Self-Driving Lab for Photopolymer Synthesis and Mechanical Testing for Expedited Material Discovery

Marcus Rocco Fratarcangeli

Active Materials &
Additive Manufacturing

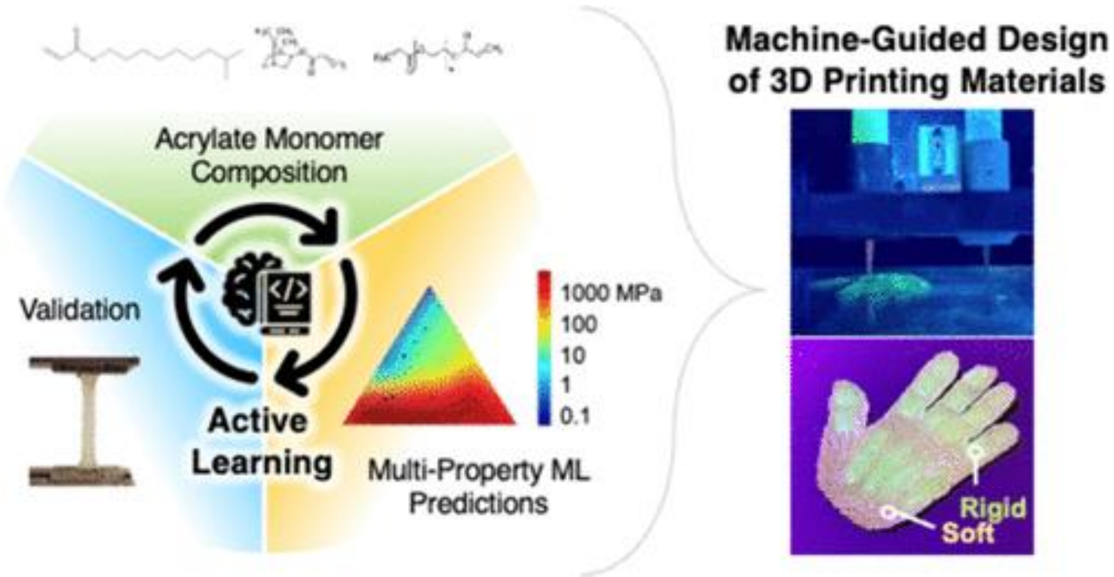
Georgia Tech

Contents

Introduction

Introduction

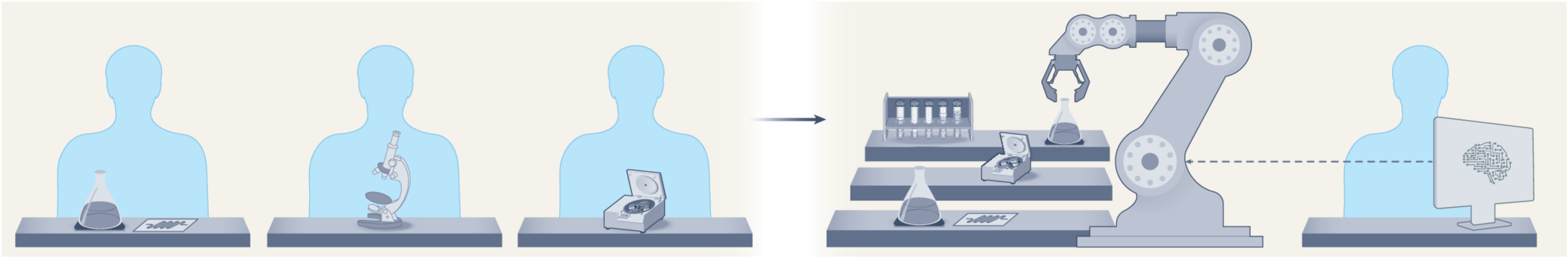
- Materials discovery has a high research budget
- Previous work tested photopolymers in small design space
- 720 tests were performed manually



Jain, A., Armstrong, C. D., Joseph, V. R., Ramprasad, R., & Qi, H. J. (2024). Machine-Guided Discovery of Acrylate Photopolymer Compositions. ACS Applied Materials & Interfaces, 16(14), 17992-18000.

Introduction

- Increasing capabilities of self-driving labs (SDLs)
- Automate tedious and time-consuming processes
- Help reach research goals faster



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Abolhasani, M., Kumacheva, E. The rise of self-driving labs in chemical and materials sciences. *Nat. Synth* **2**, 483–492 (2023). https://doi.org/10.1038/s44160-022-00231-0

Self-Driving Labs

- Three main components: processing, characterization, decision-making

Processing & characterization

Decision-making

<table>
<tr><th>Hardware / Software</th><th>Manual</th><th>Automated task/ experiment</th><th>Automated workflow</th><th>Automated laboratory</th></tr>
<tr><td>Human ideation</td><td>Level 0</td><td>Level 1</td><td colspan="2">Level 2</td></tr>
<tr><td>Single iteration</td><td>Level 1</td><td>Level 2</td><td colspan="2">Level 3</td></tr>
<tr><td>Multiple iterations</td><td rowspan="2">Level 2</td><td rowspan="2">Level 3</td><td colspan="2">Level 4</td></tr>
<tr><td>Generative</td><td></td><td>Level 5</td></tr>
</table>

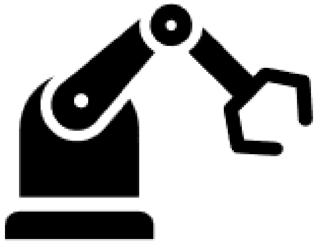
Self-driving lab levels of automation

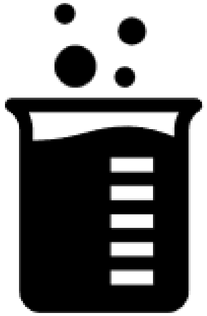
We are here

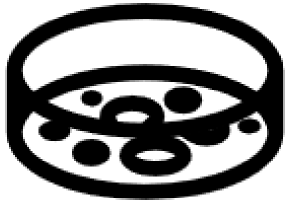
Gary Tom, Stefan P. Schmid, Sterling G. Baird, Yang Cao, Kourosh Darvish, Han Hao, Stanley Lo, Sergio Pablo-García, Ella M. Rajaonson, Marta Skreta, Naruki Yoshikawa, Samantha Corapi, Gun Deniz Akkoc, Felix Strieth-Kalthoff, Martin Seifrid, and Alán Aspuru-Guzik, Chemical Reviews 2024 124 (16), 9633-9732, DOI: 10.1021/acs.chemrev.4c00055

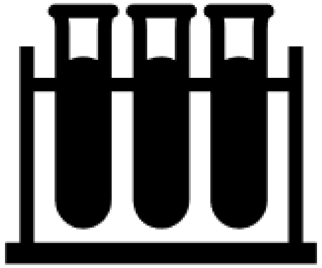
Processing

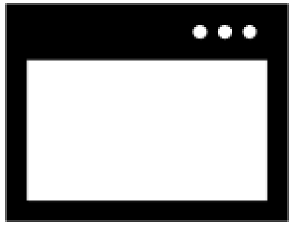
- Creating samples to be tested
- Transforming material into testable format


Robotic handling


Curing

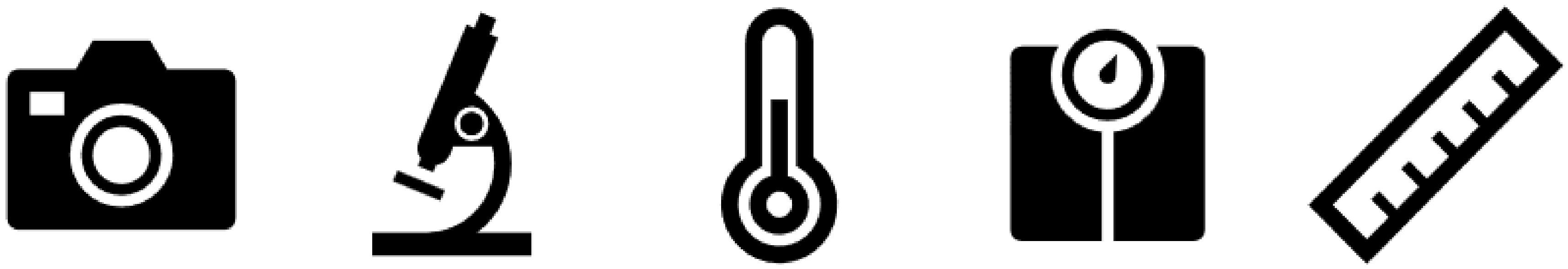

Growth


Chemical mixing


Heating/cooling

Characterization

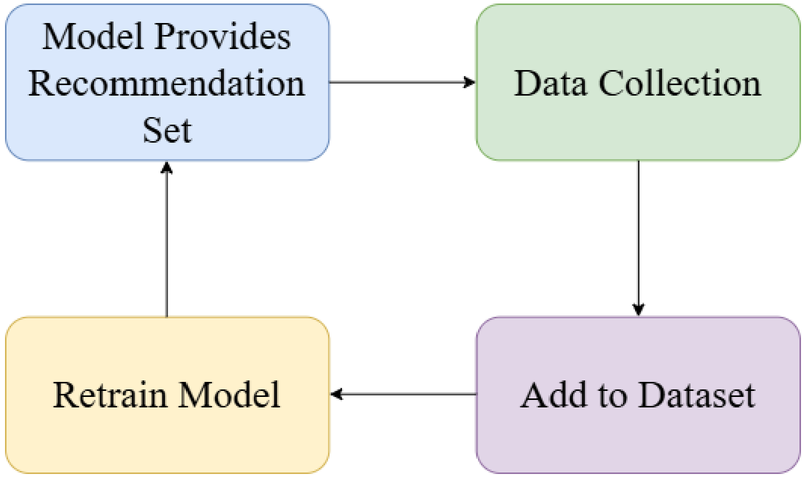
- Data collection from samples
- Contact or non-contact



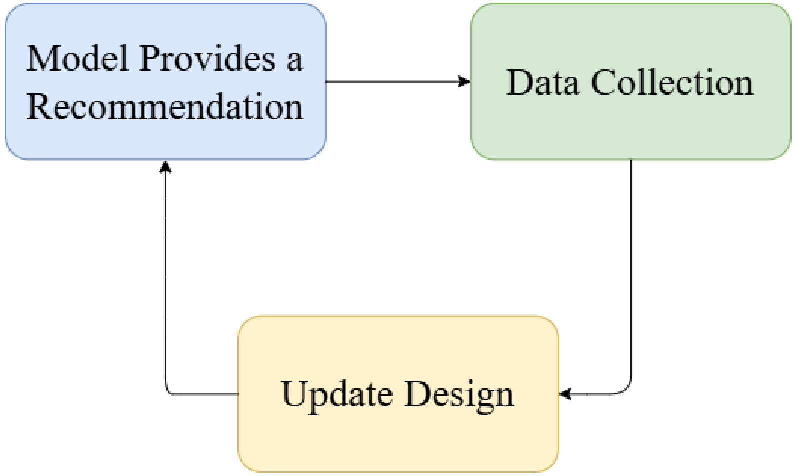
Imaging | Microscopic analysis | Thermal testing | Weighing | Measuring

Decision-making

- Choosing which samples to test to efficiently reach research goals
- Increase in size of design space calls for more data and better decision-making algorithms



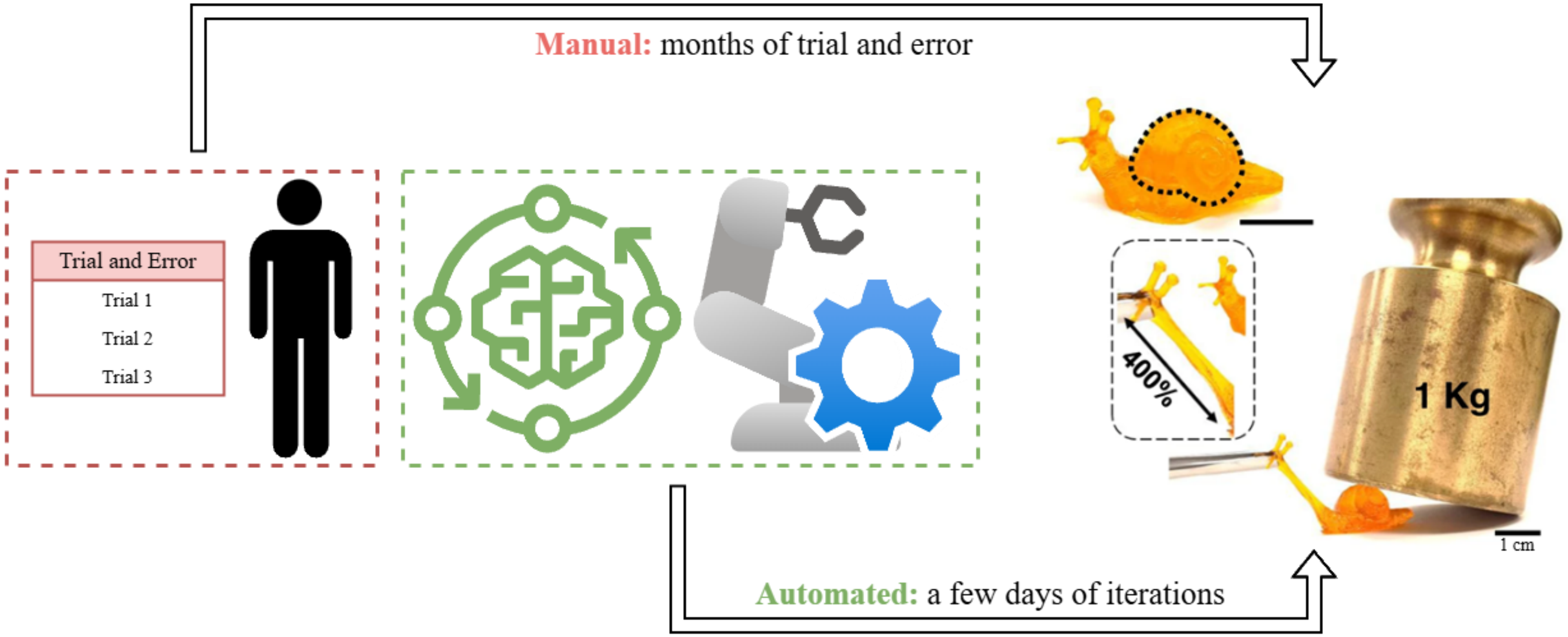
Batch update



Incremental update (Bayesian)

Objective

- Leverage SDLs for discovery of photopolymers for digital light processing (DLP) 3D printing
- Find relationships between photopolymer components to efficiently discover ideal compositions for specific tasks



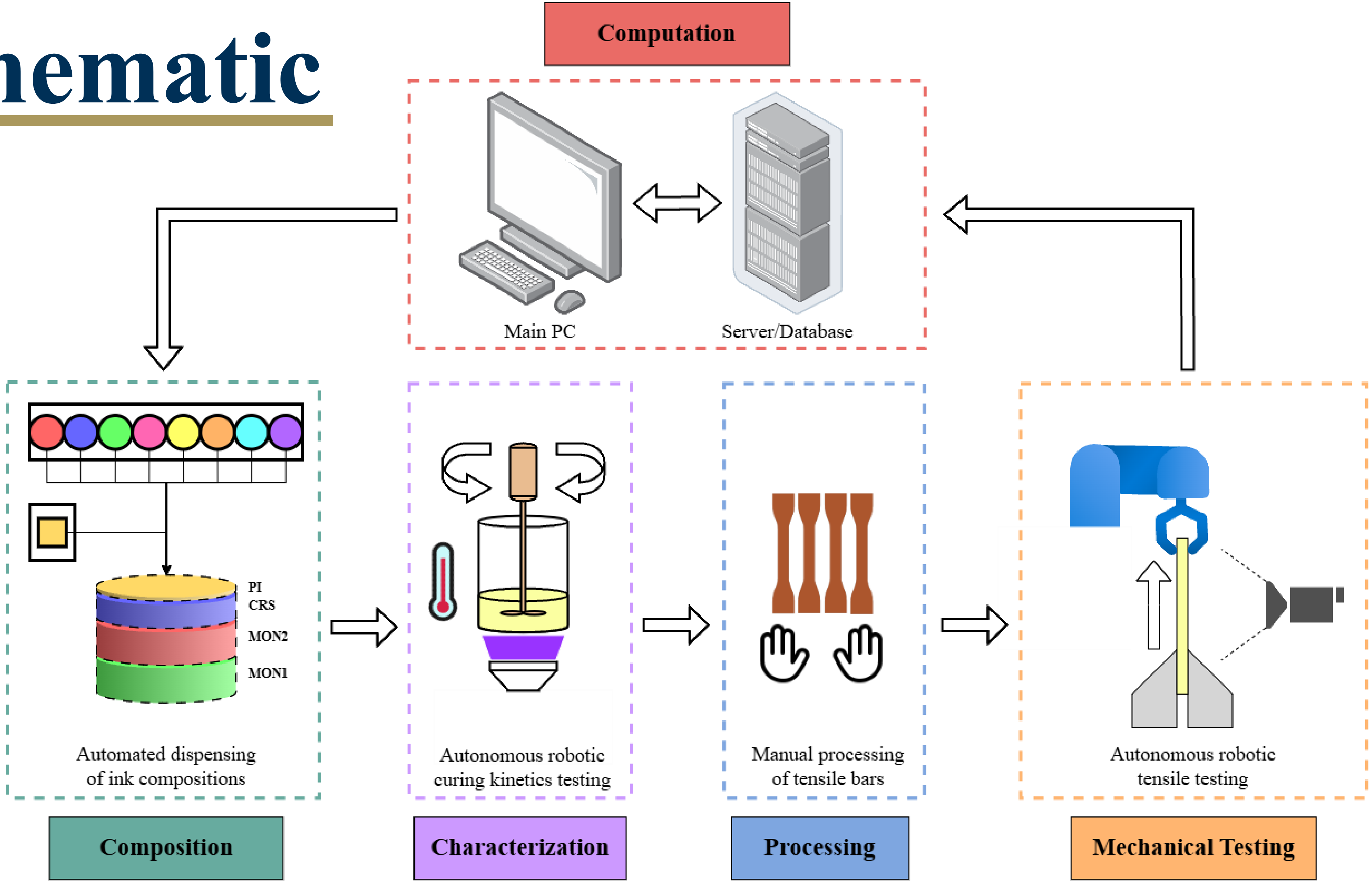
Yue, L., Macrae Montgomery, S., Sun, X. et al. Single-vat single-cure grayscale digital light processing 3D printing of materials with large property difference and high stretchability. Nat Commun 14, 1251 (2023). https://doi.org/10.1038/s41467-023-36909-y

Summary

- Self-driving labs have potential to more efficiently reach research goals
- Three parts of SDL: processing, characterization, decision-making
- Discover novel photopolymers for DLP 3D printing using an SDL
- Efficiently find ideal photopolymers for specific applications

CH.2 Photopolymer SDL System Design

Schematic



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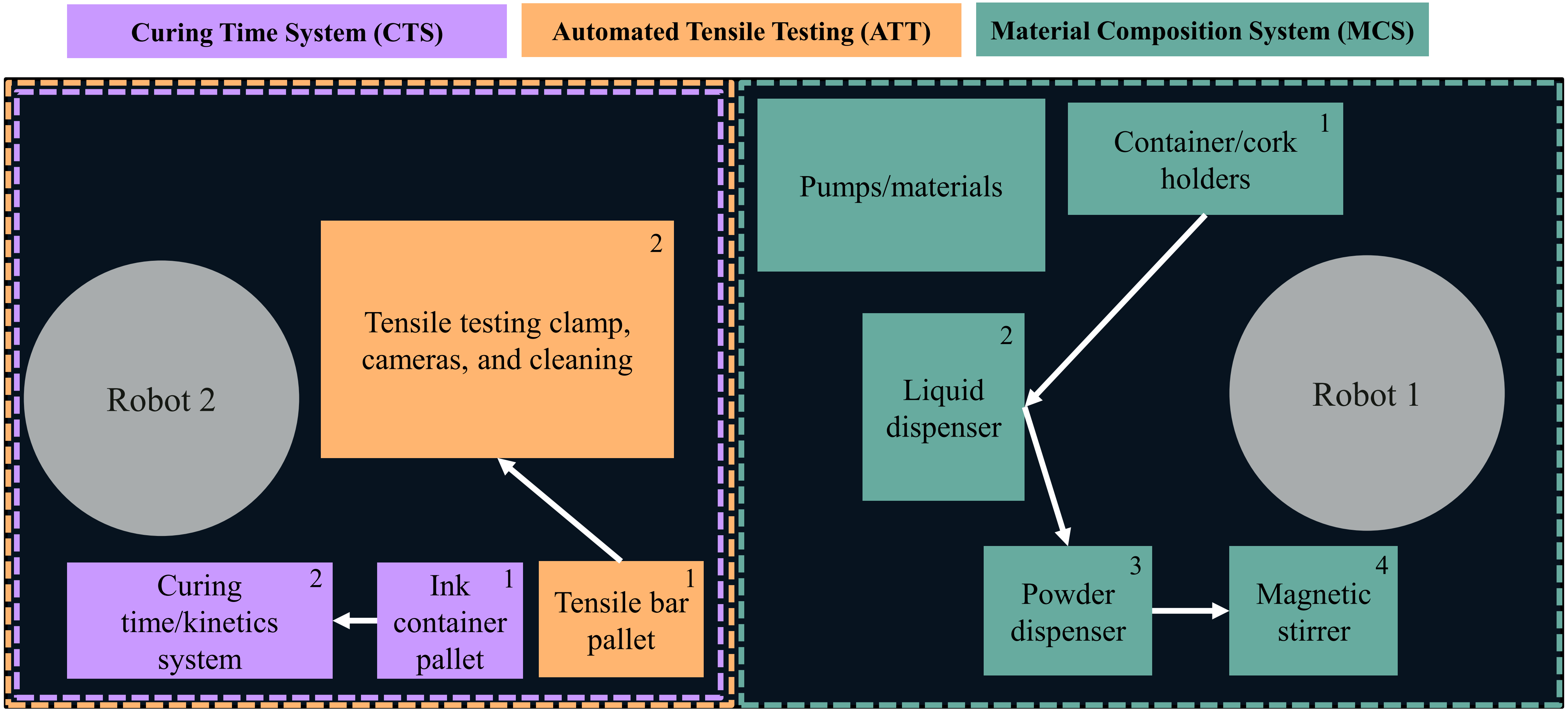
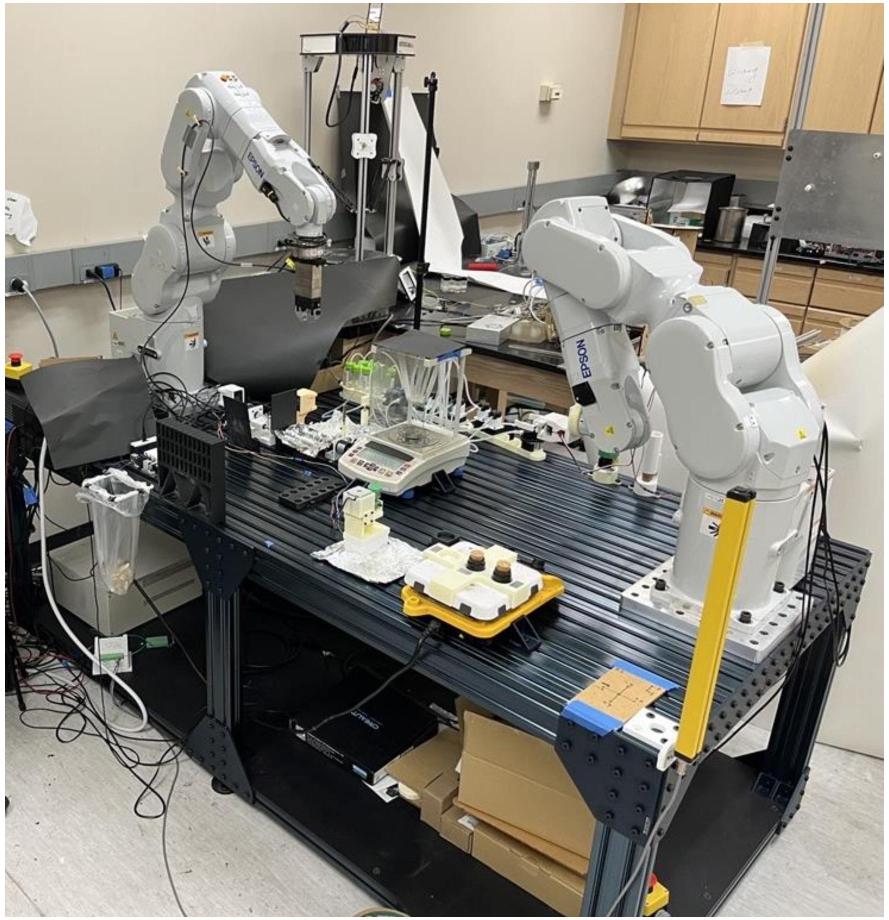
Physical Layout



SDL Table

Physical Layout



Processing

Material Composition System (MCS)

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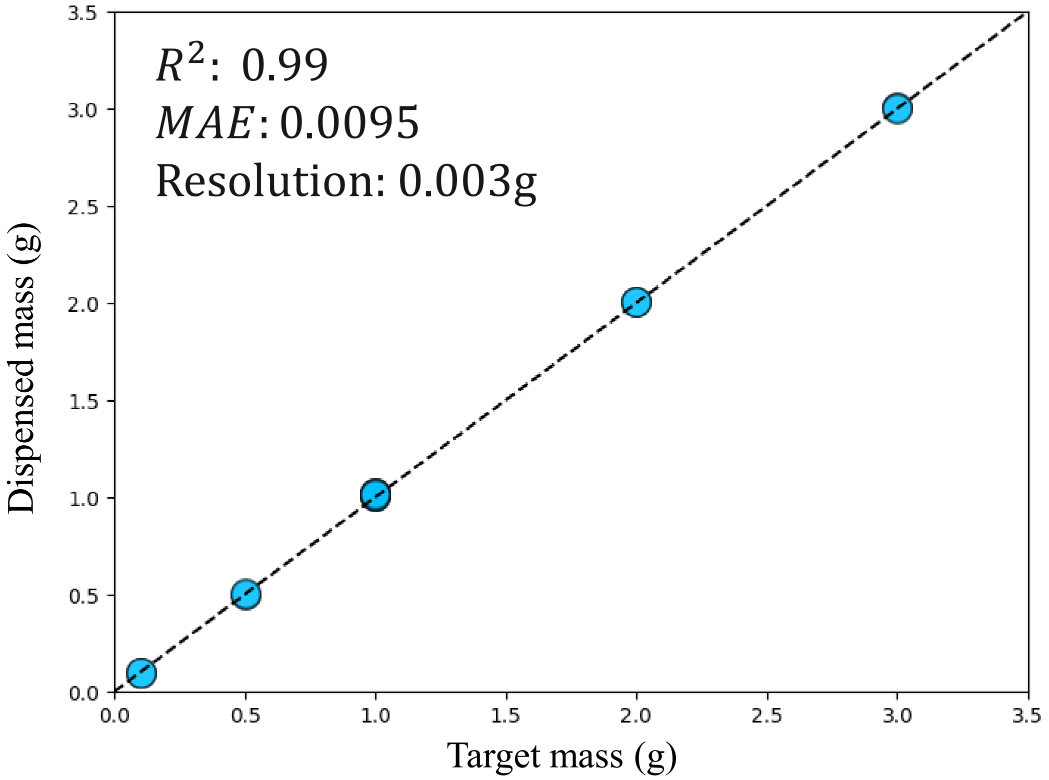
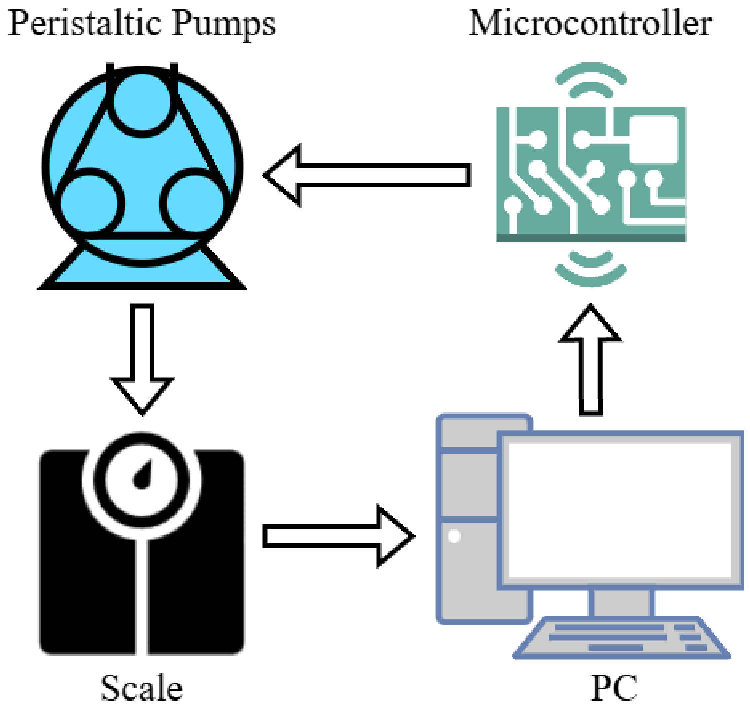
Liquid Dispensing

- Closed loop PID control circuit for monomer/crosslinker dispensing



Dispensing residual plot



Closed loop dispensing

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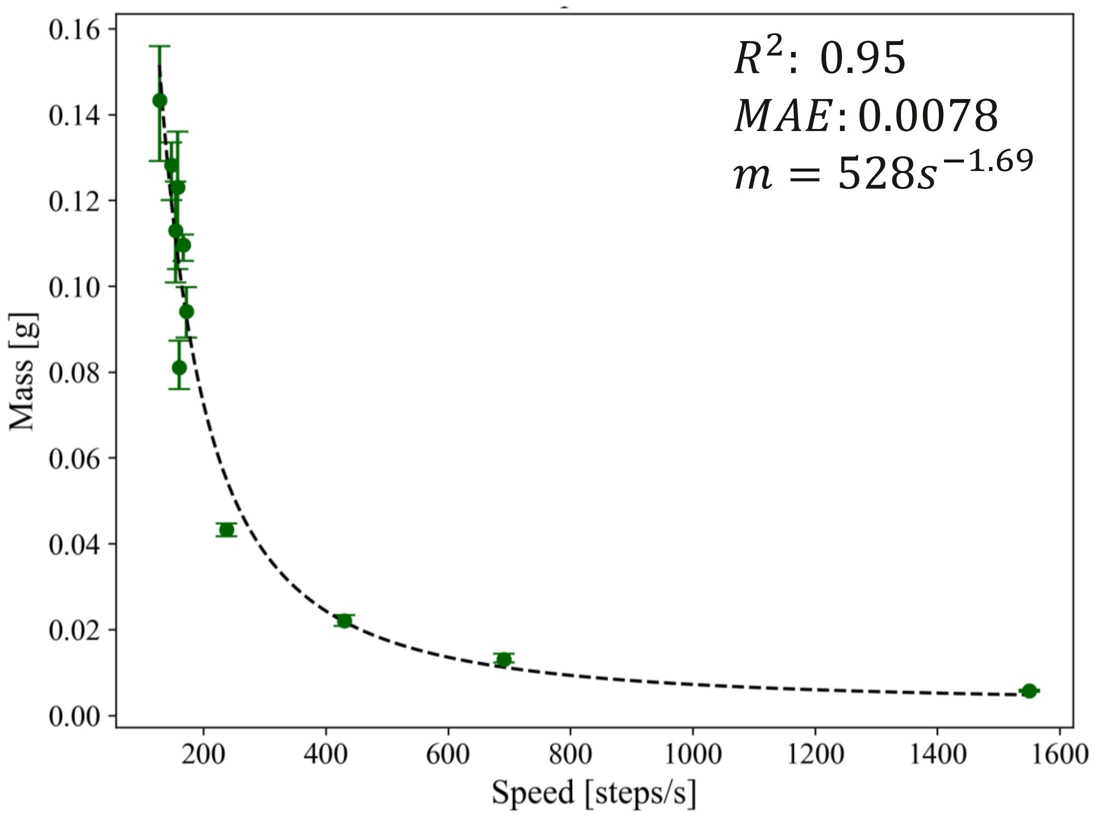
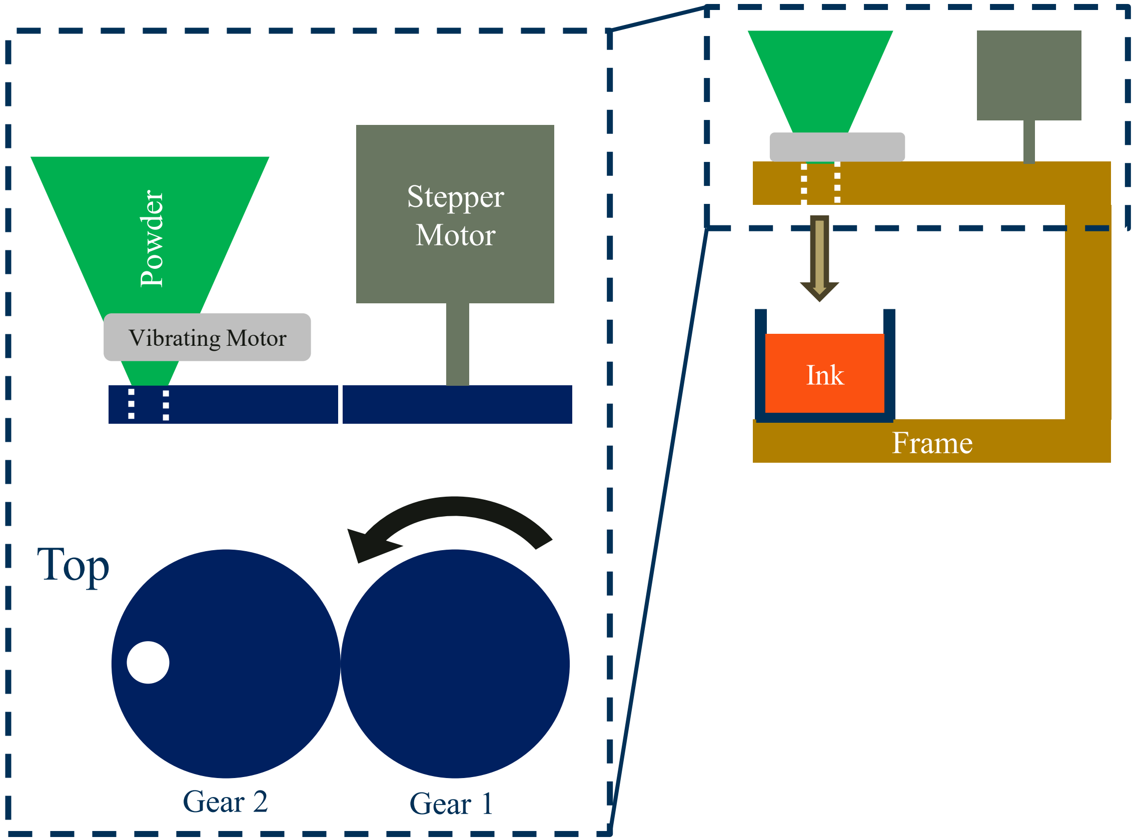
Powder Dispensing

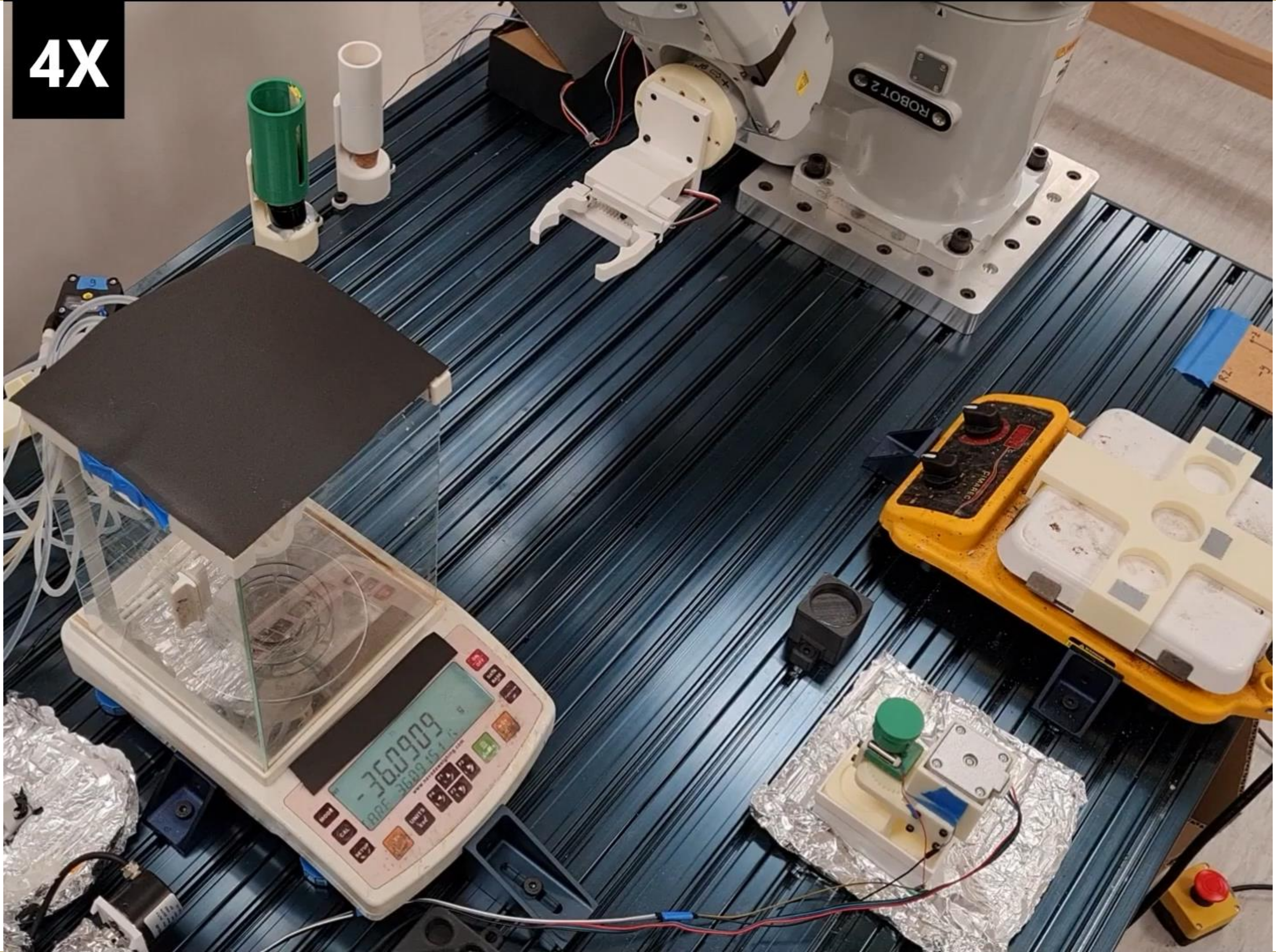
- Powder dispensing for photoinitiator
- Speed determines amount dispensed



Dispensed mass curve fit



Depiction of powder dispenser


4X
ROBOT 2

Characterization

Curing Time/Kinetics System (CTS)

Curing Time System (CTS)

- Measures curing kinetics of inks
- Determines printability for DLP
- Utilizes robotic arm with force sensor

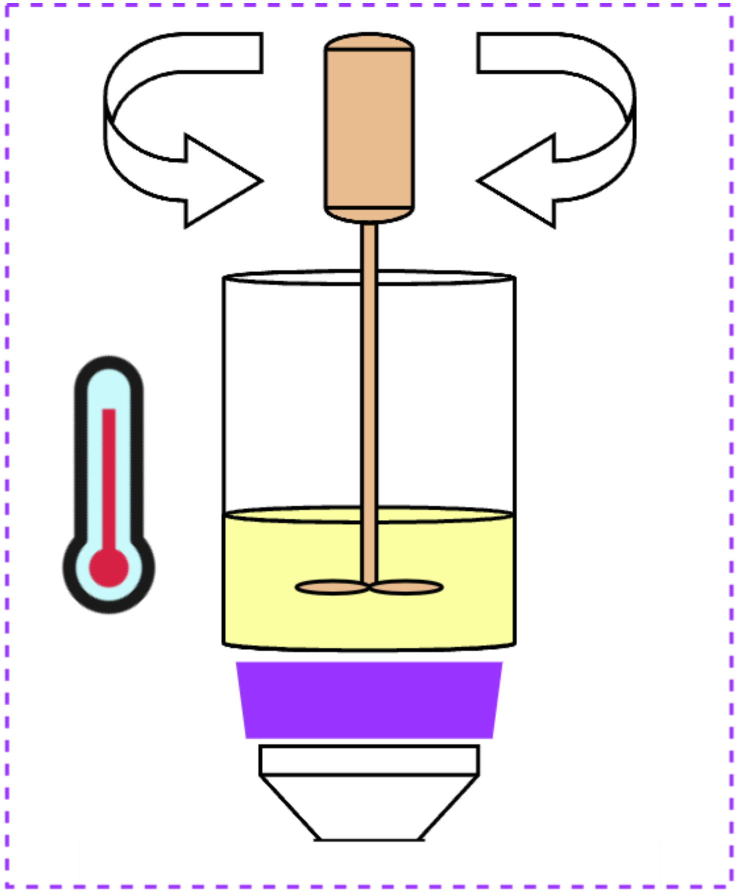
Input:
inks in glass containers

→

Curing kinetics system

→

Output:
curing time
temperature
realizability



Depiction of system

Assumptions

- Polymerization reaction is exothermic
- Temperature increases as bonds are formed during reaction
- Release of heat does not guarantee crosslinked network
- Ink will harden if network is formed

Conservation of energy: $\varrho C_p \frac{\partial T}{\partial t} = \kappa \nabla^2 T + \frac{d[\mathrm{M}]}{dt} \Delta H$

Rate of monomer consumption: $\frac{d[\mathrm{M}]}{dt} = -k_p [\mathrm{R}][\mathrm{M}]$

Measure temperature and hardness of ink to discover basic curing kinetics

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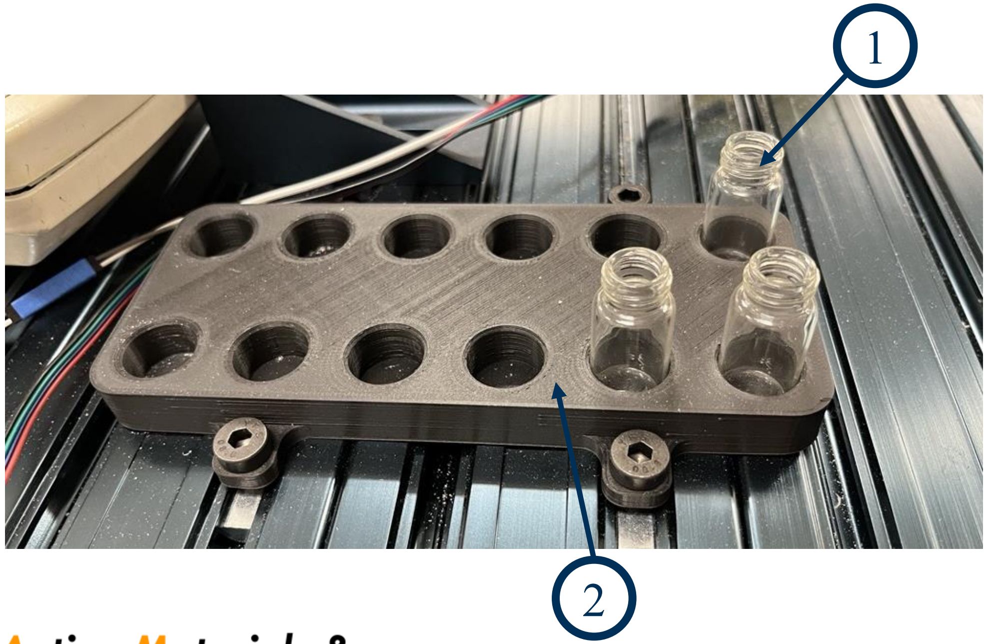
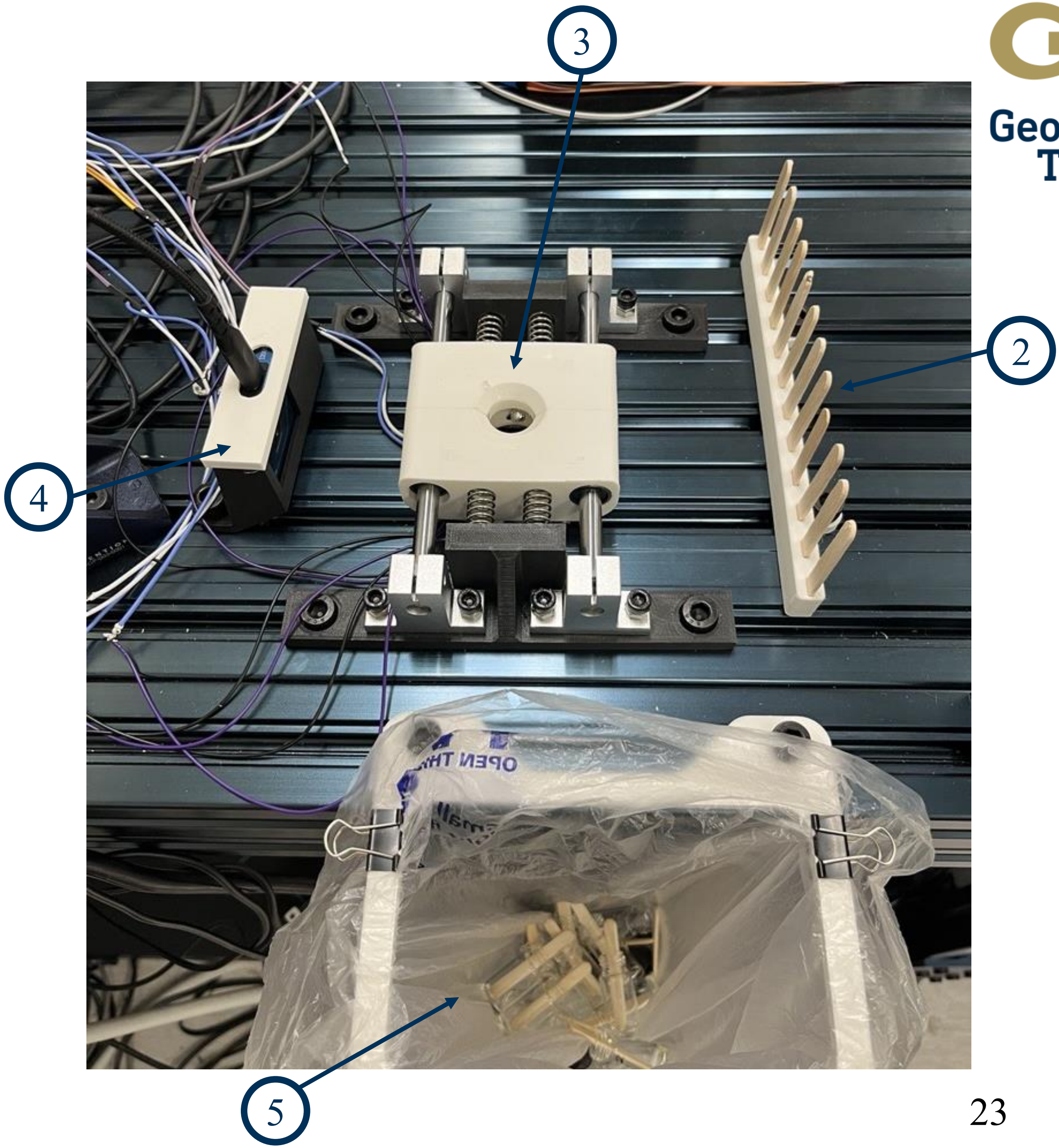
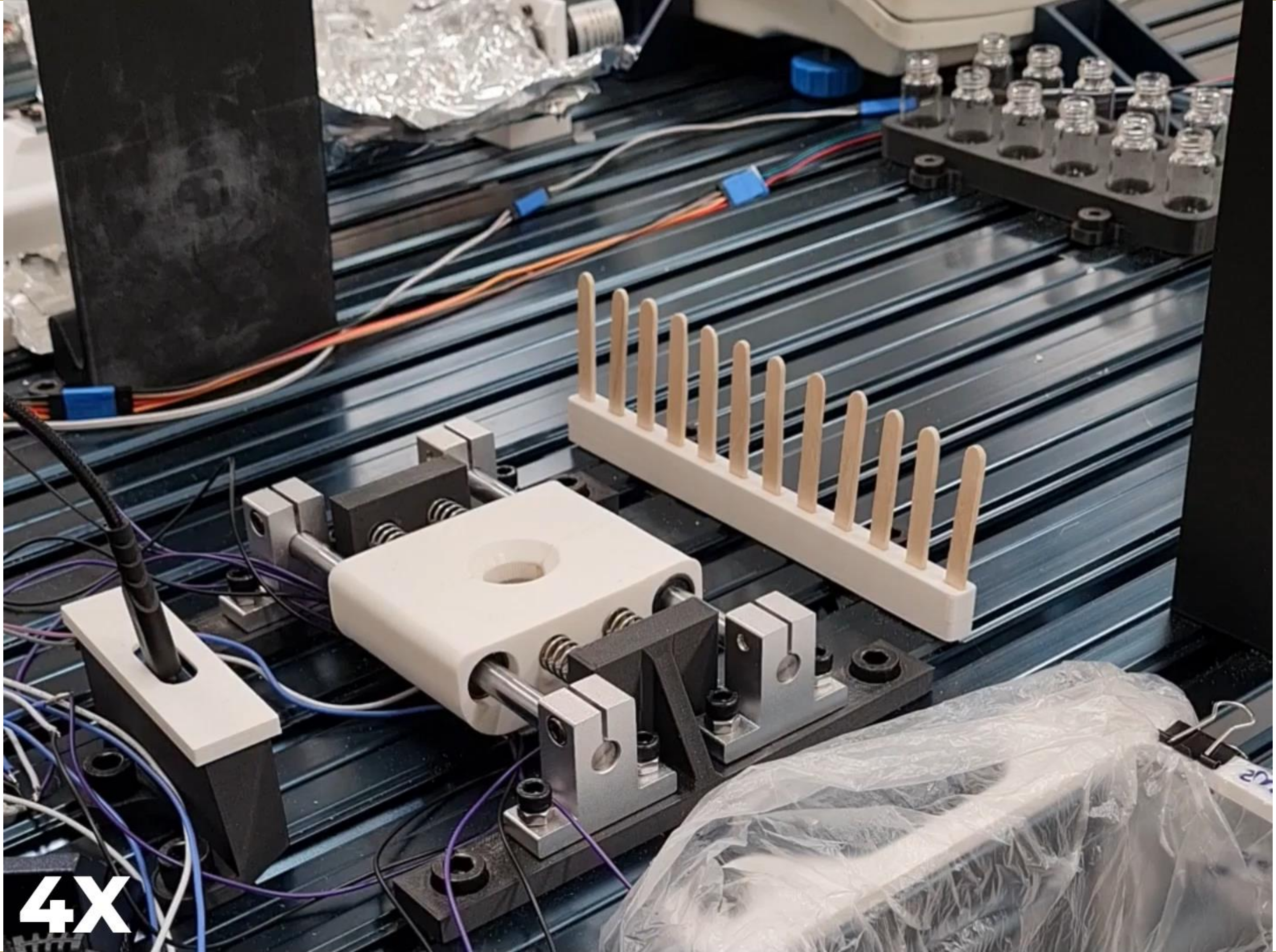
Fang, N., Sun, C., & Zhang, X. (2004). Diffusion-limited photopolymerization in scanning micro-stereolithography. Applied Physics A, 79, 1839-1842.

Hardware

1. Inks are tested in small containers
2. Pallets to hold containers and probes
3. Passive clamp with UV LEDs
4. Thermal camera
5. Disposal for completed tests

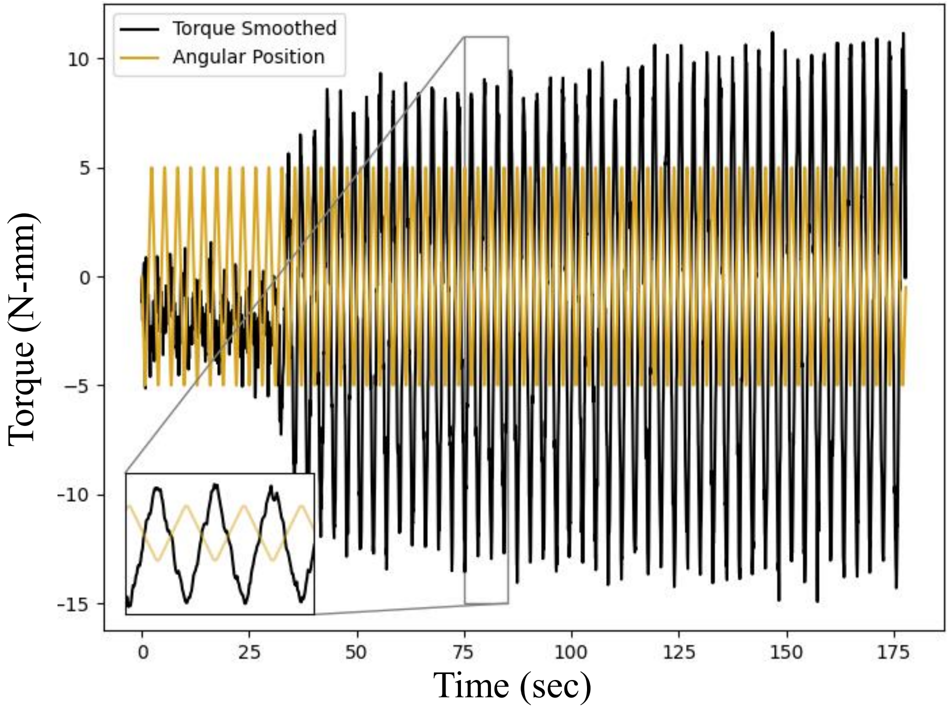




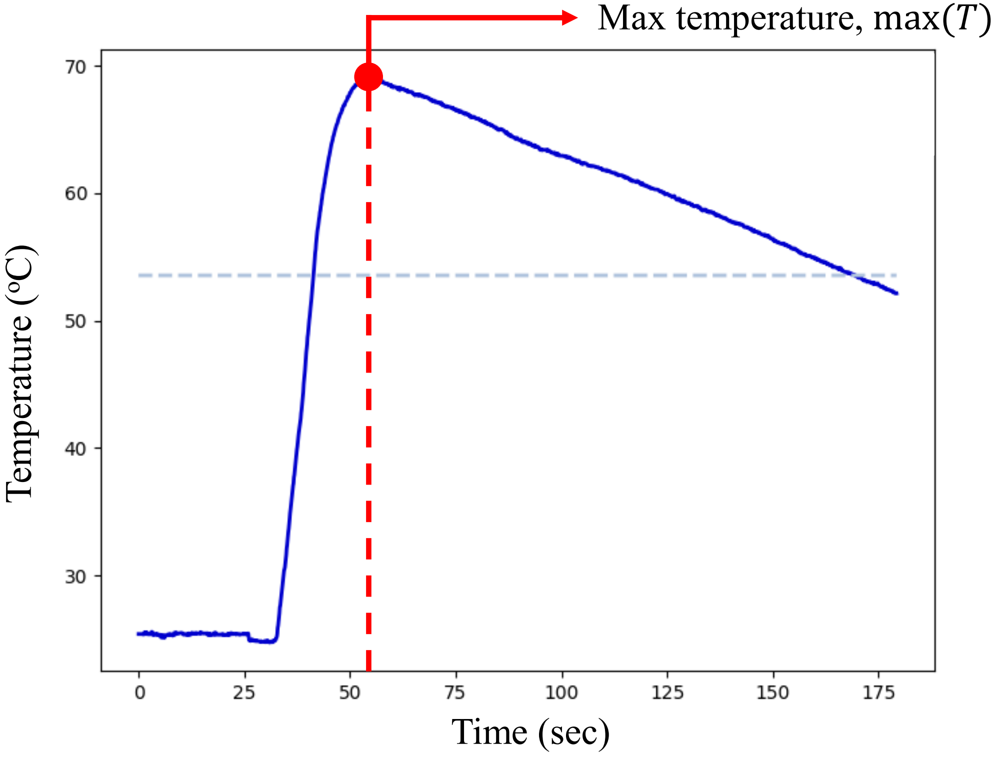

4X

Data Analysis

- Two outputs with time: temperature and torque
- Use torque to find cure time and status
- Use temperature for verification of cure



Raw torque curve



Temperature curve

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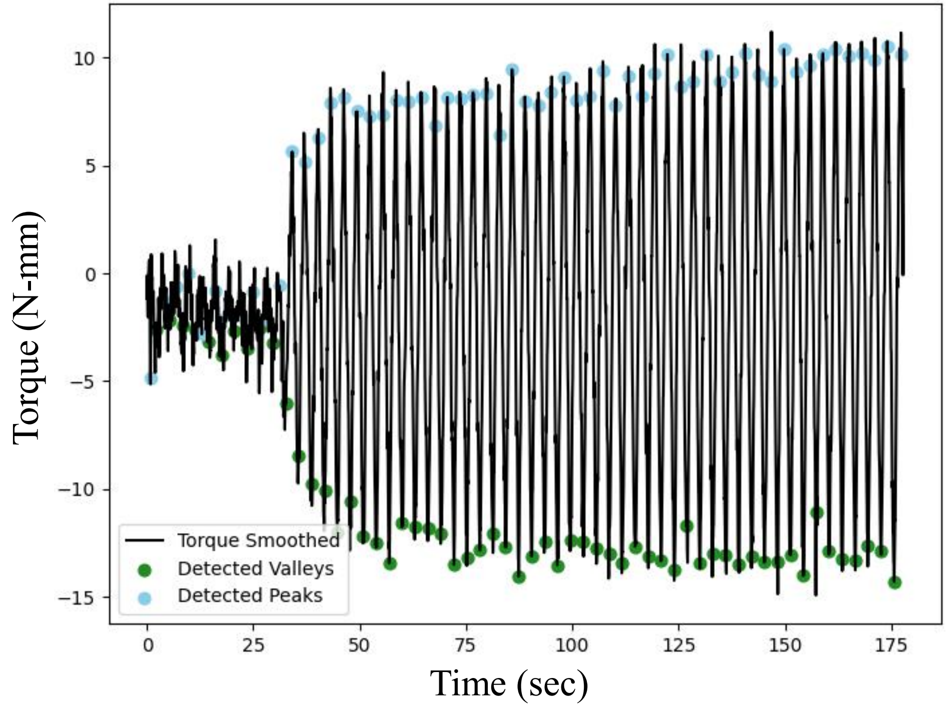
Data Analysis

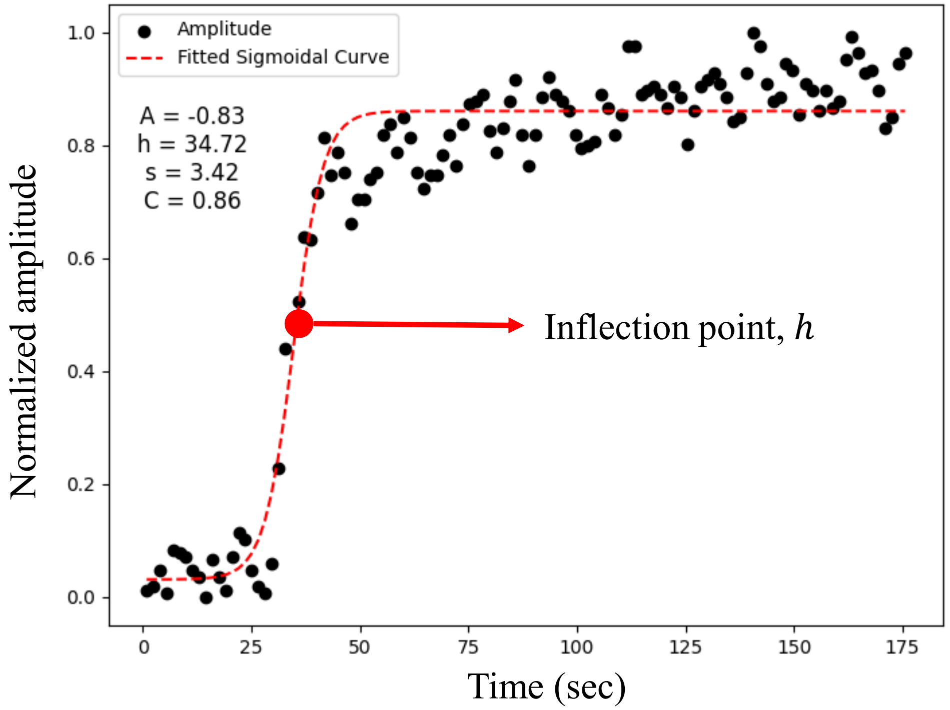
- Find peaks and valleys related to angular position
- Calculate amplitudes and normalize
- Fit sigmoid curve

Sigmoid fitting equation:

$$\frac{A}{1+\exp\left(\frac{x-h}{s}\right)}+C$$



Raw torque with peaks and valleys



Torque amplitude curve

Data Analysis

Conditions:

Curing time:
- $t_{CTS} = h - 30$

Maximum temperature:
- $\max(T)$

Realizability (true):
- $t_{\max(T)} < 150$
- $s \neq 0$
- A curve fit is possible
- $30 < h < 150$

Example:

Curing time:
- $t_{CTS} = h - 30 = \mathbf{4.72\ seconds}$

Maximum temperature:
- $\max(T) = \mathbf{68.7\ {}^{o}C}$

Realizability (true):
- $t_{\max(T)} = 56.2$ sec → **True**
- $s = 3.42$ → **True**
- A curve fit is possible → **True**
- $h = 34.72$ → **True**

DLP Map

- Estimate DLP printing time using CTS time

Assume degree of cure (DoC) is proportional to *It*

$$\frac{I_{CTS}}{I_{DLP}} = \frac{e^{-\mu h_c}}{e^{-\mu h_p}} = e^{-\mu(h_c - h_p)} \approx e^{-\mu h_c}$$

To reach the same DoC, we have

$$I_{CTS} t_{CTS} = I_{DLP} t_{DLP} \rightarrow \frac{t_{DLP}}{t_{CTS}} = \frac{I_{CTS}}{I_{DLP}}$$

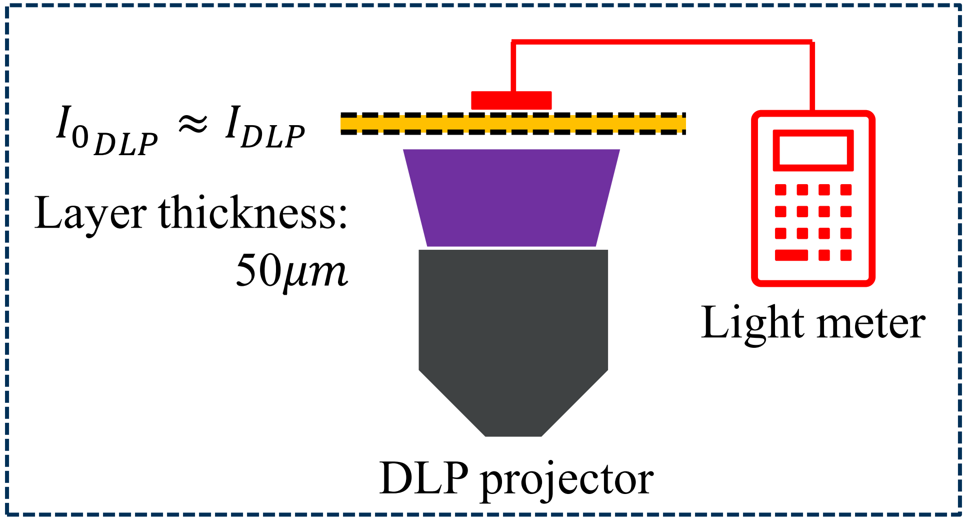
As a rough estimate

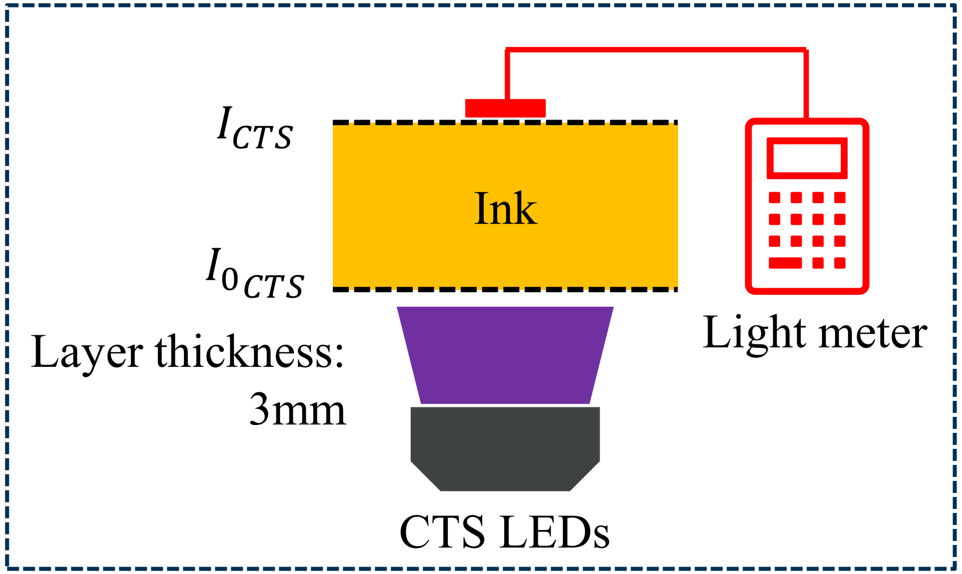
$$t_{DLP} = t_{CTS} \frac{I_{CTS}}{I_{DLP}} \rightarrow \boldsymbol{t_{DLP} \approx \frac{t_{CTS}}{10}}$$

DLP Map

- Experimental determination of values
- Incident light same as initial light for DLP

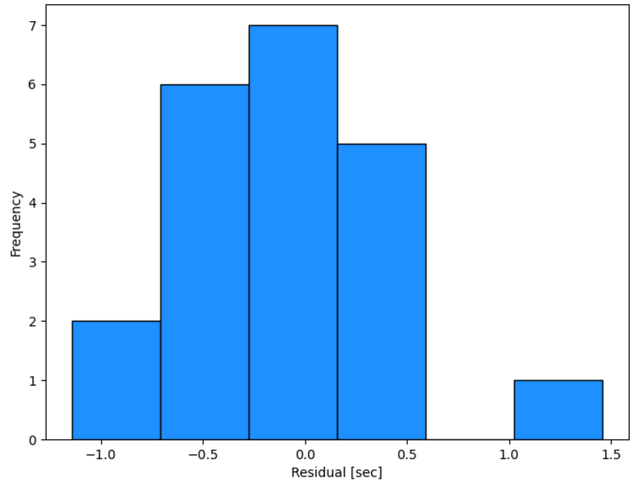
$$t_{DLP} = t_{CTS}\frac{I_{CTS}}{I_{DLP}} = t_{CTS}\frac{1.03\,\frac{\mathrm{W}}{\mathrm{cm}^2}}{10.11\,\frac{\mathrm{W}}{\mathrm{cm}^2}} \rightarrow \boldsymbol{t_{DLP} \approx \frac{t_{CTS}}{10}}$$



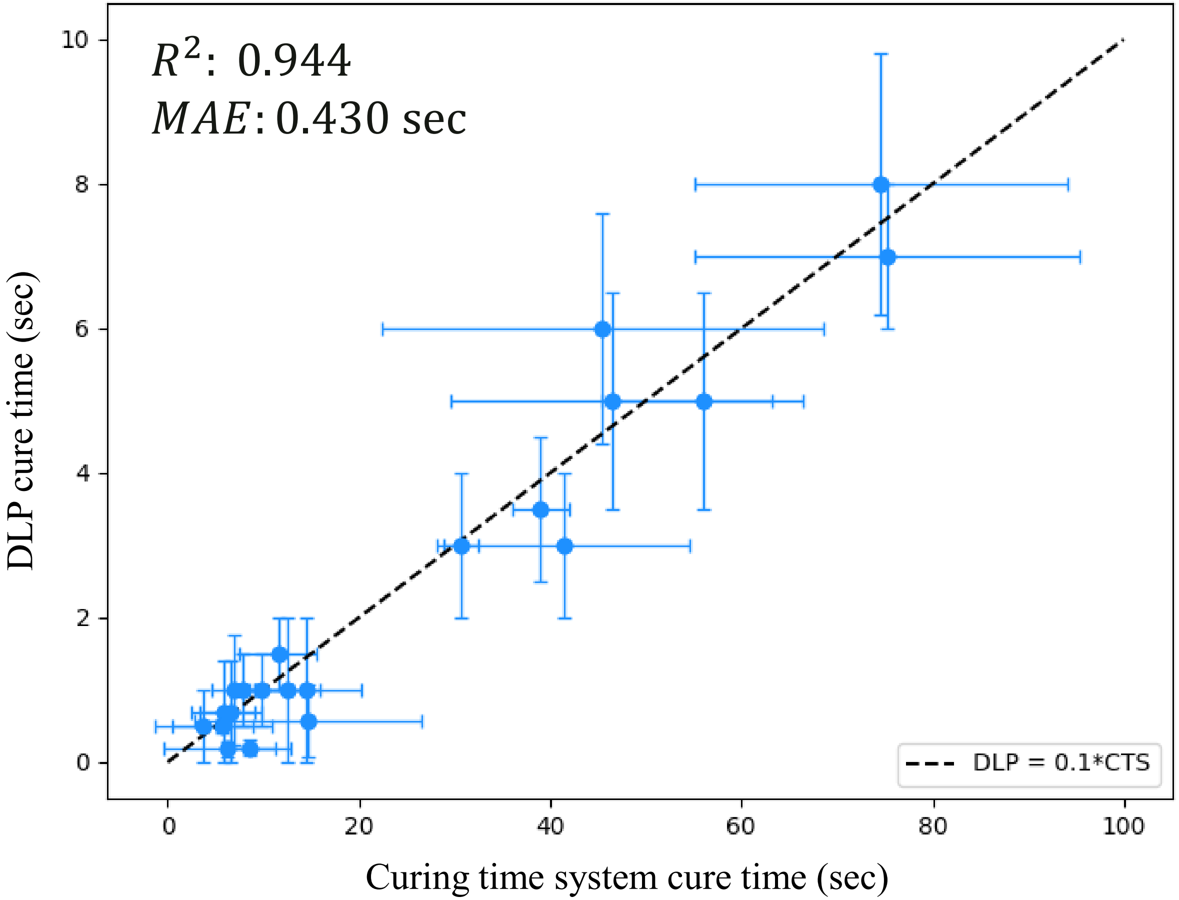


DLP Map

- Experimental verification
- Uncertainty increases with cure time



Residual Distribution



t_{CTS} to t_{DLP} Comparison

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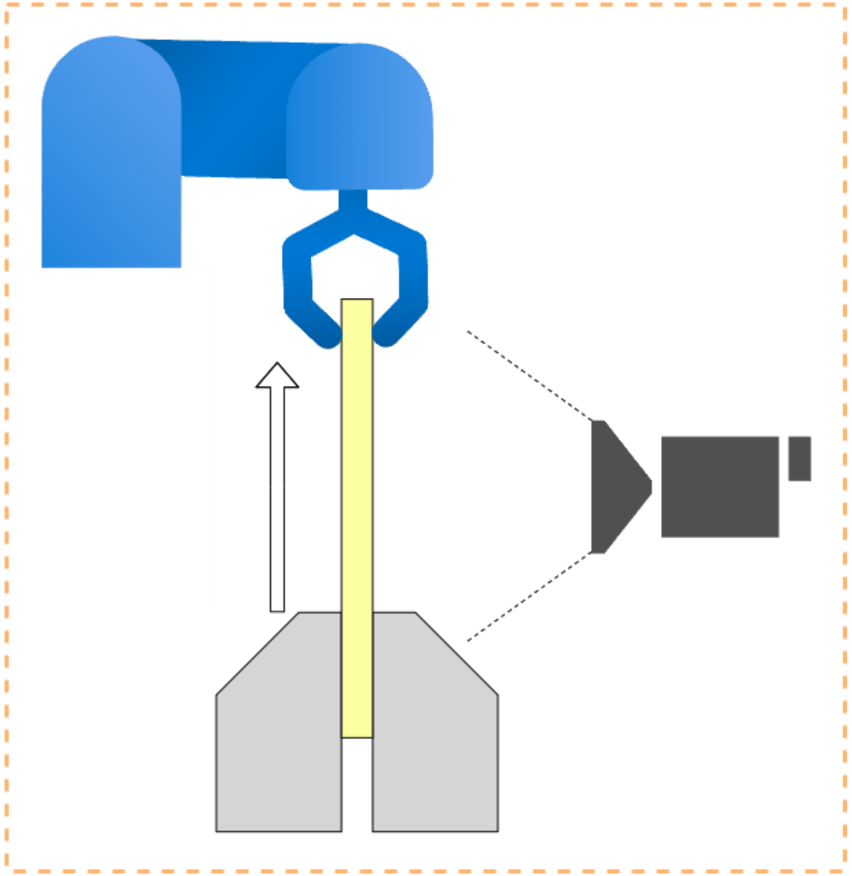
Characterization

Automated Tensile Testing (ATT)

Automated Tensile Testing (ATT)

- Uses robotic arm with force sensor
- Robot location is tracked
- Load capacity of 200N

Input: tensile bar samples → **Automated Tensile Testing System** → **Output:** modulus ultimate tensile strength (UTS) elongation



Depiction of system

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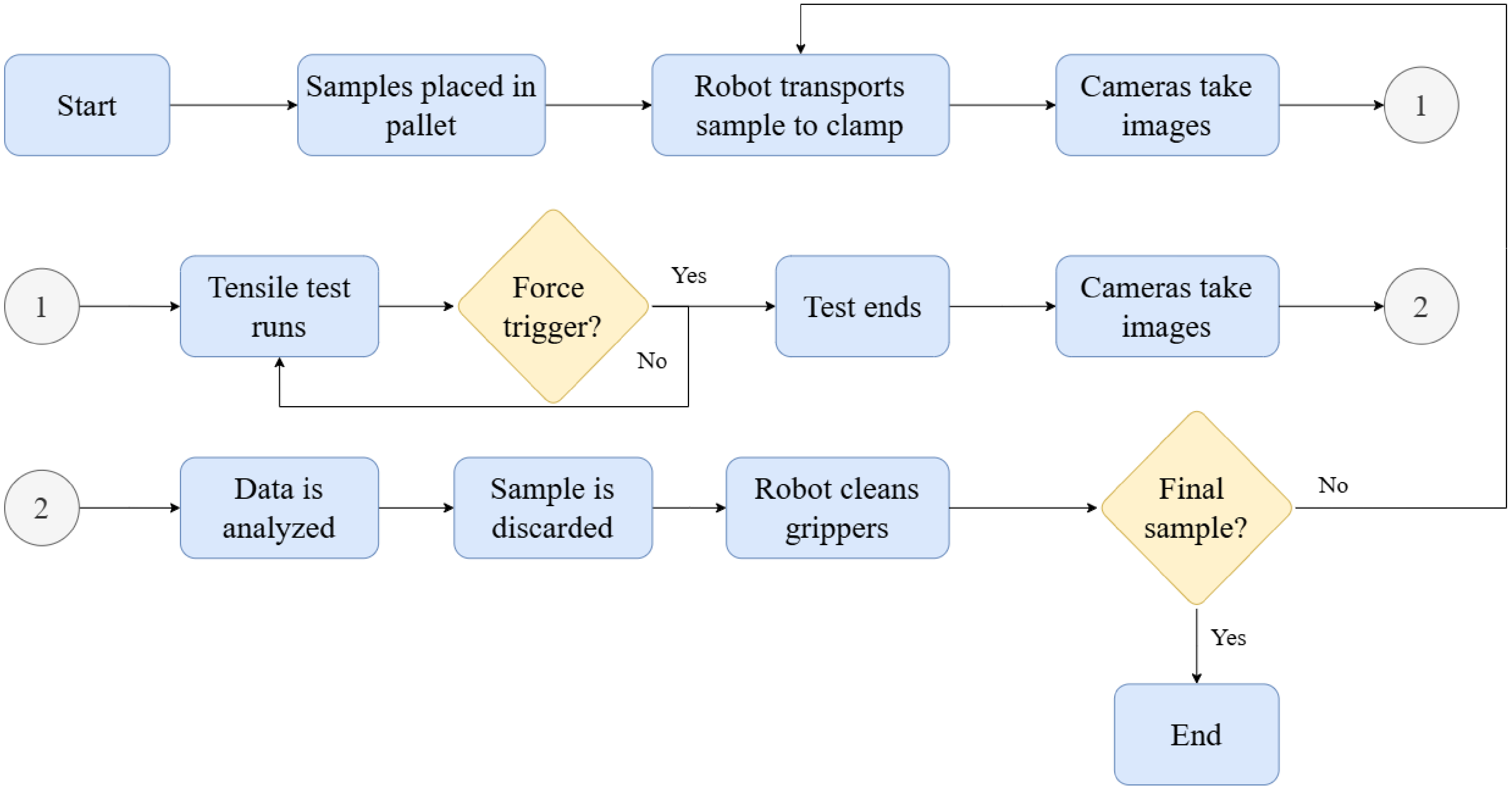
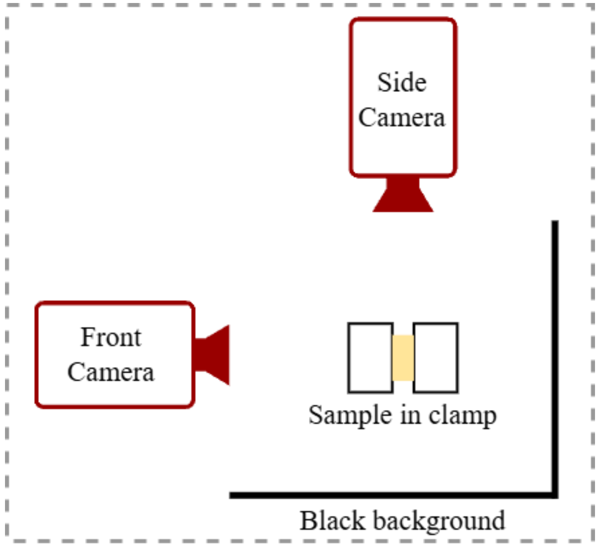
Tensile Testing Workflow




8X


Dimension Detection

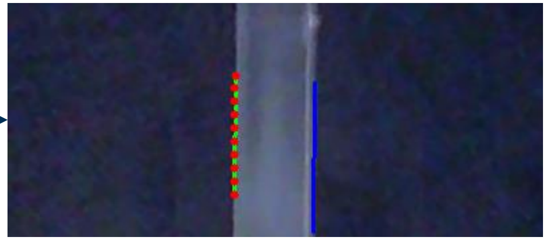
- Canny edge detection algorithm
- Measures average width across several points



Top view of physical setup

Raw image

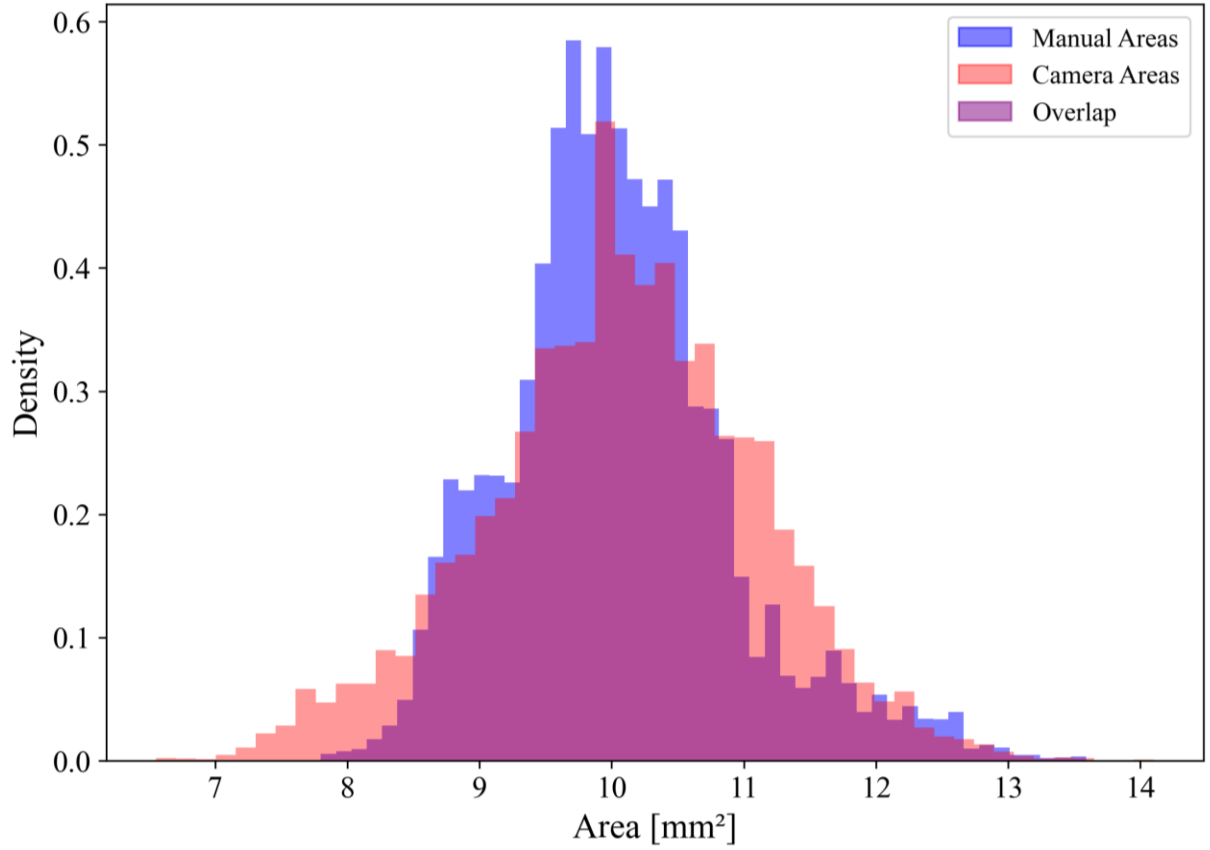
Canny edges



Outermost edges with points for distance

Dimension Detection

- Verification by examining dimension distributions
- Manual → measured with calipers



Cross-sectional area distributions

Metrics

Manual:
Mean = 10.045
STD = 0.851
CV = STD/Mean = 8.472%
Skewness = 0.647

Cameras:
Mean = 10.075
STD = 1.034
CV = 10.263%
Skewness = -0.111

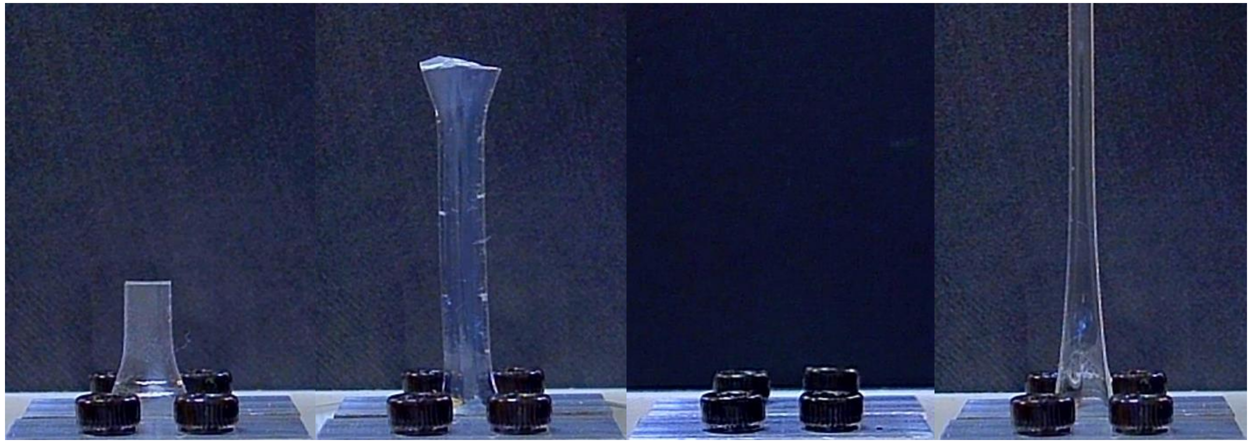
Wasserstein Distance:

$W_1(M, C) = \frac{1}{n}\sum_{i=1}^{n} |x_i^M - x_i^C|$

$= 0.193 \text{ mm}^2 = 1.93\%$

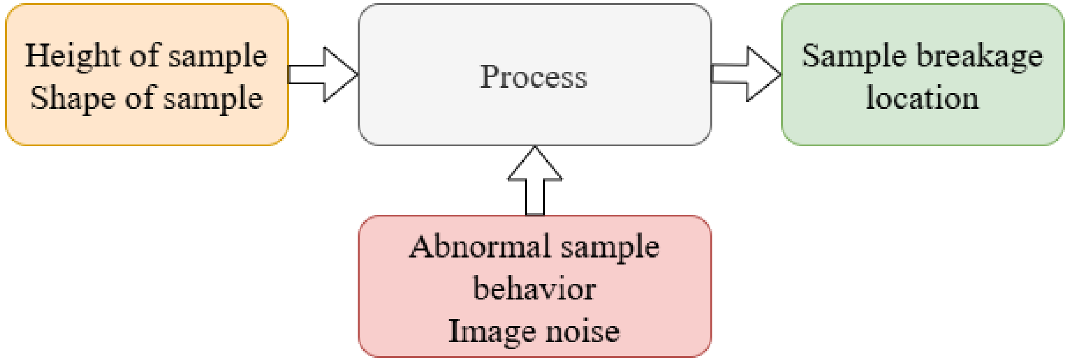
Sample Breakage Model

- Determine state of sample after test is complete
- Dataset contains post-test sample images
- Four classes: gauge region, high break, low break sample stretched
- Each camera has separate dataset



Gauge break (class 0) | High break (class 1) | Low break (class 2) | Stretched (class 3)

Examples from each class



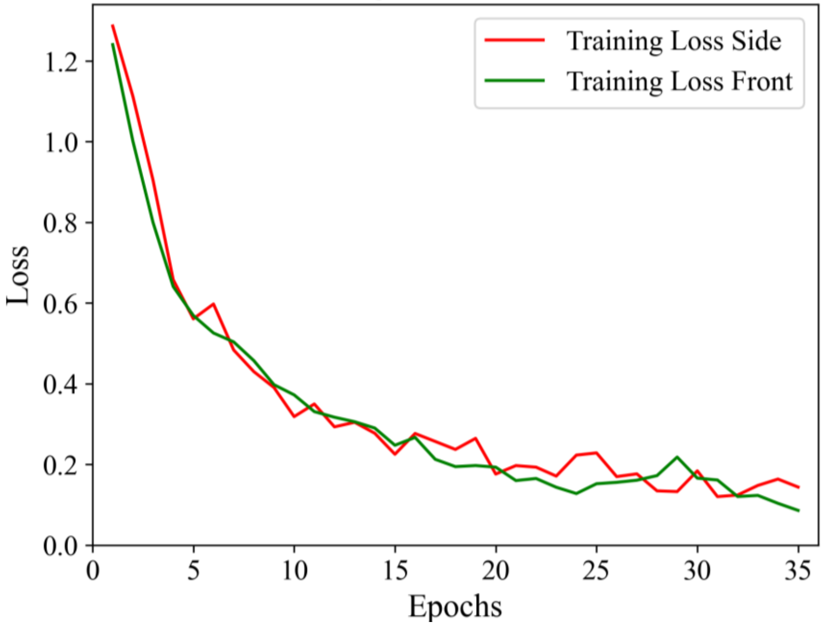
Process model

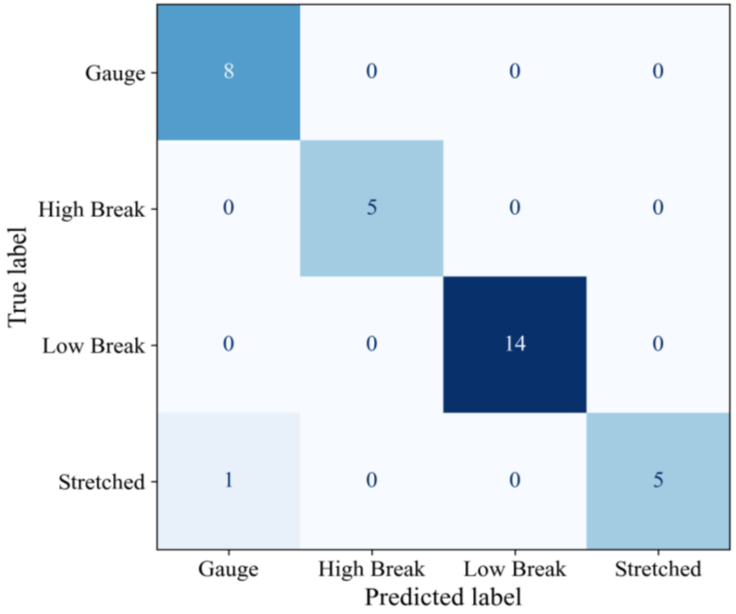
Sample Breakage Model

- Data gathered from real tensile tests
- Total images: 660, train test split: 90/10
- Side model can struggle with borderline samples

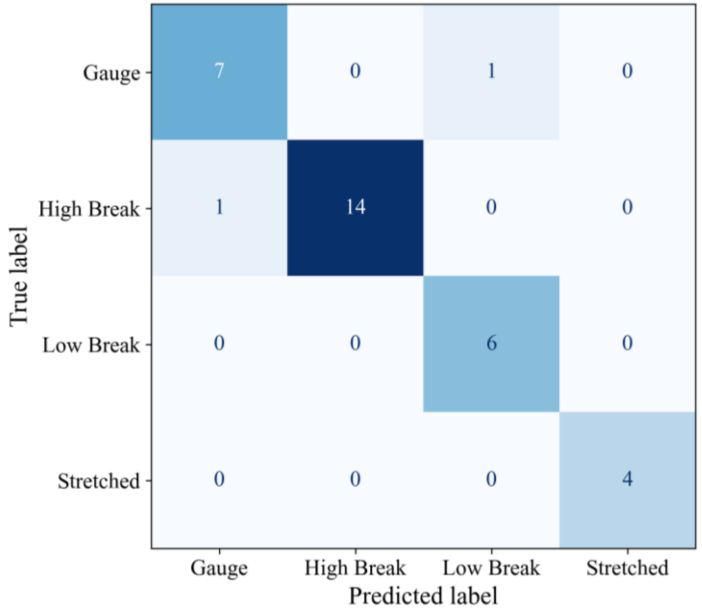
Dataset

Class	%
0	29.2%
1	28.0%
2	30.1%
3	12.7%





Front model



Side model

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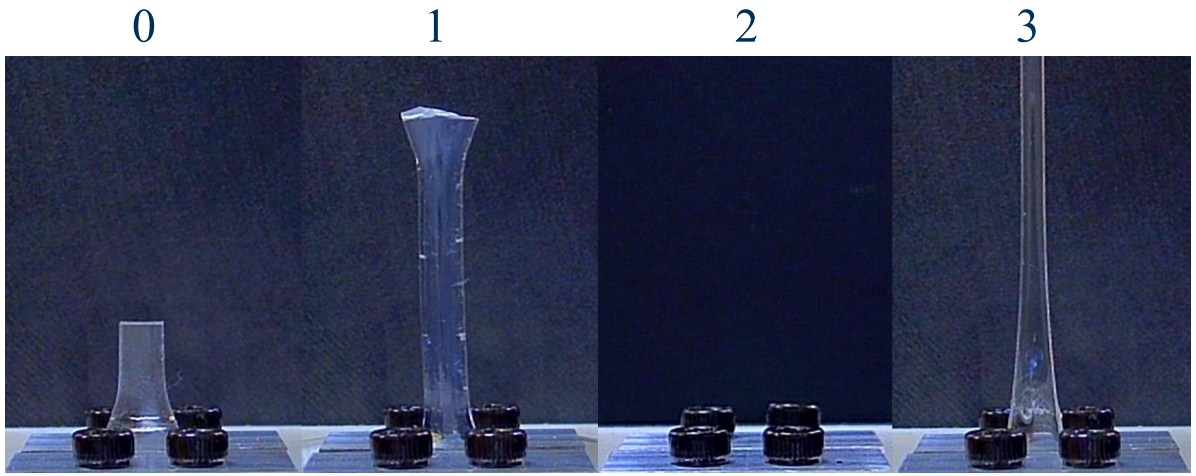
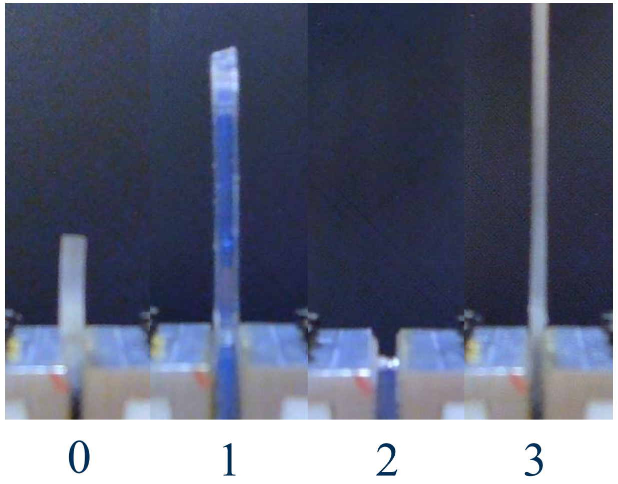
Sample Breakage Model

- Each model outputs probabilities of classes
- Ensemble method: predictions compared
- Validation of each with clear cases

Front Pred.	Prob.	Side Pred.	Prob.	Final Pred.	Ground Truth
0	84.8%	0	93.9%	**0**	**0**
1	97.5%	1	91.7%	**1**	**1**
2	99.3%	2	95.9%	**2**	**2**
3	94.8%	1	32.8%	**3**	**3**

Predictions and their probabilities for each image





Front and side validation images

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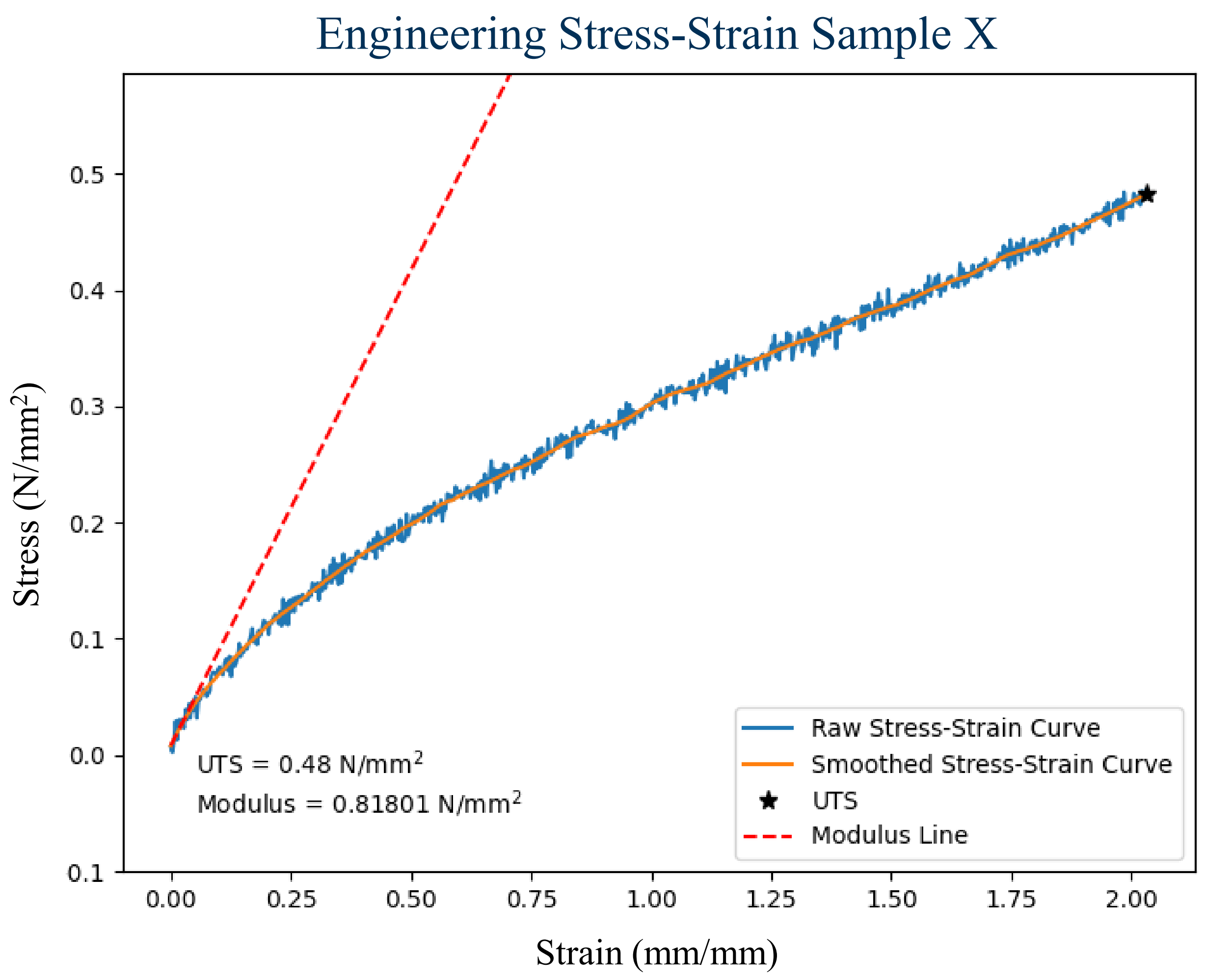
Data Analysis

- Reads robot position and force
- Dimensions found from cameras
- Second derivative of tensile curve to find where elastic region ends

$$\sigma_{Eng} = \frac{F}{A_0}, \varepsilon_{Eng} = \frac{\Delta L}{L_0}$$



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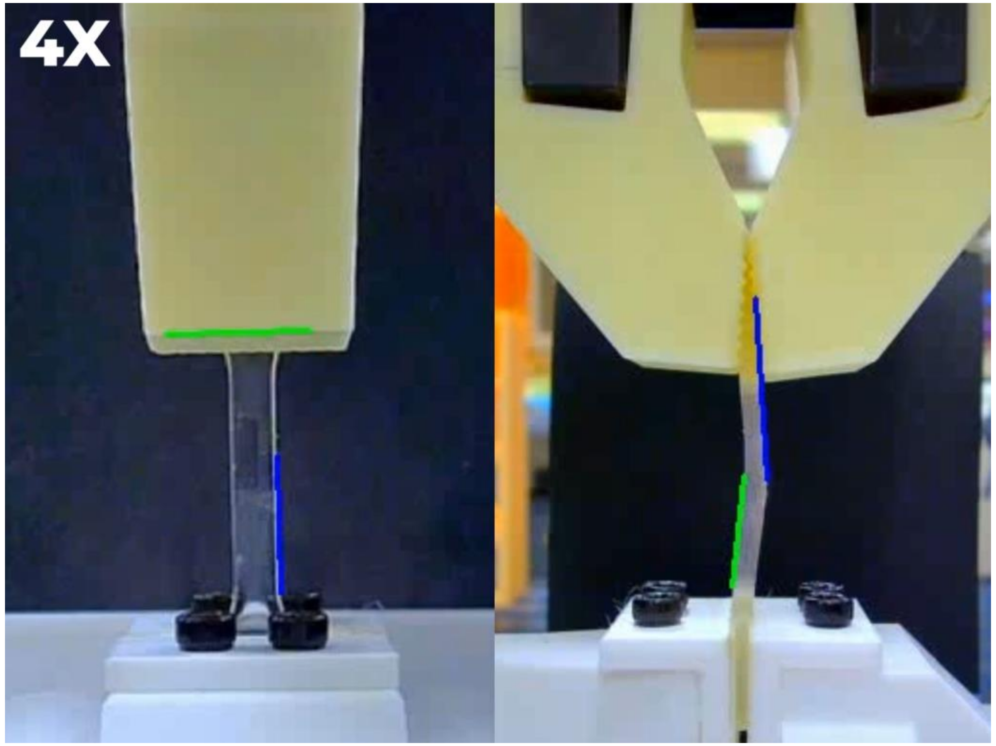
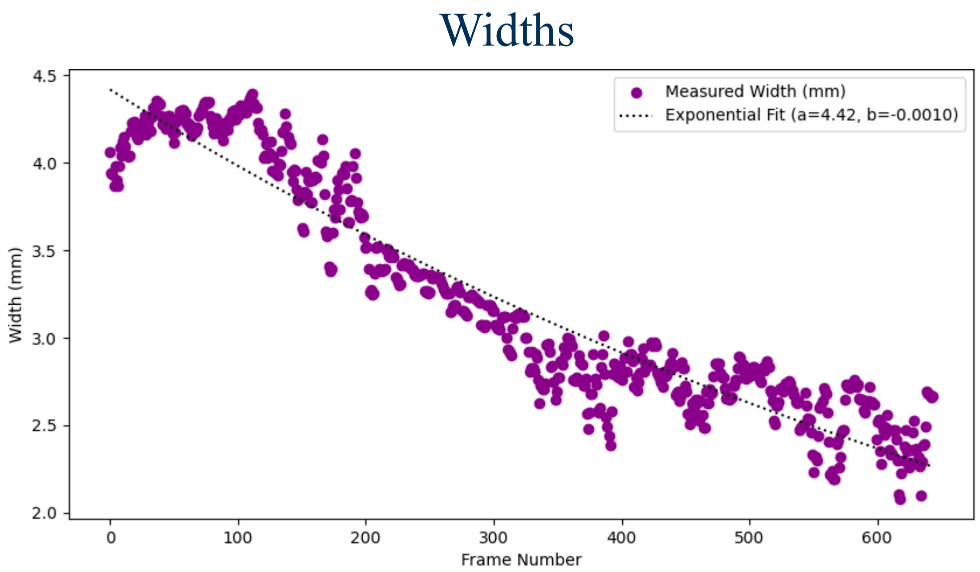
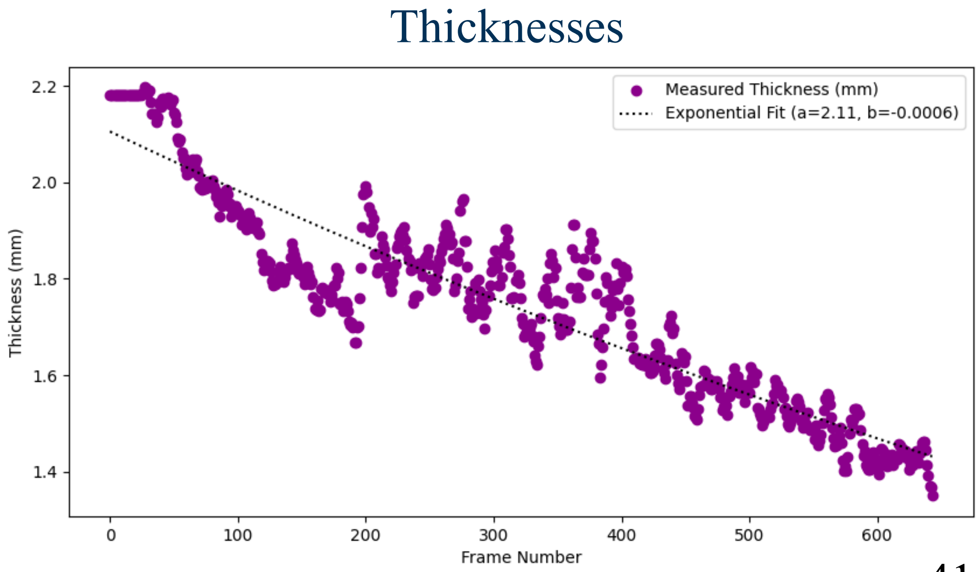
Data Analysis

- True stress and strain can be estimated
- Find average dimension of each frame



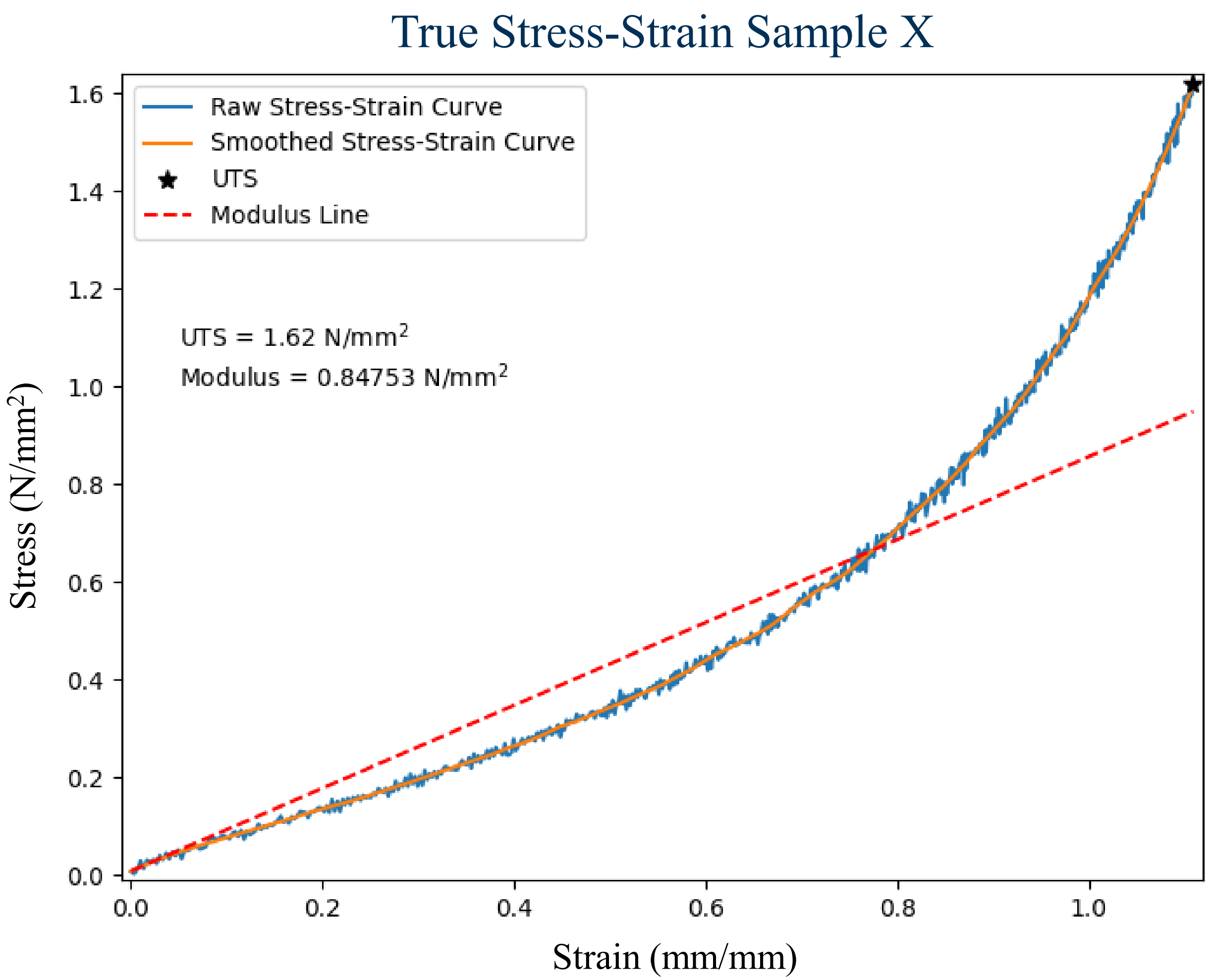




Data Analysis

- Apply exponential fit to the tensile data
- Same data as previous plot

$$\sigma_{True} = \frac{F}{A_i},\ \varepsilon_{True} = \ln\left(\frac{L_i}{L_0}\right)$$



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Summary

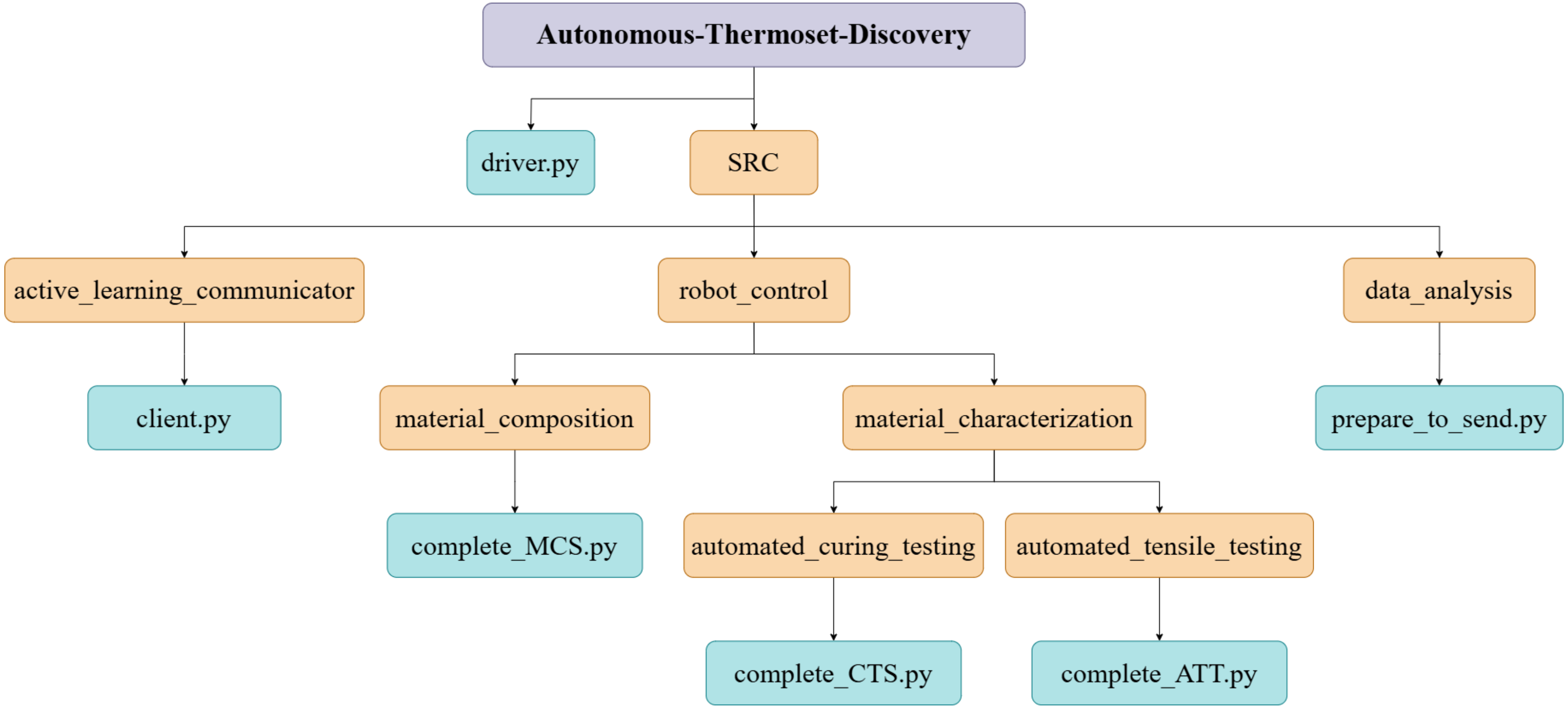
- Autonomous workflows facilitated by robotic arms and various machines
- Material composition system (MCS) to process photopolymer inks
- Curing time/kinetics system (CTS) to find curing time, temperature, and realizability of compositions
- Automated tensile testing (ATT) to find modulus of elasticity, UTS, and elongation of samples

CH.3 Optimized Discovery of Novel Photopolymers

Georgia Tech

Integration

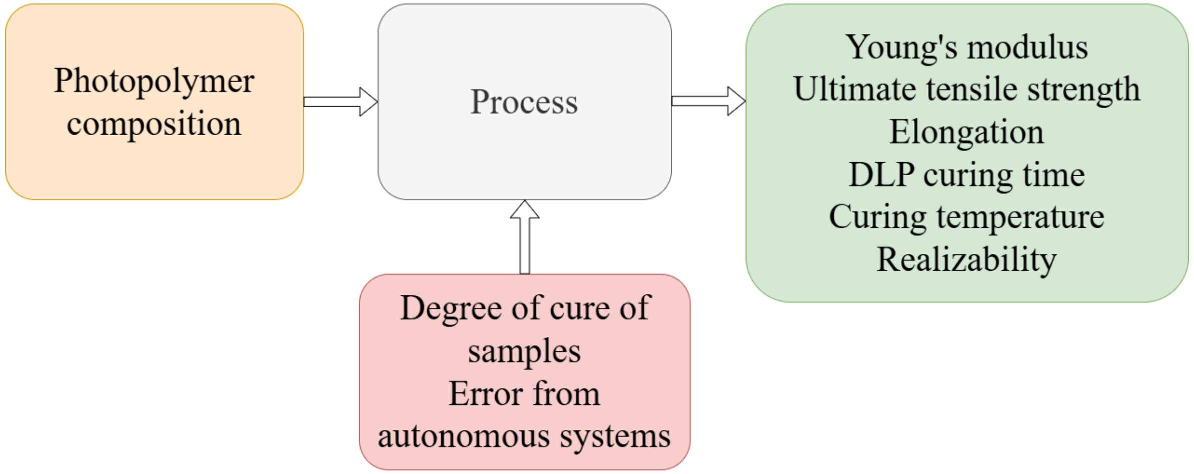
- GitHub repository connects systems
- Server contains database and decision-making algorithm



Repository tree structure

Process Model

- Two goals:
  - Find ideal photopolymers for specific applications
  - Discover new and unique photopolymers



Forward process model

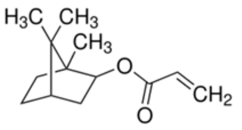
Reverse process model

Design Space

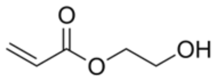
- Nine components chosen for variety
- Each composition has two monomers and one crosslinker
- Compositions chosen at 5 wt% intervals

6840
total possible compositions

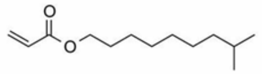
Monomers



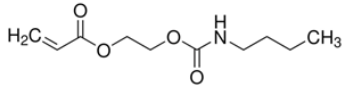
Isobornyl acrylate



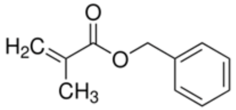
2-Hydroxyethyl acrylate



Iso-decyl acrylate

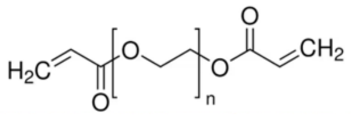


2-[[(Butylamino)carbonyl]oxy]ethyl acrylate

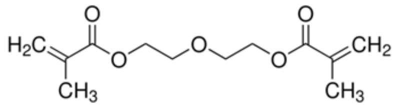


Benzyl methacrylate

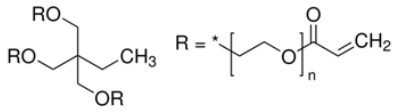
Crosslinkers



Poly(ethylene glycol); Mn 250 & 700



Di(ethylene glycol) dimethacrylate



Trimethylolpropane ethoxylate triacrylate

Initial Results

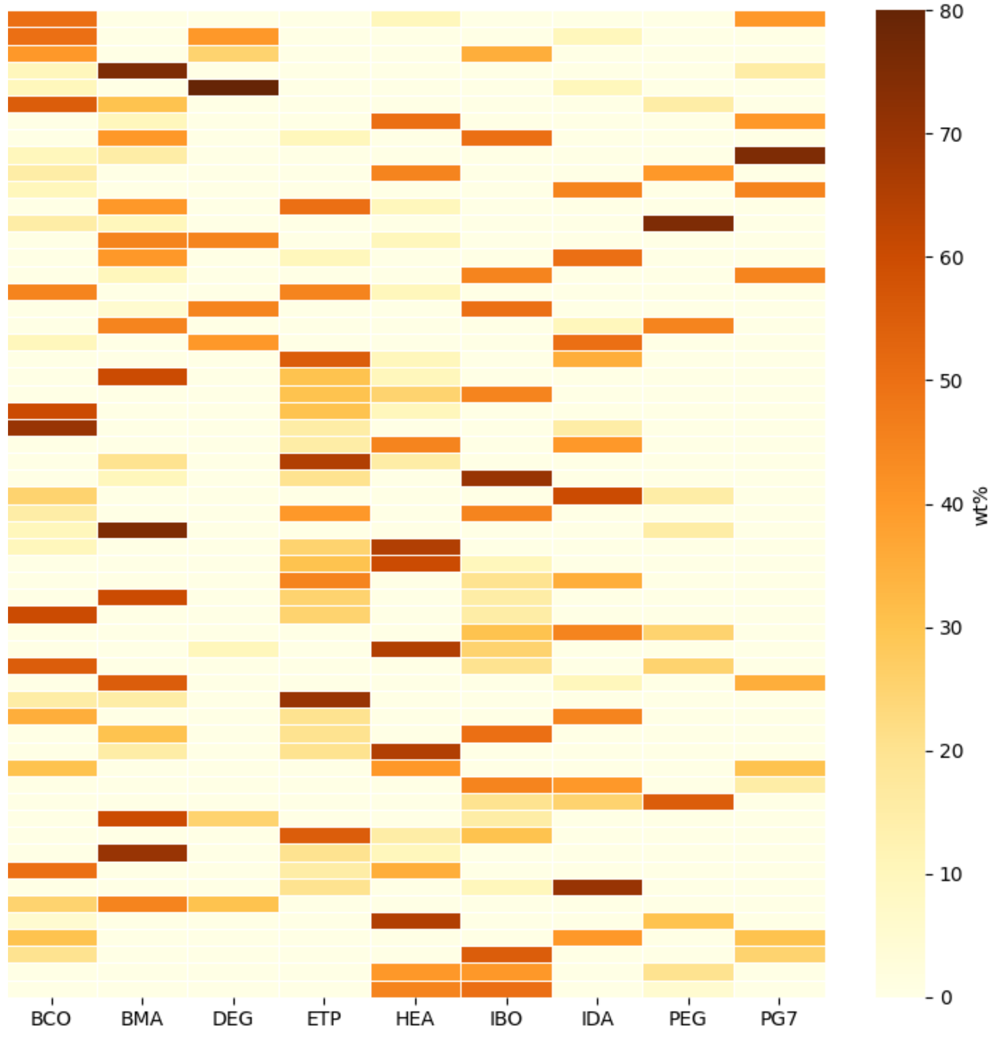
- 56 compositions tested so far, 14 iterations
- One iteration, i, is four compositions
- Total run time ≈ 63 hours

Metric	Value	Material Composition System	Curing Time System	Automated Tensile Testing
Time per sample	t_s	15 min	4 min	5 min
Samples per composition	s_c	1	3	8
Samples per iteration	$s_i = s_c * 4$	4	12	32*
Time per iteration	$t_i = t_s * s_i$	60 min	48 min	160 min
Total samples tested	$s_T = i * s_i$	-	174	480*
Total run time	$t_T = i_T * t_i$	14 hrs	11 hrs	37 hrs

*Only realizable samples are mechanically tested, true values are lower

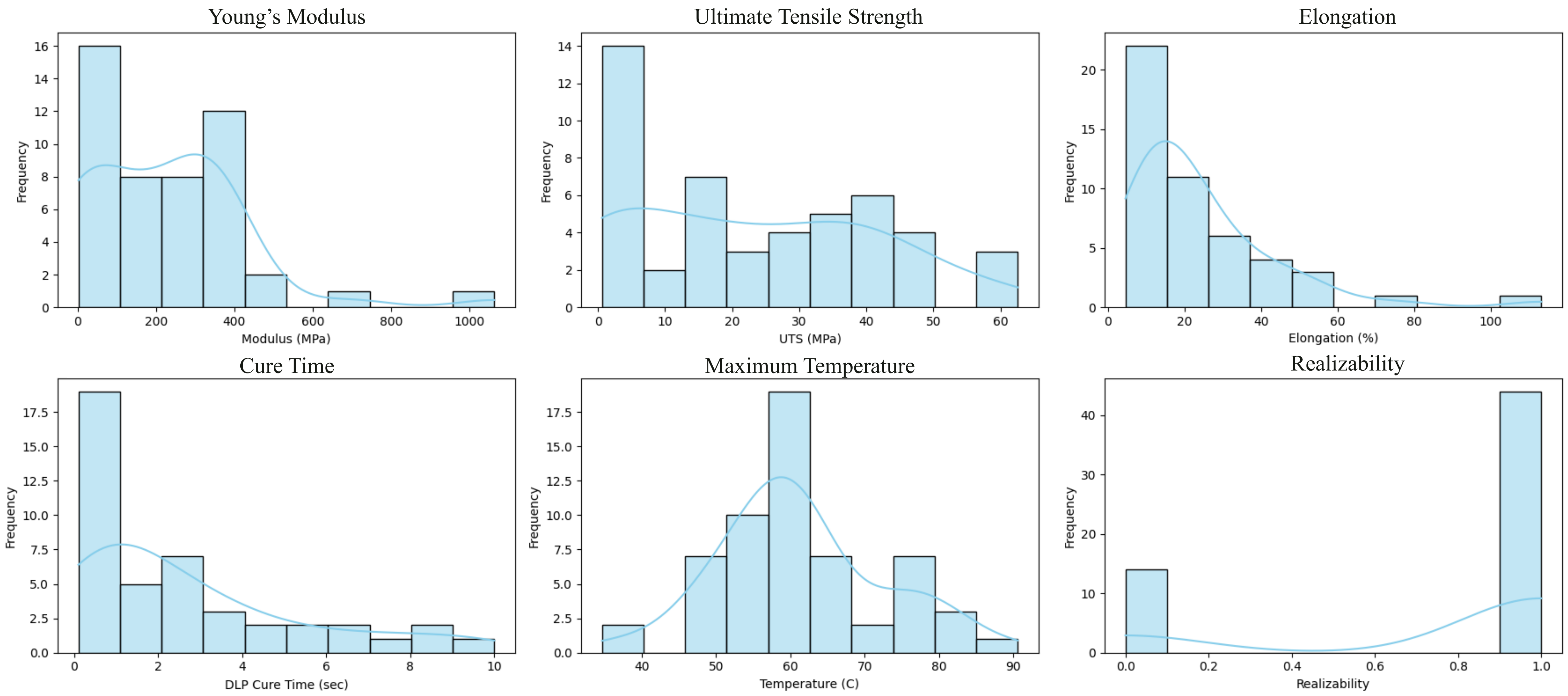
Initial Results

- Only exploration thus far
- Chosen based on highest uncertainty
- Sparse data



Factor composition heatmap

Initial Results



Response distributions

Summary

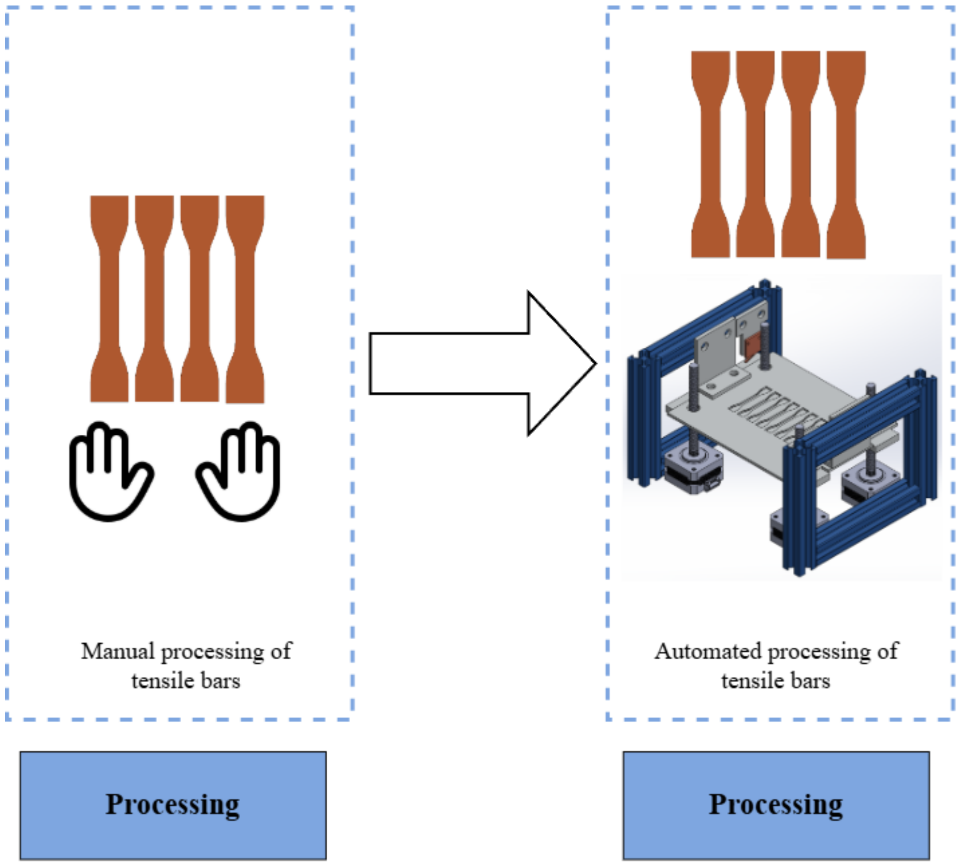
- Design space consists of a variety of common monomers and crosslinkers
- Active learning paired with autonomous systems enables efficient data collection

CH.4 Conclusions and Future Work

Conclusions

- Automated systems can be used for efficient photopolymer processing and characterization
- Iterations and time consumption of composing and testing inks to explore a design space can be greatly reduced
- Reliable photopolymer data can be collected autonomously and paired with an active learning model

Future Work



Close the loop to make entire system automated

Design Space Expansion:

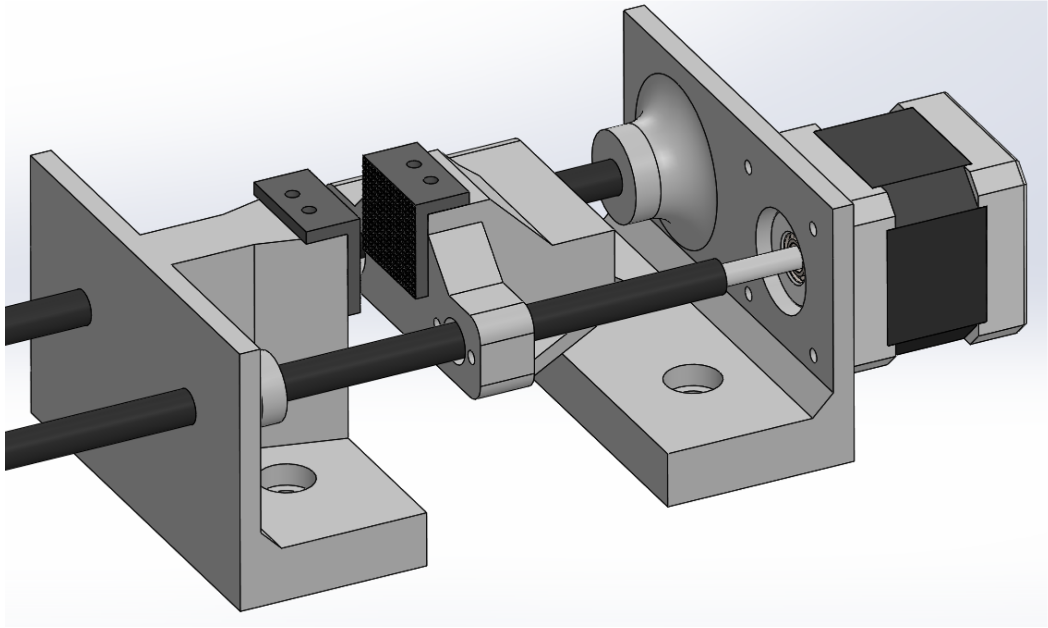
- Increase from 3 to 4 components
- Remove crosslinker requirement

122,094
total possible compositions

Supplementary

Automated Clamp

- Bottom grip for tensile testing
- Stepper motor controls linear stage
- Uses rotary encoder to track position
- Serrated metal grips

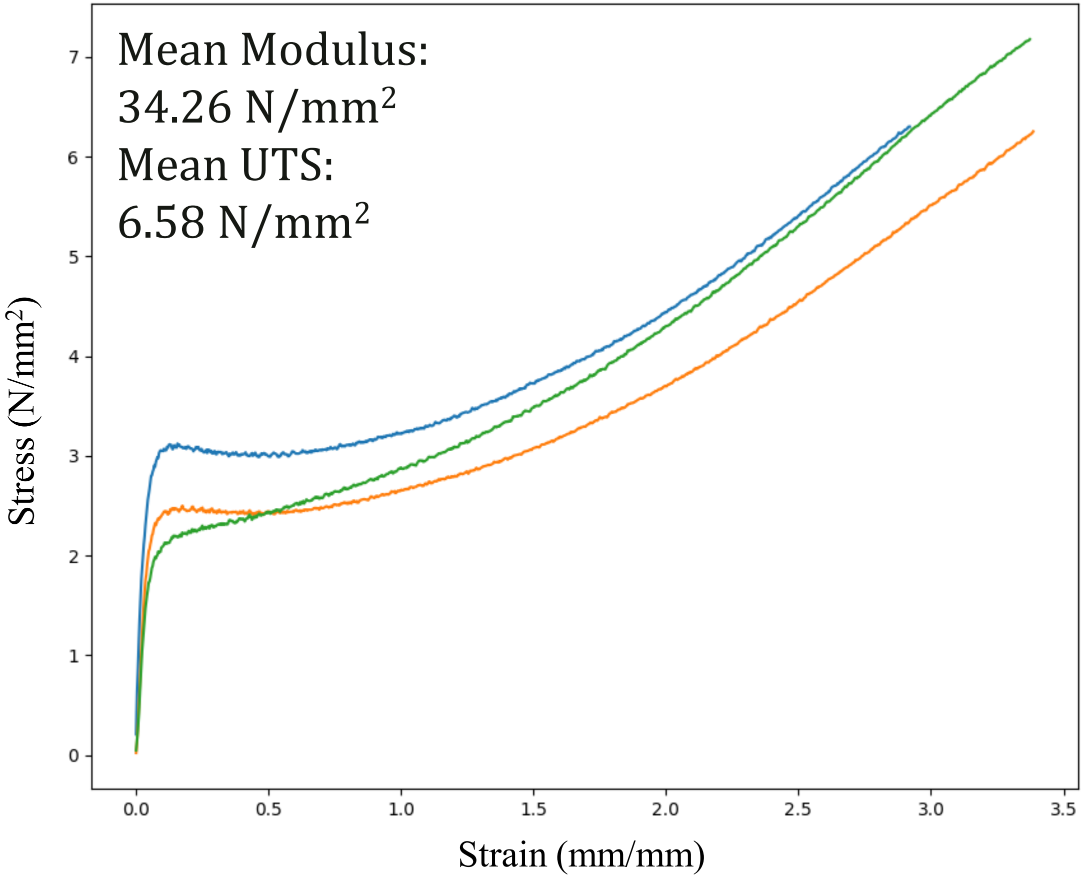


Automated parallel gripper design

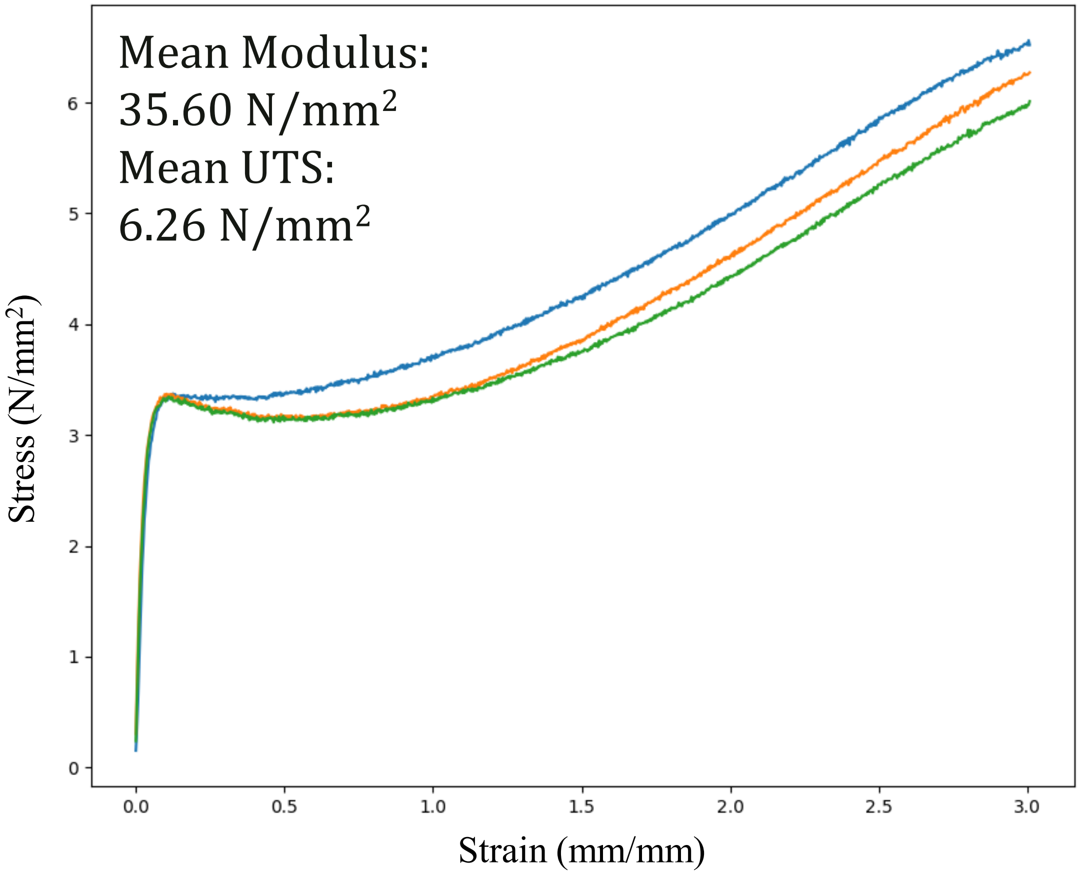
Implementation

ATT Validation

MTS Machine Tensile Test Sample Y



Robot Tensile Test Sample Y



Powder Dispenser Error

- Error is around 5% in dispensing
- Minimal effect on properties

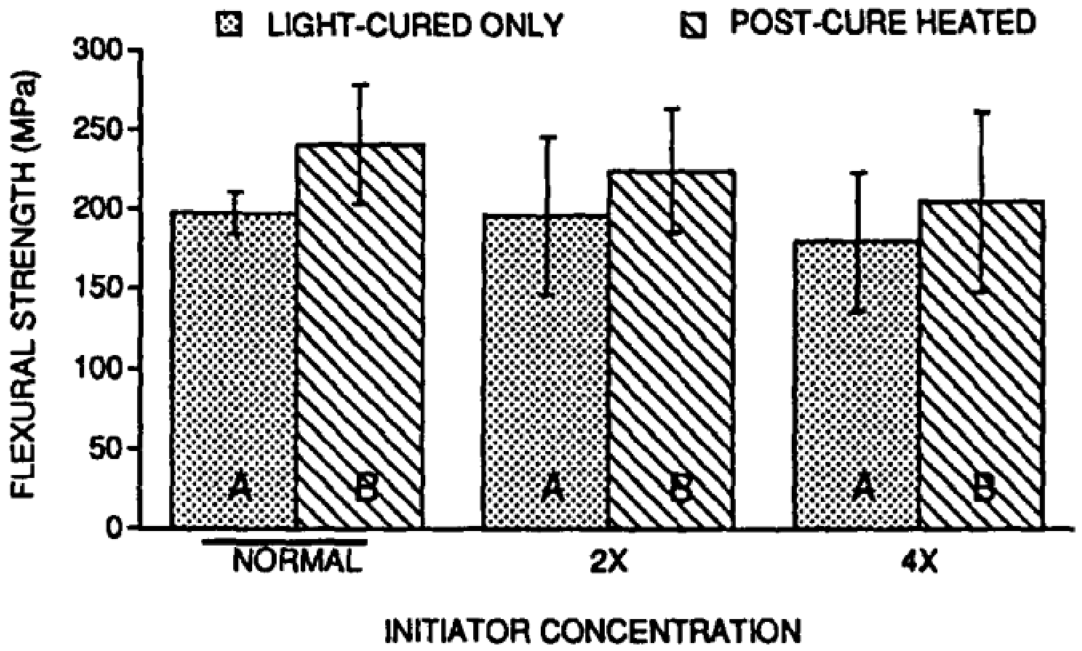


Fig. 1. Relationship between biaxial flexural strength and level of photoinitiator when only light-cured and after post-cure heating were used. n = 10 per group. Vertical bar = ± 1 standard deviation. Horizontal bar indicates statistical difference between groups. Similar letters indicate statistically equivalent groups

Rueggeberg, F. A., Ergle, J. W., & Lockwood, P. E. (1997). Effect of photoinitiator level on properties of a light-cured and post-cure heated model resin system. Dental Materials, 13(5-6), 360-364.