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Multiscale simulation on the membrane formation process via thermally induced phase separation accompanied with heat transfer

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ABSTRACT

A novel methodology based on dissipative particle dynamics (DPD) simulation and the results of macroscopic mathematical models was established to obtain multiscale understanding on the membrane formation process via thermally induced phase separation (TIPS) method accompanied with heat transfer between the polymer solution and coagulation bath, taken into account polyvinylidene fluoride - diphenyl carbonate (PVDF-DPC) system. The phase separation process simulated by this methodology could be close to a real membrane formation process by adopting a linear cooling algorithm based on the macroscopic model results and providing much larger scales. The simulation results indicated that the temperature gradient in the polymer solution resulted from the heat transfer at the polymer solution-coagulation bath interface had a significant influence on the phase separation process, thereby different parts in the polymer solution possessed different cooling rates and coarsen time, which resulted in a microporous membrane with anisotropic structure. Secondly, as the polymer concentration increased, the system became much denser and the phase separation rate got lower due to a decline in the flexibility of the system. The results proved that a further deep understanding could be obtained by this methodology.

1. Introduction

Dissipative particle dynamics (DPD) is a particle-based mesoscale method that bridges the gap between microscopic and macroscopic simulation methods, which facilitates the studies of thermodynamic and dynamic properties of soft matter and polymer systems at physically interesting larger lengths and time scales [1–3]. In the preceding work of our group, a methodology based on the DPD simulation technique has been established for the first time to conduct some thermodynamic and dynamic researches on the membrane formation process via thermally induced phase separation (TIPS) method that has been considered as a prominent way to prepare porous polymer membranes [4–9]. This methodology has been acknowledged by several researchers to be an alternative effective approach to explore the membrane formation mechanism, and the simulation results enable researchers to examine the effects of various processing factors individually as well as visualize the development of membrane morphology [10–12].

In the membrane preparation by TIPS process, a homogeneous polymer solution with an elevated temperature is cast onto a substrate or spun, and then immersed in a coagulation bath that usually contains water. Since the temperature of the coagulation bath is below the spinodal line, there is heat transfer at the polymer solution – coagulation bath interface, thereby the polymer solution starts to separate into a polymer-rich phase and a solvent-rich phase. During a certain period of the phase separation, the growth of the two phases is influenced by the local cooling rate, and then the polymer-rich phase is solidified as a membrane matrix by crystallization or glass transition, while the solvent-rich phase develops pore structures. Consequently, the heat transfer at the polymer solution–coagulation bath interface is important for the structures and the properties of the resultant membranes.

Intensive researches have been conducted in plenty of literatures concerned the effects of the coagulation temperature and cooling rate on the membrane structures and properties. Several experimental results have shown that the quenching temperature

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could effectively influence the growth rate of polymer-lean phase as well as a high quenching temperature or a low cooling rate would lead to a larger pore size membrane in general [13–16]. However, the phase separation process via TIPS can hardly be observed by experimental methods. On the other hand, some macro mathematical models have been built to simulate the growth of the solvent-rich phase. The results have revealed the effects of the coagulation bath temperature or the cooling rate on the concentration and temperature profiles in polymer solution, which indicated that the droplet size could be simulated to predict morphologies of polymer membranes [17–19]. Nevertheless these model results can only reflect the temperature changes without the evolution of the phase separation process. Also, some attention has been paid to study the phase separation dynamics by mathematical modeling incorporating Cahn–Hilliard theory and Flory–Huggins theory, and the results have shown that an anisotropic morphology could be developed when a temperature gradient was imposed along the polymer solution sample [20–21]. Whereas, the results are not intuitive and the microscopic information could hardly be included.

In the latest work of our group, a hypothetical coagulation bath was added to investigate the membrane formation process via TIPS accompanied with mass transfer across the interface between the polymer solution and the coagulation bath, in which the homogeneous polymer solution was directly quenched to the low temperature without considering the cooling rate and the temperature gradients resulted from the heat transfer [7]. The quenching process of the previous methodology did not conform to the real process and the terminal of the phase separation could not be determined. Therefore in this work, the effect of heat transfer at the polymer solution-coagulation bath interface on the phase separation will be firstly discussed via a novel methodology that combines the DPD simulation method and the results of the macroscopic mathematical models from the literatures [17,19–22]. As mentioned above, the temperature gradient in the polymer solution resulted from the heat transfer during TIPS process can be calculated by those macro models and the results have shown that the temperature gradients are generally nearly linear, which means that the solvent-rich phase in different parts of the polymer solution can be regarded as possessing a linear cooling rate and having different time to develop. In this work, in order to be closer to the real membrane formation process and extend the application of this method further, the original methodology has been improved by adopting a linear cooling algorithm based on the macro model results and implementing the DPD simulations on a single graphics processing unit (GPU) to provide a much faster computation speed and larger scales [23]. Subsequently, the phase separation process via TIPS is simulated to analyze the effects of the temperature gradient and the polymer concentration on the membrane formation via TIPS on the basis of the new methodology, taken into account polyvinylidene fluoride - diphenyl carbonate (PVDF-DPC) system.

2. Method and methodology

2.1. DPD method

DPD was originally proposed by Hoogerbrugge and Koelman [24]. It is based on particle methods in which a “fluid” particle represents a small region of fluids or molecular groups that is larger than molecular scale, but is still macroscopically small. Particles interact with each other via soft potentials and their time evolutions are assumed to be governed by the Newton's equations of motion and GW-VV algorithm [1,25],

$$\begin{aligned}
r_i(t+\Delta t) &= r_i(t) + \Delta t v_i(t) + \frac{1}{2}(\Delta t)^2 f_i(t),\\
\tilde{v}_i(t+\Delta t) &= v_i(t) + \lambda \Delta t f_i(t),\\
f_i(t+\Delta t) &= f_i\left(r(t+\Delta t), \tilde{v}(t+\Delta t)\right),\\
v_i(t+\Delta t) &= v_i(t) + \frac{1}{2}\Delta t\left(f_i(t) + f_i(t+\Delta t)\right)
\end{aligned} \tag{1}$$

According to our previous work [4], $\lambda=0.65$ and $\Delta t=0.01\tau$ (τ will be defined in Section 2.2) are adopted to ensure the simulation having high efficiency and a better temperature control.

The pairwise interactive force acting on a particle i by particle j is characterized by three parts: the conservative force ($\vec{F}_{ij}^{C}$), the dissipative force ($\vec{F}_{ij}^{D}$), and the random force ($\vec{F}_{ij}^{R}$). All of the three forces are acting within a certain cutoff radius r_c (r_c is chosen as the length unit in the simulations, which will be illustrated in the following section). The conservative force is given by,

$$\vec{F}_{ij}^{C} = \begin{cases} \alpha_{ij}\left(1 - r_{ij}/r_c\right)\vec{e}_{ij}, & (r_{ij} < r_c) \\ 0 & \left(r_{ij} \ge r_c\right) \end{cases} \tag{2}$$

Where $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, $r_{ij} = \left|\vec{r}_{ij}\right|$, and $\vec{e}_{ij} = \vec{r}_{ij}/r_{ij}$. α_{ij} is the maximum repulsion strength between particle i and particle j as well as is the only one parameter in DPD simulations, which can be considered as a characterization of the interaction between the particles. As the interaction becomes weaker, α_{ij} gets bigger, as illustrated in Table 2. The connection between the simulation and the real system can be established by α_{ij} as shown in the literature [1]. The remaining two forces between the interacting particles are dissipative and random forces, and they couple together to form a momentum-conserving thermostat. They are respectively given by,

$$\vec{F}_{ij}^{D} = -\gamma\omega^D(r_{ij})\left(\vec{e}_{ij}\cdot\vec{v}_{ij}\right)\vec{e}_{ij}, \tag{3}$$

$$\vec{F}_{ij}^{R} = \sigma\omega^R(r_{ij})\theta_{ij}\vec{e}_{ij}, \tag{4}$$

where $\vec{v}_{ij} = \vec{v}_i - \vec{v}_j$, θ_{ij} is a random number with zero mean and unit variance. The noise level is taken to be $\sigma = 3.0$ for a better temperature control and the relationship between σ and γ is given by $\sigma^2 = 2\gamma k_B T$. The weight functions ($\omega^D\left(r_{ij}\right)$ and $\omega^R\left(r_{ij}\right)$) follow the relation $\omega^D(r) = [\omega^R(r)]^2$ to satisfy the fluctuation–dissipation theorem [24]. For simplicity, the general function form of $\omega^R(r)$ is,

$$\omega^R(r) = \begin{cases} (1-r) & (r < 1) \\ 0 & (r \ge 1) \end{cases}, \tag{5}$$

The polymer chain is constructed by connecting the adjacent particles via a harmonic spring,

$$\vec{F}_{ij}^{S} = -Kr_{ij}, \tag{6}$$

where K is the spring constant. According to the preceding work [7], K is chosen to be 4.0.

In the DPD simulations, the reduced units are used to decrease the computation complexity. The real particle mass m' and the

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

Molecule	Particle / Molecular volume V (Å^3)	Monomer number per bead
PVDF	2200	15
DPC	220	10