume between the polymer chains, restricting its swelling capacity and compressibility.

When a thin PDMS film is used as an active layer in a SRNF experiment, it may be subjected to two opposing phenomena. On the one hand, as described above, solvent-induced swelling increases the interchain free volume through relaxation of the polymer network. On the other hand, the membrane is subjected to a high level of applied pressure (usually 20–40 bar) which flattens the swollen

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List of abbreviations

δ	Hildebrand solubility parameter (MPa ^{1/2})
ϵ	membrane strain (mm.mm ⁻¹)
σ	applied stress (MPa)
χ	interaction parameter
μ	liquid dynamic viscosity (Pa.s)
ρ	density (g.cm ⁻³)
τ	tortuosity factor
B_0	specific permeability of the membrane (m ²)
D	diffusion coefficient (m ² .s ⁻¹)
ΔP	transmembrane pressure (Pa)
HS	Hildebrand solubility
J	solvent flux (L.h ⁻¹ .m ⁻² or m ³ .s ⁻¹ .m ⁻²)
K	partition coefficient
L	membrane thickness (m)
Mc	molecular weight between cross-links (g.mol ⁻¹)
p	porosity
PDMS	polydimethylsiloxane
r	average pore radius (m)
S	swelling ratio
SRNF	solvent resistant nanofiltration
TR	thickness reduction factor
v	molar volume (cm ³ .mol ⁻¹)

Subscripts

l	length
m	membrane
s	solvent
w	weight

PDMS. If compaction and/or swelling restriction of the membrane really occur in SRNF, how far would they influence permeation properties? Would there be obvious morphological changes in the swollen polymeric network? Linearity was reported when plotting flux as a function of the transmembrane pressure [6–8]. This observation suggested that no membrane compaction occurred. By contrast, swollen PDMS polymers showed a dual visco-elastic and poro-elastic behaviour when submitted to applied pressure, with poro-elastic relaxation being restricted by the migration of the solvent [9,10]. Moreover, Tarleton et al. [11] noted that an applied-pressure of 20 bar led to 80% reduction of the swelling in heptanes as compared to the value obtained at atmospheric pressure. In agreement with the swelling restriction of the PDMS membranes when submitted to applied pressure, Ogieglo et al. [12] showed, using spectroscopic ellipsometry for in-situ measurements, that a progressive reduction in membrane thickness was observed when the upstream pressure increased. In addition, the significant amount of time needed to reach the steady filtration state was attributed to membrane compaction under pressure in other studies [13,14].

Currently, the SRNF transport mechanism is one of the most discussed means of investigation. It is well known that a solvent can migrate through a polymer matrix by convection and/or diffusion. Convection occurs mainly when the free volume between crosslinks is much larger than the size of a single solvent molecule. However, when the mesh size of the polymer network is equivalent to the solvent's molecule size, its migration is better described as diffusion [15]. The question debated in the SRNF community is: can a swollen polymer be considered a “porous medium”? By definition, a dense polymer does not exhibit any pores in its structure. However, since solvent-induced swelling increases the interchain free-volume, the resulting swollen system properties might be similar to those of a porous one. Solvent fluxes through PDMS membranes have been shown to be mostly influenced by both the swelling state and the thickness of the membrane [16–19], as well as solvent viscosity, polarity [18,20] and affinity for the membrane [17,21]. Furthermore, although the Hagen–Poiseuille equation has been reported valid for describing solvent transport through PDMS membranes [18,20], other studies invalidated this transport mechanism solely based on viscous flow [8,12,21,23].

In the present study, a thicker but pure PDMS commercial membrane was chosen over a composite one in order to avoid any possible swelling restriction or polymer chain intrusion into the macroporous support [6,24,25]. The impact of the swelling, the transmembrane pressure applied and the solvent on the PDMS permeation properties during NF experiments was studied with several solvents, chosen for exploring a broad range of swelling capacities. First, the polymer was characterized through swelling experiments and uniaxial compression tests. Then, permeation measurements were carried out to determine the parameters that had the most influence on the transport of solvent through the PDMS membrane. Finally, a study of the solvent transport by employing the most commonly used models in SRNF was carried out.

2. Theoretical background

The two main theories commonly used to study solvent transport through nanofiltration dense membranes are the pore flow and the solution-diffusion models [26,27]. The first is depicted by the Hagen–Poiseuille equation that describes the flux value for a viscous flow as:

$$J = \left(\frac{pr^2}{8L\tau} \right) \frac{\Delta P}{\mu} \quad (1)$$

where J (m³.s⁻¹.m⁻²) is the solvent flux, p the porosity, r the average pore radius (m), ΔP the transmembrane pressure (Pa), L the membrane thickness (m), μ the liquid dynamic viscosity (Pa.s) and τ the tortuosity factor. Basically, it is admitted that there are no pores in a dense polymer. However, solvent sorption and consequent relaxation of the polymer network may induce paths through the membrane that are significantly larger than the diameter of a single permeating molecule. The so-called “channels” formed in the polymeric network would mean that membrane mesh sizes need to be taken into account, hence, this

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