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A model for wet-casting polymeric membranes incorporating nonequilibrium interfacial dynamics, vitrification and convection

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ABSTRACT

A new model is developed for wet-casting polymeric membranes that address how the concentrations at the interface between the casting solution and nonsolvent bath adjust from initial nonequilibrium to equilibrium values on the binodal. Properly describing the evolution of the interface concentrations enables this new model to predict vitrification, which has been observed experimentally but not predicted heretofore. This new model also incorporates densification-induced convection that arises owing to density changes associated with the concentration gradients and contributes to the mass-transfer fluxes. The predictions for the cellulose acetate, acetone, and water system indicate that densification-induced convection can increase the mass-transfer flux by nearly two orders-of-magnitude shortly after initiating wet-casting. This increased mass-transfer flux can have a marked effect on the properties of the functional layer of asymmetric membranes that is formed early in the casting process. The predictions for initial casting-solution thicknesses of 75 and 125 μm are markedly different. When densification-induced convection is included, the 125 μm film is predicted to enter well into the metastable region, thereby allowing supersaturation that promotes macrovoid defects. Hence, this new model provides an explanation for the effect of casting-solution thickness on the occurrence of macrovoids.

1. Introduction

The wet-casting process is a phase-inversion method for polymeric membrane formation. In the wet-casting process a homogeneous polymer solution (casting solution) is prepared with polymer and solvent (and sometimes nonsolvent) and cast into a thin film or hollow fiber geometry. The casting solution then is immersed into a precipitation bath of nonsolvent. Due to the concentration differences, solvent is transferred from the casting solution into the bath, while nonsolvent is transferred from the bath into the casting solution. As a result, the local composition at any point in the casting solution changes with time. The homogeneous casting solution eventually becomes thermodynamically metastable or unstable, which leads to phase separation and formation of the solid polymeric matrix of the membrane. The structure of the membrane is strongly dependent on the local composition in the casting solution. However, measuring this local composition as a function of time and position is very difficult due to the very rapid change within the thin film of casting solution [1]. Therefore, a mathematical model is useful for providing insight into the influence of various parameters that determine the structure and performance of a membrane. Prior modeling studies of the wet-casting process have made limiting and in some cases tenuous assumptions that are addressed in this study.

The first attempt to model the wet-casting process was made by Cohen et al. [2]. Their description of the mass-transfer process was based on a steady-state diffusion model. Several researchers [3,4] have pointed out that this assumption is not reasonable.

McHugh and Yilmaz [4] improved on this model by using an unsteady-state pseudo-binary mass-transfer formalism whereby any diffusion of the polymer is ignored. Hence, their governing equations are simplified by assuming zero polymer flux in the casting solution and negligible mass-transfer dynamics in the nonsolvent bath. Moreover, the pseudo-binary formalism implies no convective contribution to the mass-transfer flux within the casting solution.

A convective contribution to the mass-transfer flux can arise during membrane casting owing to local density changes associated with the concentration gradients created by the mass transfer. In principle, this densification can cause either free convection that arises owing to buoyancy effects or can cause bulk flow in the absence of any gravitational body forces because of the interplay

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between the density and velocity dictated by the continuity equation. Free convection is not possible in conventional wet-casting owing to the very large solution viscosity and thin liquid film. However, convection can arise during wet-casting owing to the solvent removal and nonsolvent addition that causes the polymer molecules to assume a more compact configuration. The terminology *densification-induced convection* used henceforth in this paper will refer to this bulk flow effect that can arise solely due to density changes in the absence of any buoyancy effects.

Reuvers et al. [5,6] further improved on the previous models by coupling the bath dynamics with the diffusion in the casting solution. They utilized a phenomenological approach based on nonequilibrium thermodynamics to describe the coupling effect of diffusion in both the casting solution and nonsolvent bath. Their detailed and appropriate description of the polymeric system was a significant improvement that has made their model a standard for many successive studies. However, they assume an infinitely thick casting solution and ignore any densification-induced convection, although they mention a calculation methodology for incorporating a finite thickness. The assumed continuity of mass fluxes at the interface between the casting solution and nonsolvent bath in their model greatly reduces the computational effort, but is valid only when the thickness of the casting solution does not change owing to densification-induced convection. They claim that the measured onset time for phase separation shows close agreement with their model predictions. However, since their model assumes that the interfacial composition of the casting solution is instantaneously located on the binodal, it cannot accurately predict the onset time for phase separation. This assumption implies that the phase separation should start nearly immediately rather than after the relatively long time (several seconds) determined by their experiments.

Tsay and McHugh [7] improved on the model of Reuvers et al. [5,6] by allowing for a variable interfacial composition with time. Moreover, they formulated the ternary conservation of species equations in terms of mass fluxes relative to the volume-average velocity. If one assumes Flory–Huggins theory, the volume-average velocity is identically zero. Hence, the approach of Tsay and McHugh avoids having to explicitly account for any densification-induced contribution to the mass-transfer flux since this is implicitly incorporated into the diffusive fluxes in their describing equations. However, this approach is valid only for an equation-of-state for which the volume-of-mixing is identically zero. Indeed, it might be expedient to invoke Flory–Huggins theory to describe the solution thermodynamics while using an empirical equation for the density that does not imply that the volume-of-mixing is identically zero. Moreover, the approach of Tsay and McHugh does not permit assessing the importance of the densification contribution to the mass-transfer flux since it is implicitly incorporated into the diffusive flux terms. This assessment would require comparing the model predictions with and without the densification contribution to the mass-transfer flux. The only way to suppress the contribution of densification to the mass-transfer flux in the approach of Tsay and McHugh would be to assume a constant mass density; however, this would compromise the ability of the model to predict changes in the casting-solution thickness. The manner in which the composition at the interface between the casting solution and nonsolvent bath changes from its initial value to an equilibrium concentration on the binodal is also not considered in the model of Tsay and McHugh. Kesting [8] reports that a significant polymer accumulation can occur at the interface of the casting solution that can lead to skin formation via vitrification. Predicting the latter requires an accurate description of the interfacial composition from the inception of the casting process.

Radovanovic et al. [9,10] showed that the description of diffusion in the bath made by Reuvers et al. [5,6] is in error and proposed a modified version of the model. Their resulting diffusion model and experimental results showed that the structure of a polysulfone membrane strongly depends on the onset time of demixing.

Cheng et al. [11] further modified the model of Reuvers et al. [5,6] by allowing for a finite casting-solution thickness. Although an advanced numerical method is used in their calculations, they do not allow for any densification contribution to the mass-transfer fluxes.

Fernandes et al. [12] presented a simple mathematical model using the Fickian diffusion equation to describe the wet-casting process. In spite of utilizing an advanced computational method, their model is overly simplified since it neglects the coupling effects of diffusion and assumes an ideal solution.

This brief review of prior wet-casting studies indicates that no model has properly allowed for the transition of the concentration at the casting solution interface between its initial nonequilibrium to an equilibrium composition on the binodal. This will result in an inaccurate description of the properties of the functional layer of the membrane since these are determined shortly after the initiation of the casting process. In particular, it will compromise the ability of a model to describe vitrification that can occur very rapidly after the initiation of casting. This review also indicates that only the model of Tsay and McHugh [7] has accounted for the effect of densification on the mass-transfer flux. However, their approach is restricted to the equation-of-state implied by modified Flory–Huggins theory since it formulates the mass fluxes relative to the volume-average velocity. Moreover, it does not permit assessing the relative contribution of densification to the mass flux. Clearly an improved model is needed for the wet-casting process that properly accounts for the transition from the initial nonequilibrium to a local equilibrium condition at the interface between the casting solution and nonsolvent bath and provides a general framework for incorporating densification-induced convection.

Recently, Lee et al. [13] developed a rigorous method for obtaining an explicit equation for the mass-average velocity that arises owing to densification and thereby contributes to the total mass-transfer fluxes. They applied their method to develop a coupled heat- and mass-transfer model for the dry-casting process for membrane formation. Their improved model was shown to agree more closely with the real-time data of Shojaie et al. [14] for the instantaneous overall casting solution mass and surface temperature and for the time required for the onset of phase separation for the dry-casting of the cellulose acetate, acetone, water system. This argues strongly for applying their method for incorporating densification-induced convection into an improved wet-casting model. However, this is not a trivial extension of the work of Lee et al. [13] for the dry-casting process since the wet-casting process presents two major complications. The first is that the mass-transfer dynamics in the nonsolvent bath are more complex than those encountered in the dry-casting process. The second is that an appropriate methodology must be developed to account for the change in the interfacial concentrations from their initial nonequilibrium values to a composition located on the binodal. This paper then is focused on the development of an improved wet-casting model that results in the following novel contributions: (1) a description of the mass-transfer dynamics in the nonsolvent phase justified by scaling analysis; (2) a proper description of the transition of the composition at the casting solution interface from nonequilibrium to local thermodynamic equilibrium; (3) a generalized framework for determining the mass-average velocity arising from densification; (4) the prediction of vitrification at the upper membrane surface in agreement with prior observations; and (5) an explanation for the effect of initial casting-solution thickness on the propensity to form macrovoid pores.

This paper is organized as follows. First, the model equations incorporating densification-induced convection are described. The