The Effect of Solidification on Entrained Air Bubbles in a Polymer Membrane

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Introduction

Polymer membranes have a wide range of applications in areas such as automotive, aerospace, biomedical, energy conversion and several others. When doped with an acidic substance, the membrane can then serve as a proton conductor and be used as an electrolyte in a polymer electrolyte membrane (PEM) fuel cell, for example. Although, often the membrane acts as a separator to prevent the mixing of gases and/or liquids; thus, it is important that the membrane be free of defects to prevent cross-contamination or mixing [1]. Defects such as air bubbles and pinholes can arise in the membrane during processing (liquid phase) and remain entrained after the membrane has solidified. The presence or absence of these defects depends on the processing conditions used to fabricate the membrane. Specifically, the membrane must be processed within the bounds of a casting window to be defect free [2].

Casting windows are generally obtained based on the liquid phase characteristics of the cast film. In this study, the behavior of air bubbles, entrained in a highly viscous non-Newtonian fluid, is investigated as the solution solidifies, to determine if the casting window can be extended based on air bubbles diffusing out of the film during solidification. The class of solution of interest is for relatively high viscosity, non-Newtonian membrane solution used in PEM fuel cells, known as polybenzimidazole doped with polyphosphoric acid (PBI/PPA) membrane solution. Expansion of the casting window can provide more manufacturing flexibility and speed for these solutions, which exhibit a narrow casting window [3].

The solidification during an injection molding process was modeled using the crystallinity of the material [4]. However, in this case crystallinity cannot be used to observe defects since a defect or a portion of the material that is yet to solidify is not distinguishable in an area of low crystallinity. Other methods based on mass transfer equations have been applied to model defects generated due to stresses developed in a drying polymer film [5,6]. However, such methods are useful for modeling defect nucleation during solidification, not for defects that already exist in the liquid phase. A suitable method to model solidification with defects originating while in the liquid phase is the enthalpy-porosity technique. It has been applied to model the solidification of liquid metal extrusion [7], aluminum alloy ingot casting [8], and injection molding of high-density polyethylene [9]. In this study, the enthalpy-porosity technique is used to model the behavior of air bubbles entrained in a PBI solution during slot die casting.

Theory

A two-dimensional, two-phase, non-isothermal, transient model was setup and solved in the commercial computational fluid dynamics (CFD) software ANSYS FLUENT 13.0, based on a slot die casting process. A 2-D representation of the slot die casting process is shown in Figure 1. As shown in the schematic, the solution exits the slot die at speed v_{in} and is cast on a substrate moving at a speed u_w to produce a membrane which is *d* thick. Also, D represents standoff height and W represents the slot gap. The PBI/PPA solution is a shear thinning non-Newtonian fluid with viscosities ranging from 30 Pa.s to 7000 Pa.s depending on temperature and strain rate, which was captured by an empirical relation developed by Harris [10]. In the CFD model, the volume of fluid (VOF) method was used to track the interface between the two phases; namely, PBI/PPA solution and air. The VOF model solves for the volume fraction of PBI/PPA, α_{pbi}, in the continuity equation:

$$\frac{\partial \alpha_{pbi}}{\partial t} + \vec{u} \cdot \nabla \alpha_{pbi} = 0$$

where $\vec{u}$ is the velocity vector. Once α_{pbi} is found, the volume fraction of air is then found by $\alpha_{air} = 1 - \alpha_{pbi}$. The solidification was modeled by the enthalpy-porosity technique, which shows up in the energy equation, including an enthalpy term *H* and a source term *S*:

$$\frac{\partial}{\partial t}(\rho H) + \nabla \cdot (\rho \vec{u} H) = \nabla \cdot (k \nabla T) + S$$

where ρ, k, and T, are the density, thermal conductivity, and temperature, respectively. The total enthalpy H is the sum of the sensible heat h, and the latent heat ΔH, given as $H = h + \Delta H$. The latent is given by $\Delta H = \beta L$, where L is the latent heat of the material and β is the liquid fraction. The liquid fraction, which essentially captures the solidification based on the liquid T_l and solidus T_s temperatures of the material, is given by:

$$\beta = \begin{cases} 1 & \text{if } T \geq T_l \\ \dfrac{T - T_s}{T_l - T_s} & \text{if } T_s < T < T_l \\ 0 & \text{if } T \leq T_s \end{cases}$$

Therefore, a liquid fraction value of zero represents solid, and a value of one represents liquid.

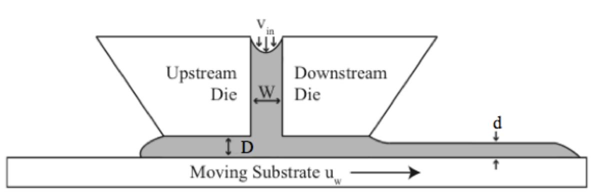

Figure 1: Schematic of a slot die casting process.

Results and Discussion:

The simulations were executed at a fixed standoff height of 250 micrometers and a slot gap of 250 micrometers. The inlet velocity v_{in} was 3.5 mm/s, and the substrate speed u_w was 5.5 mm/s. Shown in

Figure 2 is a contour plot of the liquid fraction. Since the liquid fraction is used to distinguish between solid and liquid, the results from the enthalpy-porosity model will equal to a liquid fraction of one for the PBI/PPA in its liquid state and air. Hence, as depicted in Figure 2, the PBI begins to solidify, transitioning to the mushy zone, and as the PBI progresses downstream it reaches a fully solidified state. Slight anomalies can be seen in the contour plot due to the air bubbles entrained in the PBI. These air bubbles are better depicted in a volume fraction contour plot shown in Figure 3.

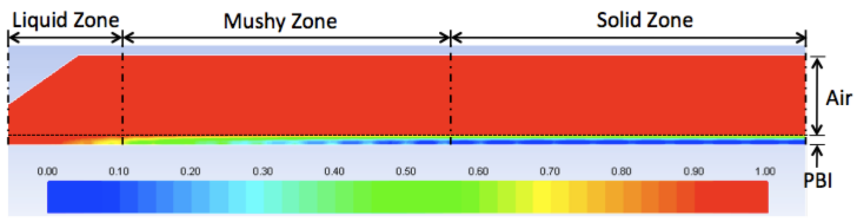

Figure 2: Contour plot of the liquid fraction depicting solidification of the PBI solution.

Shown in Figure 3 is the inception of air bubbles below the slot die and how they progress through the PBI solution while in its liquid state Figure 3a. The mushy zone roughly starts at the x = 0.005 m marker in Figure 3b and stretches to approximately x = 0.009 m. As a result of the solidification, the viscosity drastically increases in the mushy zone and these affects the flow field and pressure locally. However, due to the relatively high viscosity, the air bubbles remain entrained in the PBI and do not diffuse out.

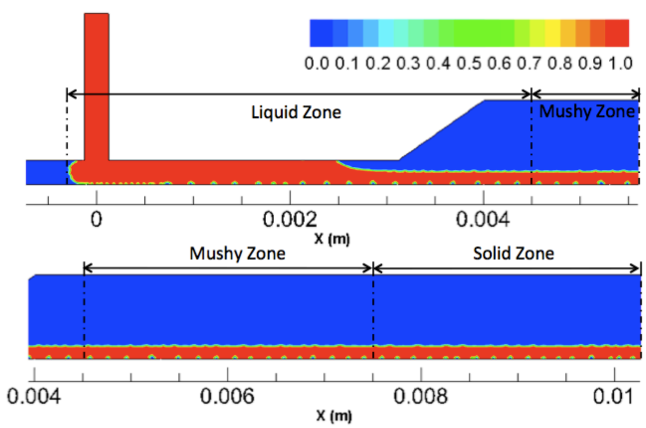

Figure 3: Contour plot of the volume fraction showing the entrainment of air bubbles in the PBI solution while (a) in its liquid state, shown in the top plot, and (b) while the PBI solidifies, shown in the bottom.

Conclusion:

A two-phase, non-isothermal, and transient CFD model was used to study the behavior of air bubbles entrained in a PBI/PPA solution, in an attempt to expand the casting window. The volume of fluid method was used to solve for the air-PBI/PPA interface and the enthalpy-porosity technique was used to solve for the liquid fraction (solidification). As the air bubbles originated below the slot die and progressed downstream through the mushy zone, it was found that the bubbles would not diffuse out of the solution, despite local changes in pressure. This is mainly due to the relatively high viscosity of the solution. Hence, it is suggested that the casting window cannot be expanded for this class of solutions after air has been generated or engulfed into the cast film.

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