

Investigation of Poly(ether-*b*-amide)/Nanosilica Membranes for CO₂/CH₄ Separation

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Abstract The results of molecular dynamics (MD) simulations on transport process of CO₂ and CH₄ gases in poly(ether-*b*-amide) (PEBAX)/nanosilica membranes are discussed. The diffusion coefficients for CH₄ and CO₂ gases at 6 cases with different amounts of nanosilica loading in the simulation boxes are presented. The results show that diffusion coefficients for CO₂ gas in all cases are larger than those for the CH₄ one. Moreover 10% nanosilica loading case shows maximum effects on diffusion coefficients and improves them by more than 68% and 157% for CO₂ and CH₄ gases, respectively. Additionally, the results of 3-D Cartesian trajectories and displacements curves are presented and the jumping attempt of CO₂ is significantly more than that of CH₄. Due to the rubbery state of PEBAX membranes in ambient temperature, the results confirm that channel lifetimes are very short and then back diffusion is not observed for this polymer.

Keywords: Gas separation; Polymeric membrane; Molecular dynamics; Diffusion coefficient.

INTRODUCTION

One of the most important issues in the world over the last century is energy production for consuming in many fields such as industry, domestic consumption, agriculture, and some others. As it can be realized from reported statistics, natural gas is one of the most important energy supplies in the world. The consumption of natural gas is increasing the most in comparison to other non-renewable energy sources in recent years. In just 20 years, global production of natural gas has increased by about 1.7 times and according to US Energy Information Administration its consumption rate will be double by 2020^[1].

Undoubtedly, natural gas sweetening which is known as the separation of acidic gases such as CO₂ and H₂S from natural gas components is a critical step in gas treatment process. Existence of these two gases in natural gas causes considerable corrosion in pipe lines and industrial equipments. In domestic consumption, their leakage into the environment causes poisoning and in some cases death. In addition, elimination of acidic gases is economically important because these gases reduce the heating value of natural gas. Over the recent decades, polymeric membranes have found an incredible and a significant progress in separation processes especially gas separation and gas sweetening^[2, 3].

Poly(ether-block-amide) copolymers which are called PEBAX empirically consist of two blocks of polyamide and polyether. This structure causes high mechanical and transport properties, respectively. These copolymers have extremely high polar/nonpolar groups which make them potentially interesting to remove acidic gases such as CO₂ and H₂S from natural gas.

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The general chemical structure of these copolymers is shown in Fig. 1.

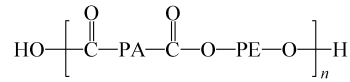


Fig. 1 General chemical structure of PEBAX

PA and PE are related to aliphatic polyamide “hard” block and polyether “soft” block segments. The common PA and PE blocks which can be used in PEBAX copolymers are PA6, PA12, poly(imino(1-oxododecamethylene)) for PA and PEO, PTMO for PE^[4–6].

Molecular dynamics (MD) simulation makes an enough powerful virtual lab that some experiments are performed to predict membrane characteristics. MD simulation has been used for calculation of some transport properties of separation materials and methods, especially polymeric membranes. Prediction of diffusion coefficients, permeability and selectivity is one of the specific applications of MD simulation in polymer-penetrant systems^[4, 7].

Some researchers have had some investigations on gas permeation through polymeric membranes especially PEBAX copolymers membranes with MD simulation^[8–20]. Recently, usage of nanoparticles to increase mechanical or transportation properties of polymeric material has attracted extremely high interest among researchers^[21–23].

The main objective of this study is calculation of diffusion coefficients for CO₂ and CH₄ gases through poly(ether block amide) membranes with different nanosilica contents (pure polymer, 5%, 10%, 15%, 20% and 25% nanosilica) by using simulation method. The diffusion coefficients are presented to explain the nanosilica particle effect on the under investigation structures. Fraction of free volume (FFV), radial distribution function (RDF), penetrant displacement, 3-D Cartesian trajectories plots of penetrant molecules are used to explain the accessed results.

SIMULATION METHOD

MD simulations were carried out using amorphous cell, discover and sorption modules of Materials Studio (MS) software which has been developed by Accelrys. All atomistic relationships were modeled using COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field^[24]. COMPASS which is presented in Eq. (1) has known as a powerful force field supporting atomistic simulations of materials.

$$\begin{aligned} E = & \sum_b \left[K_2 (b - b_0)^2 + K_3 (b - b_0)^3 + K_4 (b - b_0)^4 \right] + \sum_\theta \left[H_2 (\theta - \theta_0)^2 + H_3 (\theta - \theta_0)^3 + H_4 (\theta - \theta_0)^4 \right] \\ & + \sum_\varphi \left[V_1 \left[1 - \cos(\varphi - \varphi_0^1) \right] + V_2 \left[1 - \cos(2\varphi - \varphi_0^2) \right] + V_3 \left[1 - \cos(3\varphi - \varphi_0^3) \right] \right] + \sum_x K_x x^2 \\ & + \sum_b \sum_{b'} F_{bb'} (b - b_0) (b' - b_0') + \sum_\theta \sum_{\theta'} F_{\theta\theta'} (\theta - \theta_0) (\theta' - \theta_0') \\ & + \sum_b \sum_\theta F_{b\theta} (b - b_0) (\theta - \theta_0) + \sum_b \sum_\varphi (b - b_0) [V_1 \cos\varphi + V_2 \cos 2\varphi + V_3 \cos 3\varphi] \\ & + \sum_\varphi \sum_\theta \sum_{\theta'} K'_{\varphi\theta\theta'} \cos\varphi (\theta - \theta_0) (\theta' - \theta_0') + \sum_{i>j} \frac{q_i q_j}{\epsilon r_{ij}} + \sum_{i>j} \left[2 \left(\frac{A_{ij}}{r_{ij}^9} \right) - 3 \left(\frac{B_{ij}}{r_{ij}^6} \right) \right] \end{aligned} \quad (1)$$

The first four terms in this equation are sums that reflect the energy needed to: 1. stretch bonds (b), 2. bend angles (θ) away from their reference values, 3. rotate torsion angles (φ) by twisting atoms about the bond axis that determines the torsion angle, 4. distort planar atoms out of the plane formed by the atoms which they are bonded to (χ). The next five terms are cross terms that account for interactions between the four types of internal coordinates. The final two terms represent the non-bond interactions as a sum of repulsive and attractive Lenard-Jones terms as well as Columbic terms, all of which are a function of the distance (r_{ij}) between atom pairs.

Molecular Dynamics Details

PEBAX-3533 (Fig. 2) was selected for investigation of diffusion coefficients and other related properties.

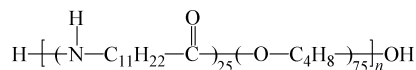


Fig. 2 Chemical structure of PEBAX-3533^[6]

As can be seen, this polymer contains PA12 and PTMO as hard and soft segments, respectively. The contribution of PTMO in PEBAX-3533 is 75 mol%. Also, α -quartz nanosilica is used as a filler in this study. The dimensions of these nanosilica particles were considered in the range of 5–10 nm. The simulated structures of PEBAX-3533/nanosilica and α -quartz nanosilica used in this study are presented in Fig. 3. The structure of constructed cells and their related characteristics for six composites with different nanosilica contents are presented in Table 1.

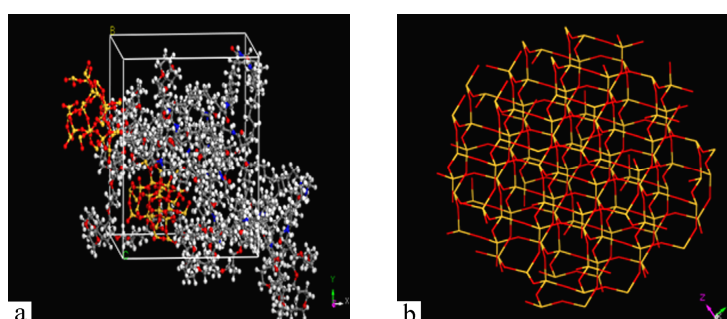


Fig. 3 Visual simulated structure of (a) PEBAX-3533/nanosilica and (b) α -quartz nanosilica

Table 1. Features of the constructed simulation cells

Cases	Pure	5% silica	11% silica	15% silica	20% silica	25% silica
Density (g/cm ³)	0.94	0.97	1.00	1.02	1.05	1.08
Number of atoms	1675	1703	1731	1753	1781	1831

The polymer chain and nanosilica at different ratios of PEBAX-nanosilica have been inserted in simulation boxes, while the initial density of these boxes was considered as 0.1 g/cm³. Periodic boundary condition was applied to the cubic simulation cells.

After insertion of the investigated structures into the simulation boxes, the energy minimization of these structures was performed using smart minimizer by 5000 steps to eliminate all closed contacts. For dynamics part Discover module was used. The 250 ps NPT run (constant number of atoms, temperature and pressure at 298 K and 0.1 MPa) was employed with a time step of 1 fs. Anderson and Berendsen methods were applied to control temperature and pressure as thermostat and barostat, respectively. The cutoff distance was considered as 0.95 nm for non-bond interaction (with a spline width of 0.1 nm and a buffer width of 0.05 nm) all over the simulations. Annealing of systems is performed with consideration of temperature increment from initial temperature 300 K to mid-cycle temperature 500 K and 5 heating ramps per cycle for 5 annealing cycles. The atomic trajectories were recorded every picoseconds (ps) to analyze structural and thermodynamic equilibrium properties.

Calculation of Diffusion Coefficients

Eight molecules of CH₄ or CO₂ gases are inserted in simulation boxes to calculate diffusion coefficients through the polymer bulk, and after reaching equilibrium every boxes are inserted into 600 ps NVT run with time step 1 fs. Diffusion coefficients are calculated by using Einstein equation (Eq. 2).

$$D = \lim_{t \rightarrow \infty} \frac{\langle (r(t) - r(0))^2 \rangle}{6t} \quad (2)$$

Where $\langle (r(t) - r(0))^2 \rangle$ is known as the mean square displacement (MSD). It is essential to note the Einstein equation is valid when it is possible to assume a random walk motion for diffusing particles, in other word, when MSD-t curve is linear.

Radial Distribution Function Analysis

The average RDF for significant atom i with different atoms j was evaluated for distances up to 1 nm in intervals of 0.01 nm as:

$$g_{i,j} = \frac{N_j(r)}{\rho_j N_i N_f 4\pi r^2 dr} \quad (3)$$

where $N_j(r)$ is the number of atoms of type j in a spherical distance between r and $r + dr$ from another atom, ρ_j is the bulk density of atoms in the polymer, N_f is the total number of frames used in the analysis and N_i is the number of i molecules.

Fractional Free Volume

The fractional free volume can be calculated by Eqs. (4) and (5) as shown below:

$$\text{FFV} = \frac{V - V_0}{V} \quad (4)$$

$$V_0 = 1.3 V_{\text{vdW}} \quad (5)$$

where V is the cell volume at $T = 298$ K, and V_{vdW} is the van der Waals volume obtained from the van der Waals surface without using Bondi's group contribution method. By consideration of hard spherical particles, the accessible volume of structures can be calculated.

X-ray Scattering

The estimation of X-ray scattering or X-ray diffraction (XRD) can be probed based on independently equilibrated configurations under periodic boundary conditions with Cu K $_{\alpha}$ radiation, $\lambda = 0.154$ nm using Forcite module. The scattering intensity can be expressed by:

$$I(Q) = \sum_i \sum_{j, i \neq j} \frac{f_i f_j (\sin Q r_{ij})}{Q r_{ij}} \quad (6)$$

where I is scattering intensity, Q is the magnitude of the scattering vector, which is equal to $4\pi \sin(\theta/\lambda)$ where 2θ is the scattering angle and λ is the radiation wavelength, f is the atomic scattering factor and r_{ij} is the distance between i and j atoms. Inter-chain spacing or d -spacing is measured by Bragg's equation according to Eq. (7).

$$n\lambda = 2d \sin(\theta_{\text{max}}) \quad (7)$$

RESULTS AND DISCUSSION

Validation of Simulation

In order to access reliable results for transport coefficients of gas molecules through the polymeric membrane, it is essential to indicate the initial structure has been simulated consistently. At previous studies, there was less information about structural features of PEBAX-3533. The experimental XRD data of PEBAX-3533 were found in the work of Kim *et al*^[23]. The wide-angle X-ray diffraction pattern of pure PEBAX-3533 is simulated at the atomistic level in this work as shown in Fig. 4. The XRD shows a relatively broad peak near 20° (2θ) that can be

ascribed to diffraction from amorphous regions of simulated structure. This result is consistent with that of the experimental work. The XRD data shows that the simulated and equilibrated structures are able to be used as consistent structures to estimate the desirable data. The measurement shows the experimental d -spacing of 0.44 nm, calculated by Bragg's law $n\lambda = 2d\sin(\theta_{\max})$ is close to the calculated value (0.47 nm) in this work.

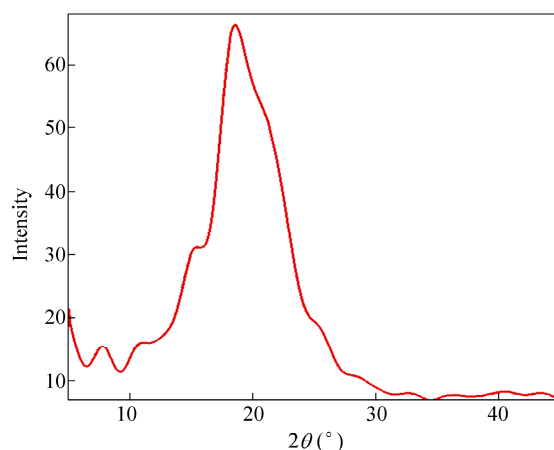


Fig. 4 Wide-angle X-ray diffraction of pure PEBAX-3533

Diffusion Coefficient

Figures 5 and 6 show the mean squared displacement (MSD) plots of the gas penetrant molecules. These figures demonstrate the normal diffusion regimes of the penetrant molecules have been accessed, because MSD curves verses time should have linear trend.

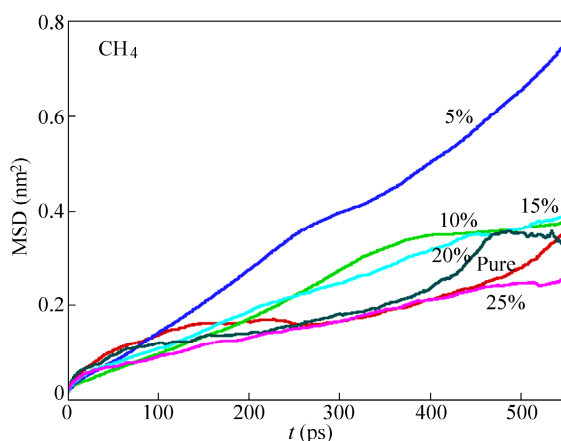


Fig. 5 Mean square displacement (MSD) of CH₄ molecule in membranes with different contents of nanosilica

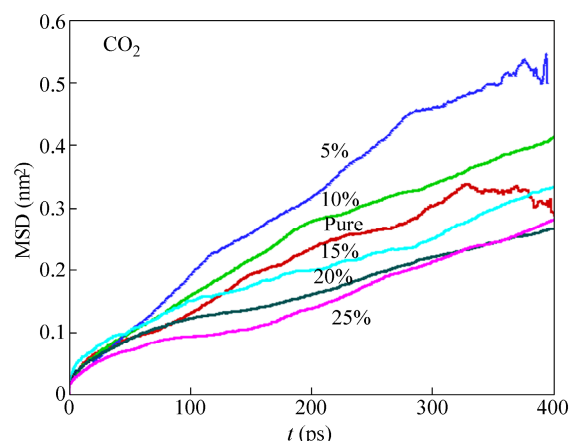


Fig. 6 Mean square displacement (MSD) of CO₂ molecule in membranes with various contents of nanosilica

Diffusion coefficients of CO₂ and CH₄ gases through membranes with various content of nanosilica are presented in Fig. 7. Obviously due to different gas kinetic diameters, the CO₂ diffusion coefficients are higher than those for CH₄ gas. The kinetic diameters for CO₂ and CH₄ penetrants are 0.33 nm and 0.38 nm as previously reported^[11]. The results show that the nanosilica loading into the pure PEBAX-3533 membrane improves the diffusion coefficients by 68.5% and 157.5% for CO₂ and CH₄ gases respectively, at 10% nanosilica loading. There is a peak in the diffusion coefficients for both CO₂ and CH₄ gases by increasing in amounts of nanosilica. The diffusion coefficients increase from pure case to 10% nanosilica loading and after that the

diffusion coefficients decrease, obviously. The diffusion coefficient of membrane with 5% nanosilica is larger than that of the pure one, which can be due to rising in amount of fraction of free volume for the membrane with 5% nanosilica according to Fig. 8. On the other hand, it can be seen that the diffusion coefficient further increases up to 10% nanosilica loading, while the fraction of free volume is decreased. For finding the reason behind this phenomenon, it should be referred to XRD graphs of all investigated cases. Figure 9 shows the XRD graphs of all cases. As can be seen from this figure, there is a peak at about $2\theta = 19^\circ$ for pure polymer while this parameter decreases for membranes with 5% and 10% nanosilica. It shows that the d -spacing between adjacent chains is increased. The d -spacing according to Bragg's law for pure membrane is equal to 0.479 nm and that for membranes with 10% nanosilica increases to 0.509 nm. Figure 10 shows the radial distribution function (RDF) of carbon-carbon (C—C) for pure state polymer chains and confirms that the first peak occurs at 0.47 nm. On the other hand, the distance between polymer chains is equal to this amount. Also, the results show that the intensity of samples with 5% and especially 10% nanosilica is more than that of the pure case. This issue indicates the free

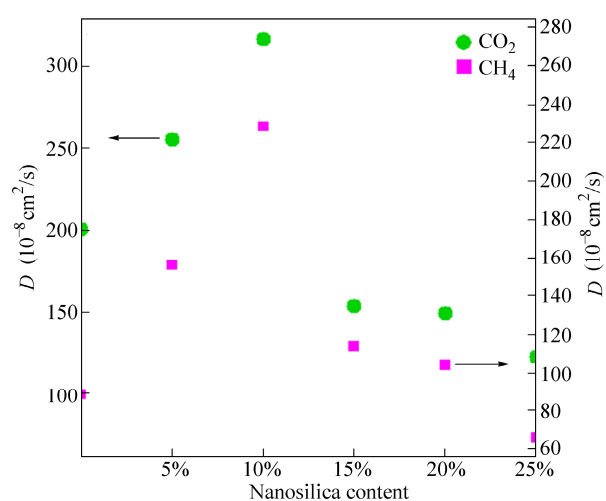


Fig. 7 Diffusion coefficients of CO₂ and CH₄ gas molecules at various contents of nanosilica loading

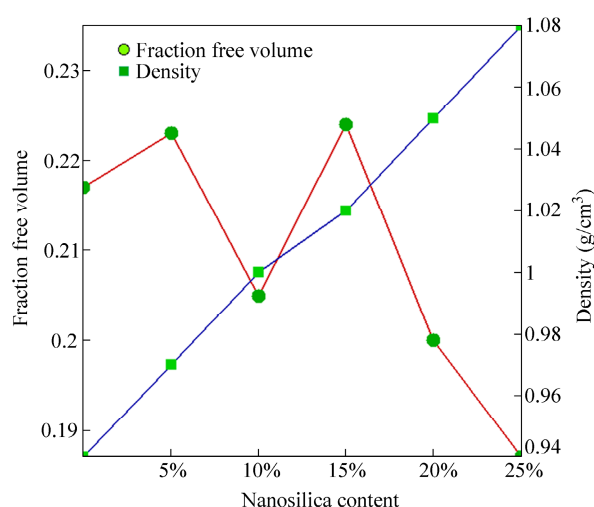


Fig. 8 Density and free volume fraction of the simulated boxes at various contents of nanosilica loading

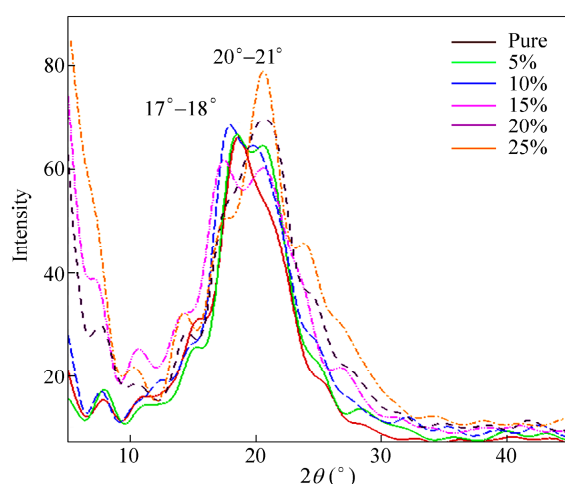


Fig. 9 X-ray diffraction (XRD) of the simulated boxes at various contents of nanosilica loading

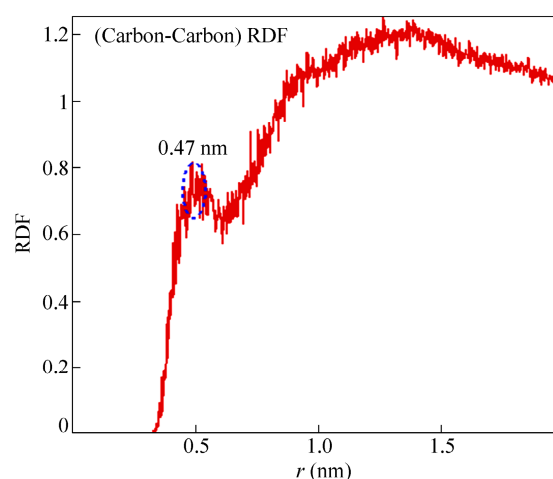


Fig. 10 Radial distribution function (RDF) of carbon-carbon (C—C) for pure polymer

volume has more regularity at impure cases. It shows the cavity size distribution of samples with 10% nanosilica is more suitable than that in pure and 5% cases. It can be considered that the second peak for the nanosilica loading membrane is caused by silica phase. It can be seen when nanosilica loading increases above 10%, the first peak intensity decreases while the second one increases. Then it can be estimated that the diffusion coefficients for both gases decrease in higher nanosilica loading membranes. In Table 2, the diffusion selectivity of penetrant gases is presented. As it can be observed from this table, the diffusion selectivity has opposite trend than the diffusion coefficients.

Table 2. Diffusion selectivity for CO₂/CH₄ ratio at different nanosilica loadings

Cases	Pure	5%	10%	15%	20%	25%
Diffusion selectivity (CO ₂ /CH ₄)	2.263	1.633	1.390	1.348	1.431	1.861

3-D Cartesian Trajectory Graphs

Besides the predictive capabilities concerning calculation of transport properties especially the diffusion coefficient, molecular dynamics simulations prepare powerful facilities to have better sight of structures and dynamic behavior of simulated polymers. Consequently, the mobility of the polymeric chains and movement details of each molecule through the simulation boxes can be directly checked by using 3-D Cartesian trajectory graphs.

Figures 11 and 12 show the trajectories of both CO₂ and CH₄ gases in the simulated boxes, respectively. As can be seen from these figures, CO₂ molecule has more jumps than CH₄ penetrant molecule (the spaces with low concentration of line).

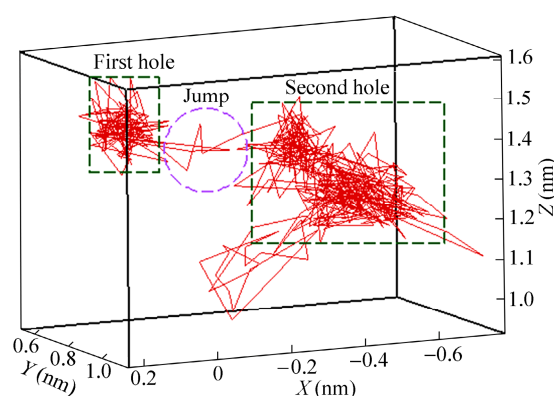


Fig. 11 3-D cartesian curve of CH₄ molecule movement in simulated box

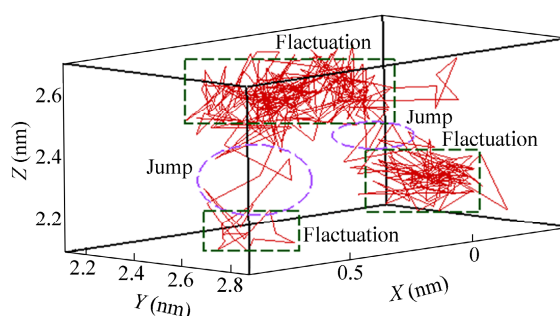


Fig. 12 3-D Cartesian curve of CO₂ molecule movement in simulated box

Nevertheless, CH₄ molecule remains more in a hole and fluctuates in it. Also, it can be understood that the line concentration of CO₂ molecule related to a hole is less than that of CH₄. This shows that the residence time of CO₂ molecule may be less than that of CH₄ one.

Investigation of gas diffusivity by using 3-D Cartesian trajectory curves cannot show jump times, fluctuation time in a cavity, jump length, and many other useful data which can help to have a deep sight how penetrants can move through a polymeric membrane structure.

However, if displacements versus time curves of penetrant molecules are plotted, it can prepare some suitable data to analyze them decently. Figures 13 and 14 are associated to CH₄ (Fig. 11) and CO₂ (Fig. 12) gas molecules. Figure 13 shows that the CH₄ molecule has a successful and an unsuccessful jump during the simulation time. Moreover, this figure shows that this successful jump and two fluctuations occur in a short time at 100 ps and 300 ps, respectively. The jump length is approximately equal to 0.5–0.6 nm. As a result, it can be estimated that the second cavity (hole) size is larger than the first one, because the range of oscillation is broader for second hole. Correspondingly, Fig. 14 shows CO₂ molecule has 4 successful jumps during its runtime. Figure 14 also shows that the first jump of CO₂ molecule occurred at about 100 ps or even less than 100 ps. It can be considered that the oscillation amplitude depends on the size of the visited hole and these positional fluctuations are not effective for the diffusive behavior. Also, CO₂ molecule has more attempts to have a successful jump. A more precise investigation of these figures shows that none of these gas molecules remarkably have back and forth jumps between two neighboring holes due to polymer rubbery structure of this copolymer. Rubbery polymers unlike glassy ones try to change the constant channel form and then, the channel lifetime in these polymers is short.

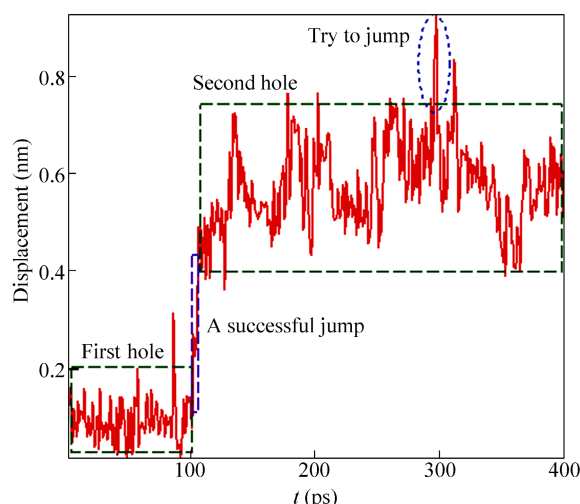


Fig. 13 3-D Cartesian trajectory curve of CH₄ molecule through pure PEBAX

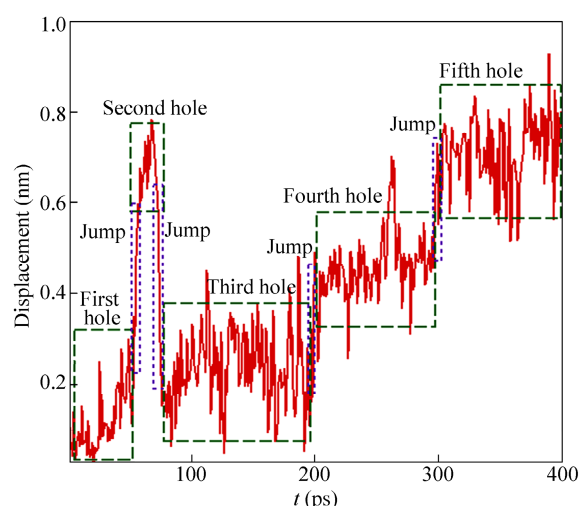


Fig. 14 3-D Cartesian trajectory curve of CO₂ molecule through pure PEBAX

CONCLUSIONS

In this study, the effect of nanosilica loading on diffusion coefficients of CO₂ and CH₄ gases penetrants through PEBAX membranes was investigated using molecular dynamics (MD) simulations. Six different contents of nanosilica (pure, 5%, 10%, 15%, 20%, and 25%) were loaded in PEBAX membranes. The results show that the CH₄ diffusion coefficients are less than those of CO₂ molecules. It was expressed that molecule kinetic diameter is the basic factor affecting diffusion coefficients of gases at constant condition of simulated boxes. The kinetic diameters of CO₂ and CH₄ are 0.33 nm and 0.38 nm, respectively. Moreover, the results show that there is a peak for diffusion coefficients for both gases at 10% nanosilica loading in PEBAX composite membranes. The 10% nanosilica loading case shows maximum effects on diffusion coefficients and improves them by more than 68% and 157% for CO₂ and CH₄ gases, respectively. It can be understood from XRD curves that the intensity of XRD curve of 10% case is more than that of the 5% one. Then, cavity size distribution (regularity of it) as an effective parameter influencing diffusion coefficient is increased, rather than the fractional free volume, at 10% case than

5% one. Moreover, for better investigation of simulated structures, it was plotted the 3-D Cartesian trajectory and displacement plots of CO₂ and CH₄ gas molecules. The results showed the residence time of CH₄ molecule in a hole is more than that of CO₂ molecule. The residence time for CO₂ is approximately 100 ps, while it is 100 ps or 300 ps for CH₄. Also, the results from 3-D and displacement curves showed that the attempts to have a successful jump for CO₂ molecules are obviously more than those of the CH₄ ones due to smaller size (kinetic diameter) of CO₂ molecules.

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