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Phase field simulations of early stage structure formation during immersion precipitation of polymeric membranes in 2D and 3D

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Abstract

The immersion precipitation process makes most commercial polymeric membranes, which enjoy widespread use in water filtration and purification. In this work, a ternary Cahn–Hilliard formulation incorporating a Flory–Huggins homogeneous free energy function is used to simulate the liquid–liquid demixing stage of the immersion precipitation process, which determines much of the final morphology of membranes. Simulations start with a non-solvent/solvent/polymer ternary system with periodic boundary conditions and uniform initial conditions with small random fluctuations in two-dimensional (2D). Results in 2D demonstrate the effects of M_{ij} (mobilities) and K_{ij} (gradient penalty coefficients) on phase separation behavior. A two-layer polymer–solvent/non-solvent initial condition is then used to simulate actual membrane fabrication conditions. 2D and 3D simulation results show an asymmetric structure of membrane morphology, which strongly agrees with the experimental observation. Then this system is coupled with the Navier–Stokes equations to model hydrodynamics in two dimensions. The results show that fluid flow destabilizes the top layer of membrane.

Keywords: Immersion precipitation; Polymeric membrane; Ternary Cahn–Hilliard; Spinodal decomposition; Fluid flow

1. Introduction

Polymeric membranes have been developed for a variety of industrial applications, including microfiltration, ultrafiltration and reverse osmosis [1]. Each application imposes specific requirements on the membrane material and pore structure. The final morphologies of the membranes will vary greatly, depending on the properties of the materials and the processing conditions. Most commercial membranes are prepared by the immersion precipitation process. In this process, a homogeneous polymer solution is cast on a substrate and then immersed into a coagulation bath containing a non-solvent (usually water). The non-solvent begins to diffuse into the polymer solution and the solvent begins to diffuse into the coagulation bath, while the polymer diffuses very little due to its low mobility. The inter-diffusion of non-solvent and solvent brings the composition of the polymer solution into the miscibility gap of the corresponding ternary phase diagram. Hence, the homogeneous polymer solution starts to decompose into two phases: a polymer-rich phase and a polymer-poor phase. At a certain stage during phase demixing, the polymer-rich phase is solidified into a solid matrix by crystallization or vitrification, while the polymer-poor phase develops into pores. The performance of this membrane depends largely on the morphology formed during phase separation and solidification.

The thermodynamic basis of immersion precipitation, which is the free energy function and the phase diagram of the non-solvent/solvent/polymer ternary system, is well developed [2–4]. Some mass transfer models in 1D have been done to understand the kinetics of the immersion precipitation process before phase separation happens [5–9]. A small number of studies have looked at the onset of phase separation. Saxena and Caneba [10] used a 1D phase field model based on the Cahn–Hilliard equation incorporating the Flory–

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Nomenclature

D_{ij}	diffusivity of species i in the matrix of species j
E	energy
f	homogeneous free energy density
F	total free energy
$\vec{F}$	force per unit volume
Fp	dimensionless force parameter
K_{ij}	gradient penalty coefficient
K_ij	dimensionless gradient penalty coefficient
L	characteristic length scale of simulation domain
m_i	degree of polymerization of component i
M_{ij}	mobility of species i due to a gradient in species j chemical potential
M_ij	dimensionless mobility
R	gas constant (8.314 J/K/mol)
Sc	Schmidt number
t	time
$\overline{t}$	characteristic diffusion time scale of polymer ($L^2/\langle D_{pp}\rangle$)
$\tilde{t}$	dimensionless time
T	temperature
u	velocity in x direction
v	velocity in y direction
v_{site}	volume per reference site
V	total volume

Greek letters

φ_i	volume fraction of component i
λ	dominant wavelength
μ_i	chemical potential of component i
ω	vorticity
Ψ	dimensionless Flory–Huggins free energy density

Subscripts

p	polymer
s	solvent
n	non-solvent

Huggins free energy model to simulate phase separation in the membrane and showed 1D periodicity of concentration profile during the initial stage of decomposition. Barton and McHugh used the Cahn–Hilliard equations in a ternary system, but the concentrations are constrained to change only along a tie line across the miscibility gap, to study membrane formation by thermal quenching, and showed the coarsening rate of the particle size in the late stage follows the 1/3 power law [11–13]. In 2002, Akthakul et al. [14] showed experimental evidence of pore formation via spinodal decomposition in asymmetric membrane formation and then used the Lattice Boltzmann method to simulate membrane formation in 2D [15]. The simulation results captured motion of the interface between coagulation bath and polymer solution and the asymmetric morphology of membranes.

However, the Lattice Boltzmann method is strongly anisotropic, causing the final result to exhibit a morphological bias in the diagonal direction. Furthermore, Lattice Boltzmann requires a regular lattice, which makes it difficult to apply on the irregular simulation domain. Extending to 3D is also not straightforward since there is no regular lattice which could produce isotropic results in 3D. The inherently 3D nature of the process and final product, with connected solid and pore phases, requires a 3D model which can simulate the whole process in the ternary system.

Toward that end, the present work provides a methodology capable of simulating the entire process of membrane structure formation via spinodal decomposition [14]. A single set of partial differential equations simulates the initial diffusion and liquid–liquid phase separation steps using a complete ternary description of the system in two and three dimensions. This will later be extended to solidification of the polymer-rich phase to lock in the membrane structure. In the model, a ternary Cahn–Hilliard phase field formulation incorporating a Flory–Huggins homogeneous free energy function is used to model the phase behavior in this heterogeneous kinetic system. The theory of phase field is discussed in Section 2, including the derivation of the governing equations and the assumptions of the model. Then, the simulation results are presented in Section 3. The first simulations presented begin with uniform initial conditions with small random fluctuations in 2D, later simulations start with two-layer polymer–solvent/non-solvent initial conditions to simulate actual membrane fabrication conditions in 2D and 3D. Then, hydrodynamic effects are added to the 2D system by coupling with fluid flow driven by surface tension. Model limitations and future work are discussed in 4. Finally, the work is concluded in Section 5.

It is worth noting here that the present work is limited to uniform mobilities and viscosities, though with different mobilities for the polymer and solvent. While non-uniform properties are necessary for accurate simulation of the physical system, many important features of the process can be explained by this model even with uniform properties. Furthermore, non-uniform mobility in particular adds considerable complexity to the system behavior, and will be addressed in a separate paper.

2. Theory

2.1. Ternary phase field model

In modeling studies on immersion precipitation, it is common to separate the initial diffusion and phase separation steps into two distinct processes since they appear to be very different phenomena. However, they share the same underly-