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Predicting extent of anisotropy in anisotropic hollow fiber membrane formation

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ABSTRACT

The relationships between processing conditions and ultimate membrane properties that exist in the spinning of hollow fiber membranes are not fully understood. To address the need for a widely applicable fiber spinning model, the present work builds on the thin filament analysis (TFA) model of the fiber spinning process and predicts the variation of fiber size, velocity, and temperature in the draw zone, including the effects of surface tension. By modeling concentration gradients in the draw zone, this model also predicts both the extent of anisotropy (portion of membrane thickness containing a pore size gradient) and degree of anisotropy (indicative of the pore size range across the membrane thickness). For typical hollow fiber membrane spinning, predicted membrane extent of anisotropy is most sensitive to the diffusion coefficient. The predicted degree of anisotropy is most sensitive to the viscosity activation energy, affected significantly by the diffusion coefficient and spinning temperature, and affected slightly by the air gap length. Trends in the model-predicted and experimental measurements of final fiber outer diameter, ratio of outer to inner diameter (OD/ID), and extent of anisotropy agree. While model sensitivity studies show that surface tension can reduce the rate of fiber elongation, it has little effect on the predicted degree and extent of anisotropy. Furthermore, this analysis allows prediction of counter-intuitive concentration changes associated with temperature dependence of the diluent vapor pressure: for some cases, the degree of anisotropy can increase and then decrease along the draw zone during spinning. Reducing the dependence of vapor pressure on temperature eliminates this phenomenon.

1. Introduction

Hollow fiber spinning processes are important to a number of applications. Hollow fiber membranes in particular are of interest commercially, with applications such as bioseparations (dialysis and virus removal from blood), gas separations (purification of natural gas), and membrane contactors (alternatives to gas absorbers and liquid/liquid extraction columns) at the forefront of research. However, many of the relationships between hollow fiber membrane spinning conditions and the final structure and properties of a given membrane are poorly defined. As a result, membrane optimization is a trial-and-error process involving costly and time-consuming experimentation [1]. Development of a model to predict membrane macrostructure (inner and outer diameter) and microstructure (porosity, pore size, pore size distribution, and membrane anisotropy) as a function of processing conditions and material properties is the ideal solution to this problem.

Previous efforts to model hollow fiber membrane spinning for various polymer–diluent systems generally involve monitoring the phase separation process, choosing a mechanism by which phase separation occurs, and relating that to evolution of the domains representative of the membrane microstructure. However, such analyses are system-specific, forcing the user to specify the phase separation mechanism and characterize the complicated kinetics of the process. In addition, the solution scheme may involve extensive and costly computational time, and most of these analyses deal with solid fibers rather than hollow fibers [2].

Ohzawa et al. [3,4] and Chandler et al. [5] are responsible for some existing solid fiber transport models of solution spinning. However, these models are simplified to predict average concentration values over the fiber cross-section, supplemented in some cases with a separate calculation of the surface concentration, but otherwise unable to predict radial concentration gradients. Simon [6,7] presents work for air gap wet spinning of solid fibers, in which phase separation occurs through solvent exchange in a coagulation bath. Mass transfer in the air gap is ignored, and hollow fiber spinning is not addressed.

Gou and McHugh [8–10], building on the work of Brazinsky et al. [11], present a model that includes radial concentration variation for dry spinning solid fibers; however, experimental data is related to average concentration only, with no directly demonstrated correlation of the modeled radial concentrations with physical fiber structure. Tsai et al. [12] developed a model to calculate radial concentration gradients for the optical fiber spinning process, but

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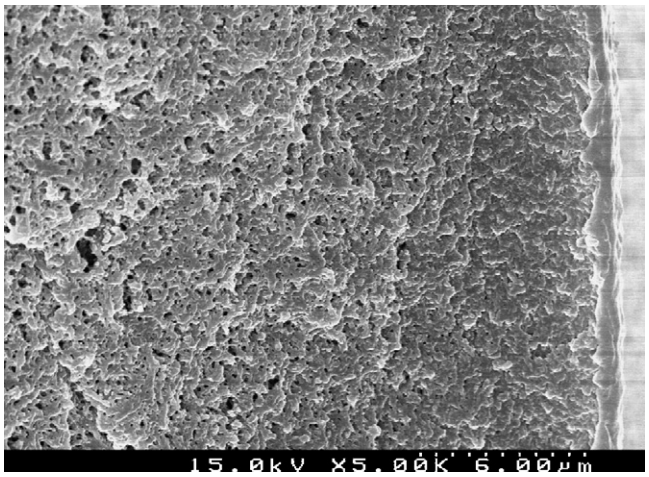

Fig. 1. Typical PE–dodecanol hollow fiber membrane cross-section SEM: the fiber outer radius appears on the right hand side of the image.

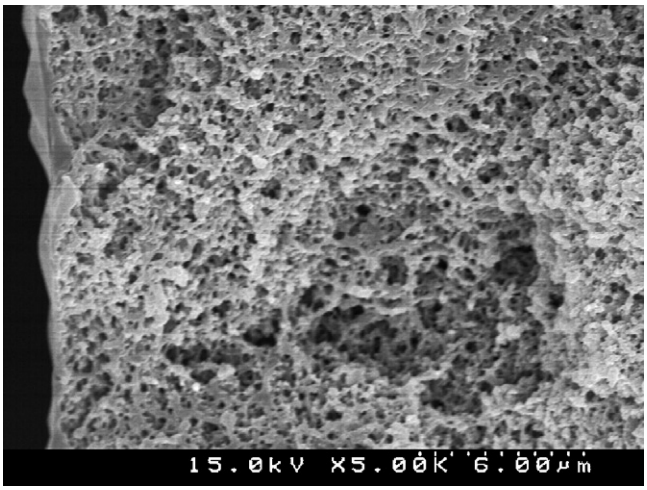

Fig. 2. Typical PE–dodecanol hollow fiber membrane cross-section SEM: the fiber inner radius appears on the left hand side of the image.

it ignores changes in the filament diameter, and no experimental comparison is made to validate model predictions.

In terms of previous hollow fiber spinning model efforts for solution spinning, existing work by Castellari et al. [13] focuses on membrane formation via phase inversion, but solvent evaporation is described empirically. Existing models for hollow fiber membranes made via the thermally induced phase separation (TIPS) process such as the work of Berghmans et al. [14] and Batarseh [15] focus on the heat and mass transfer for the spinning process, with some predictions of radial concentration gradients. However, these models neglect momentum transfer; thus, hollow fiber dimensional changes due to draw-down cannot be considered.

The present work applies to hollow fiber membranes and builds on the thin filament analysis (TFA) model of the fiber spinning process [16]. It involves using a boundary layer analysis to model concentration gradients that evolve in the fiber spinning solution, or clad, during the spinning process, and the concomitant evaporative cooling effects. Knowledge of this data is useful because the local concentration and temperature at the time of phase separation determine the kinetics involved in the phase separation process [17]. Thus, prediction of radial concentration gradients and axial temperature profiles is an important fundamental step toward predicting final membrane structure as a function of spinning system physical parameters and process variables. Specifically, a concentration gradient leads to a pore size gradient, and in asymmetric or anisotropic hollow fiber membranes, the predicted radial concentration gradients from the present modeling efforts can be used to estimate membrane extent of anisotropy (that is, the fraction of the membrane cross-section exhibiting a pore size gradient), and degree of anisotropy (that is, an indicator of the range of pore sizes present in the membrane [15]).

Figs. 1 and 2 show scanning electron micrographs (SEMs) of a typical polyethylene (PE)–dodecanol hollow fiber membrane; pictured are cross-sections adjacent to the outer and inner radii, respectively. These membranes were spun using a pure nitrogen gas core. A radial pore size gradient near the outer radius is evident in Fig. 1, in contrast to virtually no changes in pore structure near the inner radius in Fig. 2. Thus, only outer wall membrane anisotropy is investigated in this work.

The thin filament analysis (TFA) is a widely accepted approximate analysis of solid fiber spinning of non-volatile pure polymer melts based on the assumption of a small fiber diameter relative to draw zone length. The TFA has been extended in separate efforts by Freeman et al. [18], Lipscomb [16], and Chung et al. [19] to model hollow fiber spinning. There are discrepancies among these hollow fiber TFA modeling efforts, most notably with the treatment of the core gas pressure. Moreover, all these analyses neglect the effects of surface tension, and for solution spinning, the effects of evaporative cooling; both of these effects are included in the model presented here. Regarding surface tension, existing literature links it to the occurrence of spinning instabilities such as draw resonance [20–23], thus providing an additional reason to explore its effects on other spinline variables.

The procedure developed herein for modeling concentration gradients and membrane anisotropy requires little computational time and is applicable to hollow fiber membranes spun under a variety of conditions. Another advantage of the modeling procedure developed here is that knowledge of the phase separation kinetics or even the phase separation mechanism is not required for predicting the membrane extent of anisotropy. Supplementary to the model derivation, experimental results illustrating the extent and degree of anisotropy for spinning hollow fiber membranes are presented.

2. Model development

The hollow fiber spinning process is represented by the schematic in Fig. 3. The thin filament analysis (TFA) is developed through radial averaging of the axisymmetric conservation of mass, momentum, and energy equations, and it predicts the variation of fiber inner and outer diameters, velocity, stress, and temperature with axial distance. The TFA of hollow fiber spinning focuses on the draw zone where the fiber is drawn to the desired size prior to phase separation, corresponding to the air gap region in Fig. 3.

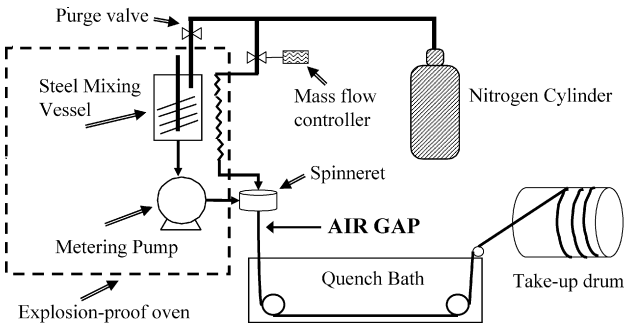

Fig. 3. Schematic of the hollow fiber spinning process.