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Molecular dynamics simulation of diffusion of gases in pure and silica-filled poly(1-trimethylsilyl-1-propyne) [PTMSP]

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Abstract

Nanocomposites have been extensively applied, and molecular dynamics simulation techniques have been applied to study the diffusion of gases (H_2, O_2, N_2, CO_2, CH_4, n-C_4H_{10}) through pure and filled with silica particle poly(1-trimethylsilyl-1-propyne) [PTMSP]. The aim for this research is to explore and investigate the effect of silica particle on the diffusion of gases in polymer. The diffusion coefficients of gases were determined via NVT molecular dynamics simulation using the COMPASS force field up to 500 or 1000 ps simulation time. We have focused on the effect of the concentration and the size of the silica particles on diffusion coefficients of gases and the changes of free volume and translational dynamics and intermolecular energies. It has been found that the addition of silica particle to PTMSP increased the diffusion coefficients of gases by enhancing the free volume of polymer.

Keywords: Molecular dynamics simulation; Silica; PTMSP

1. Introduction

Recently, organic–inorganic hybrid materials have received tremendous attention, for they seemingly offer a relatively accessible means for altering the properties of existing materials without requiring synthesis of entirely new chemical species. In molecular separations, ongoing efforts continue to explore the utility of incorporating porous particles, such as highly selective zeolites, into dense polymeric membranes to improve gas separation properties [1–4], In theory, such materials might combine the excellent size selectivity of zeolites with the desirable mechanical and processing attributes of polymers. In practice, however, attaining this synergy is difficult. Often, hybrid membrane performance is compromised by the formation of relatively non-selective defects caused by dewetting of polymer chains from the surface of micrometer-sized zeolite particles. These problems with zeolite/polymer adhesion, as well as inadequate particle dispersion in the polymer phase, have hindered the development and implementation of such membranes.

In addition to porous zeolite particles, many types of non-porous, inorganic fillers are added to polymers for a variety of reasons. Traditionally, the incorporation of non-porous fillers, such as metal oxides, silica, or carbon blacks, into polymers reduces gas or vapor permeability. This decreased permeability is the result of a reduction in the amount of polymer through, which transport may occur and an increase in the diffusion path length that penetrant molecules experience [5] as they are forced to take a tortuous course around filler particles to traverse a film.

However, recently incorporation of nanoscale, non-porous fumed silica (FS) particles into high-free-volume, poly(4-methyl-2-pentyne) [PMP] have been discovered to increase gas permeability organic vapor [6–7], and this highly unusual and counterintuitive result suggests that the volume filling and tortuosity effects are offset by the ability of these tiny particles to disrupt packing of rigid polymer chains, thereby subtly increasing the amount of free volume in the polymer. Such nanoscale hybridization represents an innovative means to tune the separation properties of glassy polymeric media through systematic manipulation of molecular packing. Poly(4-methyl-2-pentyne) [PMP] is the member of a family of substituted acetylene polymers that exhibit poor polymer chain packing in

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part due to rigid backbones, low interchain cohesion, and bulk substituents. These glassy polymers are characterized by low densities, high fractional free volumes, high gas permeabilities, and in some cases, highest selectivity for organic vapors over permanent gases. Poly(1-trimethylsilyl-1-propyne) [PTMSP] is also the member of a family of substituted acetylene polymers, and it has the similar attributes with PMP, and the people implemented a lot of research on PMP and PTMSP in experiment and theory [8–18].

Although experimental works have pointed that gas permeability was increased for silica–PMP and silica–PTMSP nanocomposites, at the molecular level, the interaction between silica nanoparticle and polymer, and the influence of silica particle on the mobility, structure, free volume of polymer was unknown. For the above reasons, it was interesting to undertake a study of such a system using a molecular dynamics simulation technique. In present paper, we selected silica–PTMSP as research object. PTMSP has the highest gas permeability in known glass polymers. It has been proved that the addition of silica particle to PTMSP had little effect on the solubility of gases in PTMSP in experiment, so we only have simulated the diffusion of several gases (H_2, O_2, N_2, CO_2, CH_4, n-C_4H_{10}) through pure and filled PTMSP systems, and have discussed the effect of the concentrations and the sizes of silica particles on diffusion coefficients and free volume of PTMSP, at the same time, have researched the interaction between silica nanoparticle and PTMSP and the influence of the addition of silica to PTMSP on the flexibility of the backbone of PTMSP.

2. Simulation details

According to the literatures [8,11], an atactic chain of 50 repeat units with a 50:50 probability for the occurrence of monomers with trans and cis configurations (Fig. 1) was build. To create some roughly spherical silica particles, a α-quartz supercell crystal structure was first created, then all Si and O atoms outside a radius of 9 Å from the center were discarded. The resulted cluster contained 78 Si atoms and 156 O atoms and was electrically neutral (Fig. 1). However, it should be borne in mind that silica particle obtained by this method was an ideal model compared with that used experimentally in the work of Merkel et al., which had different size and morphology of the particle. The gases (H_2, O_2, N_2, CO_2, CH_4, n-C_4H_{10}) were used in the simulation, respectively. For pure PTMSP systems, the unit cell included five single gases and one PTMSP chain and the unit cell size is about 23.18×23.18×23.18 (Å^3) (Fig. 2), and for filled PTMSP systems, the unit cell included five single gases and one PTMSP chain and one silica particle with the radius of 9 Å and the unit cell size is about 28.24×28.24×28.24 (Å^3). As for force field, the newly developed COMPASS force field of Accelrys was used in all cases, and van der Waals (vdW) and Coulomb non-bond interactions were treated using Ewald summation method, About this point, we need to say more. When we tried to use atom-based and group-based summation method, the big gases (CO_2, CH_4, n-C_4H_{10}) did not implement jumping diffusion even up to 500 ps simulation time, however, using Ewald summation method, they could implement enough jumping diffusion in 500 ps simulation time. So we decide to use Ewald summation method for every gas.

Every unit cell was minimized using smart minimizer method in order to eliminate local non-equilibrium, then a MD run (NPT, 500 ps) was performed for each of the models in order to further equilibrate the models before using them for data production, following a MD run (NVT, 500 ps) was performed for the models with the gases (H_2, O_2, N_2, CO_2, CH_4)for production, and 1000 ps was done for C_4H_{10} vapor, and the output frequency was every 0.1 ps and the time step of 0.001 ps was taken to be constant for all the simulations of this study. The Andersen thermostat and Berendsen barostat were used to maintain a constant temperature (300 K) and a constant

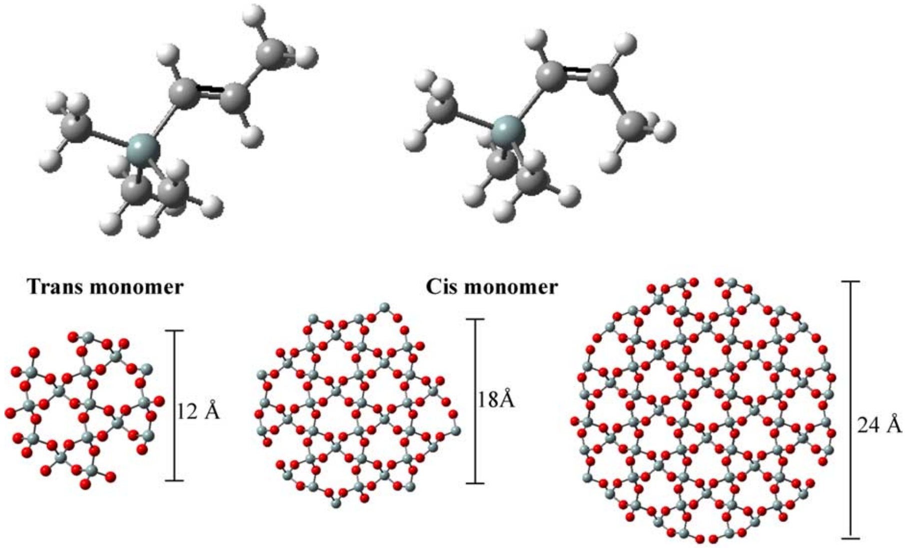

Fig. 1. Molecular model of *trans*/*cis* PTMSP monomer/silica nanoparticle.

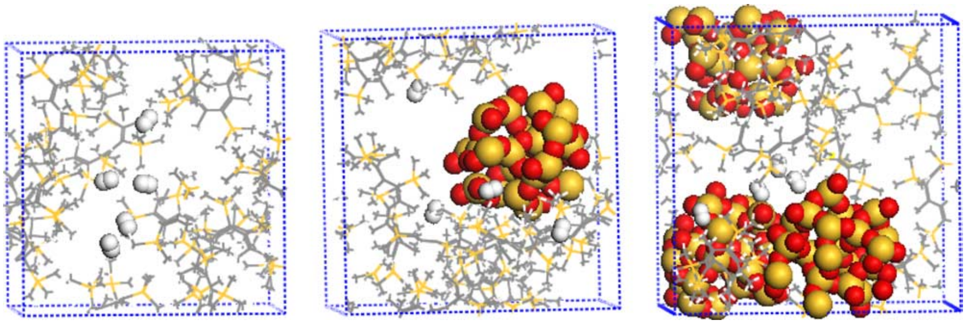

Fig. 2. Schematic representation of unit cell model with hydrogen and silica particle. Hydrogen gas molecules and silica particle are represented in space-filling models, and PTMSP are represented in wire-frame models.

pressure (10^5 Pa). The diffusion coefficients were computed by Einstein–Smoluchowski equation:

$$\langle|\mathbf{r}(t)-\mathbf{r}(0)|^2\rangle = 6Dt \tag{1}$$

In Eq. (1), D is the diffusion constant, t is time, $\mathbf{r}(t)$ is the position vector of the gas molecules in space at time t; and the brackets denote an ensemble average, which in these simulations is obtained from averaging over all gas molecules in the polymer system and all time origins ($t=0$), this equation only applies in the limit of large times at which the simulated gas molecules have performed enough jumps for their trajectories to become a random walk in the polymer model.

The simulations were mostly performed using Material Studio 2.2 molecular simulation software [19] on personal computer.

3. Result and discussion

3.1. Diffusion of gases through pure and filled PTMSP

Firstly, every model was minimized, then equilibration runs for 500 ps were carried out, at last the density of unit cell for pure and filled PTMSP was fluctuated within the range of ± 2% of the experiment density (0.75 g/cm^3 for pure PTMSP and 0.80 g/cm^3 for filled PTMSP), for example, the change of the unit cell density during the equilibrium stage for pure and one silica particle filled PTMSP was shown in Fig. 3 and the average of the density of the last 100 ps for pure and filled PTMSP unit cell was 0.759 and 0.786 g/cm^3, respectively, following a MD run (NVT, 500 ps, only1000 ps for C_4H_{10}) was done for data production. The gases in every model began to perform normal fickian diffusive over 500 ps (1000 ps for C_4H_{10}), and Fig. 4 shows that the displacement vs. time for H_2 through pure and filled PTMSP, and the blue arrowhead denotes that the gas performs jumping diffusion, and it can be seen from the figure that the displacements of the gas in pure and filled PTMSP are obviously different after about 200 ps after which the displacements of the gas in filled PTMSP are greatly increased. Table 1 presents the detailed diffusion coefficient of every gas through pure and filled PTMSP. Hofmann [18] showed the simulated diffusion coefficients for gases (O_2, N_2, CO_2, CH_4) through the pure PTMSP were 3.6, 1.5, 0.8, and 1.7×10^{-5} cm^2/s, respectively. In present work, the diffusion coefficients for gases (O_2, N_2, CO_2, CH_4) were 5.0, 4.8, 3.3, and 3.8×10^{-5} cm^2/s, respectively, and they were 5.2, 4.4, 3.3, and 3.6×10^{-5} cm^2/s in the experiment, respectively. So it was concluded that the diffusion coefficients gained by the present work were comparable with that gained by Hofmann [18], though the two simulation works was different in simulation size (50 repeat units for present work and 499 repeat units for the work implemented by Hoffmann). And this conclusion was also consistent with that in Ref. [21], Paulaitis et al. [21] detailedly discussed the effect of simulation size on the diffusion coefficients. They found that simulation

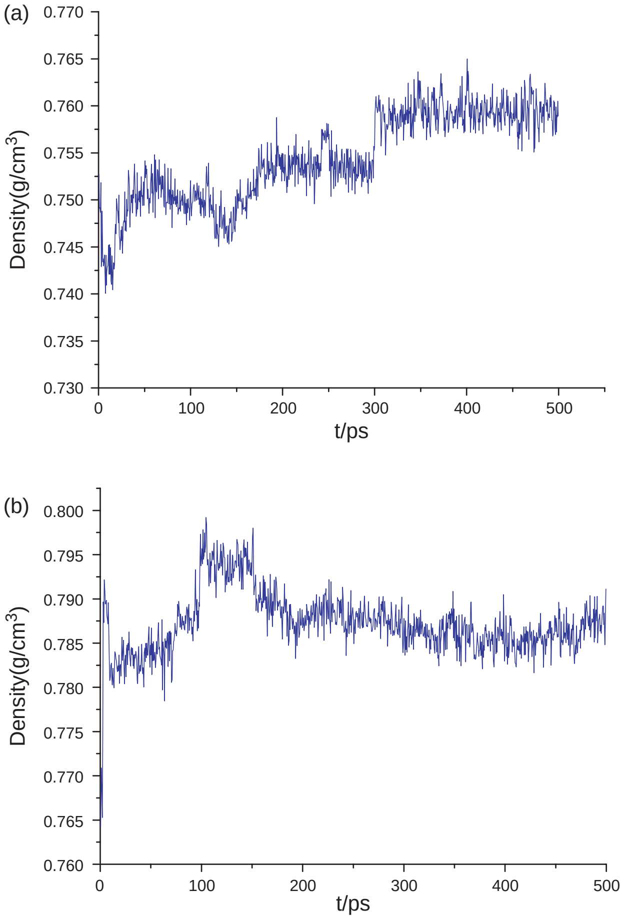

Fig. 3. The change of the unit cell density during the equilibrium stage (a) for pure PTMSP (b) for one silica particle (9 Å) filled PTMSP.

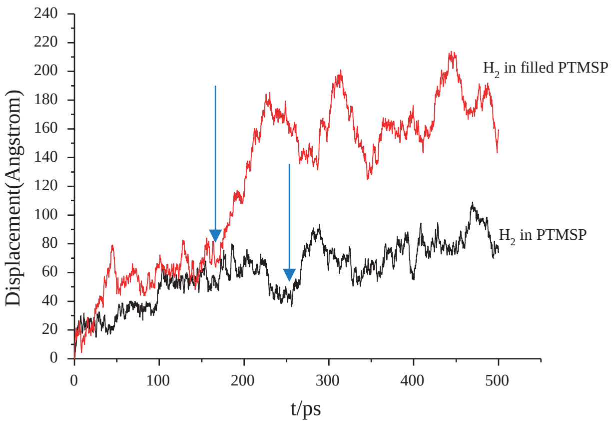

Fig. 4. Displacement of H_2 in pure and filled PTMSP at 300.0 K.

size did not have a significant effect on the diffusive motion of any of the penetrants for a periodic structure. Besides, our simulation results were also comparable with experimental data. At the same time, it can be seen from the table that gases diffusion coefficients in polymer were increased when silica particle was incorporated in PTMSP, and Merkel [9] showed H_2 and CH_4 diffusion coefficients in 40 wt% silica particle filled PTMSP approached to 80.07×10^{-5} and 9.0×10^{-5} cm^2/s, respectively. In our simulation, the fraction of silica particle was 45.1 wt%, and H_2 and CH_4 diffusion coefficients were 92.1×10 and 9.2×10^{-5} cm^2/s, respectively, and so the present simulated data was comparable with the reported experimental data.

3.2. Effect of the concentrations and of the sizes of silica particles on gases diffusion

To examine the effect of silica particle concentrations on gases diffusion, we simulated the diffusion of three gases (H_2, CH_4, C_4H_{10}) in PTMSP with different silica particle filled concentrations, respectively. The used silica particle radius was 6 Å, which was gained as the same method as the silica particle with the radius of 9 Å, and this particle totally included 26 Si atoms and 52 O atoms. We simulated the diffusion of three gases in PTMSP, which filled by silica particles from one to six, and the corresponding silica concentration was 20.83, 34.47, 44.11, 51.27, 56.81, and 61.22, respectively. The change of diffusion coefficients with silica concentrations is shown in Fig. 5, and it is clear from the figure that the diffusion coefficients of the gases are enhanced gradually with the increasing of silica particle concentrations for three gases. In addition, the change of diffusion coefficients for H_2 with the silica particle concentrations is more obvious than the other gases (CH_4, C_4H_{10}), and this results from the change of the mechanism of diffusion for H_2, and diffusion coefficients for H_2 have reached to the range of free phase transport such as Knudsen flow. This relation between gases diffusion coefficients and silica particle concentrations was qualitatively consistent with the reported experimental result [13]. In a word, the diffusion coefficients of gases were enhanced when the concentrations of filler silica particles were increased.

To discuss the effect of particle size on diffusion coefficients of gases, we simulated the diffusion of gases (H_2, CH_4, C_4H_{10}) in PTMSP, which was filled by different size silica particles at the almost same silica filler contents (67%). In order to keep the constant particle filler concentrations, we built three unit cells for every gas, which, respectively, included one particle ($R=$ 127 Å) and two particles ($R=9$ Å) and eights particles ($R=$ 67 Å). The effect of particle size on diffusion coefficients of gases in filled PTMSP at constant filler fraction of 67 wt% was displayed in Fig. 6, and it is clear from the figure that diffusion coefficients of gases are increased with the reduction of silica particle radius. This relation was consistent with that found by Toy [16]. In conclusion, the diffusion coefficients of gases were enhanced by reducing filler particle size.

3.3. Effect of silica particle on the backbone of PTMSP

3.3.1. Translational motion of the backbone of pure and filled PTMSP

The effect of silica particle on the mobility of the backbone of PTMSP can be proved by mean-square displacements (MSDs), as showed in Fig. 7, and it can be seen from the figure that MSDs of the atoms of the backbone of filled PTMSP are greatly increased in comparison with that of pure PTMSP, and the diffusion coefficients are 0.7×10^{-7} and 4.7×10^{-7} cm^2/s for pure and filled PTMSP, respectively. So it can be concluded that the mobility of the backbone of filled PTMSP is enhanced, but in general [22], the mobility of the backbone of filled polymer is decreased, which probably because Si atoms exist in PTMSP and attribute to increase the electrostatic repulsive interaction between PTMSP and silica particle. In order to confirm the conclusion, we simulated two kinds of silica filled polymers, and one polymer was that Si atoms of PTMSP were displace by C

Table 1
The diffusion coefficients of gases in pure and filled PTMSP with the particle radius of 9 Å ($cm^2\ s^{-1}\times10^{-5}$)

	Pure PTMSP				Filled PTMSP
	Present simulation	Simulation		Experiment [20]	Present simulation
		[18]	[8]		
H_2	35.6			26	92.1
O_2	5.0	3.6	2.38	5.2	6.9
N_2	4.8	1.5	2.05	4.4	6.8
CO_2	3.3	0.8	0.40	3.3	5.0
CH_4	3.8	1.7	1.67	3.6	9.2
C_4H_{10}	0.9				2.0

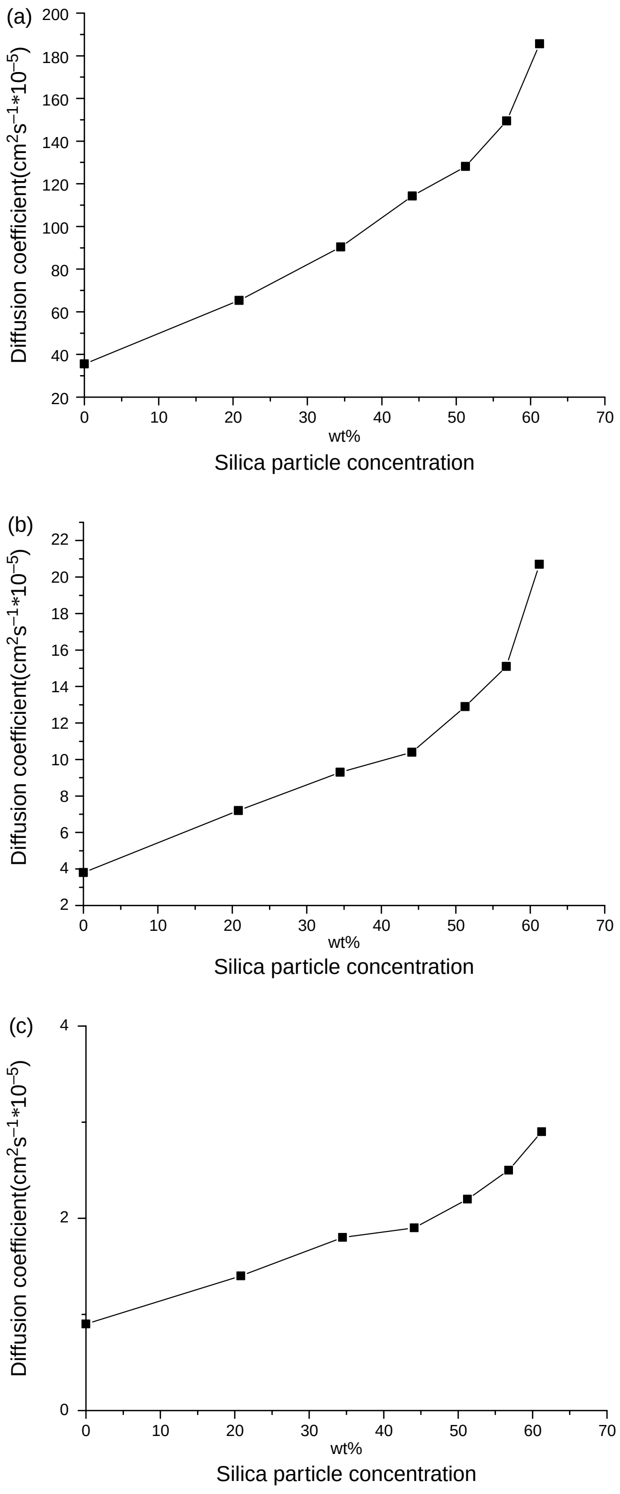

Fig. 5. Effect of silica particle concentrations on diffusion coefficients of gases in filled PTMSP (a) hydrogen (b) methane (c) *n*-butane.

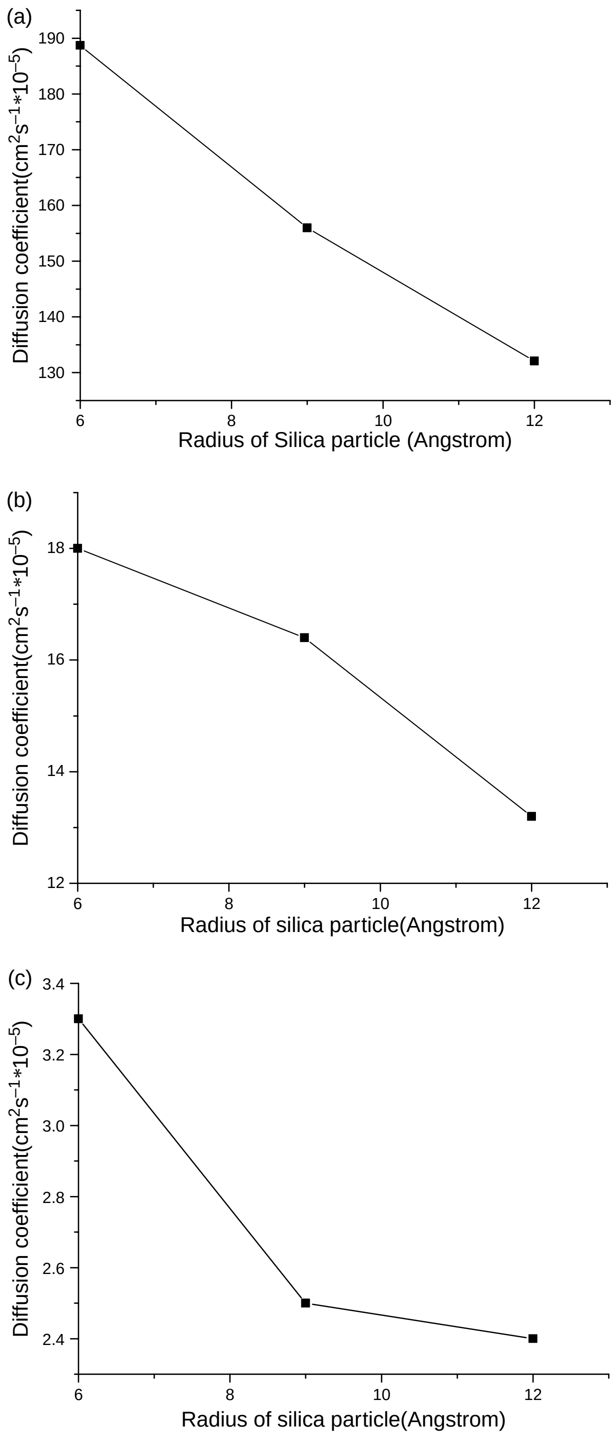

Fig. 6. Effect of filler particle sizes on diffusion coefficients of gases in filled PTMSP at constant filler fraction of 67 wt% (a) hydrogen (b) methane (c) *n*-butane.

atoms, the other polymer was poly(dimethylsiloxane) (PDMS). It can be found that the mobility of the backbone of the former filled polymer was decreased, but the mobility of backbone of the latter was increased, as showed that our conclusion was right. The mobility of the backbone of polymer can influence the dynamic free volume, so the enhancement of the mobility of the backbone of filled PTMSP can add the number and the size of the dynamics free volume and accordingly can result in the enhance of diffusion coefficients of gases.

3.3.2. Rotational motion of the backbone of pure and filled PTMSP

To examine the effect of silica particle on the backbone of PTMSP, rotational motion of the backbone of pure and filled

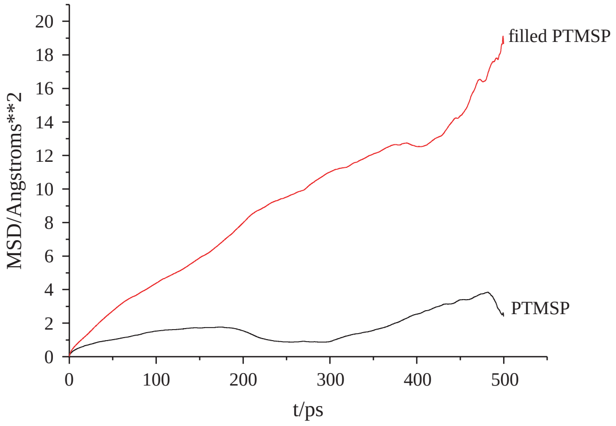

Fig. 7. MSD vs. time for atoms of the backbone of pure and filled PTMSP.

PTMSP was investigated by measuring rotational time correlation function $m_1(t)$, $m_1(t)=\langle\mu(t_0)\cdot\mu(t_0+t)\rangle$, where $\mu(t)$ denotes a unit vector characterizing the orientation at a time t, in this simulation $\mu(t)$ is defined as the vector connecting the first atom of and the last atom of the backbone of PTMSP. The rotational time correlation function of the backbone of pure and filled PTMSP is displayed in Fig. 8, it is seen that from the figure that the relaxation curves decay no exponentially and the relaxation curves for filled PTMSP decay much faster than pure PTMSP, so it can be concluded that the backbone of filled PTMSP is more flexible than pure PTMSP, and the fast decay for filled PTMSP results from the interaction between silica particle and the backbone of PTMSP.

3.4. Free volume

There are two phases in a polymer membrane: a solid phase occupied by polymer chains and a space phase named as free volume. The occupied volume of polymer chains is similar to 1.3 times the van der Waals volume of polymer chains in a separation membrane, and the free volume is the outlines of the van der Waals surface of polymer chains. The well-known definition of fractional free volume (FFV) is defined by specific volume of membrane and occupied volume of polymeric molecules. The FFV was calculated from the formula: $\mathrm{FFV}=1-V_0/V_\mathrm{s}=1-1.3V_\mathrm{vdW}/\mathrm{V}_\mathrm{s}$, where V_s is the specific volume, V_0 is occupied volume of polymer chains and V_vdW is van der Waals volume of polymer chains, respectively. In this research, we assumed that the van der Waals volume of polymer is calculated from the volume occupied by van der Waals surface of polymer. The free volume sizes and morphology are very important parameters to the permeability of the polymer. Generally speaking, the more fractional free volume of separation membrane, the higher diffusivity or solubility of membrane that will be obtained. The change of fractional free volume with the concentrations of silica particle and the sizes of silica particle is displayed in Figs. 9 and 10, and the free volume in the figures represents the free volume of the polymer/particle composite with the contribution from the particles removed, and it can be seen that from the two figures that the fractional free volume is gradually increased with the addition of silica particle concentration, which is consistent with the relation between diffusion coefficients and the

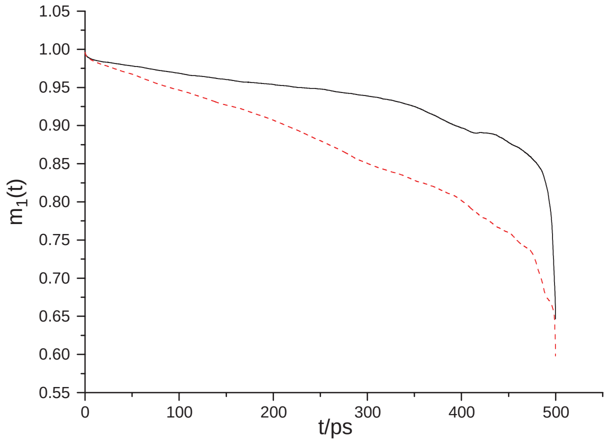

Fig. 8. The rotational time correlation function of the backbone of pure and filled PTMSP. Pure PTMSP is denoted by a black solid line and filled PTMSP is denoted by a red broken line.

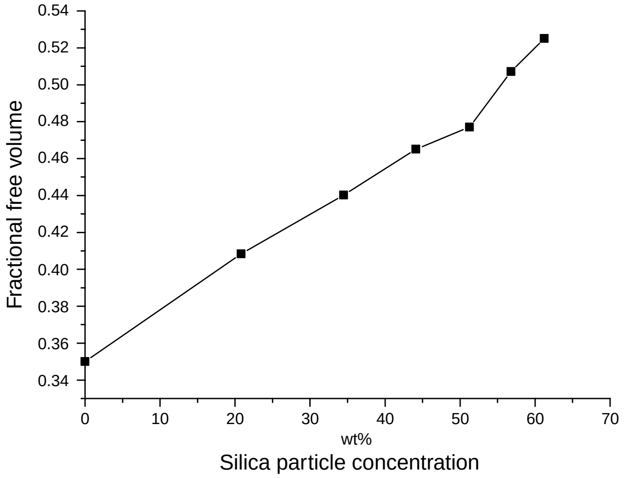

Fig. 9. Effect of filler particle concentrations on the fractional free volume of filled PTMSP.

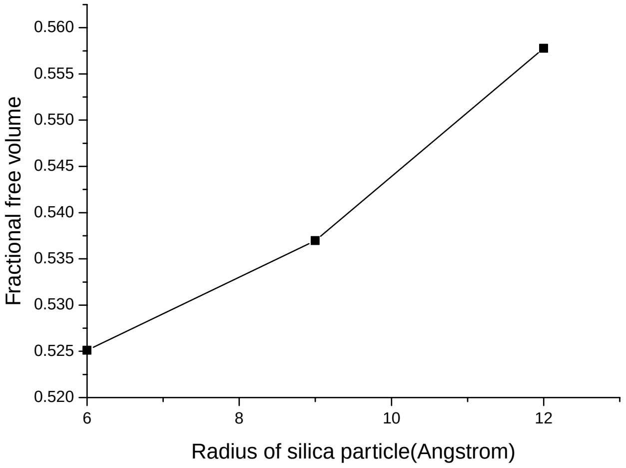

Fig. 10. Effect of filler particle sizes on the fractional free volume of filled PTMSP at constant filler fraction of 67 wt%.

Table 2
Each specific energy component of pure and silica filled PTMSP (kcal/mol)

	$E_{\text{pure PTMSP}}$	$E_{\text{filled PTMSP}}$	ΔE
$\langle E_{\text{total potential}} \rangle$	915.50	-3982.43	-388.68
$\langle E_{\text{internal}} \rangle$	2677.22	2838.87	-282.80
$\langle E_{\text{non-bond}} \rangle$	-1761.72	-6821.30	-105.89
$\langle E_{\text{vdW}} \rangle$	69.56	-177.93	-257.69
$\langle E_{\text{vdWrepulsive}} \rangle$	2692.35	2982.46	-1371.15
$\langle E_{\text{vdWdispersive}} \rangle$	-2622.79	-3160.39	1113.46
$\langle E_{\text{ele}} \rangle$	-1831.28	-6643.37	151.81

concentration of silica particle. The fractional free volume is gradually reduced with the decreasing of the radius of silica particle, from the above discussion, we know that the diffusion coefficients are increased with the reduction of the size of particle, generally speaking, the free volume would be increased if the diffusion coefficients were increased, however, the present results is contrary, as is not expected by us. Probably the effect of the size of particle on diffusion coefficients is related with not only interfacial free volume, but also the interaction between silica particle surfaces and the gases, and we will further probe into the question in future.

3.5. Thermodynamics data

The averages of various thermodynamic properties are given in Table 2 for the pure and filled PTMSP systems at 300 K, quoted in kcal/mol. Averages were taken over the last 500 ps simulation, and we estimated the change in important energy components associated with mixing PTMSP and silica, ΔE, to $E_{\text{PTMSP–silica}}$ minus the sum of $E_{\text{pure-PTMSP}}$ and E_{silica}, namely, $\Delta E = E_{\text{PTMSP–silica}} - E_{\text{pure-PTMSP}} - E_{\text{silica}}$. The total energy is reduced 388.68 kcal/mol, and vdW energy is decreased 257.69 kcal/mol, while the total electrostatic energy is increased 151.81 kcal/mol. In summary, the addition of silica particle to PTMSP made the system more stable.

4. Conclusions

Fully atomistic equilibrium MD simulations of pure and filled PTMSP systems were performed, and we draw several conclusions as follows:

(1) Si atoms of PTMSP play an important role in non-bond interaction between gases and PTMSP, and the treating method of non-bond interaction can affect the diffusion coefficients of the gases.
(2) The diffusion coefficients of gases (H_2, O_2, N_2, CO_2, CH_4, n-C_4H_{10}) are increased to different degree.
(3) The diffusion coefficients are increased with the enhancement of the concentrations and the reduction of the size of silica particles.
(4) The addition of silica particle to PTMSP can increase free volume by disruption of polymer chain packing.
(5) Silica particle can enhance the flexibility of the backbone of PTMSP.

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