

Effect of PDMS cross-linking degree on the permeation performance of PAN/PDMS composite nanofiltration membranes

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Abstract

This work focuses on the effect of poly(dimethyl siloxane) (PDMS) cross-linking on the permeation performance of the poly(acrylonitrile) (PAN)/PDMS nanofiltration (NF) composite membrane. PDMS membrane of various cross-linking degrees could be obtained by changing the ratio of a vinyl-terminated pre-polymer over a hydride cross-linker, 10/0.7, 10/1 and 10/2.

The hexane permeability (P_{hexane}) through the PAN/PDMS composite membrane prepared at pre-polymer/cross-linker ratio of 10/0.7 is higher than at ratio of 10/1 (4.5 and 3.1 $\text{lm}^{-2} \text{h}^{-1} \text{bar}^{-1}$, respectively), due to the higher membrane swelling. The P_{hexane} through the PAN/PDMS prepared at pre-polymer/cross-linker ratio of 10/2 is however higher than through the composite membrane prepared at 10/1 ratio (4.1 and 3.1 $\text{lm}^{-2} \text{h}^{-1} \text{bar}^{-1}$). This result is not consistent with the swelling findings of the dense, free-standing PDMS membranes and might be due to the lower pore intrusion of the composite membrane prepared at ratios of 10/2 compared to 10/1 and/or due to the heterogeneous quality of the silicone network. The “apparent” viscosity inside the membrane and the membrane swelling are the most critical factors affecting the hexane permeability through all composites. Nevertheless, the composite membranes prepared at various pre-polymer/cross-linker ratios have similar oil and/or PIB retention probably due to the high swelling of the silicone network.

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1. Introduction

The mass transport of organic molecules through poly(dimethyl siloxane) (PDMS) dense membranes is based on the solubility and diffusivity of the penetrants into the polymer [1–4]. By introducing extra cross-links in the PDMS network, the membrane swelling may be restricted and the diffusivity of the penetrant through the PDMS would decrease. Several studies [1,2,5–8] used PDMS-based NF membranes in various non-aqueous media due to the high affinity of PDMS for non-polar organic solvents. Bhanushali et al. [5] indicated that cross-linking degree of the silicone network may be a very important parameter determining the permeation characteristics of the NF membranes. However, no systematical study has been performed concerning the influence of the PDMS cross-linking degree on the transport properties

of silicone-based NF membrane, mainly because the studied membranes are commercial and the exact nature of their selective layer has not been fully revealed. Concerning gas and vapour transport through dense silicone membranes, Hagg [9] reported a significant effect of the PDMS cross-linking degree on the permeability of Cl_2 , O_2 , and N_2 while Nguyen et al. [10] studied the significance of the cross-linking degree on the pervaporation of water–ethyl acetate mixtures through the dense PDMS membranes.

In an earlier study [1], we used poly(acrylonitrile) (PAN)/PDMS membranes prepared at pre-polymer/cross-linker weight ratio of 10/1 (which is the recommended ratio by the supplier General Electric, The Netherlands). This ratio corresponds to the stoichiometry of the reaction between the pre-polymer of vinyl-type and the cross-linker of hydrosilane-type. However, when the pre-polymer/cross-linker ratio varies, the PDMS swelling is expected to change considerably [11–13]. This may increase the flux of the PAN/PDMS composite membranes without compromise for

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Nomenclature

a_{pen}	penetrant activity
$c_{\text{PIB,f}}$	concentration in the feed side (% (w/w))
$c_{\text{PIB,p}}$	concentration in the permeate side (% (w/w))
$D_{i,j}$	diffusion coefficient
E_{m}	elastic modulus (MPa)
J	flux through membrane
K	partition coefficient
l	membrane thickness (μm)
M_{c}	average molecular weight between cross-links (g mol^{-1})
M_{SD}	membrane swelling degree (%)
MW	molecular weight (g mol^{-1})
MWCO	molecular weight cut-off (Da)
Δp	transmembrane pressure (bar)
P	permeability of hexane through the membrane
R	membrane retention
t	time (h)
T	temperature (K)
w_{PDMS}	weight fraction of PDMS at swelling equilibrium

Greek letters

$\alpha_{\text{CO}_2/\text{N}_2}$	gas selectivity of membrane for CO_2 over N_2
χ	interaction parameter
ϕ_{pen}	penetrant volume fraction
η	viscosity (cSt)
$\Delta\pi$	osmotic pressure (bar)
ρ	density (g cm^{-3})
v	molar volume ($\text{cm}^3 \text{mol}^{-1}$)

the membrane retention, an aspect very important for practical (industrial) applications. Therefore, in this work, we systematically study the influence of cross-linker amount (6.5, 9.1, and 16.7% (w/w), corresponding to the pre-polymer/cross-linker ratios of 10/0.7, 10/1, and 10/2, respectively) on the membrane swelling and permeation properties. For the PAN/PDMS prepared at pre-polymer/cross-linker ratio of 10/1, we reported earlier [1] that the “apparent viscosity” inside the membrane and the membrane swelling (due to the interaction of PDMS/hexane/solute) are the most critical factors affecting the hexane permeability. It would be interesting to see whether similar conclusion can be drawn for the hexane transport through the composite membranes prepared at other pre-polymer/cross-linker ratios.

2. Theoretical background

The hydrosilylation reaction relies on the ability of the hydrosilane bond of the cross-linker (SiH) to add across

a carbon–carbon double bond that belongs to the pre-polymer in the presence of Pt catalyst [14,15] (Fig. 1). In the ideal case, the SiH reacts only with the $-\text{CH}=\text{CH}_2$ groups along the pre-polymer chains, allowing a good control over the cross-links distribution. The stoichiometric ratio of the PDMS system is defined as the ratio of hydrosilane to vinyl groups, being 1/1. For the ideal case, the molecular weight and molecular weight distribution of chains in the network are those of the pre-polymer chains prior to their linking into the network structure [14,15]. In practice, the formed network may deviate from ideality due to the steric hindrance or the unbalanced stoichiometry of the curing reaction. Few experimental studies on the effect of the pre-polymer/cross-linker ratio upon physical properties of the PDMS as well as the gas/vapour transport are available in literature [9,10,16–19]. Simpson et al. [16] reported that an excess (from the stoichiometrical amount) of the cross-linker slows down the curing rate for the PDMS films of various thicknesses. The excess of tetrafunctional cross-linker was, however, reported to improve the adhesion of the silicone to the substrate [17]. Venkataraman et al. [18] studied the dynamic storage modulus as a function of the pre-polymer/cross-linker ratio. In the absence of any side reaction, balanced stoichiometry leads to the PDMS network with a high elasticity. Shefer [19] studied the changes in the PDMS glass transition temperature (T_{g}) as a result of various cross-linking degree, indicating that the highest T_{g} is at the stoichiometrical ratio of the silicone network. Hagg [9] measured the permeability of Cl_2 , O_2 , and N_2 through the “standard”, stoichiometrically cross-linked PDMS and the γ -radiated PDMS composite membranes (with a higher degree of cross-linking than the “standard” PDMS), at pressure range of 1–3 bar. The membranes showed a decrease in gas permeability and a slight increase in gas selectivity with the increase of cross-linking degree. Nguyen et al. [10] performed pervaporation of water–ethyl acetate mixtures through PDMS cross-linked membranes at different conditions (pre-polymer/cross-linker ratios and temperatures). They observed a decrease of both water and ester permeation fluxes, attributed to the decrease of sorption of the components in the membrane.

Sometimes, the non-porous, gel membranes are described as swollen polymeric networks with “pores” of molecular size, usually between 20 and 100 Å [20,21]. In our view, the term “pore” might be misleading and as de Gennes pointed out [22], a more appropriate term could be “macromolecular mesh”. Non-porous, gel membranes include most types of hydrogels such as water-swollen networks of poly(vinylalcohol) and related polymers, as well as other hydrophobic polymers swollen in the appropriate organic solvents (as PDMS in hexane) [1]. The investigation of swelling equilibrium could help to elucidate the structure of the PDMS network. According to the Flory–Huggins solution theory (applicable for the good solvents in PDMS [9,23]), the equilibrium volume fraction of the penetrant, ϕ_{pen} , can be related to the activity of the penetrant, a_{pen} , by the following

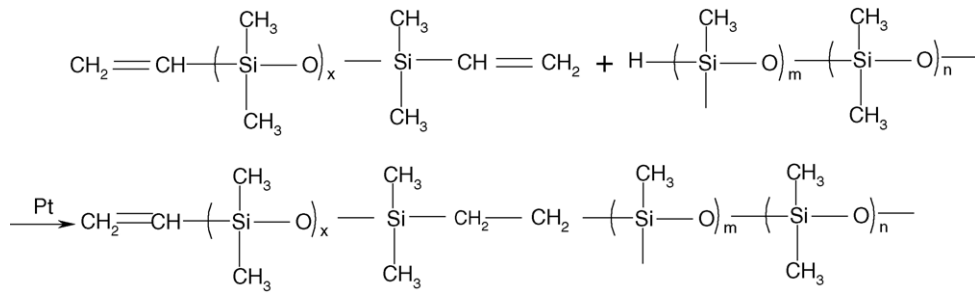


Fig. 1. Scheme of the cross-linking reaction for the silicone network formation.

expression:

$$\ln a_{\text{pen}} = \ln \phi_{\text{pen}} + (1 - \phi_{\text{pen}}) \left(1 - \frac{\nu_{\text{pen}}}{\nu_{\text{PDMS}}} \right) + \chi(1 - \phi_{\text{pen}})^2 \quad (1)$$

where χ is the PDMS—penetrant interaction parameter. The ratio of penetrant to PDMS molar volumes ($\nu_{\text{pen}}/\nu_{\text{PDMS}}$) is assumed negligible. For the pure liquid, the χ parameter is calculated by setting $\ln a_{\text{pen}} = 0$. In order to gain further insight into the swelling process in relation to the morphological characteristics of the network, the PDMS volume fraction in the swollen state, ϕ_{PDMS} , is estimated using the equation [12]:

$$\phi_{\text{PDMS}} = \frac{w_{\text{PDMS}}/\rho_{\text{PDMS}}}{(1 - w_{\text{PDMS}})/\rho_{\text{hexane}} + w_{\text{PDMS}}/\rho_{\text{PDMS}}} \quad (2)$$

where w_{PDMS} is the weight fraction of the polymer at the swelling equilibrium and ρ_{PDMS} and ρ_{hexane} is the density of the PDMS and hexane, respectively. The polymer volume fraction is calculated assuming the polymer–solvent volume additivity.

The Flory–Rehner equation [23], however, takes into account the effect of cross-linking degree on the elastic forces contribution and may be used for systems involving the same polymer at various cross-linking degrees [12]:

$$\ln a_{\text{pen}} = \ln(1 - \phi_{\text{PDMS}}) + \phi_{\text{PDMS}} \left(1 - \frac{\nu_{\text{pen}}}{\nu_{\text{PDMS}}} \right) + \chi \phi_{\text{PDMS}}^2 + \frac{\nu_{\text{pen}} \rho_{\text{PDMS}}}{M_c} \left(1 - 2 \frac{M_c}{M^*} \right) \left(\phi_{\text{PDMS}}^{1/2} - \frac{1}{2} \phi_{\text{PDMS}} \right) \quad (3)$$

where M_c is the molecular weight between cross-links and M^* is the average molecular weight of the initial pre-polymer, before cross-linking.

The solution–diffusion model [24,25] has already been used to describe the mass transport through the swollen PDMS membrane [1]. We will briefly remind the main equations. The flux of the pure solvent i can be calculated by:

$$J_i = P_i(\Delta p - \Delta \pi) \quad (4)$$

where P is constant equal to $\frac{D_i K_i c_{if} \nu_i}{l R_g T}$ and is called the solvent permeability. D_i is the diffusion coefficient of i through the

membrane, K_i is the partition coefficient, l is the membrane thickness, c_{if} is the feed concentration of species i , ν_i is the partial molar volume of species i , Δp and $\Delta \pi$ is the difference in applied and osmotic pressure across the membrane, respectively, R_g is the gas constant and T is the temperature. Similarly, the flux of the solute j is:

$$J_j = \frac{D_j K_j}{l} \left[c_{jf} - c_{jp} \exp \left(\frac{-\nu_j (p_f - p_p)}{R_g T} \right) \right] \quad (5)$$

Eq. (4) indicates a linear increase in solvent flux with increasing transmembrane pressure difference, whereas Eq. (5) indicates that the solute flux is less affected by the pressure difference. This leads, in general, to an increasing solute retention with increasing solvent flux. The primary assumption of this model is that the flux of the solute and solvent are independent.

3. Experimental

3.1. Materials

The PAN support membranes with molecular weight cut-off (MWCO) of 30 kDa were provided by GKSS, Germany. The selective top layer of the composite was PDMS (RTV 615 type, kindly supplied by General Electric, The Netherlands). The silicone kit was a two-component system, consisting of a vinyl-terminated pre-polymer (RTV A) and a cross-linker containing several hydrosilane groups (RTV B). The curing of the PDMS-membrane occurred via Pt-catalysed hydrosilylation reaction to form a densely cross-linked polymer network. The poly(isobutylenes) (PIB), Glissopal[®] of MW 550, 1000, 1300, and 2300 were kindly provided by BASF, Germany and of MW 350, by Janex S.A., Switzerland (see Table 1). The *n*-hexane (Merck, The Netherlands) and the PIB were used as supplied, without further purification.

4. Membrane preparation and characterization

The free-standing, thick PDMS films were prepared from 75% (w/w) PDMS/hexane solution, at room temperature, by mixing the pre-polymer and cross-linker at 10/0.7, 10/1 or

Table 1
Specifications of the PIB used in this work

MW _{PIB} ^a (g mol ⁻¹)	Producer	Polydispersity ^b
350	Janex	1.8
550	BASF	2.1
1000	BASF	2.9
1300	BASF	3.6
2300	BASF	1.8

^a Given by the producer.

^b Defined as the ratio of M_w to M_n , determined by GPC.

10/2 (w/w) ratios. The PAN/PDMS tailor-made composite membranes were prepared following a two-step coating procedure described in detail elsewhere [1].

The density of the dense PDMS films was measured with a pycnometer (Micrometrics Accupyc 1330). The elastic modulus of the dense PDMS films was determined by performing tensile testing on a Zwick Z020 (Germany) machine. In order to obtain the stress–strain diagrams, the uniaxial deformation of the sample (dumb-bell test piece, according to ISO37, type 2) was measured under 10 N loading. The molecular weight between cross-links (M_c) was calculated [26,27] by:

$$M_c = \frac{3\rho_{\text{PDMS}}R_gT}{E_m} \quad (6)$$

where E_m is the elastic modulus.

Pure gas permeation measurements with N_2 and CO_2 were performed, using the set-up and procedure described in [1]. No significant differences in gas permeability through the composites as a function of cross-linking degree were found. For the PAN/PDMS composite membranes, the gas selectivity, α_{CO_2/N_2} was 9.8 ± 1.4 , independent on the cross-linking degree. These values are close to the PDMS intrinsic selectivity (=11.6), indicating good quality of the PDMS top-layer.

For the swelling measurements, pre-weighed dry dense PDMS membranes (M_{dry}) were immersed in pure hexane or PIB/hexane solutions until equilibrium swelling was reached (M_{wet}). The swelling degree (M_{SD}) of the dense membrane was calculated by:

$$M_{\text{SD}} (\%) = \left(\frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \right) \times 100 \quad (7)$$

For PIB/hexane solutions, at the end of the swelling experiments, the samples were removed from the liquid solutions and dried. From the difference between the initial and final dry weight, the concentration of the PIB in the membrane ($c_{\text{PIB,membrane}}$, % (w/w)) was measured and the PIB partition coefficient K_{PIB} was calculated by:

$$K_{\text{PIB}} = \frac{c_{\text{PIB,membrane}}}{c_{\text{PIB,f}}} \quad (8)$$

where $c_{\text{PIB,f}}$ is the PIB concentration in the immersed solution.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used for the characterization of PDMS at various cross-linking degrees. The penetration

depth of the infrared beam ranged from 0.5 μm at 3000 cm^{-1} to 2 μm at 700 cm^{-1} for the ZnSe crystal with a 90° angle of incidence for PDMS network analysis. Gel permeation chromatography (GPC, Waters 515 GPC instrument, using tetrahydrofuran as solvent) was used to determine the molecular weight of the pre-polymer and cross-linker. ¹H NMR spectroscopy (Bruker AC 250 spectrometer, 400 MHz, using deuterated chloroform) was used to determine the structure of the pre-polymer and cross-linker. The morphology of the composite membranes was visualized by scanning electron microscopy (SEM, Microscope Jeol JSM-5600LV, at 15 kV).

All the liquid permeation experiments through the composite membranes were performed at room temperature (24 ± 3 °C), with the set-up and experimental protocol described in [1]. Helium gas was used to apply pressures in the range of 1–7 bar. The flux through the membrane was calculated by dividing the amount of the collected permeate over the membrane area and permeation time. The permeate volume was calculated by dividing the collected weight to the permeate density (measured by a digital density meter, model DMA 50). The PIB concentration in the feed ($c_{\text{PIB,f}}$, % (w/w)) and the permeate ($c_{\text{PIB,p}}$, % (w/w)) solutions was analyzed by refractive index measurements, at 25 °C, using a Abbe-3 refractometer, from Carl Zeiss, Germany. The PIB retention was calculated using the equation:

$$R = \left(1 - \frac{c_{\text{PIB,p}}}{c_{\text{PIB,f}}} \right) \times 100 \quad (9)$$

Values and error bars reported in the tables and figures are based on at least three different membranes samples.

5. Results and discussion

5.1. Pre-polymer and cross-linker characterization

Fig. 2 presents a typical result of the GPC analysis of the pre-polymer and cross-linker, as received from the supplier. The data indicate that both have mainly a bimodal character of molecular weight (pre-polymer: 4000 and 67,000 g mol^{-1} , cross-linker: 1500 and 60,000 g mol^{-1}). The molar masses of the pre-polymer and cross-linker obtained by ¹H NMR analysis (data not shown here) are in good agreement with the GPC results. Theoretically, the hydrosilylation reaction is very specific since the hydrosilane groups should react only with the vinyl groups at the end of the chains, the stoichiometric ratio being 1/1. Generally, an excess of the hydrosilane part is used in order to compensate for the steric hindrance: the reaction between vinyl and hydrosilane groups becomes more and more difficult since reactive species become scarcer, and the network becomes tighter as the reaction progresses [14]. In the absence of any significant side-reaction, balanced stoichiometry should lead to a network with average molecular weight between cross-links, M_c , that equals the molecular weight of the pre-polymer chains prior to their end linking

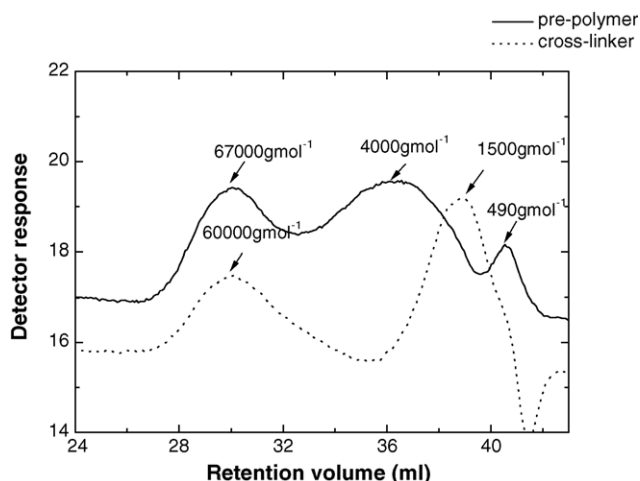


Fig. 2. The molecular weight of the PDMS pre-polymer and cross-linker determined by GPC.

and few, if any, dangling-chains (those chains attached to the network at one end only) [14,15].

5.2. ATR-FTIR and mechanical analysis of the dense PDMS membrane

ATR-FTIR was used for the spectroscopic characterization of the dense, free-standing PDMS membranes prepared at various pre-polymer/cross-linker ratios. Fig. 3 presents a typical result for the membrane prepared at ratio, 10/1. The typical peaks of the C–H methyl stretch at 2965 cm^{-1} , the silicon–methyl bond at 1260 cm^{-1} , and the broad polymer backbone absorption band between 1130 and 1000 cm^{-1} are found [28]. The amount of the unreacted vinyl and hydrosilane (SiH) groups (after cross-linking at $65\text{ }^{\circ}\text{C}$ for 4 h in N_2 oven) can be determined by following the change in intensity of the absorption band at 1410 cm^{-1} (for vinyl) and 2140 cm^{-1} (for SiH). If no side reaction occurs, the changes in the intensity of these bands could be attributed to the con-

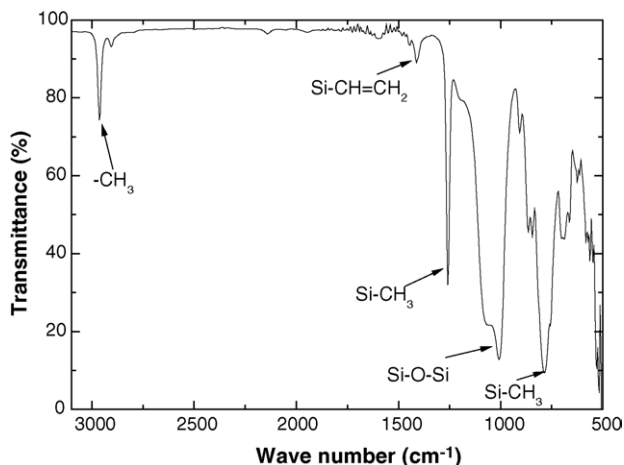
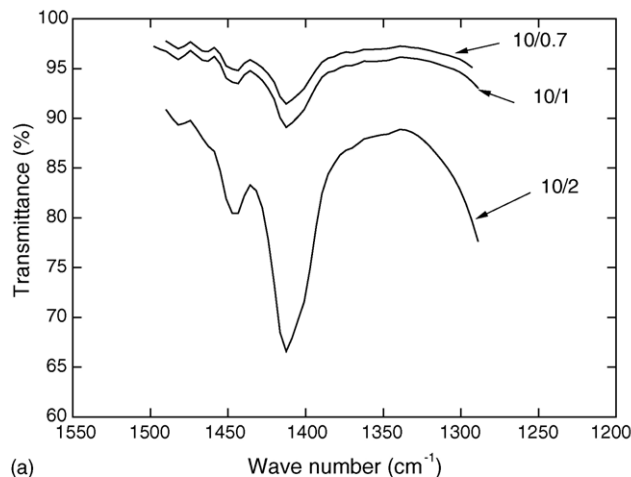
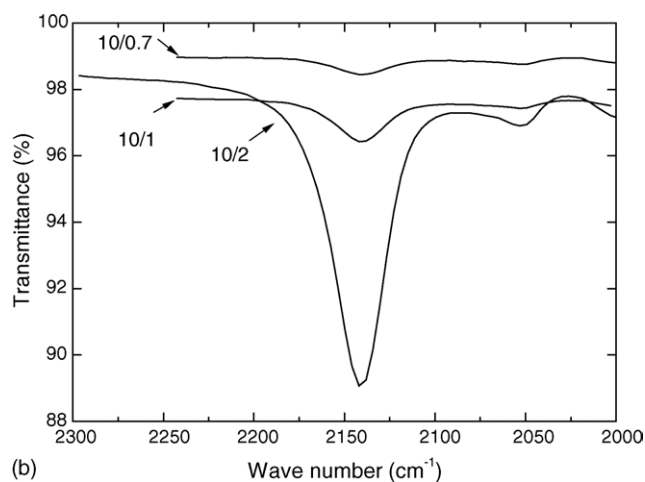


Fig. 3. ATR-FTIR spectra of the PDMS membrane prepared at ratio of 10/1.



(a)



(b)

Fig. 4. ATR-FTIR spectra of the dense PDMS membrane prepared at various pre-polymer/cross-linker ratios: (a) vinyl group; (b) SiH group.

sumption of these groups upon cross-linking reaction. Fig. 4 presents typical ATR-FTIR spectra of the dense PDMS films of various pre-polymer/cross-linker ratios at these specific wavelengths. For the PDMS prepared at pre-polymer/cross-linker ratio of 10/2, the intensity of the absorption band at 1410 cm^{-1} is high (see Fig. 4a), indicating the excess of vinyl groups. In Fig. 4b, the SiH absorption band cannot be clearly detected for the PDMS membranes prepared at pre-polymer/cross-linker ratios of 10/0.7 and 10/1, indicating almost total SiH consumption upon the cross-linking reaction. In contrary, for PDMS of 10/2 ratio, the SiH peak is high, suggesting that not all the hydrosilane groups have reacted. Nguyen et al. [10] reported similar results for an excess of cross-linker in the pre-polymer/cross-linker mixture. They suggested that the silicone network is a blend of unreacted silicone (still containing vinyl and SiH groups) and fully-cured silicone (without unreacted groups) [10]. These experimental findings seem to support the hypothesis of heterogeneous cross-linker “agglomeration” or “branching” [29] that decreases the cross-linking reaction extend due to steric hindrance. This leads to the formation of an

Table 2
Density, Young's modulus and average molecular weight of chains between cross-links for PDMS prepared at various pre-polymer/cross-linker ratios

Pre-polymer/ cross-linker ratio	ρ (g cm ⁻³)	E_m (MPa)	M_c (10 ³ g mol ⁻¹)
10/0.7	1.052 ± 0.009	0.35 ± 0.08	22.3 ± 4.5
10/1	1.055 ± 0.006	0.50 ± 0.02	15.6 ± 0.8
10/2	1.064 ± 0.007	0.77 ± 0.06	10.3 ± 0.7

“imperfect” PDMS network at pre-polymer/cross-linker ratio of 10/2. Such network is expected to have a lower swelling degree compared to the homogeneous network. Table 2 presents the density (ρ), the Young's modulus (E_m), and the calculated average molecular weight of chain between the cross-links (M_c , see Eq. (6)) of the PDMS prepared at various pre-polymer/cross-linker ratios. The elastic modulus of the dense, free-standing PDMS membrane increases with the amount of cross-linker, as expected, since an increase in cross-linker content forms a tighter network. Similar trend was reported by Nguyen et al. [10]. Thus, the average molecular weight between cross-links decreases from 22,300 to 10,300 g mol⁻¹.

5.3. Swelling experiments of dense PDMS membrane in hexane

Fig. 5 presents the effect of the cross-linker content upon the swelling of free-standing, dense PDMS membranes prepared at pre-polymer/cross-linker ratios of 10/0.7, 10/1, and 10/2, corresponding to 6.5, 9.1, and 16.7% (w/w) cross-linker content, respectively. The lower the amount of cross-linker, the higher the swelling degree of the membrane. Such behaviour can be explained by the decrease in chain length between cross-links with increase of the cross-linker amount (see Table 2). The shorter the chains between cross-links, the stronger the elastic resistance to the swelling stress (higher

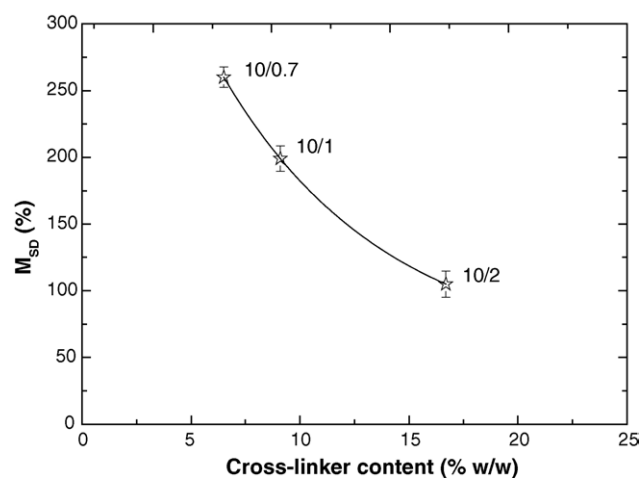


Fig. 5. The effect of the cross-linker content upon the swelling degree (M_{SD}) of PDMS dense membranes in hexane.

Table 3
Equilibrium results of the swelling experiments for the dense free-standing PDMS membranes prepared at various pre-polymer/cross-linker ratios

Pre-polymer/ cross-linker ratio	w_{PDMS}	ϕ_{PDMS}	$\chi_{Flory-Huggins}$	$\chi_{Flory-Rehner}$
10/0.7	0.28 ± 0.02	0.19 ± 0.02	0.57 ± 0.02	0.58 ± 0.02
10/1	0.33 ± 0.03	0.24 ± 0.02	0.59 ± 0.02	0.59 ± 0.02
10/2	0.50 ± 0.03	0.38 ± 0.03	0.68 ± 0.02	0.66 ± 0.02

elastic modulus) and the lower the swelling degree of the membrane [14]. Table 3 summarizes the results of swelling experiments of the dense PDMS membranes in hexane: the weight fraction of PDMS (w_{PDMS}), the volume fraction of PDMS (ϕ_{PDMS}), and the interaction parameter (χ) calculated using the Flory–Huggins and the Flory–Rehner equations. For the Flory–Rehner equation (Eq. (3)), the M_c obtained from the mechanical analysis (Table 2) and the M^* of 35,000 g mol⁻¹ taken from the GPC analysis, Fig. 2) are used. The data show that the volume fraction of PDMS in the swollen network increases with the amount of cross-linker. This increase, however, does not affect much the interaction parameters of the hexane–PDMS membranes prepared at pre-polymer/cross-linker ratios of 10/0.7 and 10/1. Nevertheless, for PDMS prepared at pre-polymer/cross-linker ratio of 10/2, the χ parameter is higher. Such finding has already been reported in literature [10,30–32]. The origin of this behaviour could be attributed to the fact that the mixing and the elastic free energies are not strictly separable in the description of swelling equilibrium [10,32]. The increase of cross-linking degree causes an increase in the elastic energy for polymer network deformation, reducing the free energy of mixing [10]. Besides, this behaviour may be due to the difference in the quality of the PDMS network prepared at pre-polymer/cross-linker of 10/2 ratio. The ATR-FTIR spectra of PDMS prepared at pre-polymer/cross-linker ratio of 10/2 indicates that the silicone network contains unreacted hydrosilane and vinyl groups. The response of such “imperfect” network to the swelling stress would not be as ideal as supposed in the Flory–Huggins and Flory–Rehner models. Two main simplifications employed, namely the Gaussian distribution of the polymer chains (which was found to not be always valid for the bimodal PDMS elastomers [33]) and the phantom network (which ignores the intermolecular effects, therefore the topological constraints), may not be valid for this silicone network [34]. Interestingly, the values of χ parameter calculated using Flory–Huggins and Flory–Rehner equations are similar, indicating that the elastic contribution of the PDMS network towards the swelling in hexane is negligible. We attribute this to the relative high M_c (see Table 2). In fact, the elastic part of the Flory–Rehner equation induces very little modification to the Flory–Huggins equation, unless the PDMS network has a very small M_c [9]. Similar findings were also reported [9,10] for the PDMS network with the M_c in the range of 640–12,700 g mol⁻¹.

5.4. Swelling of dense PDMS membranes in PIB/hexane solutions

The equilibrium swelling degree of the dense, free-standing PDMS membrane in PIB/hexane solutions was investigated as well. For this study, PIB of various MW have been used. Fig. 6 presents a typical result concerning the PIB of MW 550 g mol⁻¹. Similar results were obtained for PIB of other MW, too. In this concentration range, the swelling degree of the PDMS does not change significantly with molecular weight of the solute [1]. In this range, the solute size might be smaller than the mesh size of the silicone gel formed by the highly swollen network in hexane. The effect of pre-polymer/cross-linker ratio on the swelling degree of the PDMS membrane in PIB/hexane solutions is similar to the pure hexane, i.e. the lower the amount of cross-linker, the higher the membrane swelling. In addition for all membranes, the PDMS swelling degree decreases when the PIB concentration of the PIB/hexane mixture increases. From the results of pure PIB ($a_{\text{pen}} = 1$) and by using Eq. (1), the interaction parameter between PDMS/PIB is found to be 2.11 ± 0.02 [1]. This value is much higher than the χ value of 0.58 corresponding to PDMS/hexane system, indicating that the sorption of hexane to PDMS is thermodynamically much more favourable than PIB. Besides, swelling experiments of PDMS membranes in PIB/hexane solutions of 8% (w/w) were performed (at 22 ± 1 °C). From the difference between the initial and final dry weight, the concentration of the PIB (c_{PIB} , % (w/w)) within the membrane was determined (see Fig. 7). Generally, the concentration of PIB decreases when the MW of PIB increases, indicating a decrease in PDMS-PIB/hexane solution interaction with increasing PIB MW. This finding is consistent with the dependence of the interaction parameter on the molar volume of the penetrant [1,35]. In addition, the concentration of PIB inside PDMS seems to decrease slightly with increasing the cross-linker amount. Such behaviour

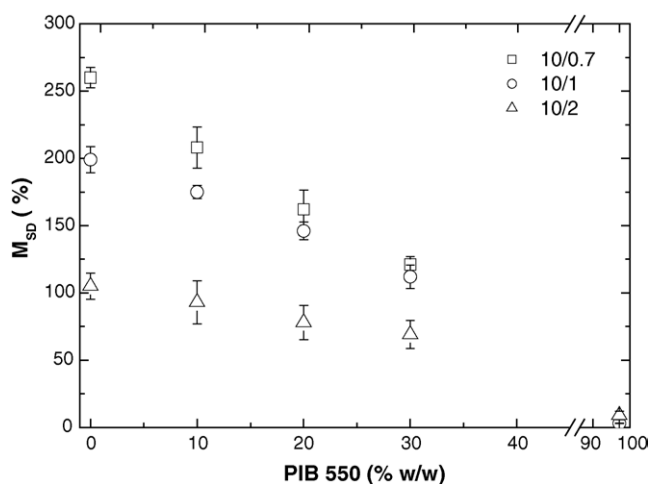


Fig. 6. The effect of the PIB/hexane solution concentration upon swelling degree of the PDMS dense membranes prepared at various pre-polymer/cross-linker ratios.

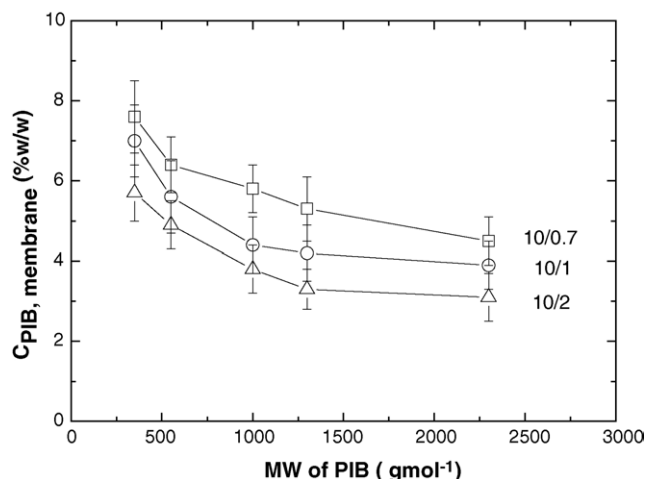


Fig. 7. The effect of MW of PIB on the concentration of PIB inside PDMS dense membrane prepared at various pre-polymer/cross-linker ratios.

could be due to the decrease of the chain length between cross-links with the increase of the cross-linker amount: the shorter the chains between cross-links, the stronger the elastic resistance to the swelling stress, thus the lower the swelling of the membrane, and therefore, the lower the PIB amount inside the PDMS network. Fig. 8 presents the PIB partition coefficient, $K_{\text{PIB, membrane}}$ calculated from the results of Fig. 7 using Eq. (8). The $K_{\text{PIB, membrane}}$ in highly swollen, free-standing silicone membranes (PDMS gel) is affected by the cross-linked density, as well as, by the penetrant size similarly as the concentration inside the membrane of Fig. 7. Similar effects of the cross-linking degree on the partition coefficient of myoglobin in block copolymer membrane of PEO-PDMS membrane was reported by Harland and Peppas [36].

5.5. Permeation experiments

Fig. 9 presents the hexane flux through the PAN/PDMS composites of various cross-linking degrees as a function

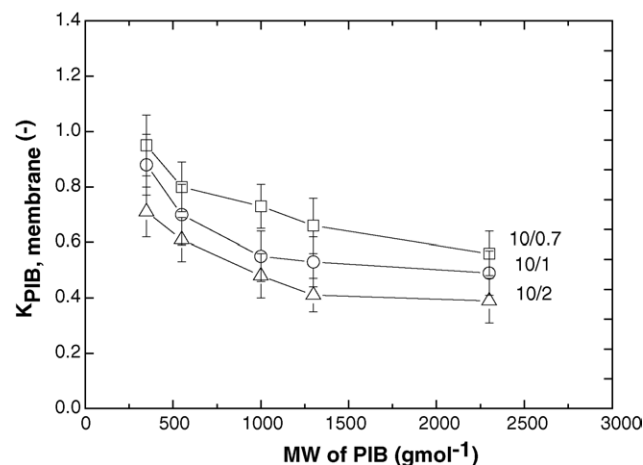


Fig. 8. The PIB partition coefficient for the PDMS dense membranes prepared at various pre-polymer/cross-linker ratios.

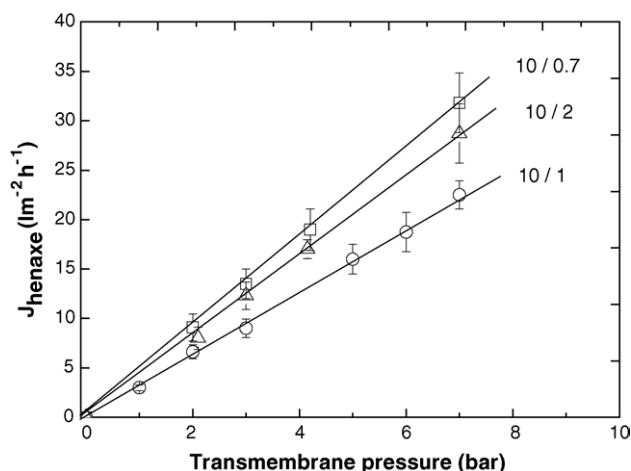


Fig. 9. Hexane flux as a function of the transmembrane pressure for the PAN/PDMS membranes prepared at various pre-polymer/cross-linker ratios.

of transmembrane pressure. The hexane flux increases linearly with the applied pressure in all cases, indicating that no compaction of the membrane occurs over the applied pressure range. From the slopes of the plots of Fig. 9, the hexane permeability coefficient, P_{hexane} , can be calculated (see Table 4). For the PAN/PDMS composite prepared at pre-polymer/cross-linker ratio of 10/0.7, the hexane permeability is higher in comparison to that through the composite prepared at 10/1. This finding is consistent with the swelling results of the corresponding dense, free-standing PDMS membranes: the PDMS membrane prepared at pre-polymer/cross-linker ratio of 10/0.7 swells much more (260% (w/w)) than that at 10/1 (200% (w/w)). However, the hexane permeability through the PAN/PDMS membrane prepared at pre-polymer/cross-linker ratio of 10/2 ratio is not consistent with the swelling results of the corresponding dense membranes. The P_{hexane} through the PAN/PDMS prepared at ratio of 10/2 is higher ($4.1 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) than of 10/1 ($3.1 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) although the swelling degree of the corresponding dense PDMS membrane is lower. This indicates that another parameter, besides swelling of the cross-linked network, might be important, in this case. Probably, the pore intrusion is different for the PAN/PDMS prepared at pre-polymer/cross-linker ratios of 10/1 and 10/2. Table 4 compares the PDMS thickness visualized by SEM and the effective thickness of the PDMS calculated from CO_2 permeability measurements, assuming that the gas transport is completely determined by PDMS. Typical SEM pic-

Table 4

Effective and visualized PDMS top layer thickness, and hexane permeability of the PAN/PDMS composite membranes prepared at various pre-polymer/cross-linker ratios

Pre-polymer/ cross-linker ratio	$l_{\text{eff}}(\text{CO}_2)$ (μm)	l_{SEM} (μm)	P_{hexane} ($\text{l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$)
10/0.7	1.9 ± 0.2	0.9 ± 0.2	4.5 ± 0.5
10/1	2.0 ± 0.2	1.0 ± 0.2	3.1 ± 0.4
10/2	2.2 ± 0.3	1.8 ± 0.3	4.1 ± 0.5

tures of the cross-section of the PAN/PDMS prepared at pre-polymer/cross-linker of various ratios are shown in Fig. 10. For the PAN/PDMS composite membranes prepared at pre-polymer/cross-linker ratios of 10/0.7 and 10/1, the difference between the effective and visualized thickness is about $1 \mu\text{m}$. This indicates that probably an intermediate layer exists where the PDMS penetrates into the pores of the support. For the composite membrane prepared at pre-polymer/cross-linker ratio of 10/2, however, the difference between the effective and visualized thickness is small, indicating that the

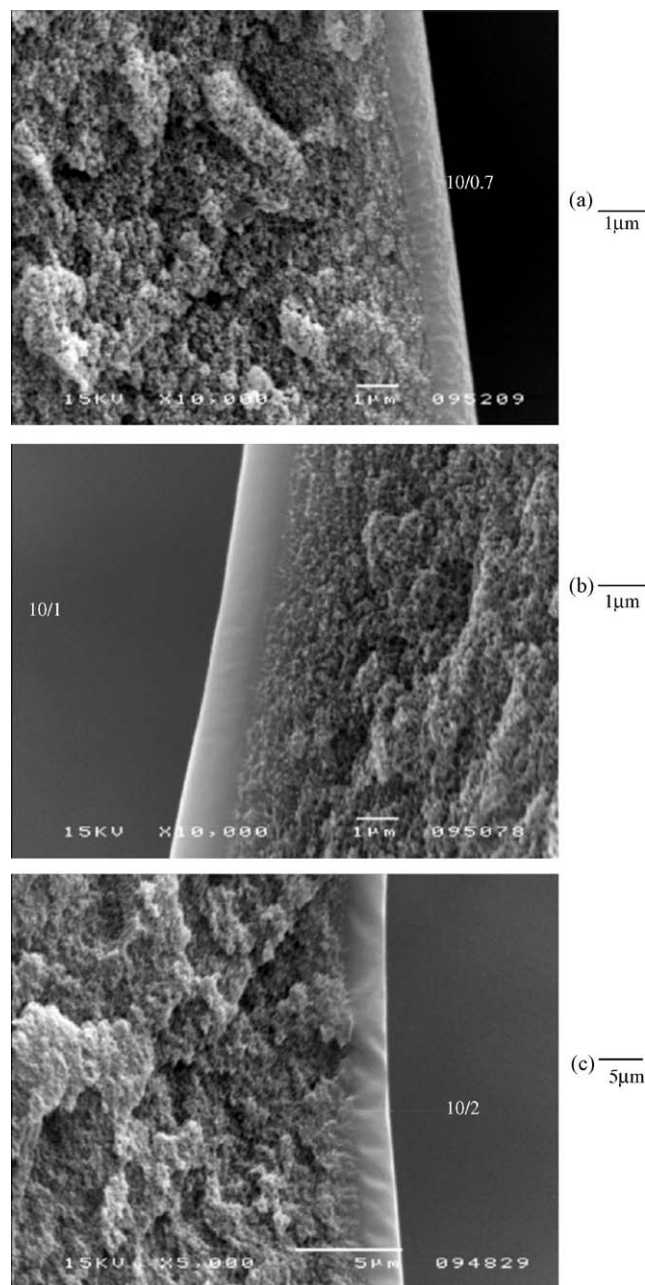


Fig. 10. SEM pictures of the cross-section of PAN/PDMS composite membranes prepared at pre-polymer/cross-linker ratio of: (a) 10/0.7 (magnification 10000 \times); (b) 10/1 (magnification 10000 \times); and (c) 10/2 (magnification 5000 \times).

pore intrusion in this membrane might be less than for the other two composites. This might be the reason for the relatively high hexane permeability observed for this membrane, even though the membrane swelling is expected to be less than for the other two membranes. A pore confinement generally restricts the swelling of the PDMS network immobilized inside the pores due to the rigidity of the support matrix. Similar results were reported by Vankelecom et al. [37] for the pervaporation of water/ethanol with PDMS/Zirfon composite membrane that had various degrees of pore intrusion. Apparently, the cross-linking degree in combination with the pore intrusion of the silicone network, determine the hexane flux through the composite membranes.

Fig. 11 presents the effect of the feed pressure on the hexane flux through the composite membranes for various PIB1300/hexane concentrations. The hexane permeability coefficient (calculated from the slopes of the graphs) decreases with the increase of PIB1300 concentration due to the increase in feed viscosity. Similar trend has been reported in literature [1,38–41] for various organic systems. In all cases, the linearity of the J_{hexane} with the applied pressure indicates that no compaction of the membrane occurs over the applied pressure range. Hence, the hexane transport through the membrane can be reasonably described by Eq. (4). For all composites, osmotic phenomena are observed and can be interpreted using the van't Hoff equation:

$$\Delta\pi = \frac{R_g T \Delta c}{MW} \quad (10)$$

$\Delta\pi$ is the osmotic pressure (in bar), Δc is the solute concentration difference across the membrane (in g l^{-1}) and MW is the solute molecular weight (in g mol^{-1}). The x -intercepts (at $J_{\text{hexane}} = 0$) for each PIB1300/hexane concentration are in very good agreement, within experimental error, with those of $\Delta\pi$ calculated using Eq. (10). For example, for the PAN/PDMS composite prepared at pre-polymer/cross-linker ratio of 10/0.7, x -intercept/calculated $\Delta\pi$ value is 1.0 bar/0.8 bar for 8% (w/w) feed and 2.3 bar/2.1 bar for 19% (w/w) feed solutions. For the PAN/PDMS prepared at pre-polymer/cross-linker ratio of 10/1, we reported earlier [1] that the “apparent viscosity”, η , inside the membrane and the membrane swelling degree (M_{SD}) (due to the interaction of PDMS/hexane/solute) were the most critical factors affecting the hexane permeability. It would be interesting to see if similar conclusion can be drawn for the hexane transport through the other composites. Table 5 presents this normalization $P\eta/M_{\text{SD}}$ for the PAN/PDMS membranes prepared at various pre-polymer/cross-linker ratios and at same experimental conditions (feed of 8% (w/w) PIB/hexane, at $24 \pm 3^\circ\text{C}$). For the normalization, the value of the “apparent viscosity” inside the membrane is estimated from the concentration of PIB in a hypothetical hexane/PIB phase inside the membranes (Fig. 7) and the plots of viscosity versus PIB/hexane concentration, presented elsewhere [1]. For the swelling degree, the results of the dense PDMS membranes are used. For all membranes, a constant normalized value $P\eta/M_{\text{SD}}$ is found,

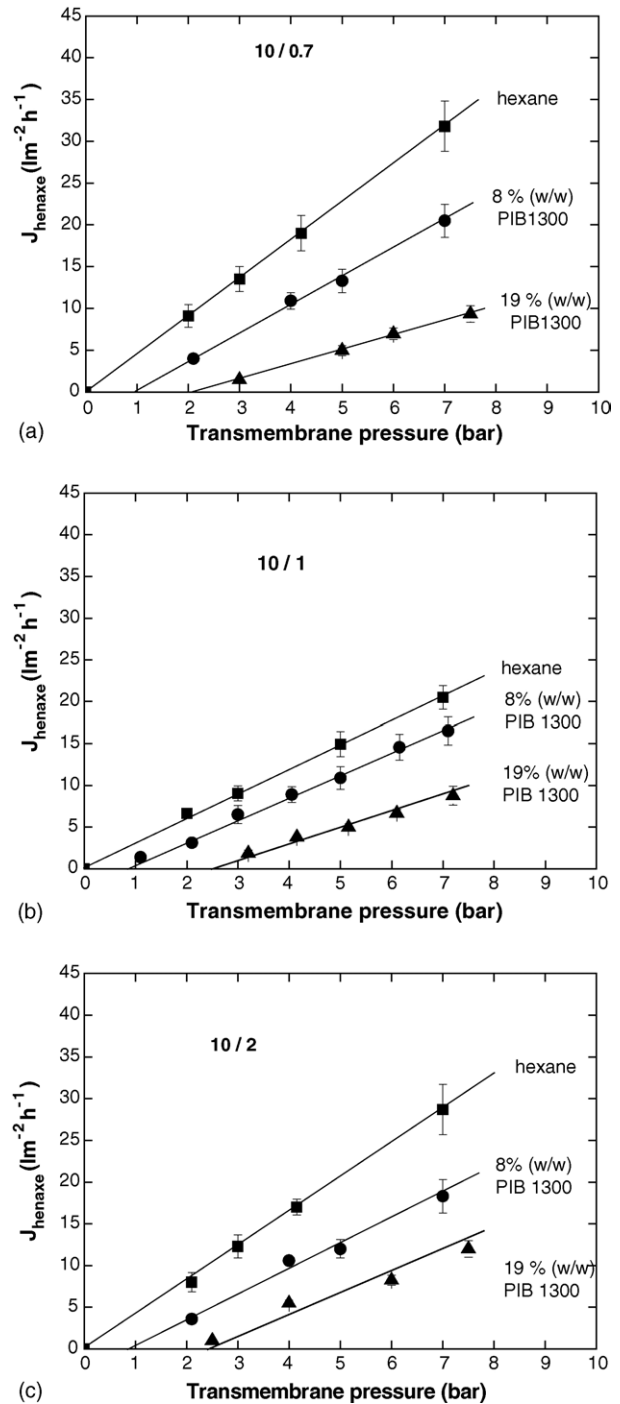


Fig. 11. Hexane flux through PAN/PDMS membrane as a function of transmembrane pressure for various PIB 1300/hexane feed concentrations. Pre-polymer/cross-linker ratios: (a) 10/0.7; (b) 10/1; and (c) 10/2.

the magnitude of which depends on the cross-linking degree of the PDMS. For the PAN/PDMS membranes prepared at pre-polymer/cross-linker ratios of 10/0.7 and 10/1, the normalized hexane permeability, $P\eta/M_{\text{SD}}$, is similar (about 1). However, for the composites prepared at ratio 10/2, the normalized value is higher (range of 2.1–2.4) due to the lower M_{SD} of the dense PDMS membrane compared to 10/0.7 and

Table 5

Parameters concerning the transport of PIB/hexane solutions through the PAN/PDMS composite membranes

MW of PIB (g mol^{-1})	η_{apparent} (cSt)	P_{hexane} ($\text{lm}^{-2} \text{h}^{-1} \text{bar}^{-1}$)	$M_{\text{SD}}/100$	$P\eta 100/M_{\text{SD}}$ ($\text{lcSt m}^{-2} \text{h}^{-1} \text{bar}^{-1}$)
(a)				
350	0.56 ± 0.06	4.1 ± 0.5	2.1 ± 0.1	1.0 ± 0.2
550	0.57 ± 0.06	3.7 ± 0.6	2.1 ± 0.1	1.0 ± 0.2
1000	0.60 ± 0.06	3.3 ± 0.6	2.1 ± 0.1	0.9 ± 0.2
1300	0.62 ± 0.07	3.2 ± 0.5	2.1 ± 0.1	0.9 ± 0.2
2300	0.63 ± 0.08	3.0 ± 0.4	2.1 ± 0.1	0.9 ± 0.2
(b)				
350	0.55 ± 0.06	2.8 ± 0.3	1.8 ± 0.1	0.9 ± 0.2
550	0.56 ± 0.06	2.7 ± 0.3	1.7 ± 0.1	0.9 ± 0.2
1000	0.57 ± 0.06	2.6 ± 0.2	1.6 ± 0.1	0.9 ± 0.2
1300	0.59 ± 0.07	2.7 ± 0.2	1.6 ± 0.1	1.0 ± 0.2
2300	0.61 ± 0.08	2.7 ± 0.2	1.7 ± 0.1	1.0 ± 0.2
(c)				
350	0.54 ± 0.07	3.9 ± 0.6	0.9 ± 0.1	2.4 ± 0.4
550	0.55 ± 0.06	3.5 ± 0.5	0.8 ± 0.1	2.4 ± 0.4
1000	0.56 ± 0.07	3.1 ± 0.6	0.8 ± 0.1	2.2 ± 0.4
1300	0.57 ± 0.08	2.9 ± 0.4	0.8 ± 0.1	2.1 ± 0.3
2300	0.58 ± 0.08	2.8 ± 0.4	0.8 ± 0.1	2.1 ± 0.3

Experimental conditions: feed of 8% (w/w), at 24 ± 3 °C. Pre-polymer/cross-linker ratio: (a) 10/0.7; (b) 10/1; (c) 10/2.

10/1. If we assume that the solution–diffusion model could be applied for this system, then we could interpret the apparent viscosity as a measure for the diffusion coefficient of hexane inside the membrane and the swelling as a measure for the solubility.

The solution–diffusion, however, does not consider the solute–solvent coupling (solvent-induced solute dragging). For the PAN/PDMS composite membrane prepared at pre-polymer/cross-linker ratio of 10/1, we have already found [1] that the flux of the solute increases linearly with the solvent flux, showing the existence of flux coupling or solvent-induced solute dragging. Fig. 12 shows that the dragging of hexane to the solute occurs for the PAN/PDMS composites at various cross-linking degrees, too. At the same PIB 1300/hexane feed concentration (8% (w/w)), the PIB flux increases linearly with the hexane flux. The flux of PIB 1300 through the PAN/PDMS composite prepared at pre-

polymer/cross-linker ratio of 10/0.7 is the highest and for the composite prepared at ratio 10/1 is the lowest, consistent with the results of Fig. 9.

5.6. Retention performance

Fig. 13 presents the results of the membrane retention for 8% (w/w) PIB/hexane solutions at transmembrane pressure of 7 bar, for all PAN/PDMS composites. The indicated MW of PIB is provided by the manufacturers (the polydispersity of PIB of various MW is presented in Table 1). The relatively high membrane retention is probably due to the differences in solubility/diffusivity of hexane compared to PIB. Having in mind the poly-dispersity of the PIB, we can conclude that

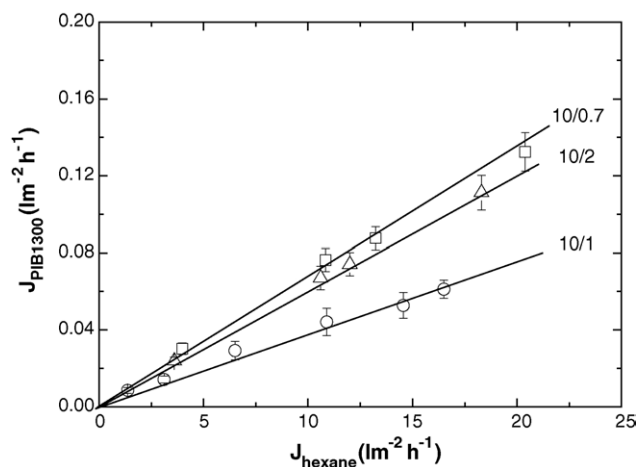


Fig. 12. The flux of PIB 1300 as a function of hexane flux for the composites prepared at various cross-linking degrees. Feed concentration: 8% (w/w).

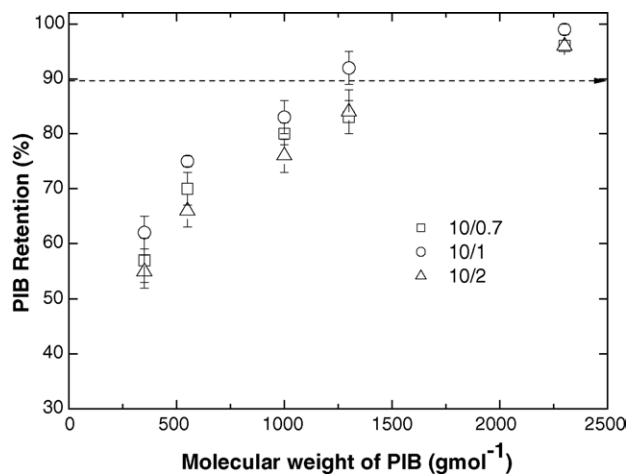


Fig. 13. PIB retention by the PAN/PDMS composite membranes prepared at various pre-polymer/cross-linker ratios as a function of the PIB molecular weight. Experimental conditions: feed concentration of 8% (w/w), $\Delta p = 7$ bar, at 24 ± 3 °C.

the retention performance is almost the same for all composite membranes. Besides, the membrane retention increases with the increase of the molecular weight of PIB. Although hexane-induced dragging increases the PIB flux, the strong effect of pressure on the chemical potential raises the hexane flux stronger than the dragging raises the PIB flux. Paul [42] stated recently that the consequence of the coupling effects in reverse osmosis might exist but they are too small to be noticeable. The results of Fig. 13 allow us to estimate a MWCO (defined as the MW of the solute that is rejected for 90% by the membrane) of around 1200–1250 Da for all composites. The fact that the cross-linking degree of PDMS has little effect on the MWCO of the membrane might be attributed to the highly swollen state of the silicone network and the PDMS polydispersity.

6. Conclusions

In this work, dense free-standing PDMS films and PAN/PDMS composite membranes of various cross-linking degrees were prepared and characterized. The swelling of the dense, free-standing PDMS membrane of various cross-linking degrees in hexane and PIB/hexane solutions decreases when the pre-polymer/cross-linker ratio increases. The partition coefficient of PIB decreases with the increase of cross-linker content and with the increase in PIB molecular weight.

The transport properties of pure hexane and PIB/hexane solutions through the composites were systematically investigated. For the PAN/PDMS composite membranes the main findings were:

- The hexane permeability (P_{hexane}) through the PAN/PDMS prepared at pre-polymer/cross-linker ratio of 10/0.7 was higher than at ratio of 10/1 (4.5 and 3.1 $\text{lm}^{-2} \text{h}^{-1} \text{bar}^{-1}$, respectively) probably due to the higher membrane swelling. The P_{hexane} through the PAN/PDMS prepared at ratio of 10/2 was higher than through the composite prepared at ratio of 10/1 (4.1 and 3.1 $\text{lm}^{-2} \text{h}^{-1} \text{bar}^{-1}$). This behaviour was not consistent with the swelling findings of the corresponding free-standing PDMS membranes and could be attributed to the lower pore intrusion of PDMS compared to 10/1 and/or due to the heterogeneity of the silicone network.
- Osmotic phenomena were observed for all composite membranes and could be interpreted using the van't Hoff equation.
- The cross-linking degree of PDMS seemed to have no effect on the membrane retention, most probably due to the highly swollen state of the silicone network. Therefore, the PAN/PDMS membrane prepared at pre-polymer/cross-linker ratios of 10/0.7 and 10/2 might be attractive for a practical application due to their higher hexane permeability without compromise for the membrane retention.

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References

- [1] N. Stafie, D.F. Stamatialis, M. Wessling, Insight into the transport of hexane–solute systems through tailor-made composite membranes, *J. Membr. Sci.* 228 (2004) 103–116.
- [2] I.F.J. Vankelecom, K. De Smet, L.E.M. Gevers, A. Livingston, D. Nair, S. Aerts, S. Kuypers, P.A. Jacobs, Physico-chemical interpretation of the SRNF transport mechanism for solvents through dense silicone membranes, *J. Membr. Sci.* 231 (2004) 99–108.
- [3] L. White, Transport properties of a polyimide solvent resistant nanofiltration membrane, *J. Membr. Sci.* 205 (2002) 191–202.
- [4] L.G. Peeva, E. Gibbins, S.S. Luthra, L.S. White, R.P. Stateva, A.G. Livingston, Effect of concentration polarisation and osmotic pressure on flux in organic solvent nanofiltration, *J. Membr. Sci.* 236 (2004) 121–136.
- [5] D. Bhanushali, C. Kurth, D. Bhattacharyya, Performance of solvent-resistant membranes for non-aqueous systems: solvent permeation results and modeling, *J. Membr. Sci.* 189 (2001) 1–21.
- [6] D.R. Machado, D. Hasson, R. Semiat, Effect of solvent properties on permeate flow through nanofiltration membranes. Part I. Investigation of parameters affecting solvent flux, *J. Membr. Sci.* 163 (1999) 93–102.
- [7] J.P. Robinson, E.S. Tarleton, C.R. Millington, A. Nijmeijer, Solvent flux through dense polymeric nanofiltration membranes, *J. Membr. Sci.* 230 (2004) 29–37.
- [8] R. Subramanian, M. Nakajima, K.S.M.S. Raghavarao, T. Kimura, Processing vegetable oils using nonporous denser polymeric composite membranes, *J. Am. Oil Chem. Soc.* 81 (2004) 313–322.
- [9] M.-B. Hagg, Membrane purification of Cl_2 gas: I. Permeabilities as a function of temperature for Cl_2 , O_2 , N_2 , H_2 in two types of PDMS membranes, *J. Membr. Sci.* 170 (2000) 173–190.
- [10] Q.T. Nguyen, Z. Bendjama, R. Clément, Z. Ping, Poly(dimethylsiloxane) crosslinked in different conditions. Part II. Pervaporation of water–ethyl acetate mixtures, *Phys. Chem. Chem. Phys.* 2 (2000) 395–400.

- [11] E. Favre, Q.T. Nguyen, P. Schaetzel, R. Clement, J. Neel, Sorption of organic solvents into dense silicone membranes. Part I. Validity and limitations of Flory–Huggins and related theories, *J. Chem. Soc., Faraday Trans.* 89 (1993) 4339–4346.
- [12] Z.J. Tan, R. Jaeger, G.J. Vancso, Crosslinking studies of poly(dimethylsiloxane) networks: a comparison of inverse gas chromatography, swelling experiments and mechanical analysis, *Polymer* 35 (1994) 3230–3236.
- [13] J.S. Yoo, S.J. Kim, J.S. Choi, Swelling equilibria of mixed solvent–poly(dimethylsiloxane) systems, *J. Chem. Eng. Data* 44 (1999) 16–22.
- [14] S.J. Clarson, J.A. Semlyen, *Siloxane Polymers*, PTR Prentice Hall, New Jersey, 1993.
- [15] J.M. Ziegler, F.W.G. Fearon, *Silicon-Based Polymer Science: A Comprehensive Resource*, American Chemical Society, Washington DC, 1990.
- [16] T.R.E. Simpson, B. Parbhoo, J.L. Keddie, The dependence of the rate of crosslinking in poly(dimethyl siloxane) on the thickness of coatings, *Polymer* 44 (2003) 4829–4838.
- [17] S. Perutz, E.J. Kramer, J. Baney, C.Y. Hui, C. Cohen, Investigation of adhesion hysteresis in poly(dimethylsiloxane) networks using the JKR technique, *J. Polym. Sci.: Polym. Phys.* 36 (1998) 2129–2139.
- [18] S.K. Venkataraman, L. Coyne, F. Chambon, M. Gottlieb, H.H. Winter, Critical extent of reaction of a polydimethylsiloxane polymer network, *Polymer* 30 (1989) 2222–2226.
- [19] M.G.A. Shefer, Effect of crosslinks on the glass transition temperature of end-linked elastomers, *Macromolecules* 25 (1992) 4036–4042.
- [20] N.A. Peppas, C.T. Reinhart, Solute diffusion in swollen membranes. Part I. A new theory, *J. Membr. Sci.* 15 (1983) 275–287.
- [21] N.A. Peppas, *Hydrogels in Medicine and Pharmacy*, CRC Press, Boca Raton, 1986.
- [22] P.G.d. Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, 1979.
- [23] P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1964.
- [24] H. Lonsdale, U. Merten, R. Riley, Transport of cellulose acetate osmotic membranes, *J. Appl. Polym. Sci.* 9 (1965) 1341.
- [25] J.G. Wijmans, R.W. Baker, The solution–diffusion model: a review, *J. Membr. Sci.* 107 (1995) 1–21.
- [26] Q.T. Nguyen, Z. Bendjama, R. Clement, Z.H. Ping, Poly(dimethylsiloxane) crosslinked in different conditions. Part I. Sorption properties in water–ethyl acetate mixtures, *Phys. Chem. Chem. Phys.* 1 (1999) 2761–2766.
- [27] E.M. Barrall II, M.A. Flandera, J.A. Logan, A thermodynamic study of the crosslinking of methyl silicone rubber, *Thermochim. Acta* 5 (1973) 415–432.
- [28] J. Pickering, D. van der Meer, G. Vancso, Effects of contact time, humidity, and surface roughness on the adhesion hysteresis of polydimethylsiloxane, *J. Adhes. Sci. Technol.* 15 (2001) 1429–1441.
- [29] J.E. Mark, Recent studies of rubber elasticity, *Macromol. Chem. Suppl.* 2 (1979) 87–97.
- [30] G.B. McKenna, K.M. Flynn, Mechanical and swelling behaviour of crosslinked natural rubber: consequences of the Flory–Rehner hypothesis, *Polym. Commun.* 29 (1988) 272–275.
- [31] L.Y. Yen, B.E. Eichinger, Vapor sorption isotherms for benzene and n-heptane with poly(styrene-co-butadiene), *J. Polym. Sci.: Polym. Phys.* 16 (1978) 121–130.
- [32] R.W. Brotzman, B.E. Eichinger, Volume dependence of the elastic equation of state. 3. Bulk-cured poly(dimethylsiloxane), *Macromolecules* 15 (1982) 531–535.
- [33] C. Menduina, J.J. Freire, M.A. Llorente, T. Vilgis, Correctly averaged non-Gaussian theory of rubberlike elasticity. Application to the description of the behavior of poly(dimethylsiloxane) bimodal networks, *Macromolecules* 19 (1986) 1212–1217.
- [34] J. He, K. Horie, R. Yokota, Characterization of polyimide gels crosslinked with hexamethylene diisocyanate, *Polymers* 41 (2000) 4793–4802.
- [35] D.W. van Krevelen, P.J. Hoftijzer, *Properties of Polymers, their Estimation and Correlation with Chemical Structure*, Elsevier, Amsterdam, 1976.
- [36] R.S. Harland, N.A. Peppas, Hydrophilic/hydrophobic, block and graft copolymeric hydrogels: synthesis, characterization, and solute partition and penetration, *J. Controlled Release* 26 (1993) 157–174.
- [37] I.F.J. Vankelecom, B. Moermans, G. Verschueren, P.A. Jacobs, Intrusion of PDMS top layers in porous supports, *J. Membr. Sci.* 158 (1999) 289–297.
- [38] H.J. Zwijnenberg, A.M. Krosse, K. Ebert, K.-V. Peinemann, F.P. Cuperus, Acetone-stable nanofiltration membranes in deacidifying vegetable oil, *J. Am. Oil Chem. Soc.* 76 (1999) 83–87.
- [39] K. Ebert, F.P. Cuperus, Solvent resistant nanofiltration membranes in edible oil processing, *Membr. Technol.* 107 (1999) 5–8.
- [40] L. Lin, K.C. Rhee, S.S. Koseoglu, Bench-scale membrane degumming of crude vegetable oil: process optimisation, *J. Membr. Sci.* 134 (1997) 101–108.
- [41] L.P. Raman, M. Cheryan, N. Rajagopalan, Deacidification of soybean oil by membrane technology, *J. Am. Oil Chem. Soc.* 73 (1996) 219–224.
- [42] D.R. Paul, Reformulation of the solution–diffusion theory of reverse osmosis, *J. Membr. Sci.* 241 (2004) 371–386.