Impact of Polymer Film Thickness and Cavity Size on Polymer Flow during Embossing: Towards Process Design Rules for Nanoimprint Lithography

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Impact of Polymer Film Thickness and Cavity Size on Polymer Flow during Embossing: Towards Process Design Rules for Nanoimprint Lithography

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Abstract
This paper presents continuum simulations of polymer flow during nanoimprint lithography (NIL). The simulations capture the underlying physics of polymer flow from the nanometer to millimeter length scale and examine geometry and thermophysical process quantities affecting cavity filling. Variations in embossing tool geometry and polymer film thickness during viscous flow distinguish different flow driving mechanisms. Three parameters can predict polymer deformation mode: cavity width to polymer thickness ratio, polymer supply ratio, and Capillary number. The ratio of cavity width to initial polymer film thickness determines vertically or laterally dominant deformation. The ratio of indenter width to residual film thickness measures polymer supply beneath the indenter which determines Stokes or squeeze flow. The local geometry ratios can predict a fill time based on laminar flow between plates, Stokes flow, or squeeze flow. Characteristic NIL capillary number based on geometry-dependent fill time distinguishes between capillary or viscous driven flows. The three parameters predict filling modes observed in published studies of NIL deformation over nanometer to millimeter length scales. The work seeks to establish process design rules for NIL and to provide tools for the rational design of NIL master templates, resist polymers, and process parameters.
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Nomenclature

NIL  nanoimprint lithography
$T_g$  glass transition temperature
nm  nanometer
$\mu$m  micrometer
mm  millimeter
°C  degrees Celsius
$X_o$  characteristic length, tool width
$P_o$  characteristic pressure, applied load
$T_o$  characteristic time
$U_o$  characteristic speed
$\eta_*$  polymer viscosity
$*v$  material dimensionless velocity
$*v_m$  mesh dimensionless velocity
$I^*$  dimensionless fluid stress tensor
$Re$  Reynolds number
$\rho$  density
$\hat{n}$  normal vector
$Ca$  Capillary number
$H^*$  dimensionless curvature
$P_{rep}^*$  dimensionless repulsive force
$d'$  dimensionless distance of the polymer boundary normal to the solid indenter
$\sigma$  surface tension
$\Gamma_i^*$  dimensionless elastic stress tensor
$P^*$  dimensionless body force of the embossing load
$\mu$  Lame mu coefficient
$\lambda$  Lame lambda coefficient
$E^*$  dimensionless small deformation strain tensor
$\varepsilon^*$  dimensionless small deformation volume strain
$\eta_{inf}$  infinite shear limit of polymer viscosity
$\eta_o$  zero shear limit of polymer viscosity
$\omega$  polymer time constant
$\dot{\gamma}$  second invariant of shear rate tensor
$n$  shear thinning exponent
$a$  dimensionless parameter describing transition between low-rate and power-law
$t$  fill time
$t_r$  ramp time
$S$  indenter width
$W$  cavity half width
$h_i$  initial polymer film thickness
$h_c$  cavity height
$t_h$  half the time to onset of filling
$t_o$  time to onset of filling
$t_f$  time when polymer has covered half master cavity floor
\( h_r \)  residual film thickness
\( \Delta P \)  pressure difference across the fluid interface
\( R_1, R_2 \)  principal radii of curvature
1. Executive Summary

Nanoimprint lithography (NIL) is a high resolution, high-throughput, economical alternative to standard silicon based fabrication technologies. For NIL to become a viable manufacturing technology, a deep understanding of local polymer flow within simple geometries is required for rational process and master tool design.

This report presents continuum simulations of polymer flow during NIL, investigating the effects of imprint cavity geometry, polymer film thickness and properties, and process parameters. The simulations capture the underlying physics of polymer flow from the nanometer to millimeter length scale and examine geometry and thermophysical process quantities affecting cavity filling. Simulations investigate embossing of single rectilinear cavities of viscous dominant flows with no elastic stress relaxation, i.e. Reynolds number $<< 1$, Deborah number $<< 1$, and Capillary number $>> 1$. A uniform pressure applied to the silicon cavity presses the indenter into the viscous polymer film. No-slip conditions prescribed at the polymer-indenter and polymer-substrate interface model the contact while a capillary surface with surface tension captures the physics of the free polymer surface. Independent variation of imprint pressure, polymer viscosity, polymer film thickness, indenter width, and cavity width and height allows examination of parameters influencing local cavity filling time and polymer deformation mode.

Variations in embossing tool geometry during viscous flow distinguish different flow driving mechanisms. Three parameters predict polymer deformation mode: cavity geometry and polymer thickness ratio, polymer availability, and Capillary number. The ratio of cavity width to initial polymer film thickness defines the directional flow ratio, predicting the importance of deviatoric stress in determining single or dual peak deformation. Single peak flow is governed by the time required for the polymer to enter the cavity, while dual peak flow is governed by the time required for the indenter to penetrate the polymer. The ratio of indenter width to residual film thickness defines the polymer supply ratio, predicting the influence of squeeze flow and relative filling times independent of material rheological properties. Characteristic NIL Capillary number based on Stokes, squeeze, or single peak pipe flow fill time distinguishes between capillary or viscous driven flows, predicting flow driving mechanism to separate necessary process design from external embossing setup and internal material physics. The three parameters predict filling modes observed in published studies of NIL deformation over nanometer to millimeter length scales. The work seeks to establish process design rules for NIL and to provide tools for the rational design of NIL master templates, resist polymers, and process parameters.
2. Introduction

In nanoimprint lithography (NIL), a nanofabricated master tool having three-dimensional topography embosses a thermoplastic substrate, forming a negative relief of the master in the substrate. NIL offers scalable manufacture of nanoelectronics and nanoelectromechanical systems (NEMS) with resolution better than 10 nm [1] over areas greater than 1000 cm² [2]. Recent studies have improved NIL resolution below 5 nm [3] and to the molecular scale [4]. A deep understanding of polymer flow during NIL is critical for rational design of embossing tools and processes. This paper investigates viscous polymer flow during NIL for a wide range of master tool geometry and establishes a framework for NIL process design based on geometric ratios, polymer thickness, and Capillary number.

Several groups have investigated polymer flow during imprint lithography with different embossing geometries and length scales, resulting in several competing phenomenological models of polymer flow [5-11]. Experiments and simulations conducted from the millimeter to nanometer scale resulted in markedly different polymer deformation modes although length scale has not been the apparent cause of differentiation. Figure 1, showing single and dual peak viscous flow, illustrates two polymer deformation modes reported in NIL. Differences in deformation mode and replication fidelity have been attributed to a variety of factors, notably shear and extensional stretching, viscous flow and localized stress, residual stress release, shear-thinning and buckling, and surface tension.

![Single Peak](image1)

![Dual Peak](image2)

**Figure 1.** Nanoimprint lithography polymer deformation modes, exhibiting either single or dual peak deformation.
Studies of embossing on the millimeter to micrometer scale have consistently cited the impact of shear deformation on replication while also noting other case-specific effects. Simulations and experiments at the millimeter scale [5] used a cavity of height 800 µm, width 3.5 mm, and spacing 3 mm to emboss a viscous PMMA film of thickness 1200 µm at 40 °C above its glass transition temperature (T_g). This system resulted in polymer flow with shear deformation at the mold surface and extensional stretching at the cavity center. Experiments at the micrometer scale [6] studied microembossing with indenter width 2 µm, cavity height 4 µm, and cavity widths 30 µm, 50 µm, and 100 µm and 15 – 20 µm thick PMMA films over a temperature range from T_g - 10 °C to T_g + 20 °C. A region of localized high strain occurred near the cavity sidewall, resulting in a deforming polymer peak that spread laterally and vertically to fill the cavity. The microembossing conditions resulted in viscous flow, localized stress, and shear-thinning phenomena dominant over surface tension effects. Indentation experiments at the micrometer to nanometer scale [7] pressed cylindrical micrometer sized cavities of height 2 µm and diameter 10 µm into glassy polymer films of thickness 450 nm and 1.7 µm. In the 450 nm film, the sharp cavity entrance produced extensive shear resulting in dual polymer peak filling. Indentation into the thicker films resulted in dual peak deformation for high loads and single peak deformation for low loads. Residual stress release on demolding influenced final replicated feature size, a phenomenon also noted in [12].

A few NIL studies investigated polymer deformation for film thicknesses and cavity heights in the 100 – 300 nm range. A large area flow experiment [8] studied cavity filling of 200 nm thick PMMA films embossed at T_g + 100 °C by cavities of width 20 µm, height 175 nm, and spacing 40 µm. The resulting deformation was a flat dual peak profile with vertical sidewalls and a central buckled region, attributed to effects from squeeze flow and shear-thinning at the indenter edge and compressive stresses in the interior of the cavity. This experimental work was followed by finite element simulations of a Newtonian fluid with surface tension [9]. These simulations showed the buckling region was the result of capillary forces acting over the large cavity width, where the polymer preferentially wetted the master surface. When surface tension effects were removed from the simulations, smooth single or dual peaks were observed dependent on cavity width, as observed in viscous flow experiments [6]. Other simulations and experiments [10, 11] investigated purely nanometer scale geometries and film thicknesses. Elastic solid simulations modeled the polymer with the nonlinear stress-strain behavior of a Mooney-Rivlin material. The studies showed both single and dual peak flow confined near the master sidewall as described above [6, 7], and noted the effect of film thickness to retard deformation. The authors concluded that polymer in NIL shows rubber-like elastic dynamics above T_g with volume compression under high loads in thick polymer films, suggesting that the elastic component of polymers plays a large role in deformation even at temperatures well above T_g.

Simulations and experiments investigating embossing and imprint lithography from the millimeter to nanometer scale have yielded the common features of single or dual peak deformation that depends on a thermophysical property or process quantity. Each of the above-referenced studies offers a different phenomenological explanation of the observed
behavior and there is little agreement about the relative importance of nonlinear elasticity, residual stress, linear and nonlinear viscous flow, compressive stresses, and capillary forces. There is a need for detailed and systematic study of geometric and material constraints over the length scales of interest. The lack of a comprehensive understanding of polymer flow in the 10 nm – 100 µm range limits NIL process design to ad-hoc or recipe-based approaches.

This paper presents simulations of liquid polymer deformation and filling modes during NIL under viscous-dominant conditions. Independent variation of imprint pressure, polymer viscosity, polymer film thickness, indenter width, and cavity width and height allows examination of parameters influencing cavity filling time and polymer deformation mode. A simple model of laminar flow between plates, Stokes flow, and squeeze flow characterizes the polymer filling time. The simulation regime is completely non-dimensionalized and the results are easily extrapolated for comparison to experiments investigating polymer flow in the 10 nm – 5 mm range. The simulation results predict behavior seen during all previously published NIL deformation studies. We suggest that three characteristic parameters, specifically, geometry ratios, polymer availability, and Capillary number, could form the nucleus of NIL process design rules.
Prior simulations of NIL have treated the polymer as either a viscous Newtonian fluid [9] or nonlinear elastic solid material [10, 11]. Solid mechanics simulations with a Mooney-Rivlin constitutive model [10, 11] used the commercially-available MARC program, based on the finite element method and rectangular plane strain elements, to model the polymer as a rubber elastic above \( T_g \). Fluid mechanics simulations [9] used the commercial computational fluid dynamics code CFD-ACE, based on the finite volume method, to simulate NIL on an Eulerian grid using the volume of fluid method (VOF) to track the deforming polymer interface. VOF methods have also been used to model micro injection molding [13, 14], but the methods sacrifice boundary shape accuracy for a faster speed of solution [15]. The free boundary or moving boundary simulations presented in this paper are ideally suited for \textit{GOMA} [16], a Galerkin finite element program specialized for analysis of manufacturing flows having one or more transport fields such as those that exist in two-phase flows or for the freely-moving polymer surface of NIL.

\textit{GOMA} allows the liquid polymer and the solid indenter to be treated in an arbitrary Langrangian/Eulerian (ALE) reference frame, thereby separating the polymer and solid motion from the mesh motion thus allowing for large free boundary deformations [15, 17]. All surfaces move as part of a fully-implicit, fully-coupled algorithm [15] that links the mesh motion to the material motion through surface kinematic conditions. A Newton-based solution algorithm enables the mesh motion and the rest of the problem physics to be solved simultaneously. For the simulations presented here, an implicit Backward-Euler time integration is used with a classical Gaussian elimination LU decomposition method. The maximum dimensionless time step size is 0.01 with a residual less than \( 10^{-7} \) at each time step. The mesh uses 9-node isoparametric quadrilaterals with smaller elements near the indenter-polymer interface and larger elements at the cavity center for accurate and swift solution convergence.

Figure 2 shows the finite element model with prescribed boundary conditions. The model assumes the embossing geometry is adequately vented or under vacuum conditions. To improve computation time and convergence, the problem is non-dimensionalized by choosing a characteristic length \( X_0 \) equivalent to the tool width, pressure \( P_0 \) equivalent to the applied load, time \( T_o \) equivalent to the ratio of polymer viscosity \( \eta \) to applied load, and speed \( U_o \) equivalent to the ratio of characteristic length to characteristic time. The characteristic time is chosen to match the timescale of microembossing experiments previously reported [6] and the characteristic speed is chosen to balance the viscous and pressure forces for computational ease. The scaled conservation equation for mass is

\[
\nabla^* \cdot \mathbf{v}^* = 0, \tag{1}
\]

and the scaled liquid momentum conservation equation is
\[
Re \left( \frac{\partial \mathbf{v}^*}{\partial t} + (\mathbf{v}^* - \mathbf{v}_m^*) \cdot \nabla \cdot \mathbf{v}^* \right) = \nabla^* \cdot \mathbf{\Gamma}^*,
\]

(2)

where \( Re \) is the Reynolds number based on polymer zero shear viscosity, \( \mathbf{v}^* \) and \( \mathbf{v}_m^* \) are the material and mesh dimensionless velocity, respectively, and \( \mathbf{\Gamma}^* \) is the dimensionless fluid stress tensor. The dimensionless Reynolds number is \( \rho U_o X_o / \eta \), where \( \rho \) is the density.

Figure 2. Nanoimprint lithography cavity and deforming polymer, showing simulation boundary conditions, geometry variables, and polymer peak deformation location measurement.

The boundary condition on the free surface of the liquid is modeled by a force balance of the fluid traction with capillary forces:

\[
n \cdot \mathbf{\Gamma}^* = \frac{1}{Ca} 2H^* n + \frac{1}{\eta U_o} \nabla^* \sigma + \frac{1}{X_o^4 d^4} P_{rep}^*,
\]

(3)

where \( n \) is the normal vector, \( Ca \) is the Capillary number, \( H^* \) is the dimensionless curvature, \( P_{rep}^* \) is an arbitrary dimensionless repulsive force, and \( d^* \) is the dimensionless distance of the polymer boundary normal to the solid indenter. The Capillary number \( Ca = \eta U_o / \sigma \) is a ratio of viscous forces to surface tension forces, where \( \sigma \) is the surface tension. Equation 3 represents a force balance at the polymer-air interface that balances the surface tension force due to curvature of the surface, the gradient of surface tension along the surface, the normal stress from the fluid and the contact force due to the proximity of the solid surface. The contact force \( P_{rep}^* \) is not significant physically and is arbitrarily chosen to ensure no liquid penetration of the solid surface. The repulsive term is applied to the liquid surface normal to the contact plane, allowing the liquid to slip along the solid surface without penetrating the solid. The ALE framework allows the capillary boundary condition to define the material shape of the free surface and a
kinematic mass balance condition ensures that the mesh location conforms to the material location at the boundary:

\[ n \cdot (v^* - v_m^*) = 0. \quad (4) \]

The body of the liquid can still be represented by an immaterial mesh that does not introduce artificial stress or deformation while the capillary surface can determine the motion of the moving boundary. A no-slip condition is applied to the fluid at the initial fluid-solid interface with the indenter and substrate.

While the stress and strain in the solid master is important for NIL process design, the fluid deformation is of primary interest here so the simulations use a single solid cavity of small mass. Conservation of momentum transfers load from the solid to the fluid. Assuming elastic forces are much larger than inertial forces, solid momentum conservation is

\[ \frac{1}{X_o} \nabla^* \cdot \Gamma_s^* + P_o^* = 0, \quad (5) \]

where \( \Gamma_s^* \) is the dimensionless elastic stress tensor and \( P^* \) is the dimensionless body force of the embossing load. The elastic stress tensor is

\[ \Gamma_s = 2\mu E^* + \lambda e^* I, \quad (6) \]

where \( \mu \) and \( \lambda \) are the Lame elastic coefficients, \( E^* \) is the dimensionless small deformation strain tensor, and \( e^* \) is the dimensionless small deformation volume strain. At the fluid-solid indenter interface, a stress balance is prescribed where the stresses in the fluid directly replace the stresses in the solid material residual equation at the interface. The balance in equation form is

\[ \frac{P}{\mu} n \cdot \Gamma^* = n \cdot \Gamma_s^*. \quad (7) \]

\( GOMA \) is capable of modeling a variety of liquid constitutive equations. Both Newtonian fluid models and non-Newtonian Carreau-Yasuda models are used, where the Carreau-Yasuda model is given in unscaled form by

\[ \eta = \eta_{inf} + (\eta_\infty - \eta_{inf}) \left[ 1 + (\omega \dot{\gamma})^\gamma \right]^{(n-1)/\alpha}, \quad (8) \]

where \( \eta_{inf} \) and \( \eta_\infty \) are the infinite shear limit and zero shear limit viscosity, respectively, \( \omega \) is the polymer time constant, \( \dot{\gamma} \) is the second invariant of the shear rate tensor, \( n \) is the shear thinning exponent, and \( a \) is a dimensionless parameter describing the transition between the low-rate and power-law region. With proper constants, the model fits well
the material properties described by Fuchs et al [18]. A Newtonian viscosity model better matches the time scale of microembossing experiments near $T_g$ [6], hence a Newtonian material model is used for the majority of simulations.

To address the largest possible solution space, nondimensionalization reduces the number of simulation variables. Applied pressure $P_o$, polymer viscosity $\eta$, and initial film thickness $h_i$ are chosen as the dimensional parameters, reducing the number of independent dimensionless variables to a dimensionless time to fill $tP_o/\eta$, ramp time $t_rP_o/\eta$, density $\rho P_o h_i^2/\eta^2$, indenter width or cavity spacing $S/h_i$, tool width $(2S+2W)/h_i$, and cavity height $h_c/h_i$. The fill time is $t$, the ramp time is $t_r$, the indenter width is $S$, the cavity half width is $W$, and the cavity height is $h_c$. Under viscous-dominant conditions, variations in density do not significantly influence the simulations. Ramp time is not thoroughly investigated for effects on shear rate. For a given applied pressure and polymer viscosity, the ratios of indenter width to film thickness, tool width to film thickness, and cavity height to film thickness are systematically varied to determine their effects on polymer deformation mode and time to fill. The dimensionless ramp time is constant for all cases.
4. Results

Simulations investigated polymer deformation during cavity filling for viscous-dominant conditions, i.e. $Re \ll 1$ and $Ca \gg 1$, where the time scale of relaxation is less than the time scale of flow. Figure 2 shows a representative rectangular cavity having indenter width $S$, cavity height $h_c$, and cavity half width $W$. Of particular interest is the location and size of the polymer peak(s), and the time required to fill the cavity. Simulations modulated cavity geometry, polymer film thickness, and process conditions and examined their effect on polymer deformation mode. Most simulations modeled the polymer as a Newtonian fluid, but a few modeled the polymer as shear-thinning. Cylindrical cavities were briefly investigated as well.

4.1. Polymer Deformation Mode

Figure 3 shows the effect of rectangular cavity width and film thickness on polymer deformation, where dimensionless cavity size is the ratio of cavity width to tool width $W/(S+W)$ and dimensionless cavity height is the ratio of cavity height to film thickness $h_c/h_i$. The indenter width is constant and only the cavity width or polymer film thickness changes. For each configuration, deformation profiles are shown for four times: the start of imprinting $t_i$, half the time to onset of filling $t_h$, onset of filling $t_o$, and the time when polymer has covered half of the master cavity floor $t_f$. Onset of filling occurs when the polymer peak first touches the master cavity floor. As cavity width increases, the deformation mode changes from single peak to dual peak deformation. The polymer deformation also transitions from single to dual peak as the initial polymer film thickness decreases, as shown in Fig. 3b. For the largest cavity widths and thinnest polymer layers, the two peaks are highly localized near the vertical cavity walls and do not interact.

For all of the simulations of this paper, the polymer deformation occurs near the indenter sidewall. Figure 3c shows the transition from single to dual peak flow based on cavity half width $W$ and initial film thickness $h_i$. The single to dual peak transition is clearly observed at $W/h_i$ near 1.2. The polymer peak remains located roughly $h_i$ from the indenter sidewall regardless of any other parameter. Small variations in peak location for a given value of $W/h_i$ are due to polymer shear limits or complete cavity filling. The polymer peak will spread laterally but not indefinitely as the lateral motion of the peak is driven by shear near the indenter sidewall.

The degree of fluid shear-thinning behavior influences peak location, shown in Fig. 4. Deformation profiles are shown at a dimensionless time of 1.0 for a Newtonian fluid and shear-thinning fluids of varying degree, where $\eta_{inf}$ and $\eta_o$ differ by four orders of magnitude. A shear-thinning fluid of power law exponent 0.15 moves the polymer peak 10% closer to the sidewall than a Newtonian fluid and decreases the required time to fill by nearly 50% compared to the Newtonian fluid for this cavity. In general, a shear-dependent fluid will affect polymer flow where shear is greatest, which occurs for small indenter widths, large cavity widths, and small film thickness. The decrease in polymer shear modulus above $T_g$ also promotes increased influence of shear-thinning parameters.
Figure 3. Deformation profiles for (a) increasing cavity width holding indenter width and film thickness constant and (b) decreasing film thickness holding cavity geometry constant. (c) Impact of resist film thickness on cavity filling. The location of the deforming polymer peak location is always a distance from the cavity vertical sidewall approximately equal to the polymer thickness.
Figure 4. Effect of shear-thinning on deformation. Decreasing shear-thinning exponent from 1 (Newtonian) to 0.15 (highly shear-thinning) reduces the polymer viscosity near the vertical cavity wall, moving the polymer peak closer to the indenter sidewall and decreasing the time to fill.
The general trends of polymer flow are similar for cylindrical, as opposed to rectangular, embossing tools. Figure 5 compares Newtonian flow for a rectangular cavity and a cylindrical slot with equivalent cavity width and diameter. At $W/h_i = 1.4$, the cylindrical slot is in single peak deformation mode while the rectangular cavity deforms in a dual peak mode. Circumferential confinement in the cylindrical slot delays the transition from single to dual peak deformation to higher values of $W/h_i$. The cylindrical slot also requires longer time to fill than the rectangular cavity because of the same confinement.

**Figure 5.** Comparison of geometric configuration for given cavity diameter or width. Confined geometry of a cylindrical slot delays the transition from single to double peak for increased cavity diameter. Cylindrical slot also requires longest time to fill.
4.2. Cavity Filling Times

Figure 6 shows the impact of rectangular cavity geometry and film thickness on fill times for a viscous Newtonian fluid, for several values of $W/(S+W)$ and constant $S+W$. In general, wider cavities fill faster than narrower cavities, and taller cavities on thin polymer films fill slower than shorter cavities on thick polymer films. In all cases, single vs. dual peak deformation mode affects cavity filling time, as the degree of shear in the polymer drives the filling. In both single and dual peak flow, it is possible to increase cavity width and/or decrease indenter width to promote shear. Figure 7 shows the effect of dimensionless cavity height on fill time. In general, taller cavities fill slower than shorter cavities. The wider cavities reach filling onset more rapidly than the narrower cavities but the overall filling time is not necessarily governed by cavity width. As Fig. 7 shows, once filling begins, the main restriction to polymer flow is not inside the cavity but between the indenter and the hard substrate, resulting in a squeeze flow. Figure 7b shows that squeeze flow in the polymer film becomes important as the indenter width $S$ becomes greater than the residual film thickness $h_r$, i.e. when $S/h_r > 1$. 
Figure 6. Impact of cavity size and cavity height to film thickness ratio on cavity filling. Increasing cavity height to film thickness ratio increases time to fill. For both single and dual peak deformation, increasing the indenter width or decreasing the cavity size increases time to fill. Time to fill levels off at decreasing dimensionless cavity size as deformation transitions to single peak and begins to decrease for single peak flow. As cavity size continues to decrease, time to fill eventually increases dramatically as evenly distributed pressure forces polymer to travel thru confined slot.
Figure 7. Impact of polymer availability on filling time. (a) Small cavity sizes require longest time to begin filling. (b) When the indenter width becomes greater than the residual film thickness, squeeze flow between the indenter and the substrate causes time to completely fill to dramatically increase. (c) Deformation profile showing the increasing time between fill onset and full filling.
5. Discussion

The polymer deformation predicted here agrees well with a number of articles that measure and model polymer deformation from the 10 nm to 1 mm scale. Nearly every report observed deforming polymer peaks located \( \sim h_1 \) from the master sidewall [5-7, 9-11, 19], with single peak deformation when the cavity half width was less than polymer film thickness, \( W < h_1 \), and dual peak deformation for cavity half width greater than polymer film thickness, \( W > h_1 \). The value \( W/h_1 \) defined dual vs. single peak polymer deformation for measurements on films of thickness 1.2 mm [5], 500 \( \mu \)m [19], and 20 \( \mu \)m [6]. Experiments in 1.7 \( \mu \)m films [7] found single peak deformation at \( W/h_1 > 2 \) while the present simulations predict dual peak deformation at \( W/h_1 > 1.2 \), however the discrepancy can be attributed to stress relaxation following elastic rather than viscous deformation. Simulations that excluded surface tension examined embossing of 200 nm thick polymer films and produced single peak deformation for \( W/h_1 < 1 \) and dual peak deformation for \( W/h_1 > 1 \) [9]. The Newtonian liquid deformations presented here agree with nonlinear solid elastic deformations [10, 11] that also noted cavity geometry and initial film thickness modulate deformation mode.

The effects of film thickness and cavity geometry on filling time also agree well with reported values over a significant breadth of length scales. All of the referenced studies state that decreasing \( h_1 \) or increasing \( h_c/h_1 \) increases either the filling time [7, 8, 20] or the filling pressure [10, 11]. For the present viscous liquid simulations, time and pressure are linearly related in the non-dimensionalization. In solid mechanics simulations [11], both low and high aspect ratio structures required higher pressures to fill the cavity than intermediate aspect ratios. The present simulations agree with this previous finding and explain the phenomena by linking filling time to deformation mode, as shown in Figs. 6 and 7.

The ratio \( W/h_1 \) accurately predicts single vs. dual peak deformation, indicating whether the polymer flow is mostly vertical or mostly lateral. As such \( W/h_1 \) can be thought of as the directional flow ratio. Figure 8 shows contours of the mean shear rate (deviatoric shear stress) for three cavity widths on the same polymer film, for which there is single and dual peak deformation and free shear flow between the indenter and substrate, and also for dual peak flow and squeeze flow between the indenter and substrate. For the cases that there is no squeeze flow between the indenter and the substrate, there is a plug of non-deforming polymer in the cavity center. This plug is pushed upward in single-peak flow, but does not move in the case of dual peak flow, as it is too far from the indenter sidewall to be affected by the induced shear. When the polymer film between the indenter and substrate becomes thin, squeeze flow dominates the polymer filling, with consequences for filling time as well as deformation mode as illustrated in Fig. 7.
Figure 8. Mean shear rate or deviatoric stress profile. Single peak flow pushes non-shearing fluid plug vertically in a single polymer peak. Dual peak flow results from shear near the indenter sidewall with non-shearing fluid plug in cavity center. As flow transitions from shear dominant to squeeze dominant, a plug develops underneath the indenter as well as in the cavity center.

The three different characteristic flow profiles in Fig. 8 suggest cavity geometry governs filling behavior. Simple viscous flow theory, based on mold geometry ratios, can estimate a characteristic NIL filling time, \( t_{\text{NIL}} \), for the filling of each geometry. The case of single peak flow, occurring when \( W/h_i < 1 \) regardless the value of \( S/h_r \), resembles the classic fluid mechanics problem of steady laminar flow between infinite plates or within a pipe. Assuming fully developed flow and no slip conditions at the boundaries, a characteristic single peak pipe flow fill time can be defined as

\[
t_{\text{NIL}} = \frac{12\eta c h_i^2 S}{P(2W)^2(S+W)} \tag{9}
\]

and a characteristic velocity, \( V_{\text{NIL}} \), may be found by dividing the distance the polymer must travel, i.e. the cavity height, by \( t_{\text{NIL}} \):

\[
V_{\text{NIL}} = \frac{P(2W)^2(S+W)}{12\eta c h_i S}. \tag{10}
\]

Fill times estimated by Eq. 9 correlate well with single peak fill times simulated here when \( W/h_i < 0.5 \). However, when \( W/h_i > 0.5 \), Eq. 9 underestimates simulated fill times by a factor of ~3 - 5. For these cases, simulated fill times seem to resemble flow through an abrupt expansion from a flow channel of \( h_i \) to \( h_i + h_c \), resulting in roughly 60 - 80% head loss for the geometries simulated here [21]. Modifying Eq. 9 accounting for the expansion loss coefficient provides a better estimate for fill time when \( 0.5 < W/h_i < 1 \). For the case of dual peak squeeze flow, when \( W/h_i > 1 \) and \( S/h_r > 1 \), the cavity filling time can be estimated by applying the lubrication approximation when assuming a fluid is squeezed out between infinite plates of width twice the indenter width moving at constant
velocity due to an applied load. The situation of cavity filling in NIL cannot be accurately defined so simply since the polymer is expelled into a finite pressure field due to confinement and because the effective pressure decreases as more polymer comes into contact with the cavity surface, thus slowing the imprint. A reasonable characteristic squeeze flow filling time can be estimated as the time required to squeeze a fluid from the initial film thickness to the residual film thickness by infinite plates of width twice the tool width weighted by the ratio of indenter width to tool width:

\[
t_{\text{NIL}} = \frac{\eta (S+W)^2}{2P} \left( \frac{1}{h_r^2} - \frac{1}{h_i^2} \right) \left( \frac{S}{S+W} \right). \tag{11}
\]

This time is similar to the fill time defined by [8] but different by choice of plate width and weighting. Ignoring elastic effects, the residual film thickness \(h_r\), or mold flash, is defined in terms of the master tool dimensions and initial polymer thickness

\[
h_r = h_i - \frac{Wh_i}{S+W}. \tag{12}
\]

A characteristic squeeze flow velocity can be found by dividing the difference in initial film thickness and residual film thickness by \(t_{\text{NIL}}\): \(V_{\text{NIL}} = (h_i - h_r)/t_{\text{NIL}}\). \(V_{\text{NIL}}\) is therefore

\[
V_{\text{NIL}} = \frac{2P}{\eta S(S+W)} \frac{h_i^2 h_r^2}{h_i + h_r} \tag{13}
\]

This velocity is close to the imprint velocity defined by [9] but again different by choice of plate width and weighting. The squeeze flow characteristic fill time best approximates simulated fill times at large \(W/h_i\) when the polymer squeezed from beneath the indenter meets low pressure resistance in the cavity center. For dual peak shear free flow when \(W/h_i > 1\) and \(S/h_r < 1\), a different characteristic fill time may be defined based on Stokes flow [22]. Like squeeze flow filling, shear flow filling will be slowed as more polymer contacts the cavity surface. Hence a practical estimate for a characteristic Stokes fill time can be defined using the tool width, rather than the indenter width, as the indenting surface, giving

\[
t_{\text{NIL}} = \frac{6\eta}{P(S+W)} (h_i - h_r) \tag{14}
\]

and a corresponding characteristic Stokes velocity of

\[
V_{\text{NIL}} = \frac{P(S+W)}{6\eta} \tag{15}
\]

Regardless of length scale, directional flow ratio \(W/h_i\) and polymer supply ratio \(S/h_r\) can determine appropriate \(V_{\text{NIL}}\), which in turn can define a Capillary number characteristic of
the imprint process, \( Ca_{NIL} = \eta V_{NIL}/\sigma \). From Eqs. 10, 13, and 15, the viscosity dependence of \( V_{NIL} \) eliminates the viscosity dependence of \( Ca_{NIL} \).

Three parameters, \( Ca_{NIL} \), \( W/h_i \), and \( S/h_r \), can predict all of the previously reported polymer deformation modes during NIL. \( Ca_{NIL} \) determines viscous vs. capillary driven flow, the directional flow ratio \( W/h_i \) predicts single or dual peak flow, and the polymer supply ratio \( S/h_r \) determines shear-dominant Stoke’s flow vs. squeeze flow. Table 1 lists imprint parameters from a number of articles that examined polymer flow during embossing and also lists \( Ca_{NIL} \), \( W/h_i \), and \( S/h_r \). Figure 9 shows two regime maps of polymer filling modes and plots the simulations and experiments listed in Table 1. Figure 9a shows the determination of \( V_{NIL} \) from \( W/h_i \) and \( S/h_r \), and Fig. 9b shows flow driving mechanism defined by \( W/h_i \) and \( Ca_{NIL} \). When located on the regime maps of Fig. 9, all of the experiments and simulations of Table 1 fall within their region of reported flow behavior. For the present simulations and the viscous deformation measurements of cited references [5-7, 19], the single vs. dual peak deformation is independent of capillary number and is determined by geometry only. A cylindrical slot can shift the transition from single to dual peak deformation to a higher value of \( W/h_i \) than occurs in rectilinear cavities.
Table 1. Comparisons of millimeter, micrometer, and nanometer scale imprinting. All studies are for negligible Reynolds number flows \((Re < 10^{-14})\). Using a characteristic velocity derived from viscous flow theory, all different flow regimes reported may be characterized by capillary number and geometry ratios. The NIL capillary number is independent of viscosity.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>(h_r) (nm)</th>
<th>(h_r/h_i)</th>
<th>(W/h_i)</th>
<th>(S/h_i)</th>
<th>(V_{NIL}) (nm/sec)</th>
<th>(Ca_{NIL})</th>
<th>Flow Profile</th>
</tr>
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<tr>
<td>Rowland [6]</td>
<td>5.67 x 10^3</td>
<td>63.0%</td>
<td>1.11</td>
<td>0.35</td>
<td>6.00 x 10^1</td>
<td>2.02 x 10^3</td>
<td>Single Peak Viscous</td>
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<tr>
<td>Rowland [6]</td>
<td>5.30 x 10^3</td>
<td>58.8%</td>
<td>2.78</td>
<td>0.38</td>
<td>1.35 x 10^2</td>
<td>4.55 x 10^3</td>
<td>Dual Peak Viscous</td>
</tr>
<tr>
<td>Rowland [24]</td>
<td>2.67 x 10^3</td>
<td>44.4%</td>
<td>4.17</td>
<td>1.88</td>
<td>1.18 x 10^1</td>
<td>3.98 x 10^2</td>
<td>Dual Peak Viscous Squeeze</td>
</tr>
<tr>
<td>Heyderman [8]</td>
<td>1.56 x 10^2</td>
<td>78.1%</td>
<td>50.0</td>
<td>192</td>
<td>5.48 x 10^0</td>
<td>5.54 x 10^4</td>
<td>Dual Peak Capillary Squeeze</td>
</tr>
<tr>
<td>Jeong [9]</td>
<td>1.94 x 10^2</td>
<td>97.2%</td>
<td>2.50</td>
<td>77.2</td>
<td>3.96 x 10^1</td>
<td>3.99 x 10^3</td>
<td>Dual Peak Capillary Squeeze</td>
</tr>
<tr>
<td>Jeong [9]</td>
<td>1.99 x 10^2</td>
<td>99.7%</td>
<td>0.25</td>
<td>75.2</td>
<td>5.73 x 10^3</td>
<td>5.79 x 10^1</td>
<td>Dual Peak Capillary-Viscous Squeeze or Confined Single Peak (Wet-dependent)</td>
</tr>
<tr>
<td>Cross [7]</td>
<td>1.29 x 10^3</td>
<td>75.7%</td>
<td>2.94</td>
<td>4.66</td>
<td>9.83 x 10^1</td>
<td>3.31 x 10^1</td>
<td>Dual Peak Viscous</td>
</tr>
<tr>
<td>Cross [7]</td>
<td>1.29 x 10^3</td>
<td>75.7%</td>
<td>2.94</td>
<td>4.66</td>
<td>7.45 x 10^0</td>
<td>2.51 x 10^2</td>
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<tr>
<td>Cross [7]</td>
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<td>11.1</td>
<td>163</td>
<td>1.74 x 10^4</td>
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<tr>
<td>Hirai [10]</td>
<td>-1.5 x 10^1</td>
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<td>Hirai [10]</td>
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<td>4.35</td>
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<tr>
<td>Hirai [10]</td>
<td>2.25 x 10^2</td>
<td>62.5%</td>
<td>1.39</td>
<td>2.22</td>
<td>1.35 x 10^1</td>
<td>4.53 x 10^1</td>
<td>Dual Peak Viscous</td>
</tr>
<tr>
<td>Juang [5]</td>
<td>6.40 x 10^5</td>
<td>53.3%</td>
<td>2.92</td>
<td>2.34</td>
<td>5.98 x 10^3</td>
<td>2.01 x 10^4</td>
<td>Dual Peak Viscous</td>
</tr>
<tr>
<td>Shen [19]</td>
<td>4.50 x 10^5</td>
<td>90.0%</td>
<td>0.20</td>
<td>0.22</td>
<td>1.20 x 10^2</td>
<td>4.04 x 10^3</td>
<td>Confined Single Peak Viscous</td>
</tr>
<tr>
<td>Austin [3]</td>
<td>9.50 x 10^1</td>
<td>95.0%</td>
<td>0.07</td>
<td>0.07</td>
<td>3.43 x 10^1</td>
<td>1.15 x 10^2</td>
<td>Confined Single Peak Capillary (Non-wetting)</td>
</tr>
<tr>
<td>Yu [25]</td>
<td>4.64 x 10^1</td>
<td>22.1%</td>
<td>1.07</td>
<td>7.01</td>
<td>2.11 x 10^0</td>
<td>7.10 x 10^2</td>
<td>Single Peak Capillary (Non-wetting)</td>
</tr>
</tbody>
</table>
Figure 9. NIL polymer deformation regime maps for NIL capillary number $Ca_{\text{NIL}}$, directional flow ratio $W/h_i$, and polymer supply ratio $S/h_r$. All of the NIL flows reported in the reference of Table 1 are located on the maps, and fall into the polymer flow regime predicted by the theory of the present paper. The dotted square indicates the simulation space of this work. (a) Directional flow ratio and polymer availability determine characteristic velocity governing polymer deformation. (b) The effect of cavity geometry and polymer film thickness on polymer deformation. $Ca_{\text{NIL}}$ governs viscous vs. capillary flow, and $W/h_i$ governs single vs. dual peak polymer deformation.
Surface tension can influence the single to dual peak transition in capillary flows. As capillary forces become significant relative to viscous forces, the transition from single to dual peak deformation can occur at higher values of $W/h_i$ than in purely viscous flow as the surface forces act to minimize the polymer surface area. The region where viscous forces are comparable to capillary forces is shaded in Figure 9. Competing viscous and capillary forces can explain the flat deformation profile resulting from a wetting fluid filling a thin cavity observed by [9]. In the strictly capillary region, transition from single to dual peak deformation depends strongly on surface chemistry. For a wetting fluid having a small contact angle with the master sidewall, the fluid will wet the master surface and climb the indenter sidewalls in a dual peak mode, independent of $W/h_i$. This wetting behavior has been observed by [8, 9, 20]. The deformation behavior for a non-wetting fluid is more complex than for a wetting fluid, and can depend on surface tension, contact angle, viscosity, pressure, film thickness, and cavity spacing. For a non-wetting fluid with large contact angle, polymer flow will be governed by the ratio of pressure and surface tension. The classical form of the Young-Laplace equation relates the radius of curvature of a fluid surface with the surface tension:

$$\Delta P = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right),$$

(13)

where $\Delta P$ is the pressure difference across the fluid interface and $R_1$ and $R_2$ are the principal radii of curvature. For a surface confined in only one direction, $R_1$ is finite while $R_2$ is infinite. The range of surface tension values for common engineering materials spans only 1-2 orders of magnitude [21] and thus for a given cavity, changes in embossing pressure will affect the curvature of the deforming polymer. While in the viscous regime, $W/h_i$ alone modulates single to dual peak transition, for a non-wetting fluid in capillary flow, the single to dual peak transition also depends on surface tension and contact angle, and in general occurs at larger $W/h_i$. Furthermore, for a non-wetting fluid capillary flow, the impact of cavity curvature is more important than for rectangular cavities, and thus single to dual peak transition in a cylindrical cavity is shifted to higher $W/h_i$ than for a rectilinear cavity.

The three parameters $W/h_i$, $S/h_{i*}$, and $C_{NIL}$, can guide NIL process design. The directional flow ratio $W/h_i$ distinguishes between vertical and lateral mold filling, which is important for replicating smooth surfaces of unfilled cavities as in the NIL manufacture of optics components. The polymer supply ratio $S/h_{i*}$ gauges the tradeoff between relative filling time and residual film thickness. The residual film thickness is critical for nanoelectronics fabrication where the mold flash must be removed before further processing. High values of the polymer supply ratio may also be unattainable in glassy or glass-like polymer systems [7, 23]. $C_{NIL}$ determines the dominant flow driving mechanism in NIL and defines the imprint regimes where surface chemistry must be considered. In the viscous regime, modulating polymer viscosity through pressure or temperature can improve replication time.
6. Conclusions

This paper performs simulations of viscous polymer flow during nanoimprint lithography, investigating the effects of imprint cavity geometry, polymer film thickness and properties, and process parameters. Polymer deformation and fill time is governed by location and rate of polymer shear during imprinting, exhibiting deformation predominantly close to the vertical indenter sidewall that can result in single peak or dual peak deformation modes. The continuum simulations capture the NIL physics observed by numerous published articles from the 10 nm to 1 mm scale.

Three parameters, \( \frac{W}{h_i} \), \( \frac{S}{h_r} \), and \( Ca_{NIL} \), accurately predict polymer deformation and filling mode. The directional flow ratio \( \frac{W}{h_i} \) predicts importance of deviatoric stress determining single or dual peak deformation and hence vertical or lateral flow. The polymer supply ratio \( \frac{S}{h_r} \) predicts the influence of squeeze flow and relative filling times independent of material rheological properties. The NIL Capillary number, \( Ca_{NIL} \), predicts flow driving mechanism to distinguish necessary process design from external embossing setup and internal material physics. The three parameters \( \frac{W}{h_i} \), \( \frac{S}{h_r} \), and \( Ca_{NIL} \) combine to allow rational and predictive NIL process design and provide a step towards establishing design rules for NIL. Rather than rely on improvised trial and error, it is possible to use these tools to appropriately tailor tool geometry, process conditions, and polymer rheology and surface chemistry for optimal NIL.
7. References


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