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Investigation on the membrane formation process of polymer–diluent system via thermally induced phase separation accompanied with mass transfer across the interface: Dissipative particle dynamics simulation and its experimental verification

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ABSTRACT

A new dissipative particle dynamics (DPD) simulation methodology was established to investigate the membrane formation process via thermally induced phase separation (TIPS) accompanied with mass transfer across the interface between the polymer solution and the coagulation bath, taken into account polyvinylidene fluoride–diphenyl carbonate (PVDF–DPC) system. The simulation results indicated that the polymer solution mainly underwent spinodal decomposition and if the coagulation bath medium had a good compatibility with the diluent, diluent and bath particles could engulfed or ejected across the polymer solution–coagulation bath interface, which caused a thin and dense polymer layer was formed near the interface. In addition, as the coagulation temperature decreased, the spinodal decomposition became faster and the coagulation bath had a less effect on the membrane formation process. Second as the compatibility between the diluent and coagulation bath declined the mass transfer got indistinct and the polymer layer disappeared gradually. To verify above simulation results, experiments were performed, whose conclusions were consistent with the simulations. The observation and conclusion in this study are beneficial to the understanding of the membrane formation of polymer–diluent system via TIPS.

1. Introduction

Dissipative particle dynamics (DPD) is introduced in 1992 [1] as a novel method for performing mesoscopic simulations of complex fluids [2,3]. Since then, DPD has received significant theoretical refinement [4,5] and has been applied to fluid dynamics in numerous research areas such as material science and molecular biology, where membranes, vesicles, and molecular systems have been modeled [6,7]. In the preceding work of our group, the DPD simulation methodology in two and three dimensions is established first to gain a full fundamental understanding about the membrane formation kinetics via a thermally induced separation (TIPS) process, which can be regarded as one of the most important microporous polymeric membrane preparation techniques [8]. The simulation methodology has been acknowledged by several researchers that it should be considered as a supplement on the mesoscale between the microscale theories and the macroscale experiments [9–11], and the results are able to give some useful information to the researchers working on the membrane preparation [12].

The TIPS is a useful technique for the preparation of polymeric membrane and have been applied to many polymers, such as polypropylene and polyvinylidene fluoride (PVDF) [13]. During the TIPS membrane formation process, a homogeneous polymer solution at a high temperature is cast into a desired shape and then immersed in a coagulation bath at a low temperature to induce phase separation and solidification. Therefore, the heat transfer and the mass transfer across the interface between the polymer solution and the coagulation bath are both very important for the phase separation process and the ultimate membrane morphology [14–18]. In the previous studies, the methodology has investigated the dynamics of phase separation for a polymer–dilute system after a quench but has not included the interface between the polymer solution and the coagulation. As far as we know, several experimental studies have been performed with respect to this problem. Matsuyama in 2002 prepared poly(methyl methacrylate)

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porous membrane by immersion in the cooled nonsolvent and he found that a thin skin layer was formed due to the outflow of the diluent near the top surface contacted with the nonsolvent [19]. Rajabzadeh et al. prepared porous PVDF hollow fiber membranes by the TIPS process in a ternary system of PVDF/triacetin/glycerol. It was found that two kinds of structures including interconnected and spherulite structure were formed simultaneously, and the addition of glycerol was effective to increase the outer surface porosity [20]. Li et al. reported that different membrane morphologies can be obtained by changing the nonsolvent content in solvent and the coagulation bath temperature [21]. Cha and Yang employed the modified TIPS process to explore the possibility of structural control of the hollow fiber membranes prepared from PVDF/γ-butyrolactone system. With introducing solvent into coagulant, water flux and mean pore size increased due to the removal of the dense top layer and the suppressed crystal growth [22]. Ji et al. used liquid paraffin as the bore liquid for purpose of replacement of the droplets near the inner surface, which leaded to larger pores were formed at the inner surface of the hollow fiber [23].

However, the problem is still unresolved since the dynamic behavior for the evolution of polymer solution systems cannot be directly observed during experiments. Therefore as the first step to include the mass transfer and investigate the influence of the interface on the membrane formation, a hypothetical coagulation bath is added to form a new DPD simulation methodology and the polyvinylidene fluoride–diphenyl carbonate (PVDF–DPC) system that undergoes a liquid–liquid phase separation is chosen to investigate the membrane formation process via TIPS accompanied with mass transfer across the interface between the polymer solution and the coagulation bath. First, a new simulation methodology based on DPD is constructed, and then the influences of mass transfer on the membrane formation process are studied by the simulation methodology via varying the coagulation temperature and the coagulation medium (the interaction between the diluent and the coagulating bath). Finally experiments are carried out to verify the conclusions obtained by the simulations.

2. Methods and materials

2.1. DPD method

DPD adopted here is as the same as that used before and GW-VV algorithm is also employed here [8]. Besides that, a polymer chain here is constructed by connecting the adjacent particles via a harmonic spring,

$$\vec{F}^{S}_{ij} = -K r_{ij}, \tag{1}$$

where K is the spring constant. According to our preceding work, K is chosen to be 4.0.

In the simulation, the reduced units are used to decrease the computation complexity. The particle mass and the interaction range are chosen as units of mass and length, hence $r_c = m = 1$. The temperature is determined by the energy unit $(k_B T)'$. Due to the soft potential used in DPD simulation, the particle number density ρ should be larger than 3 to make sure that the equation of state can be fulfilled [3], nevertheless considering the computational efficiency, $\rho = 3$ is a proper choice. Note that all the quantities with superscripts are expressed in natural units, otherwise are in reduced units.

2.2. Physical length and time scales

The simulation system is composed of polymer (PVDF), diluent (DPC) and the (hypothetical) coagulating bath particles. Each particle represents a large number of atoms or molecules, while different beads are assumed to be equal volume, which is necessary to conform to the standard DPD model [3]. The molecular models of PVDF, vinylidene fluoridethe (VDF), DPC are shown in Fig. 1, together with their mappings on the coarse-grained DPD particle models. Table 1 shows the excluded volumes of molecules calculated by the molecular simulation method. Since it is almost impossible to obtain the exact molecule volume by experimental observation, the solvent-excluded volume raised from the solvent-excluded surface (also called Connolly surface) is always regarded as a valuable estimation of molecular volume [24]. It is observed from Fig. 1 and Table 1 that DPC molecule is a little bigger and composed of two parts. Therefore in this simulation, DPC molecule is regarded as two particles which are connected by a spring which is stronger than the polymer chain because the bond energy of C–O bond is bigger. Hence each bead represents a liquid volume of 110 Å^3, which approximately equals to the volume of two PVDF monomers and 1 bath particle. Because the simulated bead density is $\rho = 3$, a cube of $r_c'^3$ contains three beads and therefore corresponds to a volume of 330 Å^3. Thus, the physical size of the cutoff radius is found to be,

$$r_c' = \sqrt[3]{110 \times 3} = 10(\text{Å}) \tag{2}$$

According to Table 1, the molar mass of one bead is approximately equal to 110 g/mol, thus the unit mass in natural unit m' is 1.83×10^{-22} g. Substitute these values into Eq. (3) and the simulated time can be obtained in natural unit [8].

$$\tau' = r_c' \sqrt{\frac{m'}{(k_B T)'}} = 2.2 \times 10^{-10}(\text{s}) = 220(\text{ps}) \tag{3}$$

In the simulations, a constant time step of $\Delta t = 0.01\tau$ is used, thus, the time step of $\Delta t = 2.2$ ps.

2.3. Repulsion parameters

In this work, the conservative interaction parameter between the same type particles α_{ii} equals to 25 $k_B T$ to correctly describe the compressibility of water. The conservative interaction parameters of different types of particles α_{ij} are chosen according to the linear relation with Flory–Huggins parameter χ_{ij} by Eq. (3),

$$\alpha_{ij} = \alpha_{ii} + 3.497\chi_{ij} \quad (\rho = 3), \tag{4}$$

There are two ways to obtain Flory–Huggins parameter χ_{ij} for a polymer–diluent system: experiment [25] and molecular simulation

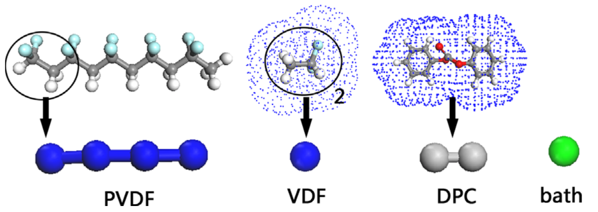

Fig. 1. Mapping model used in the simulation. (Upside: molecular models of PVDF, VDF, and DPC; downside: coarse-grained mapping models).

Table 1
Parameters of molecular volume and monomer number per particle of PVDF and DPC in the simulations.

Molecule	Monomer/molecular weight (g/mol)	Monomer/molecular volume V (Å^3)	Monomer number per bead
PVDF	64.1	55	2
DPC	214.2	220	1/2
Bath		110	1