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Mesoscopic simulations of thermally-induced phase separation in PVDF/ DPC solutions



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ABSTRACT

We present a phase-field model of thermally-induced phase separation in polymer solutions, calibrated for the polyvinylidene fluoride (PVDF)/diphenyl carbonate (DPC) system. Large-scale three-dimensional computer simulations were performed for isotropic and anisotropic thermal quenches, and the evolution and structure of the resulting two-phase morphology is analyzed. Isotropic quenches, in which the temperature is uniformly reduced below the binodal temperature, were conducted to understand the initiation and coarsening of the polymer-rich and polymer-poor phases throughout time. Anisotropic quenches, in which the system is cooled from one particular surface, were also conducted to understand how gradients in the characteristic domain size develop for varying conditions. In these anisotropic quenches, we observe the formation of a dense skin layer adjacent to the cooling surface, the thickness of which depends on several parameters including the polymer volume fraction, the assumed bath temperature that is maintained at the cooling surface, and the rate of thermal conduction through the polymer solution. The model here can be adapted to other polymer/solvent systems by modifying the thermodynamic and kinetic parameters specific to the two species.

1. Introduction

Porous polymer membranes are typically fabricated from a polymer solution that is made to undergo an internal phase separation process [1–4]. This process is thermodynamically driven by either a change in temperature (known as thermally-induced phase separation, TIPS) or the introduction of a second solvent (known as solvent-induced phase separation, SIPS) that creates a miscibility gap leading to the co-formation of a polymer-rich phase and a polymer-poor phase. Subsequently, the polymer-poor phase is removed to form a dispersion of internal porosity, and the polymer-rich phase is solidified to form a membrane. Various geometries can be achieved with TIPS and/or SIPS processing including flat sheets and hollow fibers. The critical characteristic of the system is the morphology of the internal pores, which can vary significantly depending on the composition of the solution as well as the processing conditions. Predicting the size of the pores, the uniformity of the pore size, and the continuity/discontinuity of the pore structure is challenging, and requires consideration of both the thermodynamic and kinetic interactions between the constituent species within the solution throughout the phase separation process.

Considering the large number of variables, the complexity of the phase separation process, and the cost of parametric experimental studies, computer simulations play an important role in the on-going goal of engineering customizable membrane structures with specific pore size distributions. Various simulation techniques have been proposed and applied in the literature, falling into three broad categories based on their representative length scale: (i) molecular-scale simulations, (ii) meso-scale simulations, and (iii) macro-scale simulations.

Macro-scale simulations generally utilize continuum transport models (i.e., Fickian diffusion of mass and heat) to predict temperature and concentration profiles along entire membrane cross-sections [5,6]. Predictions of pore sizes can then be made using thermodynamic models such as Flory-Huggins theory as well as kinetic theories to describe the phase coarsening rates at particular temperatures. This approach does not explicitly track the dynamics of the polymer and solvent species, nor does it track the formation of the two-phase morphology. However, it does provide approximations of porosity variations on a membrane-wide scale.

On the other end of the spectrum, molecular-scale simulations such as molecular dynamics (MD) can predict detailed information of individual polymer chains, such as their conformational changes through time. Such details however are only possible for system sizes on the order of 10's of nanometers (or, perhaps 1–20 polymer chains), as MD simulations track every atomic trajectory. Coarse-grained models such as dissipative particle dynamics (DPD) reduce this level of detail while still capturing chain dynamics with a point-mass representation. The work of Wang et al. [7], He et al. [8], and Tang et al. [9–12] demonstrate the ability of DPD simulations to capture the formation and evolution of polymer-rich and polymer-poor phase domains during

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TIPS and/or SIPS processing. Due to computational demands, DPD simulations are limited to system sizes of approximately 10 nm, and therefore can only capture pore size distributions on this scale.

Simulation methods at intermediate length scales are particularly promising as they resolve features at the level of the pore network. These techniques capture the evolution of the phase separation process with variables stored on a computational grid that define the two distinct phases. Termonia [13–15] developed a Monte Carlo (MC) lattice diffusion model to simulate the coagulation process during SIPS, revealing various morphologies including fingerlike pores depending on the coagulation rate. He et al. [16] employed a similar technique and analyzed the pore structure as a function of polymer content. These stochastic MC studies were performed on two-dimensional lattices.

Deterministic meso-scale simulations have also been developed, most notably phase-field models utilizing the Cahn-Hilliard (CH) equation. The CH equation is essentially a diffusion equation for multicomponent mixtures that is informed by an assumed thermodynamic model for the energy of mixing, which may induce phase separation. Caneba and Soong [17] demonstrated the earliest application of the CH equation to specifically simulate the polymer membrane formation process. They conducted one-dimensional (1D) simulations of the TIPS process in a polymer-solvent system at various locations relative to a cooling surface, using the Flory-Huggins and free-volume theory models for the thermodynamic and kinetic descriptions, respectively. Their results estimated pore sizes as a function of membrane depth away from the cooling surface, thus demonstrating the versatility of this approach. However, although 1D simulations can provide predictions of pore size, they do not offer information regarding the continuity/discontinuity of a porous network.

Soon after, two-dimensional (2D) simulations of TIPS in polymersolvent systems were reported [18,19] that assumed isotropic quenches focusing in particular on the growth and coarsening rates of the polymer-rich and polymer-poor phases. The effect of temperature gradients (i.e. anisotropic quenches) were studied by Lee et al. [20,21] and Kukadiya et al. [22] with 1D and then 2D simulations. Recently, Mino et al. [23] conducted three-dimensional simulations of the TIPS process, including the effects of a polymer concentration gradient that leads to an anisotropic structure. The SIPS process has also been simulated with phase-field models [24–27] to investigate the coagulation process. Due to the significant hydrodynamic transport processes associated with SIPS during the exchange of the two solvents, recents efforts to simulation SIPS have employed fluid-based simulation methods, including the lattice-Boltzmann method [28] and the multi-fluid model of Tree et al. [29,30].

In this work, we have utilized a CH model to simulate the TIPS process in three dimensions for both isotropic and anisotropic quenches. We have chosen the PVDF/DPC polymer/solvent system which is commonly used in TIPS membrane processing [31,32]. The size and interconnectivity of the pore structures are analyzed for varying polymer volume fractions and temperature quench rates. In our anisotropic quench simulations, we observe the formation of a dense skin layer, as observed in experiments [33], whose thickness is found to depend on the bath temperature and the thermal conductivity of the polymer solution.

2. Methods

The CH equation employed here evolves in space and time a conserved field variable, ϕ_p , representing the local polymer volume fraction in a solution. We assume a binary solution of polymer and solvent, hence $\phi_p + \phi_s = 1$ at any location, and only ϕ_p is required to represent the system. The equation is given by:

$$\frac{\partial \phi_p}{\partial t} = \nabla \cdot \left(M_p \nabla \left(\frac{\partial F_{mix}}{\partial \phi_p} - 2\kappa \nabla^2 \phi_p \right) \right) + \xi, \tag{1}$$

where M_p is the temperature- and concentration-dependent polymer mobility, F_{mix} is the free energy of mixing between polymer and solvent, κ is a term that scales the interfacial energy between the polymer-rich and polymer-poor phases, and ξ is a random number centered at zero associated with thermal fluctuations. The CH equation is essentially a diffusion equation which we are applying to investigate a liquid-liquid phase separation process. We acknowledge that the model does not account for convective mass transport. However, unlike the SIPS process that involves long-range fluid transport of solvent species which justifies a fluid model [28–30], the TIPS process is a more local redistribution of polymer and solvent during quenching in a very viscous system, thus diffusion is the dominant mode of transport.

The Flory-Huggins (FH) free energy of mixing of a polymer-solvent system is used for F_{mix} :

$$F_{mix} = k_b T \left[\frac{\phi_p}{N} \ln \phi_p + \phi_s \ln \phi_s + \chi \phi_p \phi_s \right]$$
(2)

where the substitution $\phi_s = 1 - \phi_p$ is made, *N* is the degree of polymerization set to a value of *N* = 150, and χ is the polymer-solvent interaction term, which is temperature dependent and expressed by:

$$\chi = \frac{425}{T} - 0.338,\tag{3}$$

where T is assumed to be in Kelvin. The values used in this equation have been shown previously to be appropriate for the PVDF/DPC system [31,12]. The binary phase diagram of PVDF/DPC is depicted in Fig. 1, and the FH energy curves are shown in the sub-plot. We have also included images of small 2D simulations with our model, demonstrating the variations in morphology with *T* and ϕ_p . As ϕ_p is increased, the morphology transitions from discrete droplets of the polymer-rich phase, to a bicontinuous morphology, to discrete droplets of the polymer-poor phase. In the PVDF/DPC system, the critical temperature calculated using Flory-Huggins with the above interaction parameter and degree of polymerization is approximately 460 K and the crystallization temperature is approximately 390 K [31]. Hence, we only present the phase diagram in this temperature range, which is associated with the liquid-liquid phase separation that occurs during TIPS. In our simulations, we do not observe phase separation in regions above the binodal line on the phase diagram, as expected. In Eq. (1), we assign $\kappa = 0.5$ which is chosen to keep the diffuse interface widths at 5–7 grid spacings (ideal for the CH model), and ξ is a random number chosen in



Fig. 1. Phase diagram for PVDF/DPC superimposed with simulation images of isothermal quenches at different temperatures and ϕ_p . Various morphologies appear including droplets of the polymer-rich phase, bicontinuous domains of both phases, and droplets of the polymer-poor phase. The inset plot shows the Flory-Huggins free energy of mixing, Eq. (2), for four different temperatures.

the interval [- 0.1,0.1].

The polymer mobility M_p is closely related to the self-diffusivity of a polymer chain in solution D_p according to the relationship [19]:

$$M_p = \frac{D_p}{\frac{\partial^2 F_{mix}}{\partial \phi_p^2}}.$$
(4)

The polymer self-diffusivity is highly dependent on temperature and the local ϕ_p . An experimentally-validated model developed by Phillies [34,35] is used here to describe the dependence of D_p on ϕ_p :

$$D_p = D_0 \exp(-\alpha c^{\nu}) \tag{5}$$

where D_o is the diffusivity of a single chain in an infinitely dilute solution, and *c* is the polymer concentration in g/L calculated by $c = \phi_p \frac{M_v}{M_w}$ where M_v is the molar volume and M_w is the molar weight of the monomer in the polymer chain. We use values of $M_v = 38.2 \text{ mL/mol}$ and $M_w = 64.03 \text{ g/mol}$, suitable for a monomer of PVDF [36]. The parameters α and ν are system-dependent scaling coefficients which are generally fit according to experimental data. Diffusion data specific to PVDF/DPC was not found in the literature, so we choose values of $\alpha = 0.2$ and $\nu = 0.4$, which fall in reasonable bounds for many other polymer solutions [34,35]. The diffusivity of a single polymer chain in a dilute solution is given by the Einstein equation:

$$D_0 = \frac{k_b T}{f},\tag{6}$$

where f is a friction factor. Eqs. (5) and (6) together account for the temperature- and concentration-dependence of D_p .

The self-diffusivity of PVDF in DPC has not been reported, hence we assume a value of 1×10^{-7} cm²/s at the critical temperature of 460 K. Fig. 2 plots the diffusivity versus ϕ_p at three temperatures: T = 460 K, 391 K and 389 K. The inset of Fig. 2 plots the polymer mobility M_p versus ϕ_p . At T = 460 K, the decrease in polymer diffusivity with increasing ϕ_p is accounted for by Eq. (5). Diffusivities at temperatures below 460 K can be obtained by linearly scaling the diffusivity at 460 K, according to Eq. (6). However, at the crystallization temperature of 390 K, the diffusivity can be expected to abruptly drop due to the state change. To account for this, at temperatures below 390 K, we reduce the diffusivity by a factor of 10^3 (i.e., we divide the calculated D_p by 1000). Hence, in Fig. 2 we plot diffusivities at 391 K (just above the crystallization temperature) and 389 K (just below the crystallization temperature), showing the abrupt drop in values.

To execute our simulations, we solve Eq. (1) with a straightforward explicit finite difference scheme on a rectilinear grid with uniform spacing between nodes. To reduce round-off error, the equations are



Fig. 2. Polymer diffusivity versus ϕ_p calculated by Eq. (5) for three temperatures - two above the crystallization temperature and one below. The inset plot shows the polymer mobility versus ϕ_p for the same three temperature.

solved with reduced units of length (\bar{l}) and time (\bar{t}) , whereby the grid spacing $\Delta x = 1 \bar{l}$ and the time step size is $\Delta t = 0.005 \bar{t}$, a value that ensures numerical stability. The reduced diffusivity is set equal to unity at T = 460 K, and linearly scaled for temperatures below that, taking into account the reduction below the crystallization temperature. In all simulations herein, the maximum temperature is 460 K, assigned as the initial temperature, followed by either an isotropic or anisotropic quench in which the temperature is reduced through time. Following the simulations, we convert all length and time scales back into physical units by assuming $\bar{l} = 35$ nm (hence, each grid node represents a box with side lengths of 35 nm) and $\bar{t} = \bar{l}^2 / 10^{-7} \text{cm}^2 / \text{s} = 1.225 \times 10^{-4} \text{ s}$. Our choice of \overline{l} is somewhat arbitrary, however in order to satisfy the meanfield representation of the polymer solution, it should be larger than the chain radius of gyration, hence the physical length and time herein are relevant for such a condition. Choosing a different \overline{l} will effectively rescale the physical time duration for the simulations.

Isotropic quenching was conducted by reducing the temperature uniformly at a constant linear rate throughout the entire domain:

$$T(t) = T_i - \left(T_i - T_f\right) \times \left(\frac{t}{\Omega}\right)$$
(7)

where T_i is the initial temperature (always set to 460 K), T_f is the final temperature, t is the current simulation time, and Ω is the total simulation time. Different quench rates were achieved by varying Ω . In our isotropic quenches, T_{final} was set to the crystallization temperature, and periodic boundary conditions were applied in all three directions.

Anisotropic quenching was also performed to more accurately capture the effects of temperature gradients on the phase separation process, ultimately leading to anisotropic pore morphologies. For anisotropic quenching, we assumed a uniform, initial temperature of 460 K. One surface of the domain (at x = 0) was kept at a constant cool temperature, and the temperature profile is obtained from the solution to a 1D, semi-infinite heat equation:

$$T\left(t, x\right) = T_{bath} + \left(T_i - T_{bath}\right) \times \operatorname{erf}\left(\frac{x}{2\sqrt{\alpha_T t}}\right)$$
(8)

where T_{bath} is the temperature of the cool surface, assumed to be in contact with a bath, and α_T is the thermal diffusivity of the polymer solution (in units of cm²/s), assumed to be uniform and equal in both the polymer-rich and polymer-poor phases. To relate the thermal diffusivity and the polymer diffusivity, and make the results more general, we utilize the non-dimensional Lewis number defined as $Le = \frac{\alpha_T}{D_0}$ [37]. We used several values of *Le* to determine its effect on pore morphology, including *Le* = 50, 100, and 150. In our anisotropic quenches, periodic boundary conditions were applied in the *y*- and *z*-directions, while no-flux boundaries (for ϕ_p) were applied in the *x*-direction. We also used three different bath temperatures, $T_{bath} = 273$ K, 298 K, and 333 K, and analyzed its effect on pore morphology.

We implemented a variety of analysis tools to evaluate the nature of the pore morphology. First, the average pore size was calculated by conducting one-dimensional sweeps along columns of grid points in each direction and calculating the average distance between interfaces within the polymer-poor phase (with an interface being defined as a location where $\phi_p = 0.25$). The average distance between interfaces was then averaged for all columns of grid points in the *x*-, *y*-, and *z*- directions. Second, we evaluated the interconnectivity of the porosity using a Hoshen-Kopelman (HK) cluster counting algorithm [38]. The HK algorithm identifies and labels individual domains of a phase, in our case the polymer-poor phase associated with the porosity. We then compute a continuity parameter Γ_c that represents the continuity of the pore network in space [39]. This parameter is calculated by dividing the volume of the largest pore (V_L) by the total volume of all the porosity (V_T):



Fig. 3. Progressive snapshots in time of an isotropic quench simulation with an initial temperature of 460 K and a final temperature of 390 K. Here, the average volume fraction is $\bar{\phi}_p = 0.15$, the quench rate is 56 K/s, and the domain size is 9 × 9 × 9 µm. The white regions correspond with the polymer-rich phase, and the blue semi-transparent regions correspond with the polymer-poor phase. The final structure on the right depicts a bicontinuous morphology.

$$\Gamma_c = \frac{V_L}{V_T}.$$
(9)

The value of Γ_c quantifies the interconnectivity of the pore network, whereby $\Gamma_c = 1$ represents the case where all the porosity is associated with a single pore (complete interconnectivity). Otherwise, as Γ_c approaches zero, the largest pore is a small fraction of the total porosity, which is thus discrete and discontinuous.

All simulations were executed on 16-core CPU nodes, parallelized by domain decomposition along the *x*-direction. Each simulation typically required a few hours of wall time to complete.

3. Results

3.1. Isotropic quench

First, we performed isotropic quenches in which the temperature throughout the simulation domain was decreased uniformly from an initial value of 460 K to a final value of 390 K (i.e., the crystallization temperature). We conducted three-dimensional simulations with grid sizes of $256 \times 256 \times 256$, corresponding to $9 \times 9 \times 9 \mu m$. Fig. 3 depicts the evolution of the two-phase morphology through time. The system is initialized by assigning values of ϕ_p about an average polymer volume fraction $\bar{\phi}_p$ with an initial random variability of \pm 0.05. The images in Fig. 3 correspond to $\bar{\phi}_n = 0.15$ and a quench rate of 56 K/s. At the initial temperature, the solution is fully soluble and there is no thermodynamic driving force for phase separation. As temperature decreases, a continuous change in F_{mix} leads to phase separation along with a continuous change in M_p that governs the rate of phase separation. Polymer-rich and polymer-poor domains form, and the local polymer content in these domains continuously changes during quenching according to the binodal line of the phase diagram. At the end of the simulation, the domain has a temperature of 390 K, and a two-phase morphology exists in which the polymer-rich domains have ϕ_n values of approximately 0.5 and the polymer-poor domains have ϕ_p values very near zero.

In our isotropic quench study, we varied two key parameters: $\bar{\phi}_p$ and the quench rate. Throughout the simulations, we computed the average pore size defined as the average distance between interfaces through the polymer-poor phase. This data is shown in Fig. 4. The left plot shows the average pore size versus temperature (which is analogous with time for our isotropic quenches) with $\bar{\phi}_p = 0.15$ for four different quench rates: 56, 70, 93, and 140 K/s. The right plot shows the average pore size at the end of the quench versus $\bar{\phi}_p$ for the same quench rates. Overall, we see a trend in which a higher quench rate (i.e., a faster quench) results in a smaller pore size. There are two factors accountable for this relationship. First, lower quench rates allow more time for the two-phase morphology to coarsen. A lower quench rate permits the system to remain at higher temperatures (yet, below the binodal line) where the polymer mobility is higher for longer times. Second, a higher quench rate results in a delay in the onset of phase separation, due to a delay in overcoming the nucleation barrier. We see evidence of this in the left plot of Fig. 4, where the data points depart from the x-axis at different temperatures (or, equivalently, different times). Lower quench rates allow more time for nucleation to occur when the system first crosses the binodal line. Due to these two effects, at the end of the quench, the pore size is larger for lower quench rates.

In addition, when examining the right plot of Fig. 4, we see that the pore size is highly sensitive to the average polymer fraction. This is to be expected, given that the porosity is derived from the polymer-poor phase, the quantity of which is determined from a tie line using the lever rule with a fulcrum at $\bar{\phi}_p$. There is also a secondary factor associated with the polymer mobility. The average mobility in the system as a whole is higher for smaller values of $\bar{\phi}_p$, due to the fact that D_p decreases exponentially with ϕ_p . Hence, the coarsening rate will be higher for lower values of $\bar{\phi}_p$.

The continuity of the porosity for these systems was also computed using the HK algorithm discussed above. Fig. 5 plots the continuity parameter Γ_c versus $\bar{\phi}_n$ for three quench rates. For values of $\bar{\phi}_n$ below 0.175, the porosity is completely interconnected, as evident by values of $\Gamma_c = 1$. Within the plot, we added images of different structures at the end of their quenches. The blue-white images on the left depict the polymer volume fraction. The multi-colored images on the right depict the porous regions in the domain (i.e. the polymer-poor phases). The pores are shaded according to their respective volume, with a red shading corresponding to a large pore volume and a blue shading corresponding to a small pore volume. These images show the transition from an interconnected porosity to a discrete disconnected porosity, which abruptly occurs in the range 0.175 < $\bar{\phi}_p$ < 0.25. The inter-connectivity of the pore network is inherently important to the separation performance of polymer membranes. The quench rate was seen to influence the pore morphology only within a range of polymer volume fractions ($\bar{\phi}_p = 0.17 - 0.25$). Below this range the system is within the spinodal region and the relatively equal quantities of polymer-rich and polymer-poor phases strongly favor a bicontinuous structure. Above this range, the polymer-poor phase is a minority phase and forms discontinuous droplets regardless of quench rate.

3.2. Anisotropic quench

The temperature quenching that occurs in an actual TIPS processing procedure occurs in an anisotropic manner. One of the surfaces of the polymer-solution is brought into contact with a cooling bath, which leads to a one-dimensional heat transfer process. Anisotropic quenching can therefore lead to anisotropic pore structures, as the local change in temperature versus time depends strongly on the distance from the cooling surface within the polymer solution.



Fig. 4. Data plots of: (left) average pore size versus temperature during isotropic quenches for $\bar{\phi}_p = 0.15$ and four different quench rates, (right) average pore size versus $\bar{\phi}_p$ at the end of the quenches for four different quench rates. The average pore size decreases with increasing quench rate and polymer volume fraction.



Fig. 5. The calculated continuity parameter Γ_c versus $\bar{\phi}_p$ for three different quench rates. Increasing $\bar{\phi}_p$ leads to a transition in morphology from a fully continuous pore network ($\Gamma_c = 1$) to a highly discontinuous pore network ($\Gamma_c \ll 1$). The inset images show simulation snapshots of the polymer fraction on the left and the pore regions on the right colored according to pore size (red = large pores and violet = small pores). Individual pore domains are identified by the HK algorithm.

To investigate an anisotropic quench process, we conducted simulations in which the x = 0 surface was held at a constant temperature correlating with the temperature of the bath, T_{bath} . The rest of the domain was assigned the initial temperature, $T_i = 460$ K. Eq. (8) was then solved within the domain to determine the local temperature at a specific point in space and time. Our anisotropic quenches differ from those of Mino et al. [23] by the fact that we utilize a non-uniform and time-dependent temperature field, whereas Mino et al. assumed an initial polymer concentration gradient (to represent a preliminary solvent evaporation) followed by an isotropic temperature quench.

We elongated the domain in the *x*-direction, and the overall grid sizes used in this section were $500 \times 70 \times 70$, corresponding with $17.5 \times 2.45 \times 2.45 \mu$ m. Fig. 6 shows snapshots of the anisotropic phase-separation process at progressive instances in time for a polymer volume fraction of $\bar{\phi}_p = 0.15$. The initial temperature of the polymer



Fig. 6. Progressive snapshots of an anisotropic quench simulation which is cooled from the top surface that is held at a constant temperature $T_{bath} = 298$ K. The one-dimensional heat flux leads to a non-uniform decrease in temperature according to Eq. (8), and a resulting non-uniform pore network. The images were taken at times of 0 s, 0.179 s, 0.358 s, and 0.894 s (the final time). The domain size is $17.5 \times 2.45 \times 2.45 \mu$ m, the polymer volume fraction is $\bar{\phi}_p = 0.15$, and the Lewis number is Le = 50.

solution was $T_i = 460$ K, the bath temperature was $T_{bath} = 298$ K. To relate the mass diffusivity of the polymer with the thermal diffusivity of heat in the material, we utilize the dimensionless Lewis number defined as $Le = \frac{\alpha T}{D_0}$ [37] (again, D_o is the diffusivity of a polymer chain in a dilute solution at 460 K). For the images in Fig. 6, Le = 50. In Fig. 6, the final simulation time is 0.894 s, which is the required time to reduce the temperature throughout the domain to a value below the crystallization temperature, 390 K. This time span is perhaps shorter than that occurring in laboratory TIPS processing, a result of the fact that the depth of our simulation domain is less than the thickness of a typical polymer membrane (e.g. 170 µm).

The anisotropic quenching clearly results in a gradient in pore size



Fig. 7. A close-up image of the dense skin layer near the cooling surface. An isosurface (drawn at $\phi_p = 0.15$) is included to better visualize the structure. Within the skin layer, a small degree of phase separation has occurred, which was essentially halted early in the simulation due to the local temperature dropping below the crystallization temperature.

in the *x*-direction. Most notably, at the top of the domain near the cooling surface, there exists a region where complete phase separation has not fully occurred. Within this region, the temperature dropped quickly below the crystallization temperature, and very little time was available for the phase-separation process. This region, however, does not have a completely uniform polymer concentration. Fig. 7 shows a close-up view of the structure, with an isosurface drawn to depict $\phi_p = 0.15$, which is the average polymer fraction. Clearly, variations in the polymer fraction exist in this region, corresponding therefore to a distribution of very small pores. Polymer-rich and polymer-poor domains have begun to develop in this region, but have not fully evolved to their preferred values of ϕ_p . This dense layer near the cooling surface



Fig. 9. Images from anisotropic quench simulations for three different polymer volume fractions: (left) $\bar{\phi}_p = 0.08$, (middle) $\bar{\phi}_p = 0.15$, and (right) $\bar{\phi}_p = 0.225$. These images show the variation of skin layer depth versus $\bar{\phi}_p$, as well as the difference in the interconnectivity of the pore structures with $\bar{\phi}_p$. $T_{bath} = 298$ K and Le = 50.

represents a skin layer which is commonly observed in polymer membranes [40]. A recent experimental work [41] reveals very similar pore structures resulting from the TIPS process, including a dense skin layer and a gradient in pore size in the direction perpendicular to the skin surface.

To quantify these anisotropic pore structures, we have computed the



Fig. 8. The computed values of pore size versus depth below the cooling surface (in the *x*-direction) for all of the conditions tested in the anisotropic quench study. The left column of plots corresponds to $\bar{\phi}_p = 0.08$, the middle column to $\bar{\phi}_p = 0.15$, and the right column to $\bar{\phi}_p = 0.225$. The top row of plots corresponds to Le = 50, the middle row to Le = 100, and the bottom row to Le = 150. Within each plot, there are three data lines corresponding with three bath temperatures, as indicated.



Fig. 10. The skin layer thickness versus T_{bath} for the three different $\bar{\phi}_p$ values tested and the three different *Le* numbers tested. The skin layer thickness increases with decreasing T_{bath} , increasing $\bar{\phi}_p$, and increasing *Le*.

average pore size versus depth from the cooling surface along the *x*-direction. This was performed using the same procedure as described above, however only columns of data along the *y* and *z* directions were probed, and the average pore size for each *x* plane was computed. This data is plotted in Fig. 8 versus depth away from the cooling surface. Here, we have varied three critical parameters: $\bar{\phi}_p$, *Le*, and *T*_{bath}. Fig. 8 contains a 3 × 3 array of plots in which each column represents a particular value of $\bar{\phi}_p$, each row represents a particular value of *Le*, and each line within the plots represents a particular value of *T*_{bath}. The three bath temperatures chosen correspond to ice water (*T*_{bath} = 273 *K*), room temperature (*T*_{bath} = 298 *K*), and a hotter temperature (*T*_{bath} = 333 *K*).

The plots in Fig. 8 show several important relationships. First, the skin layer can be recognized by the small values of pore size at small depths. The pore size increases rather abruptly at the bottom of the skin layer. Below the skin layer, the pore size increases somewhat gradually along the depth of the system. Overall, an observed trend is that the pore size is larger for smaller values of $\bar{\phi}_p$, smaller values of Le, and higher values of T_{bath}. Higher bath temperatures and smaller values of Le result in lower temperature drop rates, hence longer periods of phase separation and therefore larger pore sizes. Smaller values of $\bar{\phi}_n$ correspond with less polymer content and larger pore sizes, as observed for the isotropic quenches. In Fig. 8, cases where the pore size apparently drops at the largest depths (around 15 µm) is actually due to insufficient time to initiate phase separation in those regions. Longer simulations would be required to capture phase separation in those regions. Fig. 9 shows the final states of the three different $\bar{\phi}_p$ values used, illustrating the difference in the size and interconnectivity of porosity. The $\bar{\phi}_n = 0.08$ sample has the largest pore sizes and a very interconnected pore network. Conversely, the $\bar{\phi}_p = 0.225$ sample has smaller pores which appear to be discrete and non-interconnected.

We measured the skin layer thickness, and plotted these values versus T_{bath} for the three $\bar{\phi}_p$ values and the three *Le* values, as shown in Fig. 10. These values of skin layer thickness were arbitrarily defined as the depths at which the average pore size increased by 50% in Fig. 8. We observe that skin thickness increases with decreasing T_{bath} , increasing *Le*, and increasing $\bar{\phi}_p$. These results are generally in agreement with experiments [33]. The skin layer thickness is also highly dependent on the crystallization temperature, which we kept at a constant value of 390 K, corresponding with the PVDF/DPC system [31]. This anisotropic quench process illustrates the intricate relationships between many thermodynamic, kinetic, and processing conditions that ultimately govern the resultant pore structure that forms.

4. Conclusion

To fully capitalize on the power of computer simulations in predicting membrane morphology for a particular material system and processing conditions, three-dimensional simulations and analysis must be performed. With current computer power, and with appropriate mesoscale models, simulations are now able to predict the complex networks of porosity that form within polymer membranes during fabrication. In this paper, we present a phase-field model to investigate the TIPS process through time for the PVDF/DPC material system. We conducted both isotropic and anisotropic quenches, and analyzed the pore networks for both average pore size and pore interconnectivity. In our anisotropic quenches, the domain size in the direction of heat flux was $17.5 \,\mu$ m, which is an order of magnitude smaller than typical polymer sheet membranes. Hence, a current simulation cannot predict pore structure throughout an entire membrane cross-section. Nevertheless, important insights can be made from this simulation model, which we contend is fast becoming a valuable tool for membrane manufacturers.

The current model does not capture convective transport of the polymer species within the solution during phase separation. A diffusion-based model is likely more suited to the TIPS process than the SIPS process, whereby the exchange of two solvent species occurs on longer length scales. A next step will therefore be to investigate the SIPS process, likely with an expanded model that captures flow due to interfacial forces in the system.

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