Study on Induced Stress and Strain in Direct Nanoimprint Lithography

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Induced stress and strains in direct nanoimprint process are investigated by computational works. Impact of the mold pressing velocity, the polymer thickness, and the side wall angle of the mold are studied for the model polymer and PMMA. The shear stress distribution in pattern cavity is strongly affected by the polymer thickness and the side wall angle of the mold. By inclination of the side wall, the shear stress is spread into pattern cavity in triangular shaped cavity due to polymer flow along the side wall, which may induce molecular ordering. On the other hand, stress and strain distributions are hardly affected by the mold pressing velocity under investigated conditions.

Keywords: thermal nanoimprint, induced stress, viscosity, shear stress, side wall angle

1. Introduction
Nanoimprint lithography [1] realizes direct fabrication of micro-nano structures using various functional materials such as polymers, glasses, and organic semiconductor films. Various applications have been reported utilizing specific features of the micro-nano structures fabricated by direct nanoimprint technology. For examples, sub wavelength optical devices with high aspect ratio structures or corn shaped structures, bio-medical chips using specific polymers, organic photovoltaic devices using nanostructured organic polymer, and electric devices on flexible films using direct forming by thermal direct nanoimprint.

In direct nanoimprint process, fatal damages due to induced stress are generated during press [2,3]. On the other hand, induced shear stress causes molecular orientation [4-12], or mobility enhancement of carriers or ions [13], which are profitable for device application, however there are few reports on stress.

In this report, we investigate induced stress and strain in polymer materials in various process and topological conditions in direct thermal nanoimprint lithography by computational works.

2. Computational model

To investigate behavior during press process, we focused on induced shear stress, and strain in polymers under various pressing velocity of the mold and system topology such as mold side wall shapes, and polymer thicknesses.

Figure 1 shows schematics of the computational model. A mold with line and space pattern is pressed against polymer with velocity v.

The polymer is a visco-elastic body and the mold is a rigid body. The polymer is fixed on the substrate and symmetrical boundaries are applied for both sides. The pattern width, height, and residual thickness are w, h, and d, respectively. The aspect ratio h/w is fixed to 1.0. Also the side wall angle θ of the mold and polymer thickness d is modified. The examined system dimensions are shown in Table 1.

For computational study, conventional Finite Element method is applied [14-20]. Generalized Maxwell model [21] was used for the polymer model as illustrated in Fig. 2, where the visco elastic property is expressed by combination springs and dashpots. Time dependent shear modulus of the polymer is expressed as:

\[ G(t) = G_{\text{inf}} + \sum G_j \exp(-t/\tau_j) \]

where the time constant \( \tau_j \) is defined as:
\[
\tau_i = \eta_i / G_i
\]

(2)

Temperature dependence of the viscoelastic properties is expressed based on the William-Landel-Ferry (WLF) model [22] as:

\[
\log_{10} \alpha_T = -\frac{C_1(T - T_0)}{C_2 + (T - T_0)}
\]

(3)

where \(\alpha_T\) is the shift factor, and \(T_0\) is a reference temperature.

3. Results and discussion

3.1. For simplified model polymer

We firstly investigate induced stress and strain behavior during pressing process in nanoimprint. To understand primary mechanism, a simplified polymer model by Maxwell model is studied as shown in Fig. 3, where the polymer is expressed by sequential combination of single spring and dashpot.

\[
\text{Fig. 3. Simplified model polymer by Maxwell model.}
\]

The system is expressed by the following differential equation as:

\[
\frac{d\tau}{dt} = \frac{1}{G} \frac{d\sigma}{dt} + \frac{\sigma}{\eta}
\]

(4)

\[
\tau = \frac{\sigma}{G} = \frac{\sigma}{\eta / G}
\]

(5)

where \(\gamma\) is external strain. \(G\) and \(\sigma\) are shear modulus and induced stress, respectively. \(\tau\) is the relaxation time constant.

When a step strain with amplitude \(\gamma_0\) is applied to the model polymer, the induced stress is expressed as :

\[
\sigma(t) = \sigma_0 \exp\left(-\frac{t}{\tau}\right)
\]

(6)

So, the stress is relaxed with time constraint \(\tau\) and the induced stress approximately disappear after \(3\tau\).

When an external vibration with radius frequency \(\omega\) is applied, \(\sigma\) is expressed as follows:

\[
\sigma(t) = \left(\frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} + i \frac{\omega \tau}{1 + \omega^2 \tau^2}\right)G_0 \gamma_0 \exp(i \omega t)
\]

(7)

The frequency response of modulus is expressed as follows:

\[
|G| = \left(\frac{1}{1 + 1/\omega^2 \tau^2}\right)^{1/2} G_0
\]

(8)

As a result, the modulus of the polymer decreases below frequency \(\omega < 1/\tau\).

To discuss on the mold velocity \(v\) in pressing, the relation between angular frequency \(\omega\) and mold velocity is roughly estimated as shown in Fig. 4.

The shear rate \(\dot{\gamma}\) in the pattern cavity is approximately expressed as:
On the other hand, the mold is assumed to be vibrating up and down at the frequency \( f = \frac{\omega}{2\pi} \) for stroke height \( h \). As a result the average velocity \( v \) is expressed as:

\[
\dot{\gamma} = \frac{v}{w/2}
\]

(9)

The induced shear stress distribution is shown in Fig. 6. At high speed mold pressing, the polymer acts almost elastic body and the shear rate dependence does not appear. On the other hand, the shear rate dependence will appear at low speed (frequency) pressing, which might affect the induced stress distribution.

3.1.1. Impact of Stress relaxation
Firstly, we investigate relaxation process of the induced stress. The induced shear stress distribution is shown in Fig. 6.

The stress distribution is not changed over \( 3\tau \) and the induced stress is almost the same. In the following discussions, the stress and strain distributions are studied when the polymer is nearly filled into the cavity.

3.1.2. Impact of mold pressing speed \( v \)
Impact of mold speed \( v \) on induces stress and strain distributions are investigated. As shown in Fig. 5, at high speed press region (1.0~0.1 m/s), the polymer behavior is almost elastic resin and the modulus depends on \( G \). On the other hand, at low speed region (0.01~0.001 m/s), the polymer turns to viscoelastic body and the modulus depends on the shear rate.

Figure 7 shows the stress and strain distributions in various mold velocity. When the mold velocity is high, stress and strain distributions are not modified because the polymer is almost an elastic body. On the other hand, the stress and strain distributions are almost the same even in the low speed pressing. The result is not expected and could not be explained well.

3.1.3. Impact of polymer thickness \( d \)
Impact of the initial polymer thickness \( d \) is examined. The pressing speed was fixed to 0.1 m/s. Figure 8 shows shear stress and strain distributions for various polymer thicknesses \( d \). As the polymer becomes thinner, the induced stress in residual layer increases due to squeezed lateral flow of polymer. On the other hand, induced stress does not spread in the pattern cavity.

3.1.4. Impact of the side wall angle \( \theta \)
The impact of the side wall angle of the mold cavity is investigated. Figure 9 shows shear stress distributions for various side wall angles (\( \theta = 90, 75, 60 \) degrees).

Stress distribution is spread into the pattern cavity as the side wall is inclined. This is because the polymer flows along the side wall.
Fig. 6. Stress relaxation of model polymer as the relaxation time $t$ proceeds after the polymer is almost filled into the pattern cavity ($G=100 \text{ MPa}$, $\tau = 10^{-5} \text{ sec}$, $v=0.1 \text{ m/s}$).

Fig. 7. Dependence of induced stress and strain stress on the mold velocity ($v = 0.1 \text{ m/s}$).

Fig. 8. Impact of polymer thickness ($v = 0.1 \text{ m/s}$).

Fig. 9. Impact of the side wall angle ($v = 0.1 \text{ m/s}$).
3.2. For PMMA

3.2.1 Mechanical characteristic of PMMA

Instead of the model polymer, actual materials are studied. We choose poly(methyl methacrylate) (PMMA). Characteristic parameters of the WLF low are experimentally extracted and the results are shown in Table 2 for molecular weight $M_w=350k$. The parameters $G_j$ and $\tau_j$ of the generalized Maxwell model are shown in the Table 3.

Figure 10 shows the frequency characteristics of the PMMA at 140 $^\circ$C. Due to interactions between polymer chains, there exist two steps in the frequency characteristics.

### Table 2. WLF parameter of the PMMA.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v$</td>
<td>0.499</td>
</tr>
<tr>
<td>$C_1$</td>
<td>12.796</td>
</tr>
<tr>
<td>$C_2$</td>
<td>74.787</td>
</tr>
<tr>
<td>$T_0$</td>
<td>110 $^\circ$C</td>
</tr>
</tbody>
</table>

### Table 3. Extracted parameters of Maxwell model.

<table>
<thead>
<tr>
<th>$\tau_i$ [sec]</th>
<th>$G_i$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.88E-09</td>
<td>26.7</td>
</tr>
<tr>
<td>6.00E-08</td>
<td>24.3</td>
</tr>
<tr>
<td>6.12E-07</td>
<td>32.7</td>
</tr>
<tr>
<td>6.25E-06</td>
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<td>6.38E-05</td>
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<tr>
<td>6.51E-04</td>
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<tr>
<td>6.63E-03</td>
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<td>6.91E-01</td>
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<tr>
<td>7.05E0</td>
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<tr>
<td>7.19E+01</td>
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<tr>
<td>7.34E+02</td>
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<tr>
<td>7.49E+03</td>
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<td>7.64E+04</td>
<td>0.0637</td>
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<tr>
<td>7.80E+05</td>
<td>0.00671</td>
</tr>
</tbody>
</table>

Fig. 10. Frequency characteristic of PMMA at 140 $^\circ$C

3.2.2. Impact of mold velocity $v$

Impact of mold velocity in pressing process is studied. The simulated results of the induced stress and strain are shown in Fig. 11.

When the mold velocity $v$ is high ($v = 1.0-0.1$ m/s), the induced shear stress and strain are almost the same because the PMMA reacts as elastic body under high shear ratio conditions. As the mold velocity decreases down to 0.001 m/s, the induced stress decreases but the strain distribution is spread into pattern cavity. The strain distribution is slightly different from the model polymer as shown in Fig. 7. At present, the reason is not well understood.

![Fig. 11. Impact of mold velocity for PMMA (Mw=350k, as press).](image)

3.2.3 Impact of side wall angle $\theta$

The impact of the side wall angle $\theta$ of the mold cavity is investigated. Figure 12 shows shear stress and strain distributions for various side wall angles ($\theta = 90, 75, 60$ degrees). Stress distributions are spread into the pattern cavity as the side wall is inline. These results are as same as the model polymer.

4. Summary

Impact of process conditions in direct nano imprint on the induced stress and strain in polymer
material is investigated. Using conventional visco-elastic model, induced stress and strain distributions are numerically calculated for various mold pressing velocity, polymer thicknesses, and side wall angles of the mold for the model polymer and PMMA.

The results show the shear stress distribution in pattern cavity is strongly affected by the polymer thickness and the side wall angle of the mold. In thin polymer system, the shear stress is concentrated nearby opening area of the pattern cavity due to squeezed flow from residual layer.

By inclination of the side wall, the shear stress spreads into pattern cavity due to polymer flow along the side wall, which may induce molecular ordering. On the other hand, stress and strain distributions are hardly affected by the mold pressing velocity and mechanical characteristic of the polymer under investigated conditions.

Further investigations for nano scale patterns are demanded for device applications for advanced devices.

We believe the results provide suggestions in process condition designing for functional polymer material.

Fig. 12. Shear stress distribution for various side wall angles in PMMA ($v = 0.1\text{m/s}$).

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References