Molecular-level investigation of plasticization of polyethylene terephthalate (PET) in supercritical carbon dioxide via molecular dynamics simulation

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The current study aims to use the molecular dynamics (MD) simulation method to discuss the glass transition behaviour and fractional free volume (FFV) of the pure polyethylene terephthalate (PET) and the plasticized PET induced by supercritical carbon dioxide (SC-CO\textsubscript{2}) sorption. The adsorption concentration reproduced through sorption relaxation cycles (SRC) was firstly estimated and in an order of magnitude with the known experimental results available in the reported literature. The FFV induced by SC-CO\textsubscript{2} in PET polymer changes regularly, which is proportional to the capacity of SC-CO\textsubscript{2} adsorption with the changes in temperature and pressure. The glass transition temperature ($T_g$) was further estimated to be almost identical to the known experimental values and shows a gradually decreasing tendency with the increase of pressure. Meanwhile, the plasticization of PET polymer studied by radial distribution functions showed that CO\textsubscript{2} molecules occupying the sorption sites on the PET backbone promoted plasticization by increasing the fluidity of the PET backbone chain.

1. Introduction

In recent years, supercritical carbon dioxide (SC-CO\textsubscript{2}) as a solvent existing above its critical point ($T_c = 31°C$, $P_c = 7.38$ MPa) has attracted considerable attention in many fields [1], such as...
pharmaceutical, blending [2], impregnation [3], foaming [4], extracting [5] and dyeing [6]. SC-CO$_2$ is a highly compressed fluid with numerous unique characteristics including high diffusion coefficient, zero surface tension and low viscosity. Meanwhile, SC-CO$_2$ has become the most widely used solvent as it’s low cost, recyclable, non-toxic, chemically inert and non-flammable [7]. Many polymer-related processes have been developed by the fact that the sorption of CO$_2$ by polymer leads to reducing the glass transition temperature of polymers and the swelling and plasticizing effects, resulting in the changes in the mechanical and physical properties of the polymer [6], such as material modification, the grade of polymer, small molecule penetration, polymer flick, supercritical fluid dyeing and superfine material preparation, etc [8].

A great number of studies have been published on the swelling and mechanical and physical properties of PET in SC-CO$_2$. Chen et al. [9] investigated the solubility of CO$_2$ in solid PET and showed a linear relationship with Henry’s law at low pressure (less than 8 MPa), and the solubility decreased with the increase of temperature at high pressure. Chen [10] compared the effects of temperature (50 ~ 120°C) and pressure (0.1 ~ 20 MPa) on the swelling rate of PET and obtained the polymer glass transition temperature in the supercritical fluid environment by their self-made high pressure autoclave with a view window, which detected the length change of PET film in the CO$_2$ state via a CCD camera. Han et al. [6] measured the swelling of polyester yarns under different conditions and found that the maximum theoretical value was 0.725 mm under the optimum treatment conditions ($T = 140°C$, $p = 26$ MPa, $t = 60$ min) using the response surface methodology. Hirogaki [11] investigated the influence of SC-CO$_2$ and the effects of additive modifiers on the swelling behaviour of PET, and found that SC-CO$_2$ promoted the crystallization of PET polymer, but the additional modifiers (such as alcohols) prevented the crystallization of SC-CO$_2$.

In recent years, the application of SC-CO$_2$ dyeing has attracted wide industrial and academic attention. It mainly includes the solubility of dyes [12], dyeing process, dye-design [13] and dyeing equipment development [14]. At present, the dyeing of polyethylene terephthalate fibre (PET) in SC-CO$_2$ has been industrialized [15]. In the process of SC-CO$_2$ dyeing, due to the dissolution of CO$_2$ in polymer, the swelling and mechanical and physical properties of PET improved the dyeing quality of polymer, since the swelling behaviour of polymer is directly related to its dyeability [6]. The molecular simulation has become an alternative approach to examining the glass transition temperature ($T_g$) [16], but no studies have as yet investigated the plasticization in PET polymer by simulation.

In this research, molecular dynamics (MD) simulation was used to investigate the effects of CO$_2$ on the $T_g$ and fractional free volume (FFV) of polyethylene terephthalate (PET) at different temperatures and pressures.

2. Computational details

2.1. Model building

In this work, all the molecular simulation processes were completed by Accelrys Material Studio (MS) 2017 [17]. The PET chain consisting of 100 repeat units [18] and CO$_2$ molecules were built by materials visualizer modules [19]. The cubic cells with two PET chains were constructed using an amorphous cell module, which is shown in figure 1, and were subsequently equilibrated using the Forcite module. In order to avoid chain rings catenation and spearing, the initial densities of cubic cells were set at 0.3 g cm$^{-3}$, 512 methanol molecules were added randomly into the cells [20], and the methanol molecules were deleted before the cells were started. The COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field [21] was used for all simulations. Andersen thermostats and Berendsen barostats were used to control the temperature and pressure respectively in all simulations. The non-bonded van der Waals interactions were calculated by the Atom based method with a cutoff distance of 18.5 Å, a spline width of 1 Å, and a buffer width of 0.5 Å. The non-bonded electrostatic interactions were characterized via the Ewald method with accuracy of $10^{-5}$ kcal mol$^{-1}$.

2.2. Simulation method

All the initial polymer chains, CO$_2$ molecular and cubic cells were subjected to energy minimization to remove the local non-equilibrium by geometry optimization with 10 000 steps using the Smart algorithm [17]. Firstly, the systems were subjected to MD runs in $NPT$ ensemble with 1fs time step for a total simulation time of 500 ps using the Forcite module [17] to equilibrate and remove residual stress.
Secondly, the systems were subjected to 500 ps NVT dynamics and 1000 ps NPT dynamics at room temperature and pressure. Finally, the systems were subjected to 300 ps NPT, 300 ps NVT and 500 ps NPT dynamics calculation at different temperatures. Generally, the system reaches equilibrium when the standard deviation of the energy and temperature requirements of the system is less than 10%. As presented in figure 2, the system reached equilibrium after the NPT dynamic simulation of 500 ps.

The sorption module of Materials Studio 2017 was applied to study the plasticated PET induced by CO₂ sorption. The simulation was evaluated by the Grand Canonical Monte Carlo (GCMC) ensemble at ‘fixed pressure’ task, which fixed temperature, volume and chemical potential using the Metropolis Algorithm [22]. For each case, it provides three types of operations with equal probability in the cell: displacement, creation and deletion. The total potential energy \( E \) (before one operation), \( E' \) (after the certain operation) and the variation \( \Delta E = E' - E \) are calculated from equation (2.1). Next, according to the assumed acceptance probabilities, this operation is accepted or rejected. The acceptance probabilities are \( \min \{ 1, \exp(-\Delta E/k_BT) \} \) and \( \min \{ 1, (\lambda^3N_i/V_i) \exp(-(\mu + \Delta E)/(k_BT)) \} \), respectively, where \( \lambda = \sqrt{\hbar^2/(2\pi mk_BT)} \), \( \hbar \) is the Planck constant, \( m \) is the mass of CO₂, \( T \) is the temperature, \( \mu \) is the chemical potential, \( V_i \) is the volume of the ith subspace and \( N_i \) is the number of CO₂ molecules in the ith subspace.

The temperature and pressure points were selected according to the experimental data values in the related literature [10]. For the sake of reproducing volume swelling and plasticization induced by sorption, sorption–relaxation cycles (SRC) [16,23] were used until the sorption coefficients converge. The relaxation process: at each cycle, the cell was loaded with CO₂ molecules at the considered

![Figure 1. Illustration of calculation model of PET: (a) chemical structure (b) molecular monomers (c) molecular chain (100) (d) cell model.](image1)

![Figure 2. Energy and temperature fluctuations observed during molecular dynamic simulation of 500 ps for PET (a) energy fluctuations (b) temperature fluctuations.](image2)
3. Results and discussion

3.1. Sorption of \( \text{CO}_2 \) in PET

In this study, the sorption equilibrium of \( \text{CO}_2 \) in PET at different pressures and temperatures has been simulated using SRC as shown in §2.2. From figure 3 we can see that the adsorption concentration of PET was in the ranges of pressure from 5 to 20 MPa and temperature from 50 to 110°C. The simulated adsorption concentration of \( \text{CO}_2 \) in PET was generally in an order of magnitude with the known experimental results available in the reported literatures as show in table 1. The simulation results were approximately three times larger than the experimental results [24]. In the simulating process, the authors only established the amorphous region, but did not establish the crystallization region,

\[
E = \sum_b K_2 (b - b_0)^2 + K_3 (b - b_0)^3 + K_4 (b - b_0)^4
\]

\[
+ \sum_{\theta} H_2 (\theta - \theta_0)^2 + H_3 (\theta - \theta_0)^3 + H_4 (\theta - \theta_0)^4
\]

\[
+ \sum_{\phi} \left[ (V_1[1 - \cos(\phi - \phi_1)] + V_2[1 - \cos(2\phi - \phi_2)] + V_3[1 - \cos(3\phi - \phi_3)]) \right]
\]

\[
+ \sum_{\chi} K_\chi x^2 + \sum_b \sum_{b'} F_{b b'} (b - b_0)(b' - b'_0) + \sum_{\theta} \sum_{\theta'} F_{\theta \theta'} (\theta - \theta_0)(\theta' - \theta'_0) + \sum_{b} \sum_{\theta} F_{b \theta} (b - b_0)(\theta - \theta_0)
\]

\[
+ \sum_{b} \sum_{\phi} (b - b_0)(V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi) + \sum_{\phi} \sum_{b'} (b' - b'_0)(V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi)
\]

\[
+ \sum_{\phi} \sum_{\theta} (\theta - \theta_0)(V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi) + \sum_{\theta} \sum_{\phi} \sum_{\phi'} K_{\phi \phi'} \cos \phi(\theta - \theta_0)(\theta' - \theta_0')
\]

\[
+ \sum_{i \neq j} q_{ij} e_{ij} + \sum_{i \neq j} \left( \frac{A_{ij}}{r_{ij}^n} - \frac{B_{ij}}{r_{ij}^n} \right).
\]
which resulted in more CO$_2$ molecules absorbed into the amorphous region compared with the real PET fibre. The adsorption concentration of CO$_2$ in PET decreases first and then increases gradually with the increase of temperature. Meanwhile, the decrease of the slope is gradually smaller and the increase of the slope is steeper and steeper as the pressure goes up. The tendency seems to follow the literature results [24]: at the lower densities, the adsorption concentration decreases with the increase of temperature. However, as the pressure increases, the inflection point of the change in the tendency is going up earlier and earlier. When the pressure is constant, the increase of temperature results in the decrease of CO$_2$ density, which decreases the number of molecules of CO$_2$ in the amorphous region (free volume). However, when the temperature is close to the point of $T_g$, the PET molecular chain amplitude increases, and the amorphous region becomes larger, resulting in more CO$_2$ molecules entering the amorphous region. The adsorption concentration of CO$_2$ in PET near of the point of $T_g$ starts to increase. When the temperature is constant, the adsorption concentration of CO$_2$ increases with the increase of pressure. The CO$_2$ density increases with the increase of pressure, causing more

| P/MPa | T/°C | Sim | Exp | Sim | exp | Sim | exp | Sim | exp |
|-------|------|-----|-----|-----|-----|-----|-----|-----|-----|
| 50    |      | 6.874 | * | 7.332 | * | 8.249 | * | 8.707 | * |
| 60    |      | 6.416 | * | 6.874 | * | 8.02 | * | 8.249 | * |
| 70    |      | 4.812 | * | 6.416 | * | 7.561 | * | 8.02 | * |
| 80    |      | 5.499 | * | 6.874 | 2.2 | 7.790 | * | 8.249 | * |
| 90    |      | 5.957 | * | 7.561 | * | 8.249 | * | 8.707 | * |
| 100   |      | 6.416 | 1.25 | 8.02 | 2.1 | 8.707 | * | 9.165 | 2.6 |
| 110   |      | 6.416 | * | 9.165 | * | 10.311 | * | 10.769 | * |

Table 1. The simulated and experimental adsorption concentration (g$_{CO_2}$/g$_{PET}$) for CO$_2$ in PET.

Figure 4. The curves of volume change with temperature for the PET at different pressures.
CO₂ molecules to enter the amorphous region of PET fibre. The PET molecular chain was intensified due to the intensified movement of CO₂ molecules, leading to the enlargement of amorphous region and more CO₂ molecules being absorbed into PET. As the pressure increases, the movement of CO₂ molecules becomes gradually stronger, causing the intensified movement of the PET molecular chain. The PET molecular chain begin to unfreeze at a lower temperature, leading to the increase of free volume and promoting the adsorption of more CO₂ molecules. As shown in figure 3, the inflection point of the change in the tendency is shifted to the left, and consistent with the decrease of glass transition temperature with the increase of pressure (§4.4 will discuss the relationship between glass transition temperature and pressure).

3.2. Swelling of the PET polymer

The swelling and plasticization of the PET polymer is a long process and it is a difficult task to figure out the specific mechanism through experiments under high pressure. However, molecular simulation has provided a unique opportunity to examine the swelling behaviour and plasticization of the PET polymer in the SC-CO₂ atmosphere. The sorption of CO₂ into PET polymer induced volume swelling.

![Figure 5](image1.png)

**Figure 5.** The relationship between free volume fraction (FFV) and temperature of PET at different pressures.

![Figure 6](image2.png)

**Figure 6.** (a) The curves of rate of volume change with temperature for the pure PET (b) the curves of the FFV with temperature for the pure PET.
and plasticization, causing the decrease of glass transition temperature. It has been shown that the reason for plasticization is the interactions between CO\textsubscript{2} and the polymer, and plasticization disrupts chain packing and enhances the inter-segmental mobility of polymer [25].

Figure 4 shows the volume change of PET polymer at the pressures ranging from 5 to 20 MPa and the temperatures ranging from 50 to 110 °C. It can be seen that the volume change increases and the slope of the volume change increases gradually with the increase of temperature in the meantime. Meanwhile, with the increase of pressure, the increase of the slope becomes larger and larger. For example, the volume change increases from 0.62% to 2.1% at atmospheric pressure and the temperature ranging from 50 to 110°C. Meanwhile, the volume change increases from 0.62% to 2.25% at the temperature of 50°C and the pressure rising from 0 to 15 MPa. The swelling of the above two is basically the same. Thus it is feasible to use SC-CO\textsubscript{2} for swelling and other related processes. In the process of development, the same effect is achieved by adjusting the range of pressure change at a lower temperature, which can save energy consumption and protect the environment.

3.3. Fractional free volume

The free volume theory was first proposed by Fox and Flory in 1950 [26]. According to the theory, the volume of liquid or solid consists of two parts: one is the volume occupied by molecules and the other is the unoccupied free volume. The size, morphology and spatial size distribution of free volume play an important role in the diffusion behaviour of molecules in polymer, providing the necessary space for diffusion molecules. In general, the larger the FFV of the polymer, the larger the diffusion coefficient of diffusing material will be. The free volume of the system is obtained by the hard ball probe method, which is using the ‘Atom Volume & Surface’ tool in MS software package. When the hard ball probe with a radius of \( R_p = 0 \) moves on the van der Waals surface of PET polymer, the volume surrounded by the Connolly surface formed by the contact point is the free volume. The FFV of the system can be obtained by dividing the simulated free volume by the total.
The relationship between FFV and temperature of PET polymer at different pressures is shown in figure 4.

From figure 4 we can see the FFV for PET change at the pressures ranging from 0.1 to 20 MPa and the temperatures ranging from 50 to 110°C. It can be shown that the FFV increases and the slope of the FFV starts to increase gradually near the \( T_g \) with the increase of temperature, corresponding to adsorption concentration for CO\(_2\) in PET. The FFV of high pressure (5 MPa) is about three times larger than that of atmospheric pressure, while the FFV of high temperature (110°C) is 0.5∼1% larger than that of low temperature (50°C), thus the influence of pressure is greater than that of temperature figure 5.

### 3.4. Glass transition temperature

\( T_g \) is a kind of common phenomenon of the polymer, and there is no perfect theory to exactly explain the experimental facts so far [27]. Under the \( T_g \), the molecular chain segment and the free volume are frozen and maintain at a constant value, and the sizes and distribution of free volume will remain basically fixed even with the increase of temperature. However, above the \( T_g \), the free volume begins to change from freezing into motion and the sizes of free volume gradually increase with the increase of temperature since the molecular chain segment has enough motion energy and begins to enter motion state. This may be due to the fact that the glass transition temperature is at a certain threshold temperature when the free volume reaches a critical value. Therefore, measuring the change of volume and the FFV with the temperature curve on the inflection point is a method to obtain \( T_g \).

Figure 6a shows the relationship between temperature and rate of volume change for the pure PET without CO\(_2\). The preliminary rough estimation of the point of inflection is obtained by visual inspection of the simulated data points, which explains the determination of \( T_g \). Then, the two corresponding parts under the \( T_g \) and above the \( T_g \) were fitted into two straight lines by linear regression. The \( T_g \) of PET polymer, namely the intersection point of the two lines obtained by molecular
**Table 2.** The glass transition temperature of PET at different pressures.

| pressure/MPa | 0.1 by $\Delta V/V$ | 0.1 by FFV | 5 by $\Delta V/V$ | 5 by FFV | 10 by $\Delta V/V$ | 10 by FFV | 15 by $\Delta V/V$ | 15 by FFV | 20 by $\Delta V/V$ | 20 by FFV |
|-------------|---------------------|------------|-------------------|---------|-------------------|---------|-------------------|---------|-------------------|---------|
| $T_g$ (°C)  | 82                  | 90         | 81                | 83      | 80                | 77      | 77                | 76      | 67                | 71      |
| literature [10] (°C) | 87          | 82         | 75                | 68      | 62                |         |                   |         |                   |         |
| relative error (%) | -5.75%      | 3.45%      | -1.22%            | 1.22%   | 6.67%             | 2.67%   | 13.2%             | 11.7%   | 8.06%             | 14.5%   |
simulation, was 83°C, which was close to the experimental \( T_g \) of 87°C [10]. Meanwhile, the curves of the FFV with temperature for the pure PET without CO\(_2\) are shown in figure 6b. Obviously, the \( T_g \) of the pure PET without CO\(_2\) was 90°C, which was a little slightly larger than the experimental \( T_g \) of 87°C.

The kind of curves of volume change with temperature for the PET polymer at the pressure ranging from 5 to 20 MPa were obtained, as shown in figure 7. Similarly, for the FFV dependence of temperature for the swelled PET polymer, the same kinds of curves were obtained, as shown in figure 8. The glass transition temperature at different pressures shown in table 2 is in good agreement with literature [10]. The relative error temperature is less than 10°C. As the pressure increases, the error relative increases, even exceeding 10% (less than 15%). The crystallinity and thermal treatment of the polymer have an influence on the glass transition temperature. When simulating this process, the authors only established the amorphous region, but did not establish the crystallization region, resulting in a different \( T_g \) compared with the experimental value. In general, the higher the crystallinity is, the higher the \( T_g \). However, the simulation results are larger than the experimental results in the literature, and further experiments are needed to check the crystallinity of experimental materials by adsorption experiments and to determine the glass transition temperature.

### 3.5. Radial distribution functions

The radial distribution function (RDF) is an important physical quantity used to analyze and describe the whole equilibrium trajectory of the distribution of other molecules around a studied molecule. According
to the position and intensity of the peak in the RDF, the accessibility and affinity of the adsorption site of a specific sorbate on the polymer can be determined. The typical atoms on the PET molecule chains are the single bond oxygen and double bond oxygen (labelled as O1 and O2, respectively).

Figure 9 shows the RDFs of CO2 molecules calculated at 10 MPa and 100°C around the typical atoms (sorption sites) of the PET polymer. The results indicate that the obvious peak values of O1 sites and O2 sites (a) p = 5 MPa, (b) p = 10 MPa, (c) p = 15 MPa, (d) p = 20 MPa.

Figure 11. RDFs (g(r)) of CO2 around O2 atoms in PET at different pressure (a) T = 50°C, (b) T = 60°C, (c) T = 70°C, (d) T = 80°C.
sites were 5.05 and 2.75 at the beginning of the SRC (with 13 CO2 molecules/simulation cell), reflecting the O2 sites are preferentially adsorbed compared to O1 sites. Meanwhile, the obvious peak values of O1 sites and O2 sites were 4.95 and 3.25 at the ending of the SRC (with 35 CO2 molecules/simulation cell), revealing the O2 sites were preferentially adsorbed compared to O1 sites.

Figure 10 shows the change in the CO2–polymer interactions by comparing RDFs at the beginning and ending of the sorption process. The position of the first small and highest peak of CO2–O1 moves to the left, meanwhile, the position of the first peak of CO2–O2 is unchanged. However, the intensity of the first peak of CO2–O2 becomes smaller. The adsorption capacity of the O1 sites became stronger than before compared with the O2 sites, which indicated the reorientation of the main chain caused by the flexibility of the chain during the CO2 adsorption process. CO2 molecules occupying the sorption sites on the PET backbone increased the fluidity of the chain and then promoted plasticization [15].

Figure 11 shows the RDFs of CO2–O2 in the temperature range of 50 to 110°C. As the temperature increases, the position of the first small and highest peak of CO2–O2 moves to the left, corresponding to the change trend reported in figure 3. Figures 12 and 13 show the RDFs of CO2–O2 in the pressure range of 5 to 20 MPa. The position of the first peak of CO2–O2 gradually moves to the left with the increase of pressure. The CO2–polymer interactions change from weak van der Waals force (3.1–5.0) to strong van der Waals force (2.6–3.1) and the adsorption capacity becomes stronger. With the higher pressure shown in figure 3, the adsorption concentration is correspondingly greater.

4. Conclusion

In the study, we predicted the adsorption concentration, swelling, FFV, and \( T_g \) of the PET polymer using the molecular dynamics simulation method. Firstly, the adsorption concentration reproduced through SRC was estimated in the same order of magnitude with the experimental data available in the reported literatures. Secondly, with the changes of temperature and pressure, the FFV induced by SC-CO2 in the PET polymer changes regularly, which was proportional to the capacity of SC-CO2 adsorption. Lastly, the \( T_g \) was further estimated almost identically to the known experimental values and shows a gradually decreased tendency with the increase of pressure. Thus, the changes of the PET backbone through the particular interactions with the sorption sites by the sorption of CO2 molecules promoted swelling and plasticization by increasing the FFV. Meanwhile, the plasticization of PET polymer studied by radial distribution functions showed that
CO₂ molecules occupying the sorption sites on the PET backbone increased the fluidity of the chain and promoted plasticization. In conclusion, in the absence of experimental data, MD simulation can be used to calculate the plasticization properties of PET polymers and other polymers.

Ethics. This article does not present research with ethical considerations.

Data accessibility. Our data are available from the Dryad Digital Repository: https://doi.org/10.5061/dryad.cjdfn35s [28].

Authors' contributions. F.S.: conceptualization, investigation, software, writing—original draft; H.D.: writing—review and editing; L.F.: writing—review and editing; W.W.: conceptualization, project administration, software, supervision, writing—review and editing; G.Z.: writing—review and editing; Z.Z.: writing—review and editing.

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