Permeability thickness dependence of polydimethylsiloxane (PDMS) membranes

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The paper describes a reliable technique to prepare PDMS membrane used to determine the permeability to CO₂ and He. SEM controls morphology of surface membrane and SEM/FIB measures the membrane thickness. The data show that permeability becomes thickness dependent below some tens of micrometers. The Islam’s model, based on the non-equilibrium sorption–desorption process at the interface, fits quite well with the experimental data. The comparison shows that flux models based on interface reaction could apply to describe quantitatively the thickness-dependence of the permeability. The model allows to determine the surface reactions rate constants for CO₂ and He on PDMS. The introduction of a specific characteristic thickness L provides a functional form, which describes very accurately the results of the present paper and other experiments on polymers. By reducing the membrane thickness below 200 nm, both permeability and selectivity change, indicating Knudsen diffusion as flux mechanisms responsible for permeation. In this range of thickness, SEM images reveal membrane defects.

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1. Introduction

Permeability to CO₂ and He are important parameters to determine the quality of PDMS membranes used in the process of gas separation. The permeability of PDMS membranes is affected by the membrane thickness, the type of gas, and the pressure. The permeability is defined as the rate at which gas molecules pass through the membrane per unit area per unit time. The permeability of PDMS membranes is influenced by the thickness of the membrane, which affects the resistance to gas diffusion. The permeability is also affected by the temperature, pressure, and composition of the gas mixture.

In vacuum technology, for instance, thin polymeric membranes are used in micro-pumps [10,11] and also in gas leakage measurements [7]. Smart single-chip gas sensor microsystems, based on sensitive polymeric layers are used for detecting airborne volatile organic compounds [12,13]. Very thin (600 nm) nanotube/polymer membranes [14] are proposed for high flux gas transport.

In the last decade, several papers as Refs. [15] described procedures to fabricate freestanding polymer membranes. The Refs. [16–18] extensively investigated electromechanical as well as mechanical and structural properties as function of thickness. The Refs. [19,20] studied gas transport characteristics of thin polymeric membranes, in different conditions of membrane preparation like nano particles mixing [21], in mixed-matrix membranes [22] and by plasma treatments [23,24]. Dependence of transport properties on working temperature, pressure [25], and physical aging [26] was also investigated. However, in spite of fact that very thin polymeric membranes are employed in several nanosized devices, the dependence of the measured permeability from membrane thickness L is little known. Studies on vulcanized rubber [27] and glassy polymers [28] concluded that it is independent on L, others concerning Oxygen transport in Kapton® polyimide [29] and, more recently, in nano-constrained glassy polymers [30], showed instead dependence from L. To explain the behavior Ref. [28–30] proposed a morphological change of polymer membrane with thickness accountable for fractional free volume alterations, which modifies gas transport mechanism. An alternative explanation was proposed by Islam and Buschatz [31,32], who considered non-equilibrium reactions at the interface instead of morphological changes. Under this hypothesis they noted that, for thickness such that the reactions at the interface cannot be more considered ‘near’ equilibrium, the measured permeability becomes an “apparent” permeability. This quantity deviates from the “true” permeability that is, instead, a material property independent of thickness, and is generally defined as product of solubility and diffusivity. The model showed good agreement with experiment and allowed to evaluate surface reaction rates which are generally not available in the literature. Their individual knowledge, important in determining the rate of capture from the surface [33].

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does not require sorption experiments to determine the equilibrium constant. The question if the model is still valid on smaller scales where the membrane permeability seems to be more dependent from morphology than from gas transport mechanism is still matter of investigation [9].

This paper studies the permeability of PDMS membrane to CO₂ and He for the thickness smaller than 55 μm. The reasons of the choice of PDMS are in its wide use: from gas separation membrane field, to sensors technology, and, because its biocompatibility, in life science [7–9,15]. CO₂ is extensively studied in gas capture and storage technology because its involvement in environmental science [2,5,6]. He, mostly employed in leak detection, is inert and much lighter than CO₂; a comparison with CO₂ allows an easy discrimination among different permeation mechanisms. A Scanning Electron Microscope (SEM) monitors possible morphological changes. The results show that the permeability P follows the Islam and Buschatz’s model for L > 200 nm. The data allow determination of rates of sorption and desorption for CO₂, He on PDMS not available in the literature, and show a CO₂ permeability almost ten times greater than He, thus confirming that the main mechanism of permselectivity is the solution-diffusion described in [34].

For L < 200 nm the SEM images show the appearance of pinhole defects and the selectivity and permeability strongly change. In this case He permeates better than CO₂ indicating the activation of different gas transport mechanism [35] and previous cited model is not more relevant. The results are in agreement with the studies of Ryoo et al. [9] on PDMS nano-membranes that below 200 nm become sufficiently permeable to air and methanol.

2. Experimental

2.1. Membrane support preparation

Fig. 1 reports description of the support of the polymer membrane. The set up warranties mechanical stability and adequate area exposed to gas flow. A non-permeable silicon chip coated with a 200 nm Silicon Nitride (Si₃N₄) low stress film, anisotropically etched, has a freestanding area (10² μm²) at the center of the chip as shown in Fig. 1(a). For supporting membranes with L larger than 5 μm the Silicon Nitride film is completely removed. In this case the effective membrane area is 10² μm².

For supporting membranes with L smaller than 5 μm a Focused Ion Beams (FIB) (Fig. 1(b) and (c)) drills holes in the Si₃N₄ freestanding area of the chip, varying size and number of the apertures depending on the thickness of the membrane. FIB is a part of a Dual Beam instrumentation by Zeiss, CrossBeam® 1540XB, that combines a Focused Ion Beam with an Ultra High Resolution Field Emission Scanning Electron Microscopy (UHR- FE-SEM). The instrument allows versatile and fast fabrication of the support structure.

2.2. PDMS membranes preparation

Fig. 2 reports detailed scheme of the membrane fabrication process. A glass cover slip supports a thick PDMS layer (Fig. 2(a)). The base and curing agent, mixed (10:1) (Sylgard 184 Silicone Elastomer Kit, product by Dow Corning), are degassed in a vacuum desicator for 15 min, spun on a glass cover slip (22 × 22 mm²) at 500 rpm for 60 s and finally baked at 100 °C for 1 h. The layer is next treated with an oxygen plasma (model Tucano purchase from Gambetti) for 60 s (power 30 W) and then silanized by exposing it to an anti-stiction agent of 1H,1H,2H,2H-per-FluoroOctylTrichloroSilane (FOTS, purchase from Sigma-Aldrich) in a vacuum chamber for 30 min (Fig. 2(b)). After, the PDMS film (the membrane) is spin coated on the anti-stiction layer and baked at 60 °C (Fig. 2(c)). The PDMS membranes are fabricated using different procedures depending on desired thickness. For membranes thicker than 1 μm, base and curing agent are mixed (10:1), spun on the substrate previously described varying the rotational speed and time to tune the thickness, and finally baked in an oven at 60 °C for 1 h. For thicknesses in the range 1 μm–100 nm, base and curing agent are mixed (10:1) and diluted in hexane 1:25 (w/w). After treatment in oxygen plasma for 60 s (power 30 W), the PDMS membrane is brought into conformal contact with the support of Fig. 1, gently pressed with tweezers and baked in an oven at 60 °C for 15 min (Fig. 2(d)). Finally, the PDMS membrane is transferred on the support previously described by

![Fig. 1](image-url). Membrane support. (a) Silicon chip coated with 200 nm of Si₃N₄ with a freestanding square area of 10² μm²; (b) FIB milling of holes; (c) SEM image of porous support, (d) cross-section of the support for membrane with L smaller than 5 μm.
peeling off the substrate (glass and thick PDMS) (Fig. 2(e)). For PDMS membrane with \( L \) larger than 5 \( \mu m \) as stated before the effective membrane area is \( 10^2 \mu m^2 \). For \( L \) smaller than 5 \( \mu m \) the effective membrane area is the sum of the area of the apertures (Fig. 1(d)).

2.3. SEM characterization and thickness measurement

SEM monitors the surface morphology and measures the thickness \( L \). The images record secondary and backscattered electrons with the In-Lens detector at an accelerating voltage of 4 kV and a working distance of 2 mm. The parameters avoid common SEM artefacts when imaging non-conductive samples. All the membranes studied show morphologies which are similar to those shown in Fig. 3, which are reported the most significant ones for (a) \( L = 3 \mu m \) and (b) \( L = 150 \) nm. For \( L \) larger than \( \approx 200 \) nm the membranes look smooth as the one in (a), for \( L \) smaller than \( \approx 200 \) nm a surface texture appears as in (b), presuming the presence of membrane defects.

For \( L > 1 \mu m \), SEM images, as that of shown in Fig. 3(c), allow an estimation of \( L \) with an accuracy in the worst condition better than 20\%. The mean value of repeated measurements in different positions gives the thickness estimation and the maximum error is the measurement error. For \( L < 1 \mu m \) the membranes are cross-sectioned by FIB using the procedure described in [36] and the SEM images, as that of shown in Fig. 3(d), give a maximum error on \( L \) larger than 20\%. A chemical vapor deposition (CVD) [36] coating as shown in Fig. 3(d) overcomes or reduces drawbacks of sample damages from ion beam.

2.4. Gas permeation measurements

Fig. 4 shows the final assembly to measure gas permeability. A perforated copper disk, Conflat® flange compatible, supports the PDMS membrane. A low vapor pressure epoxy (Torr Seal®) ensures vacuum sealing obtaining negligible leak losses and mechanical integrity even at pressure differences up to 1 atm.

For \( L > 1 \mu m \), SEM images, as that of shown in Fig. 3(c), allow an estimation of \( L \) with an accuracy in the worst condition better than 20\%. The mean value of repeated measurements in different positions gives the thickness estimation and the maximum error is the measurement error. For \( L < 1 \mu m \) the membranes are cross-sectioned by FIB using the procedure described in [36] and the SEM images, as that of shown in Fig. 3(d), give a maximum error on \( L \) larger than 20\%. A chemical vapor deposition (CVD) [36] coating as shown in Fig. 3(d) overcomes or reduces drawbacks of sample damages from ion beam.

Fig. 2. Multistep membrane fabrication procedure. (a) A PDMS thick layer is deposited on a glass cover slip, (b) an anti-stiction agent (FOTS) is evaporated on the PDMS layer of (a), (c) a thin PDMS layer, the final membrane, is spin coated on (b) and baked at 60 °C, (d) after oxygen plasma treatment, the PDMS membrane is brought into conformal contact with the support of Fig. 1 and then baked in an oven for 15 min, (e) the PDMS membrane (d) is transferred on the support by peeling off the substrate (glass and thick PDMS).

Fig. 3. SEM images of membranes. (a) \( L = 3 \mu m \), (b) \( L = 150 \) nm. Thickness determination of a membrane with (c) \( L = 27 \mu m \) and (d) \( L = 500 \) nm. In (d) PDMS membrane is cross-sectioned by FIB after FIB-CVD deposition of Platinum (Pt). Si₃N₄ support has \( L = 200 \) nm, PDMS membrane \( L = 500 \) nm.
The assembly of Fig. 4 inserted in the gas permeability apparatus of Ref. [37], allows performing permeability measurements. Fig. 5 sketches the apparatus. The system is similar to that assembled by Tremblay for the same purpose, and described in Ref. [38].

Eq. (1) gives the membrane permeability \( P \) as a function of thickness \( L \), upstream pressure \( p_u \), downstream pressure \( p_d \), and molar flux \( J \) through the membrane

\[
P = \frac{J}{RT} \frac{A}{L} \tag{1}
\]

The capacitive sensor (CS) on feed chamber measures the upstream pressure \( p_u \) that is varied by incremental steps up to \( 9 \times 10^4 \) Pa. He or CO\(_2\) have purity grade N5.0. The QMS measures the downstream partial pressure \( p_d \) in steady-state conditions. The IG gauge calibrates [39] the QMS by means a calibrated leak. Eq. (2) gives the molar flux \( J \) per unit effective membrane area \( A \) of the gas penetrating into the chamber through the membrane

\[
J = \frac{p_d \delta}{RT} \tag{2}
\]

\( R \) is the gas universal constant, \( T \) is the absolute temperature and \( \delta \) is the pumping speed of the TP pump.

Before measuring the membrane permeability, RP evacuates the feed chamber to \( \approx 1 \) Pa, while TP the high vacuum chamber to \( \approx 1 \times 10^{-7} \) Pa. To record the background and to obtain steady-state conditions we switch on the QMS one hour before measuring. We repeat the measurements several times to check possible aging effects [40] and we alternate fluxes of CO\(_2\) and He to test possible plasticization effects [41]. None of them is observed within 10 days.

Following Eq. (1) we calculate the error on the permeability \( P \) by the errors on molar flux \( J \), thickness \( L \) and differential pressure \( p_u-p_d \). Eq. (2) determines the error on \( J \). We did measurements of \( p_u \), with the precautions recommended in Ref. [39], so that its relative error, after IG calibration of the QMS, results of 10%, the error on the membrane area \( A \) and on the TP pumping speed, \( \delta \), are less than 2%, resulting in a relative error on \( J \) of 14%. We point out that the pressure measurement performed by the IG gauge after calibration have an accuracy much better than the 20% declared by the manufacturer. For molar flux less than \( 2 \times 10^{-11} \) mol s\(^{-1}\), the error on \( p_u \) is affected by the determination of the background pressure and the error on \( J \) results greater than 14%. The error on \( L \), as discussed in the previous section, results for \( L > 1 \) \( \mu \)m better than 20%, while below 1 \( \mu \)m becomes larger. Since in the present experimental conditions \( p_u \gg p_d \), the error on \( p_u \) is determined by the error on \( p_u \) which is less than 0.5%. The error on \( P \) is therefore roughly the sum of the relative error on \( J \) and \( L \). By taking into account possible errors arising from the lack of reproducibility in the membrane preparation, we repeat the permeability measurements on several (up to 5) membranes of the same thickness \( L \). The values of \( P \) reported in Figs. 6–8 are the weighted means and the errors are the variance of the weighted means.

3. Results and discussion

3.1. Results

Fig. 6 reports the average values of \( P \) as function of \( L \) (from 1 mm to 200 nm) for CO\(_2\) and He at \( p_u=9 \times 10^4 \) Pa and \( T=293 \) K. Above \( L \approx 50 \) \( \mu \)m the PDMS permeability \( P \) is independent from \( L \), in samples thinner than some tenths of micrometers \( P \) decreases with \( L \). The selectivity \( \beta_{CO_2/He} \) (\( \beta_{CO_2/He} = P_{CO_2}/P_{He} \) with \( P_{CO_2}, P_{He} \) the respective permeability) remains constant with \( L \) as shown in Fig. 7.

\( \beta_{CO_2/He} \) follows the reverse-selectivity behavior explained by the solution-diffusion mechanism [42] previously observed in others dense polymers [43].

By reducing the membrane thickness below 200 nm, both permeability and selectivity change, indicating Knudsen diffusion as flux mechanisms responsible for permeation. In this range of thickness, SEM images reveal membrane defects (see Fig. 3(b)). The PDMS becomes porous and the solution-diffusion [42] model generally used to explain the transport mechanism through dense
membranes does not apply because the mechanism is not the only one responsible of the permeation [35]. We do not report the experimental points since they are not meaningful for the following discussion.

3.2. Discussion

In the solution-diffusion model, based on the Fick’s and Henry’s laws, the permeability $P_{\text{Henry}}=DS$, where $D$ is the diffusion coefficient and $S$ the solubility and $P_{\text{Henry}}$ does not depend on the thickness of the membrane. This model fits the present data only for $L$ larger than 50 $\mu$m, where $P$ results independent from $L$. In this range, $P_{\text{CO}_2}=(1.5 \pm 0.4) \times 10^{-12}$ mol m$^{-1}$ s$^{-1}$ Pa$^{-1}$ and $P_{\text{He}}=(2.1 \pm 0.7) \times 10^{-13}$ mol m$^{-1}$ s$^{-1}$ Pa$^{-1}$ are, in fact, within experimental errors, equal to those measured in thick PDMS membranes and reported in Refs. [19,23,34]. For $L$ in the range 50 $\mu$m < $L$ < 200 nm, $P$ shows a strong decrease with $L$ but the selectivity does not change significantly from its value at $L=1$ mm, $P_{\text{CO}_2/\text{He}} \approx 7$, a value very close to the one reported in Ref. [23] for thick PDMS.

Islam and Buschatz [31,32] analyze in more details the steady state diffusion flux through a membrane, considering the non-equilibrium sorption–desorption process at the interface. The analysis concludes that for a given system (gas and polymer), there may exist a value of $L$ below which the surface reactions are not any more in near equilibrium and the measured permeability becomes dependent on the membrane thickness. Following Ref. [31] one may consider the measured permeability $P$ as an “apparent” permeability, deviating from the product of $D$ and $S$. To describe quantitatively this dependence, we compare the experimental results with the models of Ref. [32]. The authors propose two flux equations, which predict the conditions for which the permeability would appear thickness dependent. In one model (hereafter referred as model A) they suppose the transport coefficient $k$ is equal to cost obtaining an “apparent” permeability $P$ depending from thickness $P$ ($L$) as shown in Eq. (3) in its most general formulation. We point out in fact that the derivation of model A of Ref. [32] made by Islam and Buschatz assumes that $k \beta L ^ {2} \simeq 1$ and obtains for Eq. (3) $P \exp \left( \frac{\rho L}{a} \right) = k_{1} L$. To give more generality to the model we calculate the flux equation without this approximation and Eq. (3) becomes

$$\begin{align*}
P \left( \exp \left( \frac{P}{a} + 1 \right) \right) = k_{1} L
\end{align*}$$

(3)

where $a = \frac{\alpha L}{P}$ and $k_{1}$ is the sorption rate [32].

Similarly, they propose an analogous flux equation, which assumes constant the diffusion coefficient $D$. This model (referred as model B) gives the “apparent” permeability $P$ ($L$) of Eq. (4)

$$\begin{align*}
P = \frac{\left( \frac{L}{L \pm L_{0}} \right) L}{1 + \left( \frac{L \pm L_{0}}{L} \right)}
\end{align*}$$

(4)

where $k_{1}$ and $k_{2}$ are respectively the sorption and desorption rates as defined in Ref. [32].

Fig. 8 reports the experimental data of Fig. 6 from $L=55 \mu$m to $L=230$ nm compared with model A [Eq. (3)] and model B [Eq. (4)].

By minimizing the $\chi^{2}$, we obtained the best-fit parameter reported in Table 1.

The $\chi^{2}$ analysis shows that both models have a good $p$-Value, thus confirming the goodness of the Islam and Buschatz’s assumption and indicating that flux models based on interface reaction could apply to describe quantitatively the thickness-dependence of the permeability. It is difficult to distinguish which one is the most appropriate to fit the present experiment since both fit give similar $p$-Values. The two models seem to give also similar values for the physical parameters. For both He and CO$_{2}$ model A and model B give the same values of $k_{1}$. 

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Fig. 7. Selectivity $P_{\text{CO}_2/\text{He}}$ as function of $L$. The upstream pressure is $P_{u}=9 \times 10^{4}$ Pa and the temperature $T=293$ K. Section 2 reports error analysis.

Fig. 6. PDMS permeability $P$ against thickness membrane $L$. • He/PDMS and • CO$_{2}$/PDMS. Section 2 reports error analysis. The upstream pressure is $P_{u}=9 \times 10^{4}$ Pa, the temperature $T=293$ K.
The parameters obtained by model B allow to calculate $P_{\text{Henry}}$ and to compare it with the experimental results obtained with different experimental techniques available in the literature [19,23,34,38]. In fact, since $S = \frac{k_1}{k_2}$, results

$$P_{\text{Henry}} = \frac{1}{2} \frac{k_1}{k_2} \times 2D$$

which can be easy calculated by the best-fit parameters of Table 1. $P_{\text{Henry}}$ is independent from the thickness and represents the value of permeability for thick membranes, values that are available in the literature.

Table 2 reports comparison among $P_{\text{Henry}}$ and experiments on PDMS membranes.

**Fig. 8.** Best fit of the permeability data from $L = 55 \, \mu$m to $L = 230 \, \mu$m with model A [Eq. (3)] and model B [Eq. (4)]. (a) CO$_2$/PDMS data compared with model A (continuous line) (b) He/PDMS data compared with model A (continuous line) (c) CO$_2$/PDMS data compared with model B (dotted line) (d) He/PDMS data compared with model B (dotted line).

### Table 1
Sorption coefficient $k_1$, transport coefficient $\kappa$, desorption coefficient $k_2$ and diffusivity $D$ for He and CO$_2$ on PDMS as determined by best-fit analysis.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$k_1 \times 10^8$ (mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$)</th>
<th>$\kappa \times 10^{13}$ (mol$^2$ m$^{-4}$ s$^{-1}$ Pa$^{-1}$)</th>
<th>$\chi^2$/ndf</th>
<th>p-Value</th>
<th>$k_1 \times 10^8$ (mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$)</th>
<th>$k_2 / 2D \times 10^{-4}$ (m$^{-1}$)</th>
<th>$\chi^2$/ndf</th>
<th>p-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>$14 \pm 1$</td>
<td>$4 \pm 1$</td>
<td>10.43/8</td>
<td>0.24</td>
<td>$14 \pm 1$</td>
<td>$2.9 \pm 0.9$</td>
<td>10.98/8</td>
<td>0.20</td>
</tr>
<tr>
<td>He</td>
<td>$2.3 \pm 0.3$</td>
<td>$0.4 \pm 0.1$</td>
<td>8.662/8</td>
<td>0.37</td>
<td>$2.3 \pm 0.2$</td>
<td>$4 \pm 2$</td>
<td>8.87/8</td>
<td>0.35</td>
</tr>
</tbody>
</table>

### Table 2
Comparison of $P_{\text{Henry}}$ obtained by the best-fit parameters values of model B with the experimental measurements of permeability of thick PDMS membranes.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$P_{\text{Henry}}$ Eq. (5) $\times 10^{12}$ (mol m$^{-1}$ s$^{-1}$ Pa$^{-1}$)</th>
<th>$P$(1 mm) this work $\times 10^{12}$ (mol m$^{-1}$ s$^{-1}$ Pa$^{-1}$)</th>
<th>$P$ from the literature $\times 10^{12}$ (mol m$^{-1}$ s$^{-1}$ Pa$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>$2 \pm 1$</td>
<td>$1.5 \pm 0.4$</td>
<td>$1.59 \pm 0.07^a$</td>
</tr>
<tr>
<td>He</td>
<td>$0.3 \pm 0.1$</td>
<td>$0.21 \pm 0.07$</td>
<td>$1.27 \pm 0.02^b$</td>
</tr>
</tbody>
</table>

$^a$ Data from Ref. [19].
$^b$ Data from Ref. [21].
$^c$ Data from Ref. [23].
The agreement is very good confirming the correctness of the analysis.

Model B also allows to compare the results of the present paper with other experiments on polymers, like Oxygen on wet and dry Kapton [29] and water on rubber [27]. In fact, by setting equal to 1 the dimensionless parameter \( \alpha = \frac{L}{L_c} \) [31], which serves as a measure for the deviation of the surface reaction from equilibrium, one could determine for each gas/membrane system a specific characteristic thickness \( L_c = \frac{L}{\alpha} \) which, when introduced in Eq. (4), provides a functional form for \( \frac{P}{P_{\text{Henry}}} \). For thicknesses close \( L_c \) the permeability starts to differ from \( P_{\text{Henry}} \) and becomes thickness dependent. We remind that, according to Ref. [31], the surface reaction are “near equilibrium” \( \alpha \ll 1 \), while for \( \alpha \geq 1 \), \( P \) appears to be dependent on \( L \). By using \( L_c \) and \( P_{\text{Henry}} \) of Eq. (5), the apparent permeability \( P \) of Eq. (4) results:

\[
\frac{P}{P_{\text{Henry}}} = \frac{L_c}{1 + \frac{L}{L_c}}
\]

by plotting the values of the dimensionless quantity \( \frac{P}{P_{\text{Henry}}} \) as function of \( \frac{L}{L_c} \) one obtains the functional form as shown in Fig. 9, which is independent from gas and system. The values of \( P_{\text{Henry}} \) and \( L_c \) obtained by the values of the best-fit parameters for the present work and for the data of Refs. [27,29] are reported in Table 3.

Fig. 9 reports the behavior of the Eq. (6) for all the experimental data available. The parameter used in the plot are given in Table 3.

We notice that the characteristic length \( L_c \) indicates the deviation of the surface reaction from equilibrium. For \( L \) smaller than \( L_c \) the solution-diffusion mechanism is associated at the non-equilibrium sorption-desorption processes at the interface affecting the measured permeability, which becomes dependent on the membrane thickness. For \( L \) larger than \( L_c \) these effects are less important and the permeability results independent from \( L \) and close to the value of \( P_{\text{Henry}} \).

A recent paper [44] simulates the diffusive flux trough a composite membrane similar to those of the present study. The results indicate that the effective permeation thickness \( L_{\text{eff}} \) is bigger than the real thickness of the membrane \( L \). To take into account of this effect the authors proposed a corrected version of the equation first published by Strathmann et al. [45] for calculating \( L_{\text{eff}} \) (see Ref. [44, equation 8]). The correction affects both permeability \( P \) (Eq. (1)) and thickness \( L \) (now \( L_{\text{eff}} \)). In our case, as described in Section 2.2, the correction applies to the membranes having thickness lower than 5 \( \mu \)m. We calculate \( P (L_{\text{eff}}) \) by using Ref. [44, equation 8] and we fit the corrected values with models A and B. The parameters obtained are, within the experimental errors, the same as those reported in Table 1.

4. Conclusions

The paper describes a reliable technique to prepare thin PDMS membranes able to maintain 1 atm of differential pressure without rupturing. A SEM/FIB facility allows accurate thickness measurement as well surface characterization. A high vacuum set up equipped with a quadrupole mass spectrometer measures permeability of CO\(_2\) and He on PDMS. The investigation reveals a permeability that is thickness-dependent for thicknesses smaller than some tens of micrometers. The models of Refs. [31,32], based on the non-equilibrium sorption-desorption process at the interface, fit quite well the experimental data. A best-fit analysis determines sorption coefficient \( k_s \), transport coefficient \( \kappa \), desorption coefficient \( k_d \) and diffusivity \( D \) for He and CO\(_2\) on PDMS.

The introduction of a specific characteristic thickness \( L_c = \frac{L}{\alpha} \) provides a functional form for \( \frac{P}{P_{\text{Henry}}} \) which describes very accurately the results of the present paper and other experiments on polymers, like Oxygen on wet and dry Kapton [29] and water on rubber [27]. For CO\(_2\)/PDMS \( L_c = 30 \pm 10 \mu\)m and for He/PDMS \( L_c = 25 \pm 12 \mu\)m.

For \( L < 200 \) nm SEM shows a porous structure of membrane, confirmed by the permeability and selectivity data that indicate Knudsen diffusion as flux mechanisms responsible for permeation.

In the limits of validity of Islam and Buschat’s model, it is possible to replicate the experiments of the present paper with different types of polymers and different gas; this would enable to determine surface rate constants not available in the literature.

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References


Table 3

<table>
<thead>
<tr>
<th>Gas/Membrane</th>
<th>( L_c (\mu)m)</th>
<th>( P_{\text{Henry}} \times 10^{32} ) (mol m(^{-1}) s(^{-1}) Pa(^{-1}))</th>
<th>Gas/Membrane</th>
<th>( L_c (\mu)m)</th>
<th>( P_{\text{Henry}} \times 10^{32} ) (mol m(^{-1}) s(^{-1}) Pa(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)/PDMS</td>
<td>30 ± 10</td>
<td>2 ± 1</td>
<td>O(_2)/Kapton (dry)</td>
<td>14</td>
<td>3.8 \times 10(^{-5})</td>
</tr>
<tr>
<td>He/PDMS</td>
<td>25 ± 12</td>
<td>0.3 ± 0.1</td>
<td>Water/Rubber</td>
<td>78</td>
<td>1.0</td>
</tr>
<tr>
<td>O(_2)/Kapton (wet)</td>
<td>22</td>
<td>3.0 \times 10(^{-3})</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \) Present work Table 1.

\( ^b \) Data from Ref. [29].

\( ^c \) From Ref. [32] which contains the analysis of the data of Refs. [29,27].

\( ^d \) Data from Ref. [27].