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Investigating the permeability of atmospheric gases in polyisobutylene membranes via computer simulation

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ABSTRACT

The elastomeric polymer polyisobutylene has a remarkably low permeability to small penetrant molecules, so is often used in applications requiring a barrier to atmospheric gases. The permeation of the atmospheric gases O_2 and N_2 through polyisobutylene membranes has been investigated via a variety of computer simulation methodologies. These include particle insertion and molecular dynamics simulations. Parallel molecular dynamics simulations were carried out both for 3-dimensionally periodic (bulk) and 2-dimensionally periodic (membrane) samples of the polymer melt. Results are compared to both experiment and previous simulation works, with particular emphasis placed upon comparing the gas barrier properties of polyisobutylene with those of polybutadiene. The experimentally noted low permeability of polyisobutylene when compared with polybutadiene is reproduced well by 2-dimensional (membrane) simulations. It is found that the difference in permeability does not stem solely from a reduced solubility or diffusivity, but rather from a reduction in both.

1. Introduction

Butyl rubber is a copolymer of 98% isobutylene with 2% isoprene to allow for cross linking. It has a very low permeability to penetrant gas molecules. For example, the permeability of molecular oxygen through butyl rubber is approximately 15 times lower than that of polybutadiene, another elastomer [1]. This allows butyl rubber to be used as the impermeable linings for a range of items, from tyres to gas masks.

The gas transport properties of polyisobutylene have already been subject to some investigation via computer simulation. Müller-Plathe et al. [2] used a combination of equilibrium and non-equilibrium molecular dynamics simulations to determine the diffusivity of H_2, He, and O_2 in polyisobutylene and a Widom [3] particle insertion method to evaluate solubility. Gusev and Suter [4] used a transition state theory approach to describe the motion of gas molecules dissolved in polyisobutylene. More recently, Tsolou et al. [5] used a particle insertion technique to evaluate the sorption of gas molecules in polyisobutylene.

This work uses several different simulation methods to compare the transport of the diatomic atmospheric gases O_2 and N_2 within polyisobutylene (a good barrier polymer), and polybutadiene (a relatively poor barrier polymer) [1]. For completeness and to allow verification against previous works, transport properties in polyisobutylene are initially studied in the bulk phase, with molecular dynamics simulations used to determine the diffusivity and a particle insertion technique providing an estimate of the solubility. The novel method of Kikuchi et al. [6] was also used. This allowed the solubility and diffusivity to be studied in one molecular dynamics simulation cell. The gas transport properties of polybutadiene have been investigated in a previous work [7].

Gas transport in a polymer membrane is often described by the solution–diffusion model, which can be summarised as

$$P = SD. \tag{1}$$

The permeability (P) of a gas through a polymer membrane is equal to the product of the solubility (S) and diffusivity (D) of the gas in the polymer [8]. The solubility defines how much gas a polymer membrane can accommodate at equilibrium for a certain gas fugacity (f) external to the melt. In most cases $f \approx p$ where p represents the gas pressure external to the melt. The quantity of gas accommodated by the polymer film is measured by the concentration of absorbed gas molecules per unit volume of film (C). This defines solubility as

$$S = C/f \approx C/p. \tag{2}$$

The solubility of a gas molecule in a polymer melt has traditionally been probed using simulation via the particle insertion technique first suggested by Widom [3]. Widom insertion involves randomly inserting a gas molecule into a frozen sample of the polymer melt. The excess chemical potential associated

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with the insertion of 1 mol of gas molecules (μ_{ex}) is calculated from the net change in energy resulting from each insertion (E_i). This is shown in Eq. (3) where V is the system volume, k_BT is the thermal energy, and RT is the molar thermal energy. Angle brackets denote an average over a series of randomly positioned insertions, carried out in a series of independent melt configurations.

$$\mu_{ex} = -RT \ln\left[\langle V \rangle^{-1} \left\langle V \exp\left(\frac{-E_i}{k_BT}\right) \right\rangle \right] \tag{3}$$

This excess chemical potential affords the Henry solubility coefficient ($k_{H,cc}$) via the following equation:

$$k_{H,cc} = exp\left(\frac{-\mu_{ex}}{RT}\right). \tag{4}$$

The subscript H,cc indicates this Henry coefficient measures the solubility of the gas molecules as an equilibrium ratio of the concentration of gas absorbed within the melt to the concentration in the external gas phase. This makes $k_{H,cc}$ a unitless quantity. It is possible to convert $k_{H,cc}$ to the definition of solubility presented in Eq. (2) via the following equation:

$$S = k_{H,cc} \frac{T_{STP}}{T_{sim} P_{STP}} \tag{5}$$

where T_{sim} is the simulation temperature in Kelvin. P_{STP} and T_{STP} are the standard pressure and the standard temperature respectively (i.e. 101,325 Pa and 273.15 K).

As the particle insertions are carried out instantaneously, the Widom method does not allow for the characterisation of the dynamic response of the melt to the presence of a penetrant molecule [9]. A molecular dynamics simulation using a cell containing both a gas phase and a polymer phase could monitor this response. It has been noted by Kikuchi et al. [6] however that under NPT constraints the gas phase in such a cell has a tendency to shrink and eventually disappear. Kikuchi et al. suggested a solution to this problem by maintaining a stable gas phase via the use of 'virtual particles'. The virtual particles surround a 2-dimensionally periodic sample (i.e. a film) of the polymer melt on either side. These particles are 'virtual' as they have no interaction in any sense with the gas molecules and a purely repulsive interaction with the polymer melt. The virtual particles act to stabilise the simulation cell by communicating the action of the NPT barostat to the melt. The lack of interaction with the gas molecules means that the gas molecules are unaware of their presence meaning sorption is unaffected by their presence. Kikuchi et al. developed two different simulation cells which used virtual particles. KKF1 is an equilibrium model designed to probe sorption [6], whereas KKF2 has a concentration gradient imposed upon it to model permeation directly [10]. Previous work [7] has compared the results of KKF1 and KKF2 simulations. As a result of this work only the KKF1 simulation cell will be used during this investigation. An example of the KKF1 simulation cell is shown in Fig. 1.

The KKF1 model also allows diffusivity to be estimated within the same simulation cell as the solubility. Diffusivity (D) measures the mobility of gas molecules within a polymer melt. It is most often estimated via simulation by tracking the mean squared displacement of a small number of gas molecules moving freely within a polymer melt and the use of the following equation [12]:

$$\langle [r(t)]^2 \rangle = 6Dt^n \tag{6}$$

Fickian [13] diffusion for gas molecules within the polymer film is identified when $n=1$ in Eq. (6).

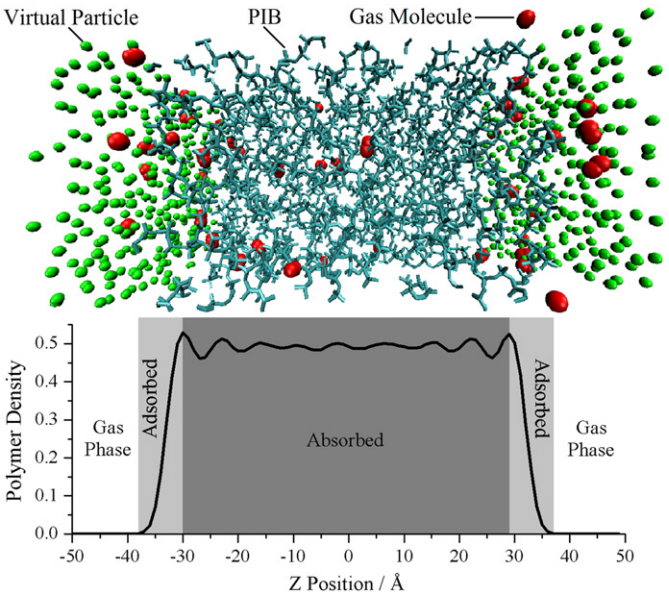

Fig. 1. An example [11] of the KKF1 simulation cell, with a plot below and to the same scale of the density of polymer atoms in arbitrary units. The plot has marked on it the zones used to classify the status of gas molecules, according to their z position. The relative sizes of the different components of the KKF1 cell have been chosen for clarity and do not represent any physical property.

2. Experimental method

2.1. Simulation details

Molecular configurations were initially created using the 'all trans chain' method of Hedenqvist et al. [14] with a 'skew start' [15] being employed to prevent chains from overlapping in periodic boundary conditions. Polyisobutylene was represented by 10 chains of 100 repeat units each. Interaction potentials were provided by the united atom (UA) force field of Tsolou et al. [5]. Gas parameterisations for O_2 and N_2 were provided by Travis and Gubbins [16] with unlike Lennard–Jones interaction parameters being calculated via the Lorentz–Berthelot combining rules [17,18]. The samples of polybutadiene (PBD) and polypropylene (PP) referred to in the results section are described by the UA force fields of Smith and Paul [19] and Martin and Siepmann [20]. Full details of methodologies employed to generate these polymer samples and undertake simulations using them can be found in previous works [7,21].

The chains were initially equilibrated in a rarefied state under NVT constraints in order to remove any artefacts from the generation of chain dihedral angles in the all trans state. The system was subject to an NPT ensemble compression to simulation conditions, an NVT ensemble thermal equilibration, followed by a long NPT ensemble equilibration. The DL_POLYv2 [22] simulation package was used to carry out all molecular dynamics simulations, with system temperature and pressure being constrained by the Nosé–Hoover method [23,24]. Thermostat relaxation times were 0.1 ps for all simulations. Barostat relaxation times were 0.4 ps for the bulk simulations and 1.0 ps for the two phase KKF1 simulation cells. Production run simulations were carried out for 40 ns with a 2 fs time step. Atomic configurations were output every 1 ps.

2.2. 3-dimensionally periodic (bulk) simulations

Solubility was approximated in the bulk state via a Widom [3] particle insertion method. A grid based insertion was used with a grid spacing of 1 Å. As O_2 and N_2 are linear molecules the insertions were also carried out in 3 orientations, with the vector connecting