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**EDITOR: STEVE TARLETON (Loughborough, UK)**
Email: filtsol@virginmedia.com; Web: www.stevetarleton.com

# DETERMINATIONS OF MEMBRANE SWELLING AND THE EFFECT ON FILTRATION PERFORMANCE

Steve Tarleton (e.s.tarleton@lboro.ac.uk)
*Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK.* (Web page: http://www-staff.lboro.ac.uk/~cgest)

This paper describes an apparatus for *in-situ* determinations of swelling where a linear inductive probe and electronic column gauge with an overall resolution of 0.1 µm was used for measurements of seven variants of polyacrylonitrile (PAN)/polydimethylsiloxane (PDMS) composite nanofiltration membranes in a range of alkane, aromatic and alcohol solvents. The unswollen membranes incorporated PDMS layers between 1 and 10 µm nominal thickness and were manufactured with a radiation and/or thermal crosslinking step.

The tested membranes exhibited a range of swelling dependent on the degree of crosslinking, the initial PDMS layer thickness and the type of solvent. With no applied pressure the PDMS layer on some radiation crosslinked membranes swelled as much as ~170% of the initial thickness whilst other membranes were restricted to a maximum swelling of ~80%. When a pressure up to 2000 kPa was applied to a membrane then swelling could be reduced to ~20% of the value obtained at zero applied pressure. By vertically stacking up to 3 membrane samples it was possible to determine the swelling of PDMS layers as thin as 1 µm, although higher imposed pressures rendered some results unreliable as the measurement resolution of the apparatus was approached. The typical influences of membrane swelling in crossflow membrane filtration are also shown.

## INTRODUCTION

Detailed knowledge of membrane properties is becoming increasingly important as membrane separation matures into new areas of technology and researchers attempt to better understand the fundamentals. For example, the development of polymeric solvent resistant nanofiltration (SRNF) membranes has attracted much attention and enabled several potential applications in the processing of organic solvent streams[1]. Although precise transport mechanisms across the convection-diffusion spectrum are an on-going topic of debate, it is generally accepted that polymer swelling plays a significant role in determining levels of flux and rejection[2-6].

Most previous efforts to quantify the swelling of nanofiltration membranes have followed the approach of Ho and Sirkar[2] whereby the weight difference between a dry and solvent impregnated polymer sample is determined. Stafie *et al.*[3] used the method with specially prepared ‘thick films’ of polydimethylsiloxane (PDMS) and measured swelling approaching 205% for hexane-solute (oil or PIB) systems. Vankelecom *et al.*[4] used ‘slabs’ of PDMS with t-butanol solvent to demonstrate 70% swelling in the unrestrained state, but only 29% swelling when a sample was clamped. The same authors also report that tetradecane solvent previously sorbed within PDMS could be removed using an applied 10 bar pressure and then restored in a reversible manner upon release of the pressure and re-immersion in the solvent.

Yoo *et al.*[5] used four variants of hydroxyl-terminated PDMS in the form of 20 mm x 10 mm x 1.5 mm blocks to measure swelling in the presence of pure solvents as well as binary and ternary mixtures. Of most relevance are the data for pure n-hexane, n-heptane and cyclohexane solvents where swelling ratios in the region of 4 were noted (i.e. ~300 % expansion). Geens *et al.*[6] also showed significant swelling with a range of solvents where prior to testing the selective top layer from three hydrophilic polymer membranes was removed using liquid nitrogen. In contrast, Piccinini *et al.*[7] describe an alternative, and relatively complex, technique where a quartz spring microbalance was used to simultaneously measure solubility, diffusion coefficient and swelling for a solvent/polymer combination of acetonitrile/polyetherurethane.

An inherent disadvantage of the Ho and Sirkar method is the need to use ‘thick films’, ‘slabs’ or ‘blocks’ of pure polymer in order to establish sufficiently accurate measurements. The extent of swelling is strongly related to the degree of polymer crosslinking as well as the affinity of the polymer for the solvent and is potentially influenced by the presence of a backing in a composite membrane which typically swells to a different extent. The use of relatively thick samples of polymer is also a problem when crosslinking is mainly achieved by exposure to radiation. As the depth of penetration is normally limited a sample will tend to experience a different degree of crosslinking toward its centre relative to that close to the exposed surfaces.

The ability to determine swelling for a composite membrane where the selective layer is measured in the ‘as manufactured’ state and in intimate contact with the backing layer(s) is a distinct advantage and one that is offered by the technique described in this paper. More realistic measurements of swelling are likely to provide for improved modelling and thus better understanding of solvent/solute transport mechanisms. There is generally a desire to use thin selective layers on membranes to maximise fluxes and, by way of example, the paper explores the potential of measuring swelling in composite membranes with PDMS layers <10 μm thickness.

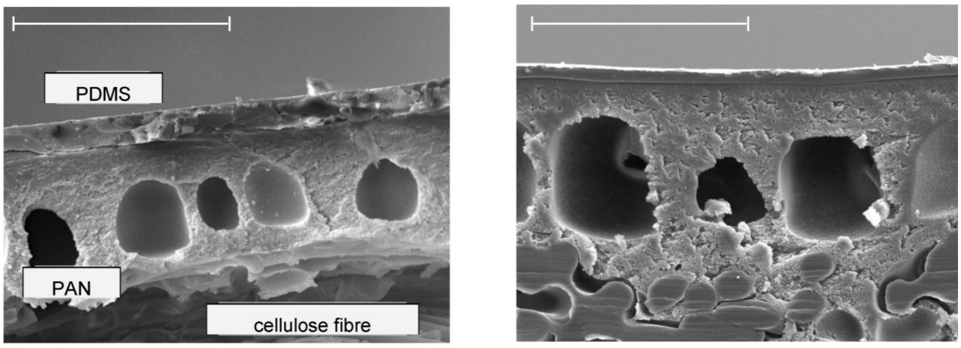
## EXPERIMENTAL

### Membrane

All swelling experiments used samples of flat sheet cellulose fibre/PAN/PDMS composite nanofiltration membranes. In total seven variants of these membrane were available for testing in their ‘as manufactured state’ and Figure 1 show some example SEMs. Although full details of membrane manufacture were not available due to issues of confidentiality, the membranes showed similar general structures where a PAN layer was sandwiched by a PDMS layer (at the top) and a cellulose fibre layer (at the bottom); neither the PAN nor cellulose fibre is thought to play any role in nanofiltration other than to provide support to the selective PDMS layer. A PAN layer had a typical thickness of 40 μm.

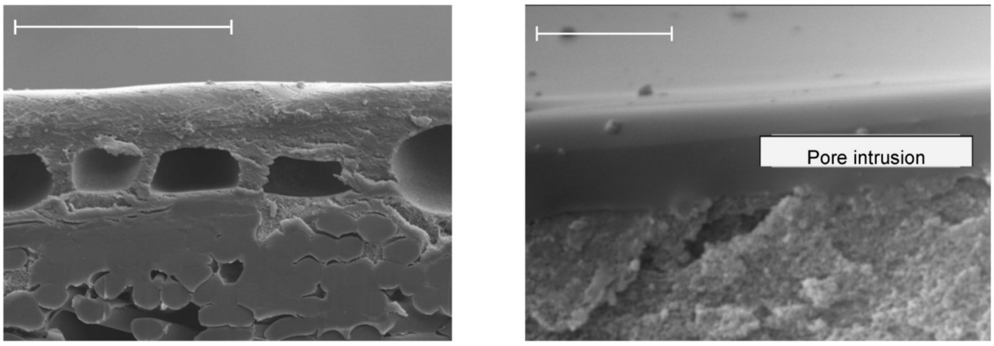
The tested membranes incorporated nominal PDMS thicknesses between 1 and 10 μm. During manufacture of six of the membrane variants, a PAN support was roll-coated with a solution containing the siloxane monomer and a catalyst, and initially subjected to a thermal treatment process to induce crosslinking. Further crosslinking of the PDMS was achieved via irradiation with an electron beam from a low energy accelerator$^{8}$. The procedure resulted in a reasonably well-defined PDMS layer with little evidence of pore-intrusion into the PAN (although the true extent of the PDMS layer was difficult to identify in some cases).

Electron beam radiation generally induces two opposing effects on PDMS composite membranes, crosslinking by the formation of radicals which subsequently combine to form covalent crosslinking bonds and degradation of the membrane material. An optimum radiation dose therefore exists which induces the maximum increase in crosslinking density with only marginal degradation of the membrane material. Three of the membranes were each exposed to a ‘standard’ radiation dose of 80 kGy during manufacture (1 kGy ≡ 1 kJ/kg) whilst three other specially prepared samples were



80 kGy radiation, 10 μm

80 kGy radiation, 2 μm



Radiation, 1 μm

Thermal, 1.5 μm

Figure 1: Micrographs of some of the tested membranes. The dimension on a sub-legend refers to the nominal PDMS thickness in the unswollen state. The size bar represents a length of 60 μm on the radiation crosslinked membranes and 2 μm on the (purely) thermal crosslinked membrane.

treated, respectively, with radiation doses of 200, 100 and 50 kGy. A seventh membrane sample was also obtained from a different source. Whilst the substrate material was similar to the other membranes, in this case the selective PDMS layer was crosslinked using a purely thermal technique and there seemed to be significant PDMS intrusion into the PAN layer.

Whilst localised variation in PDMS thickness was observed in several SEMs, nitrogen gas permeation measurements showed that the average thickness was as stated and average permeances were within 2% of the literature quoted value of 280 barrer.

### Solvents

A range of alkane (octane, hexane, heptane and cyclohexane), aromatic (xylene) and alcohol (methanol, ethanol and propanol) solvents were used in the swelling experiments. These span a range of polarity[9], and thus potential swelling capability, as evidenced by their solubility parameter $\delta$ = 14.3-29.2 MPa$^{0.5}$. All solvents were used in their as received state, had purities in excess of 99% and were obtained from Sigma-Aldrich, Fisher Scientific or Shell Global Solutions.

### Apparatus and Procedure

The form of the membrane swelling apparati are shown in Figure 2 (see also[10]). With reference to Figure 2(a), in an experiment with no applied pressure a *circa* 15 mm square sample of PAN or membrane was placed in a flat-bottomed dish. A 10 mm diameter spacer was placed on top of the sample and the linear measurement probe was positioned over the spacer and connected to the electronic column gauge. The probe/gauge combination, which essentially comprised a digital dial comparator, had a resolution of 0.1 µm. Referring to Figure 2(b), with the addition of a support frame and cantilever bar that pivoted about a bearing mount in one end, it was possible to impose a pressure upon a test sample. By adjusting the distance between the sample and pivot, and/or adding weight to the free end of the cantilever bar the applied pressure could be varied up to 2000 kPa.

In a typical swelling experiment the sample to be tested was initially mounted dry in the dish. Membranes with a 10 µm nominal PDMS thickness could be tested individually. For thinner PDMS layers the potential of using membrane 'stacks' was investigated where up to three separate membrane samples were positioned vertically, one on top of the other. With the membrane (s), spacer, probe and cantilever bar all in place, a few millilitres of solvent was quickly added to the dish to completely immerse the sample after which swelling started immediately. Sixty seconds was typically allowed for a sample to reach an equilibrium thickness before a final displacement measurement was taken; this time included a safety margin of *circa* 15-30 s and was established during a sequence of preliminary experiments where transient measurements of swelling were taken following the introduction of solvent.

The rapidity of measurements meant that any longer term fluctuations in laboratory temperature (typically 18±2ºC) had negligible influence on measurement accuracy. As a precaution, however, the apparatus was shrouded from drafts and sunlight and preliminary experiments with heptane solvent and an 80 kGy radiation, 10 µm membrane were repeatedly performed at different times over a period of days to confirm general data reproducibility.

## RESULTS AND DISCUSSION

### Swelling Measurements

Swelling tests were performed using the apparati shown in Figure 2 and the seven membrane variants.

For the PAN substrate alone and lower polarity solvents such as n-heptane and xylene there was no change in lateral dimension (i.e. below the detection limit), however, with higher polarity alcohols some

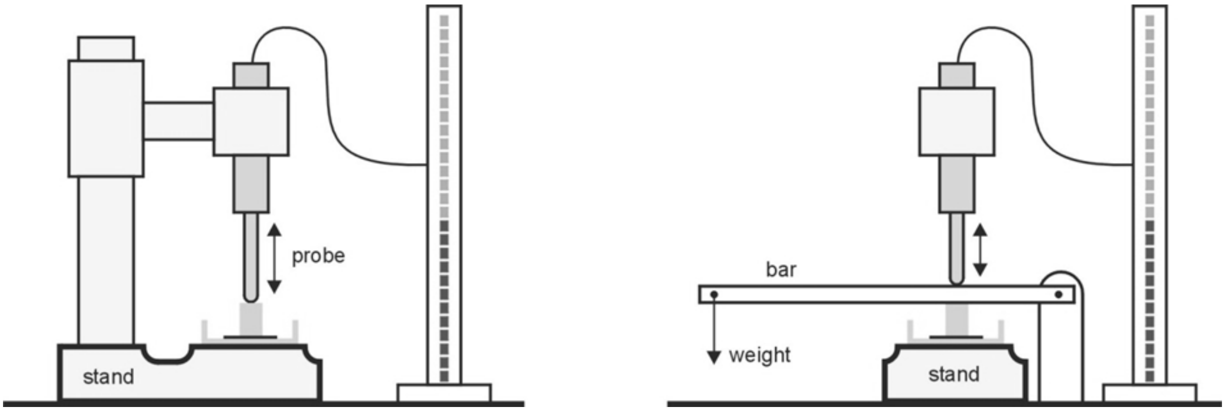


Figure 2: Schematics of apparati for measurements of membrane swelling. (a, *left*) no applied pressure, (b, *right*) with applied pressure.

shrinkage was observed (see Table 1). Experiments using the PAN/PDMS composite often showed appreciable swelling. For low polarity solvents the swelling was exclusively dictated by expansion of the PDMS, whereas with the highest polarity solvents shrinkage of the PAN substrate became progressively more comparable to dimension changes in the PDMS.

To overcome the inevitable variability's of membrane manufacture it was necessary to perform a number of repeat experiments for each membrane/solvent combination and typically between 4 and 10 measurements were taken. When evaluating swelling of the PDMS layer in a composite membrane it was assumed that any dimension change in the PAN was the same as determined in a corresponding experiment with the PAN alone. The test samples, as assessed by visual inspection at the end of an experiment, were completely wetted in all cases.

Tables 1 & 2 and the corresponding graphs in Figures 3 & 4 show a range of typical results of experiments with no applied pressure using the apparatus depicted in Figure 2(a). The data demonstrate an ability to quantify swelling and comprise average values for sample expansion/shrinkage and respective standard deviations (SDs) for the displacement measurements. As a rule-of-thumb, in the following descriptions a sequence of measurements are deemed to be acceptable when the SD is *circa* 10% (or less) of the average value. Whilst this choice is somewhat arbitrary, measurements by the Ho and Sirkar method typically yield SDs of the same level (see, for example,[3]).

Considering the 80 kGy radiation, 10 μm membrane as a reference, Table 1 and Figure 3 show that a peak swelling of 169% occurred with n-heptane solvent ($\delta$ = 15.3 MPa$^{0.5}$) which corresponds favourably with the literature reported value of solubility parameter for

| Solvent | Solubility parameter ($\delta$, MPa$^{0.5}$) | PAN alone (μm)* | 80 kGy radiation, 10 μm (μm)** | 80 kGy radiation, 2 μm (μm)** | | |
|---|---|---|---|---|---|---|
| | | | | single | double*** | triple*** |
| i-octane | 14.3 | bdl | 14.8 (0.82) | 3.10 (0.90) | 2.32 (0.21) | - |
| i-hexane | 14.7 | bdl | 16.0 (1.59) | 4.16 (1.09) | - | - |
| n-hexane | 14.9 | bdl | 16.4 (1.59) | 3.41 (0.34) | - | - |
| n-heptane | 15.3 | bdl | 16.9 (1.80) | 3.86 (0.55) | 3.48 (0.44) | 3.59 (0.82) |
| cyclohexane | 16.8 | bdl | 15.8 (0.95) | 4.66 (0.50) | 3.16 (0.27) | 3.16 (0.31) |
| xylene | 18.2 | bdl | 11.9 (0.94) | 2.55 (0.72) | 2.13 (0.38) | 1.93 (0.53) |
| i-propanol | 23.6 | -0.10 | 1.50 (0.30) | 0.54 (0.18) | 0.48 (0.28) | - |
| n-propanol | 24.9 | -0.20 (0) | 1.24 (0.34) | 0.33 (0.27) | -0.08 (0.08) | - |
| ethanol | 26.5 | -0.24 (0.09) | 0.75 (0.26) | 0.42 (0.32) | -0.35 (0.35) | - |
| methanol | 29.2 | -0.64 (0.09) | 0.07 (0.30) | 0.56 (0.17) | -1.21 (0.38) | - |

At least: *4 measurements; **9 measurements. ***Quoted SDs are for the measurements of stacks of 2 (double) or 3 (triple) membranes. bdl ≡ below detection limit.

Table 1: Lateral expansion/swelling of PAN and PDMS layers on composite membranes in pure solvents with no applied pressure; the standard deviations (SDs for a single membrane or a stack) of measurements are shown in brackets. The dimension in a membrane name refers to the nominal PDMS thickness in the unswollen state.

| Solvent | 50 kGy radiation, 2 μm (μm)* | 100 kGy radiation, 2 μm (μm)* | 200 kGy radiation, 2 μm (μm)* | Radiation, 1 μm (μm)* | Thermal, 1.5 μm (μm)* |
|---|---|---|---|---|---|
| i-octane | 2.20 (0.38) | 1.60 (0.30) | 1.77 (0.24) | 0.50 (0.12) | 0.80 (0.24) |
| i-hexane | 2.24 (0.34) | 1.73 (0.23) | 1.71 (0.28) | 0.45 (0.14) | 0.52 (0.27) |
| n-hexane | 2.24 (0.24) | 1.70 (0.23) | 1.70 (0.30) | 0.49 (0.16) | 0.53 (0.24) |
| n-heptane | 1.84 (0.23) | 1.76 (0.32) | 1.63 (0.21) | 0.53 (0.18) | 0.51 (0.33) |
| cyclohexane | 2.15 (0.22) | 1.25 (0.27) | 1.69 (0.27) | 0.78 (0.16) | 0.81 (0.20) |
| xylene | 2.29 (0.36) | 1.26 (0.29) | 1.09 (0.23) | 0.78 (0.30) | 0.76 (0.16) |
| i-propanol | 0.09 (0.14) | 0.14 (0.24) | 0.16 (0.16) | 0.01 (0.18) | 0.09 (0.06) |

*At least 9 measurements. Quoted SDs are for the measurements of stacks of 2 or 3 membranes.

Table 2: Lateral expansion/swelling of PDMS layers for composite membranes in pure solvents with no applied pressure; the SDs of measurements are shown in brackets. All '2 μm' membranes were measured with a double membrane stack whilst the '1 μm' and '1.5 μm' membranes required a triple membrane stack.

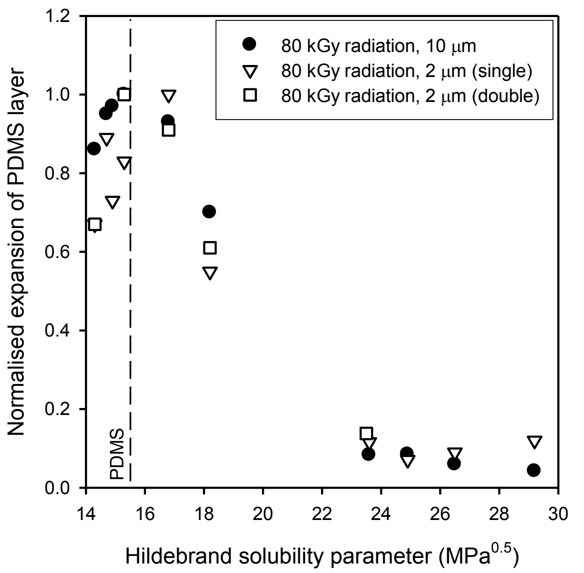


Figure 3: Normalised swelling of the PDMS layers on two radiation crosslinked membranes as induced by different pure solvents.

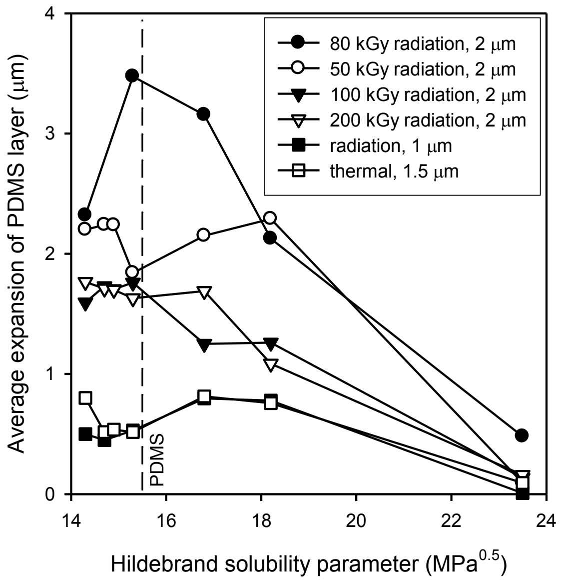


Figure 4: Swelling of the PDMS layers on a range of radiation or thermally crosslinked membranes with different pure solvents.

PDMS at $\delta$ = 15.5 MPa$^{0.5}$. Over the region $\delta$ = 15.3-23.6 MPa$^{0.5}$ the solvent polarity increases to induce progressively less swelling in the PDMS layer and at even greater values of $\delta$ the membrane swelling was reduced still further and reliable values were difficult to obtain. Corresponding results for the 80 kGy radiation, 2 µm membrane are also shown in Table 1 and Figure 3. Whilst the swelling follows a similar general trend in terms of the position of the peak, the absolute values are substantially lower as the PDMS layer is nominally 2 µm, rather than 10 µm, thick. Moreover, when a single membrane was tested there was a tendency for the measurement SDs to be somewhat larger for the membrane with the 2 µm PDMS layer; Figure 3 also shows that the average values are more scattered relative to the data recorded for the 10 µm membrane. The swelling of a single membrane with a 1 µm PDMS layer could not be measured reliably given the limiting 0.1 µm resolution of the measurement probe.

In an attempt to overcome the difficulties associated with measurements of thinner samples, tests were performed using membranes stacked vertically in double and triple configurations prior to placement of the spacer and linear probe. Whilst additional solvent/membrane interfaces are introduced by this procedure, which may interfere with overall measurement accuracy, it was expected that their influence would be negligible relative to the potential benefits. Table 1 and Figure 3 show that when two samples of the 80 kGy radiation, 2 µm membrane were stacked one on top of the other then more consistent data were obtained over the region $\delta$ = 14.3-23.6 MPa$^{0.5}$, as evidenced by the SDs which are in keeping with those recorded for the 80 kGy radiation, 10 µm membrane. The similar normalised profiles shown in Figure 3 also infer a similar degree of crosslinking.

A reduced number of experiments were also performed using a stack of three membranes, however, Table 1 shows that the benefits are limited when the starting PDMS thickness is sufficient (which in turn infers that the additional solvent/membrane interfaces introduced by the stacking procedure have little detrimental effect on measurement accuracy when low polarity solvents are used). It is noted that in the authors previous works[11-13] with low polarity systems, maximum solvent fluxes and minimum solute rejections were reported in nanofiltration experiments for the 80 kGy radiation, 2 µm and 10 µm membranes when $\delta_{solvent} \approx \delta_{PDMS}$. The data suggest that the relationship of these two parameters closely follows swelling propensity over the region $\delta$ = 14.3-18.2 MPa$^{0.5}$.

Swelling experiments with n-propanol, ethanol and methanol solvents and the 80 kGy radiation, 2 µm membrane identified a limitation of the measurement technique. Although not observed with single membrane samples, when stacks of two and three membranes were tested using higher polarity solvents ($\delta$ > ~24) unexpected shrinkage of the PDMS layer was recorded, i.e. over and above that which could be accounted for by shrinkage of the PAN substrate alone. Whilst shrinkage of PDMS in alcohol cannot be entirely discounted, at least theoretically, such results are unusual and currently unexplained but could be a consequence of introducing additional solvent/membrane interfaces by using membrane stacks.

Table 2 and Figure 4 show the results of swelling experiments with no applied pressure for the remaining membranes variants in Figure 1. For membranes with a nominal 2 μm PDMS layer a stack of two was required to give consistent results whilst a stack of three membranes was needed in the case of thinner PDMS layers. Table 2 shows that when the number of membranes used in a measurement is taken into account, the majority of swelling values for the membrane stacks exhibit acceptable standard deviations when compared to those recorded, for instance, with the 80 kGy radiation, 10 μm membrane; membranes with 1-1.5 μm PDMS layers are probably approaching the resolution limit of the current apparatus, particularly when there is intrusion of the PDMS into the PAN layer. It is evident from Figure 4 that swelling of the membrane variants differs significantly to a degree dependent on the extent of crosslinking and the unswollen thickness of PDMS.

As could be expected intuitively, the 50 kGy treated membrane generally swells to a greater extent than either the 100 or 200 kGy treated membranes as there is less crosslinking present. However, the swelling profiles of all three of these membranes differs substantially in comparison to the 80 kGy radiation, 2 μm membrane. Although exact manufacturing details were not available to the author, the results suggest that the 80 kGy radiation, 2 μm membrane undergoes additional treatment(s) during manufacture to impart different swelling properties and thus solvent flux/ solute rejection performance. Figure 4 also shows that the membranes with nominal 1 μm and 1.5 μm thick PDMS layers exhibit similar swelling profiles both in terms of form and absolute values.

A direct comparison of results for PDMS swelling with those in the open literature is difficult due to their limited availability and knowing the extent of crosslinking in a particular PDMS sample. However, for n-heptane, cyclohexane and n-hexane solvents independent measurements of swelling for thermally crosslinked PDMS blocks have been reported by Yoo *et al.*[5] with values in the region of 260-310% whilst Stafie *et al.*[3], for thick films of PDMS, report swelling in hexane of ~205%. These values are rather higher than the data reported in this paper which perhaps supports the suggestion that the presence of a PAN backing material can significantly hinder swelling of an attached PDMS layer. What is clear, however, is that nominally similar PAN/PDMS composite membranes swell to significantly different extents dependent upon their mode of manufacture and literature reported values of ‘PDMS swelling’ obtained by the Ho and Sirkar method may need to be treated with some caution, i.e. there are no generally applicable values.

A limited number of data were acquired using the apparatus shown in Figure 2(b) where the swelling of four membrane variants was assessed over the pressure range 0-2000 kPa; the results are shown in Table 3 and Figure 5 in absolute and normalised forms respectively. All of the tested membranes showed a reduction in swelling with increased pressure which is to be expected. From the data presented it is evident that an applied pressure affects PAN/PDMS membranes in different ways dependent upon factors such as the starting thickness of PDMS and the degree of cross-

| Pressure (kPa) | 80 kGy radiation, 10 μm (μm)* | 80 kGy radiation, 2 μm (μm)**, † | 200 kGy radiation, 2 μm (μm)**, † | Thermal, 1.5 μm (μm)**, † |
|---|---|---|---|---|
| 0 | 16.9 (2.90) | 3.48 (0.44) | 1.63 (0.22) | 0.52 (0.33) |
| 19 | - | 1.74 (0.27) | 1.20 (0.16) | 0.39 (0.23) |
| 68 | - | 1.70 (0.28) | 1.19 (0.3) | 0.15 (0.11) |
| 100 | 14.4 (1.40) | - | - | - |
| 131 | - | 1.69 (0.15) | 1.18 (0.09) | 0.15 (0.15) |
| 348 | - | 1.29 (0.16) | 1.12 (0.26) | 0.11 (0.11) |
| 475 | - | 1.19 (0.19) | 0.94 (0.08) | 0.11 (0.20) |
| 500 | 8.77 (2.30) | - | - | - |
| 985 | - | 1.10 (0.16) | 0.93 (0.44) | 0.09 (0.06) |
| 1000 | 6.50 (0.70) | - | - | - |
| 1500 | 4.67 (0.90) | - | - | - |
| 1622 | - | 0.97 (0.15) | 0.70 (0.21) | 0.09 (0.18) |
| 2100 | 4.33 (0.50) | - | - | - |

At least *9 measurements; **5 measurements. †Quoted SDs are for the measurements of stacks of 2 or 3 membranes.

Table 3: Lateral expansion/swelling of PDMS layers on composite membranes in pure heptane with applied pressure; the standard deviations (SDs) of measurements are shown in brackets.

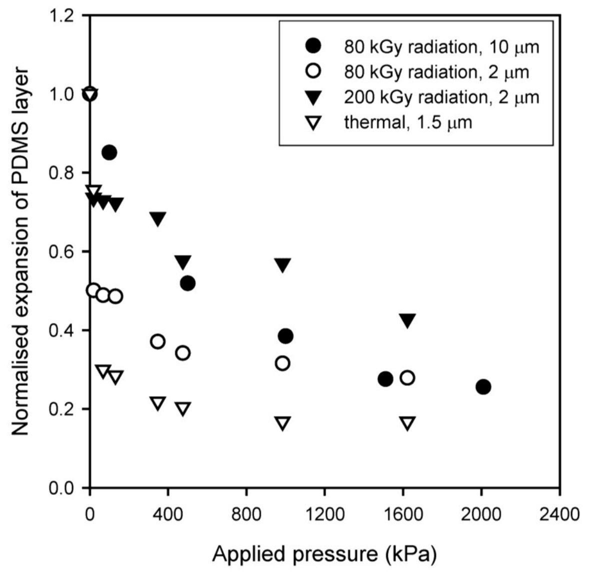


Figure 5: Swelling of the PDMS layer on four composite PAN/PDMS membranes with heptane solvent and a range of applied pressures.

linking. Swelling was influenced from the onset with pressure and there was greater effect on swelling from (say) 0-1000 kPa than over the range 1000-2000 kPa. It is noted that many of the absolute data values shown for the thermal, 1.5 µm membrane in Table 3 should be viewed with caution as the standard deviations of measurements are significant relative to the average values for swelling. However, the available evidence suggests that the PDMS layer is compressed at raised pressures.

**Solvent Flux/Solute Rejection Performance**

Although the principal intention of this paper is to report a test methodology and exemplar swelling data for PAN/PDMS composite membranes it is interesting to discuss the data obtained in the wider context of crossflow nanofiltration performance. Solvent flux and steady state solute rejection are the principal measures of performance and Figures 6 and 7 illustrate the salient features of membrane swelling on these two parameters. All crossflow nanofiltration data reported in this paper were obtained with a DESAL membrane module (wetted surface area = 75 cm$^2$) at a crossflow rate of *circa* 1 l/min. Measurements of rejection, as determined by UV-vis spectroscopy or refractive index, were typically repeatable within ±1%.

Figures 6 and 7 show that in crossflow nanofiltration with a feed comprising a low polarity solvent and polynuclear aromatic (PNA) solute at dilute concentration, the flux-pressure relationship is linear in accordance with Darcy's Law for all the tested membranes whilst solute rejection increased over the same pressure range. Several researchers have reported increasing solute rejection at raised pressures[3,14-17], frequently with obeyance of Darcy's Law. Others have reported non-linear solvent flux/pressure relationships[18-20] that are attributed to membrane compaction[18]. Sufficient data are presented to suggest that the PDMS layers on composite membranes will generally undergo com-

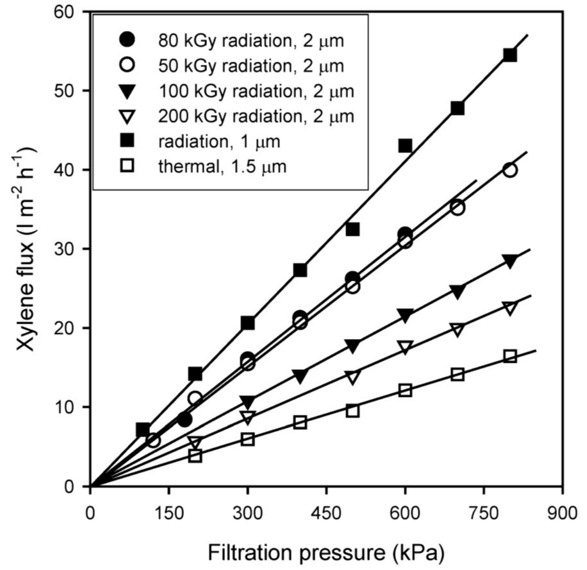


Figure 6: Flux-pressure relationships in crossflow nanofiltration with xylene solvent for a range of PAN/PDMS composite membranes.

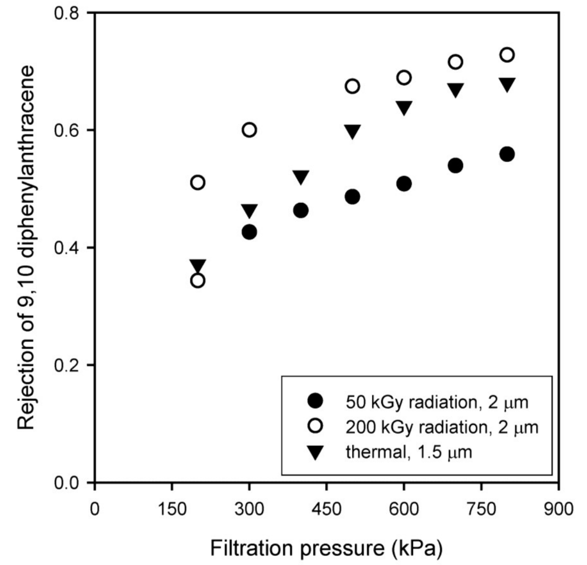


Figure 7: Rejection behaviour in crossflow nanofiltration for three membranes with xylene solvent and 9,10 diphenylanthracene (PNA) solute at a feed concentration of 20 ppm. The rejection with the other membranes showed similar trends but have been omitted for clarity.

pression during pressure driven nanofiltration, particularly over the range 0-1000 kPa. However, the overall situation presents something of a paradox, how can increasing pressure, membrane compaction and increasing solute rejection occur simultaneously with a linear solvent flux-pressure relationship? Possibilities include:

1. The polymer chains move closer together under the raised pressure to reduce free volume, diffusional solute transport subsequently slows due to a reduced diffusion rate through the denser polymer and solute rejection progressively increases. Such an arrangement could reasonably be expected to also slow diffusional solvent transport and thus cause non-linearity of the flux-pressure relationship.
2. The polymer chains move further apart during swelling to allow a greater free volume in the membrane structure which tends to promote an element of convective flow and lower rejections. When the pressure is raised the reduction in free volume naturally brings polymer chains closer together to enhance rejection by a size exclusion mechanism. For this to happen simultaneously with a linear flux-pressure relationship, the free volume/flow paths in the PDMS would have to remain sufficiently large so as not to adversely affect flow.
3. A combination of (1.) and (2.).

Both (1.) and (2.) are beneficially influenced by the potential enhancements to transport due to the reduced PDMS thickness at raised pressure. That is, respectively, a shorter distance for molecules to diffuse through the membrane or a convective flux increase in accordance with Darcy's Law. There would need to be significant coincidence for the simultaneously acting factors to induce a linear solvent-flux relationship. For fuller considerations of these hypotheses the reader is directed to previous papers by the author[11-13,21-23] where experimental arrangements and results are discussed in greater detail along with applications of nanofiltration models.

## CONCLUSIONS

A method for the *in-situ* measurement of PDMS layer swelling on composite nanofiltration membranes has been described and data presented that illustrate its capabilities and limitations. The approach offers potential advantages over more conventional techniques including the ability to test membranes in their as manufactured state, in a variety of physical arrangements (e.g. clamped, with/without imposed pressure) and the potential to determine transient measurements of swelling (e.g. as solvent progressively wets a membrane or as solvent composition is altered).

By extending the measurement range of the technique to membranes with PDMS thicknesses of *circa* 1 μm then improvements in modelling are likely to follow. The difficulties of reconciling solvent flux and solute rejection performance with membrane swelling induced by solvent(s), and the compression induced by an applied filtration pressure, are as yet largely unresolved. However, more realistic measurements of changes in membrane structure can only help to resolve the complex issues facing the membrane community.

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