Mechanical Properties of Poly-methyl methacrylate (PMMA) for Nano Imprint Lithography

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Mechanical property of a polymer over glass transition temperature is an important factor to design process conditions in nano imprint lithography or nano embossing technology. Mechanical properties such as shear modulus, retardation time and viscosity are experimentally evaluated for poly methyl methacrylate (PMMA) for various molecular weights (12k to 996k) over 100°C. Also, dependency on the shearing strain rate is evaluated using WLF law. Based on the results, process conditions are discussed for nano imprint lithography and experimentally demonstrated high aspect ratio pattern.

Keywords: modulus, viscosity, retardation time, strain rate, imprint lithography, molecular weight, poly methyl methacrylate

1. Introduction

Nano-imprint lithography or nano embossing technology is expected to fabricated nano structures by extremely low cost. There have been proposed several methods for nano imprint technology. One of the typical methods is thermal imprint lithography as shown in Fig.1[1]. In the thermal imprint process, thermoplastic polymer, which becomes soft over glass transition temperature (Tg) and turns to be hard below the grass transition temperature. Chou et al. reported sub-10nm pattern fabrication using PMMA thin film on Si substrate[2]. Using this method, large scale integrated pattern is fabricated on substrate once the mold is fabricated. Also, there are various thermal polymers for imprinting such as PMMA, poly carbonate (PC) etc. and the application field is very large such as nano optics devices, micro total analysis systems, bio-chemical systems etc.

In the imprint process, process condition is one of the important factors successful fine pattern fabrications. Usually, the imprint is performed over around 40 °C beyond the glass transition temperature, however there is a few report about the mechanical properties about these thermal polymers over glass transition temperature.

![Schematic diagram of the nano imprint lithography by thermal curing process.](image)

Fig.1. Schematic diagram of the nano imprint lithography by thermal curing process.
On the other hand, lower temperature and less pressure processing is required because the thermal expansion and damages would be suppressed in the imprinting processes. In this paper, mechanical properties of polymer such as shear modulus, retardation time and viscosity [3][4][5] are experimentally evaluated for PMMA for various molecular weights (12k to 996k) over 100 °C. Also, dependency on the strain rate is evaluated based on WLF law [6].

2. Experimental method

To evaluate the mechanical properties, we use commercial available viscoelastic measurement system (Rheology Co., MR-500). Figure 2 shows the schematic diagram of the system. Alternative strain with angular frequency $\omega$ is applied to the sample plate and the transducer measures the amplitude and the phase lag $\delta$ of the vibration. Based on them, the shear modulus $G$, degradation time $\tau$, viscosity $\eta$ is obtained.

![Schematic diagram of the measurement system for visco-elastic properties of the polymer plate.](image)

Figure 2. Schematic diagram of the measurement system for visco-elastic properties of the polymer plate.

![Photo image of the examined sample plate.](image)

Figure 3. Photo image of the examined sample plate.

The PMMA powder is hot pressed in vacuum using metal mold. The sample does not contain any solvent for PMMA solution.

Table 1 shows the measurement conditions of the samples. The mechanical properties of the PMMA are examined form 100 degree up to 170 degrees for various molecular weights.

<table>
<thead>
<tr>
<th>$M_w$</th>
<th>12k, 150k, 350k, 996k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>100~170 °C</td>
</tr>
<tr>
<td>Angular frequency</td>
<td>0.01~20 rad/s</td>
</tr>
<tr>
<td>Amplitude</td>
<td>0.1 mm</td>
</tr>
<tr>
<td>Sample diameter</td>
<td>20.0mm</td>
</tr>
<tr>
<td>Sample thickness</td>
<td>2.0mm</td>
</tr>
</tbody>
</table>

3. Experimental results and discussions

3.1 Mechanical parameters of the polymer

In this paper, we discuss about the following four mechanical parameters [3][4][5]. The first parameter is the phase lag $\delta$. When the temperature of the polymer is below the glass transition temperature ($T_g$), the value of the $\tan(\delta)$ is sufficiently small and the polymer shows elastic behavior. This means that the polymer is not enough to be soft. As the temperature increases to be around $T_g$, the viscosity of the polymer increases and the value of the $\tan(\delta)$ becomes large. The polymer shows typical viscoelastic behavior when the $\tan(\delta)$ becomes to be around 1.0 over $T_g$. In these states, the polymer becomes to be soft. The temperature rises up to be the melting temperature ($T_m$), the polymer turns to be viscous liquid and the polymer becomes to be flow. In this way, the $\tan(\delta)$ indicates specific states of the polymer, which is helpful to design the process temperature for the nano imprint process.

Next, we discuss the shear modulus $G$, which is related to the imprint pressure. In a simplified model, the polymer might be enough deformed under the equivalent pressure as same as the shear modulus.

Then, a degradation time $\tau$ is extracted. The degradation time $\tau$ is related to the holding time at nano imprint process.

Finally, we discuss about the viscously of the polymer. The viscosity is related to the flow of the polymer into the mold glove. Higher aspect ratio patterns may be easily fabricated by lower viscosity polymer.
3.2 Phase lag $\delta$

Figure 4 shows the measured results of the $\tan(\delta)$ for various molecular weight of the PMMA. As the temperature becomes high, the $\tan(\delta)$ becomes large. The PMMA polymers over 350k in molecular weight are almost the same characteristics, where the $\tan(\delta)$ increases over around 140 °C. Over 140 °C, the value of the $\tan(\delta)$ becomes to be around 0.1, which means that the polymers still shows elastic behavior. In the same way, $\tan(\delta)$ of the polymer with 120k in molecular weight increases over around 120 °C. On the other hand, lower molecular weight polymer (Mw=15k), it increases as the temperature increases. Over around 120 °C, the $\tan(\delta)$ becomes 1.0 and it continuously increases as the temperature rises. Over 160 °C, it becomes to be 10, which means that the polymer shows viscous elastic liquid behavior. These characteristics also depend on the distribution factor of the molecular weights.

![Figure 4. Measured phase lag $\delta$ for various molecular weights and temperatures ($\omega = 1$).](image)

3.3 Shear modulus $G$

Next, the static shear modulus $G$ is extracted for various temperatures and the molecular weights. Figure 5 show the results. The shear modules $G$ of the polymers with 996k and 350k in molecular weight decrease over around 140 °C, which is corresponded to the characteristics of the temperature dependence on the $\tan(\delta)$. Over 140 °C, the modulus $G$ drastically decreases. The polymers show viscoelastic properties over 140 °C where the static shear modulus decreases to be around 10 to 40 MPa. The shear modulus is about 1/100 times compared with that of at 100°C. On the other hand, the shear modulus with 120k and 15k in molecular weight gradually decrease as the temperature rises up. Also, the shear modulus becomes low as the molecular weight decreases. The modulus for the 996k in molecular weight is around 100 times larger than that for the 15k.

![Figure 5. Measured shear modulus $G$ for various molecular weights ($\omega = 1$).](image)

Based on these results, the imprint temperature is recommended over around 140 °C and the pressure is around from 1.0 to 100 MPa for PMMA resist.

3.4 Retardation time $\tau$

The retardation time is related to the holding time in the press process. It is derived based on the following relation:

$$\tau = \frac{1}{\omega \tan(\delta)} \quad (1)$$

![Figure 6. Extracted retardation time $\tau$ for various molecular weights ($\omega = 1$).](image)

Figure 6 shows the results for various molecular weights and temperatures. Over 140 °C, the
retardation times are around 1.0 s except the polymer with 15k in molecular weight.

For imprint process, the holding time during the press may be enough for about 1 min.

3.5 Viscosity $\eta$

The viscosity shows the fluidity of the polymer in various temperatures. The viscosity $\eta$ is related to the following equation:

$$\eta = G\tau$$  \hspace{1cm} (2).

Figure 7 shows the viscosity of the polymer for various temperatures and molecular weights. The viscosity is evidently lower at low molecular weight polymer. They are less than around $10^6$ Pa s over 140°C. It is reasonable value for molding process. For lower molecular weight polymer (Mw=15k), the viscosity is around 1/100 or 1/10000 times lower than other polymers over 140 °C. It may be easily flow into narrow groves and good for high aspect ratio pattern fabrication.

![Figure 7. Measured viscosity $\eta$ for various molecular weights ($\omega = 1$).](image)

3.6 Dependence on strain rate

In a non liner elastic material, the characteristics depend on the strain rate. The above discussed properties of the polymer are measured under constant angular frequency, where the $\omega =1$ rad/s. In the actual system, the strain rate is not unity and we should examine the dependency on the strain rate, however, the measurement system can not measure for wide range in the angular frequency $\omega$.

To obtain the dependency on the shear rate for wide range of the angular frequency $\omega$, time-temperature equivalence and superposition are applied based on the W.L.F law [6]. First, the frequency dependencies are measured in various temperatures within limited range of the frequency. Figure 8 shows the measured phase lag for various temperatures. In this case, the molecular weigh of the PMMA is 120k. Based on the W.L.F law, the measured curves are shifted along the $\omega$ axis by a constant amount $\log a$, where $a$ is the shift factor expressed as follows:

$$\log a = \frac{C_1(T - T_s)}{C_2 + (T - T_s)}$$  \hspace{1cm} (3).

In our experiment, the parameter $C_1$ is 8.86 and $C_2$ is 101.6 at $T_s=140$ °C.

![Figure 8. Dependence on angular frequency for the $\tan(\delta)$ in various temperatures. The molecular weight of the examined PMMA is 120k.](image)

To obtain the dependency on the shear rate for wide range of the angular frequency $\omega$, the time-temperature equivalence and superposition are applied based on the W.L.F law [6]. First, the

![Figure 9. Superposed characteristics of the phase lag $\tan(\delta)$ for widely range angular frequency. The molecular weight of the PMMA is 120k. The standard temperature is 140 °C.](image)

Figure 9 shows superposed phase lag $\tan(\delta)$ for various angular frequency $\omega$ in wide range. As the shearing frequency increases, the phase lag
decreases and the polymer shows viscoelastic behavior.

There is a local maximum point at around the \( \omega = 50 \) rad/s. At present, we can not find the reason of this phenomena.

In the same way, the shear modulus \( G \) is measured for the polymer with 120k in molecular weight. Figure 10 shows the measured experimental results for various temperature and alternative angular frequency. Figure 11 shows the superposed dependency on the alternative angular frequency.

![Figure 10](image1.png)

Figure 10. Dependence on angular frequency for the shear modulus \( G \) in various temperatures. The molecular weight of the PMMA is 120k.

![Figure 11](image2.png)

Figure 11. Superposed characteristics of the shear modulus \( G \) for widely range angular frequency. The molecular weight of the PMMA is 120k. The standard temperature is 140 °C.

In the actual imprinting system, the press speed is around \( 1 \times 10^{-2} \) m/s, which is approximately equivalent to \( 1 \times 10^4 \) rad/s for 2.0 mm thick plate. In this case, the shear modulus is around 20 MPa at \( \omega = 1 \times 10^4 \) rad/s. On the other hand, the shear modulus at \( \omega = 1 \) (in Fig. 5) is approximately 0.2 MPa. From this, the shear modulus is around 100 times larger than that of the measured results at \( \omega = 1 \). These results suggest that the polymer might be deformed by lower pressure when it would be pressed at a slow speed. However, it takes about more than 1000 s for single press process under \( 1 \times 10^{-5} \) m/s (equivalent to \( \omega = 1 \) rad/s).

4. High aspect ratio pattern fabrication

Based on the results, fabrication of a high aspect ratio pattern is demonstrated using various molecular weight PMMA (\( M_n=15k, 120k \) and 996k). Fine Si mold is prepared by an anisotropic wet chemical etching, which provides flat side wall of the etched groove. The imprint pressure is 10 MPa at 170 °C.

![Fig. 12](image3.png)

Fig.12 Imprint results for various molecular weight PMMA. The pattern width is 200nm and the height is 1.2 μm. (170 °C, 10 MPa)
Figure 12 shows the scanning electron microscope (SEM) images of the experimental results for various molecular weights. Using lower molecular weight polymer, the plastic polymer gets into the mold groove completely, however it is not enough deformed using higher molecular weight polymer.

6. Conclusions
Mechanical properties of PMMA polymer are evaluated over glass transition temperature. Shear modulus, retardation time and viscosity are obtained for various molecular weights. Almost all the polymers show viscoelastic behavior and becomes soft over 140 °C. The retardation time is around 1 s and the shear modulus is around from 1.0 to 100 MPa, which may be related to the imprint conditions.

Strain rate dependence is also investigated using time-temperature equivalence and superposition based on the W.L.F. law. The polymer might be deformed by lower pressure when it would be pressed at a slow speed.

Based on these results, high aspect ratio transfer is demonstrated using PMMA resist polymers with various molecular weighs. It is confirmed that lower molecular weight polymer is easily flow into narrow groove.

We believe there results are very useful for design and investigation of nano imprint lithography process conditions.

Acknowledgements
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References