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Dissipative particle dynamics study and experimental verification on the pore morphologies and diffusivity of the poly (4-methyl-1-pentene)-diluent system via thermally induced phase separation: The effect of diluent and polymer concentration

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ABSTRACT

Dissipative particle dynamics (DPD) simulation was performed to construct the mesophase membrane morphologies of poly(4-methyl-1-pentene) (PMP) during thermally induced phase separation (TIPS). The PMP morphologies and their fluid diffusivities relationship was established using a mesoscale 3-D tetragonal-like structure construction. The effects of PMP concentration and the use of a single diluent (dioctyl phthalate, diphenyl ether, and dibutyl phthalate) or a mixed diluent on the pore morphology were compared. The diffusivity resistance was evaluated by comparing the mean square displacement of a hypothetical fluid bead through tetragonal-like morphologies in three normal directions. The 3-D morphology and density profile results revealed that larger pores were produced after TIPS when the PMP-diluent interaction was weaker. Radial distribution function analysis showed that poor diluent and high PMP concentration could form a coarsened structure with less interconnectivity, indicating more diffusion resistance. To verify DPD simulation results, PMP hollow fibre membranes (HFMs) were fabricated via TIPS, and HFM cross-sectional morphologies proved that the pore structures agreed with the DPD-simulation 3-D evolution diagram. The structure-fluid diffusivity resistance relationship was also confirmed by porosity measurements and gas permeation testing. The DPD simulation method is promising for the fabrication and design of gas-diffusive membranes, especially in terms of the rational selection of diluent and polymer concentration.

1. Introduction

Poly(4-methyl-1-pentene) (PMP) has excellent optical clarity, a high melting temperature, a low bulk density, good chemical resistance, and outstanding gas permeability. Thus, it is widely used in medical products, especially for oxygen enrichment [1–3]. To extend the application of PMP, asymmetric PMP membranes with dense surface skins and porous sections are often employed.

Thermally induced phase separation (TIPS) is a versatile method for preparing porous membranes because different porous structures can be obtained by adjusting the thermodynamic and kinetic parameters. This technique is based on the phase separation of a homogeneous polymer solution into polymer-rich and polymer-lean phases based on a polymer solubility change induced by either the temperature or solvent composition. The final porous membrane contains a continuous rigid structure resulting from the polymer-rich phase [4,5]. This method has been extensively applied to prepare microporous polymeric membranes [6], such as PMP [7,8], polypropylene (PP) [9], polyethylene [10], poly(vinylidene fluoride) (PVDF) [11], poly(lactic acid) (PLA) [12,13], and polyacrylonitrile (PAN) [14]. Controlling the membrane morphology is very important for tailoring these membranes to specific applications, as the pore size and distribution largely determines its function. Many factors affect the final membrane morphology, including complex thermodynamic and kinetic parameters; therefore, detailed information about the phase separation mechanics and morphological changes during fabrication may facilitate the achievement of the desired

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membrane structure and function.

Dissipative particle dynamics (DPD) method, an important bridge between the atomistic and macroscopic perspectives, has been applied to a large number of computer simulations of complex fluid systems, such as polymer melts and solutions [15–17]. It is easy to adjust the component concentration as well as the Flory-Huggins interaction parameter χ by manipulating the bead fraction and repulsion parameter α_{ij}. Moreover, because DPD is a particle-based simulation method, its use of a soft potential allows this method to reflect the phase separation process and even trace the change of the morphology evolution. DPD has the advantage of having length-scales that range from a few nm to a few μm and being able to model dynamical phenomena over time-scales of 1 ms or greater due to the Lennard-Jones soft potentials [15] and coarse-grained methods [18,19] employed.

DPD simulations are helpful for investigating the membrane fabrication process and membrane diffusion process. Wang's group [20–22] reported DPD simulations of a polyolefin-diluent system during TIPS and investigated the influence of the polymer chain and diluent structure on the mesoscale evolution. To obtain a comprehensive understanding of these phenomena, the evolution of the 3-D phase structures and structure factors of the polyolefin domains were compared. Dorenbos et al. [23] combined DPD with Monte Carlo (MC) simulations to estimate the water diffusion in the pore network of an amphiphilic membrane.

DPD has also been applied to model fluid diffusion through dense polymer membranes [24,25] and porous membranes [23,26]. The diffusion coefficient of a fluid can be calculated by evaluating the mean square displacement (MSD) of all fluid beads [27].

However, few studies on polyolefin porous membrane fabrication via TIPS have applied DPD simulations to relate the constructed membrane interconnectivity to its fluid diffusivity, even though the latter is conventionally considered the most important factor in the field of gas permeation membranes. Lloyd et al. reviewed and thoroughly discussed the thermal dynamics during microporous membrane formation via TIPS, including the phase separation mechanism [9,28], thermodynamic polymer-diluent interactions [29], polymer chain crystallization kinetics [30], diluent properties [31,32], cooling rate and additives [33]. Most other published work about PMP microporous structure fabrication via TIPS has experimentally investigated the thermodynamic properties of the PMP-diluent system, PMP crystallization properties, and pore morphology evolution (pore size and porosity) [7,8,34,35], omitting a detailed discussion of the effects of pore interconnectivity and distribution on the gas diffusion properties. Therefore, using DPD simulation to predict the pore structure formation of the PMP-diluent system during TIPS can provide important information on the 3-D pore distribution, phase separation evolution, and pore interconnectivity. In addition, the effects of the polymer-diluent interaction, polymer chain properties (chain branching, fixed chain, and chain distribution), polymer concentration, additives, and mechanical load can be easily compared via specifying the bead construction, repulsion parameters, and boundary conditions.

Polyolefin hollow fibre membranes (HFMs) fabricated via TIPS for gas permeation have an asymmetric structure with a dense surface skin and porous support section. The dense surface skin is implemented to prevent pore wetting, especially in long-term gas-liquid membrane contactor processes, such as those in membrane oxygenators. Conventionally, the thickness of the dense surface skin is optimized in terms of the trade-off between an extended liquid breakthrough time and a lower diffusion resistance [36]. It is well known that the diffusion rate of the dense surface skin is much lower than that of the porous support [37], as theorized based on the open-pored, interconnected structures of the porous support section. Diversified pore morphologies can be obtained via TIPS, and the selections of the polymer concentration and diluent structure significantly influence the derived pore morphologies. Therefore, it is meaningful to investigate the morphology of the porous support section to explain its gas permeation properties. Using DPD simulations, it is possible to correlate the porous morphologies and their gas permeation properties. However, few works have investigated this relationship, except for some empirical diluent selection and membrane morphology observations [7,35,38].

The purpose of this work is to capture the evolution of the porous morphology of the PMP-diluent system during TIPS using DPD simulation and to directly investigate the diffusion resistance of the constructed morphologies. The effects of PMP concentration and the use of a single diluent (dioctyl phthalate (DOP), diphenyl ether (DPE), and dibutyl phthalate (DBP)) or a mixed diluent on the membrane formation process and pore morphology were compared and discussed. The relationship between the constructed PMP morphologies and their fluid diffusivities was evaluated by an anisotropic MSD analysis of fluid beads through a tetragonal-like structure with a longer pathway in a predefined direction. To verify the simulation results, PMP HFMs were fabricated through TIPS using different diluents and then subjected to morphology observation, porosity measurements, and gas permeation tests for oxygenator applications. The results show that DPD simulation can predict and provide helpful information for guiding membrane fabrication and may serve as a substitute for some laboratory measurements.

2. Methods and materials

2.1. DPD method

The DPD method solves the Newtonian equations of motion for particles subject to interparticle conservative, dissipative, and random forces [15], as shown in Eq. (1).

$$\frac{d\boldsymbol{r}_i}{dt} = \boldsymbol{v}_i;\qquad \frac{d\boldsymbol{v}_i}{dt} = \boldsymbol{f}_i \tag{1}$$

where $\boldsymbol{v}_i$ and $\boldsymbol{r}_i$ are the velocity and position of the ith particle, respectively. All the masses are normalized to 1 for simplicity, and the forces acting on a particle are a sum of three pairwise contributions: a conservative force $\boldsymbol{F}^C$, a dissipative force $\boldsymbol{F}^D$, and a random force $\boldsymbol{F}^R$, as shown in Eq. (2).

$$\mathrm{fi}=\sum_{j\neq i}(\boldsymbol{F}_{ij}{}^{C} + \boldsymbol{F}_{ij}{}^{D} + \boldsymbol{F}_{ij}{}^{R}) \tag{2}$$

where the sum runs over all other particles within a certain cut-off radius r_c. As this is the only length-scale in the system, we use the cut-off radius as our unit of length, $r_c = 1$. The different components of the forces are given by (Eqs. (3)–6).

$$\mathrm{fi}=\sum_{j\neq i}(\boldsymbol{F}_{ij}^{C} + \boldsymbol{F}_{ij}^{D} + \boldsymbol{F}_{ij}^{R})\boldsymbol{F}_{ij}^{C} = \begin{cases}\alpha_{ij}(1-r_{ij})e_{ij} & (r_{ij}<1)\\ 0 & (r_{ij}\geq 1)\end{cases} \tag{3}$$

$$\boldsymbol{F}_{ij}^{C} = \alpha\omega^{C}(r_{ij})e_{ij} \tag{4}$$

$$\boldsymbol{F}_{ij}^{D} = -\gamma\omega^{D}(r_{ij})(\nu_{ij}e_{ij})e_{ij} \tag{5}$$