Resin Deformation Analysis in UV Imprint Considering UV Shrinkage, Thermal Deformation, and Thermochemical Kinetics

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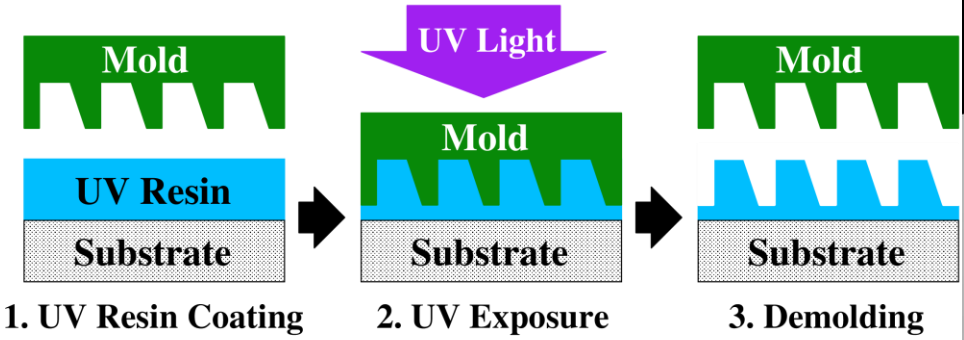
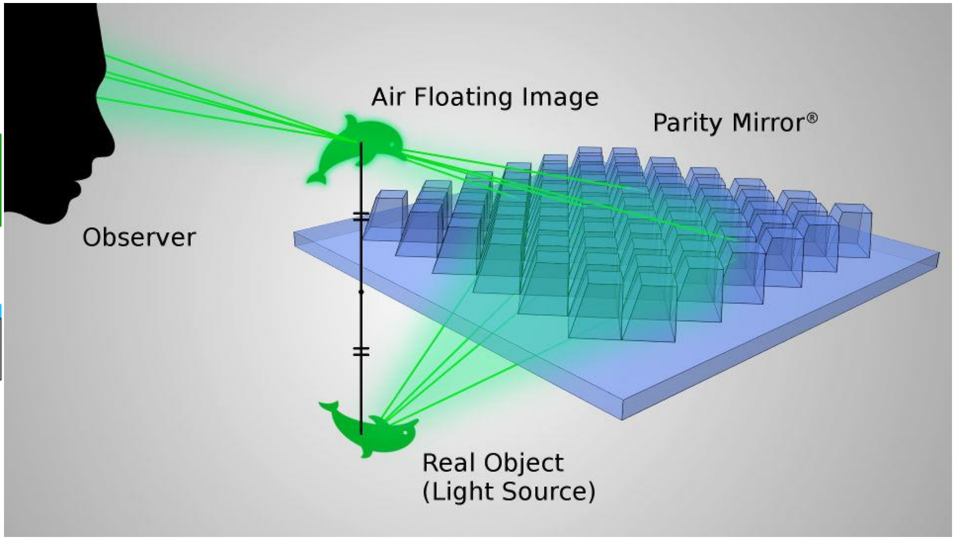
Background

- UV imprint is known as a low-cost and high-throughput nano/micro fabrication method.
- In recent years, it has been adopted as a fabrication method for micro-optical devices such as micromirror array that requires high-precision surface profiles.



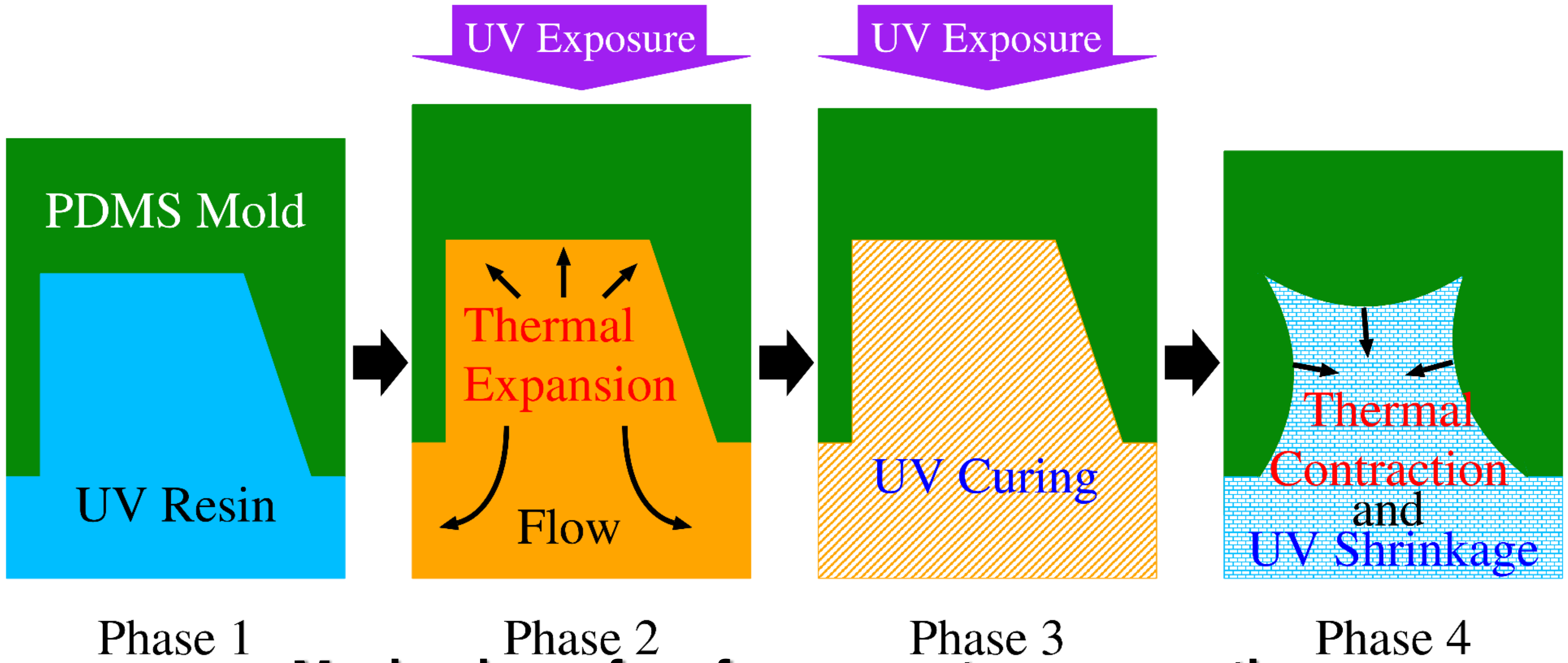
Basic steps in UV imprint.



Optical device produced by thermal imprint.
Parity Innovations Co., Ltd.
https://www.piq.co.jp/about_e.html

Issue

- UV resin undergoes several percent thermal deformation and UV shrinkage during imprint, resulting in unexpected surface curvature when a soft mold is used.



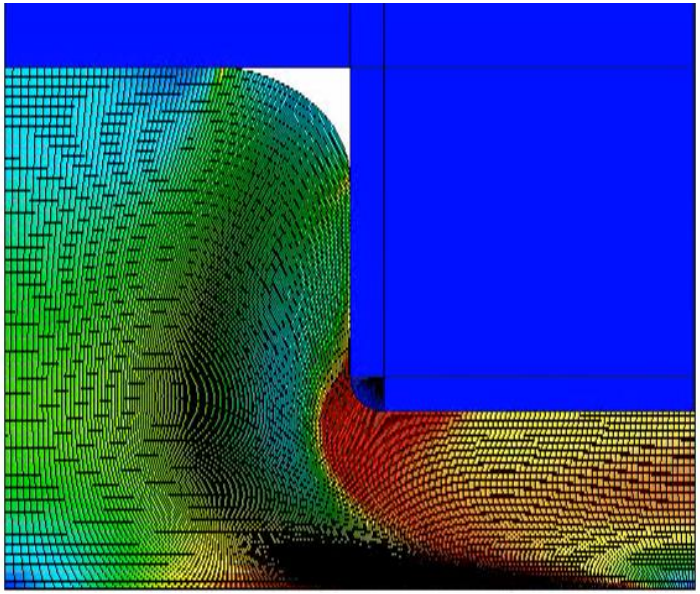
Mechanism of surface curvature generation

- We need to predict this by numerical simulation, but no numerical modeling method has been proposed yet.

Related research

A numerical modeling method for thermal imprint has already been proposed.

- Thermo-viscoelastic constitutive model for thermoplastic resin:
  - Thermal deformation: heat expansion coeff.
  - Shear behavior: viscoelastic (generalized Maxwell model)
  - Temperature dependency: time-temperature superposition (WLF law)
- Finite element method



Example of thermal imprint analysis

Idea: It may be possible to achieve UV imprint modeling with a similar approach.

Our approach

- Focusing on the analogy with thermo–viscoelastic model in thermal imprinting:
  - UV reaction progress ⟹ Cooling
  - UV curing ⟹ Cooling solidification
  - UV shrinkage ⟹ Cooling contraction

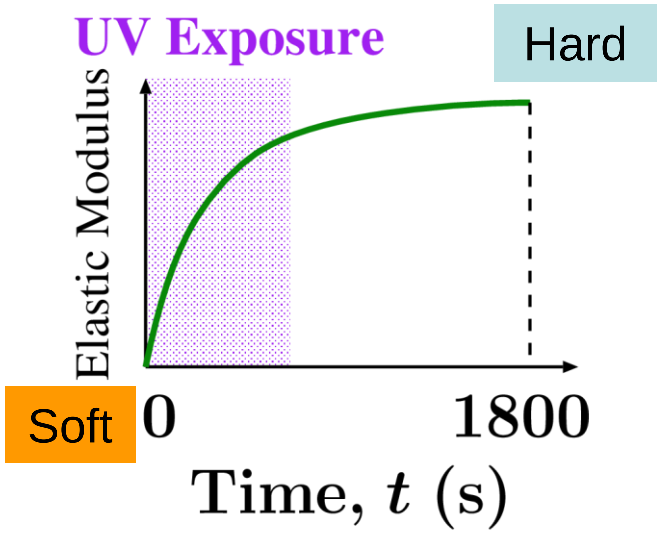
  i.e., giving a virtual cooling of UV resin.

- To give virtual cooling, we introduce the idea of "virtual temperature".

Idea of “virtual temperature”

Virtual temperature (θ^{virt}) is introduced as a measure of UV reaction progress to cool the UV resin virtually.

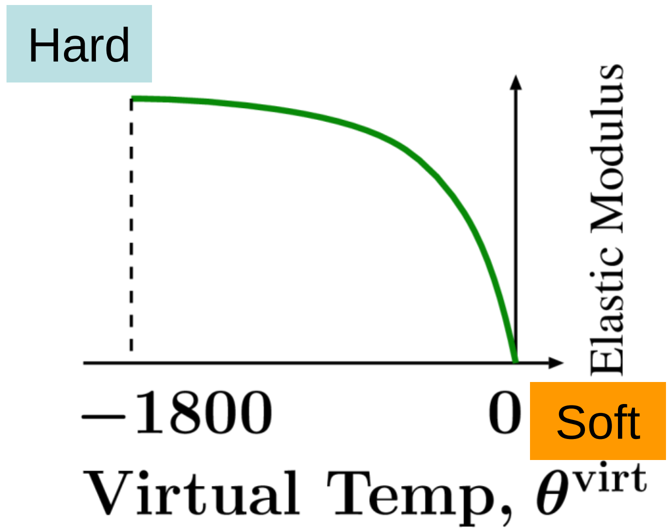
e.g., UV curing $\Longrightarrow$ Cooling solidification



UV Reaction

UV Curing

Virtual Temperature θ^{virt}



Virtual Cooling

Cooling Solidification

Objective

- Establishment of numerical modeling method for resin deformation analysis in UV imprints considering
  1. UV curing,
  2. UV shrinkage,
  3. thermal deformation, and
  4. temperature-dependent reaction rate.
- Validation of the modeling method with a micromirror array example for aerial display.

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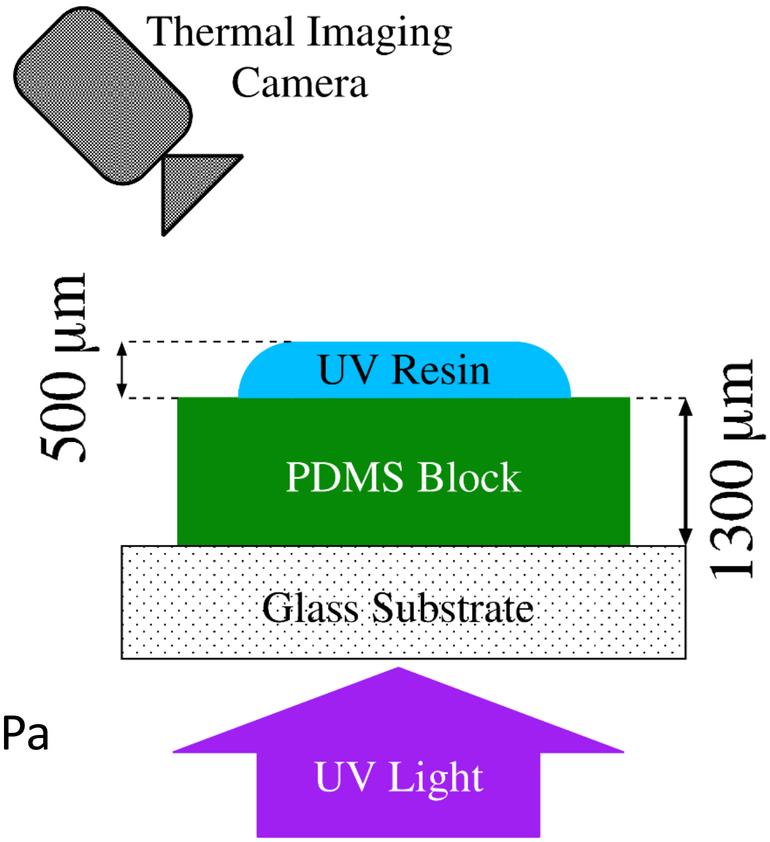
- Experiments
- Methods
- Results and discussion
- Summary

Experiments

Resin temperature measurement test

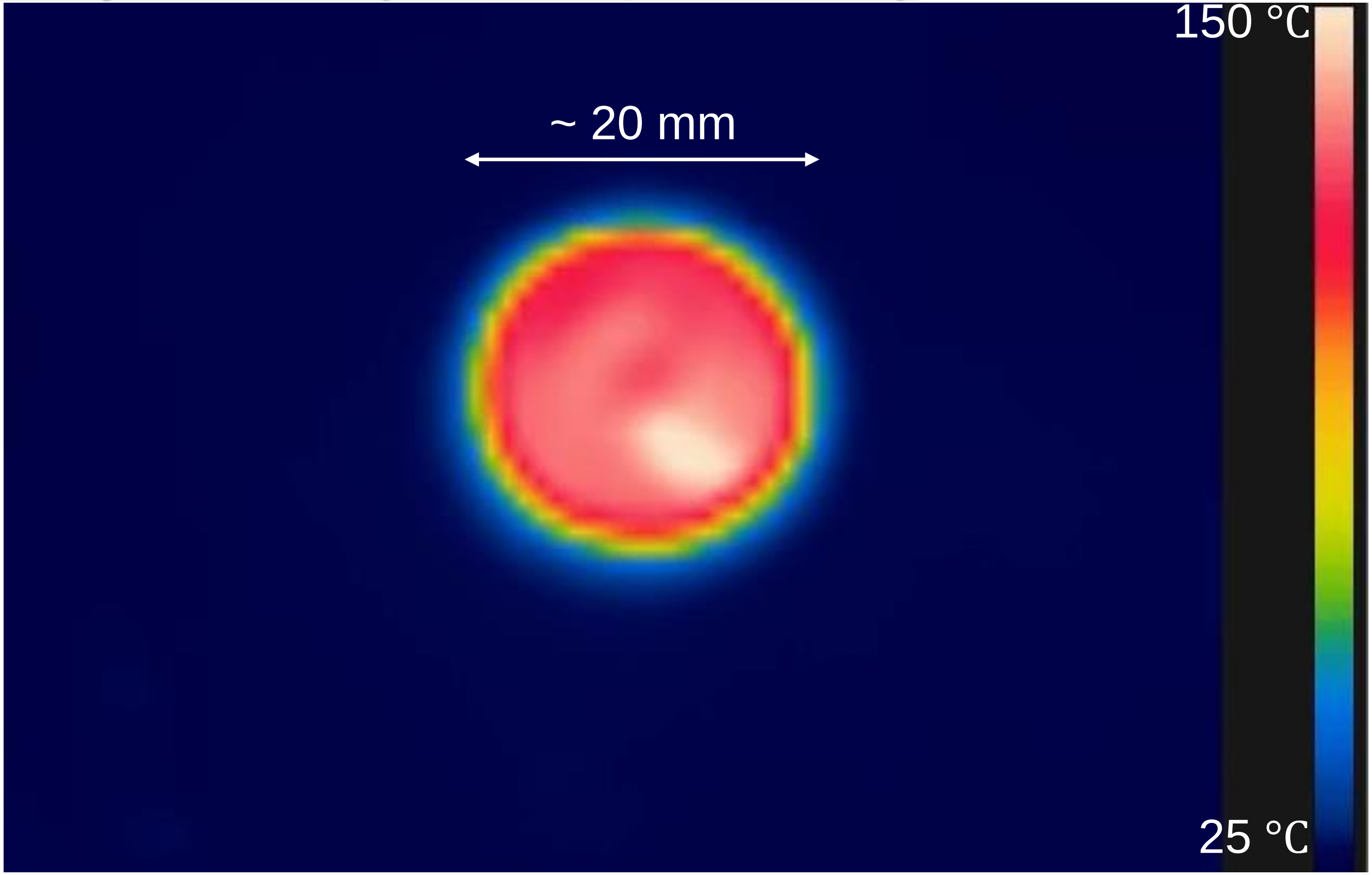
Outline

- UV resin is dropped on a PDMS block placed on a glass substrate.
- UV light is exposed from below.
- A thermal imaging camera measures resin temp. from above.
- The test specifications are identical to those of the actual micromirror array imprint.
  - Cation polymerization-type resin
  - Hard PDMS with Young's modulus of 5 MPa
  - UV-LED flat light of 365 nm
  - 30 s exposure with 50 mW/cm^2



Resin temperature measurement test

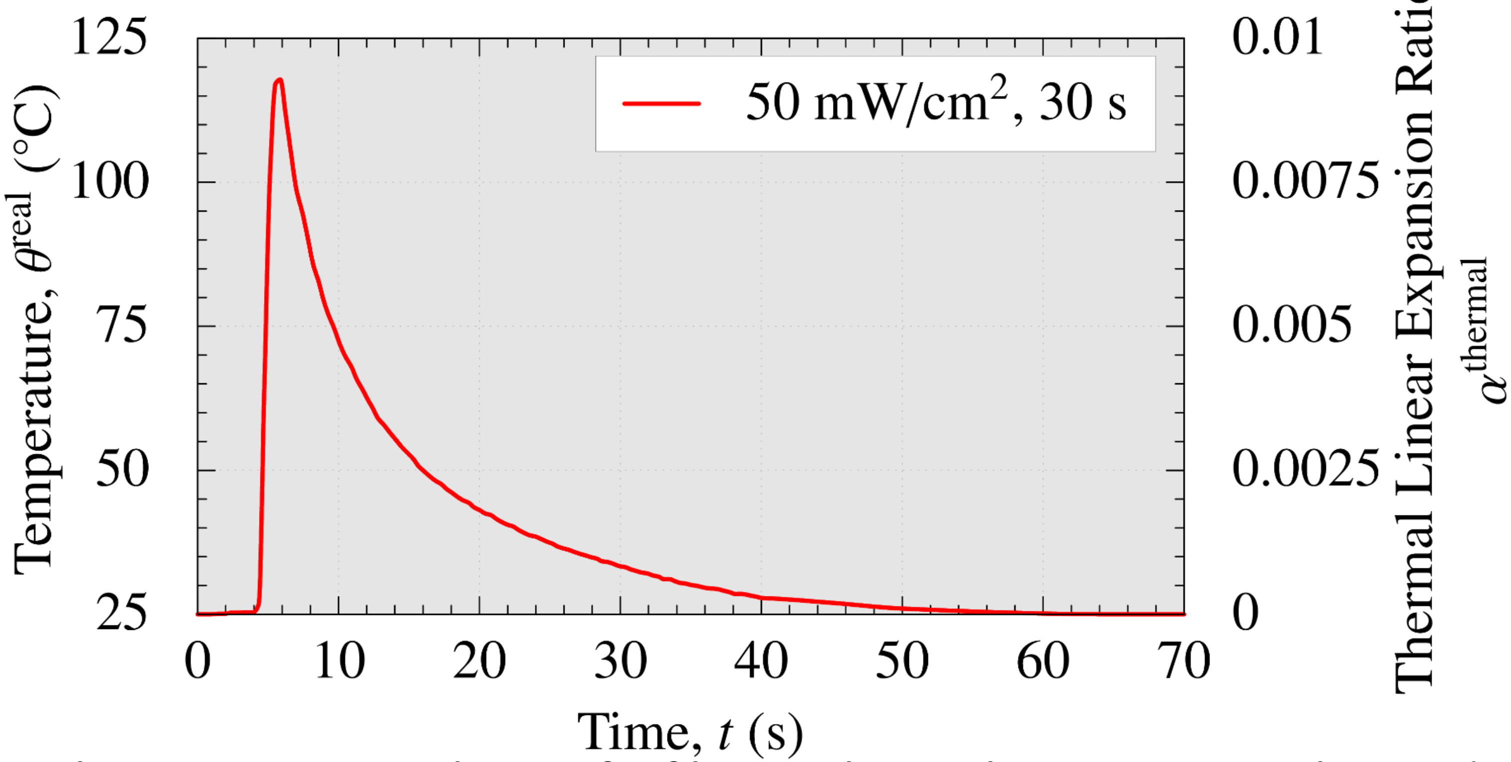
An example result (300 mW/cm^2 case)



The temp. reaches the maximum in several seconds after the start of exposure and gradually returns to room temp..

Resin temperature measurement test

Time histories of temp. and expansion (50 mW/cm², 30s)



※ From another experiment, the coef. of linear thermal expansion is obtained as 1.0×10^{-4} [1/K].

A temperature increase about 100 K causes about
1% thermal linear expansion (3% expansion in volume)
in 6 s after exposure.

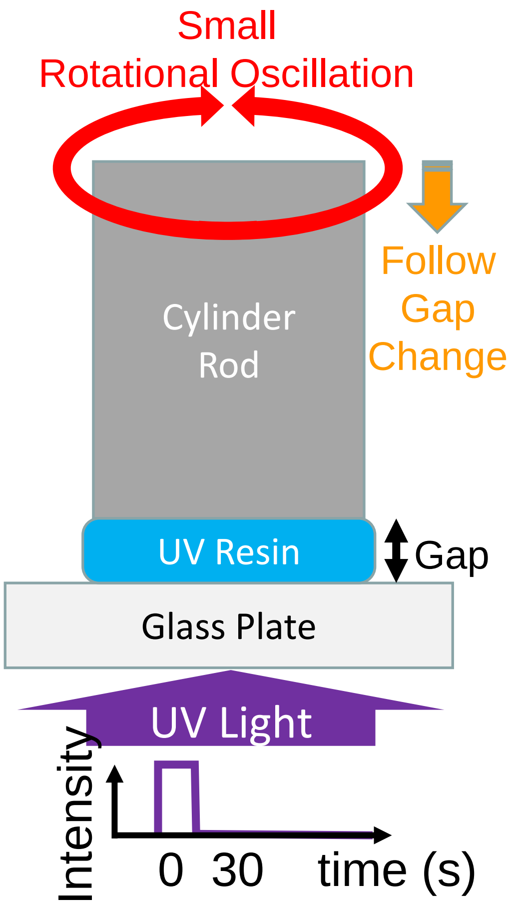
UV shrinkage & complex shear modulus meas. tests

Outline

- Rotational oscillatory rheometer.
- Small rotational oscillation is given to the UV resin under UV curing.
- Time history of UV shrinkage (gap length) is measured.
- Time history of Complex shear modulus at various temps. and freqs. is also measured.
- Resin temp. is kept constant by the aluminum rod with temp. control.

Anton Paar MCR series

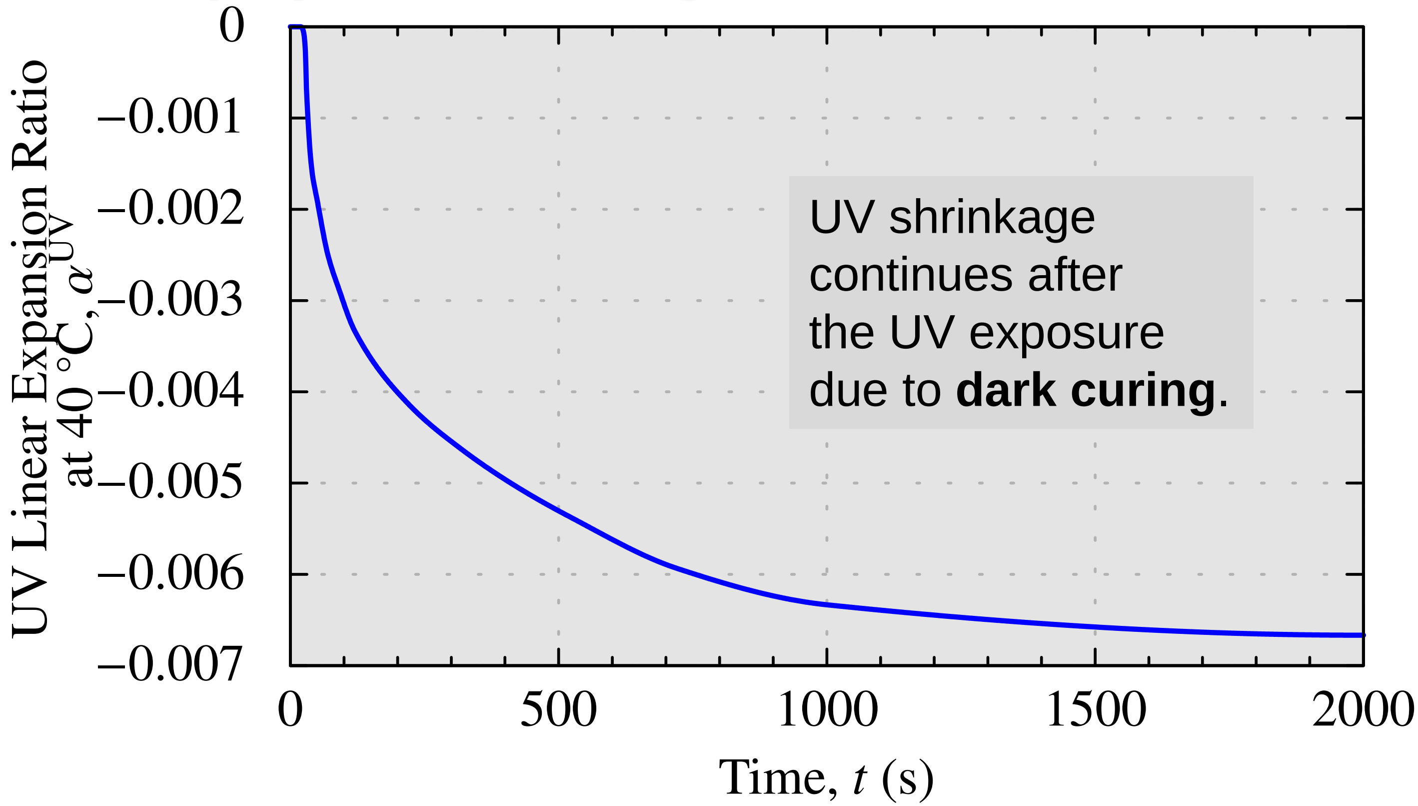
https://www.anton-paar.com/corp-en/products/details/rheometer-mcr-102-302-502/



- Same UV exposure condition as the micromirror array imprint.

UV shrinkage & complex shear modulus meas. tests

Time history of UV shrinkage (at 40 °C, independent of freq.)

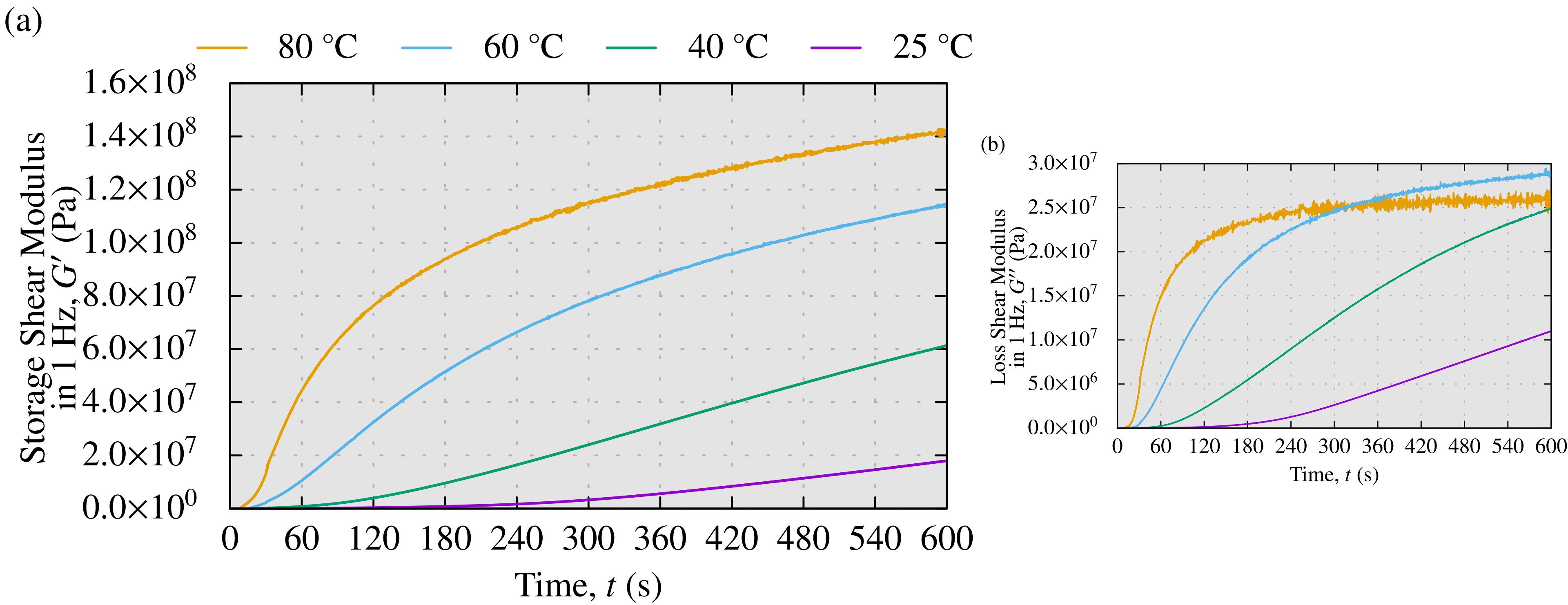


UV curing finally causes about 0.7% linear shrinkage (2% shrinkage in volume)
⟹ It seems possible to treat this as virtual “thermal” contraction by combining this with the real thermal expansion.

UV shrinkage & complex shear modulus meas. tests

Time history of complex shear modulus at various temps. (1 Hz in freq.)

Left: Storage shear modulus, Right: Loss shear modulus

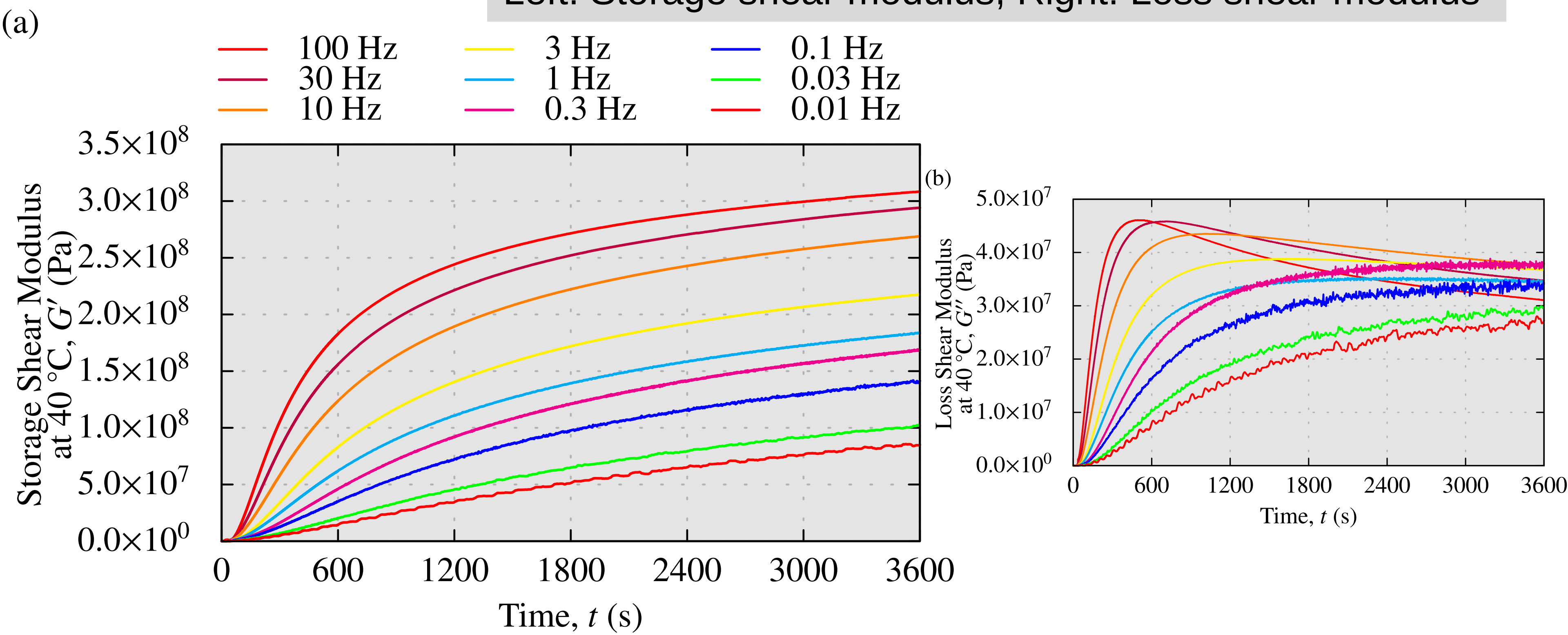


UV curing progresses faster as the temp. increases.
⟹ It seems possible to identity the temp.-dependent reaction rate constants.

UV shrinkage & complex shear modulus meas. tests

Time history of complex shear modulus at various freqs. (40 °C in temp.)

Left: Storage shear modulus, Right: Loss shear modulus

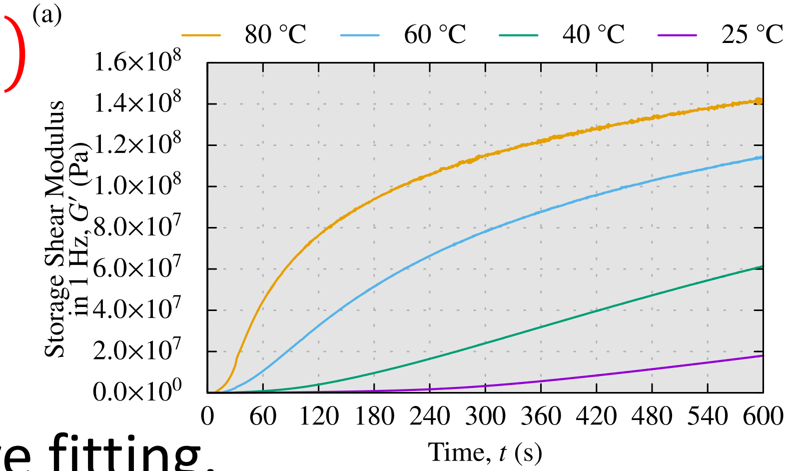


The storage modulus becomes larger as the freq. increases.
⟹ It seems possible to identify the Prony series of the generalized Maxwell model and the time−(virtual)temperature superposition law.

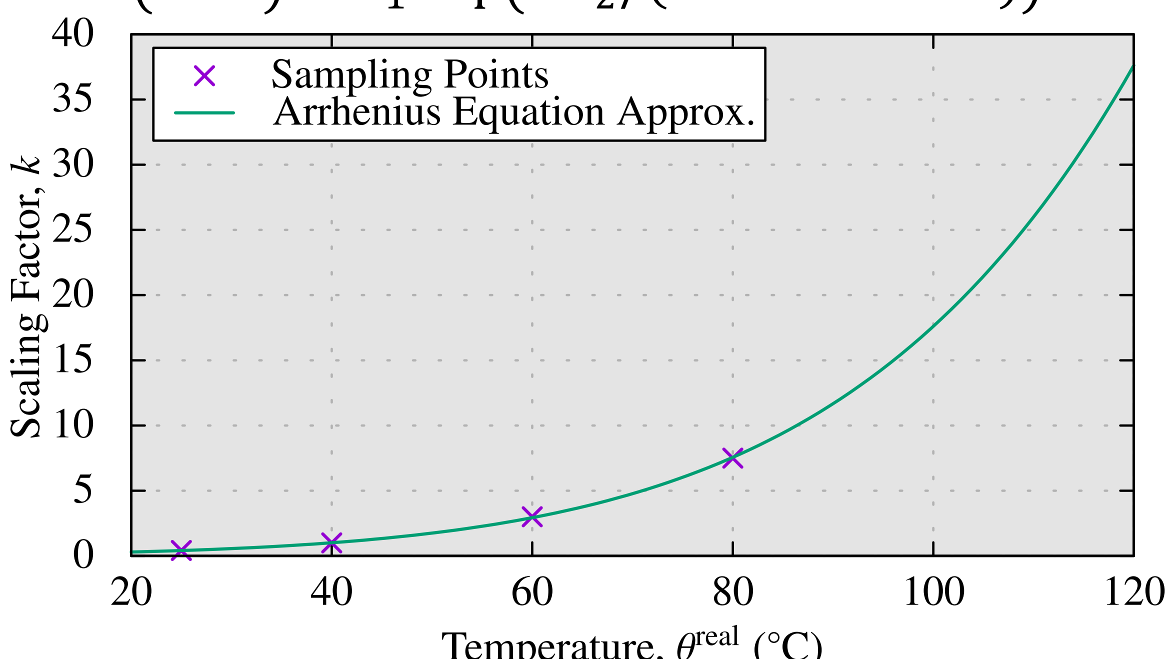
Methods

Identification of Arrhenius Constants

- The reaction rate scaling factor $k(\theta^{\mathrm{real}})$ can be identified from the time history of the complex shear modulus at various temps. (right fig.).
- Based on thermochemical kinetics, the Arrhenius equation is used for curve fitting.



$$k(\theta^{\mathrm{real}}) = C_1 \exp(-C_2/(\theta^{\mathrm{real}} + 273.15))$$



Ref. temp. is 40 °C (i.e., $k = 1$ at 40 °C)

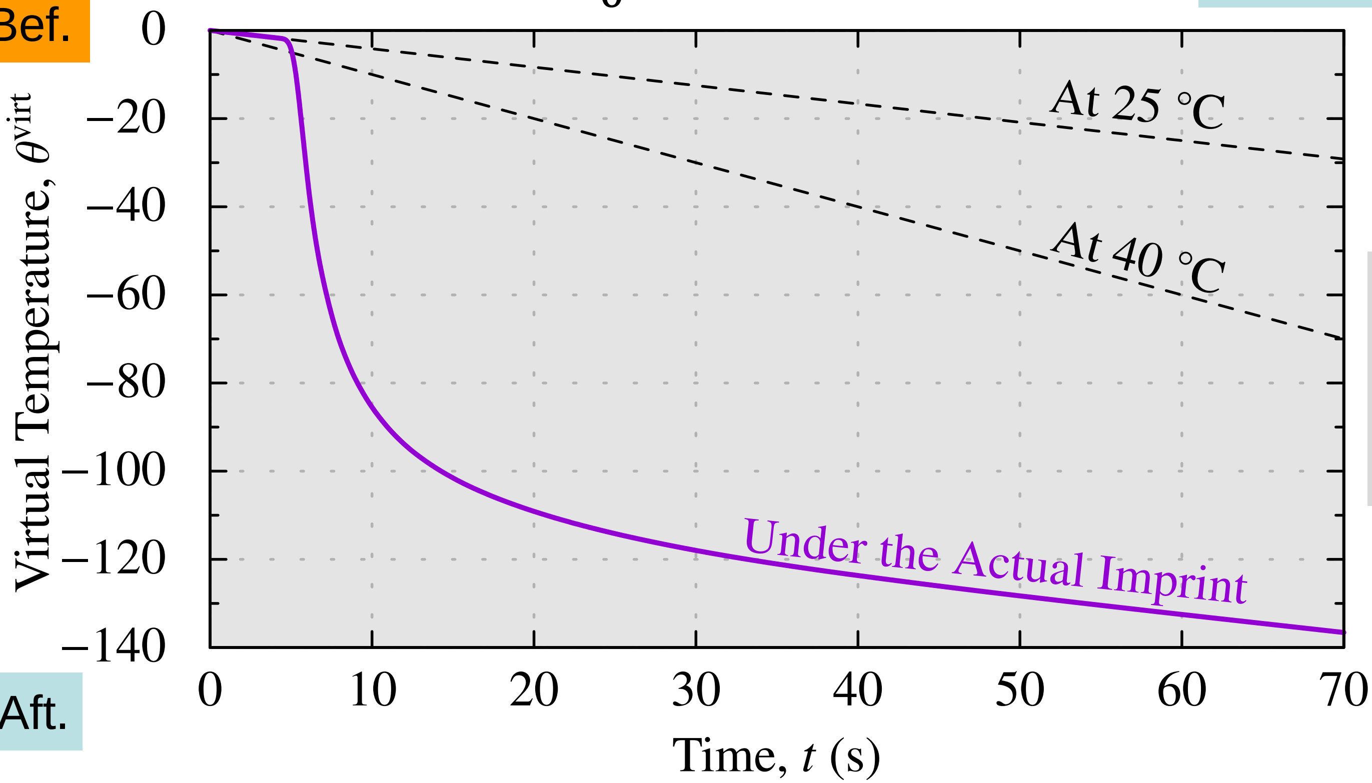
Definition of virtual temp. time history

- $\theta^{\mathrm{virt}} = 0$ before UV exposure ($t \leq 0$).
- After UV exposure, θ^{virt} is monotonically decreased according to the reaction rate factor k at each moment.

$$\theta^{\mathrm{virt}}(t) \equiv \int_0^t -k\left(\theta^{\mathrm{real}}(t)\right)\,\mathrm{d}t$$

$\theta^{\mathrm{virt}}(t)$ represents the measure UV reaction progress.

Bef.



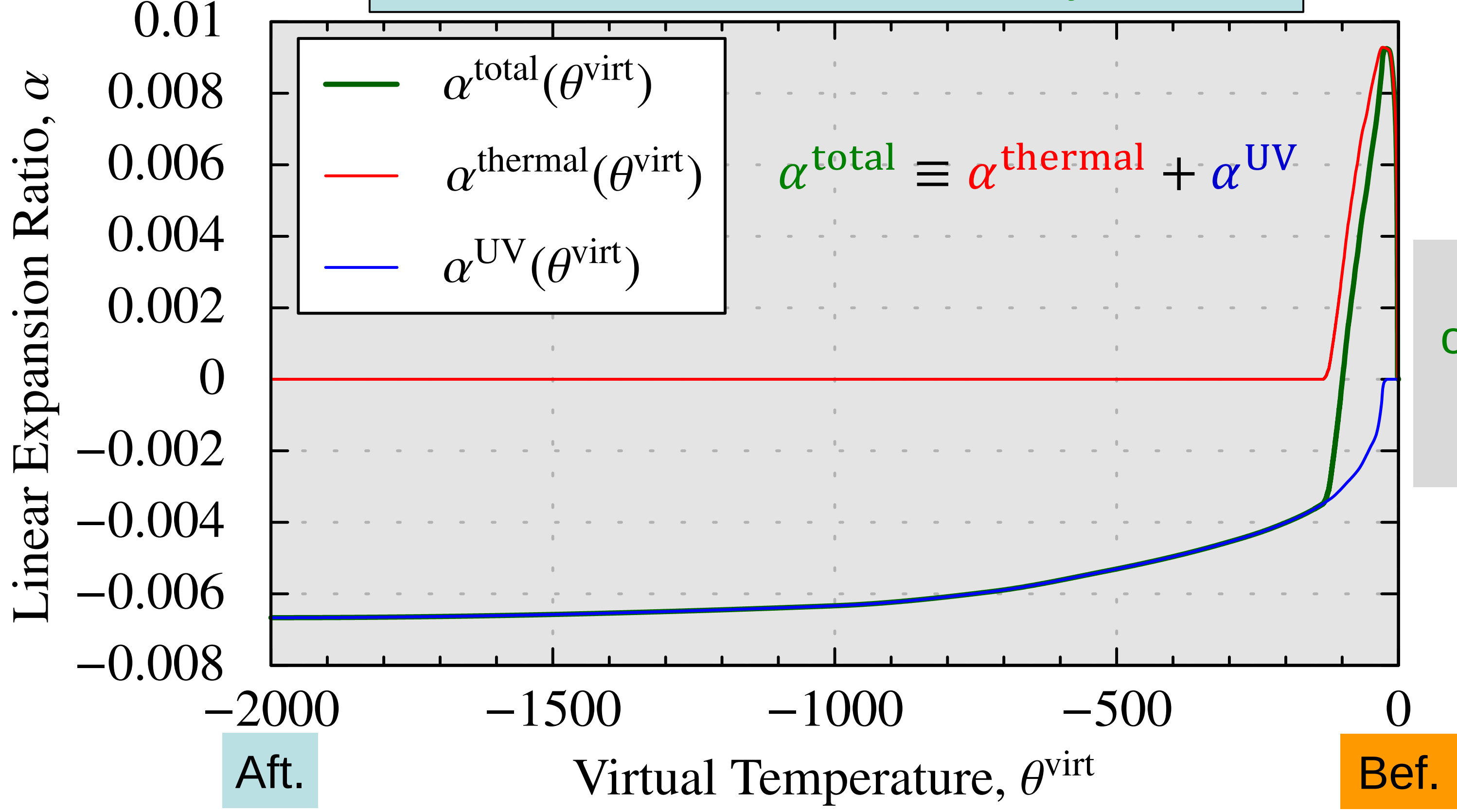
Aft.

The Curve of $\theta^{\mathrm{virt}}(t)$ is defined as a table data.

Identification of virtual temp.-dependent expansion

- The previous plots of time-dependent thermal deformation and UV shrinkage are converted into virtual temp.-dependent plots.
- The sum of the two is the virtual temp.-dependent expansion coefficient.

Thermal deformation and UV shrinkage can be considered simultaneously.



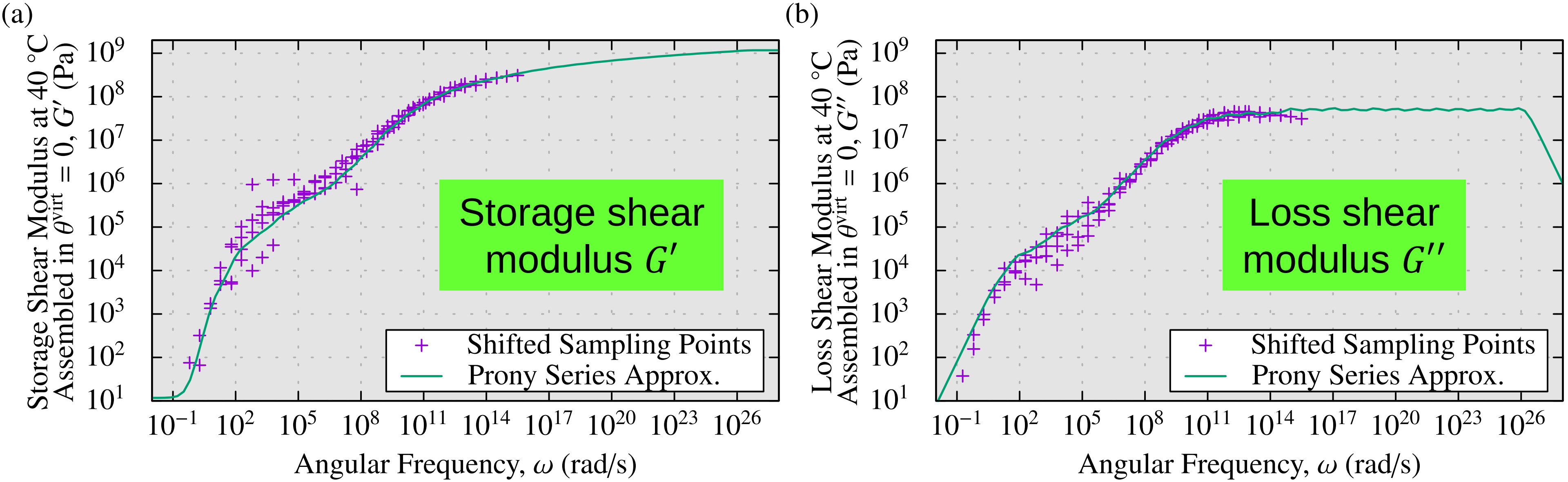
The Curve of $\alpha^{\mathrm{total}}(\theta^{\mathrm{virt}})$ is defined as a table data.

Prony series coefs.

- The Prony series coefs. (g_i, τ_i)s are identified by the curve fitting for the master curves of storage/loss shear modulus.

$$G'(\omega) = G_\infty + G_0 \sum_i \left(g_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \right)$$

$$G''(\omega) = G_0 \sum_i \left(g_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \right)$$

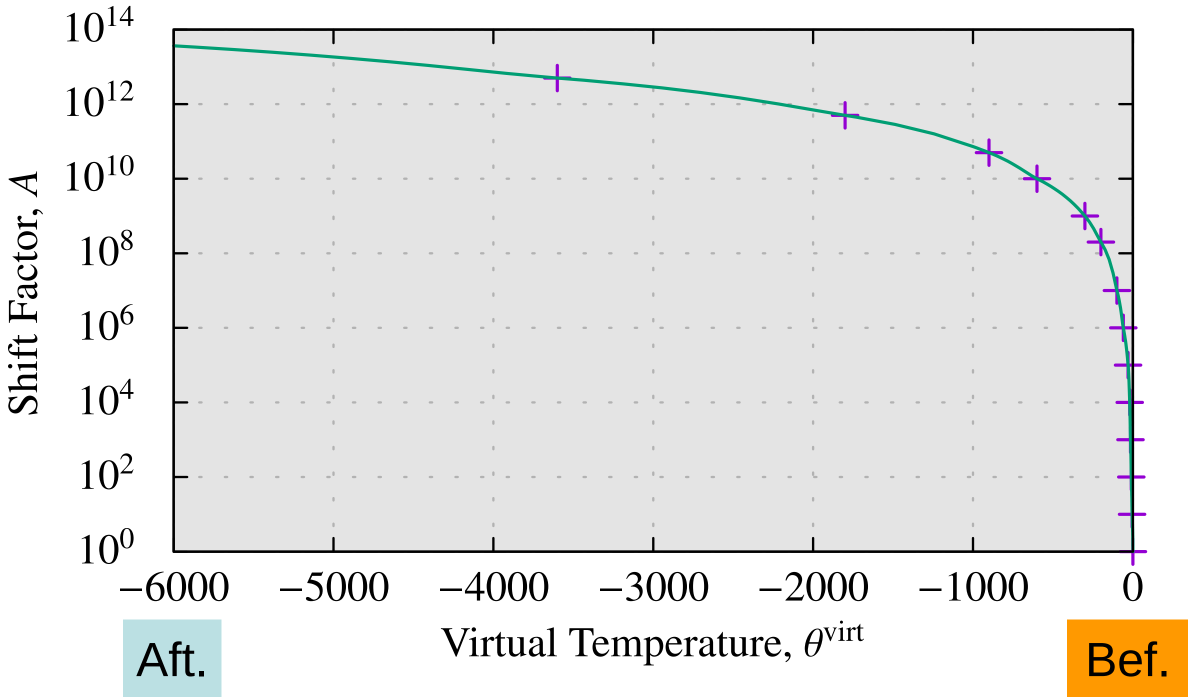


(g_i, τ_i)s are described as a table data.

Identification of thermo-viscoelastic properties

Time-virtul temp. superposition

- The shift factor $A(\theta^{\mathrm{virt}})$ for the time-virtual temp. superposition is identified by curve fitting using time shift data for the master curves.



$A(\theta^{\mathrm{virt}})$ is defined as a table data.

Now, a set of model parameters for UV resin deformation was all identified.

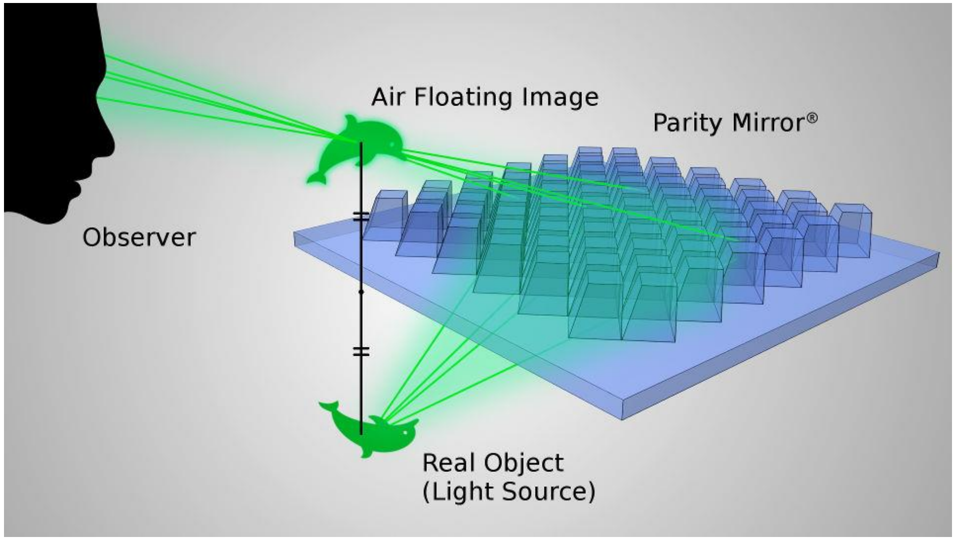
Results and Discussion

Micromirror array imprint analysis

Outline

- Target pattern is a **micromirror array** for aerial display.
- Since the mold has repetitive structure, only **one pattern is taken into account** with periodic boundary conditions.
- The initial state is when the pattern is filled with UV resin.
- Commercial finite element code, ABAQUS, is used for simulation.
- 8-node hexahedral SRI element (C3D8) is adopted.

Schematic view of micromirror array



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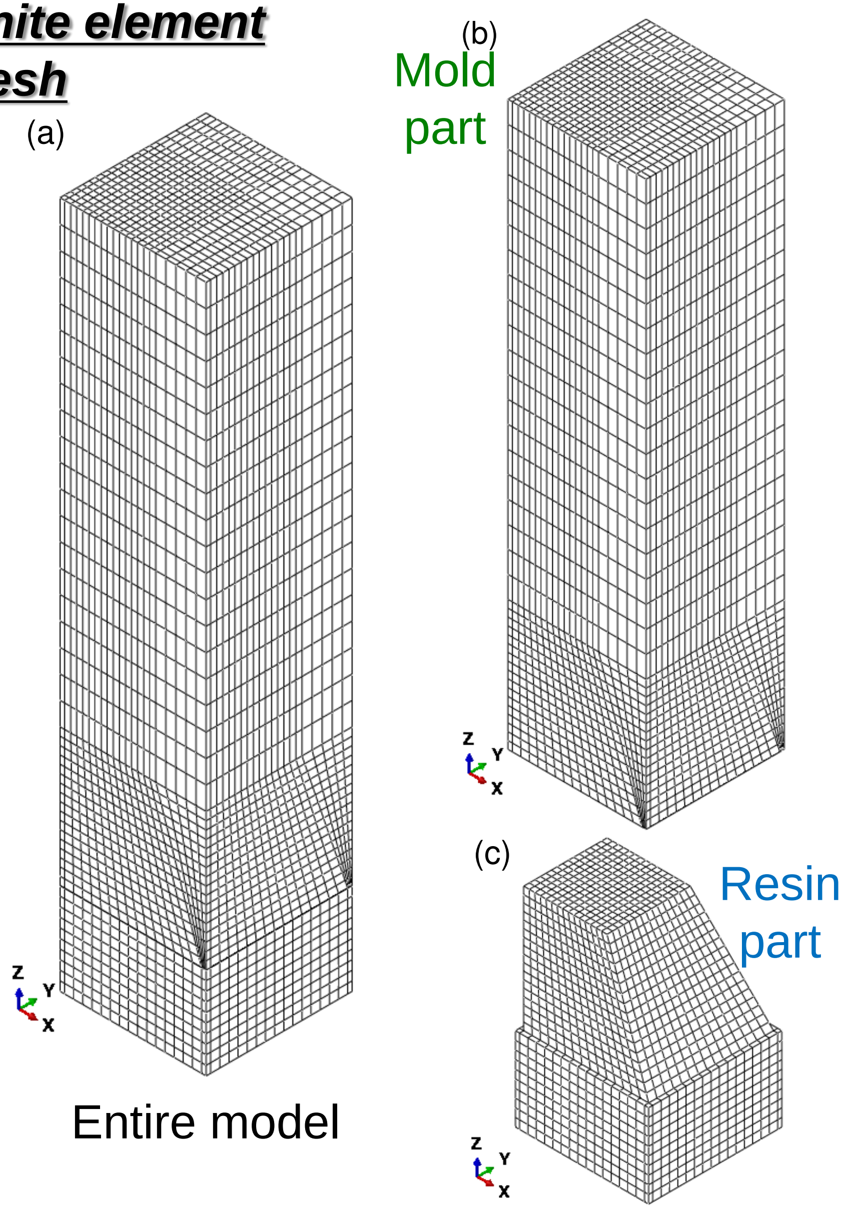
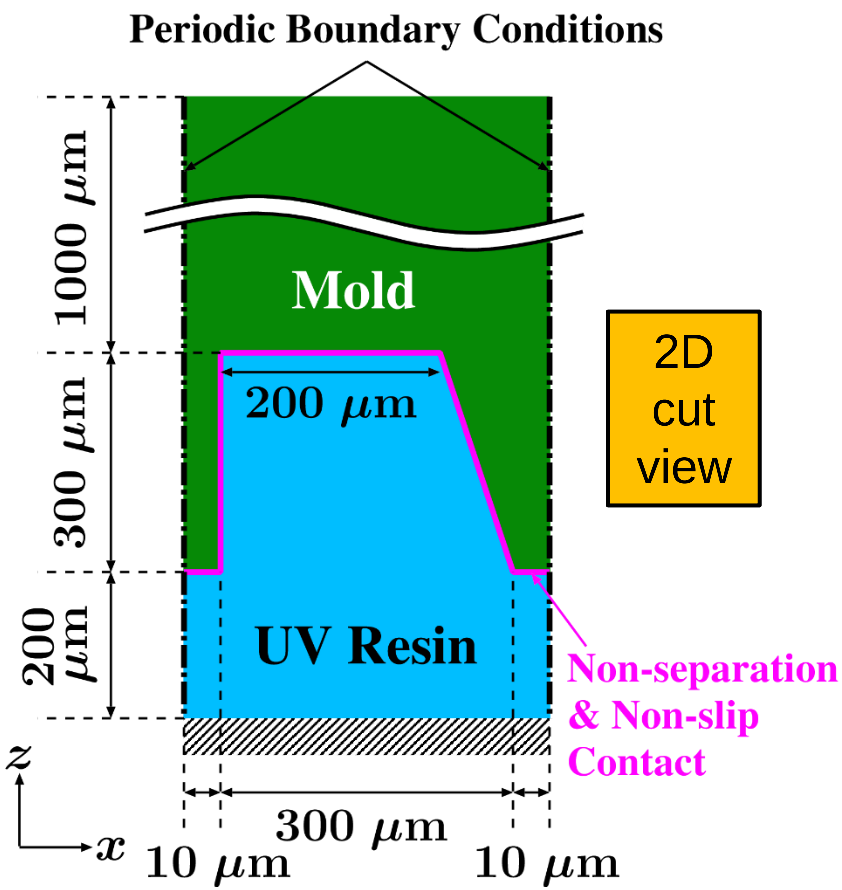
Finite element mesh



Steps for imprint simulation

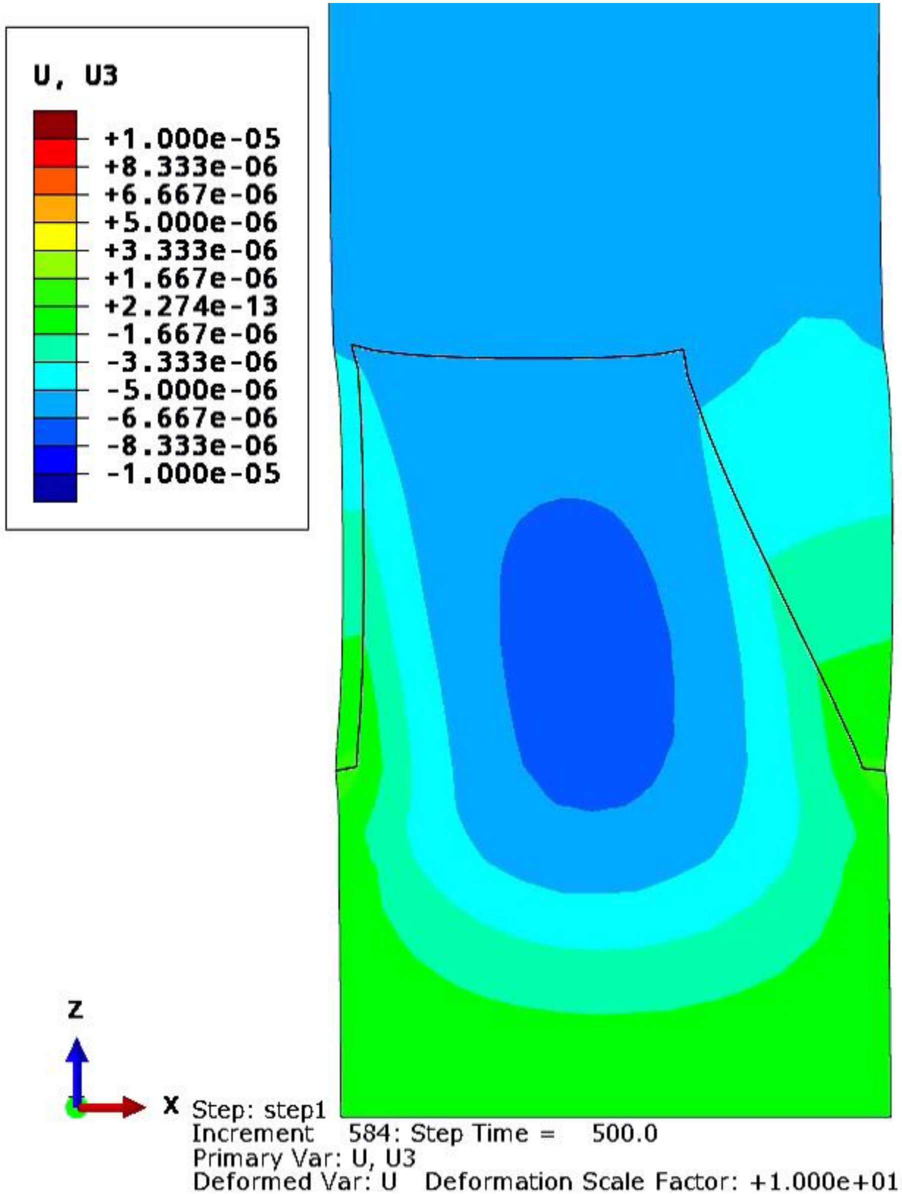
- **Step 1: Initial state (0 s)**
  - ❑ Static analysis considering gravity
  - ❑ Apply non-separation & non-slip contact
- **Step 2: UV exposure and dark curing (500 s)**
  - ❑ Quasi-static analysis (till the end)
  - ❑ Decrease θ^{virt} $(0 \rightarrow -312)$
- **Step 3: Demolding and dark curing (10 s)**
  - ❑ Remove the contact definition
  - ❑ Lift up the mold
  - ❑ Decrease θ^{virt} $(-312 \rightarrow -316)$
- **Step 4: Dark curing (100000 s)**
  - ❑ Decrease θ^{virt} $(-316 \rightarrow -41164)$



Part	Material model
UV resin	Thermo viscoelastic body with the identified params.
Mold	Neo-Hookean hyperelastic body

Simulation result

Animation of Z displ. dist. on a central Y cross-section

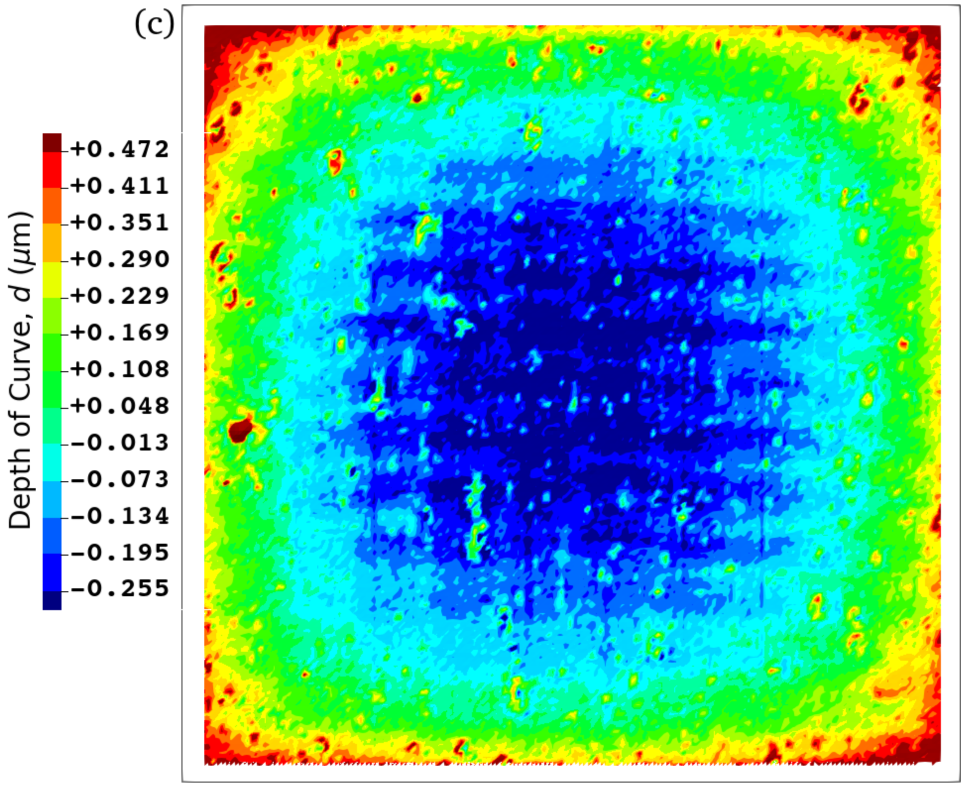


Deformation magnification: x 10

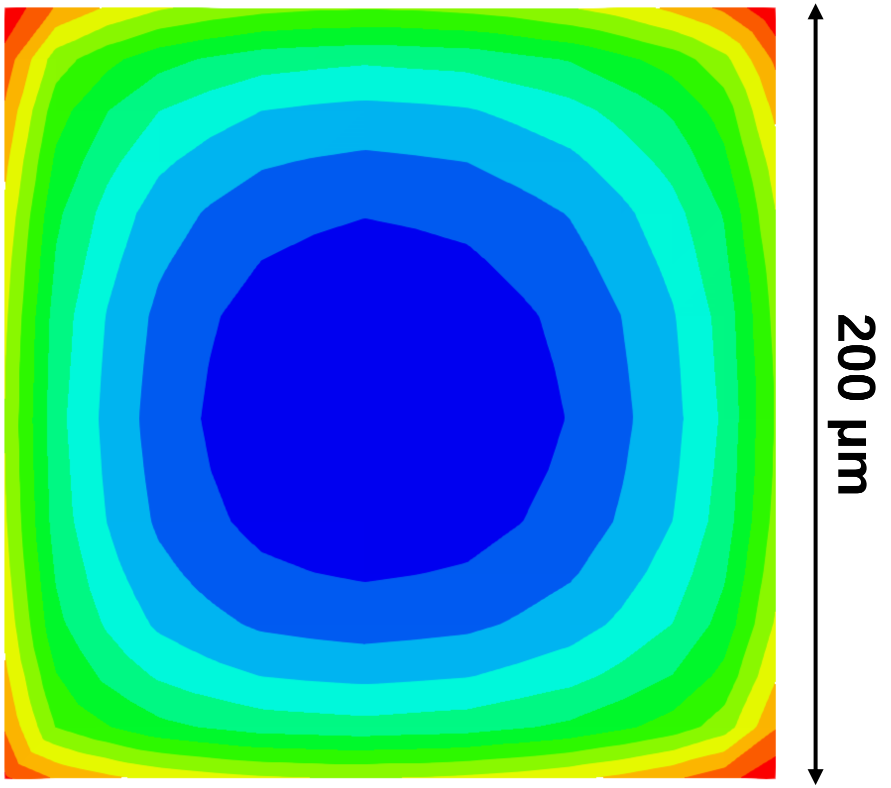
- The periodic boundary conditions are given correctly.
- Major expansion of UV resin soon after UV exposure.
- Gradual contraction of UV resin during dark curing.
- Surface curve on the PDMS mold is reproduced.

Comparison of results

Distribution of depth of curve on the top face



Actual Imprint
(measured by laser microscope)

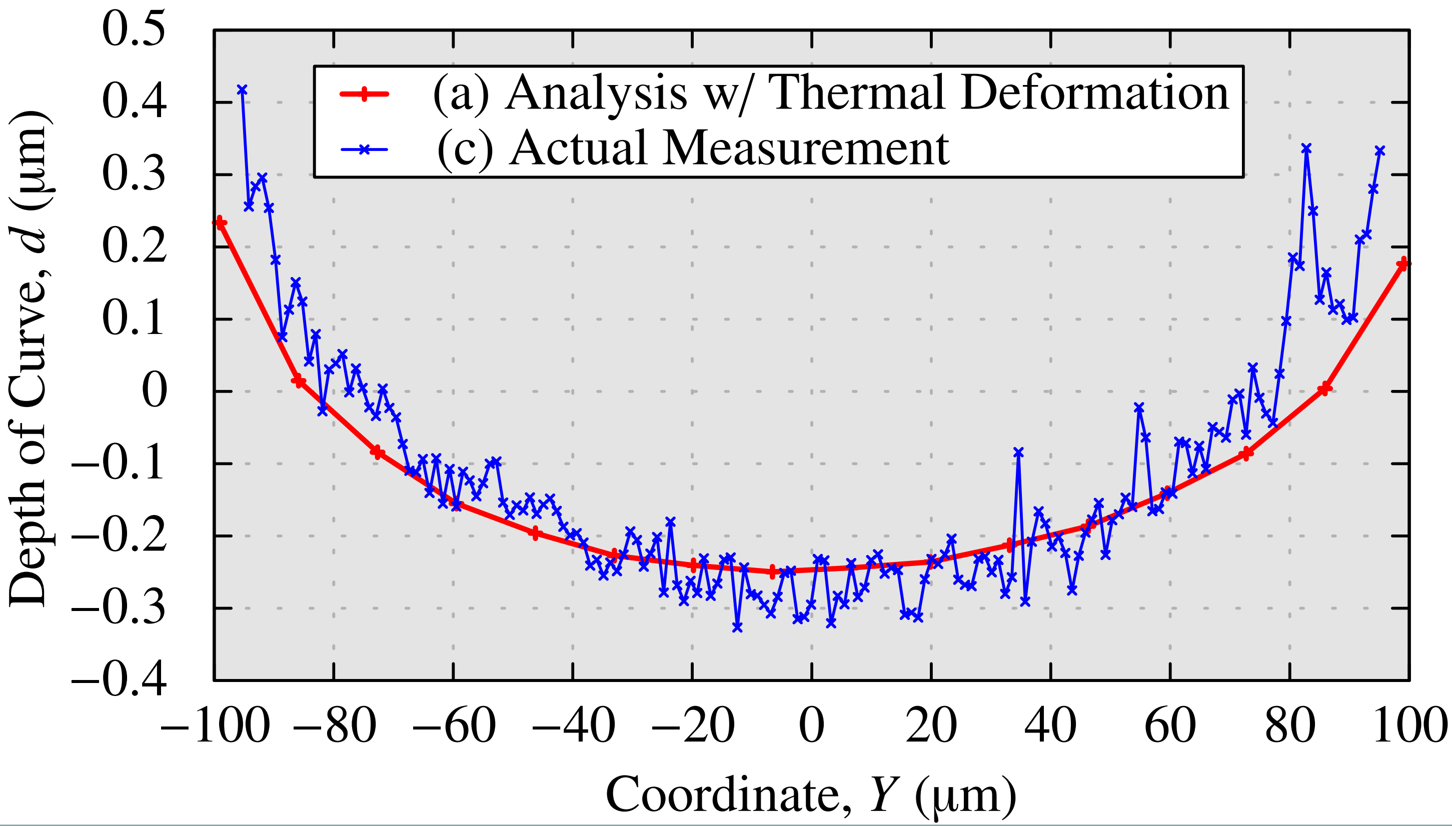


Simulation Result

The curvatures are in **good agreement**.

Comparison of results

Profiles of depth of curve on the vertical center line of the top face



The profiles are in **good agreement**, but the simulation result is about 10% shallower than the actual measurement.
It may be necessary to consider the thermal softening effect of the PDMS mold due to temperature rise in the PDMS mold.

Summary

Summary

- A novel numerical modeling method for shape deformation analysis in UV imprint was proposed.
- UV curing, UV shrinkage, thermal deformation, and temperature-dependent reaction rate were all considered simultaneously by introducing the virtual temperature, reaction kinetics, and thermo-viscoelastic constitutive law.
- A set of model parameters for UV resin was identified through the thermal camera tests and rheometer tests.
- A micromirror array imprint analysis was conducted to validate that the simulated surface curve agreed with the actual measurement with 10% error approximately.
- The temperature rise and thermal softening of the mold due to heat transfer are to be considered in the future.

Thank you for your kind attention!