Numerical modeling method to reproduce UV imprint process using thermo-viscoelastic constitutive law

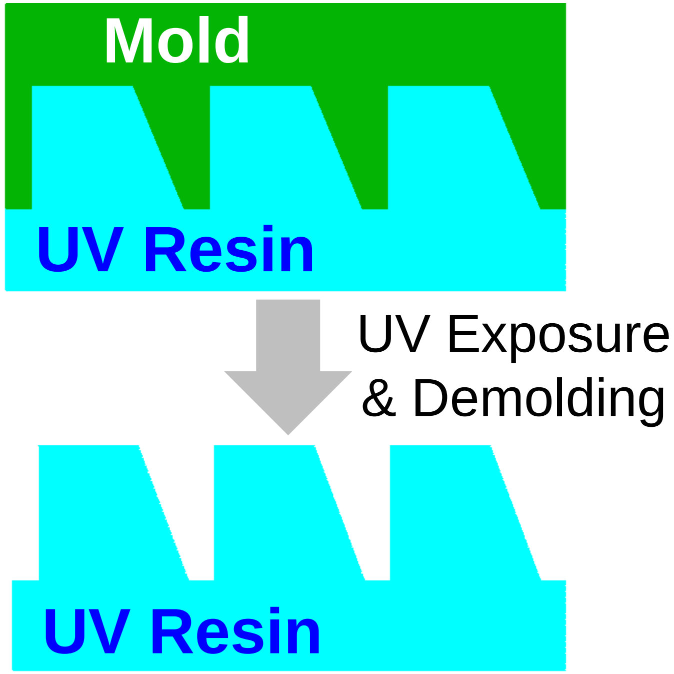
R. YAMASHITA [a], Y. ONISHI [a], K. AMAYA [a], Y. HIRAI [b]

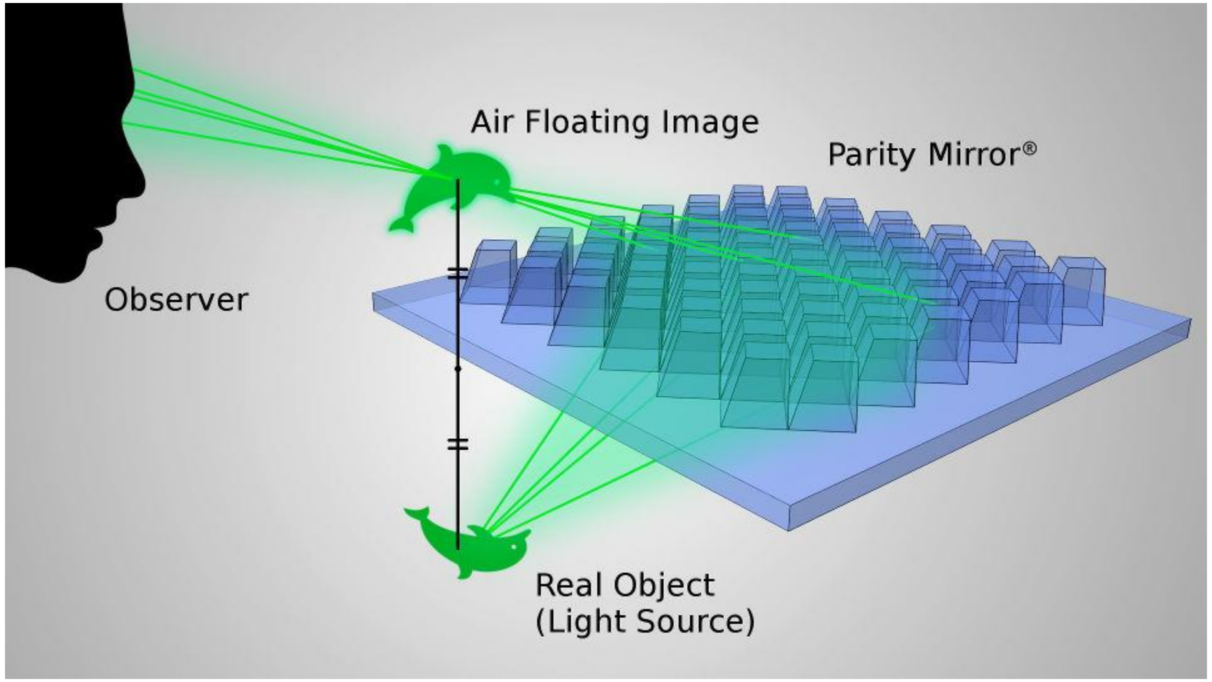
[a] Tokyo Institute of Technology, Japan

[b] Osaka Prefecture University, Japan

Background

- **UV imprinting** is a low cost and high throughput production method.
- It has been adopted to the production of various **optical devices requiring high surface accuracy** such as micromirror array.

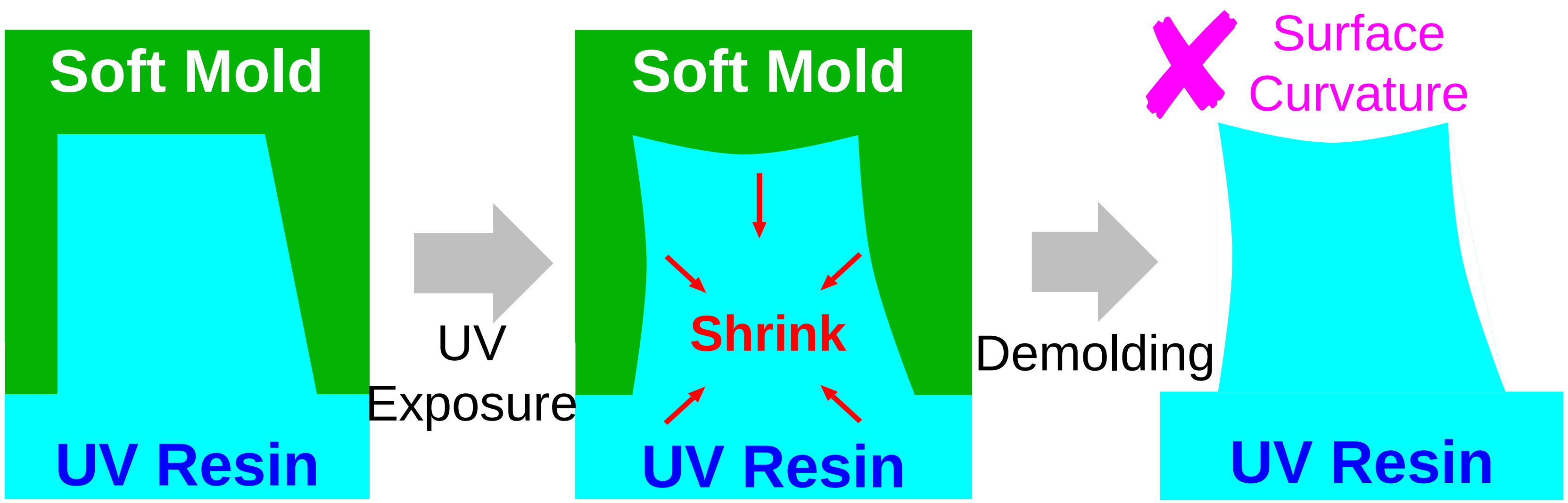


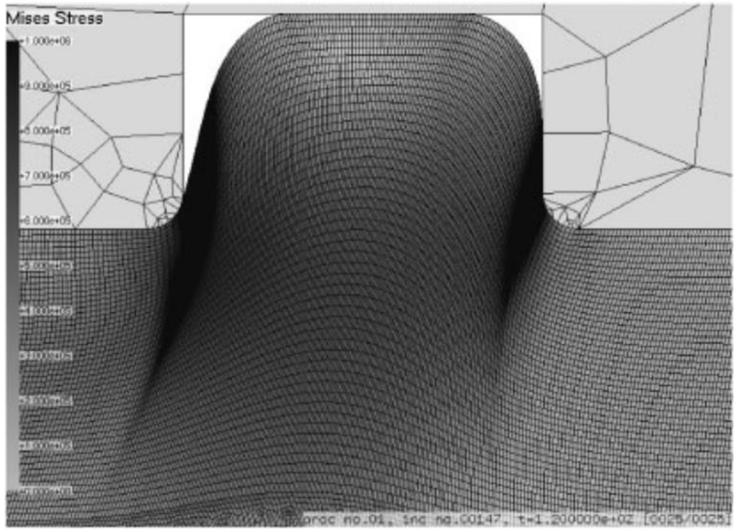


Example of optical product produced by micro imprint.
Parity Innovations Co., Ltd.
https://www.piq.co.jp/about_e.html

Issues

- In the curing process, **volume shrinkage of UV resin** arises and may cause **unintended surface curvature** when a soft mold such as PDMS is used.
- There is **no numerical modeling method** to reproduce this type of error in UV imprint, although there are a few **conventional methods for *thermal* imprint**.

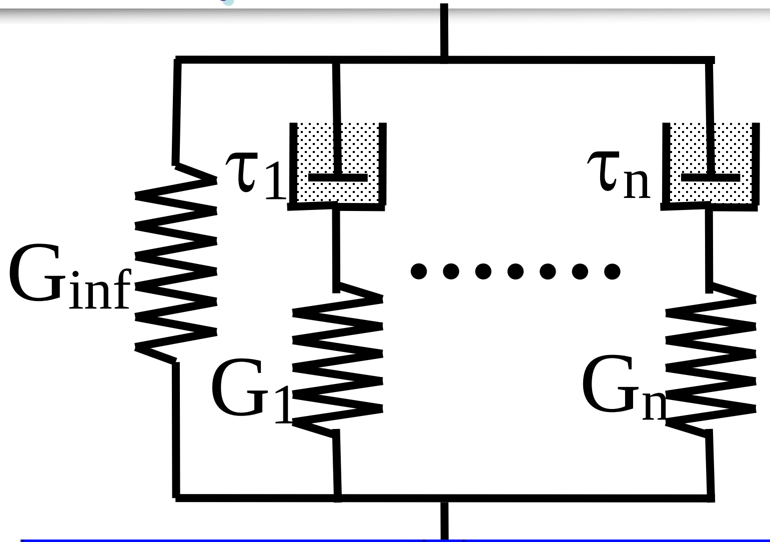


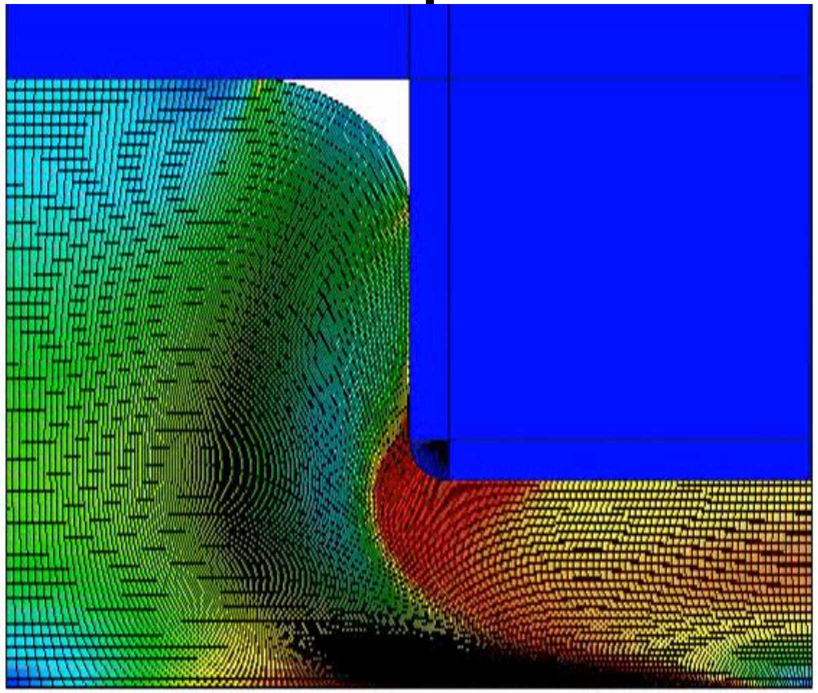


Y. Onishi *et al. Jpn. J. Appl. Phys.* **47** 5145 (2008)

Brief of Conventional Method for <u>***Thermal***</u> Imprint Simulation

- **Thermo-viscoelastic** constitutive model
  - Thermal contraction is described with **thermal expansion coefficient**.
  - Shear behavior is described with the **time-temperature superposition principle** and **Prony series** for the **generalized Maxwell model**.
  - Volumetric behavior is assumed to be independent of strain rate and temperature.
- Numerical simulation with the **finite element method (FEM)**





Our idea:
Similar numerical approach could be used for <u>***UV***</u> imprint simulation.

Objective

1. Propose a numerical method for **UV curing process simulation**.

2. Perform a **numerical analysis for validation** of the proposed numerical method.

Methods

Overview of Our Method

Considering the analogy of thermal and UV imprint,

- Our approach uses **thermo-viscoelastic** material constitutive model and replaces phenomena on UV resin as follows.
  - UV reaction progress ⟹ Cooling (temperature drop)
  - UV shrink ⟹ Cooling contraction
  - UV curing ⟹ Cooling solidification

Becomes similar to thermal imprint simulation

- **Virtual temperature θ** is introduced for the UV reaction progress measure.
- The model parameters are identified through **rheology measurement experiments**.

⇓

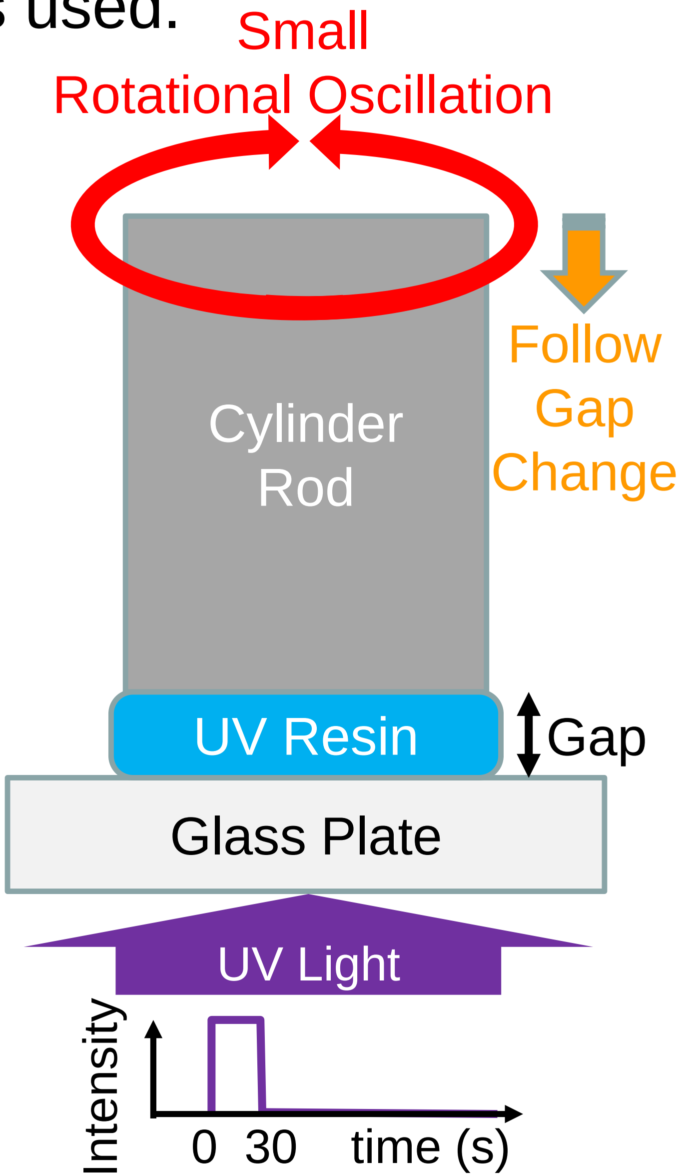
Numerical UV process simulation is realized as the result.

Experimental Conditions

- **Rotational oscillatory rheometer** (Anton Paar MCR301) is used.
- The measurement object is a cationic polymerization-type UV resin from Daicel Co..
- Room temperature is 25℃ (const.).
- UV exposure condition is constant (30 s exposure in a constant intensity).
- The oscillation frequency is varied from 0.1 to 10 Hz.
- The gap between the cylinder rod and the glass plate changes over time due to UV shrink.
- Long time measurement is conducted to consider the dark curing.

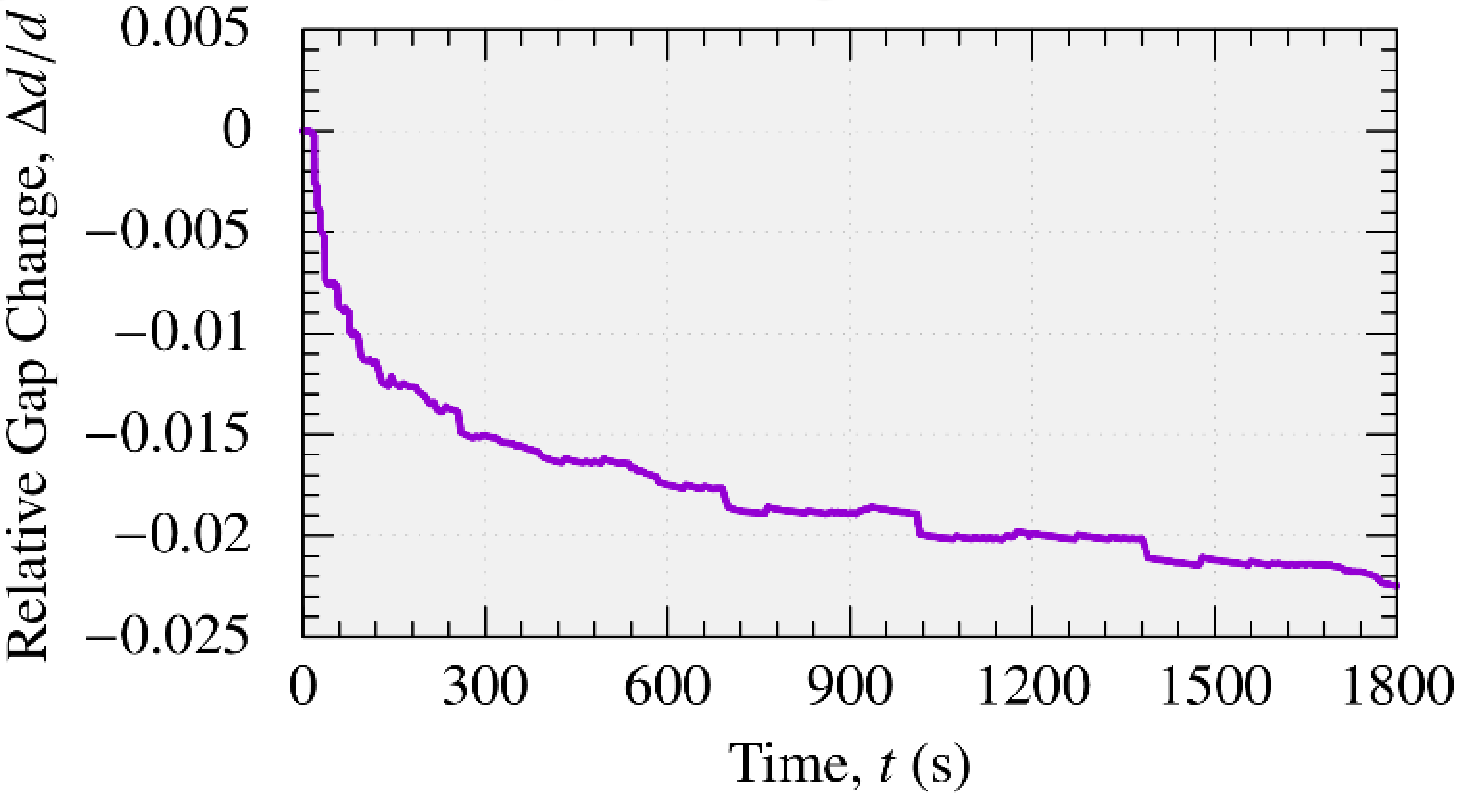
Anton Paar MCR series

https://www.anton-paar.com/corp-en/products/details/rheometer-mcr-102-302-502/



Relative Gap Change (Experimental Result)

Time History of Relative Gap Change

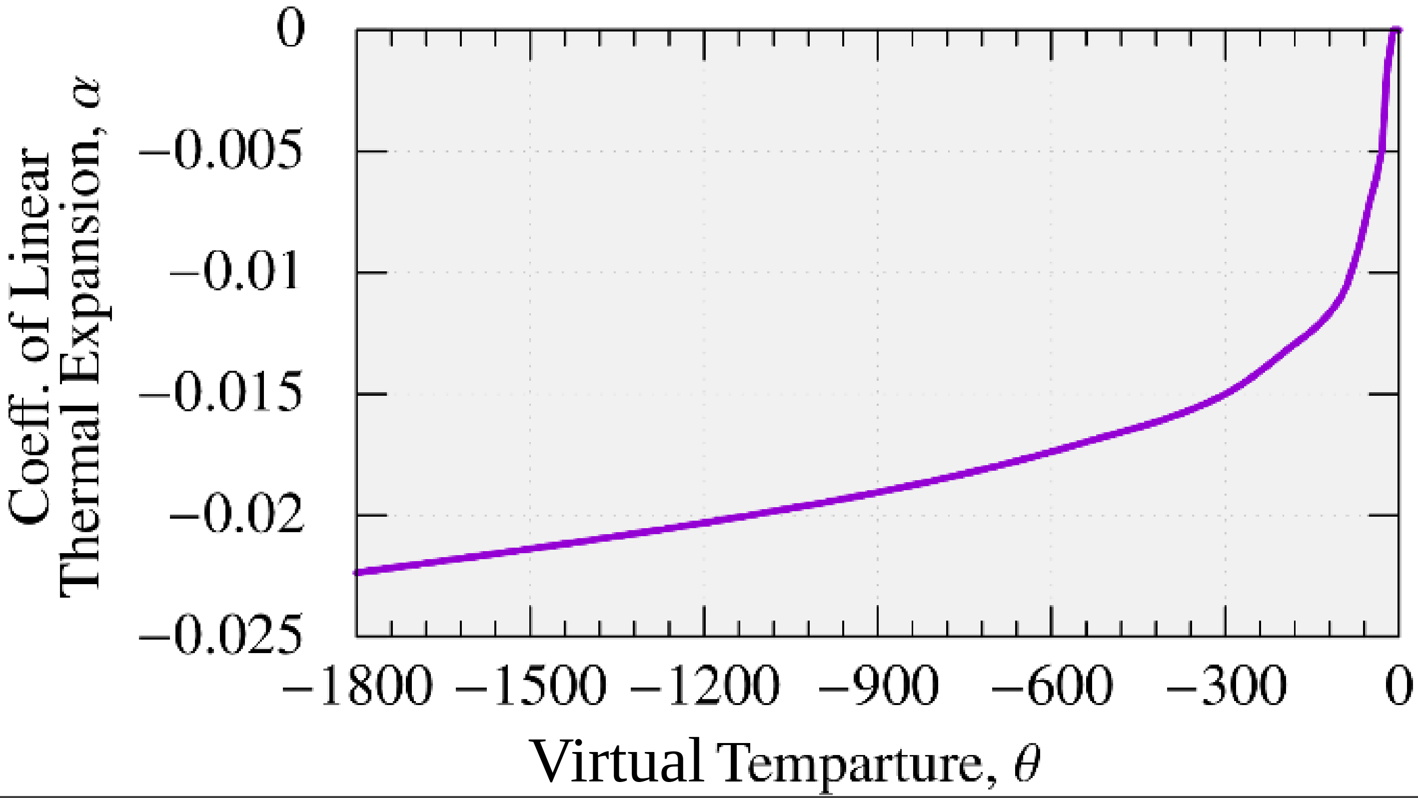


- Note: the time history of the relative gap change is always the same in all cases (∵ UV exposure condition is constant).
- UV shrink progresses with time, and the shrink speed gradually decreases.

Relative Gap Change (Model Parameter Identification)

- UV shrink is modeled as **thermal (cooling) contraction**.
- The time history of virtual temperature is given as $\boldsymbol{\theta(t) = -t}$.
  (Note that θ is not a real physical quantity but just a virtual value.)
- The time history of relative gap change is converted into the virtual temperature-dependent coefficient of thermal expansion.

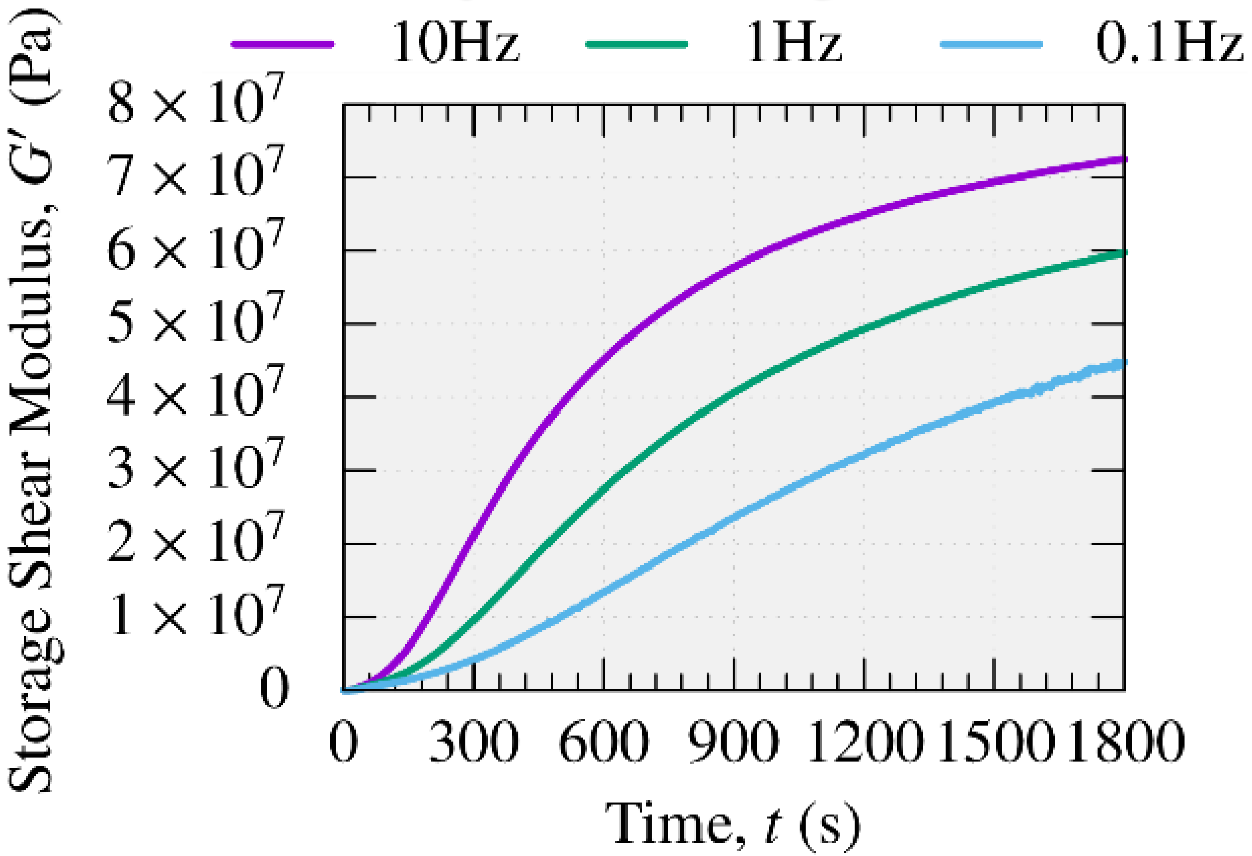
Virtual Temperature-Dependent Coefficient of Thermal Expansion

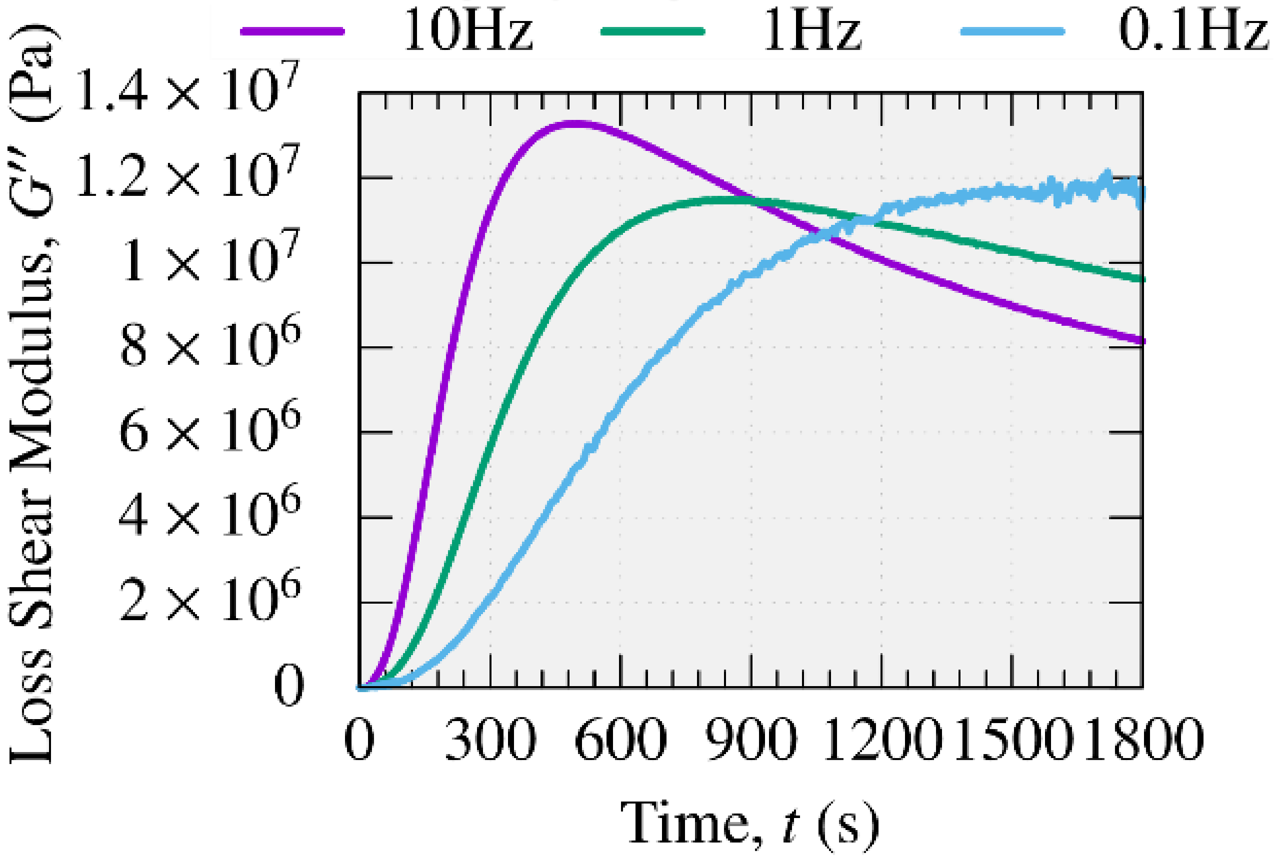


Note: α is negative because it represents the volume change compared to the initial volume.

Viscoelasticity (Experimental Result)

Time History of Storage / Loss Shear Modulus (G' / G'')





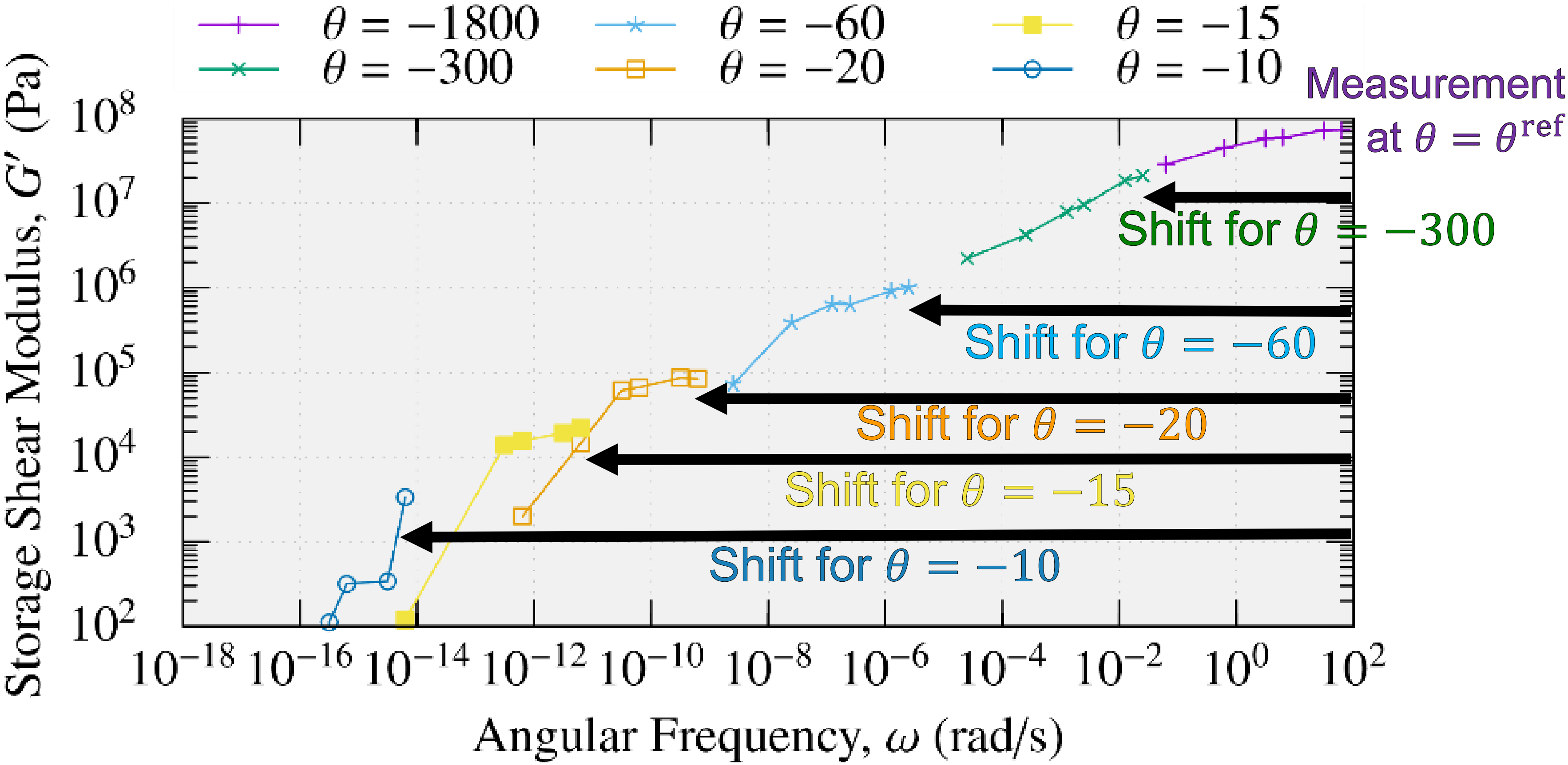
- Depending on the frequency, the time histories of G' and G'' are different (harder at higher frequencies).
- At any frequency, UV resin monotonically hardens with time.

Viscoelasticity (Model Parameter Identification 1/2)

- UV resin is modeled as viscoelastic material based on the **time-temperature superposition principle** and **Prony series** for the **generalized Maxwell model**.
- The reference virtual temperature is set as $\theta^{\mathrm{ref}} = -1800$.
- Pick G's and G''s at various θs and identify each time shift.

Time-Shifted Storage Shear Modulus $G'(\omega)$ at θ^{ref} (Master Curve)

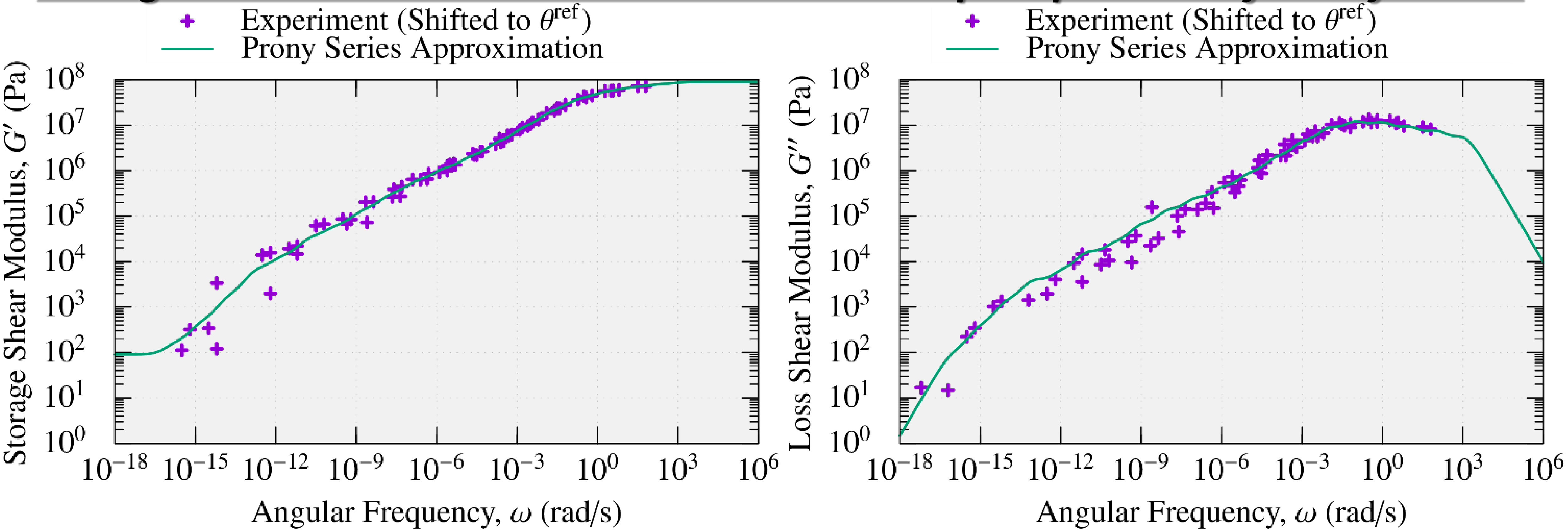
In practice, $G''(\omega)$ is also taken into consideration to determine the time shifts.



Viscoelasticity (Model Parameter Identification 2/2)

- Find the Prony series coeffs by fitting the master curve at the reference temp.

Storage / Loss Shear Modulus at Reference Temp. Expressed by Prony Series

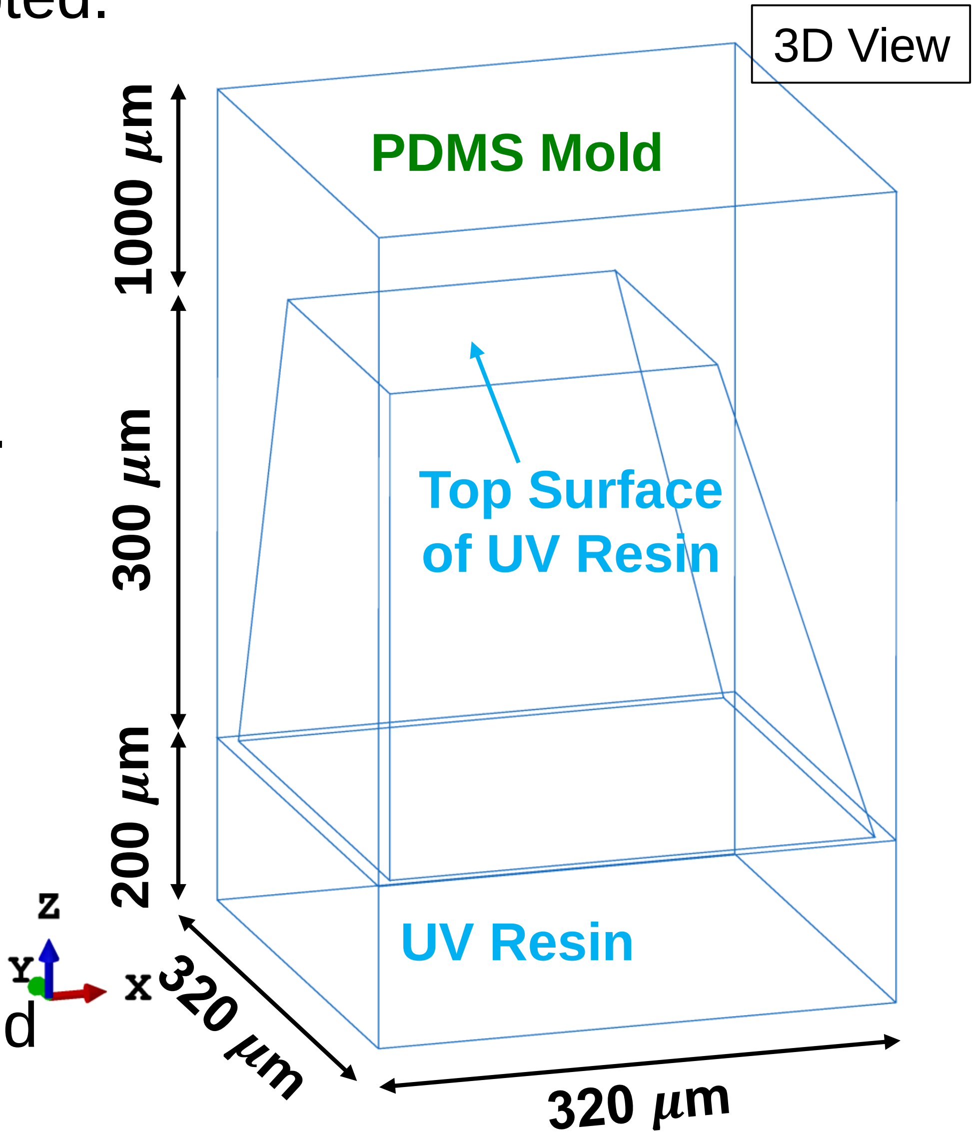


From the above, the constitutive model of thermo-viscoelasticity to simulate UV shrink and curing were identified.

Result & Discussion

UV Curing Process Simulation (Outline)

- Commercial finite element code, ABAQUS, is adopted.
- Target pattern is a **micromirror array**.
- The mold pattern is periodic and thus only **one pattern is taken into account** with **periodic boundary conditions**.
- Mold cavity is filled with UV resin at the initial state.
- Virtual temperature is given as $\boldsymbol{\theta(t) = -t}$.
- UV exposure condition is exactly the same as that of the rheology measurement experiments. (30 s exposure in a constant intensity).
- Demolding is conducted 100 s after the end of UV exposure.
- **Curvature on top surface of UV resin** is evaluated enough after the demolding (6000 s).



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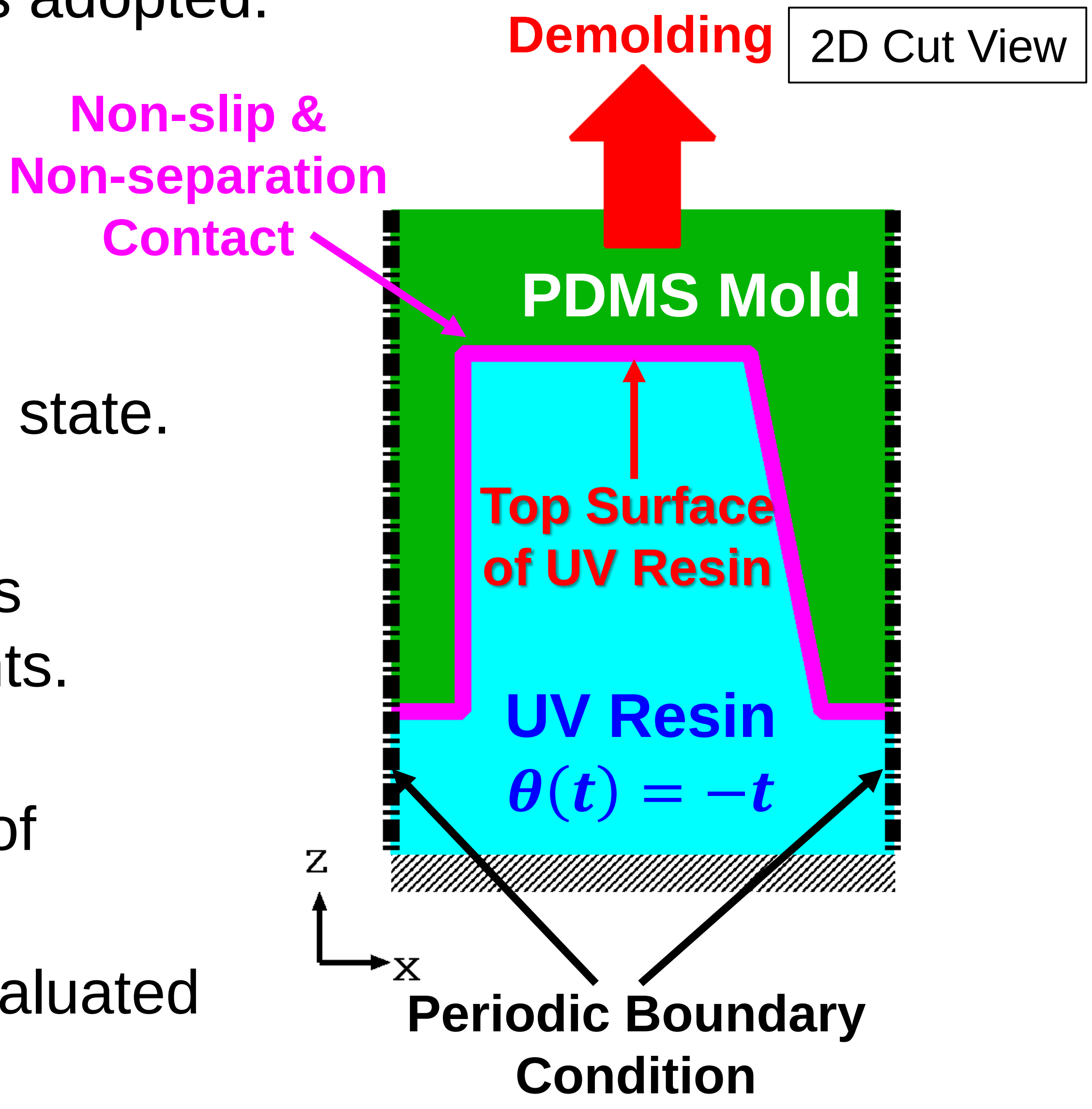
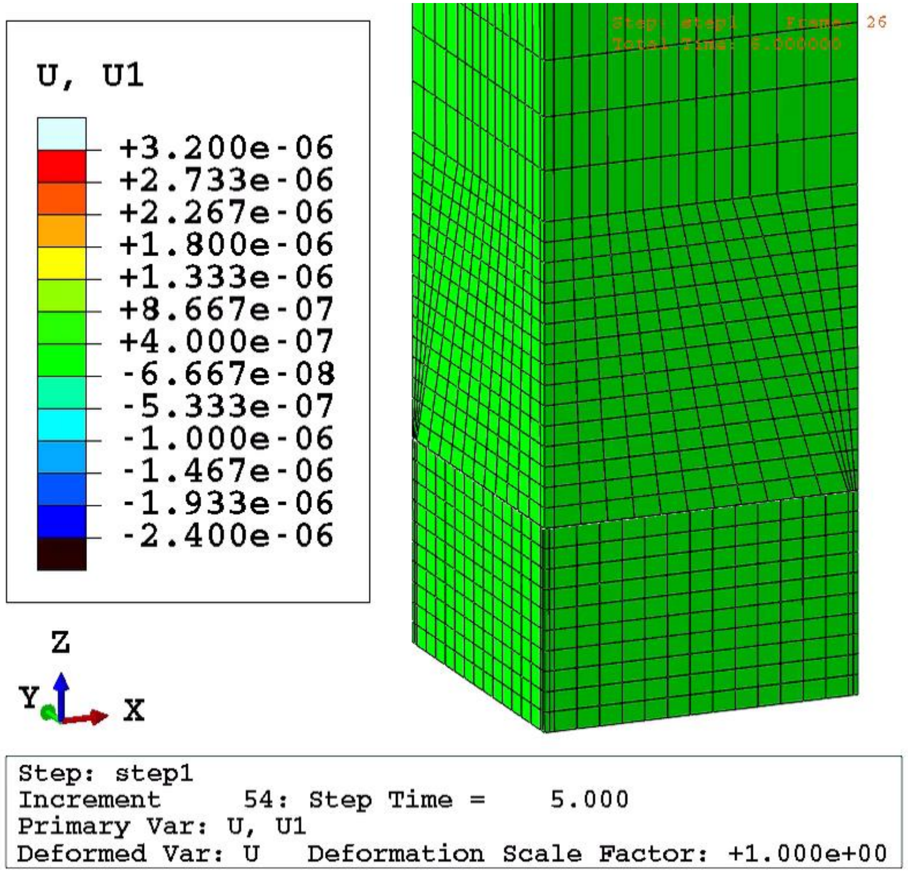


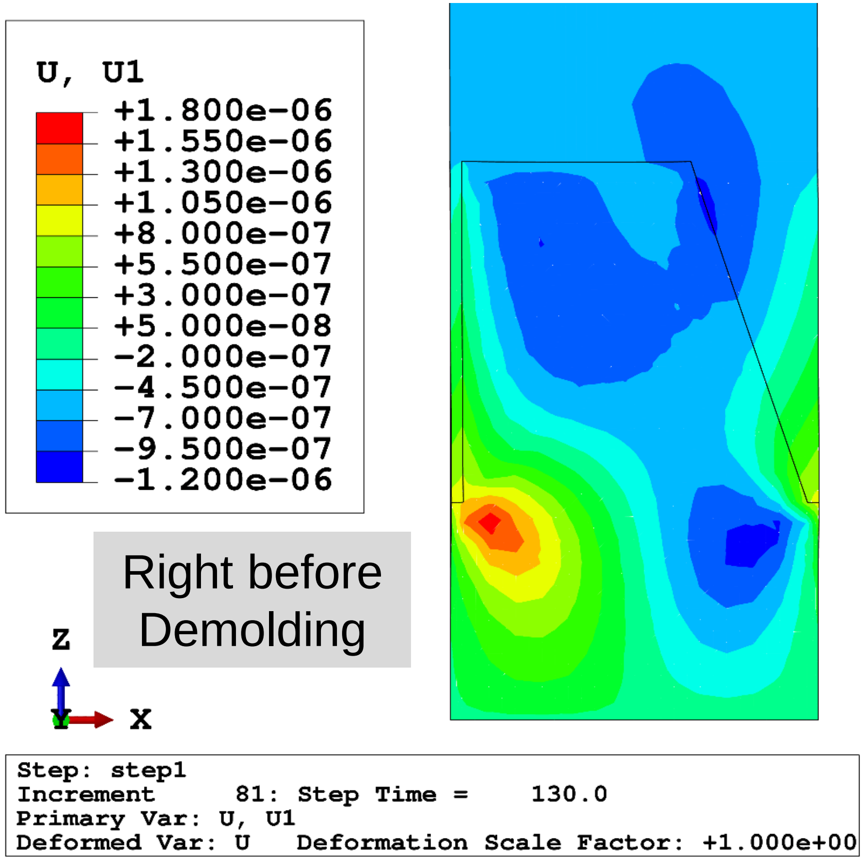
UV Curing Process Simulation (Simulation Result)

Displacement Dist. in X Direction



3D view

Surface curvature due to the UV shrink of resin and the mold deformation is observed.

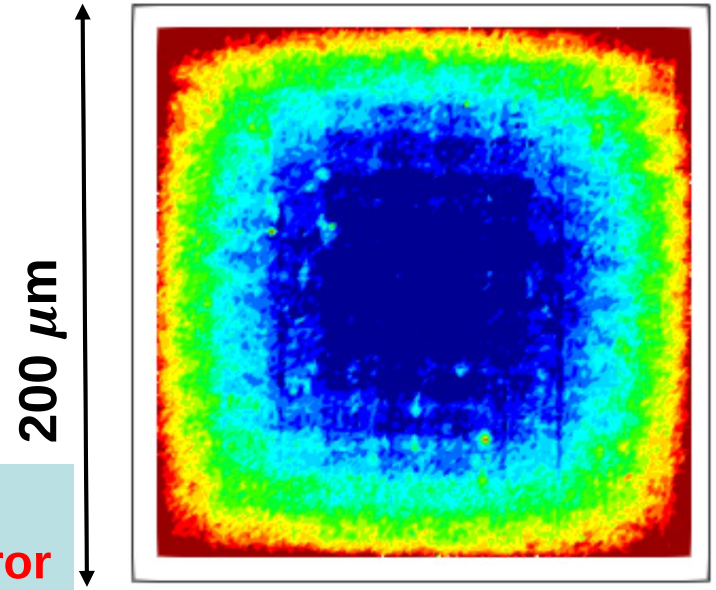


Sectional view (cut on *Y* plane)

Flow of UV resin due to the UV shrink is observed.

UV Curing Process Simulation (Validation)

Curvature Depth Dist. on Top Surface

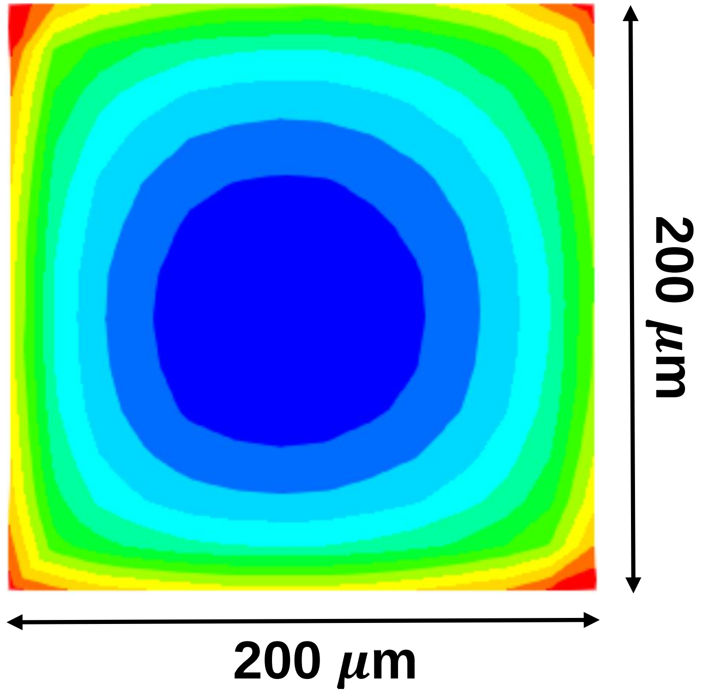


Actual micromirror array

Experimental Result

(Measured with laser microscope VK-X100, KEYENCE Co.)

Max. depth: about **0.75 µm**



Simulation Result

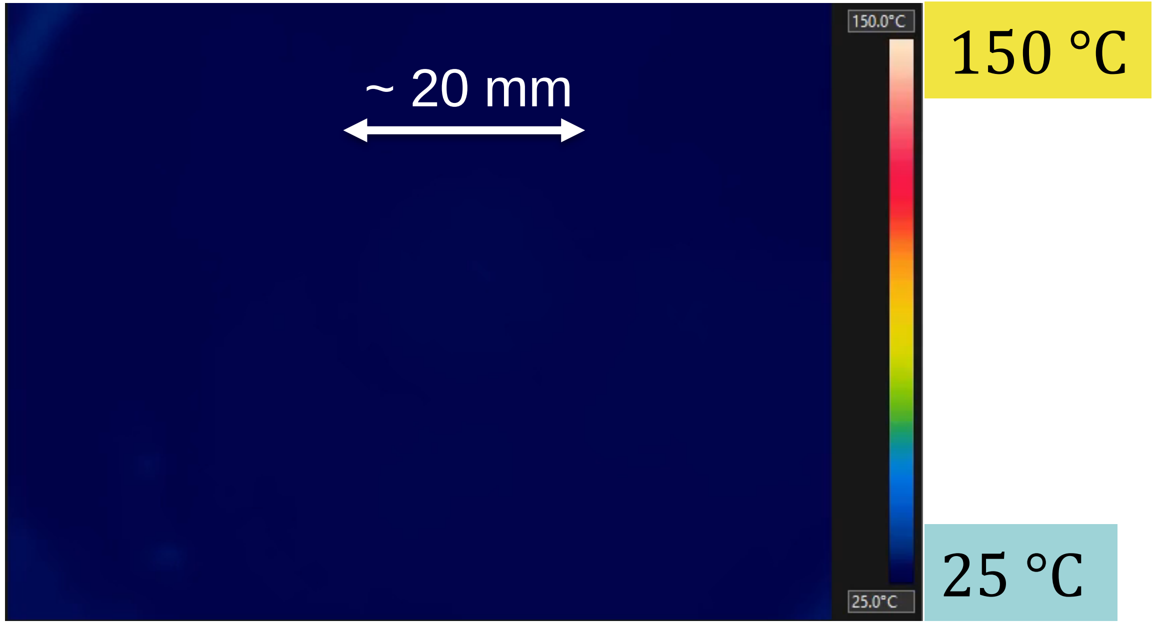
Max. depth: about **0.47 µm**

- ✔ Simulation result agreed with the experimental measurement data qualitatively.
- ✘ However, maximum curvature depth of simulation is smaller than experimental one.

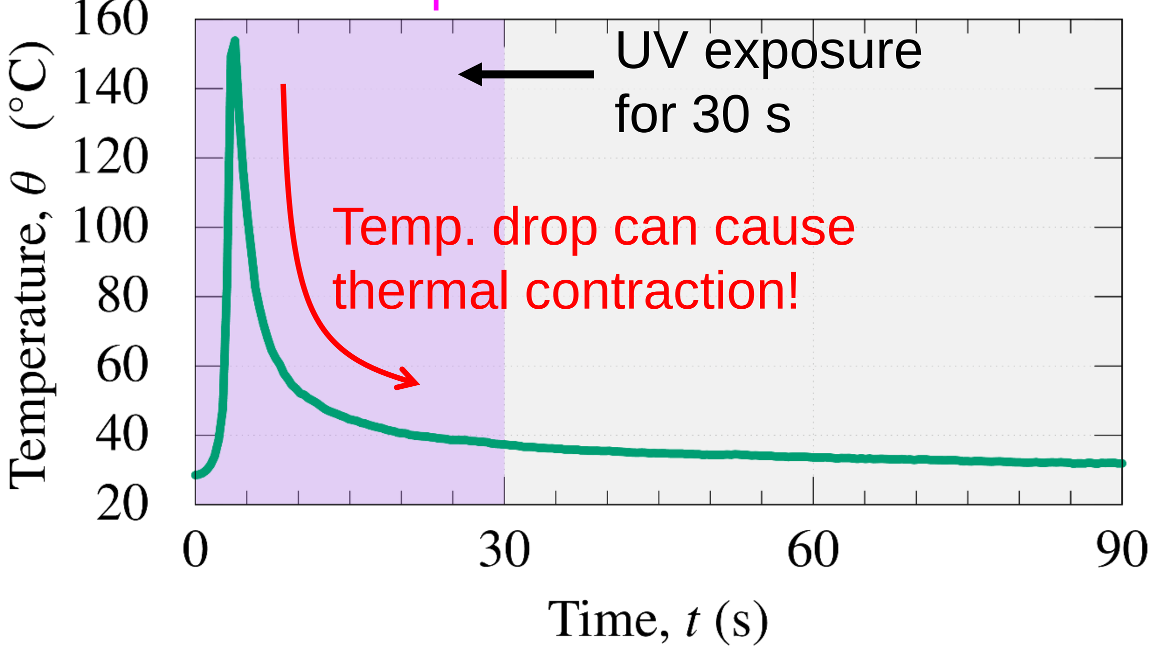
Why curvature depth of simulation is small?

Temperature time history of UV resin during UV reaction
(Stage temp. 25 °C, UV intensity 300 mW/cm^2, 500 μm thick)

Recorded by thermography (FLIR C2)



Temperature time history of resin center

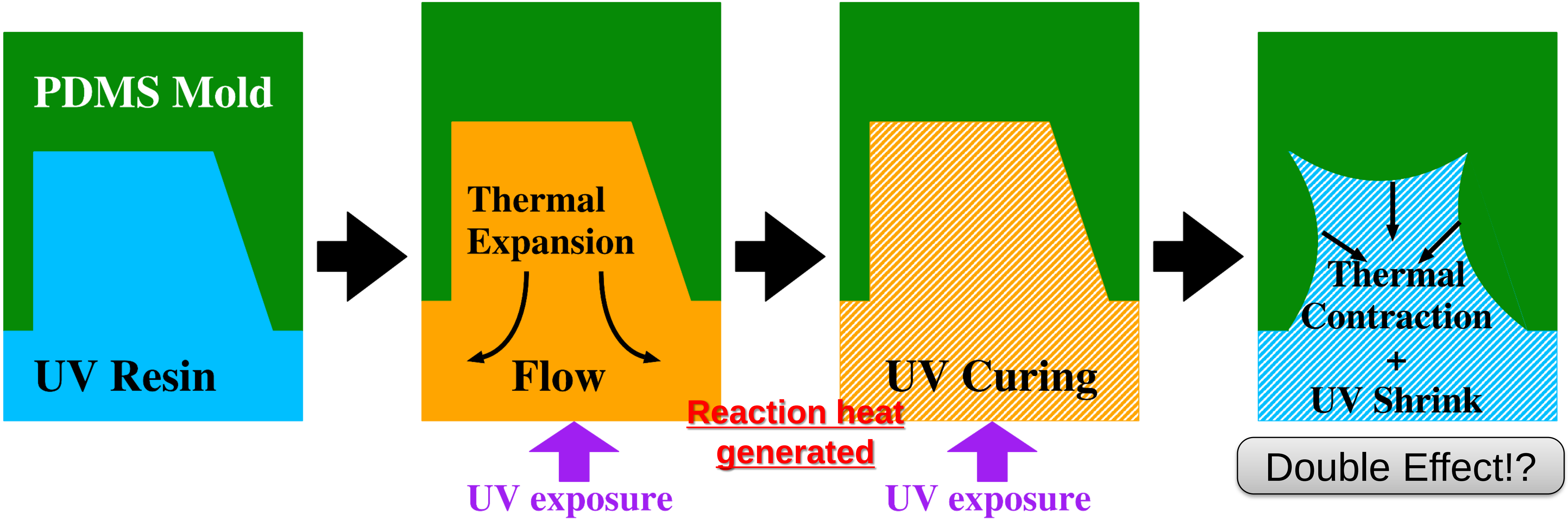


Reaction heat is quickly generated after the start of UV exposure, and the peak temperature of UV resin exceeds 100 °C.

⇒ **Thermal contraction due to cooling should be considered.**

Why curvature depth of simulation is small?

Mechanism of surface curvature of UV resin formed by thermal contraction (Hypothesis)



➢ **Temp**: low ➢ **Viscosity**: low ➢ **UV shrink**: yet	➢ **Temp**: high ➢ **Viscosity**: low ➢ **UV shrink**: yet	➢ **Temp**: high ➢ **Viscosity**: high ➢ **UV shrink**: yet	➢ **Temp**: low ➢ **Viscosity**: high ➢ **UV shrink**: done

Summary

Summary

- A numerical modeling method for **UV shrink & curing simulation** using **thermo-viscoelastic model** was proposed.
- The model parameters were identified through the **rheology measurement experiments**.
- A process simulation for micromirror array using PDMS mold validated the **qualitative accuracy on mirror surface curvature.**
- Our recent future works are below:
  - Investigate the hypothesis to achieve the **quantitative validation** of our method.
  - Improve our modeling method and simulation accuracy to aim for **practical application.**

Thank you for your kind attention.

Appendix

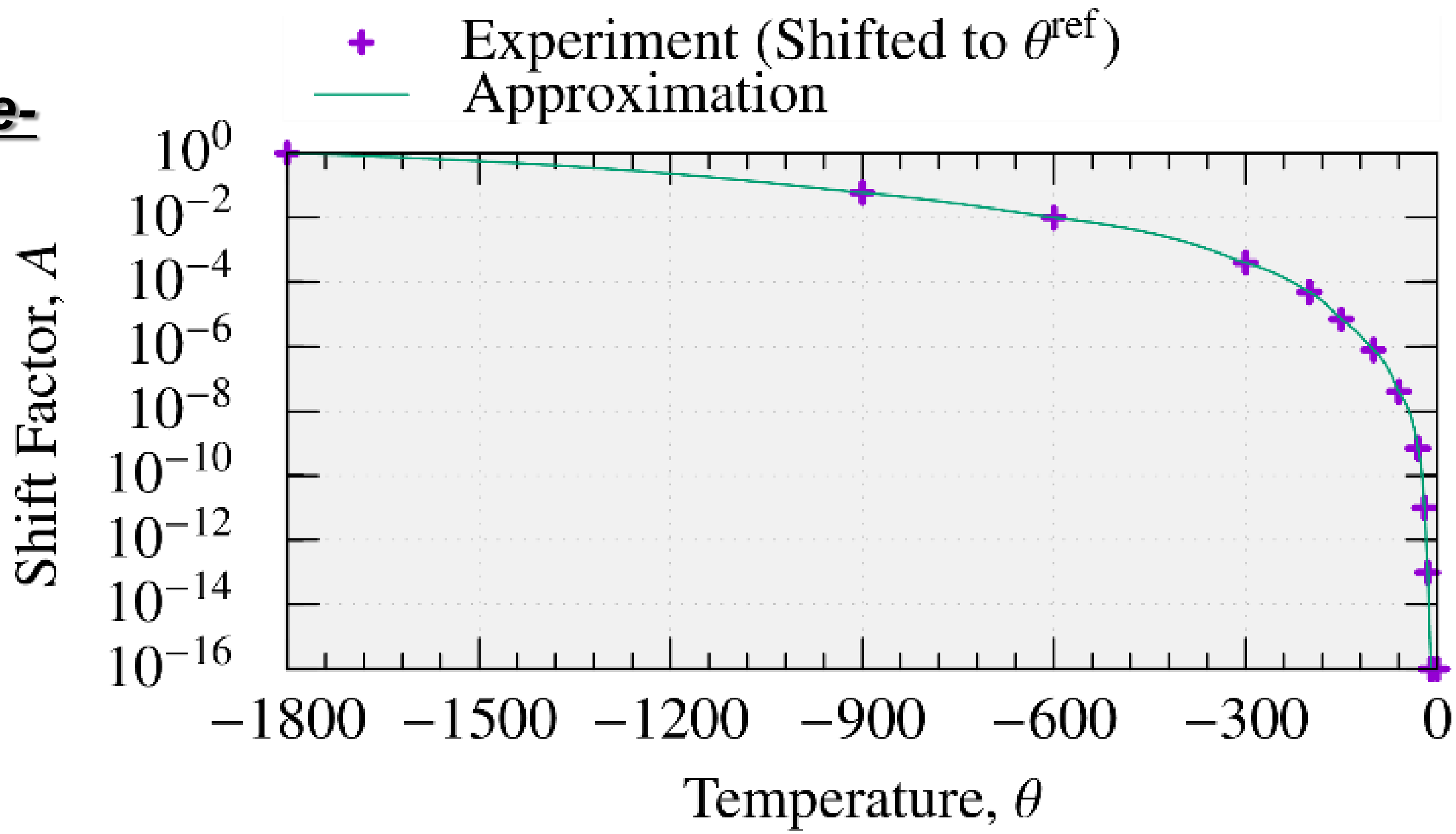
Limitation of Our Method

- UV exposure condition to simulate must be exactly the same as that on the rheology measurement experiments.
- The pattern size must be large enough to apply continuum approximation.

Viscoelasticity (Model Parameter Identification 2/3)

- A virtual temperature-dependent shift factor (i.e., time-temperature superposition) is obtained by fitting the time-shifts at various temperatures.

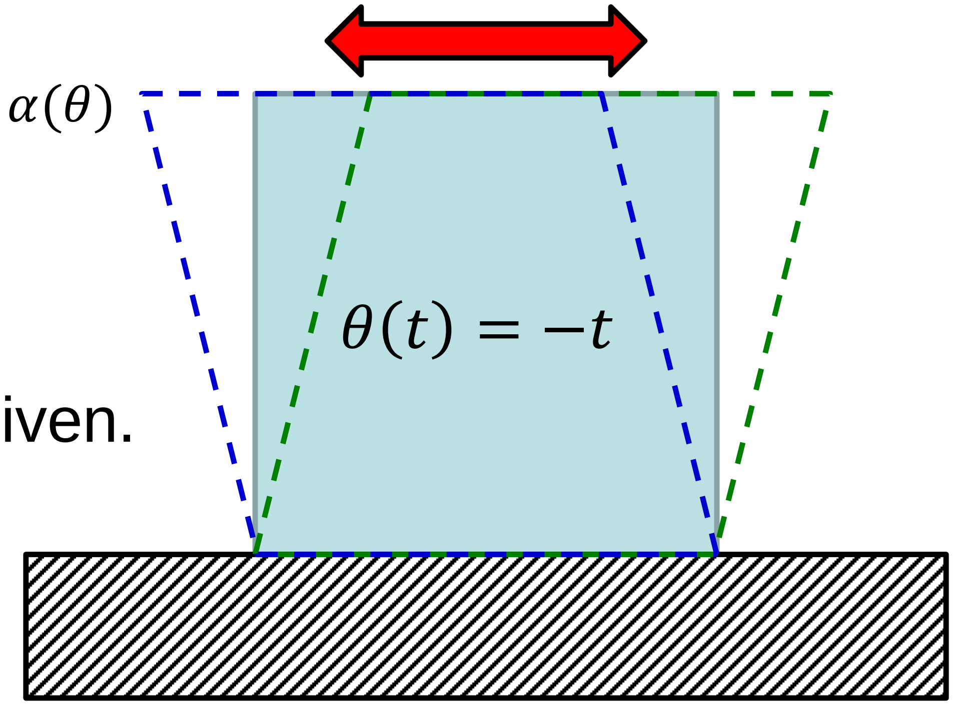
Virtual Temperature-Dependent Shift Factor $A(\theta)$



Validation of Material Constitutive Model

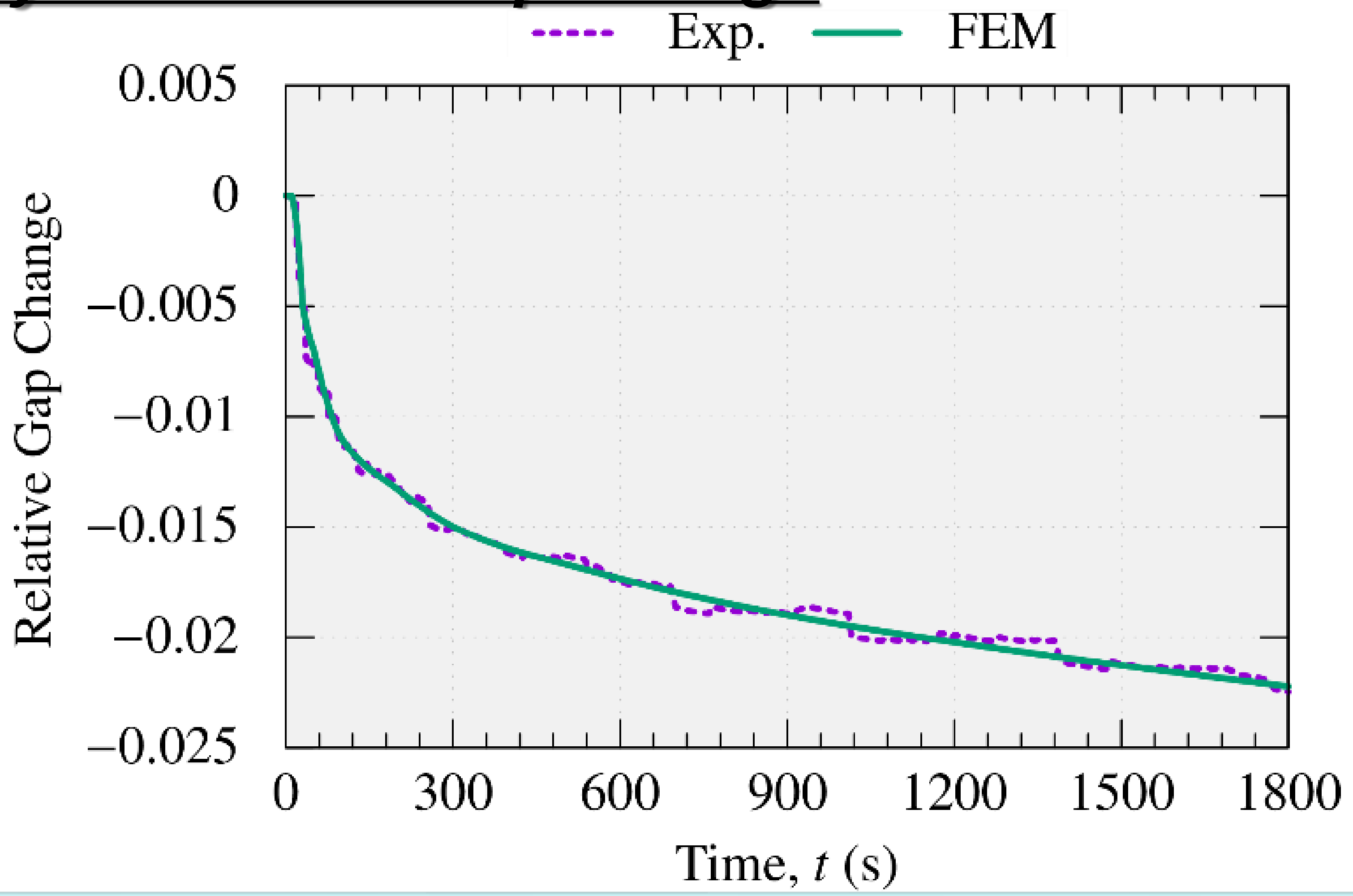
Outline

- Finite element analyses using the identified thermo-viscoelastic properties to reproduce the rheometer measurement data is conducted.
- For simplicity, time evolution analysis that gives shear vibration to one hexahedron element is performed.
- Defined thermo-viscoelastic properties are:
  - Temperature-dependent coefficient of thermal expansion, $\alpha(\theta)$
  - Temperature-dependent shift factor, $A(\theta)$
  - Prony series at reference temperature, g_i $(i = 1, \ldots, 20)$
  - Instantaneous Young’s modulus E^0 and Poisson's ratio ν^0
- Field condition of virtual temperature $\theta(t) = -t$ is given.
- Boundary conditions are:
  - Perfect constraint on the lower surface
  - Small oscillatory disp. in shear on the upper surface.



Validation of Material Constitutive Model

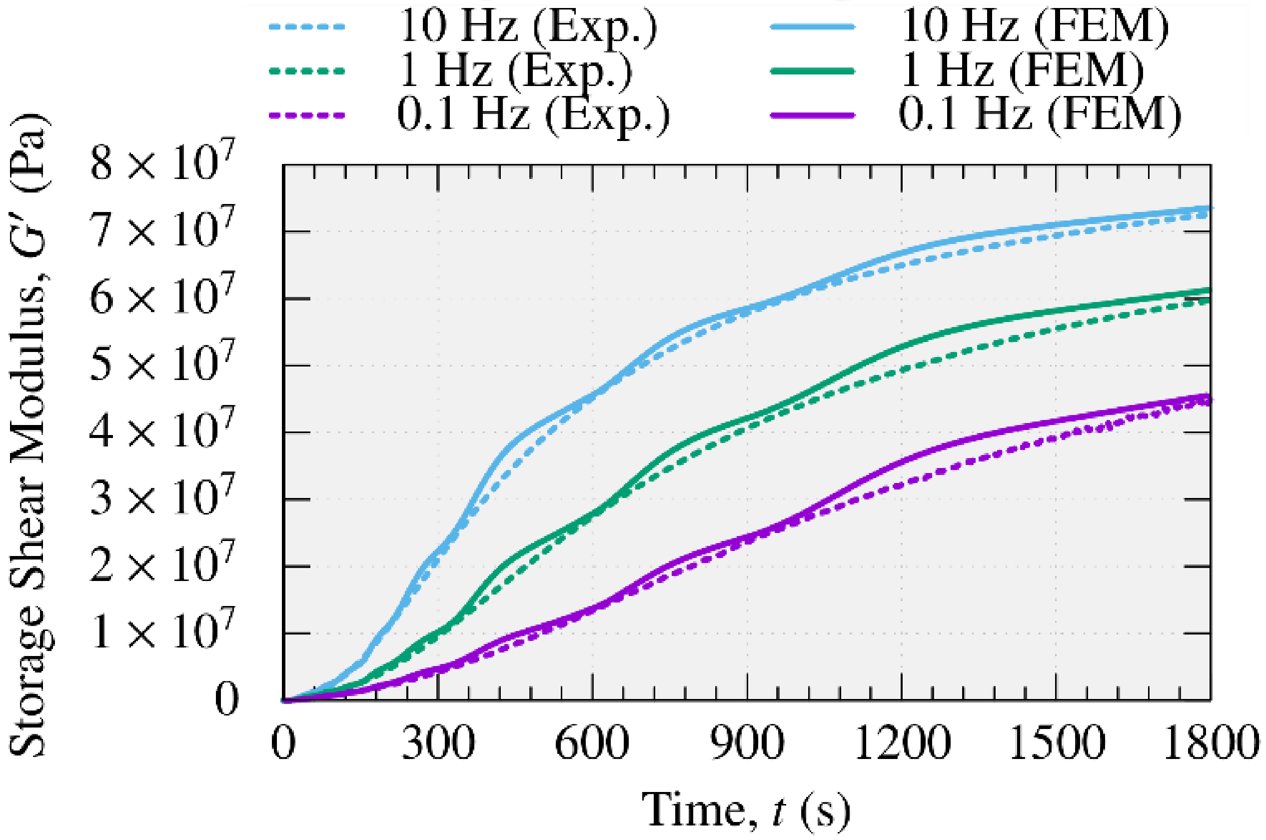
Time History of Relative Gap Change

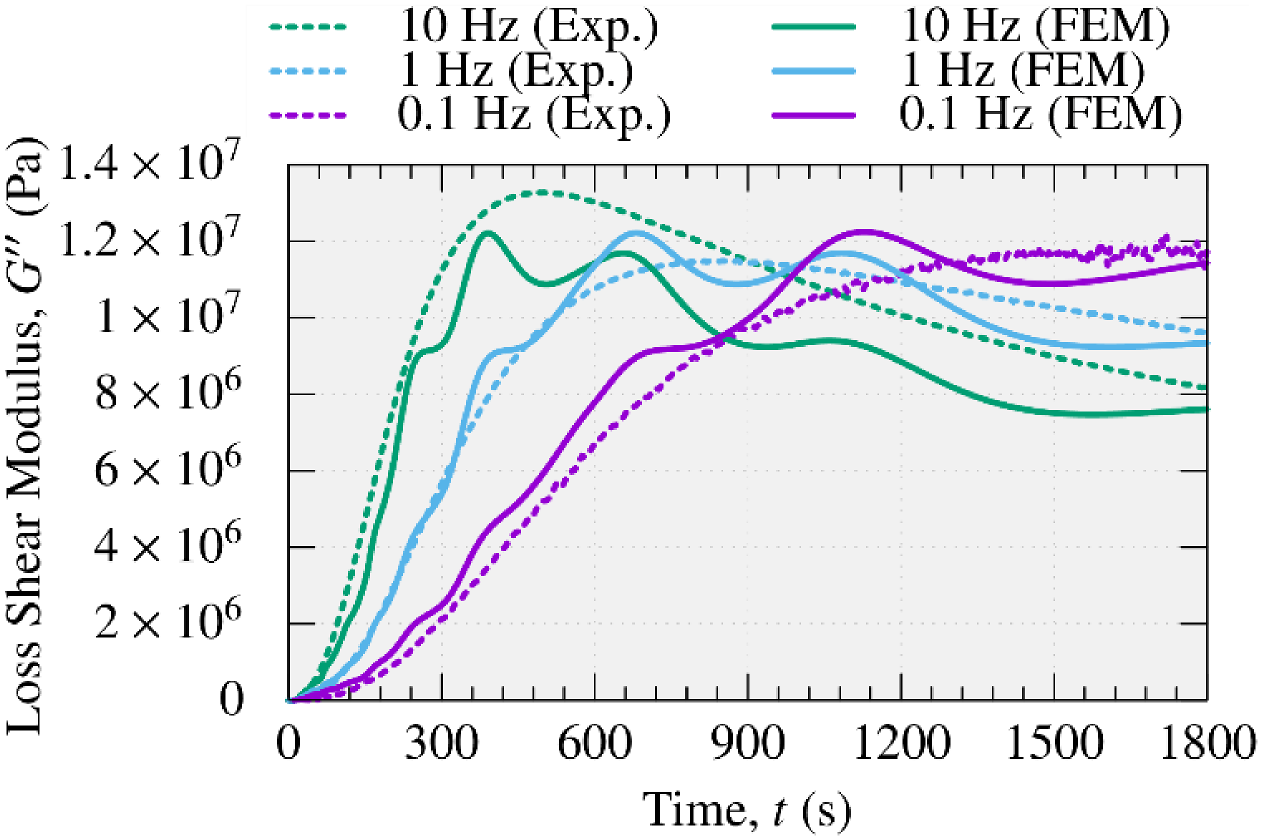


The relative gap change is accurately simulated.

Validation of Material Constitutive Model

Time History of Storage / Loss Shear Modulus





The storage shear modulus G' is accurately simulated.
On the other hand, minor problem remains in the accuracy of the loss shear modulus G'' because $G' \gg G''$.

Steps of UV Process Simulation

Step 1: Stationary (1 sec.)

- Static analysis
- Start no-slip & no-separation contact

Step 2: UV exposure & Dark curing (130 sec.)

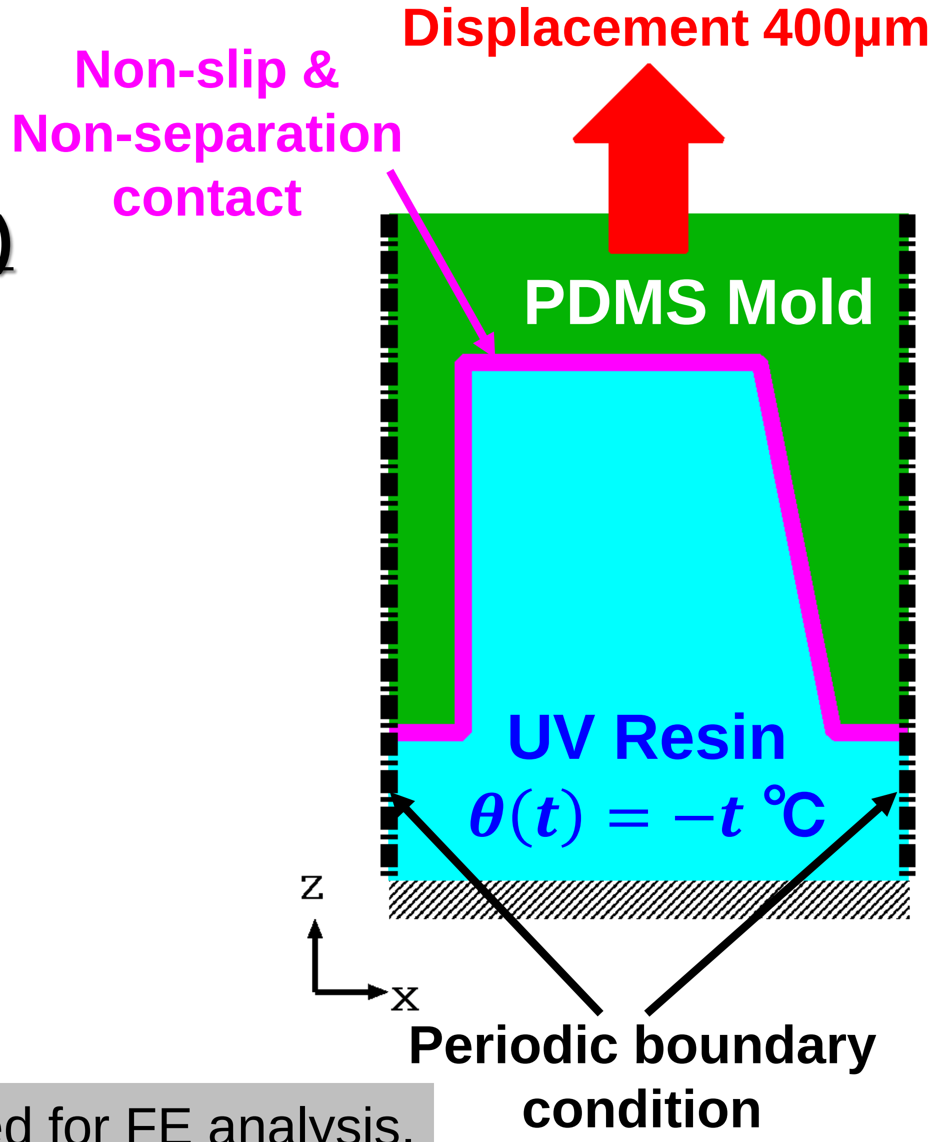
- Quasi-static analysis
- Lower UV resin virtual temperature: $\theta(t) = -t$

Step 3: Demolding w/ Dark curing (10 sec.)

- Quasi-static analysis
- Remove no-slip & no-separation contact
- Lift mold upward
- Lower UV resin virtual temperature: $\theta(t) = -t$

Step 4: Dark curing (6000 sec.)

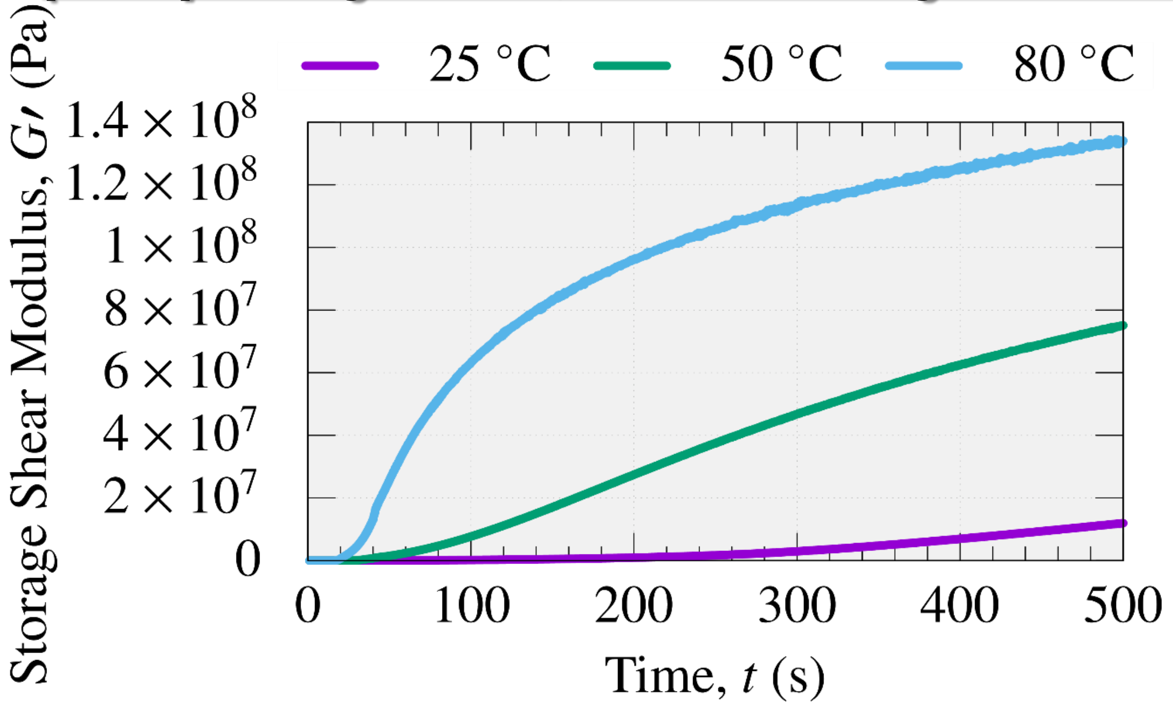
- Quasi-static analysis
- Lower UV resin virtual temperature: $\theta(t) = -t$



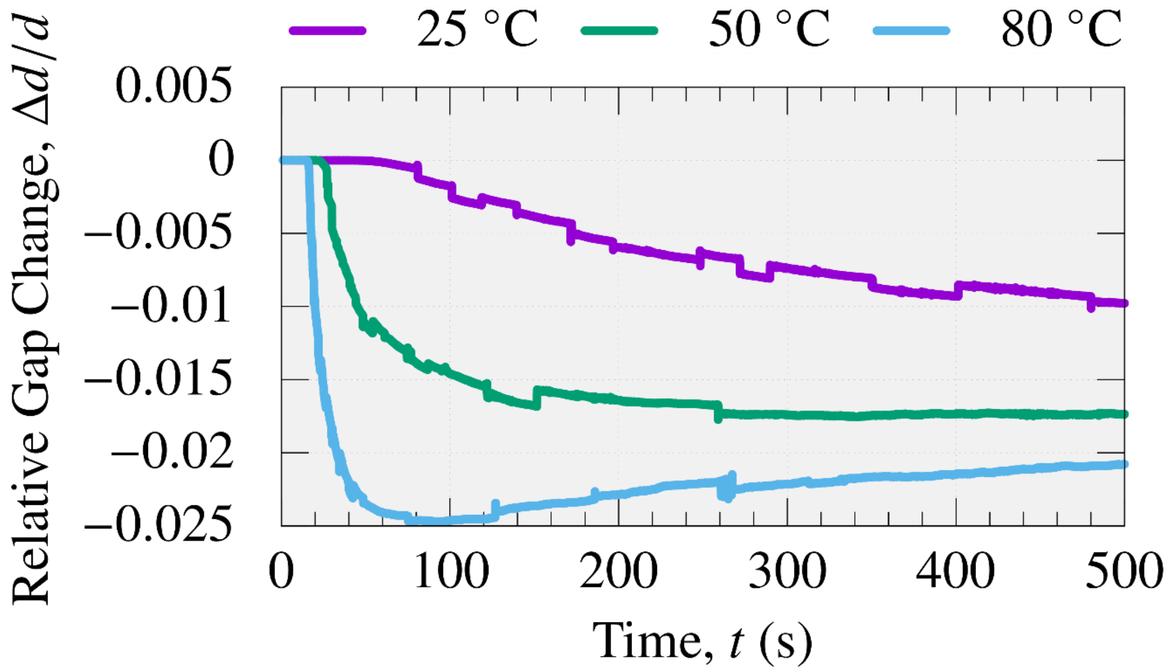
ABAQUS/Standard C3D8 is used for FE analysis.

Acceleration of UV reaction by reaction heat

Rheology measurement results at various stage temperature
(Frequency: 1 Hz, UV intensity: 25 mW/cm²)



Storage Shear Modulus G'

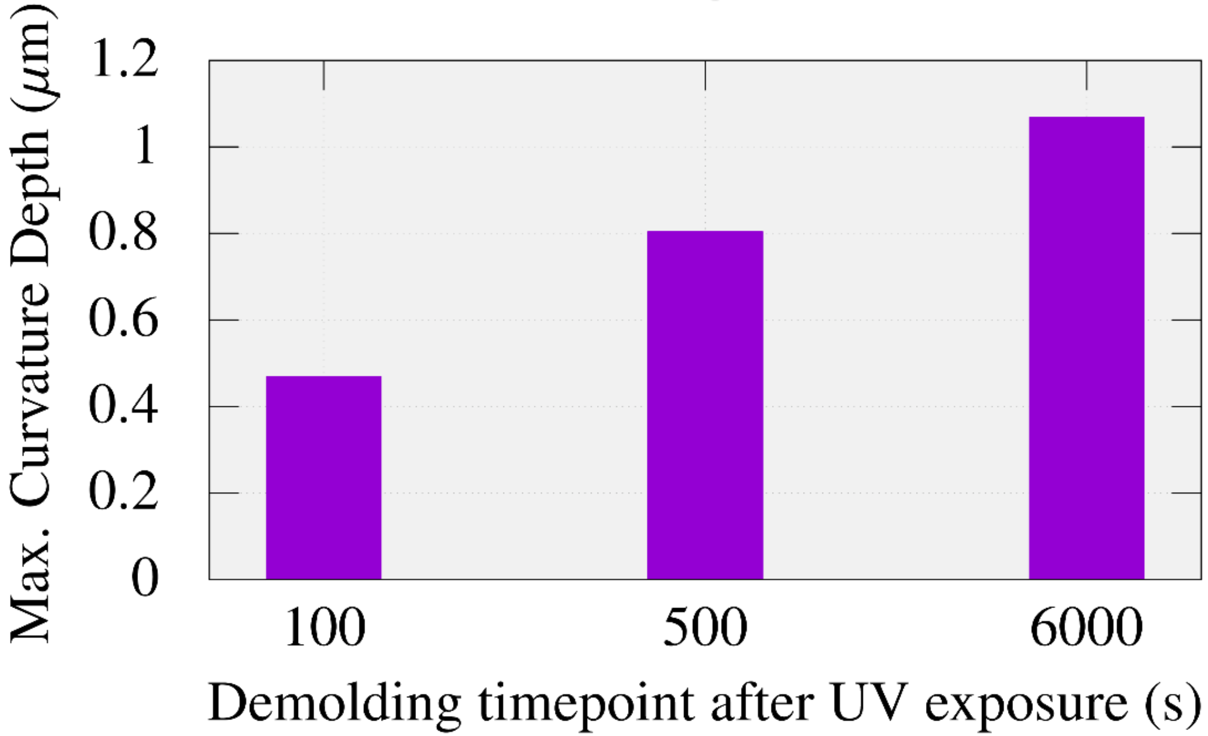


Relative Gap Change

The higher temperature, the faster the UV reaction.
⟹ In the actual process, UV shrink can be accelerated by the reaction heat.

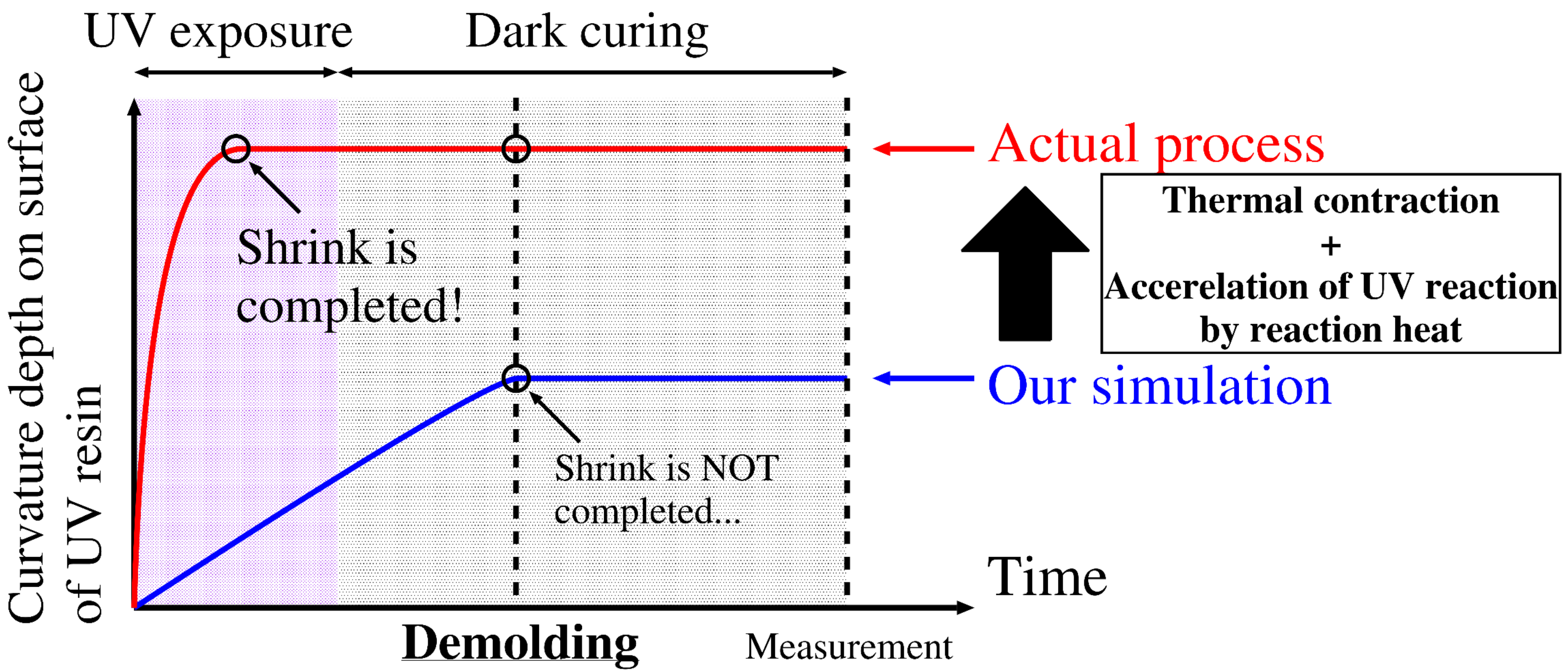
Effect of demolding timepoint on curvature depth

Relation between demolding timepoint and max. curvature depth



Delaying the demolding timing makes the surface curvature deeper.
⇒ The more UV reaction progresses until demolding timepoint, the deeper the surface curvature.

Why curvature depth of simulation is small?



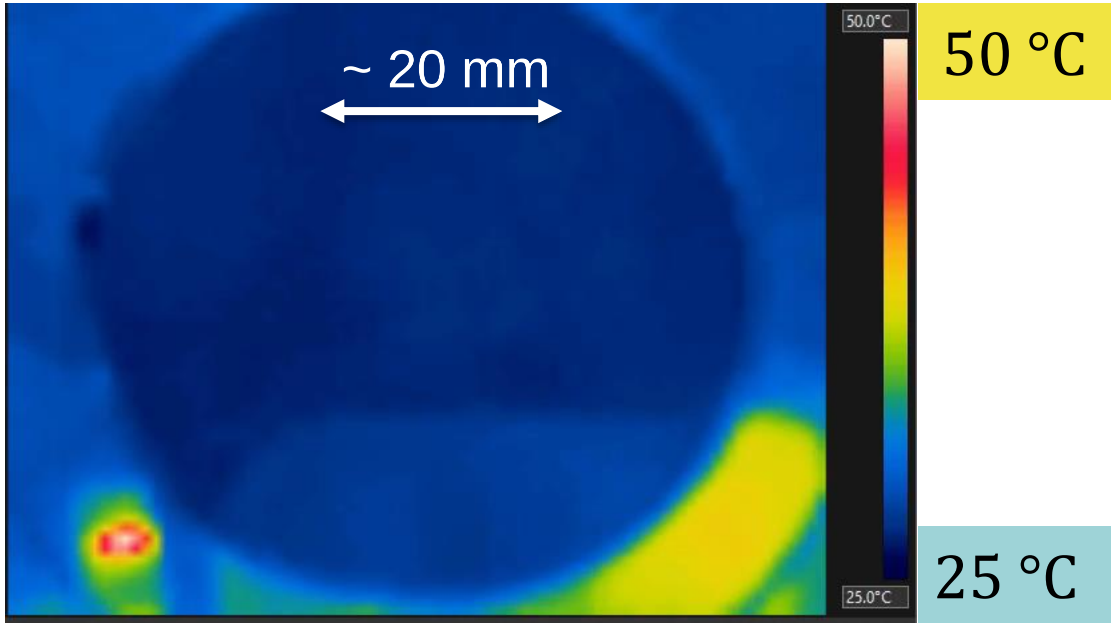
- In the simulation, UV shrink is not completed at the time of demolding, and the curvature depth at that time is observed.
- In the actual process, UV shrink with thermal contraction has been completed before demolding, therefore the curvature depth becomes deeper than our simulation's one.

Why curvature depth of simulation is small?

Temperature time history of UV resin during UV reaction

(Stage temp. 25 °C, UV intensity 50 mW/cm^2, 500 μm thick)

Recorded by thermography (FLIR C2)



Temperature time history of resin center