Additive Manufacturing by Photopolymerization

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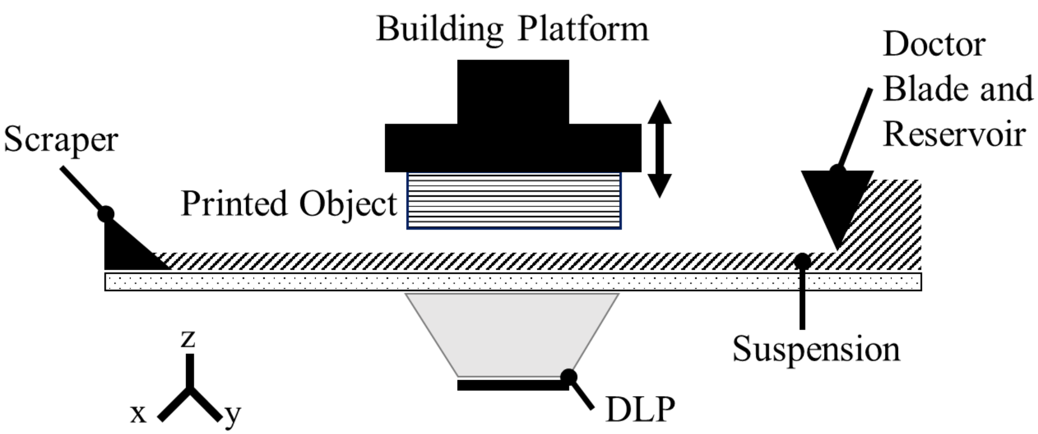
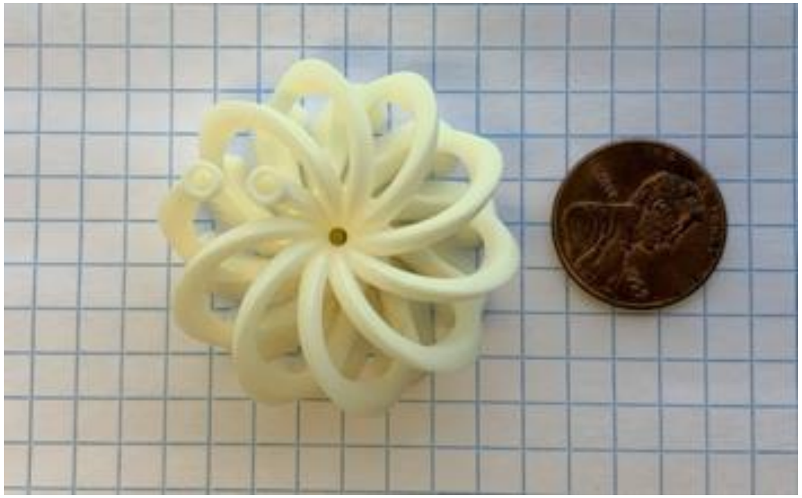
June 24, 2020

Game Changing



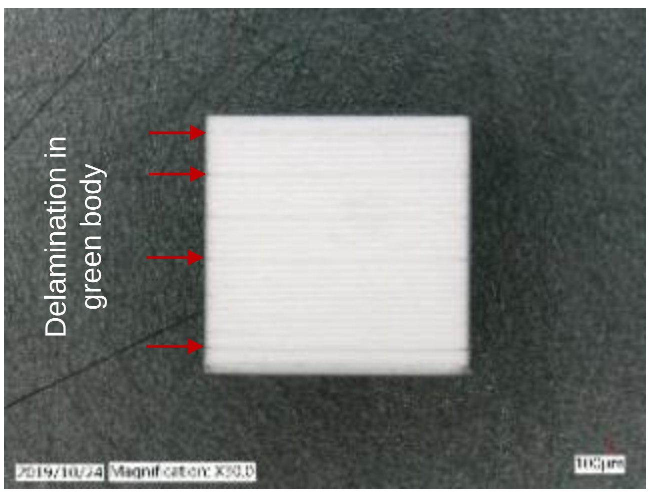


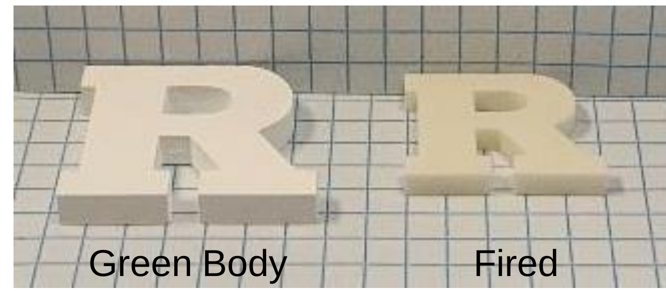
- Provides:
  - High degree of freedom
  - Less waste
  - Novel materials
  - High functional products

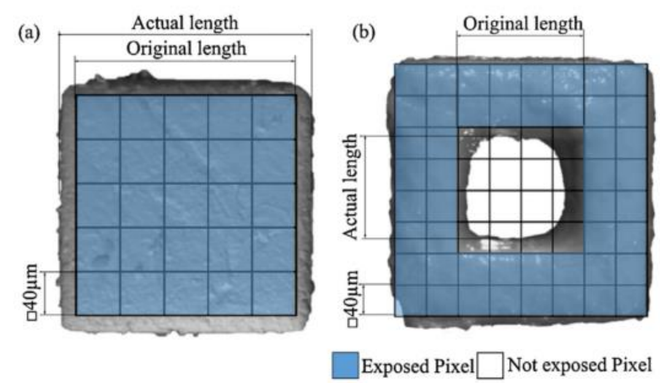
Challenges constrain the degree of freedom

- Suspensions variability
  - Binder removal
- Final products variability
  - Drying/anisotropic shrinkage/warpage
  - Dimensional and features resolution due to scattering
  - Delamination and microstructural flaws
- Dark and dense powders
- Partial polymerizations and oxygen effect upon curing?

It was found the z shrinkage can as high as 32% than xy shrinkage in fired printed







(Mitteramskogler, Gmeiner et al. 2014)

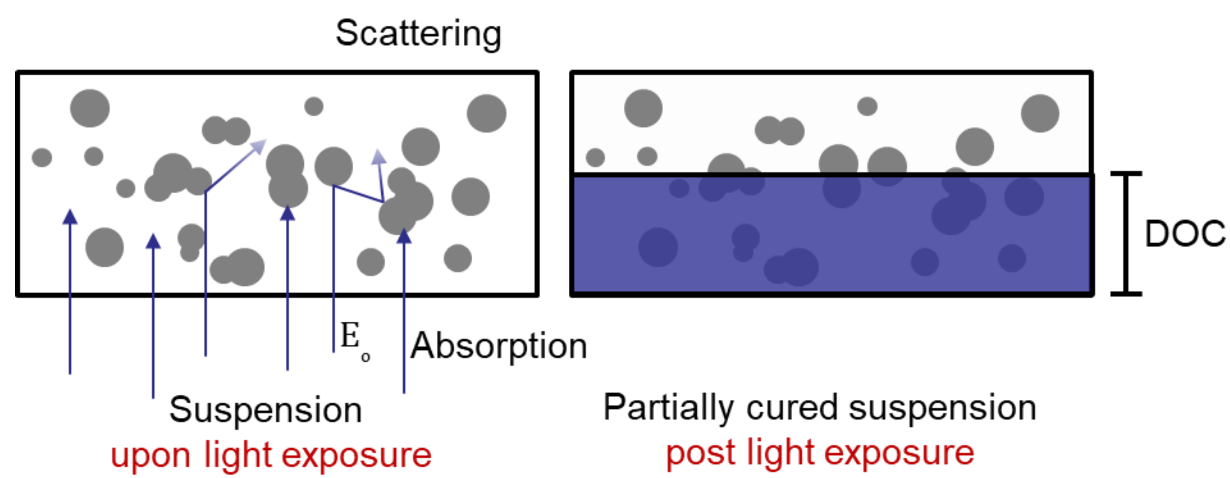
Cure depth (DOC) - An essential metric in SLA

$$DOC = S_d \ln \frac{E_\circ}{E_{crit}}$$

(Gentry and Halloran 2013)

S_d is materials sensitivity in the vertical direction and inversely proportional to the depth attenuation factor (A_d)

- Proper depth of cure is essential to achieve a good adhesion between layers



There is no specific form of DOC equation, but

Particle size
- What is the effective particle size?
- S or d are more effective?

Refractive Index difference depends on
- Powder refractive index
- Resin refractive index

$$DOC = \frac{2}{3}\frac{d}{Q^*}\frac{n_o^2}{\Delta n^2}\ln\left({}^{E_o}/_{E_{crit}}\right)$$

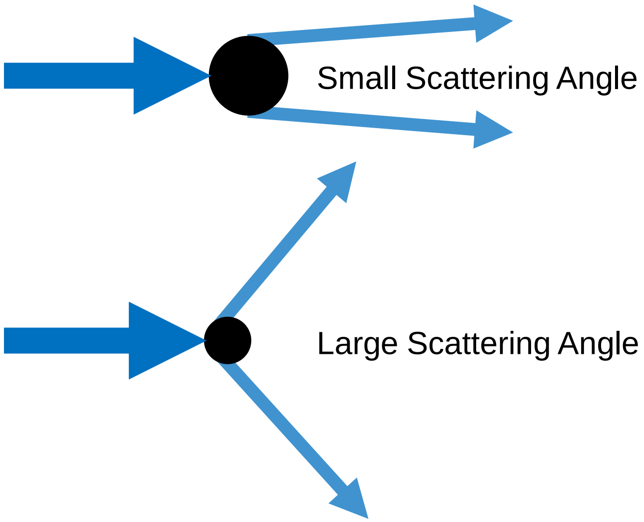
$$Q^* \propto \frac{S}{\lambda}$$

Energy dose depends on
- Exposure time
- Energy intensity
- Light scattering
- Refractive index difference

Interparticle spacing depends on
- Particle packing
- Particle size
- Solid content
- Degree of dispersion

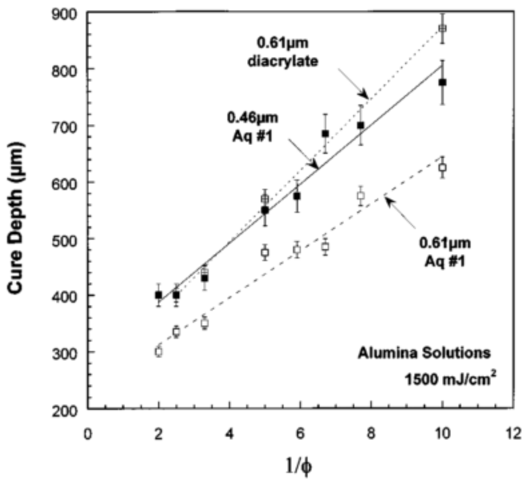
(Griffith and Halloran 1997)

In low solid content system



- **Particle Size:**
  - Large scattering angle should result in higher DOC
- **Solid Content**:
  - DOC and solid content are inversely correlated

The scattering behavior is more complex for high solid content system and a systems where there are large differences in refractive index between particle and medium



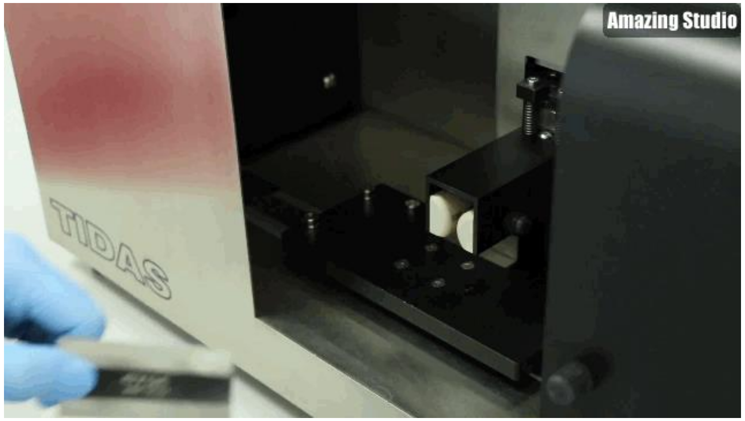
Griffith and Halloran (1997)

Our Approach

1. Developing characterization metrics
   - ✓ Quantitative analysis of degree of dispersion
2. Developing photocurable resins for ceramic and metal powders
   - ✓ Mixing methodology
3. Defining the printing limitations of ceramics

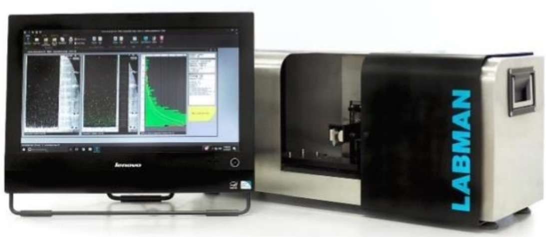
Automated FOG to define degree of dispersion

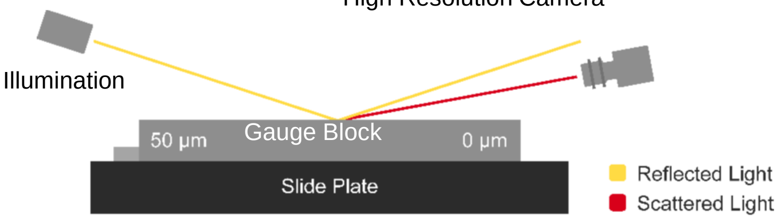
- Developed a method to evaluate SLA slurry using FOG gauge to define large agglomerates
- Provided auto drawdown measurement, thus constant shear and force
- Mitigated user error



Courtesy of Labman

courtesy of tqcsheen.com



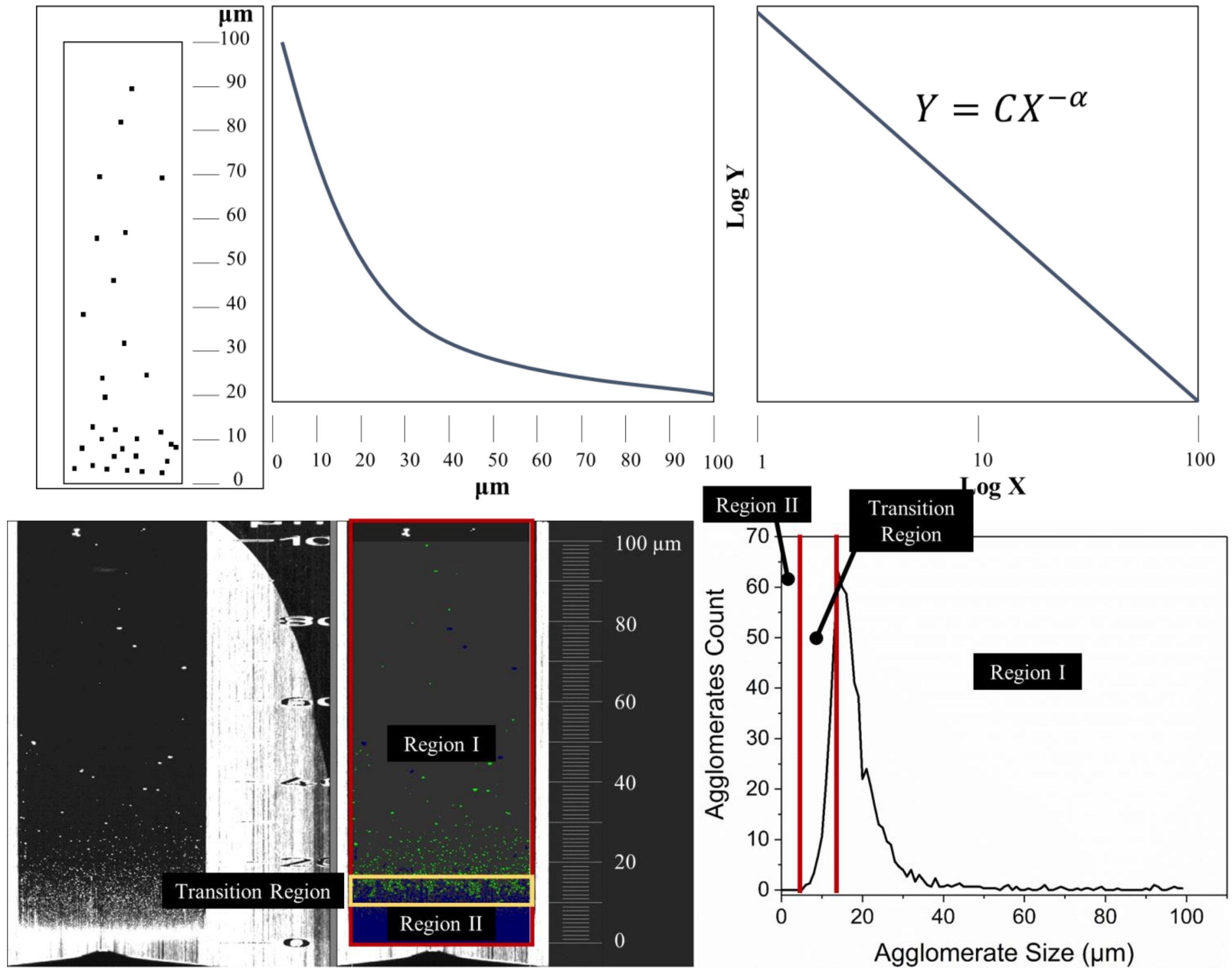


How does TIDAS work?

M. K. Alazzawi, F. F. Maniaci, B. Beyoglu, and R. A. Haber, "Degree of Dispersion Assessments of Highly Filled Stereolithography Suspension using Fineness of Grind Measurement," To be Published.

Parameters to define the agglomerate distribution

- When the plotting method fails
- To understand the effective particle size
- Ideally: power law behavior
- In reality:
  - Region I
  - Transition Region
  - Region II
- The model based on using Region I which was defined statistically



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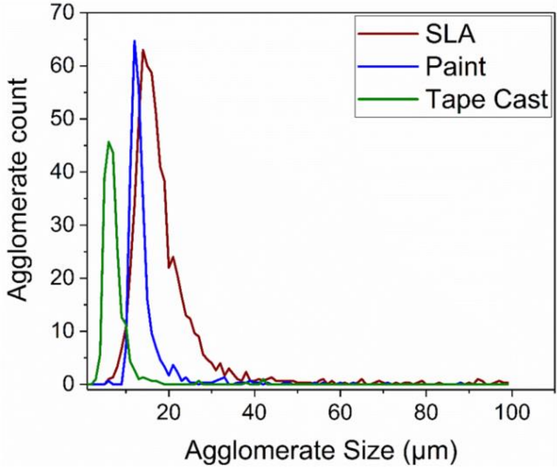
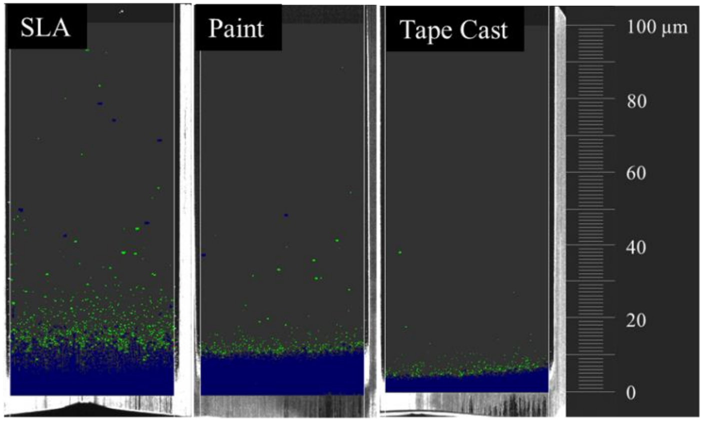
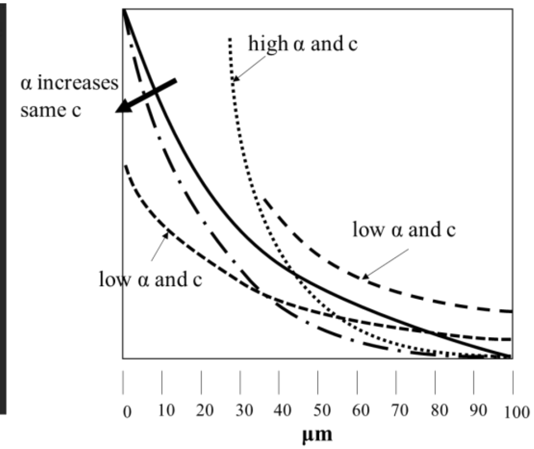
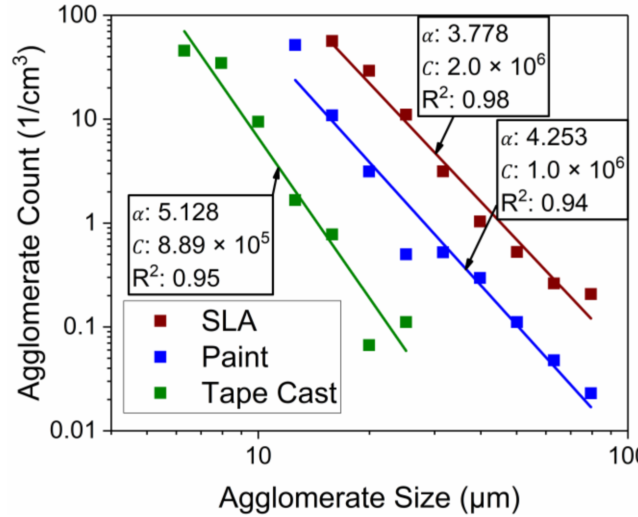






- **High *α*** when steep slope
- **Low *C***whenshifted to small agglomerate side



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Developing Unique Formulations | Challenges

Obtaining proprietary photocurable polymers and dispersants

- What are the type of polymers and dispersants?
- Collaborating with polymer companies

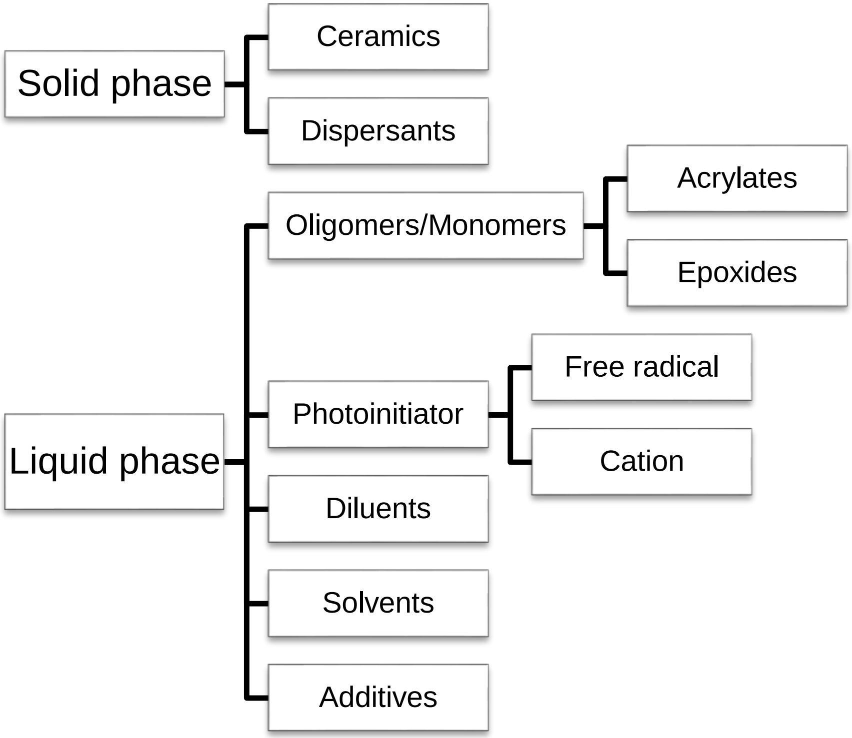
Mixing methodology

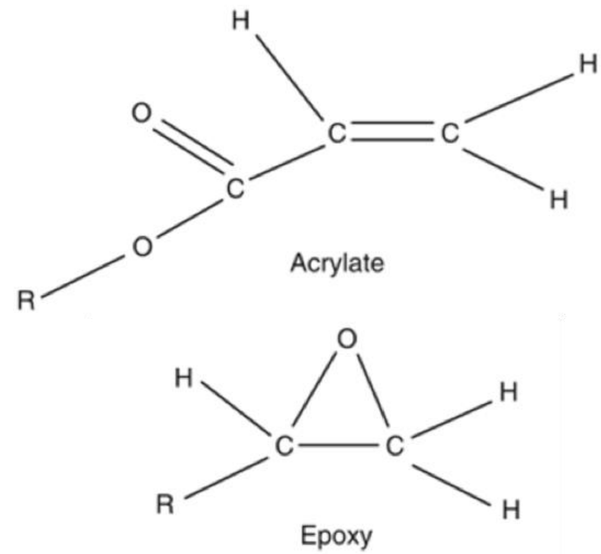
- Type of mixers
- Mixing parameters

Mixing sequence

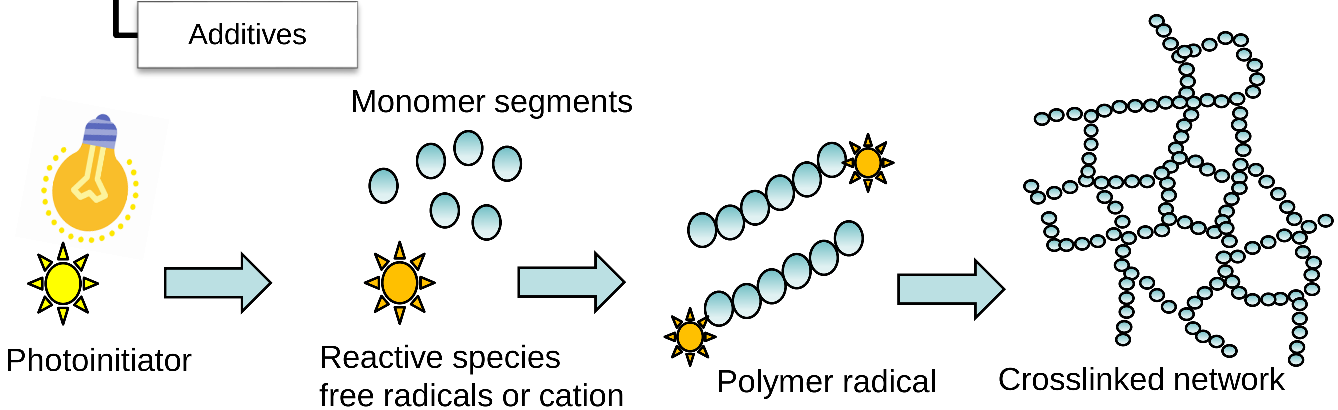
- How are the resins prepared?
- How is the dispersant added?
- How is the ceramic blended?

Photocurable Suspensions and Photopolymerization





(Gibson, Rosen et al. 2010)



Finding the right resin and dispersants

- **Criteria**
  - DOC of unfilled resin > 1000 µm
  - No curling and deformation
  - Temperature changes is minimal
  - Adhesion to the building platform
- **Requirement**
  - Oligomers were high molecular weight and high viscosity yielded in low shrinkage and high tackiness
  - Monomer or diluent to reduce the viscosity

Date	Oligomer 1	Monomer#1	Solvent	Powder	Mix#
5/3/2019	D2	M4	DMA	AA-07	34
5/30/2019	D2	M3		AA-07	35
5/31/2019	D2	M4		AA-07	35
6/4/2019	D2	M2		AA-07	35
6/5/2019	D2	M3		AA-07	36
6/6/2019	D2	M4		AA-07	36
6/10/2019	D2	M3		AA-07	37
6/11/2019	D2	M4		AA-07	37
6/12/2019	D2	M3	DMA	AA-07	38
6/13/2019	D2	M3	DMA	AA-07	39
6/14/2019	D2	M3		AA-07	40
6/17/2019	D2	M4		AA-07	40
6/21/2019	D2	M2		AA-07	40
7/11/2019	D2	M3		AA-07	43
7/23/2019	D2	M3		AA-07	49
8/2/2019	D2	M3		AA3.0(65%)+AA07(20%)+AA03(15%)	49
8/5/2019	D2	M3		AA3.0(65%)+AA07(20%)+AA03(15%)	49
8/6/2019	D2	M3		AA3.0(65%)+AA07(20%)+AA03(15%)	43
8/7/2019	D2	M3		AA-07	58
8/8/2019	D2	M3		AA3.0(65%)+AA07(20%)+AA03(15%)	58
8/9/2019	D2	M3		AA3.0(65%)+AA07(20%)+AA03(15%)	58
8/19/2019	D2	M3		AA-07	59
8/20/2019	D2	M3		AA-07	60
8/21/2019	D2	M3		AA-07	60

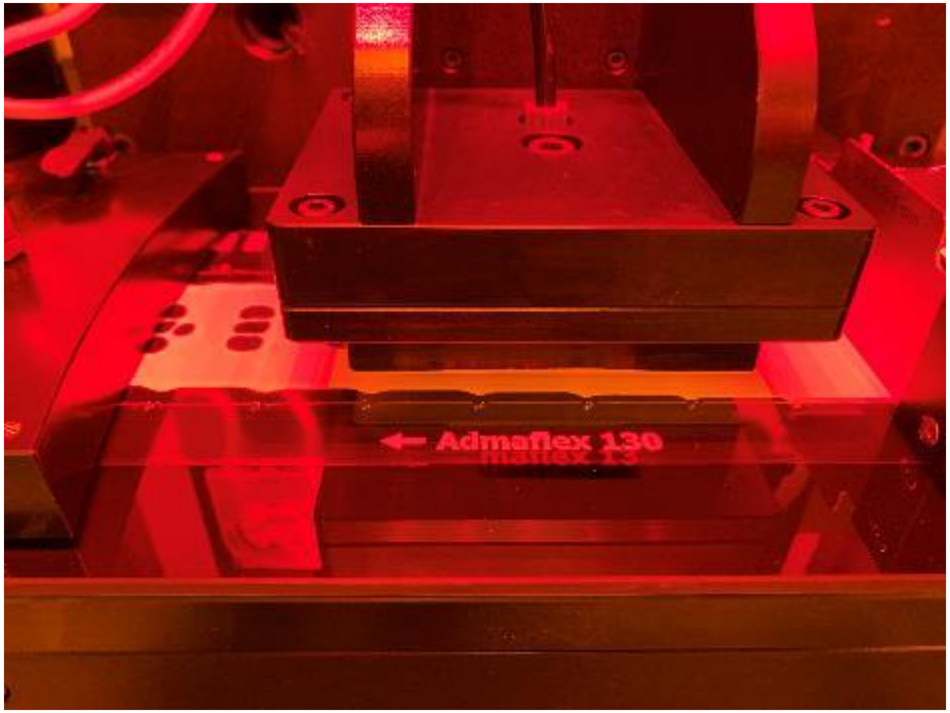
Good | Neutral | Bad

DMA : Dimethylacetamide

We have developed Center proprietary blends that we will share individually with Center members. However for this presentations, we are not including the specific polymer names

Rutgers photocurable resins

Resin	Viscosity (kcP)	Refractive Index	DOC (µm)
(Oligomer D2+ Monomer M2) Acrylate	0.53	1.4770	1300.8 ± 37.8
(Oligomer D2+ Monomer M3) Acrylate	1.43	1.4825	1356.0 ± 35.4



M. K. Alazzawi, V. R. Tsarkova, B. Beyoglu, C. Hwang, and R. A. Haber, "Stereolithography Apparatus and the Dimensional Control of Alumina Systems," To be Published.

Ceramic's factors need to be considered

Ceramic's Factors

- Solids content
- Particle packing
- Particle size
- Particle Morphology
- Dispersants

→

To Produce Suspensions with

- High solids content
- Sufficient depth of cure
- Shear thinning behavior
- Desirable degree of dispersion

→

What will it impact?

- Shrinkage
- Feature Resolution

Solid Content (%vol)	Powder	Particle Size, d_{50} (μm)	Density (g/cm^3)	Resin
34.0 – 62.0	AA07	1.35	4.01	(Oligomer D2+ Monomer M2) Acrylate
				(Oligomer D2+ Monomer M3) Acrylate
45.4	AA3	2.76	4.06	(Oligomer D2+ Monomer M3) Acrylate

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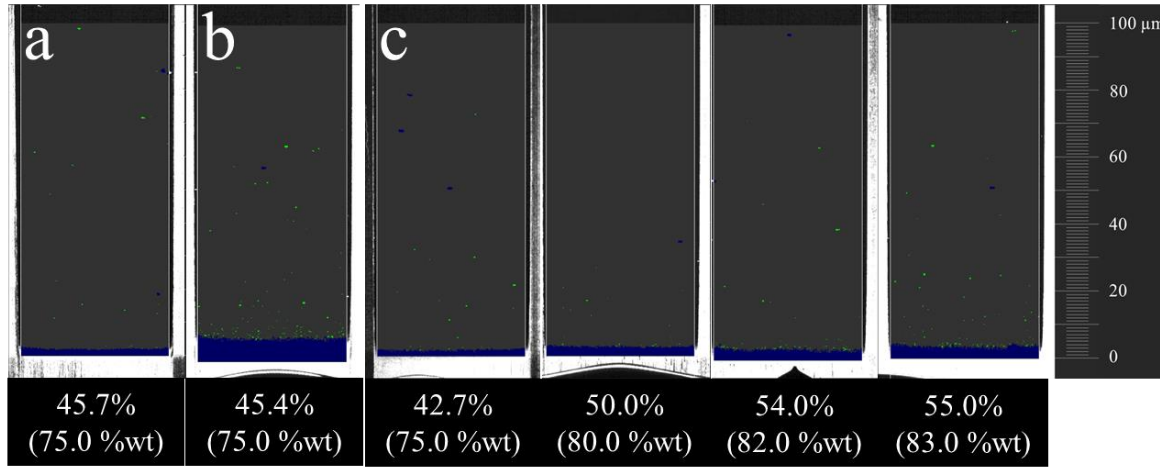
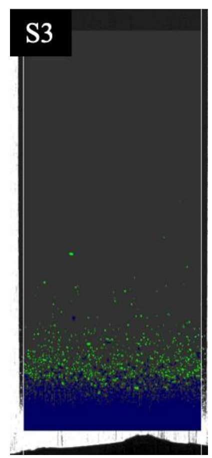
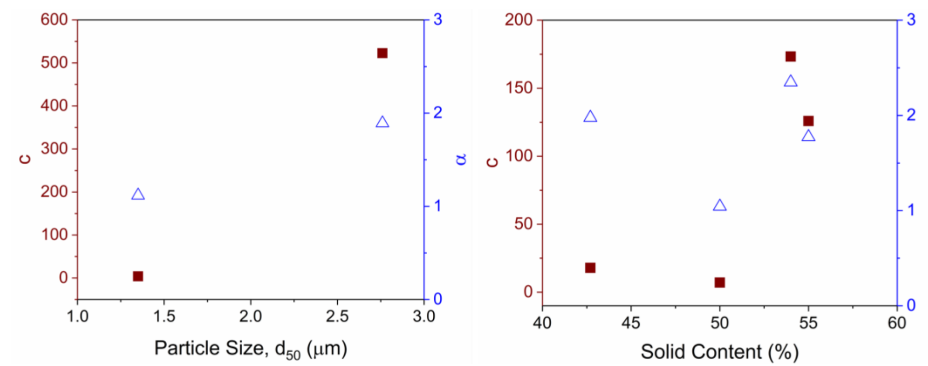
High degree of dispersion

- Regardless the ceramic parameters. The degree of dispersion was very high
- Resulted from:
  - High shearing of mixer
  - Viscosity of the base resin
- Does ceramic factors impact the DOC and viscosity?





(a) D2M3 resin and particle size of 1.35 µm
(b) D2M3 resin and particle size of 2.75 µm
(c) D2M2 resin and particle size of 1.35 µm



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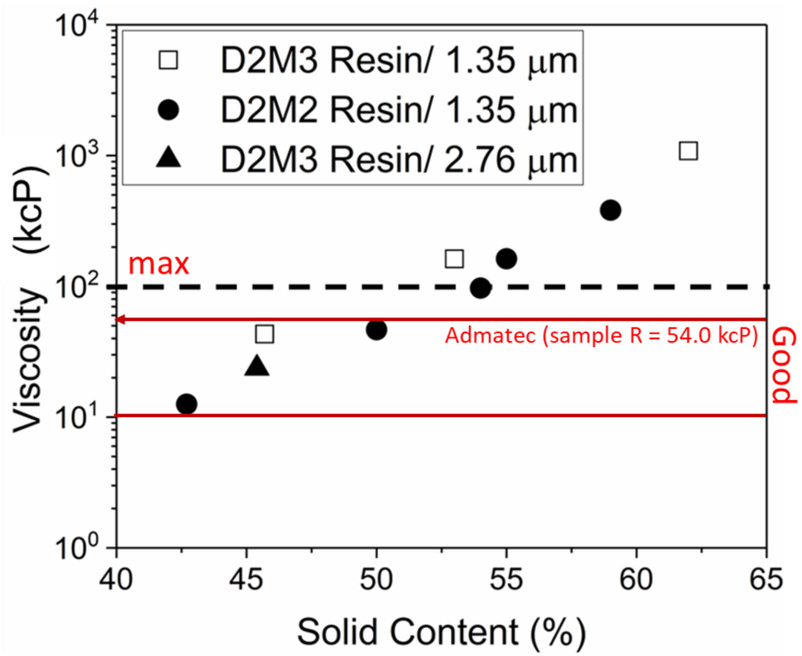
Viscosity limits

- Maximum printable viscosity was around 100.0 kcP, otherwise
  - – Can not be casted
  - – Layer detachment
  - – Severe delamination
- Good viscosity range above 10 kcP to around 60 kcP



Viscosity: RT, 1 s^{-1} , and maintained the measurement conditions constant (prehistory of stress)

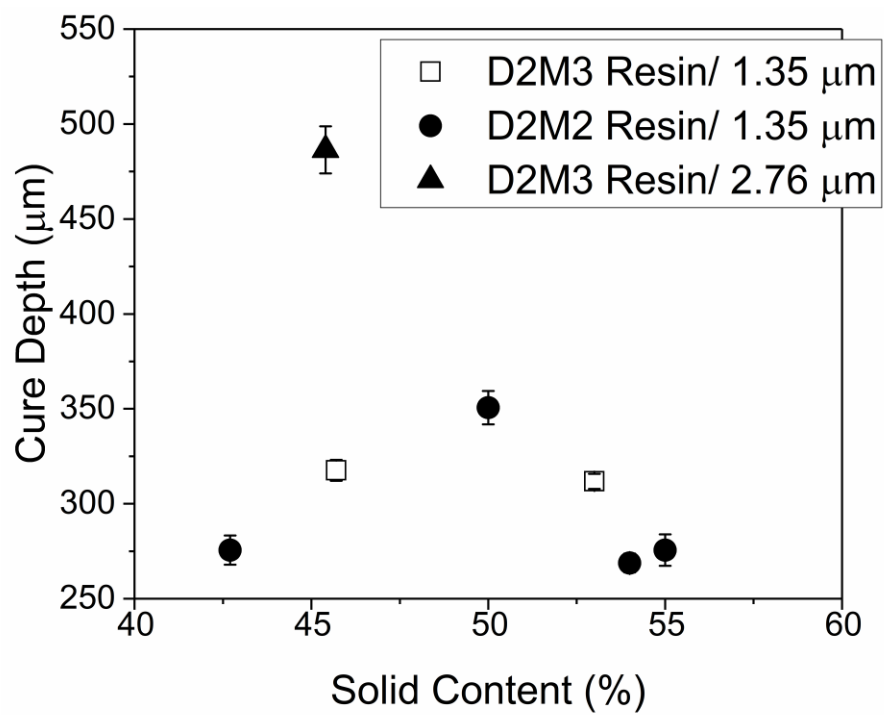
M. K. Alazzawi, V. R. Tsarkova, B. Beyoglu, C. Hwang, and R. A. Haber, "Stereolithography Apparatus and the Dimensional Control of Alumina Systems," To be Published.

Particle size showed significant impact on DOC

$$DOC = \frac{2}{3}\frac{d}{Q^*}\frac{n_o^2}{\Delta n^2}\ln\left({}^{E_o}/_{E_{crit}}\right)$$

$$Q^* \propto \frac{S}{\lambda}$$

- Solid content showed no significant impact
- Larger particle size resulted in high DOC
- DOC depend on resin type



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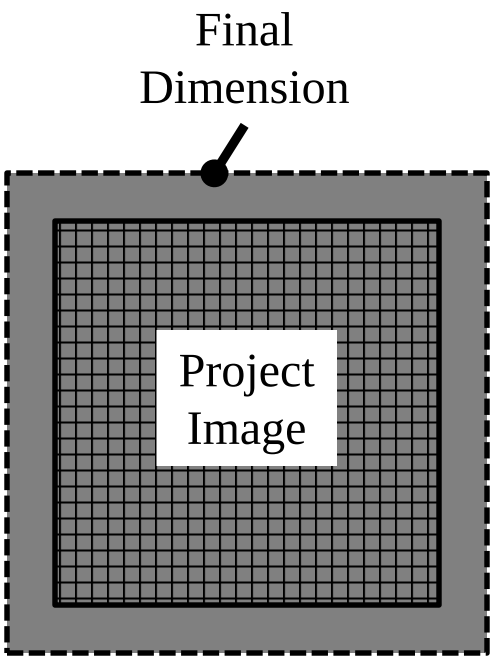
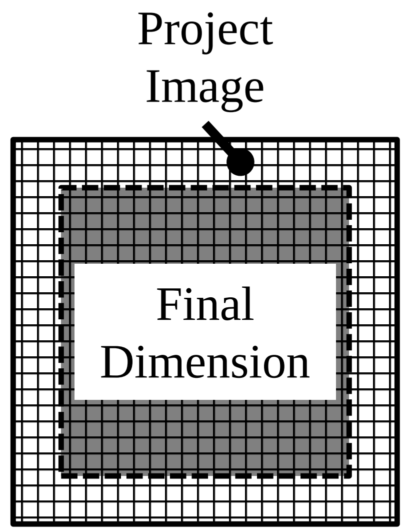
Defining print resolution



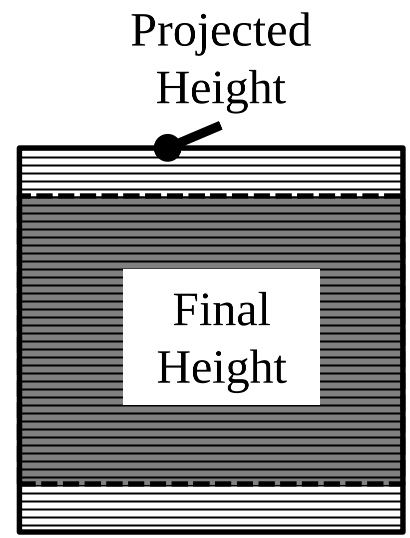
x and y

Growth in Dimensions (+)



x and y

Shrinkage in Dimensions (-)



z

Shrinkage in Dimension (-)

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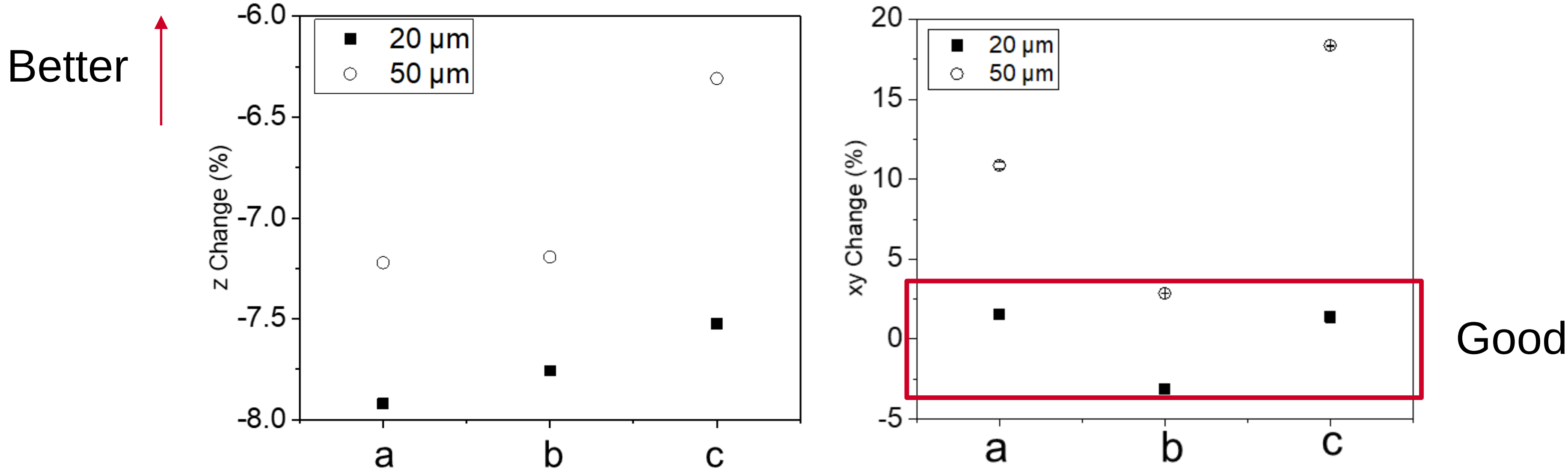
Dimensional control of "As Printed Objects"



(a) D2M3 resin and particle size of 1.35 µm
(b) D2M3 resin and particle size of 2.75 µm
(c) D2M2 resin and particle size of 1.35 µm

- 20 µm required low energy dose to reach the targeted cure depth
- Large particle size with thinner layer resulted in a high resolution
- Dimensions in z direction did not change significantly

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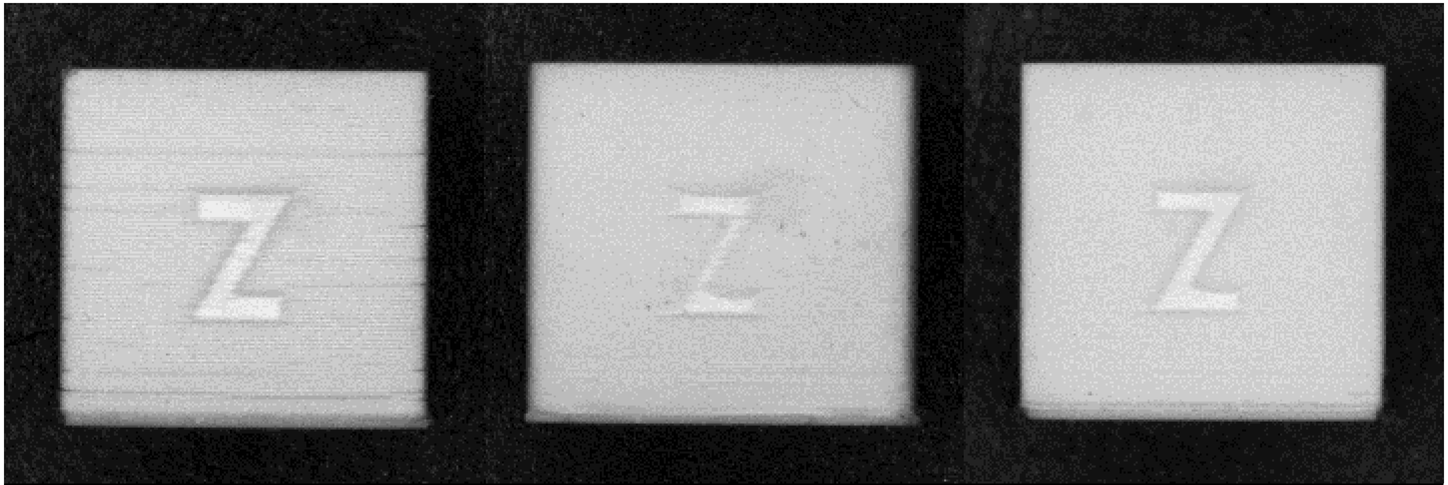
Dimensional control of "As Printed Objects"

50 µm, low energy dose	50 µm, high energy dose	20 µm, high energy dose



45.4 %vol + D2M3 resin and particle size of 2.75 µm

- Feature resolution enhanced without delamination by using thinner layers with coarser particle size
- All samples that prepared using D2M2 resin showed delamination

M. K. Alazzawi, V. R. Tsarkova, B. Beyoglu, C. Hwang, and R. A. Haber, "Stereolithography Apparatus and the Dimensional Control of Alumina Systems," To be Published.

Binder Removal

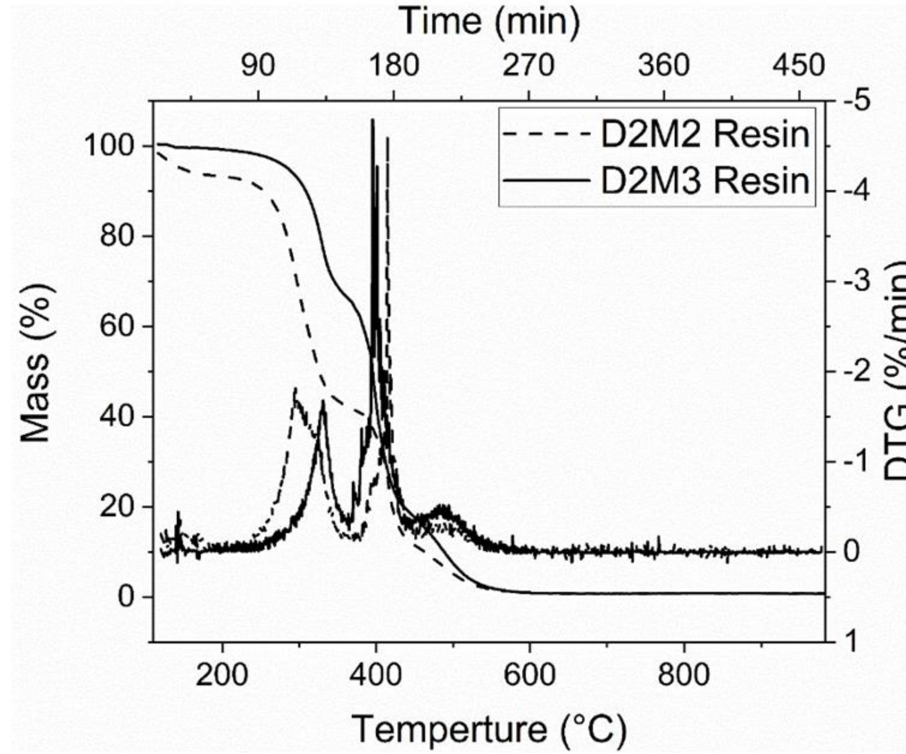
- Early stage of the study showed that cracks start between 165 °C and 180 °C
  - Trapped uncured resin
  - Low degree of polymerizations

120 °C

150 °C

165 °C

180 °C



Heating rate: 2 °C/min

Takeaways

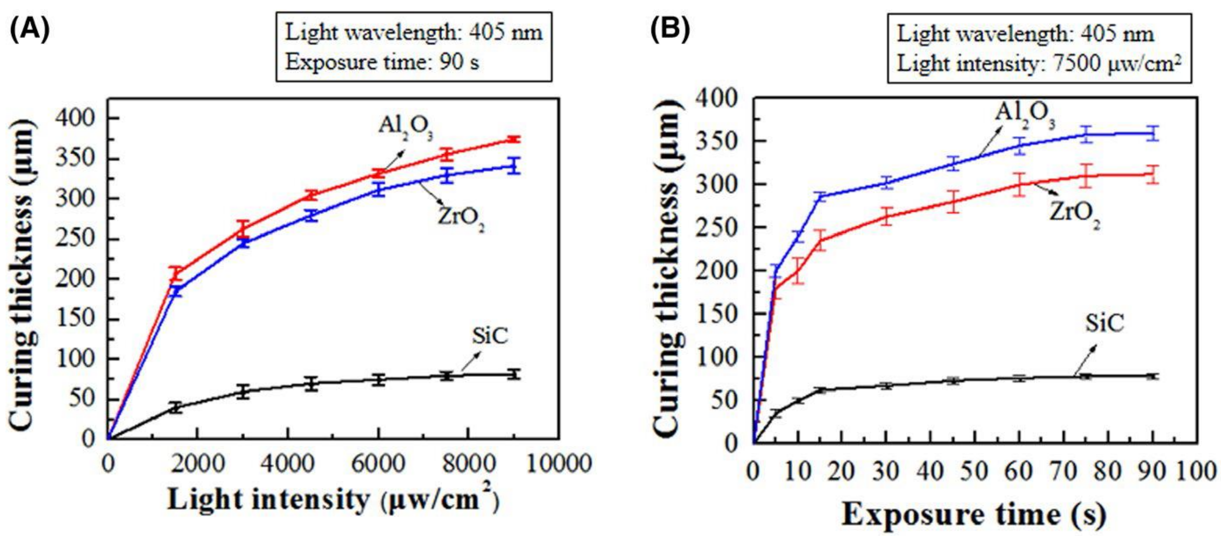
1. Developed characterization metrics
   - ✓ Quantitative analysis of degree of dispersion
2. Developed three resins
   - ✓ Developed mixing methodology for ceramics and polymers
3. The key is tuning formulations with printing conditions

Next

1. Design dark powder suspensions (Victoria Tsarkova)
   - Define printing condition
2. Continue low refractive index powder project (Frank Maniaci will start Fall 2020)
   - Examine the degree of polymerization as function of printing conditions
     - Understanding the degree of polymerization through a layer's thickness by Raman
   - Examine varying photoinitiators
   - Define a feasible washing methods
3. Additive manufacturing of multi materials (Sweta Kondapalli and Frank Maniaci)
   - Metal via direct write approach
   - Ceramic via SLA approach
4. Optimizing binder removal without causing defects in large prints (Eoin McAleer)
5. Provide a 3D analysis of the microstructure (Jon Oliver)

Establish process of dark powder

- The challenge: high refractive index would result in a lower depth of cure
  - Dark powders have increased light absorbance in comparison with white powders
- Deliverables: allowing for a more effective and economical route to manufacture advanced ceramics with complex shapes.



Ding, Guojiao, et al. 2019

Experimental plan of dark powder project

- Step 1: Establish the baseline on the formulation for Si_3N_4
- Step 2: Study the effect of dispersant on DoC
  - Effect of dispersant type: Efka PX 4701, Efka PX 4733, Efka RM 1469
  - Effect of dispersant amount: 0.1%, 0.5%, 1%
- Step 3: Study the effect of solid loading on DoC
  - Variations: 30%vol, 40%vol, 50%vol
- Step 4: Study the effect of particle size on DoC
  - Variations: 1 um, 1-3 um, >3um
- Step 5: Study the effect of refractive index difference between solid (Si_3N_4) and UV curing resin on DoC
  - Resin: D2 + M(2, 3, 4) + PI
  - Variations: M2 (1.4770), M3 (1.4825), M4 (1.4835); assuming n = 1.95 for Si_3N_4
- Step 6: Study the effect of stereolithography parameters on DoC
  - Vary light intensity and exposure time depending on targeted depth of cure (base: 60 um ± 20um)
- Step 7: Optimize & design formulation(s) for Si_3N_4
- Step 8: Test runs

Thank you ☺

- Kaavya Krishna-Kumar and Eliza Wirkijowski (Undergrad Research Assistants)
- Chuck Rohn (Malvern Panalytical)

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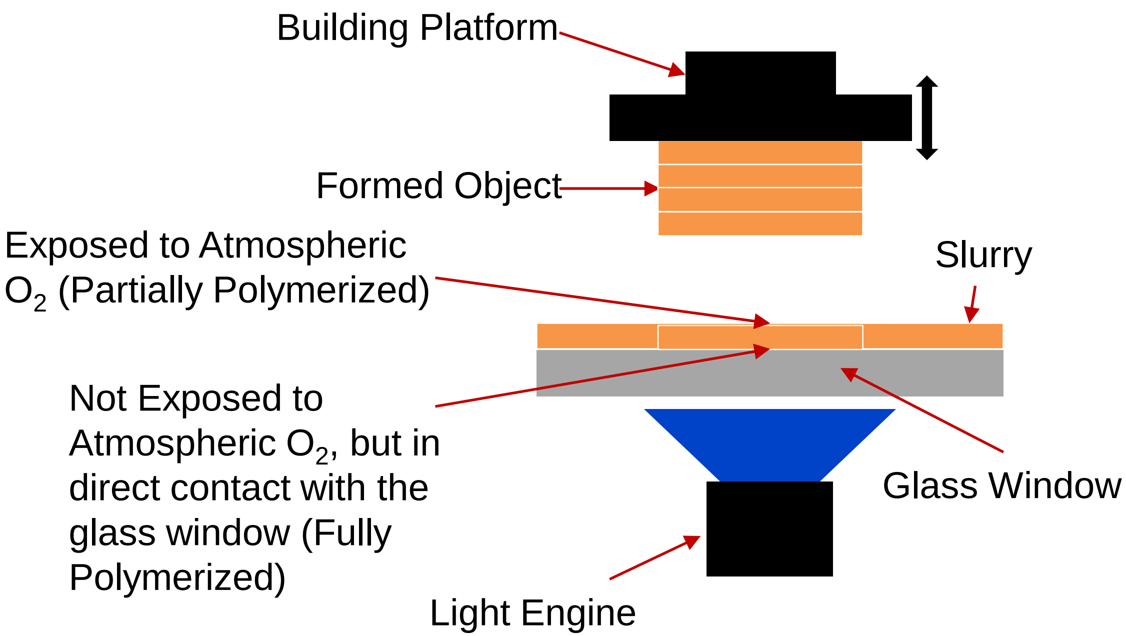
Atmospheric Oxygen and Trapped Air Impacts

Oxygen consumes free radicals produced by the photoinitiatior, therefore, it gives rise to partial photopolymerization and possibly differential shrinkage

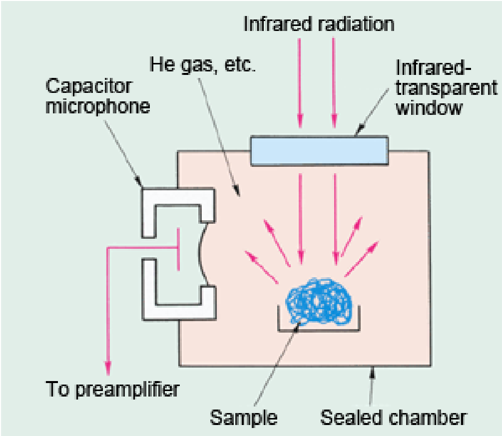
- FTIR study is on going to investigate the degree of polymerization as a function of layer thickness



The Horiba Raman will allow us to evaluate the oxygen sensitivity of photoinitiators. This is critical to do as current PI's are phosphorus containing and we need to look at non-contaminating compounds

Atmospheric Oxygen and Trapped Air Impacts | FTIR Study

- Photoacoustic signals are generated by thermal expansion due to the heat that generated by infrared radiation
- Beam intensity is modulated by changing the frequencies, $f = \nu V$, by changing mirror velocity
  - Higher velocity results in near surface scan
  - Lower velocity results in higher depth

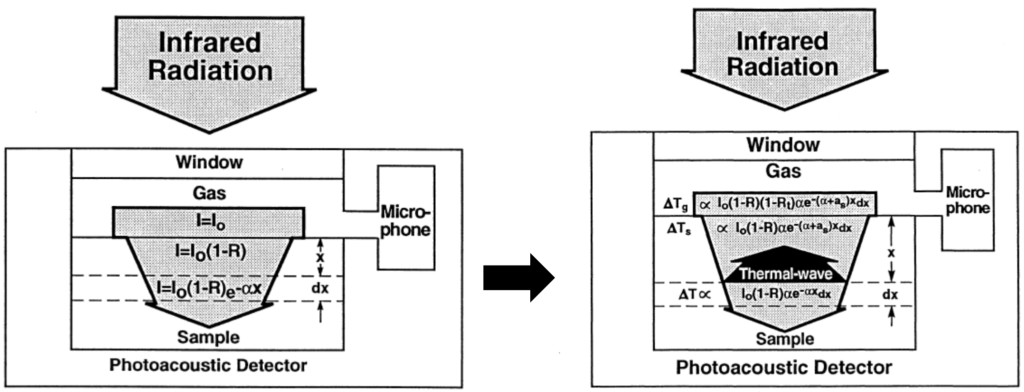


shimadzu.com

$$L = \left({}^{D}/_{\pi f}\right)^{1/2}$$

D : thermal diffusivity
ν : Wave length
V : Optical path difference velocity (mirror velocity)

Jones et. al (2002)



McClelland et al. (1992)

Atmospheric Oxygen and Trapped Air Impacts | FTIR Study

- Preliminary data showed significant changes in the peak intensity between scans at the surface compared to higher depth
- How is this related to the degree of polymerizations?
- What is the relationship between degree of polymerizations and shrinkage?