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Study of nanostructure characterizations and gas separation properties of poly(urethane–urea)s membranes by molecular dynamics simulation

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ABSTRACT

Molecular dynamics (MD) and grand canonical Monte Carlo (GCMC) have been employed for understanding the effect of urethane and urea contents on gas separation properties of poly(urethane–urea)s (PUUs) membranes. Five membranes considered in this study are based on polytetramethylene-glycol (PTMG), isophorone diisocyanate (IPDI), and designed ratios of 1,4-butanediamine (BDA) to 1,4-butanediol (BDO) as chain extenders. The glass transition temperature (T_g), density, fractional free volume (FFV), X-ray diffraction (XRD) pattern and radial distribution function (RDF) were calculated to examine the nanostructure characterizations of the membranes. The permeations of five gas molecules (O_2, N_2, CO_2, CH_4, and H_2S) through the membranes were investigated. It was found that *d*-spacing, fractional free volume and phase separation of hard and soft segments increase with increasing urea contents in the membranes. The results indicated that the permeability of the membranes increases with increasing urea linkage in the polymer configuration.

1. Introduction

In recent decades, gas separation by polymeric membranes has attracted considerable interest due to their energy efficiency, low maintenance cost, non-environmental emission, compact, and modular procedure [1–4]. Polymeric membranes are used in various areas of industry such as separation of carbon dioxide and hydrogen sulfide in natural gas purification, recovery of hydrogen from ammonia in petrochemical industries, separation of biogas and landfill gas, production of oxygen and nitrogen enriched stream from air, and food packaging [1,5–7]. Enhancement of desirable properties of polymeric membranes mainly depends on understanding of the structure–property relationship. Today, thanks to impressive progress in computer hardwares and algorithms, molecular simulations can provide accurate understanding of the microscopic mechanisms that affect material performance, and even quantitatively predict desirable properties for complex materials systems of immediate industrial interest [8]. Poly(urethane–urea)s (PUUs) are multiblock copolymers consisting of soft and hard segments which have been investigated particularly for the possibility of tailoring their transport properties by varying their microstructures [9–11]. The soft segments consist of high molecular weight polyether/polyester groups and act as permeable matrix for gas molecules. The urethane/urea hard segments are formed by extending a terminal diisocyanate with a low molecular weight diol/diamine as a chain extender, and generally, this segment performs some kind of virtual crosslinks, reinforcing filler and suppressing membrane swelling [4,12]. Type and arrangement of these PUUs segments that determine the copolymer properties can be easily and widely changed to find the structure–property relationship as well as to design material for fitting the desired separation [4]. Gas permeation through PUUs membrane can be influenced by many factors such as molecular weight of polyol, type of soft segment, and type and proportion of hard segment [13–16]. In addition, the type of chain extender by changing phase-separated domain morphology, crystallinity, density, and glass transition of the membranes, can significantly change permeation properties of the membranes [17–19].

There have been a number of experimental studies on gas transport properties of PUUs membranes. Some of these studies focused on the effect of soft segment on gas permeation for example, Freeman et al. [20] and Lee et al. [21] studied the effect of polyol type on permeation and microstructure of PUUs membranes and reported the increase in fractional free volume (FFV) and gas permeability by increasing the polyether molecular weight and soft segment content. Grabczyk and Jankowski [22] investigated gas transport

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properties of segmented polyurethanes by varying the kind of soft segments. Some researchers concentrated on hard segment effects on gas transport. Galland and Lam [23] varied the molecular weight of the polyol and evaluated the effect of hard segments content on the polyurethane gas permeability. Knight and Lyman [19] changed the length of polyols and showed that the gas permeability of the copolyether–urethane–ureas increased in a linear manner with an increase in the polypropylene glycol segment molecular weight. Huang and Lai [14] studied the effect of hard segment content of hydroxyl terminated polybutadiene based on polyurethane membranes. Ruaan et al. [13] investigated the effect of the hard-segment content on selectivity and found that hydrogen bonding between hard segments was the cause of the failure of selectivity improvement. Also, the effects of chain extender have been investigated by Sadeghi et al. [1,24] and they reported the influence of chain extender type on morphology and gas permeation of PUUs membranes and concluded that permeability of gases increases with increasing the length of chain extenders. Their results indicate that by increasing the urea linkage the chain mobility of polymers, diffusivity and permeability of gases increase but the selectivity decreases.

In recent years, molecular modeling (MM) [25–34] simulations have progressed to such a level to predict the structural and transport properties of membranes [35–37], but few studies have been done on structure–property relationship of PUUs from molecular simulation viewpoints. Tao et al. [38] applied a combination of molecular dynamics simulation and the Monte Carlo method to calculate phase diagram and degree of phase separation of polyurethanes. Raghu et al. [39] performed molecular dynamics simulation to estimate the cohesive energy density, solubility parameter, and the surface properties of the PUs and to produce X-ray diffraction (XRD) patterns for determining the phase morphology of the PUs. Ren et al. [40,41] investigated the H-bonds in polyurethane with multiple donors and acceptors. Repakova [42] characterized molecular structures and properties of polyurethanes. Rahmati et al. [43] studied the effect of degree of polymerization and operation condition on physical and structural properties of polyurethane membranes by using configuration bias grand canonical Monte Carlo (MC) and molecular dynamic (MD) methods.

In this study, MD and grand canonical MC (GCMC) simulations were carried out to examine the effect of urethane and urea linkages content on the gas separation properties, fractional free volume, and phase separation of poly(urethane–urea)s membranes. Five novel poly (urethane–urea)s membranes consisting of polytetramethylene-glycol (PTMG), isophorone diisocyanate (IPDI), and different ratios of 1,4-butanediol (BDO) to 1,4-butanediamine (BDA) as the chain extenders were constructed. To avoid changing the other structural factors, only the diol and diamine linkages in the chain extender were varied and the other factors were kept constant. The poly(urethane–urea)s membrane, used in this work, is introduced by the generic name PUUX where X represents the percent of BDA content in BDA/BDO mixture. The density, fractional free volume, XRD patterns and radial distribution functions (RDF) were calculated to characterize and verify the proposed models and then the permeability of gases (O_2, N_2, CO_2, CH_4, and H_2S) through membranes was evaluated.

2. Theory

The permeation of gas molecules through polymeric membranes is usually represented in terms of the solution–diffusion model. This model has three steps: first, the gas molecules are adsorbed on the high-pressure side of the membrane surface. Second, the molecules diffuse through the polymeric membranes, and finally, they are desorbed at the surface of the low-pressure side of the membrane [44]. The permeability coefficient is given by

$$P_A = D_A \times S_A \tag{1}$$

where P_A is the permeability coefficient expressed in Barrer (1 Barrer $= 10^{-10}$ cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}), D_A (cm^2/s) is the diffusion coefficient, and S_A (cm^3 (STP) cm^{-3} of polymer cmHg^{-1}) is the solubility. D_A reflects the dynamics of the penetrant–polymer system and S_A represents a thermodynamic factor depending on the penetrant–polymer interactions; therefore the permeability shows the ease with which the gas crosses through the polymeric membrane [45]. The ideal selectivity for gas A over gas B is defined as the ratio of their pure gas permeabilities [46]:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left[\frac{D_A}{D_B}\right] \times \left[\frac{S_A}{S_B}\right] \tag{2}$$

where D_A/D_B is the diffusivity selectivity which strongly depends on the size difference of the penetrant molecules and the size-sieving ability of the polymer matrix. S_A/S_B is the solubility selectivity, which is controlled by the relative condensability of the penetrants and the relative affinity between the penetrants and the polymer matrix [47].

2.1. Diffusion

In molecular simulation, the most widely used method to calculate self-diffusion coefficients is by means of the Einstein relationship [48,49] which is expressed as

$$D_\alpha = \frac{1}{6N_\alpha} \lim_{t\to\infty} \frac{d}{dt} \sum_{i=1}^{N} \left\langle |r_i(t) - r_i(0)|^2 \right\rangle \tag{3}$$

where N_α is the number of diffusing atoms α, $r_i(t)$ and $r_i(0)$ denote the position vector of atom i at the time t and the initial time 0, and the angular brackets denote the ensemble average of the mean square displacement (MSD) of the inserted gas molecule i within a dynamics trajectory. The limiting slope of the MSD as a function of time can be used to estimate the self-diffusion coefficient of a molecule undergoing random Brownian motion in three dimensions. It should be noted that the Einstein relationship assumes a random walk for the penetrants. In short time, a regime of anomalous diffusion may occur, in which the diffusing particles may diffuse slowly and the MSD would be proportional to t^x with $x < 1$; or if the molecule encountered no other molecules, traveling ballistically, then the distance that it traveled would be proportional to the time interval and the MSD would increase quadratically with t. For sufficiently long times (i.e. the hydrodynamic limit), diffusing particles transit from anomalous to Einstein diffusion, so the Fickian regime occurs, in which the MSD is proportional to t^x with $x \approx 1$ [45].

2.2. Solubility

The solubility of small molecules in polymers is essential for the design and operation of polymer plants. There are several methods to employ a molecular mechanics force field for calculating solubility of the gas particles in polymers. One method is a measurement of Henry's law constant by calculating the non-bonded potential energies of the gas molecules randomly inserted in a periodic cell representing the sorbing medium [50]. Another widely used method is the grand canonical Monte Carlo (GCMC) method, which is based on the calculation of the energy change between the new configuration and the previous configuration. In this method, for accepting or rejecting configurational moves (rotation and translation of the sorbate molecule) as well as for insertion and deletion, Metropolis algorithm is employed [51].

In this work, both van der Waals and Coulombic forces were included in the sorption simulation. The total number of calculating steps was set to 1,000,000 and the probability of gas creation and