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Molecular simulation study of penetrant gas transport properties into the pure and nanosized silica particles filled polysulfone membranes

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ABSTRACT

The simulation techniques have been utilized to investigate the structural, physical and separation properties of penetrant gases including oxygen, nitrogen, carbon dioxide and methane through pure and nanosized silica particles filled polysulfone (PSF) membranes. Molecular dynamics (MD) and grand canonical Monte Carlo (GCMC) simulations were performed by employing the COMPASS force field to estimate the diffusivity and solubility of the gases into the membrane. The parameters such as fractional free volume, average cavity size and cavity size distributions of pure and silica-filled PSF are calculated using an energetic based cavity-sizing algorithm. These parameters for the filled membrane are higher than those of pure PSF and increase with the amount of the filler content and as a result, the diffusion coefficient, solubility and permeability of penetrant gases in silica-filled PSF membranes are greater than pure PSF membrane. The simulated results are in agreement with the available experimental data.

1. Introduction

In the last two decades, a significant improvement have been made in the performance of membranes based polymeric materials for the gas separation and understanding of a meaningful relationship among their structural and transport properties. Polymeric membranes are more common and economical than the other conventional membranes in industrial separation of gas mixtures [1–6]. However, their application is limited by two essential parameters, gas selectivity and permeability, which highly affect their performance. In addition, their segmental flexibility, at high temperature limits their ability to discriminate similar-sized penetrants and loss of performance [2,7–12]. Inorganic membranes such as molecular sieve materials, zeolites, single wall carbon nanotubes (SWCNTs) and multiwall carbon nanotube (MWCNTs) were fragile structures, difficult and expensive fabrication stages, which restrict their applications in the industrial scale. Therefore polymeric membranes are still in attention, but their chemical structure must be modified to improve their performance [13–21].

To capture the advantages of organic and inorganic membranes (for instance, the flexibility and processability of polymers, and the selectivity and thermal stability of the inorganic membranes), the hybrid materials which are known as polymer–inorganic nanocomposite materials are used [1,7–9,12]. Generally, to improve the gas transport properties of glassy or rubbery polymer membranes, the nanoscaled particles such as nonporous silica, molecular sieve, zeolites, nanotube, TiO_2 and ZrO_2 are added [22,23]. Various factors such as (a) characteristics of each component in nanocomposite membranes (for instance, concentration, particle size and filler shape and degree of polymerization of polymer), (b) the degree of compatibility between nanoparticle and polymer matrix which is related to the amount of interaction energy between particles and polymer, (c) presence or absence of interfacial defects, (d) morphology and (e) fabrication process of nanocomposite membrane, have a considerable influence on gas transport behaviors of polymer/inorganic mixed-matrix membranes (MMMs) [24,25]. For example, in chemical industry, for the separation of hydrocarbons from their mixtures poly(1-trimethylsilyl-1-propyne)[PTMSP] was suggested as an appropriate polymeric membrane, because this polymer is extremely permeable to hydrocarbons and has high hydrocarbon/permanent gas selectivity, but the poor chemical resistance of this material due to its solubility in all liquid hydrocarbons, leads to the prohibition of its usages as an industrial membrane [26]. To overcome this problem, an alternative acetylene based polymer, poly(4-methyl-2-pentyne) [PMP] membrane was used, because PMP is stable against condensed hydrocarbon vapors, but unfortunately the organic-vapor/permanent-gas selectivity and permeability of PMP are lower than those of PTMSP. To obtain the industrial nanocomposite membrane with high stability against condensed hydrocarbon vapors

Abbreviations: PSF, pure polysulfone; PSF/*x*vol% silica, nanosized silica particles filled polysulfone membranes

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and high permeability and selectivity as well, the nonporous, nanosized silica filler was added to PMP and the permeability and selectivity of PMP as a membrane was increased [26]. This is the advantage of adding filler to pure polymer to improve its separation performance. Ahn et al. [27,28] reported the gas transport behavior of micropoeous (PIM-1)/silica and polysulfone/silica. They investigated the density, thermal stability and nanostructural morphology of composite and found that by adding nonporous silica particles to the neat polymer matrix, the free volume and volume of the void cavities of membrane increases and this modification enhances the penetrant permeability coefficients of the nanocomposites. Cao et al. [29] compared the gas separation performance and morphology of the neat poly(vinylidene fluoride)[PVDF] membrane and the PVDF composite membranes with nanosized TiO_2 particles. They evaluated the permeability of membranes by using the instrumental analysis (such as atomic force microscopy (AFM), scanning electron microscope (SEM) and x-ray diffraction (XRD)). They found that these nanosize particles obviously affected the performance and structure of the PVDF membranes. Kim et al. [30] prepared and characterized the novel nanocomposite membranes containing single walled carbon nanotubes functionalized with long chain alkyl amine (to facilitate the dispersion of the filler in the continuous phase of blend) and polysulfone matrix. They found that by increasing the weight fraction of carbon nanotubes in nanocomposite, both permeabilities and diffusivities of H_2, O_2, CH_4 and CO_2 in the membranes was increased. Wahab et al. [31] investigated the use of nanosized silica as the fillers in polysulfone to construct the asymmetric hollow fiber mixed matrix membrane (HFMMM). They observed that by adding a small amount of silica particles (0.1 wt%) into polysulfone, the selectivity of CO_2 and CH_4 of this composite was higher than the pure polysulfone. They also found that the addition of about 10 wt% of these particles tends to form aggregates and create void spaces or pathways for slow gases to permeate faster. These nanosized particles increased the permeability of CO_2 in comparison to the pure polysulfone for all samples and increased their glass transition temperature.

The empirical investigation of gas permeation performance of pure and filled polymer as membranes is difficult, time consuming and costly or needs obtaining special parameters in the critical conditions (such as high temperature and high pressure) [32–36]. On the other hand, by applying the considerable improvements in the computational calculations and using this assumption that the motions of atoms can be described by Newtons' laws and the interactions among the atoms can be calculated by using the existing empirical potential functions, the molecular dynamics (MD) simulation has provided a general and high efficient method to simulate various natural processes at the molecular level [36–41]. For instance, Chang and Kim [42] performed the molecular dynamics (MD) simulation to study the diffusivity and swelling of epoxy materials with respect to temperature and moisture concentration. Hu et al. [36] investigated the diffusion coefficient and sorption isotherm (or solubility) behavior of the CO_2 and CH_4 in coal. This group calculated the diffusion coefficient of these gases by the MD simulation in the order of 10^{-9} m^2/s and obtained the sorption isotherm by applying the grand canonical Monte Carlo (GCMC) method. Their results were in close agreement with the experimental data. Yang et al. [43] and Guo et al. [44] applied a methodology based on GCMC and *NVT* ensemble equilibrium MD techniques to simulate the ethanol/water system in contact with silicalite crystal and NaA zeolite, respectively, and calculated the mixture adsorption, diffusion and separation characteristics of these systems. Pavel and shanks [45] applied the MD simulation technique by utilizing NVE ensemble to evaluate the transport properties of oxygen and carbon dioxide as small molecule penetrants in models polyester blends of bulk amorphous poly(ethylene terephthalate) and related aromatic polyesters in a range of temperatures (300, 500 and 600 K).

In several studies, many researchers applied molecular simulation to the model systems to predict the transport properties (solubility, diffusivity and permeability) of various gases into the desirable nanocomposite polymeric membranes [26,46–49]. For example, Odegard et al. [50] simulated the silica nanoparticle/polyimide composites with various nanoparticle/polyimide interfacial treatments to predict their elastic properties. Zhou et al. [46] applied extensively the MD simulation technique to study the diffusion of gases into pure PTMSP and filled with silica particle.

Among all glassy polymers, the polysulfone (PSF) has received much attention as a polymeric based membrane and several researchers have extensively investigated the pure- and mixed-gas permeation properties of either pure PSF or filled by various nanosized filler to be used for gas separation [27,28,46,51–53]. The nonporous, nanosized silica provide a good improvement on transport properties of polymers especially PSF and the results obtained suggest that silica has higher influence on gas permeability of PSF compared with the other common fillers [51–53].

By considering the experimental results for the transport behaviors of the unfilled and silica nanoparticles filled PSF, it can be concluded that the loading of silica increases the diffusivity, solubility and permeability characteristics of gases in a nanocomposite PSF membrane, but at the molecular level, the interaction energies (repulsive and/or attractive) between silica nanoparticles and PSF, and the influence of silica particles on the mobility, structure, free volume of the polymer as the matrix of nanocomposite membrane is still need to be investigated. To provide a revealing insight into these points, it is interesting to undertake a study on the PSF/silica nanocomposite membranes by using a MD technique.

In this work, silica nanocomposite PSF membranes with different loading of nanoparticles (5, 10, 15, 20 vol%) have been simulated by the MD technique. In the first part of this article, some structural and thermal characteristics of nanocomposite membranes comprising of PSF with various amount of silica are investigated and in the next part, the transport properties of common industrial gases O_2, N_2, CO_2 and CH_4 are evaluated. Extensive search in the literature indicates that no comprehensive molecular modeling has been done to study the transport properties of gases for passage through the PSF membrane. These properties have determining effects on the behavior of these membranes when used in selecting and purification of gases. In addition not only the experimental data on the PSF membranes are scares but the characteristic properties of these membrane have not been thoroughly studied which can be attributed to several reasons such as complexity of the needed instruments and time consuming procedure of the experimental measurements. The MD and MC simulation methods proposed and utilized in this work indicated that, how effectively PSF membrane characteristics, namely; density, glass transition temperature, radius of gyration, chain end-to-end distance, fractional free volume and x-ray patterns of the membranes can be evaluated. Also the molecular simulation provided valuable information about the microstructure of the nanocomposite polymer membranes. The calculated properties such as end-to-end distance, free volume and *d*-spacing of the microstructural plates of the polymer chain which are considered as the most essential properties required in designing and construction of polymer membrane were obtained fast and computationally inexpensive, with high accuracy compared with experimental data. The simulated membranes, in this study, are denoted by PSF/*x*vol% silica. In these abbreviations, *x* refers to the volume percent of silica particles in each membrane.