HIGH PERFORMANCE MATERIALS DEVELOPED FOR 3DP

CHRISTOPHE DUQUENNE
WILLIAM WOLF
SEAN NUNEZ
KYLE SNOW

N3XTDIMENSION BY ARKEMA

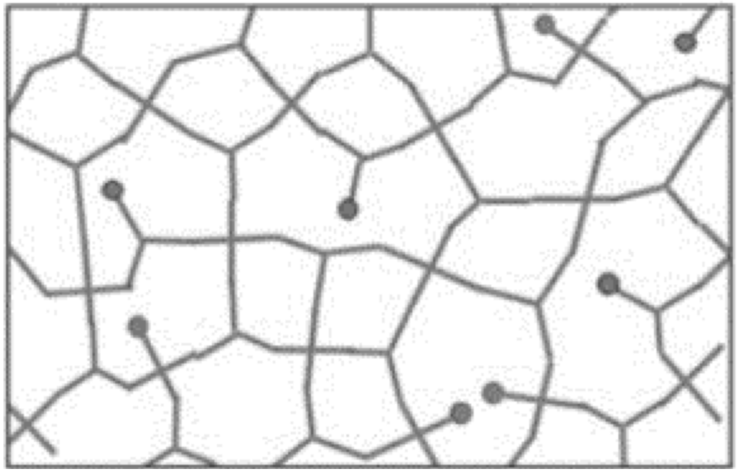
UNIQUE 3D PRINTING NEEDS

Photopolymer Framework

- Combination of thermosetting reactive species commonly acrylic or epoxide

- **Monomers**
  - Acrylic or (meth)Acrylic functionality
  - Often responsible for providing viscosity and cure speed for select platforms

- **Oligomers**
  - High Viscosity, low MW pre-polymers
  - Often provide performance enhancements to Physical Properties of final photopolymer



Thermoset Network

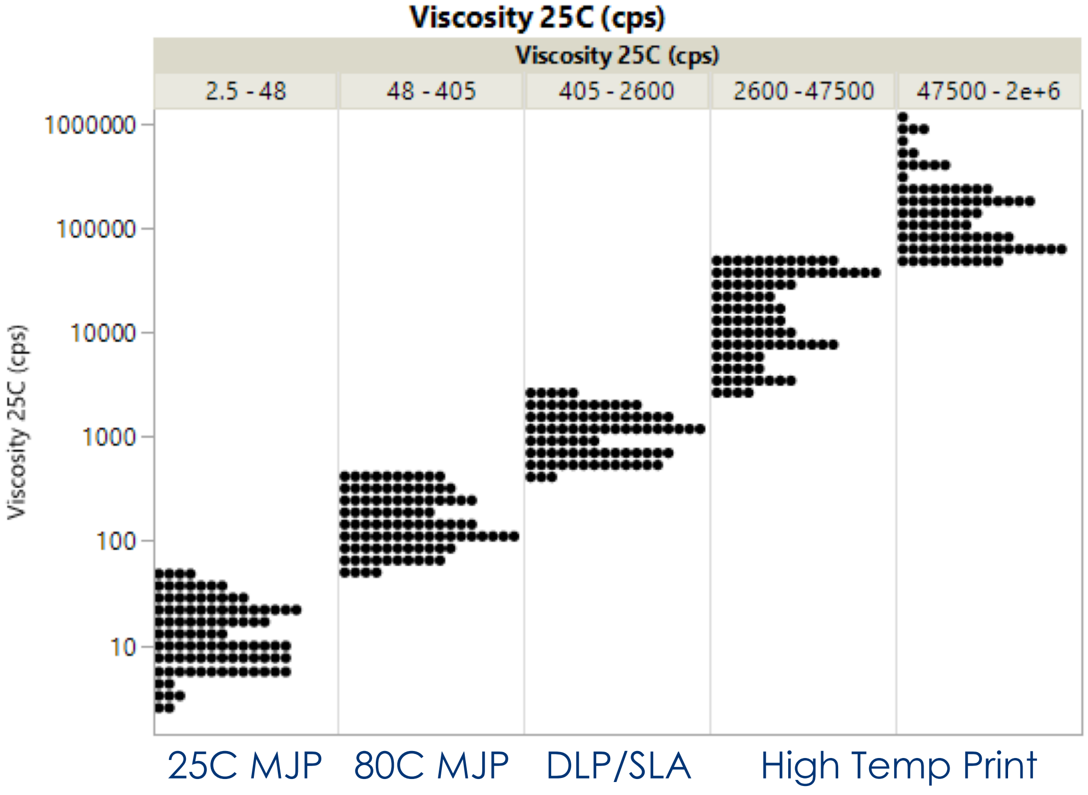
UNIQUE 3D PRINTING NEEDS

Material Science Challenge

- Reponses to stress is very different in the materials 3D printing aim to emulate.
  - **Thermoplastics** respond through their elastic component and creep over time
  - **Thermosets** will balance elastic and viscous contributions equally

Equipment Advances

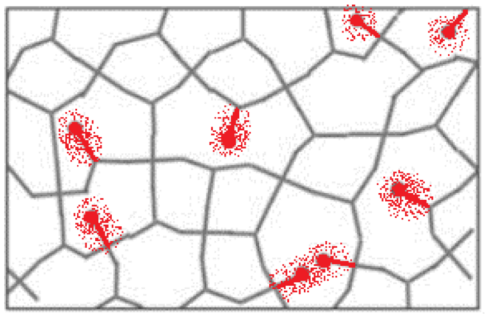
- Novel equipment expand design box
- Handling higher viscosity materials enables access to more diverse chemistry



Number of Materials driven by Viscosity Class

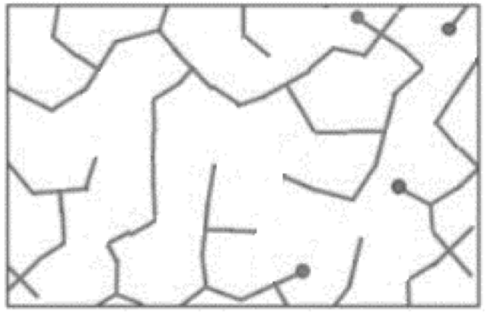
TYPICAL MATERIAL STRATEGIES

Designed Composition



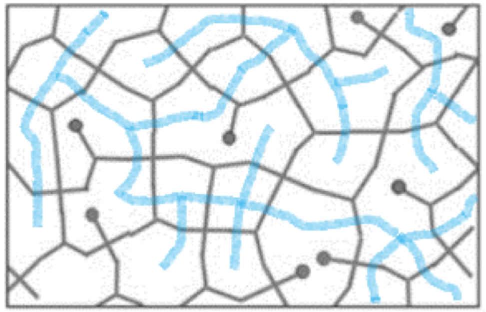
Compositionally designed to maximize particular criteria in photopolymerization.

Network Engineering



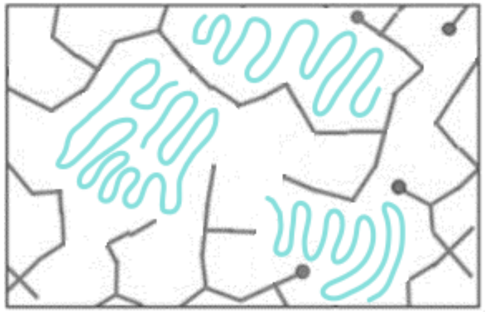
Design of crosslink density and tuning of intermolecular forces

Interpenetrating Network



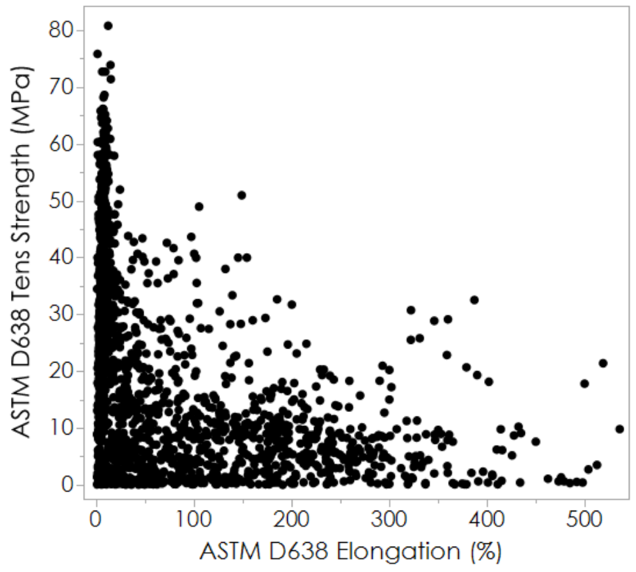
Dual orthogonal networks copolymerizing in symphony.

Photopolymer Composite



Design of microstructure where the sum of the whole is greater than the individual components

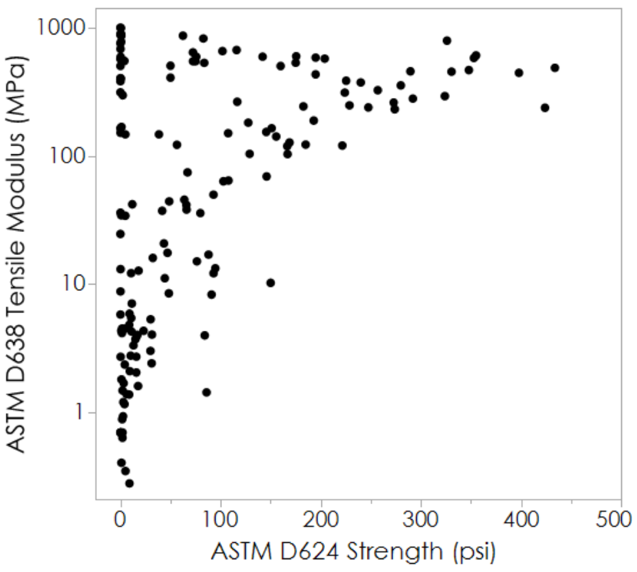
UNIQUE 3D PRINTING NEEDS ADDRESSED WITH NOVEL MATERIALS



Abs-Like

Strength, Modulus, Elongation
Thermal Resistance
Impact Resistance
Shrinkage

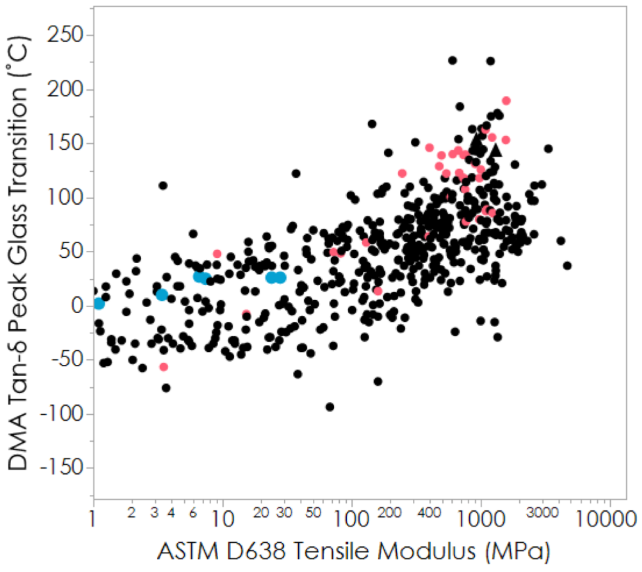
Development in this area with M1



Elastomeric

Strength, Modulus, Elongation
Tear Strength
Resilience

Developments supported by M2



High HDT

Physical Property Balance
Thermal Resistance
HDT, Onset, Tg

Developments supported by M3

ENHANCING ABS QUALITIES

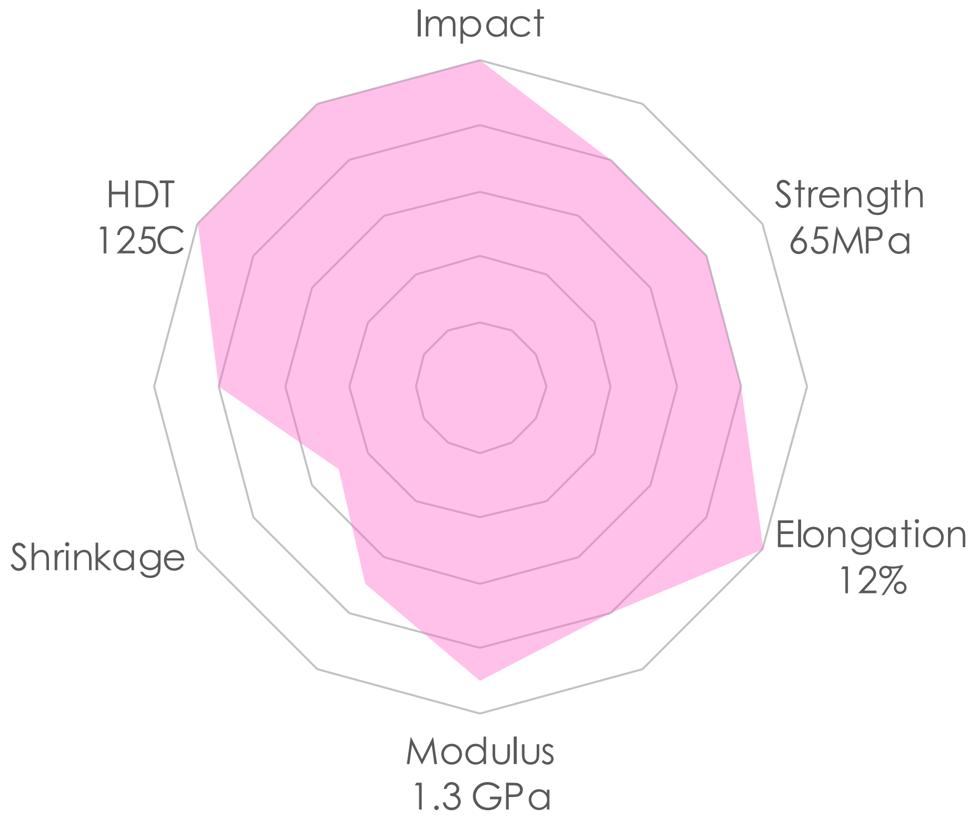
Beyond Physical Properties

- Many photopolymers can achieve the modulus, strength and elongation targets
- Notched IZOD Impact resistance, for thermosets is extremely difficult

Designed Composition Approach

- Novel high Tg, low shrinkage monomer developed to enhance these areas

PROPERTY BALANCE



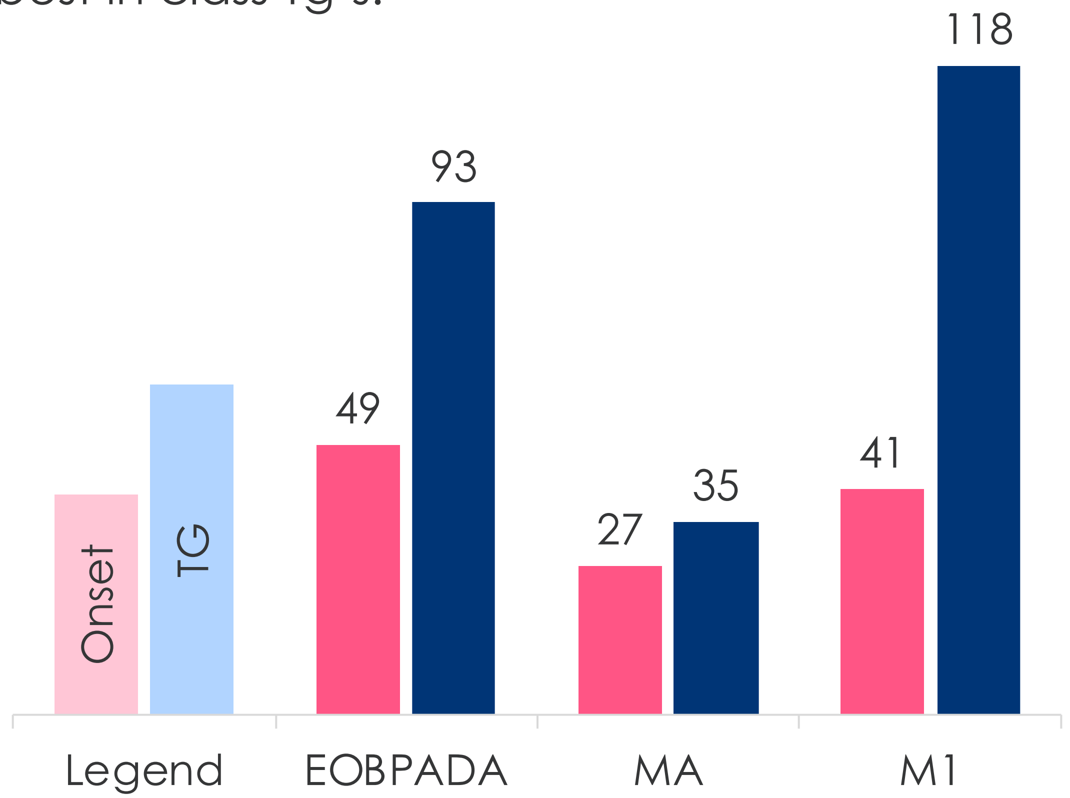
ENHANCING ABS QUALITIES

Comparative Study

- We typically observe lower functionality to result in softer, lower Tg photopolymer
- M1 shows an ability to provide maintain Onset/HDT values and provide high TG capabilities

Description	EOBPADA	MA	M1
Trifunctional URAC	50	50	50
EO BPA DA	50		
MA		50	
M1			50
Speedcure TPO-L	+1	+1	+1

M1 shows thermomechanical values similar to difunctional acrylics and best in class Tg's.



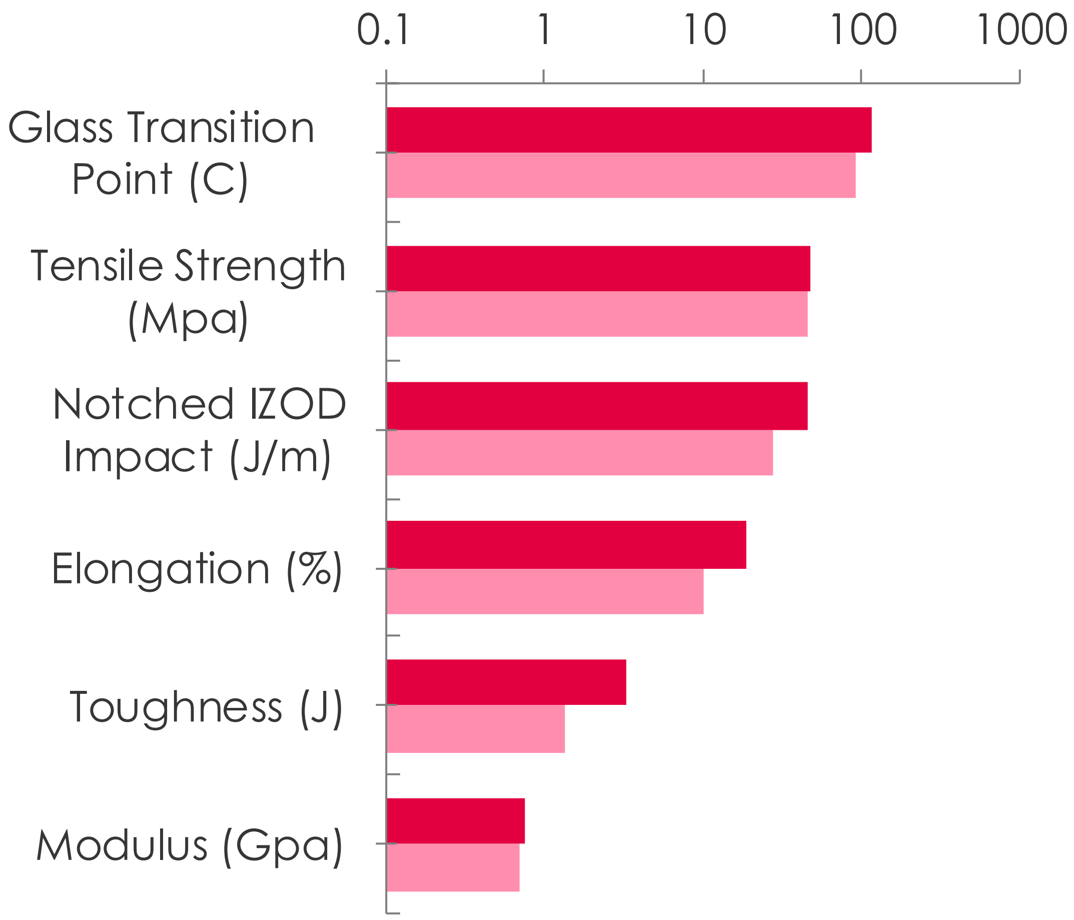
ENHANCING ABS QUALITIES

Comparative Study

- We typically observe lower functionality to result in softer, lower Tg photopolymer
- M1 provides properties similar to performance acheived with high shrinkage materials

Description	EOBPADA	MA	M1
Trifunctional URAC	50	50	50
EO BPA DA	50		
MA		50	
M1			50
Speedcure TPO-L	+1	+1	+1

Higher desire-able properties identified through the entire scope of study

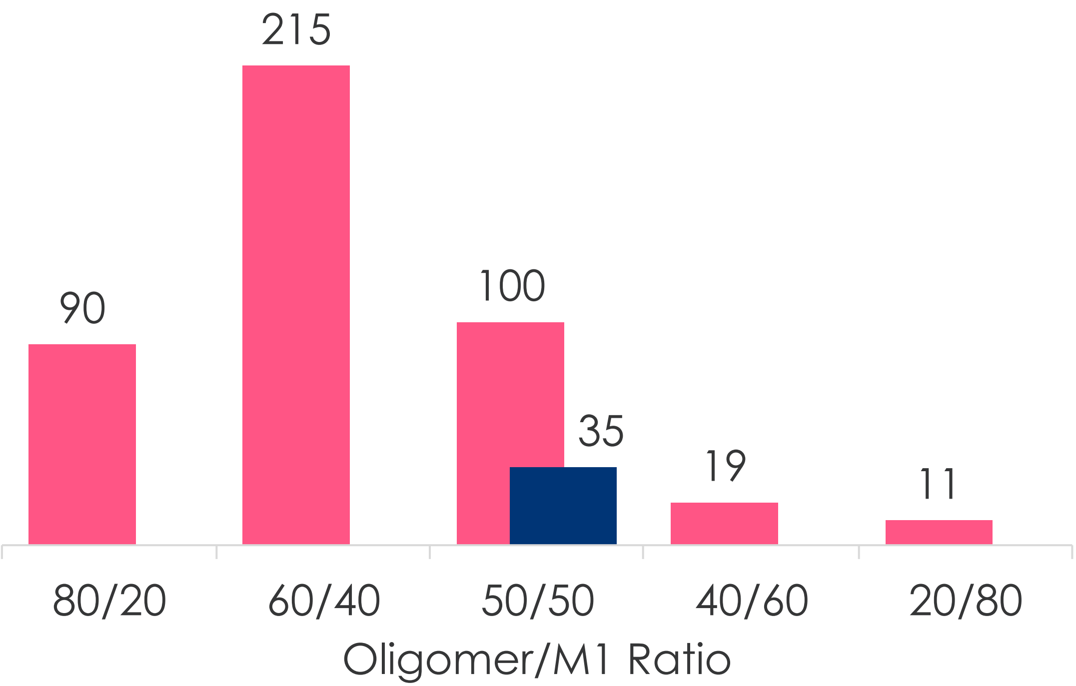


ENHANCING ABS QUALITIES

Ladder Study

- M3 demonstrated some marketed enhancements over IBOA at a 50/50 comparison for impact resistance.
- General trends show an optimum related to impact resistance towards the higher viscosity end of the spectrum.

M1 show's delivering enhanced impact resistance over a range



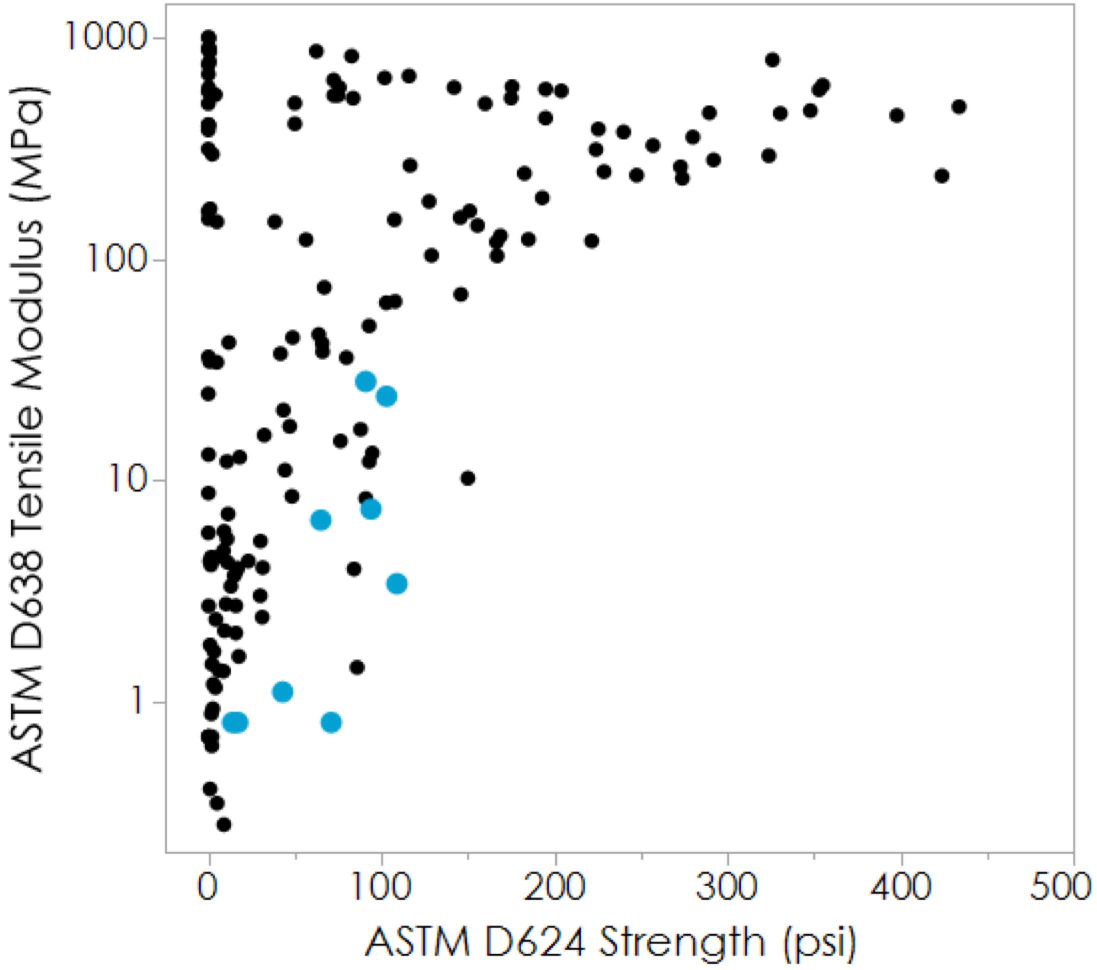
ENHANCING FLEXIBILITY

Beyond Physical Properties

- Tensile property balances are already well covered by photopolymers
- Low modulus, high tear strength is difficult

Designed Composition Approach

- Novel monomer delivers low Tg and capitalizes on key intermolecular forces
- Low glass transition point pulls the photopolymer into a rubber state at 25C
- Low toxicity requirement, enables exploratory applications



ENHANCING FLEXIBILITY

Material Design

Use of low Tg, monofunctional materials is a common strategy to achieve highly flexible systems. This particular avenue is targets reduced hazards of a highly polar monomer.

Physical Assessment

Experimental results surrounded around (2) strategies to suggest promising vectors with use.

Printability

The ultimate test in our material development pipeline.

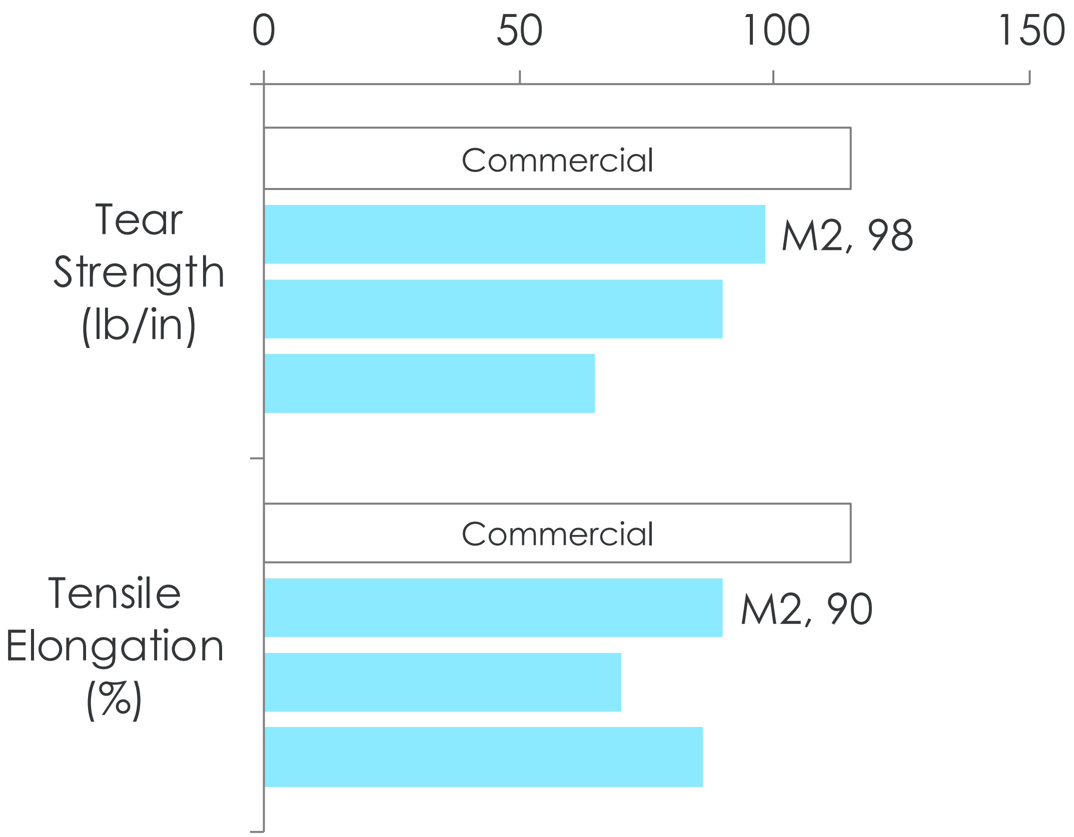
ENHANCING FLEXIBILITY

Comparative Study

- Use of monofunctional, low Tg monomers enable soft material development
- Compared to other highly polar monomers tear and elongation elevated
- Against commercial resin systems, performance is below but promising

Description	MB	MC	M2
Low MW UR Diacrylate	60	60	60
MB	40		
MC		40	
M2			40
Speedcure TPO-L	+1	+1	+1

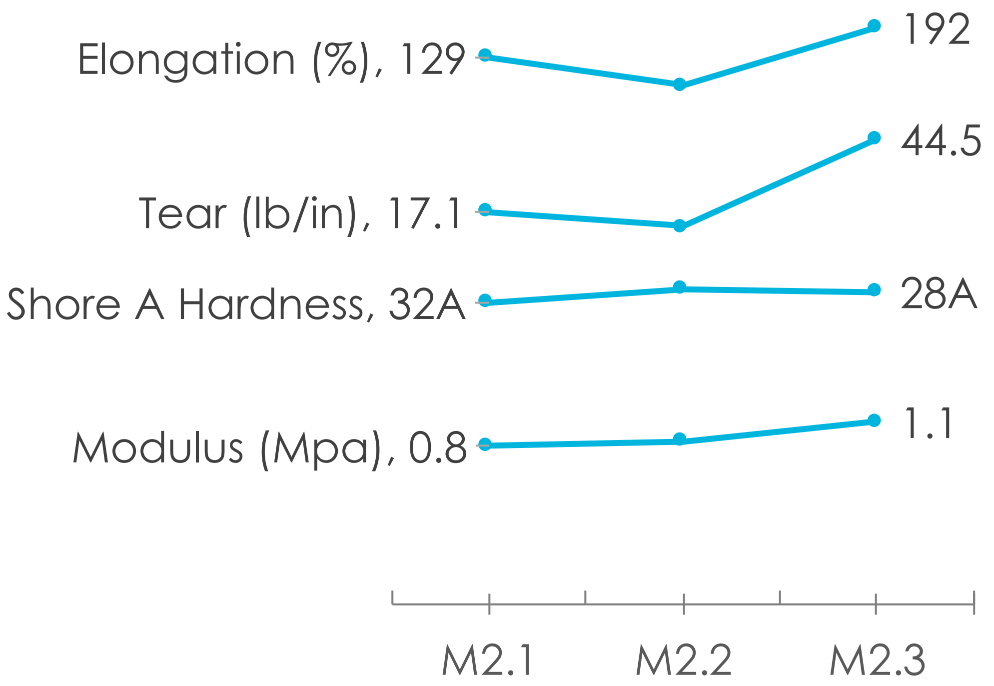
M2 show's comparable performance to other in-class highly polar monomers



ENHANCING FLEXIBILITY

Ladder Study

- M2 shows increase's to elongation and tear while maintaining polymer softness
- Slight increase's in modulus were found as M2 concentrations increased.



Description	M2.1	M2.2	M2.3
High MW URAC	20	20	20
High Tg Monomer	35	35	35
Low Tg Monomer	20	20	20
M2	15	25	35
Speedcure TPO-L	+1	+1	+1

Use of M2 show's performance trends akin with low Tg monomers while enhancing properties related to elastomer.

ENHANCING FLEXIBILITY

Ultimate Research Hurdle: Printability

Further Observations

- **Challenging to resolve fine features**
  - Fine Feature resolution depends heavily on the materials ability to build Green Strength
  - M2 delivers enhanced resolution through an accelerated modulus build.

- **Color Difference apparent**
  - Major differences in the image is simple replacement of M2.
  - Raw material quality can have a significant impact on resulting color after post-cure.

Printed on an AnyCubic LED-DLP System
30 s / layer with 5 wt% TPO-L

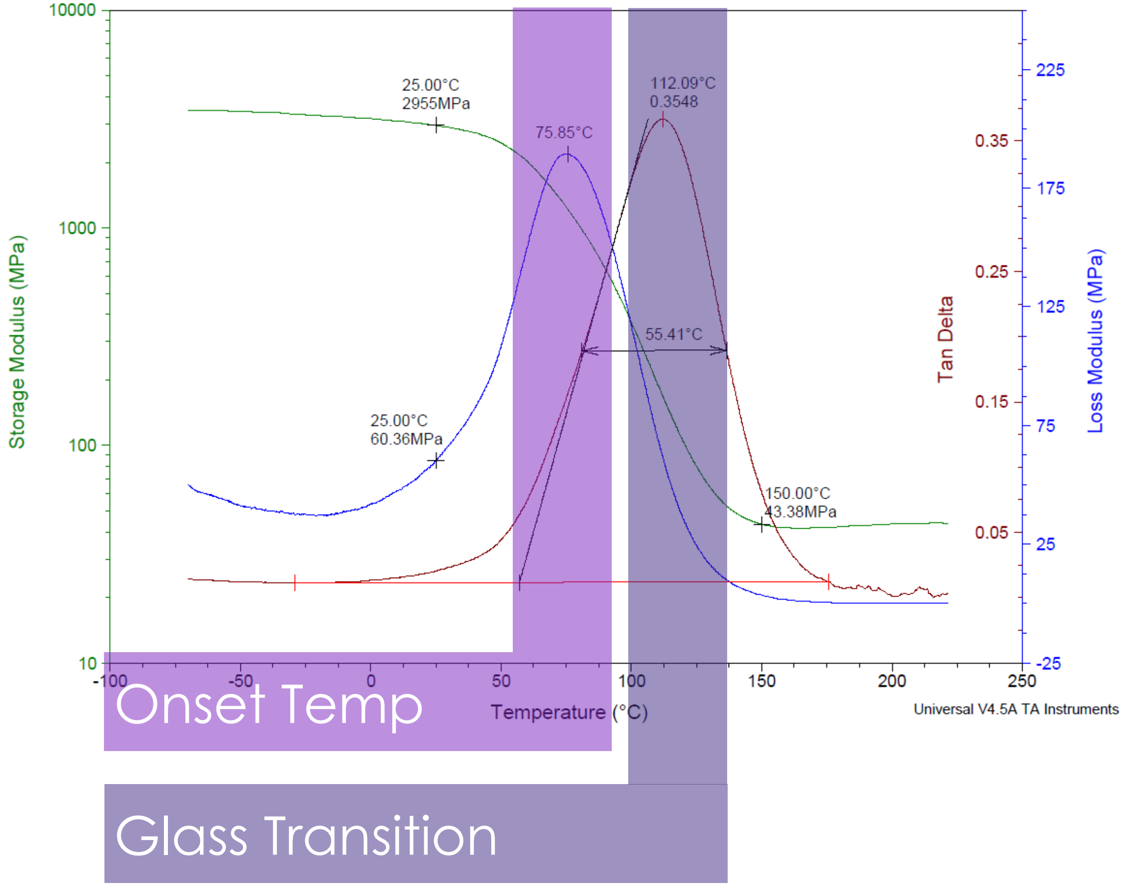
ENHANCING TEMPERATURE RESISTANCE

Beyond Physical Properties

- Photopolymers with temperature resistance is within the capabilities of acrylic systems
- Enhancing durability of these systems, is a one of the more challenging items
- Many strategies invoke shrinkage and embrittlement needing careful tuning

Designed Composition Approach

- Novel material aims to provide hydrogen bonding, and limit crosslink density



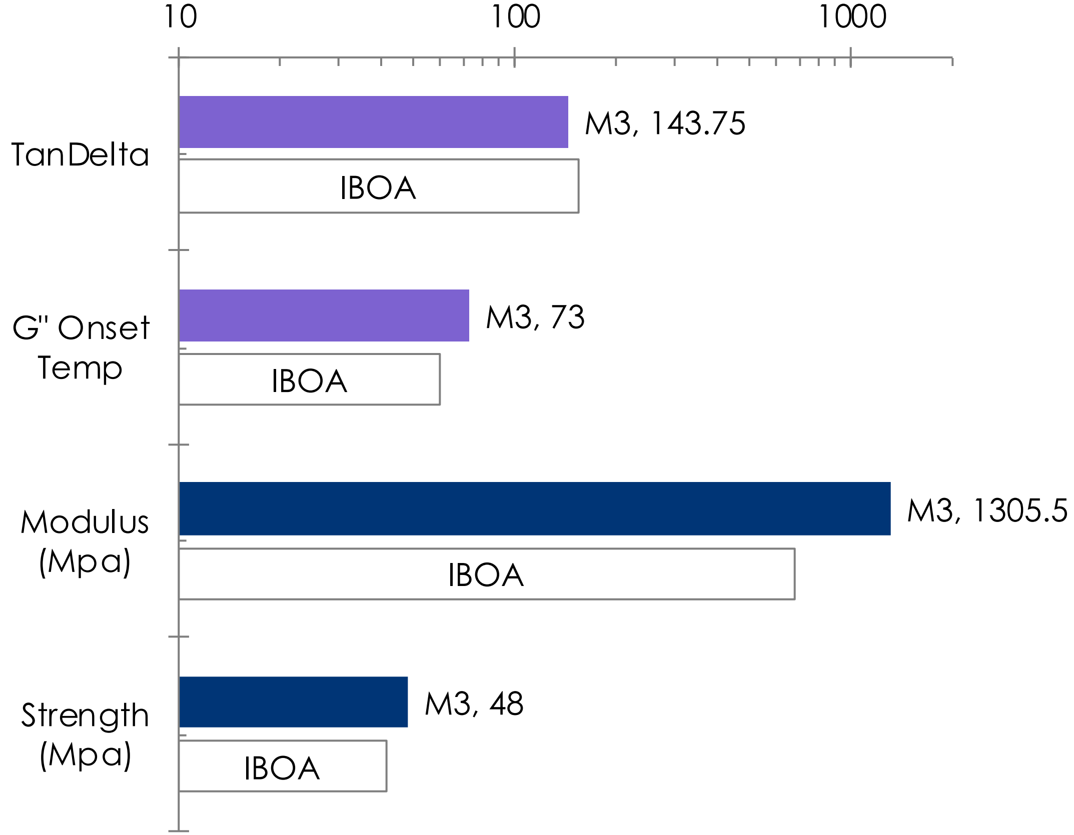
ENHANCING TEMPERATURE RESISTANCE

Comparative Study

- Against other high Tg monofunctional monomers we enhanced the G" onset.
- Wide range of physical durability seems to affect highly rigid photopolymers
- Use of M3 shows marked improvements over odorous analogs such as IBOA

Description	IBOA	MD	M1	M3
UDMA	80	80	80	80
IBOA	20			
MD		20		
M1			20	
M3				20
Speedcure TPO-L	+1	+1	+1	+1

M1 and M3 showed higher resistance to temperature and stress levels



CONCLUSION

Fundamental approach

- Extends application performance and ultimate adoption of photopolymers.
- Enables interesting balance of properties over traditional materials used industrially

Development Strategy

- Often a balance of properties can bring you into the ballpark
- Each application requires that little extra push to take it over the finish line.

?