

Processing of 3D Printed High Temperature Materials

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Amelia Davenport, Trevor Goldman, Johnathan Genther, Neil Cramer
Colorado Photopolymer Solutions
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Outline

- Background of technology
- Routes to final materials
 - Acrylate
 - Thiol Acrylate
 - Hybrid (Acrylate/cationic)
 - Silica and Alumina filled systems
- Post-Processing conditions
 - LED processing
 - Broadband UV light
 - Heat processing
 - LED and Heat
- Results
- Conclusions

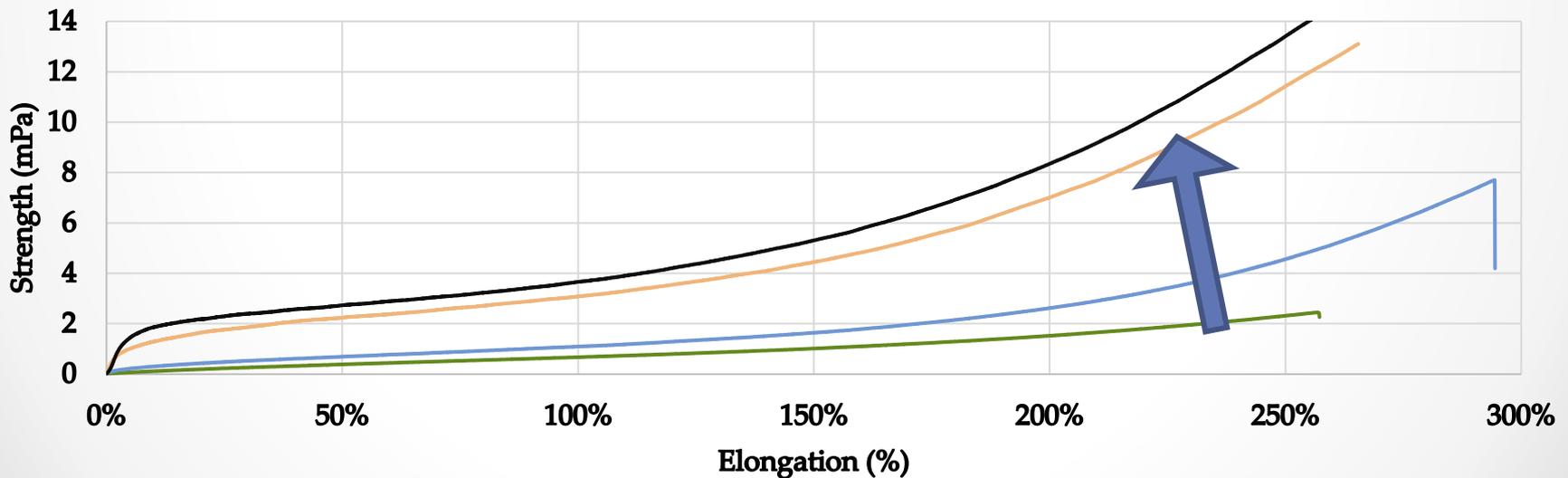


Background

- 3D printing has been primarily been used for prototyping applications
 - Material characteristics unimportant
- Additive Manufacturing (AM) - Use of 3D printing for mass production and end use applications
 - Requires material with functional properties for specific use cases
 - Casting
 - High temperature
 - Tough
 - Rubbery

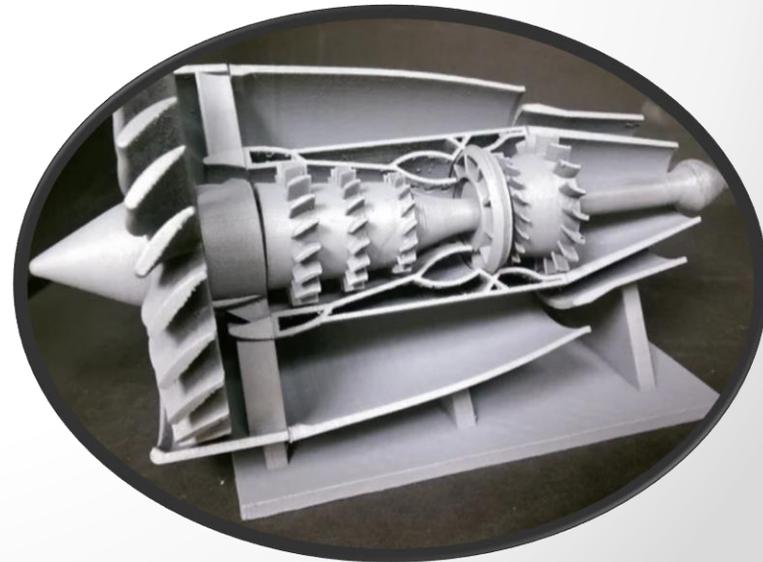
Background

- Materials come off of printers with incomplete cure, known as a “Green State”
- Requires some amount of post-processing to bring the part up to usable properties
- Final parts that are not brittle and have appropriate heat resistance



Inspiration

- Increasing viability of materials and platforms
- Need for 3D printed materials that can be used at high temperatures
 - Automotive
 - Molding
 - Solvent Resistance
 - Others
- Moderate expectations of the process



Relationship between T_g and Polymerization Temp

- For polymers that have the potential for a much higher T_g than the curing temperature, mass transfer limitations (vitrification) and the network heterogeneity combine to control T_g such that:

$$T_g \approx T_{cure} + T_{g1/2width}$$

- For systems polymerized at temps closer to their max T_g, polymer structure becomes dominate factor
- Good for chain growth and step growth mechanisms

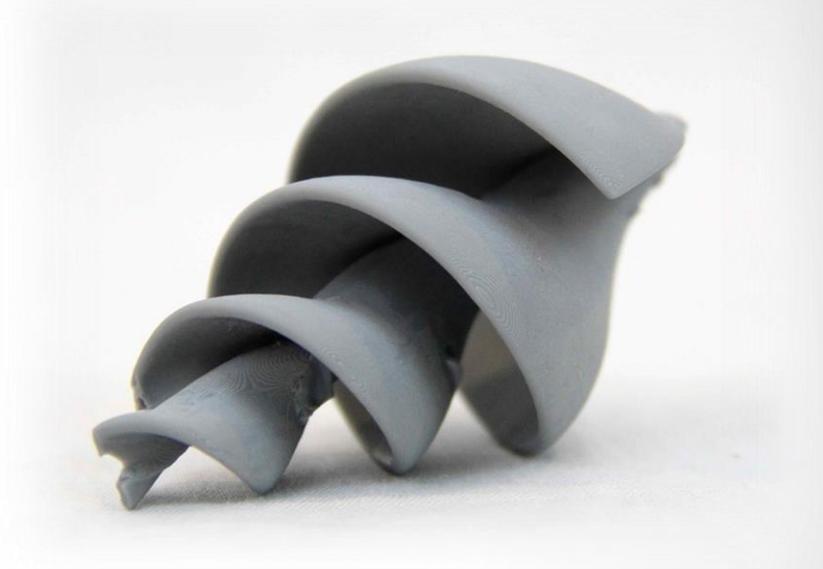
Print and Test Conditions

- Printed on Origin 3D printer
 - 100 μm layer thickness
 - 7 mW/cm^2
 - 385 nm
- Tensile
 - ASTM D638-IV
- Flexural
 - ASTM D790
- Glass Transition Temperature (T_g)
 - DMA



Material Types

- Acrylate
 - Radical chain growth
- Thiol-Acrylate
 - Radical step-chain growth
- Hybrid Radical-Cationic
 - Radical chain growth/cationic ring opening chain growth
- Filled systems
 - Acrylate – radical chain growth
 - Silica
 - Alumina

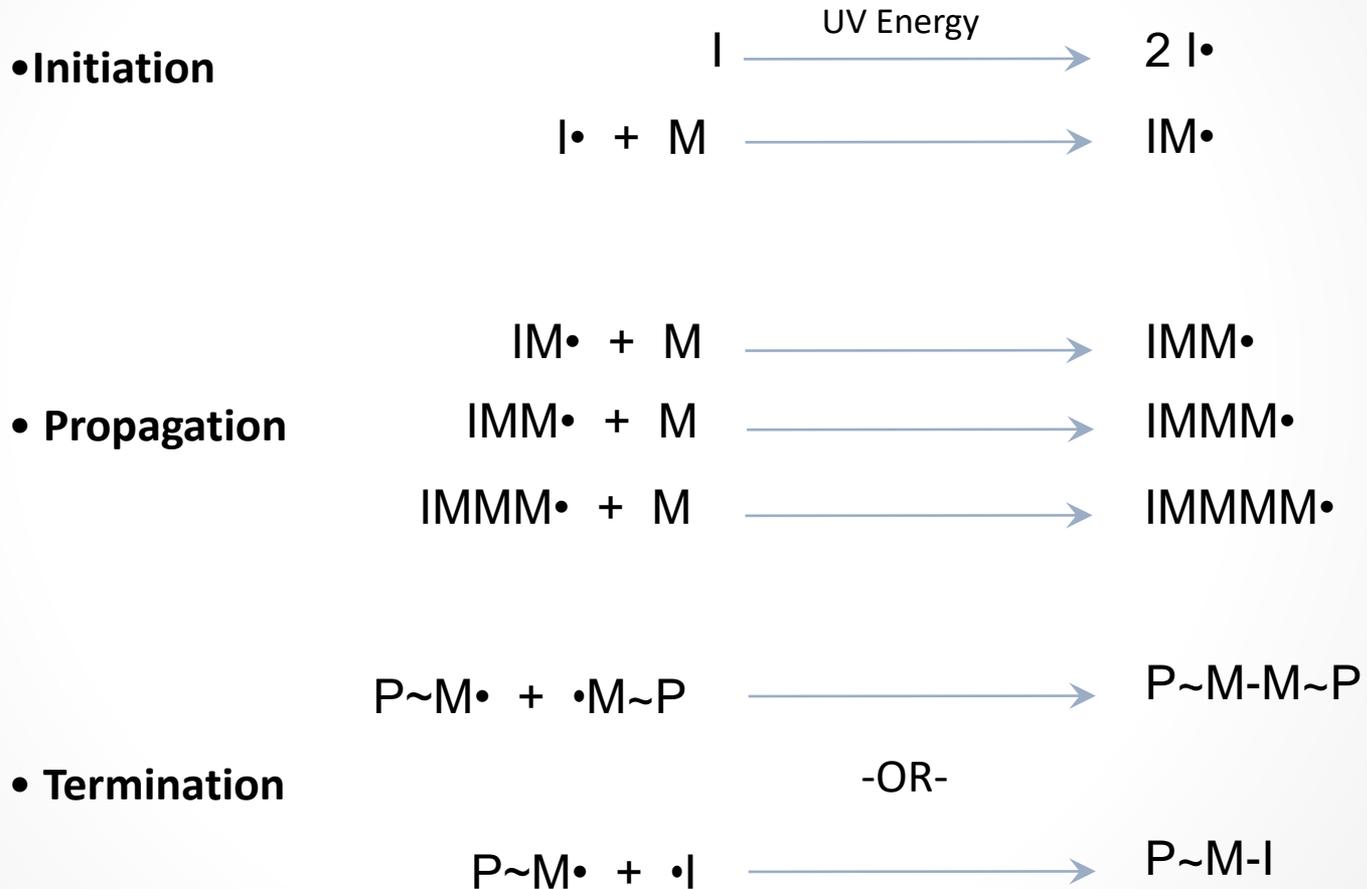


Post-Cure Conditions

- 405 nm LED
 - 10 mW/cm²- 10min a side
 - 27 °C
- LED+Heat
 - 10 mW/cm²-10 min a side
 - 100 °C
- Broadband UV
 - 80 mW/cm² -10 min a side
 - 90 °C
- Heat
 - 100 °C 1hr



Acrylate Mechanism and Characteristics

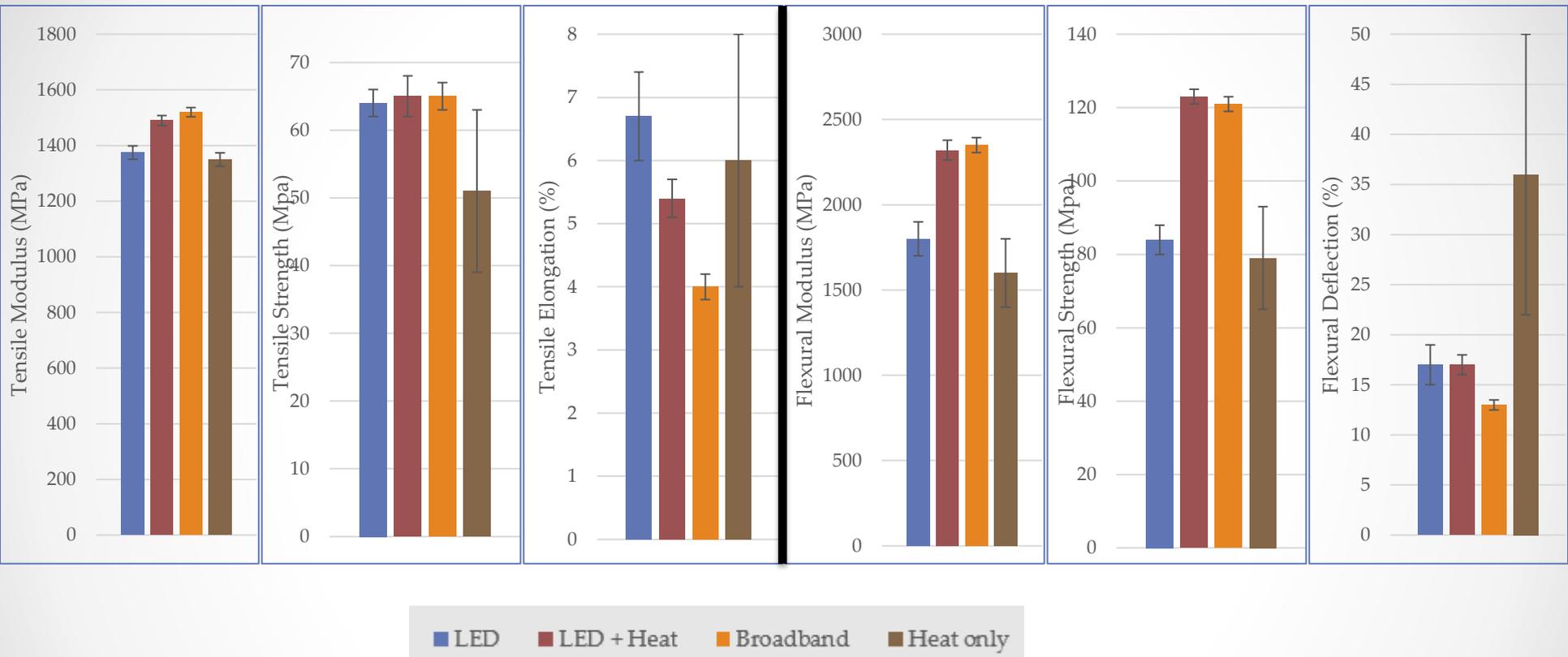


I = Initiator M = Acrylate P = Polymer chain

Acrylate Mechanism and Characteristics

- Chain growth
- Quick cure times
- Large tool box of commercial monomers
- Good photoinitiator selection for popular wavelengths
- Some shrinkage

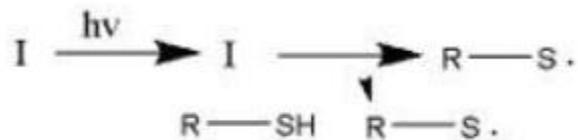
Acrylate Results



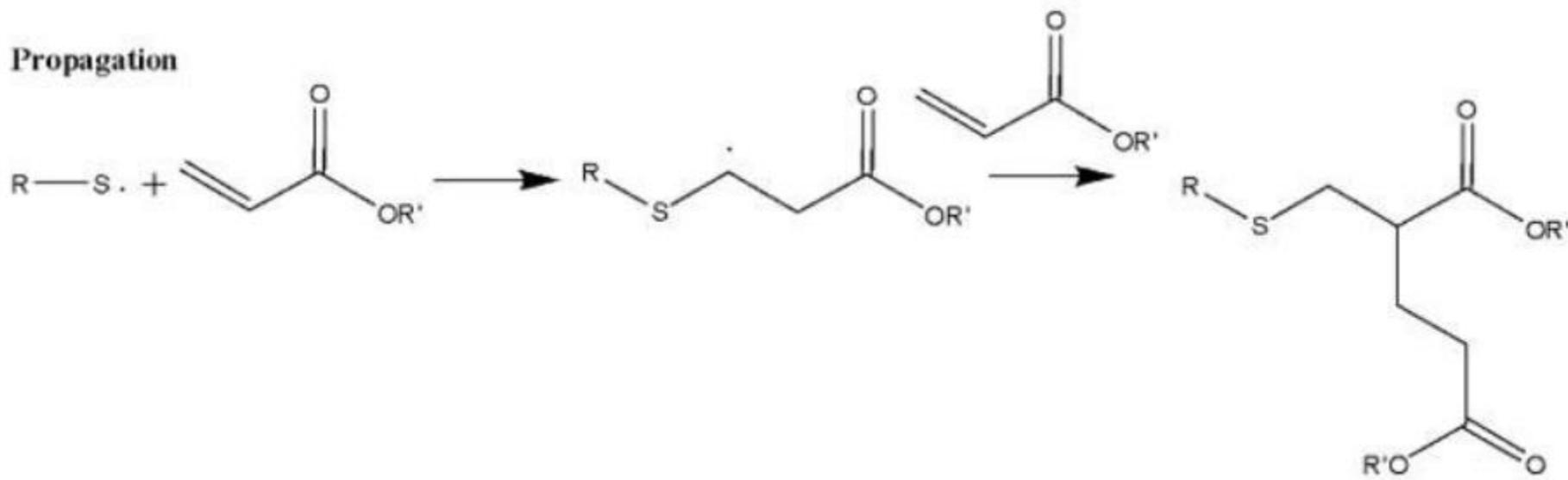
- Heat only post-cure did not yield improved properties, in this case
- Increasing temperature/ spectrum of light yields more thorough curing

Thiol-Acrylate Mechanism and Characteristics

Initiation



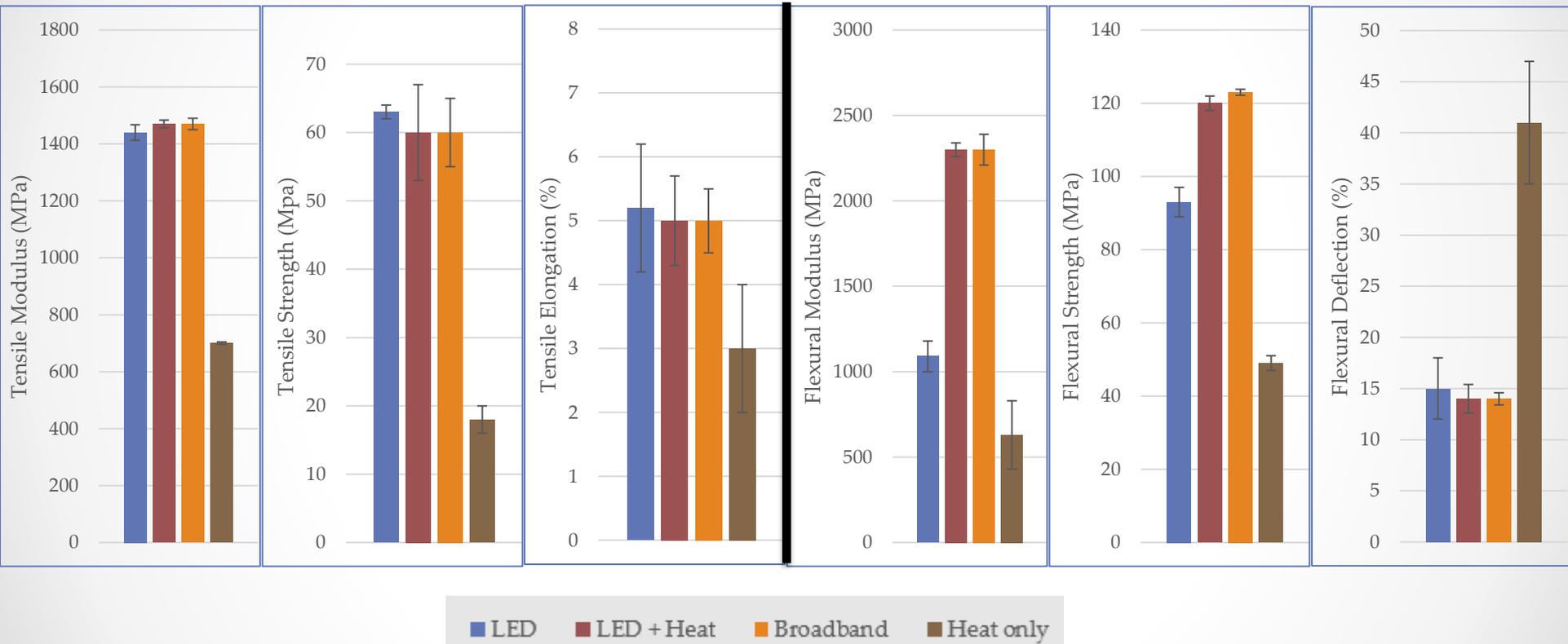
Propagation



Thiol-Acrylate Mechanism and Characteristics

- Combination of chain growth and step growth mechanisms
 - Chain transfer reduces stress and glass transition width (heterogeneity)
 - Delayed gel point- more complete conversion
- Very fast cure times
- Large tool box of commercial monomers
- Good photoinitiator selection for popular wavelengths
- Reduced shrinkage
- Reduced oxygen inhibition

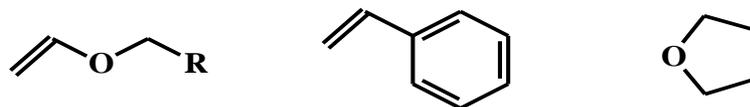
Thiol-Acrylate Results



- More homogeneous network
- Very fast cure times

Hybrid Mechanism

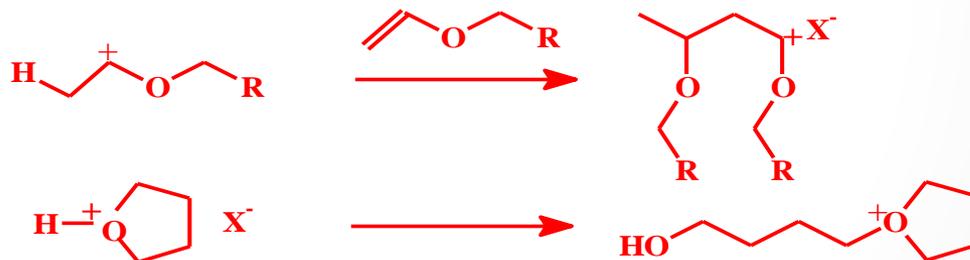
Monomers



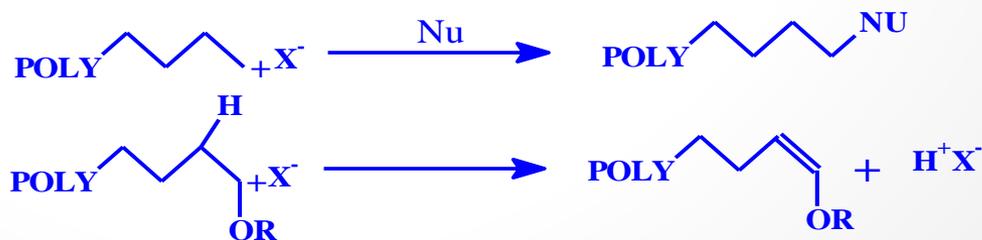
Initiation



Propagation



Termination

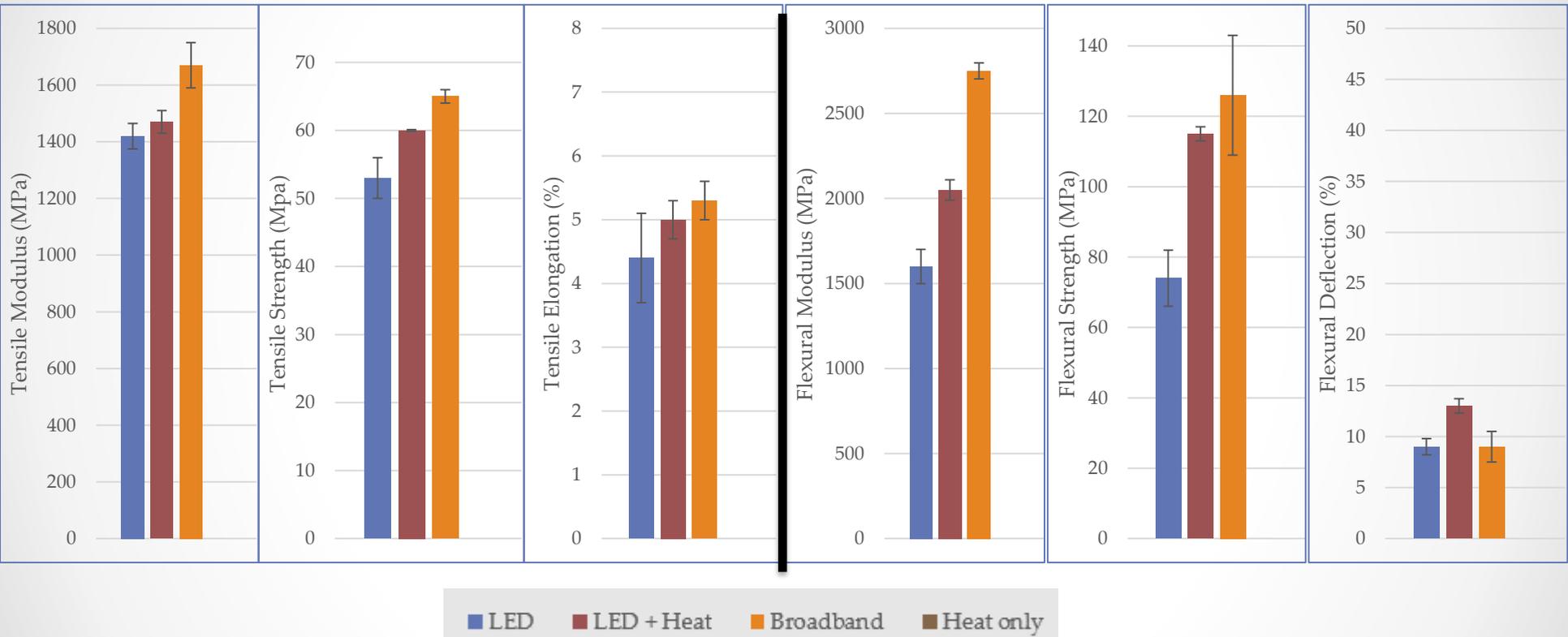


Hybrid Characteristics

- Chain growth-hybrid network
- Slower cure speeds
- Reduced shrinkage over acrylate
- Potential for dark cure

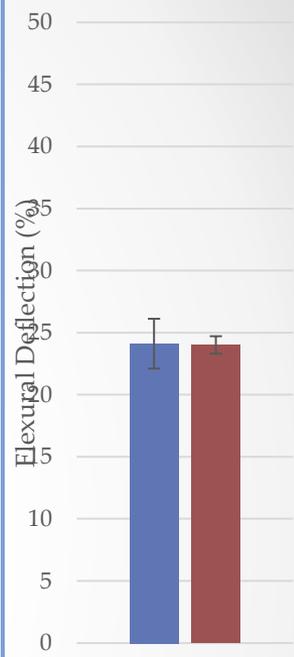
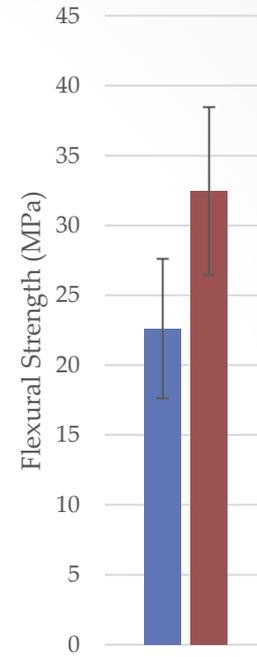
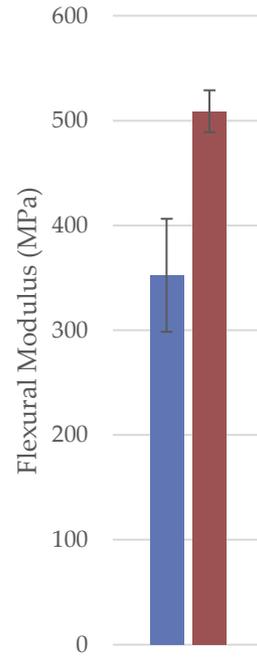
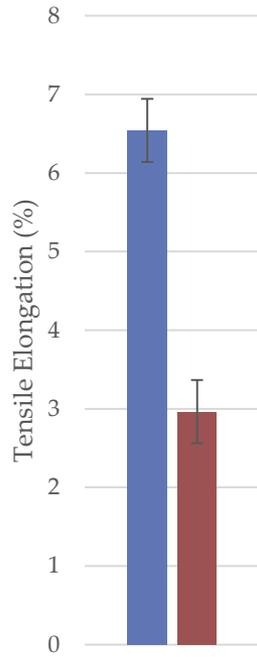
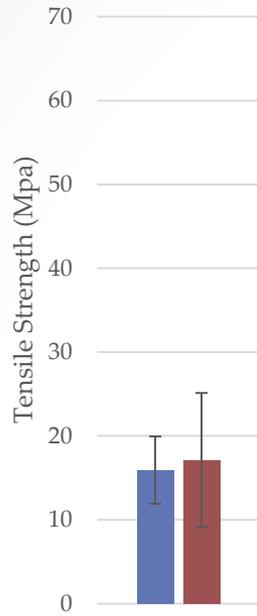
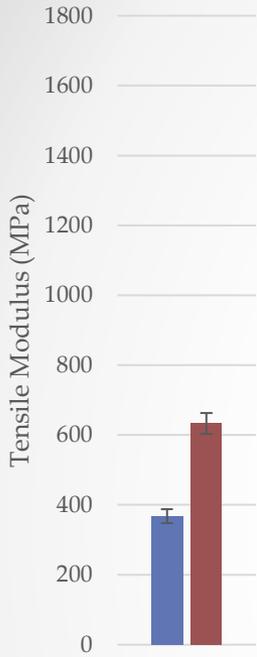
- Cationic cure is not inhibited by oxygen
- Limited number of cationic materials
- Not usually printed at 385+ nm

Hybrid Results



- Exhibited the biggest difference from LED+heat to broadband light
- Highest overall modulus

Hybrid Results



■ Hybrid 100°C 1 hr

■ Hybrid 150°C 1 hr

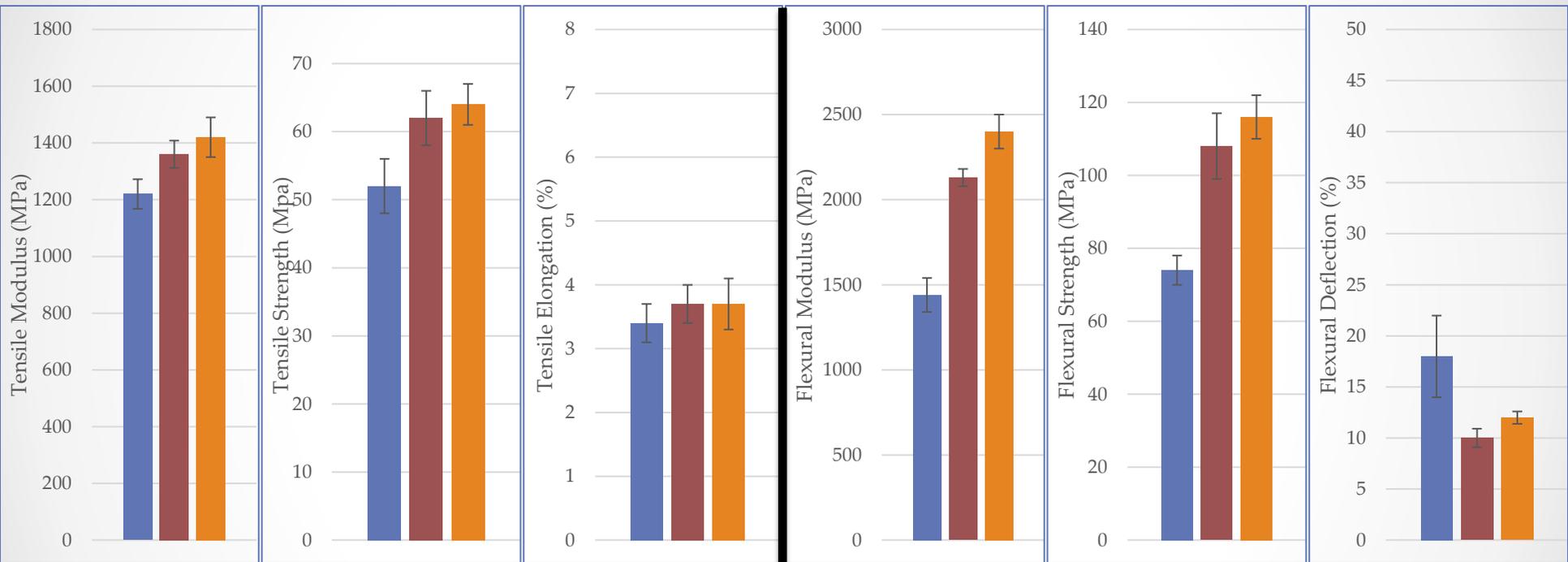
- Time between printing and post-curing is important
- Temperature of post-cure is important

Types of Fillers

- Unfilled- 500 cPs
- Alumina
 - 10 μm
 - Methacrylate treated
 - 10%- 560cPs
 - 40%- 1300 cPs
- Silica
 - 0.5 μm
 - Methacrylate treated
 - 10%- 1100 cPs
 - 18%- 2250 cPs
- Fillers can reduce shrinkage in highly crosslinked systems
- Improve temperature properties



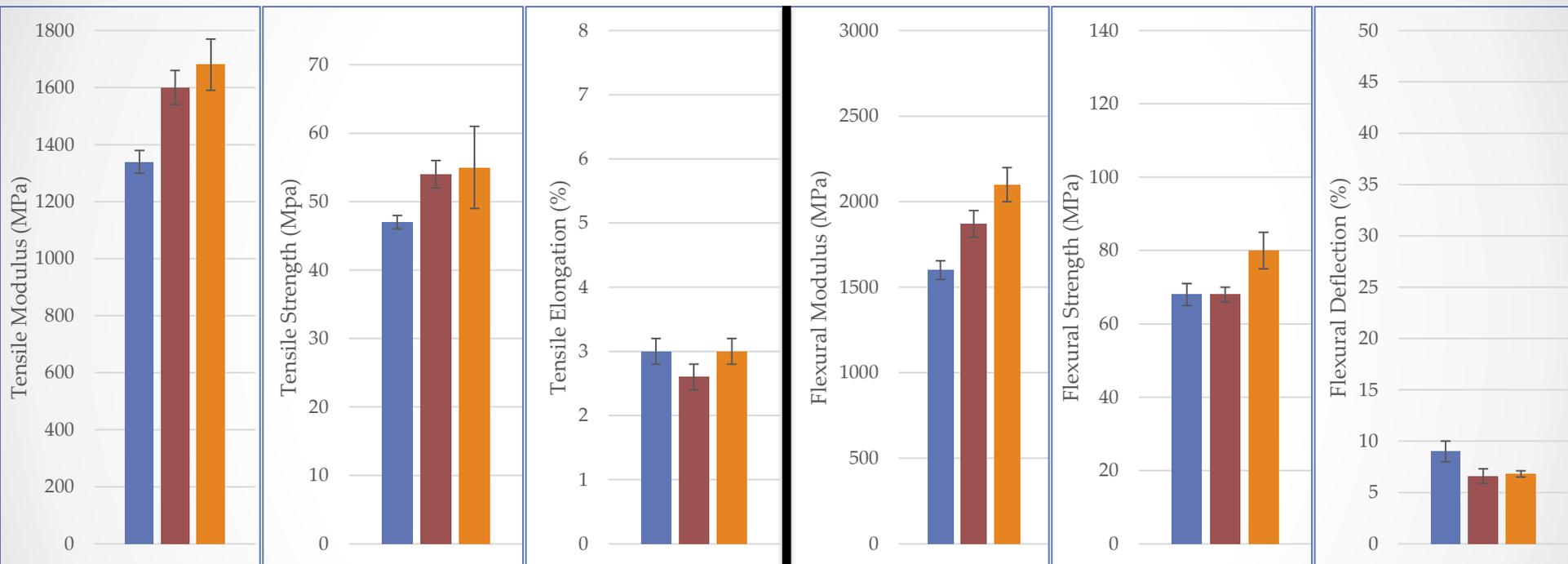
Acrylate Material filled with 10% Alumina



■ LED ■ LED + Heat ■ Broadband

- Reduced Elongation/Deflection from unfilled data
- Similar trends to unfilled material

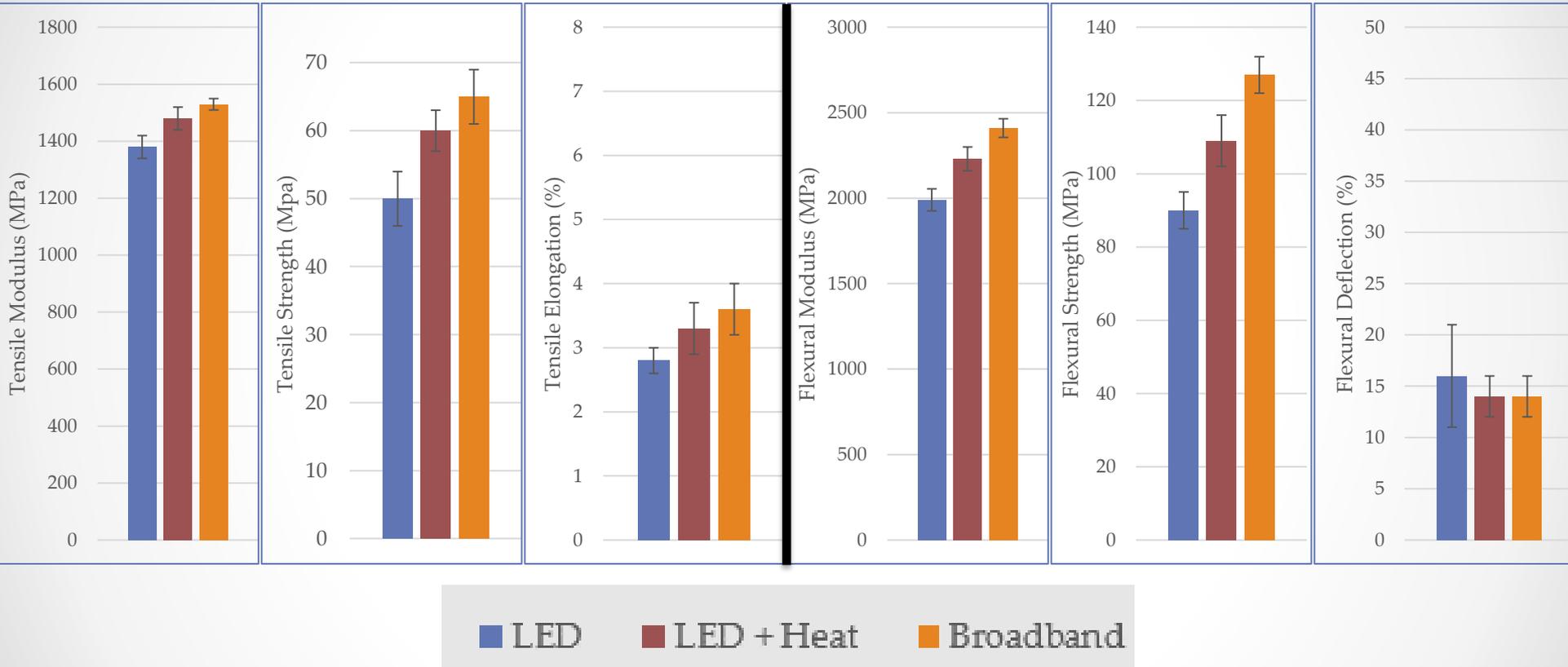
Acrylate Material filled with 40% Alumina



■ LED ■ LED + Heat ■ Broadband

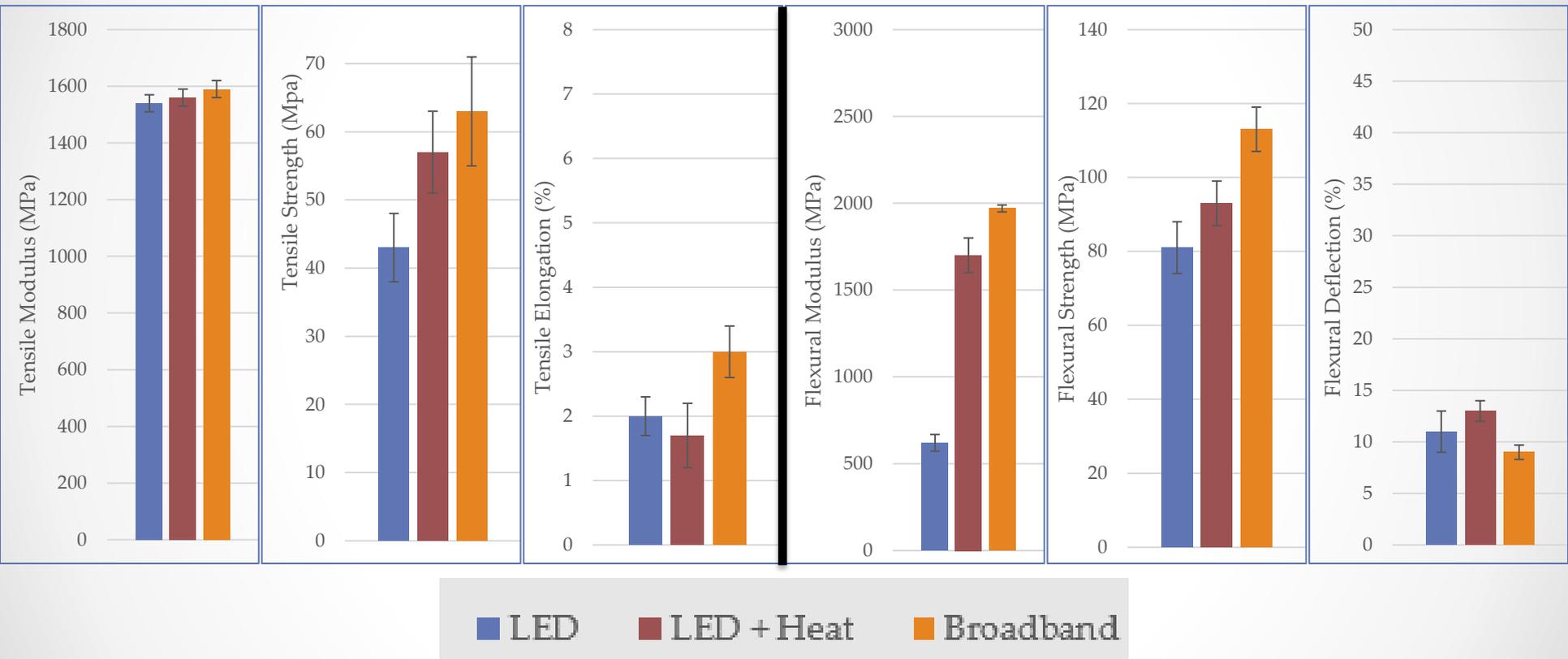
- Improved Modulus from 40%
- Optimized ratio for desired properties

Acrylate Material filled with 10% Silica



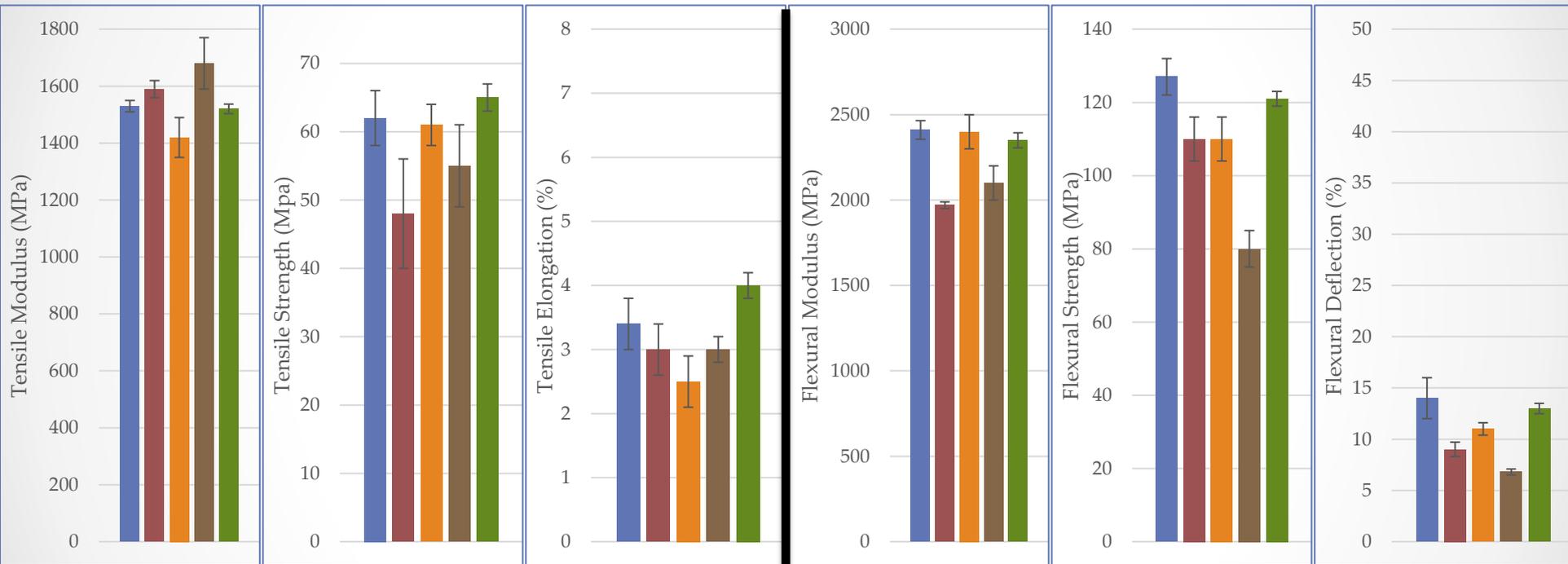
- Similar trend from unfilled material
- Unexpected improved elongation with additional curing

Acrylate Material filled with 18% Silica

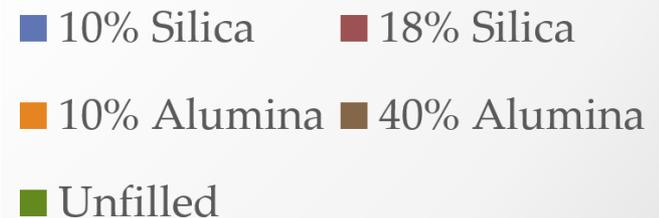


- Improved Modulus over 10% Silica
- Reduced Elongation over 10% Silica
- Optimized amount for desired properties

Filler Comparison- Broadband UV



- Fillers generally reduced Elongation/Deflection
- Find optimized amount and type of filler



Comparison of T_g (°C)

Formulation	LED	LED + Heat	BB
Acrylate	90	104	140
Hybrid	-	-	163
Thiol Acrylate	-	-	132
10% Alumina	-	-	148
40% Alumina	-	-	144
10% Silica	-	-	149
18% Silica	-	-	153

- More thorough curing leads to high T_g
- Hybrid gave highest overall T_g
- Fillers led to higher T_g

Theory on Observations

- Systems vitrify such that no additional cure will happen until the part is above the T_g of the material and loose ends can move again.
- Hybrid materials benefit more from broadband light
- Optimized amounts and types of filler can give ideal material properties and heat responses

Conclusions

- High temperature materials benefit from higher temperature post curing, with the best usual results coming from a Broadband UV set up
 - However, if a Thiol-acrylate is used, LED + heat may be enough to bring the materials up to it's full properties.
- Fillers can be used to raise the Tg of already high temperature materials
 - They require the same post-cure conditions of unfilled materials
 - Need to be optimized to reach ideal properties

Thanks!

Colorado Photopolymer Solutions

Amelia Davenport

Amelia.davenport@cspolymers.com

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