

Dissipative particle dynamics simulation on the polymer membrane formation by immersion precipitation

Xiao-Lin Wang, Hu-Jun Qian, Li-Jun Chen, Zhong-Yuan Lu*, Ze-Sheng Li

Institute of Theoretical Chemistry, Jilin University, Changchun 130023, PR China

Received 7 March 2007; received in revised form 31 October 2007; accepted 16 December 2007

Available online 23 December 2007

Abstract

The kinetics of membrane formation by immersion precipitation is investigated using dissipative particle dynamics (DPD) simulation method. We study the influences of varying the chain length (N) of the polymer composing the membrane, the solvent size in the polymer solution, and the nonsolvent size and amount in the nonsolvent bath on the liquid–liquid demixing process and the membrane morphology in detail. The results are analyzed in terms of the characteristic domain size (R) in the polymeric membrane. R is as a function of simulation time, which first decreases, then increases due to the changes of the number of the interfaces between membrane polymer and nonsolvent. Moreover, the occurrence from spinodal decomposition to late stage domain coarsening is faster for the system with $N = 40$ than $N = 100$. When we take the chain-like instead of the one-site solvent, R turns to be larger at the same simulation time for the same system. But when we enlarge the nonsolvent size, it is surprising that the nonsolvent can not diffuse into the polymer solution to exchange for solvent. In addition, the domain size increases with increasing the amount of the nonsolvent, especially in the R coarsening process.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Dissipative particle dynamics; Membrane formation; Immersion precipitation; Spinodal decomposition; Characteristic domain size

1. Introduction

In modern world polymeric membranes are widely used in industry [1–4]. Examples of industrial applications are micro-filtration, ultrafiltration, reverse osmosis and gas separation. Controlling the morphology of the membrane is of great importance in tailoring them to perform appropriately for specific applications, since it is the size and distribution of pores that largely determines their function. There are several ways to prepare porous polymeric films, such as sintering, stretching, track-etching and phase inversion [5–7]. The final morphology of the membranes obtained will vary greatly, depending on the properties of the materials and the process conditions. The majority of membranes is prepared by phase inversion, which can be induced in several ways, such as thermally induced phase separation (TIPS), air-casting of a polymer solution, precipita-

tion from the vapor phase and immersion precipitation. Among these techniques, immersion precipitation is the most efficient one. It is a technique that a polymer solution is first cast as a thin film on a support, and then is immersed into a nonsolvent bath. Precipitation can occur because the solvent in the polymer solution is exchanged for the nonsolvent due to the chemical potential imbalance. The polymer-rich phase is then solidified, after the phase separation attains a certain degree, in order to form the porous membrane. Therefore, the entire immersion precipitation process actually includes both liquid–liquid demixing and solidification.

Control over membrane structural formation is made challenging by the complex interplay of thermodynamics and kinetics during the immersion precipitation process. The thermodynamic basis of the immersion precipitation method, which is the phase diagram of the polymer/solvent/nonsolvent system, had been well developed [8,9]. Some experimental and simulation works about the kinetics of immersion precipitation process had also been done [10–29] Koenhen et al. [10] found that the growth rate of the precipitation front decreased with increasing polymer concentration. But no details of the

* Corresponding author. Tel.: +86 431 88498017; fax: +86 431 88498026.

E-mail addresses: luzhy@mail.jlu.edu.cn (Z.-Y. Lu), zeshengli@mail.jlu.edu.cn (Z.-S. Li).

phase separation processes could be detected. In 1979, Cohen et al. [11] developed the first mass transfer model of immersion precipitation. Since then, many improvements had been made by, for example, Smolders and coworkers [12,13], McHugh and coworkers [14–16], Gryte and coworkers [17–19], Kumar and coworkers [20], Mayes and coworkers [21], Kim and coworkers [22], and Munari and coworkers [23], in the past decades. Because there are many properties difficult to control experimentally, modelling and simulations have been applied on immersion precipitation process to provide a crucial insight and design guidance in recent years [24–29]. Termonia [24] used Monte Carlo simulation to study the effect of additives in the coagulant. Saxena and Caneba [25] used the Cahn-Hilliard equation incorporating the Flory-Huggins free energy model to simulate phase separation in the membrane. Furthermore, Akthakul [26,27] used the Lattice Boltzmann method to simulate the membrane formation. Maiti et al. [29] utilized a specific feature of MesoDyn that allows the concentration of the species in a model to be varied to simulate solvent exchange in nanoporous membranes. However, there still have been some arguments about the mechanisms of phase separation during immersion precipitation. Furthermore, a better understanding of the kinetics of immersion precipitation process is needed.

Dissipative particle dynamics (DPD) is suitable for this kind of system because it can involve spatial inhomogeneities over length-scales ranging between a few nm to a few μm , and exhibit dynamical phenomena over time-scales of 1 ms or greater due to the soft potentials employed [29]. Moreover, since DPD is the simulation method based on particles, thus the transport and distribution of nonsolvent particles in the polymer matrix are easily seen. It can reflect the phase separation process, and even capture the subtle change of the morphology successfully. In addition, due to the soft potential used in DPD model, the diffusion of the DPD particles is fast. This is an advantage of DPD since it can accelerate the simulation speed.

The objective of the current work is to capture the morphology during the first process of immersion precipitation, i.e., liquid–liquid demixing, and to investigate the effects of some physical parameters (i.e., the chain lengths of the polymer composing the membrane (N), the sizes of the solvent and the nonsolvent, the nonsolvent quality and quantity) on the membrane formation and morphology through DPD method. We follow a two-step strategy within the whole simulations: first we carry out the simulations to prepare different polymer solutions, then we use the final configuration obtained from the foregoing process to perform immersion precipitation by adding nonsolvent to the space above the polymer solution. The DPD model can predict the process of membrane formation and provide helpful information on the morphology of polymeric membranes.

2. Simulation method and model construction

In DPD, the time evolution of the interacting particles is governed by Newton's equations of motion [30]. GW-VV algorithm

[30,31] is used here,

$$\begin{aligned} \mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + 1/2(\Delta t)^2 \mathbf{f}_i(t), \\ \tilde{\mathbf{v}}_i(t + \Delta t) &= \mathbf{v}_i(t) + \lambda \Delta t \mathbf{f}_i(t), \\ \mathbf{f}_i(t + \Delta t) &= \mathbf{f}_i(\mathbf{r}(t + \Delta t), \tilde{\mathbf{v}}(t + \Delta t)), \\ \mathbf{v}_i(t + \Delta t) &= \mathbf{v}_i(t) + 1/2\Delta t(\mathbf{f}_i(t) + \mathbf{f}_i(t + \Delta t)). \end{aligned} \quad (1)$$

We choose $\lambda = 0.65$ according to Refs. [30,31] and $\Delta t = 0.01$ in order to ensure the simulation having the high efficiency and better temperature control. To further justify these two choices, we have tested the dependence of the system temperature on λ and Δt . λ is varied from 0.4 to 0.65, and Δt from 0.01 to 0.06. We find that with $\lambda = 0.65$ the time step can be selected as large as 0.06 without deviating from the constant temperature, as demonstrated in Ref. [30]. Moreover, the average temperature 0.99931 under the condition of $\lambda = 0.65$ and $\Delta t = 0.01$ is the best approximate value of the target temperature $k_B T = 1$.

Inter-particle interactions are characterized by pairwise conservative, dissipative, and random forces acting on a particle i by a particle j . They are given by:

$$\mathbf{F}_{ij}^C = -\alpha_{ij} \omega^C(r_{ij}) \mathbf{e}_{ij}, \quad (2)$$

$$\mathbf{F}_{ij}^D = -\gamma \omega^D(r_{ij}) (\mathbf{v}_{ij} \cdot \mathbf{e}_{ij}) \mathbf{e}_{ij}, \quad (3)$$

$$\mathbf{F}_{ij}^R = \sigma \omega^R(r_{ij}) \xi_{ij} \Delta t^{-1/2} \mathbf{e}_{ij}, \quad (4)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $r_{ij} = |\mathbf{r}_{ij}|$, $\mathbf{e}_{ij} = \mathbf{r}_{ij}/r_{ij}$, and $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$. ξ_{ij} is a random variable with zero mean and unit variance.

The pairwise conservative force is written in terms of a weight function $\omega^C(r_{ij})$, here we choose $\omega^C(r_{ij}) = 1 - r_{ij}$ for $r_{ij} < 1$ and $\omega^C(r_{ij}) = 0$ for $r_{ij} \geq 1$ such that the forces are soft and repulsive. Unlike the conservative force, the weight functions $\omega^D(r_{ij})$ and $\omega^R(r_{ij})$ of the dissipative and random forces couple together to form a thermostat. Moreover, they cannot be chosen arbitrarily. Español and Warren [32] showed the relations between the two functions,

$$\begin{aligned} \omega^D(r) &= [\omega^R(r)]^2, \\ \sigma^2 &= 2\gamma k_B T. \end{aligned} \quad (5)$$

This precise relationship between the two forces is determined by the fluctuation-dissipation theorem. We take a simple choice of $\omega^D(r)$ due to Groot and Warren [30],

$$\omega^D(r) = [\omega^R(r)]^2 = \begin{cases} (1 - r)^2 & (r < 1) \\ 0 & (r \geq 1) \end{cases}. \quad (6)$$

It should be noted that the choice of $\omega^D(r_{ij})$ is not unique, the simplest form adopted here is just because of its common usage in roughly all published works.

In our simulations we choose the cutoff distance of interaction, the particle mass and the temperature as $r_c = m = k_B T = 1$. The mass is set equal to unity, fixing the scale of mass. The cutoff distance r_c sets the length scale for the model. Correspondingly, the time scale in the simulations is defined by $\tau_0 = (m r_c^2 / k_B T)^{1/2}$. Performing the simulations in reduced units is a way to reduce the computation complexity. Due to the soft potential used in DPD simulations, the particle density should

Download English Version:

<https://daneshyari.com/en/article/638072>

Download Persian Version:

<https://daneshyari.com/article/638072>

[Daneshyari.com](https://daneshyari.com)