

Molecular simulation and mathematical modelling of glass transition temperature depression induced by CO₂ plasticization in Polysulfone membranes

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Abstract. A sequence of molecular modelling procedure has been proposed to simulate experimentally validated membrane structure characterizing the effect of CO₂ plasticization, whereby it can be subsequently employed to elucidate the depression in glass transition temperature (T_g). Based on the above motivation, unswollen and swollen Polysulfone membrane structures with different CO₂ loadings have been constructed, whereby the accuracy has been validated through good compliance with experimentally measured physical properties. It is found that the presence of CO₂ constitutes to enhancement in polymeric chain relaxation, which consequently promotes the enlargement of molecular spacing and causes dilation in the membrane matrix. A series of glass transition temperature treatment has been conducted on the verified molecular structure to elucidate the effect of CO₂ loadings to the depression in T_g induced by plasticization. Subsequently, a modified Michealis-Menten (M-M) function has been implemented to quantify the effect of CO₂ loading attributed to plasticization towards T_g .

1. Introduction

Polymeric membrane gas separation is an emerging process in industrial application ascribed to its various advantages in comparison to conventional technologies, such as occupying a relatively smaller footprint, chemical free, cost effective, high process flexibility and energy efficiency [1-5]. It has been applied extensively typically in CO₂ removal from natural gas [6]. Nonetheless, the drawback of polymeric membrane that reduces its competitive edge is CO₂ induced plasticization.

CO₂ plasticization is explained as the phenomena whereby the sorption of highly condensable gas molecules into polymer matrix increases the free volume by acting as a “lubricant”, contributing to ease of movement for chain molecules to slip over one another and thus causing polymer softening [7, 8]. Plasticization increases the polymeric segment mobility and hence permeability of all gas species [9]. However, as free volume increases, the ability of polymeric material to sieve gas molecules for



permeation becomes weaker and hence causes reduction in selectivity [10]. Therefore, it is important to elucidate the plasticization phenomena owing to the fact that it can potentially lead to excessive product lost that reduces profitability of the natural gas processing plant. Schematic representation of the plasticization phenomena that increases free volume of the polymeric glassy membrane is provided in Figure 1 [11]. Among the most apparent effect that characterizes the onset of plasticization upon sorption of compressed gases into glassy polymeric membrane is the depression of glass transition temperature, T_g .

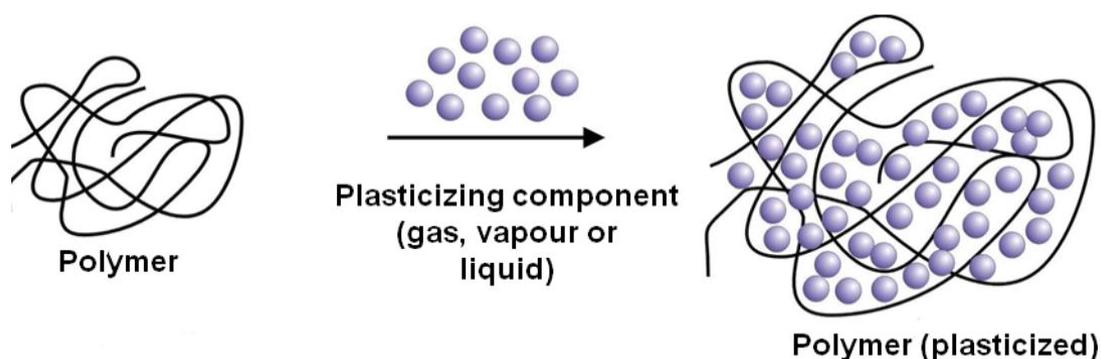


Figure 1 Schematic representation of the plasticization phenomena resulting in facilitated polymer mobility and increased free volume in the polymer matrix, adapted from Kikic *et al.* [11]

The fundamental elucidation of CO₂ induced plasticization plays a pivotal role in enhancement of separation proficiency and the development of existing and next-generation polymeric membranes with high performance. In this context, molecular simulation has been proposed as a feasible alternative to provide insights into gas transport characteristic from an atomistic point of view, usually achieved via a coupling of molecular dynamics (MD) and Monte Carlo (MC) technique [12, 13], due to the ever-growing improvement in computational technology and simulation tools [14].

Heuchel *et al.* (2006) pioneered an attempt to characterize molecular models of representative unswollen and swollen states of real polymeric membranes, namely polysulfone (PSF) and poly (ether sulfone) (PES) with and without sorbed carbon dioxide, and validated the methodology through comparison with actual experimental data [15]. Subsequently, detailed atomistic of the two unswollen and swollen reference states of PSF were associated to the common dual sorption model and site distribution model of Kirchheim by Hölck *et al.* (2006), which permitted the characterization of sorption and thereby swelling induced behavior in glassy polymers [16]. In later work by Hölck *et al.* (2008), a molecular modeling investigation of dilation effects induced by sorbed gas molecules attributed to plasticization effect in PSF and polyimide 6FDA-TrMPD (P14) has been conducted [17]. Based on a similar motivation, the sorption and swelling of glassy atactic polystyrene (PS) at elevated pressures had been mimicked by Spyriouni *et al.* (2009) through a new scheme albeit requirement of higher computational procedures and tool to achieve the designated simulation [18]. Zhang *et al.* (2010) carried out fully atomistic simulations to examine CO₂ induced plasticization of a 6FDA-ODA (6FDA = 4, 4-(hexafluoroisopropylidene) diphthalic anhydride, ODA = 4, 4-oxydianiline) polymeric membrane through introduction of different CO₂ loadings to achieve a quantitative understanding of the relation among polymer structure, its interaction with CO₂ molecules and separation performance [14]. Their work had been extended by Velioğlu *et al.* (2012), who employed molecular simulation techniques to investigate CO₂ induced plasticization in varying fluorinated polyimide membranes (e.g. 6FDA-ODA, 6FPA-DPX and 6FDA-DAM; DPX = 2,5-dimethyl-p-phenylenediamine, DAM = 2,4,6-trimethyl-m-phenylenediamine) [19]. Neyertz & Brown (2014) compared the CO₂ sorption and plasticization resistant through fully-atomistic molecular model of a *meta*-linked 6FDA-6FmDA polyimide membrane to its *para*-linked 6FDA-6FpDA isomer [20, 21]. Computational tools were applied to estimate plasticizing effect of CO₂ and to calculate CO₂- and H₂O-loading for three absorbable polyesters: polycaprolactone and two copolymers of poly-D, L-lactid- co-glycolid)-co polyethyleneglycol by Knani *et al.* (2015) [22].

As highlighted earlier, the sorption of gas into polymers contributes to increment in the segmental mobility that results in enhancement of free volume, whereby the effect at the molecular level can be macroscopically observed by the depression of glass transition temperature of the polymer-penetrants mixture. Nonetheless, to date, majority of the simulation model has been confined to construction of polymeric membrane structure ascribed to CO₂ plasticization, while molecular simulation of reduction characteristic in glass transition temperature as a direct consequence of plasticization followed by mathematical modeling of the aforementioned phenomena has received less scrutiny. Therefore, the objective of current work is to develop a molecular modeling procedure to simulate an experimentally validated membrane structure characterizing the effect of CO₂ plasticization, whence it can be subsequently employed to elucidate the depression in glass transition temperature attributed to different loadings of CO₂. A modified Michealis-Menten (M-M) function that has been previously adopted to quantify thickness dependent T_g in published work by Kim *et al.* (2000) [23], has been improvised to characterize the effect of CO₂ loading attributed to plasticization towards the T_g . To the best of our knowledge, our work is the pioneering effort to address such T_g depression in the presence of CO₂ plasticization through employment of molecular simulation tool.

2. Methodology

The methodology is subdivided into two subsections, whereby the first is molecular simulation to construct the molecular structure of the PSF polymeric membrane (with and without CO₂ plasticization effect), and the second is procedure for determination of glass transition temperature in the polymeric membranes.

2.1. Atomistic Packing Models

The molecular structure has been simulated through adaptation of Materials Studio 8.0 developed by Accelrys Software Inc [24]. Polysulfone (PSF), which is a commercial membrane commonly adapted for gas separation, has been simulated employing a series of molecular dynamics (MD) procedure in Materials Studio 8.0. The repeating unit of the PSF polymeric membrane is provided in Figure 2.

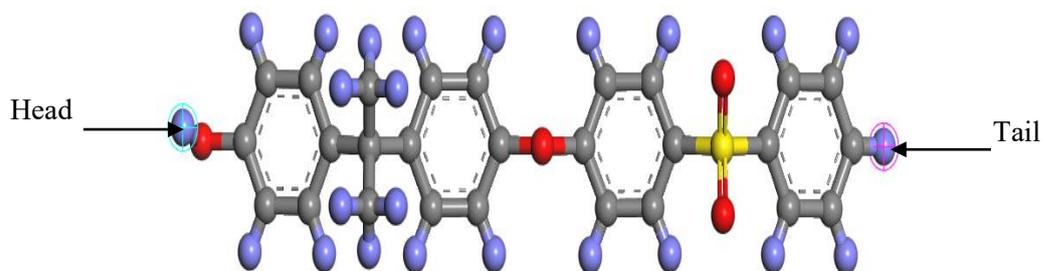


Figure 2 The chemical structure for polysulfone repeated single chain, purple: hydrogen, grey: carbon, yellow: sulphur, red: oxygen atom

The Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field has been adopted consistently. In addition, the Ewald method with an accuracy of 0.001 kcal/mol has been adopted to describe the electrostatic interactions, while the van der Waals interaction has been characterized via the Lennard-Jones-6-12 function with a cut-off-distance of ~11 Å (spline width of 1 Å and buffer width of 0.5 Å), whereby this value is selected since it is less than half of the expected cell length.

2.1.1. Unswollen Polysulfone (PSF) Polymeric Membrane Structure

A single polymer chain with 20 repeat units is constructed. The initial polymeric chain has been located in the Forcite module of Materials Studio 8.0 and has been subjected to energy minimization and geometry optimization. The COMPASS force field has been adopted alongside the smart

algorithm, which is a combination of the steepest descent; adjusted basis set Newton-Raphson (ABNR) and quasi-Newton algorithms in a cascading manner, in order to refine geometry of the initial polymeric chain. Later, the polymeric membrane chain has been folded into Amorphous Cell module adopting Construction task. The polymer chains have been embedded in the hypothetical cell under the periodic condition at initial density corresponding to 70% of the targeted experimental density. Similarly, the COMPASS force field has been adopted to pack the polymeric chains.

Then, the initial constructed atomistic configuration has been subsequently minimized and optimized adopting a series of protocols. Firstly, a 10000 step energy minimization has been conducted in order to remove any undesirable configurations including overlapping and close contact. After this stage, an annealing procedure has been performed on the polymeric structure by adopting the temperature cycle protocol embedded within Forcite module. Throughout the cycle, the system has been heated and cooled back with an interval of 293.15 K between 353.15 K and 653.15 K, which is well above the glass transition temperature of PSF. At each temperature, 100 ps isothermal-isobaric ensemble (NPT) has been conducted. At this step, in order to control the temperature at the designated heating temperature and pressure of 1 atm, the Nose thermostat with Q ratio of 0.01 and Berendsen barostat with decay constant of 0.1 ps have been employed continuously. Subsequently, in order to achieve the ideal structure, which is the lowest energy configuration with the most realistic geometry, a molecular dynamics equilibrium run has been implemented on the amorphous cell structure in the NPT ensemble with a total simulation time of 500 ps. Similarly, the pressure of the system has been maintained at 1 atm while the temperature is fixed at a constant value of 298.15 K with Nose thermostat and Berendsen barostat. Throughout this step, the equation of motions has been integrated by the velocity Verlet algorithm with a time step of 1 fs for all simulation conditions. When approaching the endpoint of the NPT run, an additional 500 ps of Canonical (NVT) ensemble at temperature of 298.15 K has been conducted on the equilibrated polymeric structure. The NPT-NVT molecular treatment has been repeated until changes in the successive density values are within predefined tolerance. The unswollen polysulfone membrane structure is named PSU throughout this study.

2.1.2. Swollen Polysulfone (PSF) Polymeric Membrane Structure

Additional packing model has been prepared for the swollen state of CO₂/ polymer system attributed to plasticization effect, which corresponds to plasticization pressure (P_{pl}) in Bos *et al.* (1999) experiment observation of 34 bar [9]. To comply with the PSF polymeric chain of 20 repeat units and solubility coefficient of 1.4 cm³(STP)/cm³.bar taken from Bos *et al.* sorption experiment, a number of 16 CO₂ molecules are required to be packed into the simulation box in addition to the PSF chain in order to induce the relaxation characteristic attributed to plasticization. A different number of CO₂ gas penetrants (i.e. 8, 16, and 24) have been packed to elucidate the effect of CO₂ loadings to the glass transition temperature of PSF polymeric membrane structure, whereby they have been named PSU8, PSU16, and PSU24 respectively in the remaining section of the paper. The applied basic techniques of packing and equilibration as described in section 2.1.1 have been employed in this context. After packing the PSF chain with designated CO₂ loadings into Amorphous Cell module adopting Construction task, the polymeric membrane structures have been subjected to a similar series of molecular treatment protocol in previous section.

2.2. Glass Transition Temperature

In this study, T_g s of PSF samples have been determined by mimicking the heating and cooling protocols in laboratory scale adapting a series of thermodynamic treatment in Forcite Module. Firstly, the optimized and equilibrated configuration for each dimension has been subjected to an additional Canonical (NVT) ensemble at 308.15 K with a time step of 1 fs and total simulation time of 10 ps by framing the output every 1000 steps. This procedure is aimed to obtain the trajectory files of PSF polymeric films with 10 frames for each thickness, such that an average T_g can be deduced to increase accuracy of the computed value when the series of thermodynamic treatment is iterated while calculating an independent T_g for each frame. Then, the individual frame located within the PSF

trajectory has been exposed to gentle heating from 300.15 K to 500.15 K, which surpasses that of the bulk glass transition temperature of PSF polymer, with an interval of 1 K. Subsequently, a 100 ps NPT dynamic ensemble has been conducted at the designated heating temperature and operating pressure. Thereafter, the system is cooled down from 500.15 K to 300.15 K with the temperature interval of 1 K while computing density of the structure at each temperature. This protocol is looped over all frames contained in the trajectory file and eventually the values are averaged at the end of the simulations.

3. Results and Discussion

In this section, the molecular simulation results related to PSF polymeric membranes at unswollen and swollen conditions have been presented, whereby it has been subdivided into two major subcategories, such as 1) molecular structure and density and 2) glass transition temperature.

3.1. Molecular Structure

As described in section 2.1, molecular dynamics simulation has been executed for all PSF polymeric films by keeping the operating parameters at the designated laboratory condition while altering the number of CO₂ molecules within the membrane structure, while the other configurations are constantly updated in quest of determining the most probable polymeric membrane film with optimized packing and molecular arrangement. The example of molecular structure within the unswollen and swollen PSF membrane with 8, 16 and 24 CO₂ loadings are depicted in Figure 3 (a), (b), (c) and (d) respectively. As it is illustrated in Figure 3 (b), (c) and (d), the CO₂ gas molecules are randomly dispersed throughout the void space within the PSF polymeric matrix, with the configuration corresponding to the optimized and most probable intermolecular interactions between the diffusants and polymeric chains.

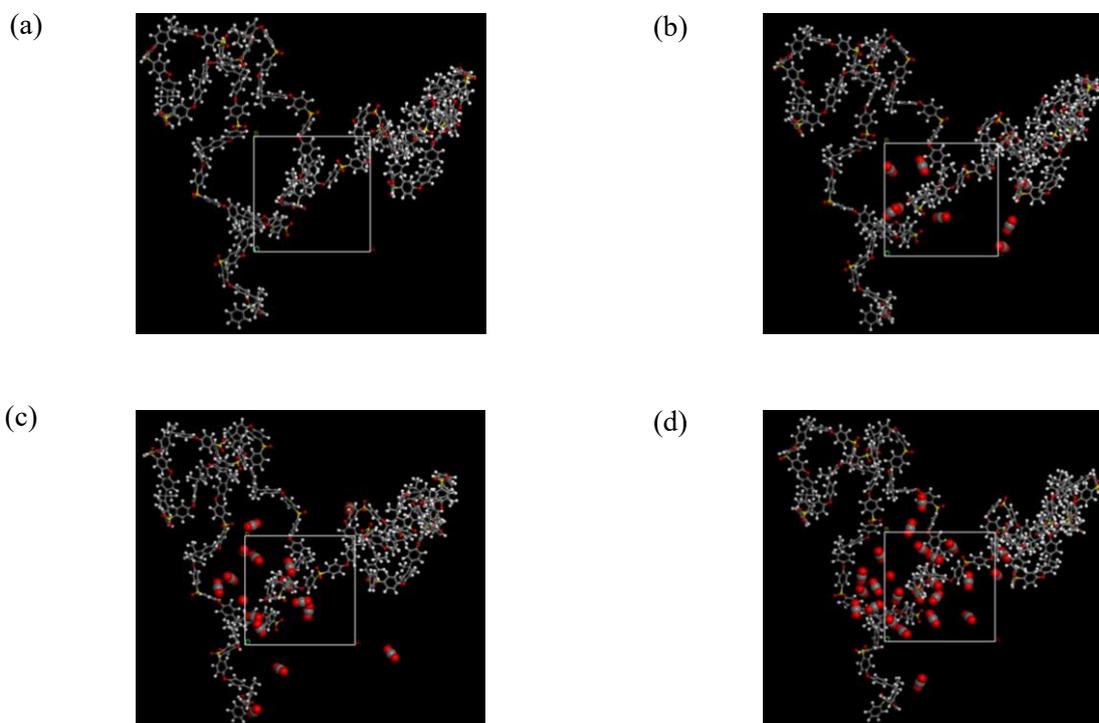


Figure 3 Molecular structure of PSF membrane structure (a) PSU (b) PSU8 (c) PSU16 and (d) PSU24

Since the system has been initialized from lower density without setting any constrictions throughout the molecular dynamics treatment, the evolution of structure, typically the structure

density, to a stable value provides intuitive reasoning that the polymeric membrane has converged towards the most plausible configuration. Hence, by analyzing physical property of the finalized molecular structure to theoretically attained value and trend with respect to effect of CO₂ loadings, which have been measured through either published experimental or molecular simulation work, accuracy of the aforementioned molecular simulation methodology can be validated. Physical properties of the constructed packing models are given in Table 1.

Table 1 Simulated cell length, density packing (inclusion of CO₂ molecules), density matrix (exclusion of CO₂ molecules) and percentage dilation as compared to unswollen packing model

| Polymer Packing | Box Length | Density Packing (g/cm ³) | Density Matrix (g/cm ³) | % Dilation |
|-----------------|------------|--------------------------------------|-------------------------------------|------------|
| PSU | 22.9935 | 1.222 (1.24) ^a | 1.222 | 0.000 |
| PSU8 | 23.1842 | 1.227 | 1.180 | 3.559 |
| PSU16 | 23.4277 | 1.234 | 1.143 | 6.912 |
| PSU24 | 23.6648 | 1.242 | 1.109 | 10.189 |

^a The number in bracket is the experimental value ([25]).

In order to verify accuracy of the simulation methodology, the simulated properties have been validated with actual experimental observations. For instance, it is found from Table 1 that the simulated density of PSU is in close agreement with previously reported density of bulk PSF with a value of 1.24 g/cm³ by Ahn *et al.* (2008) [25]. The good compliance between simulated and experimentally observed condition supports the claim that the unswollen PSF polymeric structure has been constructed via high accuracy simulation procedure since the system has been ramped from a low density configuration without confining any constraints and boundaries throughout the molecular dynamics process. Small percentage error of -1.45% between simulated and experimentally observed PSF density can be rationalized through the assumption in molecular simulation, whence cut off distance has been applied throughout the simulation cell that deemed long range molecular interaction to be negligible. As for swollen PSF polymeric membrane structure with presence of CO₂, the accuracy has been demonstrated through excellent accordance between the solubility characteristic (e.g. 1.2651 versus 1.38 cm³ (STP)/cm³ .bar) in simulated PSU16 and experimentally observed sorption experiment taken from Bos *et al.* (1999) [9] respectively.

In addition, from Table 1, it is depicted that the packing density of molecular structure increases with increment in CO₂ loadings. The observation tallies with characteristic of single packing models of PSF, as reported by Heuchel *et al.* (2006) [15], whereby PSU molecular structure with CO₂ exhibits greater density as compared to its pristine unswollen PSU configuration attributed to the presence of CO₂ that increases weight of the entire molecular system. On the other hand, density of the membrane matrix experiences a decrement when CO₂ loadings are further increased. The reduction in density of membrane matrix has been acclaimed through enhanced interaction between CO₂ gas molecule and polymeric matrix, which contributes to augmented swelling and relaxation in polymeric membrane structure [9]. The claim has been supported via incremental in box length that characterizes the degree of swelling, whereby percentage dilation rises with number of CO₂, which has been computed and tabulated in Table 1 as well.

3.2. Glass Transition Temperature

The variations in specific volume versus temperature for PSF polymeric membranes with different CO₂ loadings have been plotted and provided as examples in Figure 4. As it can be seen from Figure 4, all the polymeric membranes experience similar behavior with changes in temperature regardless of CO₂ loadings. Initially, the specific volume increases linearly with increment in temperature, and then shows an abrupt alteration in the value before continuing to embark in another linear region. Change in linear relationship is demonstrated through the difference in slope between the two curves, whereby the first at lower temperature is representative of the glassy state region, while the latter describes the rubbery state. The point at which the glassy and rubbery linear correlation meets to form an intercept provides graphical representation of the glass transition temperature, T_g . The simulated behavior is

consistent to experimental observation reported by Zoller *et al.* (1978), who investigated the pressure-temperature-volume relationships in bulk PSF over a wide range of operating conditions [26].

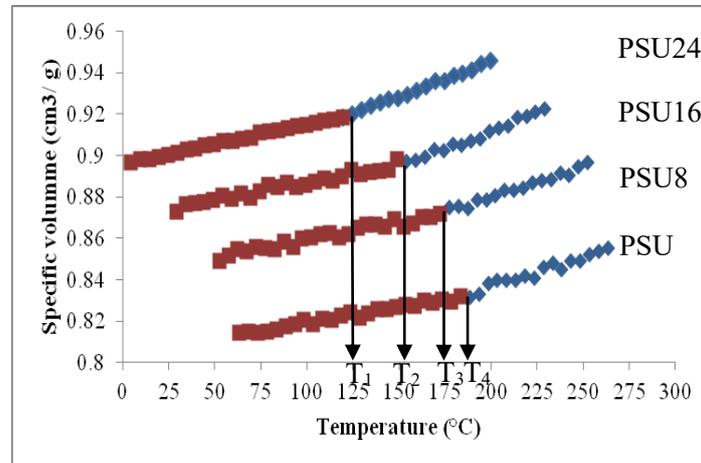


Figure 4 Effect of CO₂ loadings on specific volume of the polymeric film with respect to alteration in temperature, whereby $T_1 = 121.6$ °C, $T_2 = 151.2$ °C, $T_3 = 169.9$ °C, $T_4 = 182.5$ °C

Specific volume of the PSF structure has been found from Figure 4 to be consistently higher for configuration with CO₂ gas molecules attributed to plasticization induced dilation as described earlier that causes increment in molecular spacing. The glass transition temperature is found to experience a depression behavior when CO₂ loadings are further increased. The reduction in glass transition temperature, T_g , can be rationalized through enhanced mobility of polymeric chains in the vicinity of CO₂ gas molecules, which constitutes to amplified softening and movement for chain molecules to slip over one another, thus contributing to suppressed T_g in comparison to the unswollen PSF polymeric structure.

It has been suggested that the reduction in T_g seems to follow the form of growth with saturation, which can be described via the Michealis-Menten (M-M) function, as described in Kim *et al.* (2000) [23], whence they elucidated the effect of thickness upon confinement to reduction in T_g . In this work, a modified form of the Michealis-Menten (M-M) function has been proposed to characterize the effect of CO₂ loadings to depression of glass transition temperature since both effects originated from relaxation of polymeric chains when subjected to external operating factors. The modified Michealis-Menten (M-M) function is presented in equation (1), while fit to the proposed empirical equation and parameters employed are provided in Figure 5. In equation (1), $T_g(\text{CO}_2)$ is the depressed glass transition temperature dependent upon the amount of CO₂ loadings, $T_{g,b}$ is the bulk glass transition temperature, ε characterizes a material constant that describes the function growth saturation rate, while CO_2 is resemblance of the amount of carbon dioxide gas molecules in simulation box.

$$T_g(\text{CO}_2) = T_{g,b} \left[1 - \frac{\text{CO}_2}{\varepsilon + \text{CO}_2} \right] \quad (1)$$

As depicted in Figure 5, the suggested correlation is able to provide a satisfactory compliance with simulated glass transition temperature, which has been demonstrated through a good R^2 value.

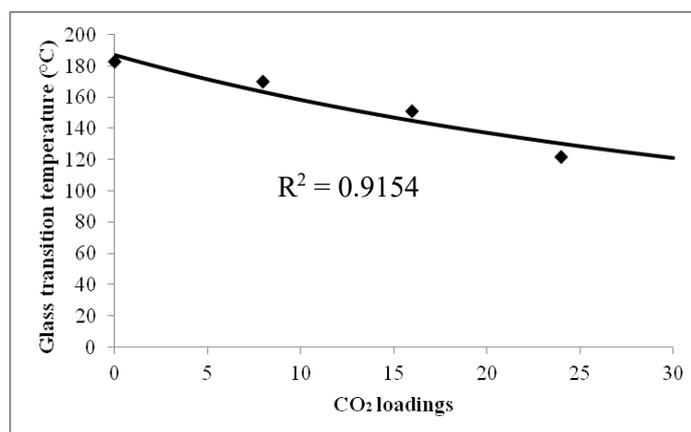


Figure 5 Effect of CO₂ loadings to the glass transition temperature, fitted with the revised Michealis-Menten (M-M) function (Equation 1), $T_{g,b} = 187.1$ K; $\varepsilon = 54.97$

4. Conclusion

In present work, a molecular modeling procedure has been proposed to construct unswollen and swollen PSF membrane structure with the presence of CO₂ in order to capture the effect of plasticization to membrane morphology. Accuracies of both the unswollen and swollen membrane structures have been verified through excellent accordance between simulated and experimental observed physical properties. The good compliance ensures applicability of the simulated membrane structure to be employed to study the impact of CO₂ loading on depression of glass transition temperature attributed to plasticization phenomena. A revised form of the Michealis-Menten (M-M) function, which has been previously adopted to quantify thickness dependency in glass transition temperature, has been employed in current work to correlate the effect of CO₂ loading to T_g . To the best of our knowledge, this work is among the first to tackle the impact of numbers of CO₂ towards the depression of T_g through molecular simulation technique, which has been employed in proposal of empirical model to address the plasticization induced T_g depression. The findings of current work can be sufficiently employed to overcome the barrier, cost and time in preparation and testing of CO₂ induced plasticization in membrane at the laboratory scale since it appears to be relatively convenient and straightforward to control operating conditions of the simulation.

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