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Time-dependent plasticization behavior of polyimide membranes at supercritical conditions

Menno Houben, Machiel van Essen, Kitty Nijmeijer, Zandrie Borneman *

Membrane Materials and Processes, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, the Netherlands

**Abstract**

The time-dependent CO₂-induced plasticization behavior of glassy Matrimid® 5218 polymer membranes at supercritical conditions up to 120 bar was investigated. Glassy polyimide membranes were conditioned with both gaseous CO₂ and liquid-like sc-CO₂. The plasticization behavior during permeation and sorption was correlated with the intrinsic membrane properties and the CO₂ fluid properties. In the gaseous region the CO₂ concentration increased slightly over time, while in the liquid-like sc-CO₂ region the CO₂ concentration remained constant over time and showed no hysteresis, indicating an induced glass transition. Contrary to the CO₂ sorption the CO₂ permeability showed more pronounced time-dependent behavior which increases with feed pressure because of polymer membrane plasticization. Despite the strong time-dependency, the CO₂ permeability was independent of the feed pressure in the liquid-like sc-CO₂ region. This difference in time-dependent behavior between sorption and permeation is due to the presence of a concentration gradient during permeation experiments. In addition, the permeability showed significant hysteresis. Exposure to liquid-like sc-CO₂ resulted in a highly plasticized membrane and changed the permeation behavior at all subsequent feed pressures, due to slow polymer chain relaxation rates. Clearly, these relationships proof that the permeation history is a critical aspect for time-dependent plasticization phenomena at high CO₂ pressures.

**Keywords:**

Supercritical CO₂, Time-dependency CO₂ plasticization, Polyimide membrane

**1. Introduction**

Glassy dense polymer membranes are commonly used in CO₂ gas separations. It is well known that high concentrations of CO₂ induce plasticization phenomena in these glassy polymer membranes [1-6]. The polymer matrix swells due to high CO₂ sorption increasing the polymer free volume and chain mobility. Consequently, the diffusivity of the permeating species increases resulting in significantly higher permeabilities. The diffusivity of especially the slower permeating species benefits the most from this increase in free volume. Therefore, plasticization generally decreases the membrane selectivity [7-9]. The extent of plasticization is closely correlated with the CO₂ concentration inside the polymer matrix and the CO₂ concentration in the polymer matrix scales with the CO₂ partial pressure [10]. Therefore, glassy polymers especially suffer from severe plasticization in high pressure applications, e.g. CO₂/CH₄ separation [9]. Additionally, at pressures and temperatures above the critical point (74 bar, 31 °C) CO₂ is in the supercritical state [11]. Supercritical carbon dioxide (sc-CO₂) has significantly different properties compared to gaseous CO₂, most notably its density and viscosity (Fig. 1) [11]. Till now, the effect of sc-CO₂ and its fluid properties on the membrane performance and the plasticization behavior is not much studied, while it does have a large impact on the performance in high pressure applications (e.g. sc-CO₂ extractions or enhanced methane recovery) [12-17].

Previous work shows that the CO₂ density is the most important fluid property influencing plasticization phenomena in polymer membranes and thus the CO₂ permeability behavior at supercritical conditions [12, 18]. Although supercritical CO₂ is often described having a liquid-like density, even within the supercritical region, a distinction can be made between a less dense gaseous-like region and a denser liquid-like region [19,20]. It is this quasi-phase transition from gaseous-like to liquid-like sc-CO₂ in the supercritical region that causes a steep increase in CO₂ density. Based on this, Shamu et al. [18] concluded that not the phase transition from gaseous to supercritical CO₂, but the quasi-phase transition within the supercritical region is the crucial transition influencing the CO₂ permeability behavior in polymer membranes.

In our previous work we showed that the CO₂ concentration profile in a glassy polyimide matrix follows the CO₂ density profile and
determines the extent of plasticization \[12\]. After the quasi-phase transition to liquid-like sc-CO\(_2\), the CO\(_2\) density and thus the CO\(_2\) concentration in the polymer matrix started to level off. Accordingly, it was hypothesized that the swelling stresses in the liquid-like sc-CO\(_2\) regime remain relatively constant. With that, also the extent of plasticization was indirectly shown not to increase further when increasing the feed pressure in this liquid-like sc-CO\(_2\) regime. However, the experimental times in our previous work were relatively short, while plasticization has a large time-dependency \[5,6,21,22\]. Above the plasticization pressure in this liquid-like sc-CO\(_2\) state, the permeability is dependent on the feed pressure and the permeation and sorption behavior are compared to discuss the plasticization phenomena at a molecular level and comprehending how key parameters play a role in the effects of plasticization is vital when developing new plasticization resistant membranes.

This study thus focuses on the time-dependent plasticization behavior of glassy polymer membranes at supercritical CO\(_2\) conditions. Glassy polyimide membranes are conditioned with both gaseous CO\(_2\) (low density) and liquid-like sc-CO\(_2\) (high density) and the observed plasticization behavior is correlated with the CO\(_2\) fluid properties and the permeation behavior. To study the time-dependency of the plasticization phenomena at supercritical CO\(_2\) conditions the CO\(_2\) permeability and sorption were measured as a function of time at different pressures in the gaseous CO\(_2\) and the liquid-like sc-CO\(_2\) region. The permeation and sorption behavior are compared to discuss the plasticization behavior on a molecular level. To further assess network dilation and relaxation kinetics at these conditions, N\(_2\) permeance decay measurements are performed after CO\(_2\) conditioning. Finally, the influence of the permeation history at low CO\(_2\) pressures on the CO\(_2\) permeability at high CO\(_2\) pressures is investigated.

### 2. Experimental

#### 2.1. Materials

Matrimid® 5218 (Matrimid), polyimide, was kindly provided by Huntsman Advance Materials (Europe). \(N, N\)-Dimethylformamide (DMF, \(\geq 99.9\%\)), was obtained from Biosolve, The Netherlands and was used without further purification. Pure gases (CO\(_2\), He and N\(_2\)) were purchased from Linde Gas with a purity of \(\geq 99.995\%\) and were used as received.

#### 2.2. Membrane preparation

Dense Matrimid films were made by casting a 20 wt% Matrimid solution in DMF on a glass substrate using a 0.5 mm doctor blade. Prior to casting, the solution was filtered to remove any remaining solid particles using a 5 \(\mu\)m aluminum filter. The Matrimid films were dried following the same protocol as in our previous work \[3\]. First, the cast films were solidified at room temperature in a nitrogen atmosphere for 48 h. Subsequently, residual solvent in the membrane films was removed in a nitrogen oven at 80 \(^\circ\)C for 24 h, 120 \(^\circ\)C for 24 h and 150 \(^\circ\)C for 48 h. The thickness of the resulting Matrimid films was measured using an IP6S Coolant Proof digital Micrometer from Mitutoyo and was found to be between 40 and 50 \(\mu\)m.

#### 2.3. High pressure gas sorption

Time-dependent gas sorption isotherms of CO\(_2\) in dense Matrimid films were determined gravimetrically using a magnetic suspension balance (MSB, Rubotherm series IsoSORP® sorption instrument). CO\(_2\) was pressurized into the supercritical state using a high-pressure syringe pump (Teledyne ISCO 260D syringe pump). The temperature was kept constant at 35 \(^\circ\)C for all experiments. Before each measurement the sample was degassed for at least 12 h. Subsequently, the time-dependency of the CO\(_2\) sorption was measured at pressures of 20, 40 and 60 bar in the gaseous CO\(_2\) state and 85, 100 and 120 bar in the liquid-like sc-CO\(_2\) state. For each conditioning pressure, the measurement consisted of a pressurization cycle where the pressure was gradually increased to the desired pressure with incremental pressure steps using a 3 h time interval, followed by three days at isobaric conditions. For all sorption measurements pristine membranes were taken to exclude any history effects. The mass uptake of CO\(_2\) in the dense Matrimid films corrected for swelling dependent buoyancy based on the initial sample weight and volume according to equation (1).

\[
\hat{m}_{\text{CO}_2} = \hat{m}_s - (V_i \cdot (1 + \gamma_s)) \cdot \rho_{\text{CO}_2} - m_0
\]

Where \(\hat{m}_{\text{CO}_2}\) is the swelling dependent buoyancy corrected mass uptake of CO\(_2\) in the polymer, \(\hat{m}_s\) is the measured mass of the sample at time \(t\), \(V_i\) is the volume of the sample in the initial state, \(\gamma_s\) is the pressure and temperature dependent volumetric swelling coefficient, \(\rho_{\text{CO}_2}\) is the density of the surrounding CO\(_2\) at the measured pressure and temperature (determined by the MSB) and \(m_0\) is the initial mass of the sample measured at vacuum. Volumetric swelling values per pressure step were calculated by the extrapolation of volumetric swelling values obtained from literature for polyimides comparable to Matrimid, as described in more detail in our previous work \[4,12\]. Although in some cases this may introduce small discrepancies between the calculated swelling values and the actual swelling values, this approach provides within the existing possibilities the most accurate swelling values.

#### 2.4. High pressure gas permeation

The high-pressure time-dependent permeation properties of dense Matrimid films were determined using a custom build high-pressure
permeation setup. The membrane under investigation was placed into a stainless steel cell with an effective permeation area of 78.8 cm² (membrane cell is described in detail by Shamu et al. [18]). Additionally, a Whatman® filter paper (Grade 50 with pore size of 2.7 μm) supported the membrane to prevent possible pressure induced punctures. The temperature during measurements was controlled with a HAAKE W19 water bath with D1 heater and all permeation measurements were performed at a temperature of 35 °C. The desired pressure was applied to the feed side of the membrane using a high-pressure Teledyne ISCO-pump 260D syringe pump, while keeping the permeate side at atmospheric pressure. Permeation flow rates were recorded using a bubble flow meter and the corresponding permeability coefficients were calculated using equation (2).

\[ P_i = \frac{J_i \cdot L}{\Delta P_i} \]  

(2)

Here \( P_i \) (cm² (STP)/cm² s cmHg) is the permeability coefficient, \( J_i \) (cm³(STP)/(cm² s)) is the flux, \( L \) (cm) is the thickness of the membrane and \( \Delta P_i \) (cmHg) is the fugacity difference of the feed and permeate. At high CO₂ pressures, the non-ideal behavior of CO₂ becomes increasingly more important. Therefore, fugacities should be used as a driving force for the calculation of the permeabilities instead of absolute partial pressures. The fugacity is the effective partial pressure, i.e., the partial pressure corrected for non-ideal gas behavior. Fugacities were calculated using the Soave-Redlich-Kwong equation of state for CO₂-CO₂ interactions.

3. Results and discussion

3.1. High-pressure CO₂ sorption

The sorption and desorption isotherms of CO₂ for Matrimid are shown in Fig. 4. The CO₂ sorption shows the non-linear sorption behavior as a function of pressure typical for glassy polymers [24,25]. In the gaseous CO₂ phase (open symbols) the CO₂ concentration increases with increasing feed pressure and can be well described with the dual-mode sorption model [26–28]. The critical CO₂ concentration of ~38 cm³(STP)/cm³, which corresponds to the plasticization pressure, is already reached at around 10 bar [1]. Thus, the effects of plasticization should be clearly visible at relatively low pressures. The extent of plasticization is dependent on the CO₂ concentration in the polymer matrix, and thus becomes more severe as the pressure increases in the gaseous CO₂ phase [10]. The phase transition from gaseous CO₂ to liquid-like sc-CO₂ at 80 bar is clearly reflected in the sorption behavior, indicated by the transition from the open symbols to the solid symbols in Fig. 4 [12]. Near the phase transition pressure (80 bar) the CO₂ density changes significantly with small changes in pressure, resulting in a slight jump in CO₂ concentration when entering the liquid-like sc-CO₂ region. After the phase transition the trend of the CO₂ concentration with increasing pressure closely resembles the trend of the CO₂ density, and both the CO₂ concentration and density start to level off [12,18,29]. Next to that, the driving force (CO₂ fugacity) also starts to level off in the liquid-like sc-CO₂ region (Fig. 2). Thus, the changing CO₂ properties ensure that the CO₂ concentration levels off at liquid-like sc-CO₂ conditions. In the liquid-like sc-CO₂ region the sorption distinctly deviates from the sorption predicted by the dual-mode sorption model. Therefore, the sorption in this liquid-like sc-CO₂ region cannot be described using this model. The CO₂ concentration in the liquid-like sc-CO₂ region reaches a plateau value, resulting in relatively constant swelling stresses in the polymer matrix with increasing pressure [12]. Based on this, we hypothesize that the extent of plasticization also remains relatively constant with increasing CO₂ pressures.

For the desorption isotherm large hysteresis is observed in the gaseous CO₂ region. This large hysteresis reflects slow chain relaxations after plasticization, which is commonly observed for glassy polymers [4]. The dual-mode sorption parameters for both sorption and desorption in the gaseous CO₂ phase are shown in Table 1 [27,28]. Since the dual-mode sorption model cannot describe the sorption in the liquid-like sc-CO₂ only the gaseous phase is considered for the calculation of the dual-mode sorption parameters [30–32]. The dual mode sorption parameters during sorption are comparable to the parameters found in literature [33,34]. When plotting, based on the dual-mode parameters,
studies proved that the glass transition temperature ($T_g$) of the polymer matrix [4, 35]. Many investigations showed that the strong plasticization effect significantly lowers the $T_g$ of the polymer matrix and marginally increase the $T_g$ of the polyimide-CO$_2$ mixture, even below the experimental temperature, is very likely. Although high hydrostatic pressures can slightly compress the polymer matrix and marginally increase the $T_g$ of the polyimide-CO$_2$ mixture, even below the experimental temperature, is very likely. Although high hydrostatic pressures can slightly compress the polymer matrix and marginally increase the $T_g$ of the polyimide-CO$_2$ mixture, even below the experimental temperature, is very likely. Although high hydrostatic pressures can slightly compress the polymer matrix and marginally increase the $T_g$ of the polyimide-CO$_2$ mixture, even below the experimental temperature, is very likely. 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CO₂ density, especially near the phase transition to liquid-like sc-CO₂ at 80 bar. In the gaseous CO₂ region, after the initial concentration build-up the CO₂ concentration in the polymer matrix remains constant over time at a pressure of 5 bar, which is expected as the magnitude of plasticization below the plasticization pressure (~10 bar for Matrimid) is very small [3, 43]. When increasing the pressure above this plasticization pressure in the gaseous CO₂ region, the CO₂ concentration increases slightly over time. This additional increase in CO₂ concentration over time is caused by the creation of extra free volume due to plasticization of the polymer matrix, which becomes more pronounced at higher pressures. Therefore, also in the gaseous CO₂ state the time-dependent increase in CO₂ concentration is more pronounced at higher pressures. Contrary to the gaseous CO₂ state different time-dependent behavior is observed when the CO₂ pressure is increased into the liquid-like sc-CO₂ region. Interestingly, in this liquid-like sc-CO₂ region the CO₂ concentration remains constant as a function of the experimental time, indicating that the kinetics of plasticization are faster when CO₂ is supplied in the liquid-like sc-CO₂ phase. The fast plasticization kinetics and constant CO₂ concentrations together with the absence of hysteresis in the liquid-like sc-CO₂ region further substantiates that indeed the high sorption of CO₂ induces a glass transition, and the polymer membrane enters its rubbery state. Typically, rubbery polymer membranes do not show any hysteresis phenomena as non-equilibrium excess free volume is absent in rubbery polymers [18, 44, 45]. Furthermore, rubbery polymers are generally much less affected by plasticization effects and therefore have no significant time-dependent sorption behavior [10, 18].

### 3.2. Time-dependent CO₂ permeability behavior

Fig. 6 shows the CO₂ permeability as a function of time for different pressures in the gaseous CO₂ region (open symbols) and in the liquid-like sc-CO₂ region (closed symbols). In the gaseous CO₂ region, the CO₂ permeabilities show time-dependent permeation behavior at all measured CO₂ conditioning pressures. The plasticization pressure of Matrimid is around 10 bar, therefore all CO₂ permeabilities are measured above the plasticization pressure of Matrimid [1, 3]. With increasing CO₂ feed pressure, the CO₂ concentration in the polymer matrix increases, resulting in a more swollen membrane. The CO₂ permeability increases by a factor 1.5 at 20 bar to even a factor 16 at 120 bar, illustrating the power of plasticization phenomena at high pressures. Above the plasticization pressure the measured permeabilities are non-equilibrium values, as they increase in time due to the non-equilibrium state of the glassy polymer [2, 6]. These time-dependent characteristics originate from large swelling stresses imposed by high CO₂ sorption. As a result, the polymer matrix swells over time increasing its free volume and therefore increasing the CO₂ permeability over time as well. The CO₂ permeability increases significantly in the first few hours due to the build-up of the concentration profile and the corresponding swelling of the membrane. Subsequently, the CO₂ permeability keeps increasing over time, but at a considerable slower rate, which is displayed by the lower slope of the permeability curves at longer experimental times.

The slopes of the permeability curves, calculated between 50 and 75 h, are shown in Fig. 7. The swelling stresses, which are determined by the CO₂ concentration in the membrane, are larger at higher pressures than at lower pressures. Therefore, increasing the pressure in the gaseous CO₂ region (20–60 bar) results in a larger time-dependent permeability increase, which is illustrated by the exponentially increasing slopes in Fig. 7.

At 35 °C the phase transition to liquid-like sc-CO₂ occurs at 80 bar [11, 19]. After the phase transition to liquid-like sc-CO₂ the permeation characteristics are independent of the sc-CO₂ pressure. In this region the CO₂ permeability curves overlap and show the exact same behavior. This behavior is correlated to the CO₂ sorption and the CO₂ density, which level off after the phase transition occurs (Figs. 1 and 4). Because the CO₂ sorption levels off, the swelling stresses in the membrane do not increase further at higher pressures in the liquid-like sc-CO₂ region. This means that in this region the swelling of the membrane, and thus the extent of plasticization, is independent of the feed pressure. This behavior is also observed in the time-dependent increase of the CO₂ permeability, as the slopes of the permeability curves are similar. Accordingly, the extent of plasticization remains constant with increasing pressure in the liquid-like sc-CO₂ region. Interestingly, the slope of the permeability curves in the liquid-like sc-CO₂ region is similar to the slope of the permeability curve at 60 bar in the gaseous CO₂ region, while the absolute CO₂ permeabilities differ significantly. This suggests that the swelling rate at 60 bar and that at pressures in the liquid-like sc-CO₂ is comparable, while the polymer matrix is more swollen in the liquid-like sc-CO₂ region. Even though the extent of plasticization does not increase with increasing pressure in the liquid-like sc-CO₂ region, the polymer matrix still plasticizes, as the CO₂ permeabilities keep increasing over time. This permeation behavior is
inconsistent with the observed CO\textsubscript{2} sorption behavior (Fig. 5). The CO\textsubscript{2} sorption shows no time-dependent behavior in the liquid-like sc-CO\textsubscript{2} region, which substantiates that the high CO\textsubscript{2} concentrations induce a glass transition in the polymer matrix [4,35]. If a similar glass transition would be induced during permeation measurements than the CO\textsubscript{2} permeability would become time-independent, as rubbery membranes are significantly less affected by plasticization phenomena [10,18]. This difference in observed behavior between permeation and sorption experiments is related to the CO\textsubscript{2} concentration in the polymer matrix [21]. During sorption all sides of the membrane are exposed to high pressure CO\textsubscript{2}, which results in a uniform CO\textsubscript{2} concentration in the membrane at steady-state conditions. On the other hand, during permeation only the feed side of the membrane is exposed to high pressure CO\textsubscript{2}, while the permeate side is at atmospheric conditions. This results in a CO\textsubscript{2} concentration gradient over the thickness of the membrane, where the CO\textsubscript{2} concentration decreases from the feed to the permeate side, as schematically shown in Fig. 8. Due to this concentration gradient, the CO\textsubscript{2} concentration will not be high enough to surpass the glass transition temperature over the entire thickness of the membrane. Only in a small part of the membrane, the part that faces the feed side, the T\textsubscript{g} drops sufficiently to end up in the rubbery phase. Therefore, the membrane primarily shows glassy behavior, which results in the increasing CO\textsubscript{2} permeabilities over time in the liquid-like sc-CO\textsubscript{2} region.

The phase transition from gaseous to liquid-like sc-CO\textsubscript{2} not only causes a steep increase in CO\textsubscript{2} density, but also a steep increase in CO\textsubscript{2} viscosity (Fig. 1). The CO\textsubscript{2} density is a thermodynamic parameter and mostly influences the CO\textsubscript{2} sorption, while CO\textsubscript{2} viscosity is a kinetic parameter, that influences the CO\textsubscript{2} diffusivity [18,46,47]. Shamu et al. [18] observed a decline in CO\textsubscript{2} permeability and diffusion coefficient for rubbery PDMS membranes in the liquid-like sc-CO\textsubscript{2} region due to the increased viscosity of CO\textsubscript{2} at liquid-like conditions. However, for glassy Matrimid membranes the CO\textsubscript{2} sorption remains constant, while the CO\textsubscript{2} permeabilities are independent of the feed pressure and keep increasing over time in the liquid-like sc-CO\textsubscript{2} region. As a consequence, the diffusion coefficient and the permeability change proportionally to each other even in liquid-like conditions due to strong plasticization, as shown in our previous work [12]. This shows that the effect of plasticization in these glassy polymer membranes dominates the effect of the increased viscosity on the CO\textsubscript{2} permeability at liquid-like conditions as seen for rubbery membranes.

3.3. N\textsubscript{2} permeability decay in time

Conditioning of the glassy polymer matrix at high pressure CO\textsubscript{2} results in increasing diffusion coefficients for all permeating species due to plasticization phenomena [1,8]. To further assess these network dilation effects, the N\textsubscript{2} permeability decay in time is measured immediately after exposure to high pressure CO\textsubscript{2}. Fig. 9 shows the N\textsubscript{2} permeability decay in time for the different CO\textsubscript{2} conditioning pressures. The measured N\textsubscript{2} permeability after CO\textsubscript{2} exposure is normalized to the initial N\textsubscript{2} permeability that is determined before the membrane has been in contact with CO\textsubscript{2}. Clearly, the conditioning of the membrane with CO\textsubscript{2} results in significant plasticization of the polymer matrix as the N\textsubscript{2} permeability is more than 2 times higher at 20 bar and more than 10 times higher at 120 bar than the initial N\textsubscript{2} permeability. The N\textsubscript{2} permeability decreases considerably during the first 25 h, which corresponds to the elastic part of plasticization. Subsequently, the N\textsubscript{2} permeability decreases slowly over time as relaxation of the plasticized polymer matrix occurs [48,49].

Fig. 9. N\textsubscript{2} permeability decay of Matrimid measured at 20 bar N\textsubscript{2} pressure and 35 °C after different CO\textsubscript{2} conditioning pressures. The N\textsubscript{2} permeability after CO\textsubscript{2} exposure is normalized to the N\textsubscript{2} permeability that is determined before the membrane has been in contact with CO\textsubscript{2}. The black dashed line corresponds to a value of 1. The open symbols represent the conditioning of the membrane in the gaseous CO\textsubscript{2} phase whereas the closed symbols represent conditioning of the membrane in the liquid-like sc-CO\textsubscript{2} phase.

Fig. 8. Authors impression of the concentration profile with increasing time under a) permeation and b) sorption conditions. The critical CO\textsubscript{2} concentration, C\textsubscript{cr}, is required to induce a glass transition in the membrane.
However, the polymer chains are unable to relax back to their initial state within the measured time interval (~100 h), indicating permanent network dilation. Over time the polymer matrix keeps relaxing to a denser configuration due to physical aging. Moreover, this process usually occurs over long timescales (months to years) for thick films, especially at temperatures far below the Tg of Matrimid [50–53].

At higher CO2 conditioning pressures, the N2 permeability increases indicating a higher degree of plasticization, and thus swelling, of the polymer matrix. Similar behavior is observed for the N2 permeability decay as for the CO2 permeability when the membrane is conditioned at pressures in the liquid-like sc-CO2 region. The N2 permeability decay follows the same course after being exposed to 85, 100 and 120 bar CO2, showing that the level of swelling and thus the extent of plasticization is independent of the CO2 conditioning pressure in the liquid-like super-critical region.

The slopes of the N2 permeability decay curves provide more information about the relaxation rate of the polymer matrix after CO2 exposure. The slopes of these curves are shown in Fig. 10 and are calculated in the time interval 50–75 h. The N2 permeability decreases more rapidly at higher CO2 conditioning pressures, implying that the polymer matrix has faster chain relaxation after being exposed to higher swelling stresses. Because the N2 permeability curves of the membranes that were exposed to liquid-like sc-CO2 are similar, the slopes of these curves are also comparable. This confirms that the relaxation rate of the polymer chains is related to the level of swelling, and thus the swelling stresses, of the polymer matrix. Overall, the slopes of the N2 permeability decay curves correspond to the swelling rate of the polymer matrix during CO2 exposure, while the slopes of the N2 permeability correspond to the relaxation of the polymer chains preceding swelling. The slope of the CO2 permeability curve at 60 bar is similar to the slopes of the CO2 permeability curves in the liquid-like sc-CO2 region (Fig. 7), while this is not the case the slopes of the N2 permeability curves. This shows that at 60 bar CO2 pressure the swelling rate of the polymer matrix is similar to the swelling rate in the liquid-like sc-CO2 region, while the absolute level of swelling is higher in the liquid-like sc-CO2 region illustrated by the higher slopes of the N2 permeability curves.

Horn and Paul [54] showed that for relatively short (~4 h) CO2 conditioning times at 32 atm thick Matrimid films have lower relaxation rates compared to thin films. However, the thick Matrimid films show almost complete relaxation back to the original N2 permeability after 200 h. In our case much longer CO2 conditioning times (~75 h) and higher CO2 pressures (20–120 bar) are applied, resulting in a higher degree of plasticization of the films. This strong plasticization is also reflected in the considerably longer relaxation times required for the film to return to its original N2 permeability. As mentioned before, in fact the membrane films do not return to their initial state within the time period of the experiment. From extrapolation of the N2 permeability curves it is estimated that relaxation times longer than 1000 h (depending on CO2 conditioning pressure) are necessary for the films to return to their initial state.

3.4. Hysteresis and permeation history

Plasticization phenomena are commonly paired with hysteresis effects upon pressurization and depressurization steps in permeation or sorption measurements [44,55–57]. Significantly higher permeabilities and concentrations are measured when the pressure is decreased step-wise after the membrane is exposed to high pressure CO2. Decreasing the pressure leaves extra free volume in the polymer matrix, and as shown with the N2 permeability decay measurements the polymer chains are unable to relax back to their initial state within the measured time interval resulting in permanent network dilation [48]. Consequently, the permeation history of the polymer membrane has a large influence on the network morphology and thus on the measured CO2 permeabilities. Fig. 11 displays hysteresis effects in the time-dependent CO2 permeability as a function of the experimental time during pressurization, depressurization and repressurization. When initially increasing the feed pressure in the gaseous CO2 region (20, 40 and 60 bar), a stepwise increase in CO2 permeability is observed, similarly as observed in literature [54]. Increasing the pressure results in a greater elevation of the CO2 permeability, due to the higher swelling of the membrane as also observed in Fig. 6. When changing the pressure into the liquid-like sc-CO2 region the CO2 permeability is only dependent on time and no longer on the feed pressure, as can be seen by the disappearance of the stepwise behavior. No difference in behavior is observed when either increasing or decreasing the pressure in the liquid-like sc-CO2 region. This is expected as the CO2 concentration remains relatively constant and no hysteresis was observed in the liquid-like sc-CO2 region (Fig. 4). This confirms that the extent of plasticization is independent of the feed pressure in the liquid-like sc-CO2 region. When the pressure is decreased further, the phase transition to gaseous CO2 occurs. A reduction in CO2 permeability is expected, because in the gaseous CO2 region the CO2 concentration starts to decrease and relaxation of the polymer matrix sets in. However, upon reducing the feed pressure to 60 and 40 bar, the CO2 permeability even slightly increases and only decreases marginally over time due to relaxation of the polymer matrix. This shows that at these pressures in the gaseous CO2 region the swelling stresses in the polymer matrix are still large enough to keep the swollen morphology of the polymer matrix intact, even though the CO2 concentration decreases (Fig. 4). Only when decreasing the feed pressure further to 20 bar in the gaseous region considerable chain relaxation occurs, illustrated by the larger decrease in CO2 permeability. This considerable chain relaxation at 20 bar is also represented by the lower CO2 permeability when increasing the pressure again during the repressurization cycle. During this repressurization cycle the CO2 permeability only increases slightly over time as the membrane is still highly plasticized from the pressurization and depressurization cycles.

In contrast to the permeation behavior during the pressurization cycle, the gaseous CO2-liquid-like sc-CO2 phase transition is not well visible in the permeation behavior during the depressurization and repressurization cycle (Fig. 12). As mentioned before in the liquid-like sc-CO2 region the CO2 permeability has no pressure dependency, but solely increases over time. This is also observed in Fig. 12 as the CO2 permeability increases with consecutive pressure steps in the liquid-like...
sc-CO\(_2\) region, independent whether the pressure is increasing or decreasing. After exposure to liquid-like sc-CO\(_2\) the membrane is highly plasticized. The swelling stresses in the gaseous CO\(_2\) region are sufficient large to keep the membrane in this plasticized state and the chain relaxations slow. This results in a relatively constant CO\(_2\) permeability as a function of pressure after exposure to liquid-like sc-CO\(_2\). Just at a feed pressure of 20 bar, the swelling stresses are small enough for significant chain relaxation to occur, indicated by a decrease in permeability. Even at this relatively low pressure the CO\(_2\) permeability does not decrease enormously over 24 h, showing that the chain relaxations are still relatively slow. Thus, exposing the membrane to liquid-like sc-CO\(_2\) significantly changes the membrane morphology and affects the permeation behavior at all subsequent feed pressures.

To study the influence of the permeation history of the membrane, membranes were exposed to CO\(_2\) for different conditioning times (Fig. 3). Fig. 13 shows the comparison of the CO\(_2\) permeability for membrane films with different permeation histories. At 20 bar no difference between the two permeabilities could be observed as this is the first pressure step and there is no prior permeation history. When the pressure increases the influence of the permeation history becomes more pronounced. The swelling stresses at lower pressures are smaller than at higher pressures \[2,6\]. Therefore, increasing the feed pressure using the different conditioning times yields a different morphological state of the polymer matrix. When using only 1 h of conditioning time at preceding pressures, the pressure and thus also the CO\(_2\) concentration increases relatively fast. Hence, the polymer matrix experiences large swelling stresses immediately. This results in higher swelling rate and thus a more

Fig. 11. Pressurization, depressurization and repressurization cycle showing hysteresis in the time-dependent CO\(_2\) permeability (based on CO\(_2\) fugacity) of Matrimid at 35 °C as a function of the CO\(_2\) conditioning time. During the pressurization cycle the pressure was gradually increased from 20 to 120 bar with a time interval of 24 h at each pressure stage. Subsequently, after the final pressure was reached the pressure was gradually decreased back to 20 bar using the same time interval of 24 h. The protocol for the repressurization cycle was identical as for the pressurization cycle.

Fig. 12. Hysteresis in CO\(_2\) permeability (based on CO\(_2\) fugacity) of Matrimid at 35 °C as a function of the CO\(_2\) conditioning pressure. Permeability values are taken after 24 h of conditioning at the corresponding pressure. The open symbols represent the gaseous CO\(_2\) phase whereas the closed symbols represent the liquid-like sc-CO\(_2\) phase.

Fig. 13. a) Comparison of the CO\(_2\) permeability (based on CO\(_2\) fugacity) of Matrimid at 35 °C as a function of pressure for different conditioning times at preceding pressures. All permeability values are taken after 24 h of permeation at the respective pressure. The open symbols represent the gaseous CO\(_2\) phase whereas the closed symbols represent the liquid-like sc-CO\(_2\) phase. b) Relative difference in permeability values at the respective pressures between the membrane films with 1hr and 24hr conditioning time. The patterned bars represent the conditioning of the membrane in the gaseous CO\(_2\) phase whereas the solid bars represent conditioning of the membrane in the liquid-like sc-CO\(_2\) phase.
swollen morphology, shown by the higher permeabilities for the membranes that have 1 h of conditioning time. Even though the membranes that have a 24 h conditioning time have been exposed to CO\textsubscript{2} above the plasticization pressure for considerably longer times, the membranes are more swollen at shorter conditioning times. Reasons for this are found in the relaxation history of the polymer matrix \cite{6,58}. When the polymer matrix is exposed to small swelling stresses at low pressures for 24 h, the swelling of the polymer matrix occurs gradually, and the polymer chains have more time to reorient. Thus, at a subsequent pressure step, the polymer matrix is not subjected to huge differences in swelling stresses. This results in less swollen membranes when longer CO\textsubscript{2} conditioning times are applied. The difference in CO\textsubscript{2} permeability for the different conditioning times becomes smaller after the transition to liquid-like sc-CO\textsubscript{2}. Given that the swelling stress is constant in the liquid-like sc-CO\textsubscript{2} region, the extent of plasticization is independent of the feed pressure and solely increases over time. Therefore, this smaller difference in CO\textsubscript{2} permeability for the different conditioning times is attributed to the different total exposure time to liquid-like sc-CO\textsubscript{2}. The CO\textsubscript{2} permeability of the membranes with 1 h of conditioning time barely increases in the liquid-like sc-CO\textsubscript{2} region. This is because the total exposure time to liquid-like sc-CO\textsubscript{2} is much lower when a 1 h conditioning time is applied compared to when 24 h conditioning time is applied at preceding pressures (Fig. 3). Hence, the total exposure time to the same swelling stress is different, which results in the smaller difference in CO\textsubscript{2} permeability with increasing pressure for the different conditioning times. However, it is expected that when the membranes are exposed to liquid-like sc-CO\textsubscript{2} for longer time the differences in morphological state of the polymer between the conditioning times will decrease, as the swelling over time will decrease and hypothetically ultimately stops.

4. Conclusions

The time-dependent CO\textsubscript{2}-induced plasticization behavior at supercritical conditions of glassy Matrimid polyimide membranes has been extensively investigated by conditioning the polyimide membranes with both gaseous CO\textsubscript{2} and liquid-like sc-CO\textsubscript{2}. The membranes were evaluated for their time-dependent gas sorption and permeation at CO\textsubscript{2} pressures ranging from 20 to 120 bar. In the gaseous CO\textsubscript{2} region, the CO\textsubscript{2} sorption could be well described using the dual mode sorption model, while in the liquid-like sc-CO\textsubscript{2} region the CO\textsubscript{2} sorption was directly dependent on the CO\textsubscript{2} density. In the liquid-like sc-CO\textsubscript{2} region the CO\textsubscript{2} concentration remained constant as a function of time and showed no hysteresis, which was attributed to a glass transition that is induced by the high CO\textsubscript{2} sorption. The CO\textsubscript{2} permeability on the other hand, showed more pronounced time-dependent behavior with increasing feed pressure as a result of polymer membrane plasticization and the increasing CO\textsubscript{2} density. In the liquid-like sc-CO\textsubscript{2} region the CO\textsubscript{2} permeability, and thus the extent of plasticization, was found to be independent of the feed pressure, but still showed a strong time-dependency. The difference between the observed time-dependent behavior during sorption and permeation experiments is proposed to be caused by the presence of a concentration gradient in the permeation experiments. Thus, during permeation the CO\textsubscript{2} concentration will not be high enough to surpass the glass transition temperature over the entire thickness of the membrane. N\textsubscript{2} permeability decay measurements revealed severe permanent network dilution and low polymer chain relaxation rates after exposure to liquid-like sc-CO\textsubscript{2}. The relaxation rate of the polymer chains is related to the level of swelling in the polymer, where a higher swelling degree resulted in a higher initial relaxation rate. The membranes showed strong hysteresis effects. Exposure to liquid-like sc-CO\textsubscript{2} resulted in a highly plasticized membrane and changed the permeation behavior at all subsequent feed pressures. Moreover, the permeation history of the membrane had a large influence on the plasticization effects, as shorter conditioning times resulted in more swollen membranes compared to longer conditioning times at preceding pressures.

CRediT authorship contribution statement

Menno Houben: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – Original Draft, Writing – Review & Editing, Visualization. Machiel van Essen: Formal analysis, Investigation, Writing - review & editing. Kitty Nijmeijer: Conceptualization, Supervision, Writing - review & editing, Project administration, Funding acquisition. Zandrie Borneman: Conceptualization, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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