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Sandia National Laboratories

THERMOMECHANICAL PROPERTIES OF POLYUREA NANOCOMPOSITES OVER EXTREME STRAIN RATES

Jessica Kopatz, Elizabeth Jones, Brett Sanborn, Justin Wagner, Christopher Riley & Christine Roberts

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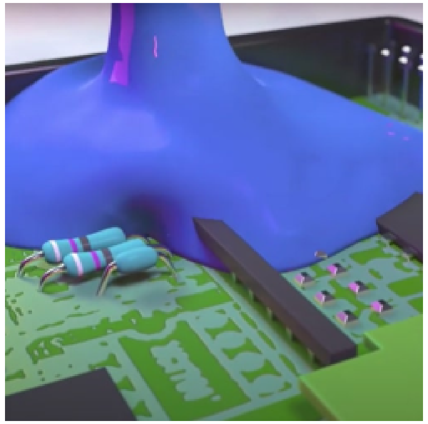
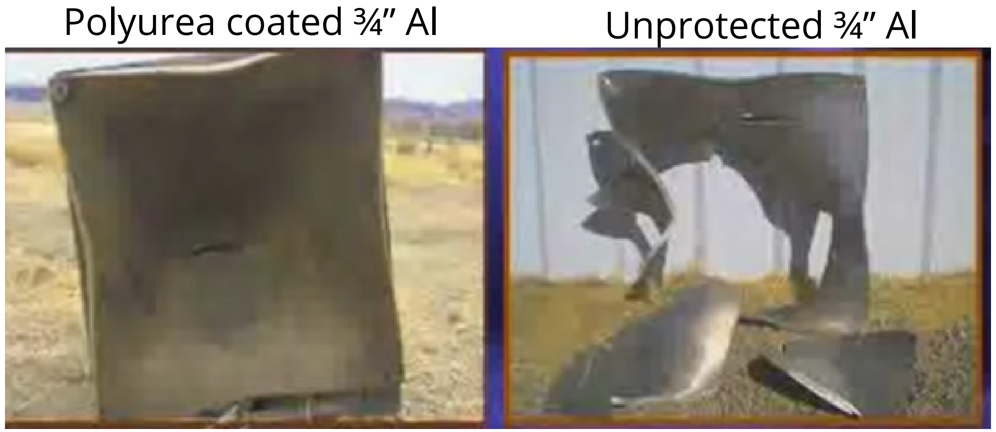
POLYUREA NANOCOMPOSITES FOR ENHANCED PROTECTION

Polyurethane uses:

- Foams
- Encapsulants
- Adhesives



Polymer-g.com



Credit: Dragonshield polyurea (TDI)

Commercial uses for Polyurea:

- Encapsulants
- Abrasion/corrosion protection
- **Blast/ballistic protection**

Hypothesis:
Polyurea nanocomposites can be engineered to be superior, multifunctional protection and dampen mechanical and thermal shock

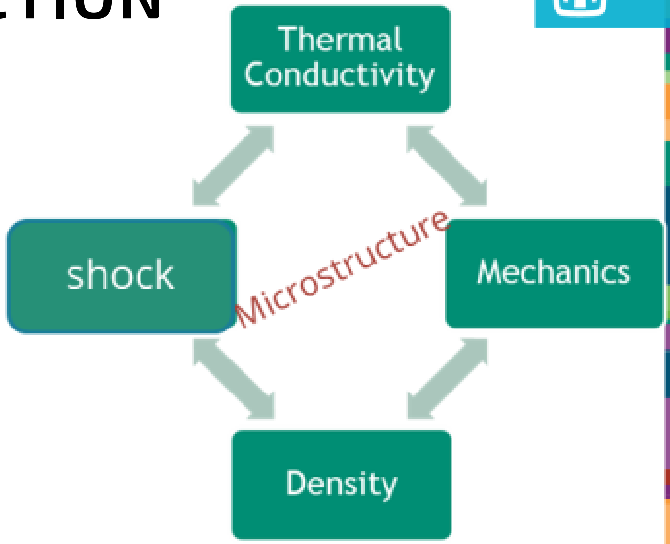
Line-X

Benefit of nanocomposites

- Mechanical properties, thermal degradation, thermal conductivity, coefficient of thermal expansion

POLYUREA NANOCOMPOSITES FOR ENHANCED PROTECTION

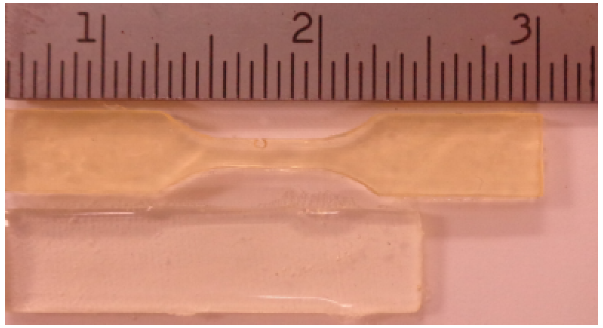
Goal: Proven, versatile matrix platform that will accept <u>any</u> engineered particle



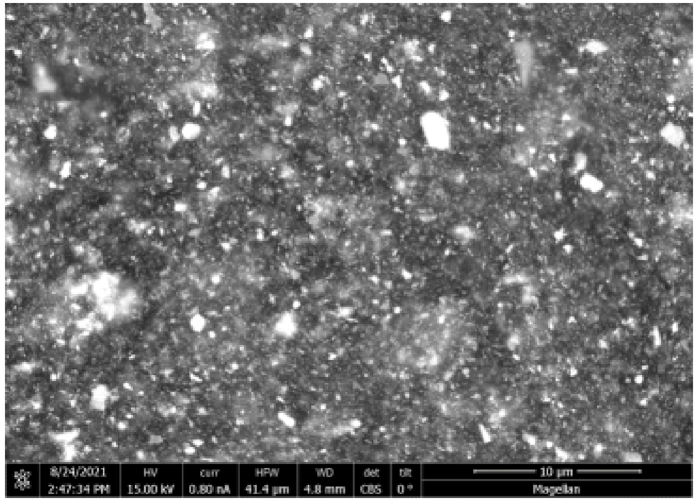
Microstructure influences all metrics of performance

Requirements:

- Nanoparticle dispersion
- High Particle-polymer adhesion
- Tailorable vol% loading



Manufacturable at large scales

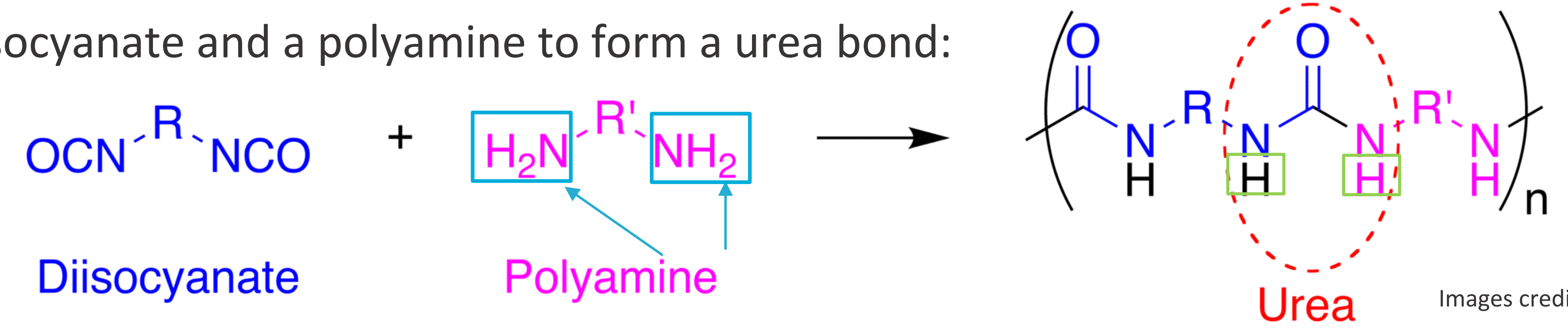


Up to 35 vol% ceria possible in dense coatings

How do polyurea nanocomposites thermo-mechanically behave across quasi-static to ballistic strain rates?

POLYMERIZATION OF POLYUREAS

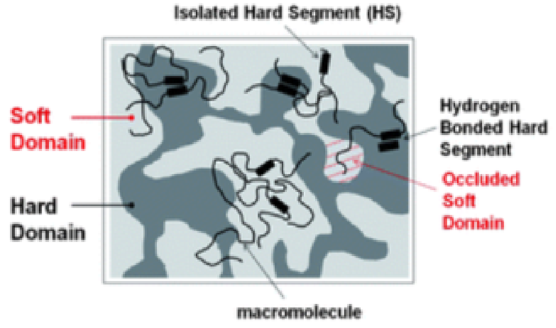
- Reacts a diisocyanate and a polyamine to form a urea bond:



Images credit: Wikipedia

****Hydrogen bonding is absent from polyurethanes****

- Identities of R and R' will influence flexibility/modulus of polyurea
  - Hard = aromatics, H-bonding
  - Soft = aliphatics (carbon chains)



Cho et al. (2012) Soft Mater

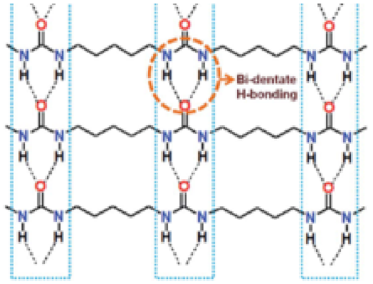


Fig. 4 Hydrogen bonding within the urea linkages in polyurea.

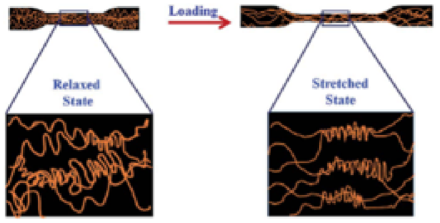


Fig. 2 Micro-structural changes in polyurea upon tensile loading.

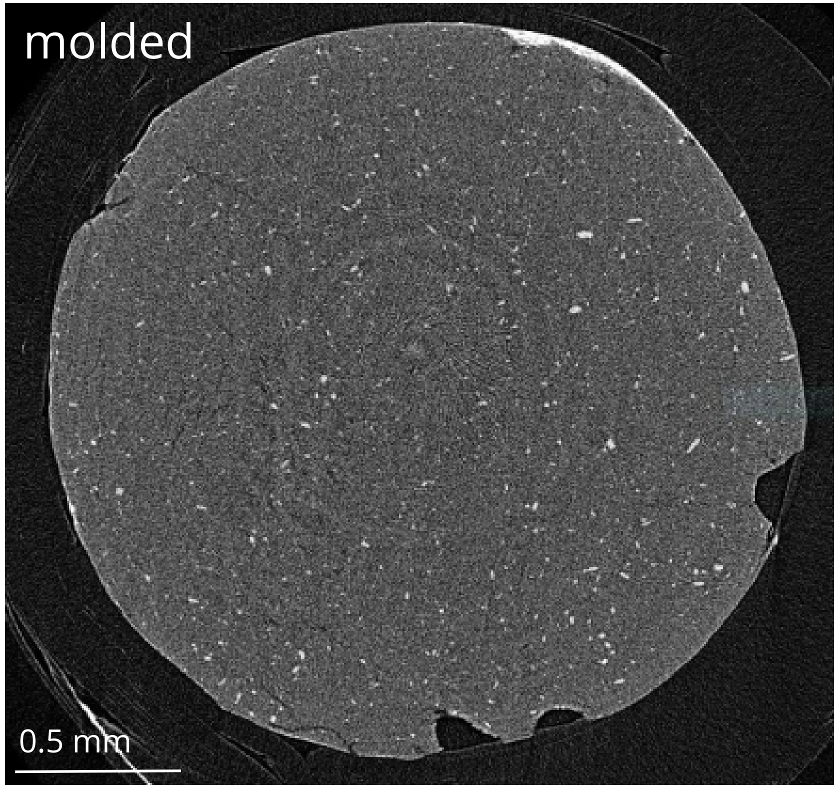
Iqbal et al. (2016) RSC Advances

Polyurea mechanics exceeds Polyurethane:
- Tolerates higher strain
- Inherently higher toughness
  - Increased energy absorbance & dissipation

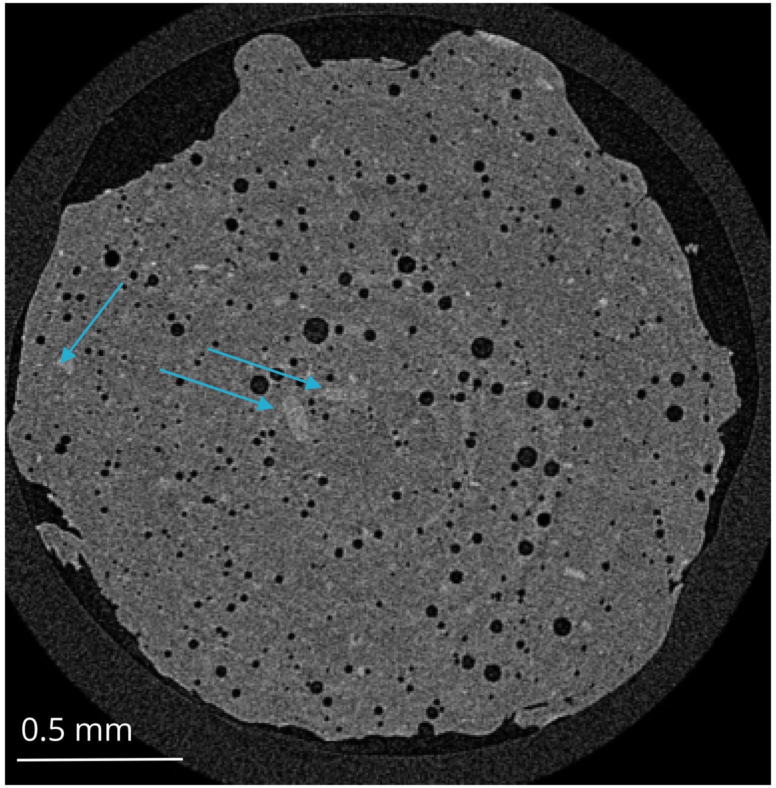
PARTICLE AGGLOMERATION IN POLYUREA

Filler	Size (nm)
Al_2O_3	400
CeO_2	10-30

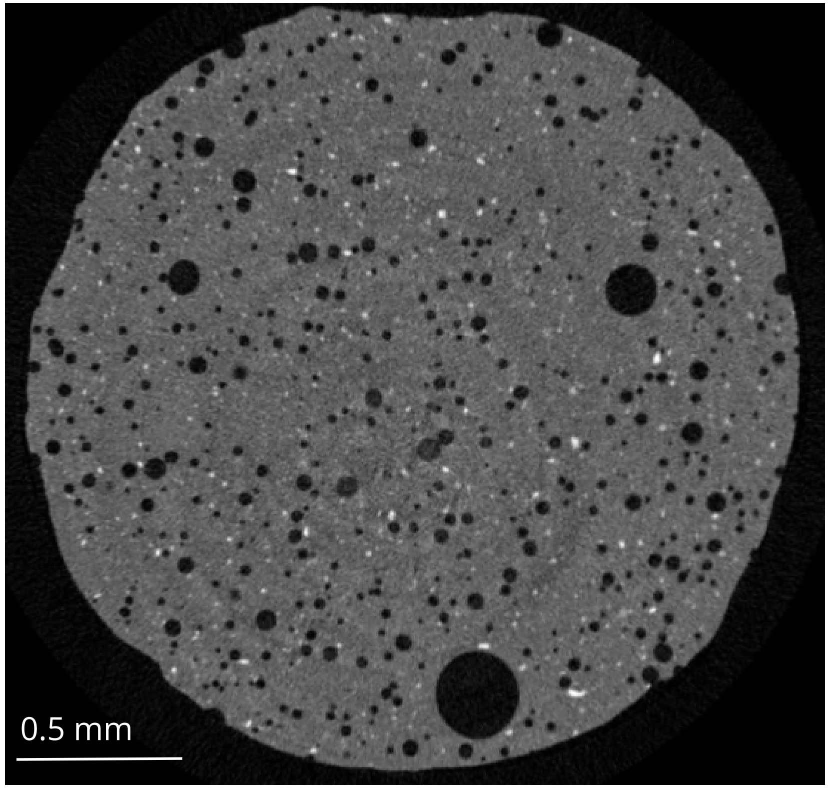
Proper surface functionalization to enable compatibility and homogeneous dispersion of the nanoparticles is necessary to realize the synergistic benefits of adding nanoparticles to the polymer matrix



20 vol% Al_2O_3



40 vol% Al_2O_3



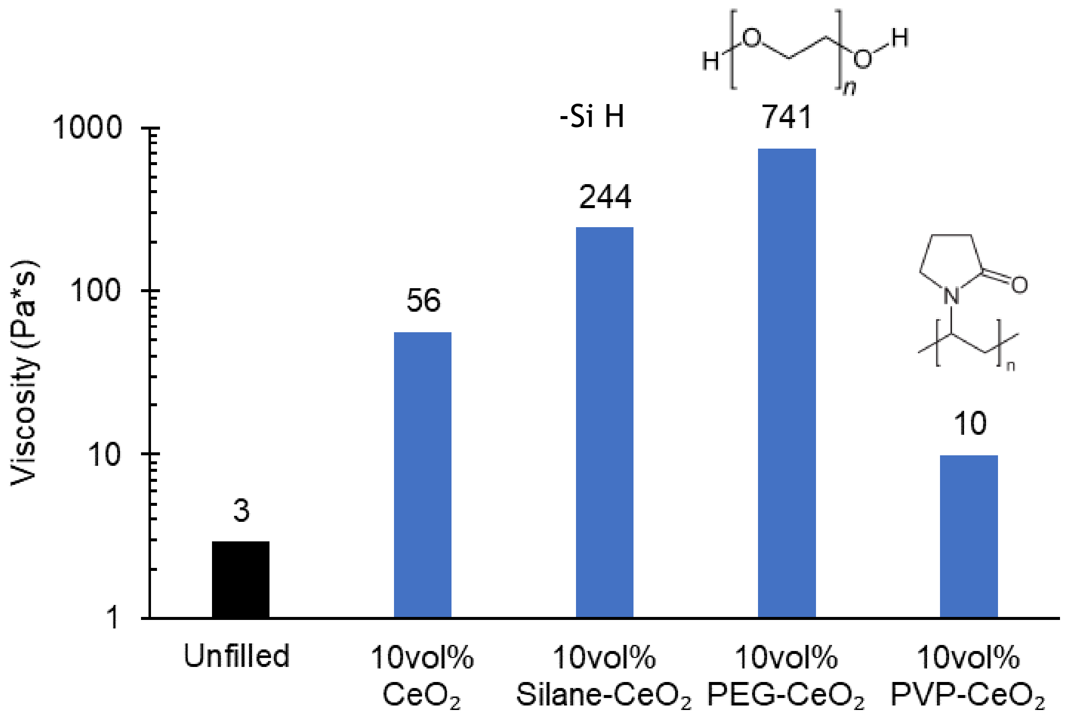
10 vol% CeO_2

Reduction of foaming reaction through limiting water exposure

SAMPLE SYNTHESIS / DESIGN

Goal: Tailorable composite, particle agnostic structure

Commercially available coated CeO_2

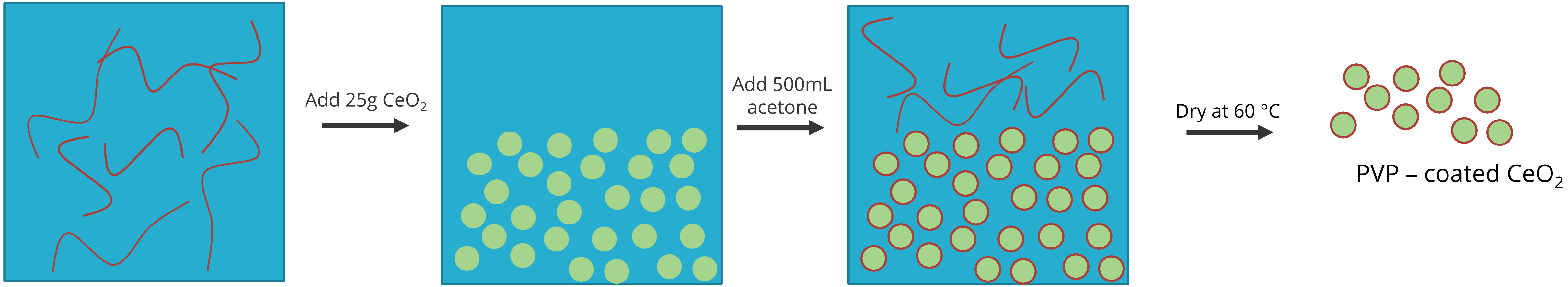


Method to determine extent of dispersion: Viscosity

Surface modification with **polyvinylpyrrolidone (PVP)** creates best compatibility with polyurea precursors due to minimal change in viscosity

Compatibility comes from similar polarity of polyurea & nanoparticle surface

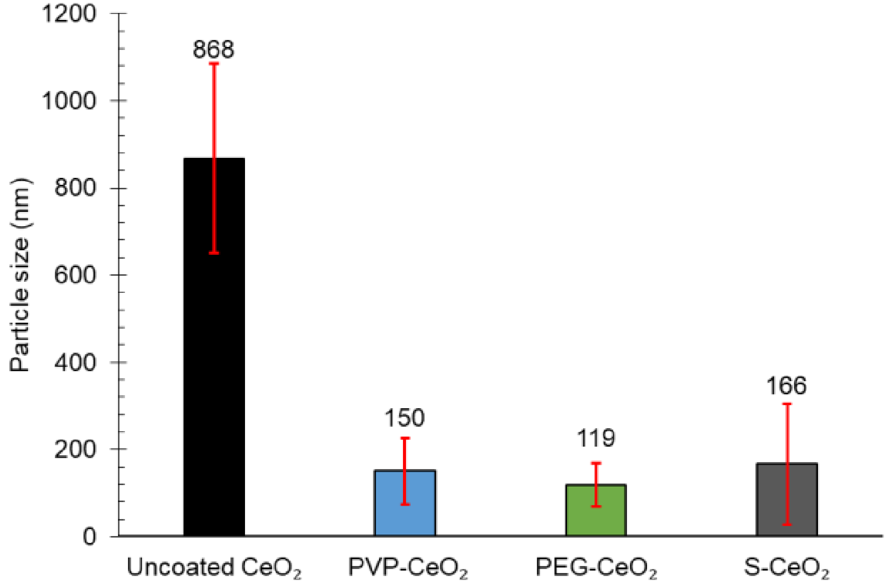
IN-HOUSE, SCALABLE PVP-COATED CEO_2 SYNTHESIS



Add & dissolve 1.5 g PVP (MW~ 10k) in 200 mL EtOH

Sonicate via cup-horn: 0.5s/0.5s total on-time: 4 hrs
Leave on bottle roller overnight

non-physisorbed PVP will separate out
Centrifuge 4k RPM, 25 min



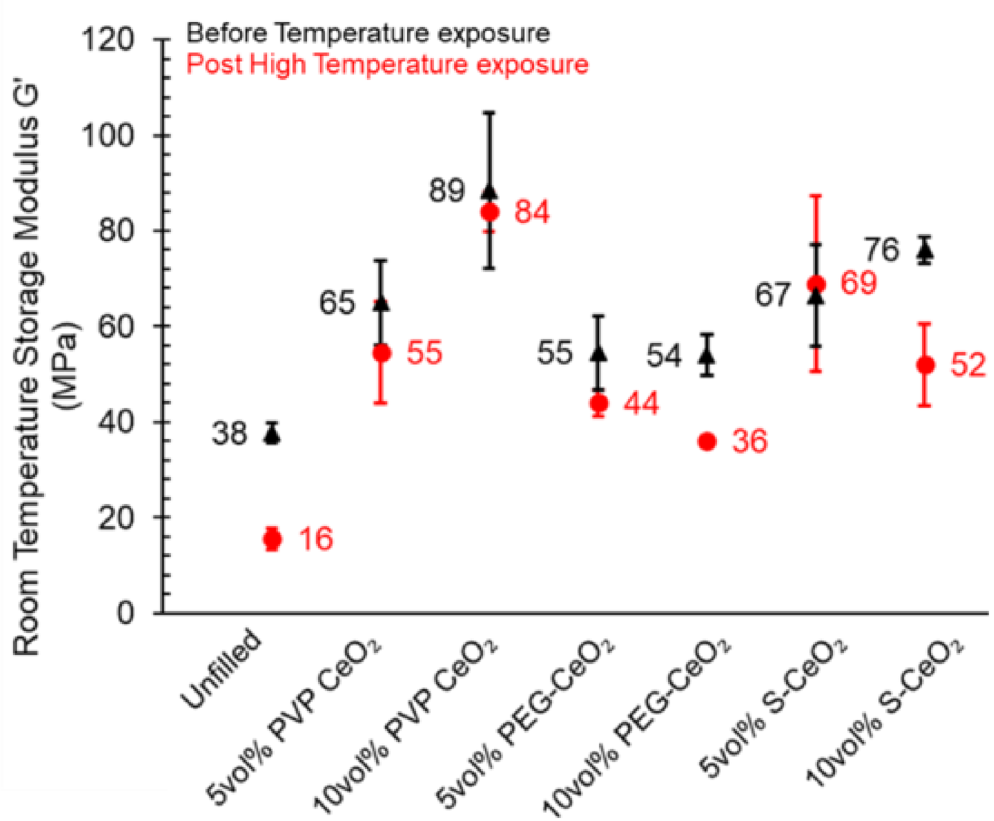
A method was created to make large-quantity batches of PVP-coated nanoparticles

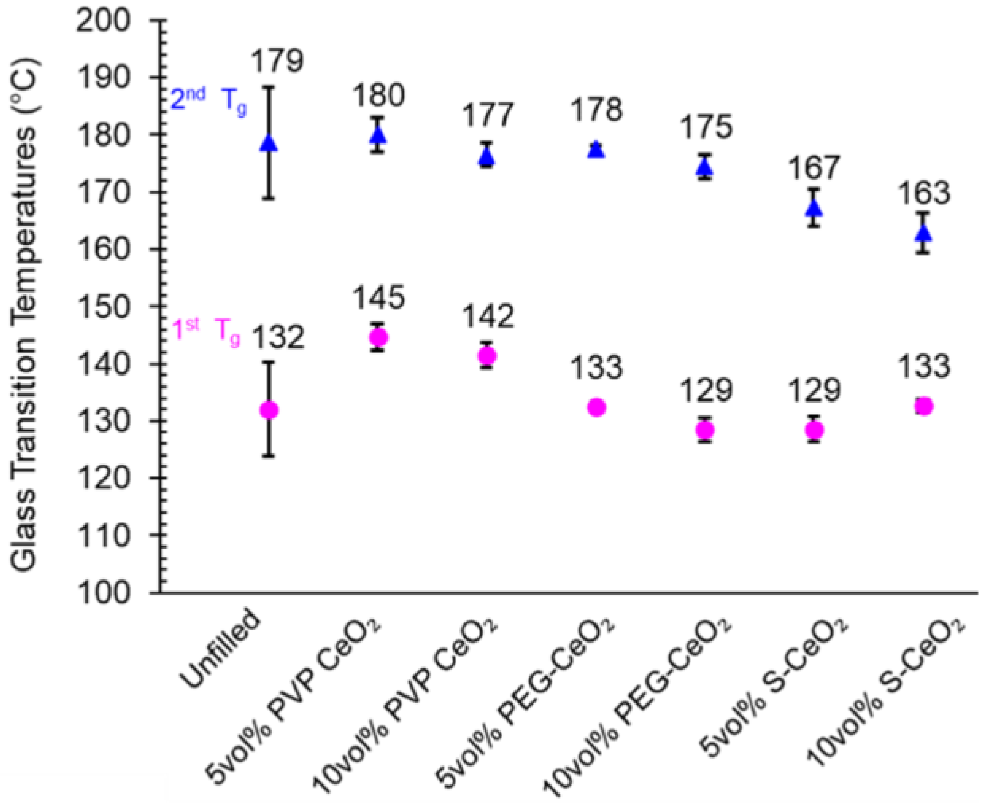
Goal: Particle Agnostic

Dynamic light scattering (DLS) utilized to determine particle size

MATERIAL PROPERTIES – DYNAMIC MECHANICAL ANALYSIS

Goal: Add functional particles without disrupting mechanics





Fillers improved thermal stability of the polyurea network

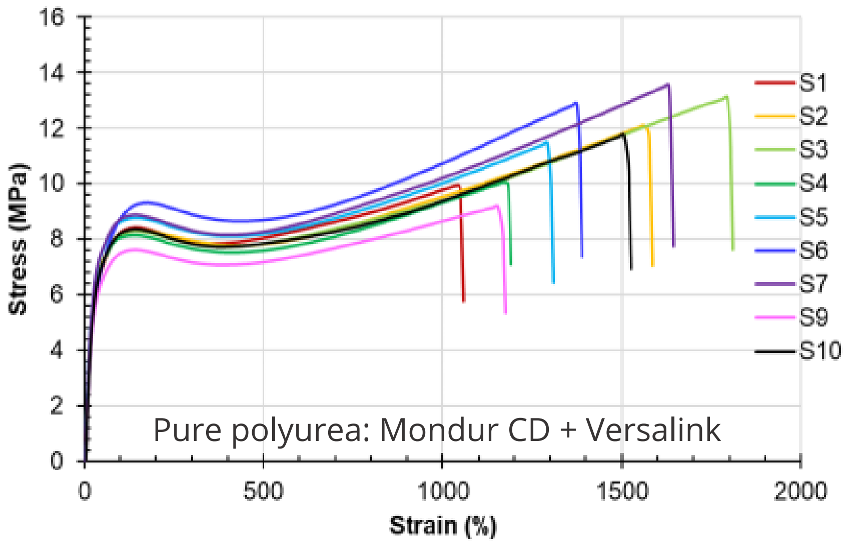
$PVP-CeO_2$ had least amount of change pre vs. post heat exposure and greatest compatibility

Glass transition is not significantly influenced by the addition of fillers

Values decreased as filler-matrix chemistry compatibility decreased

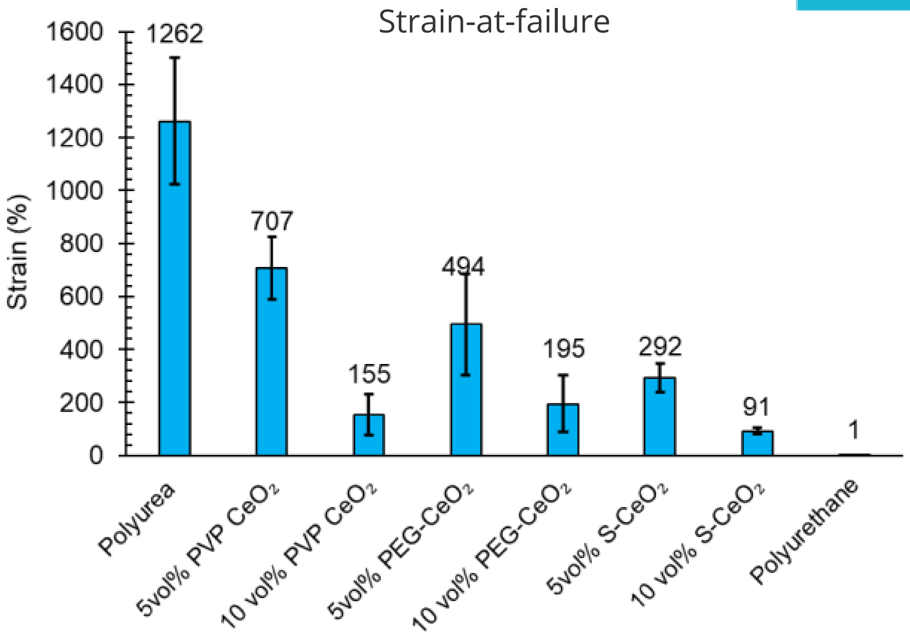
MATERIAL PROPERTIES – TENSILE TESTING

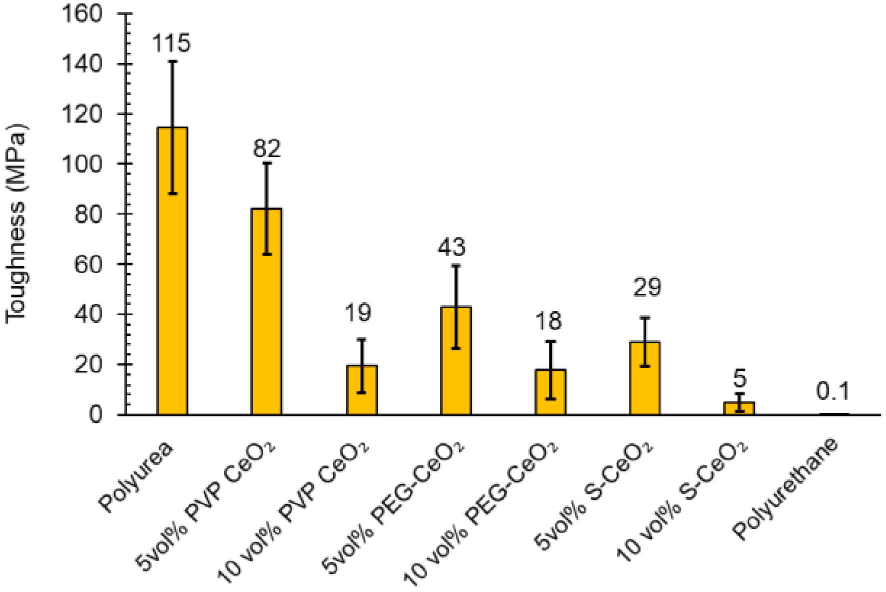
Goal: Add functional particles without disrupting mechanics



Pure polyurea: tougher than polyurethane in tension due to microstructure

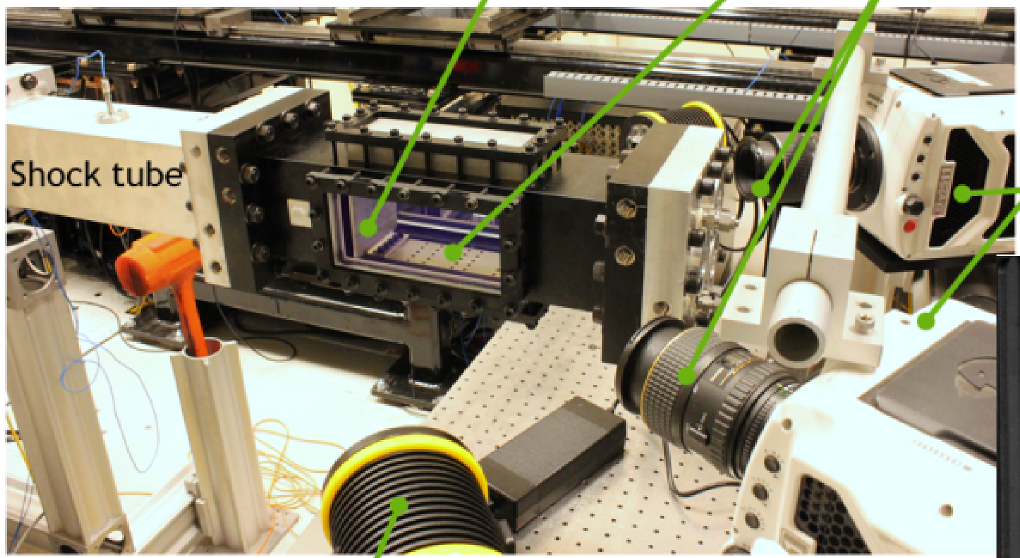
Addition of particles decreased toughness and strain-at-failure due to impeding polymer chain mobility, but PVP-coating restores some cohesive strength

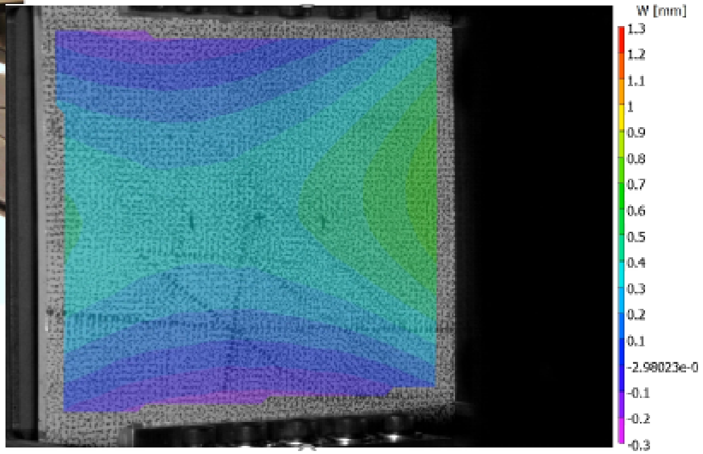




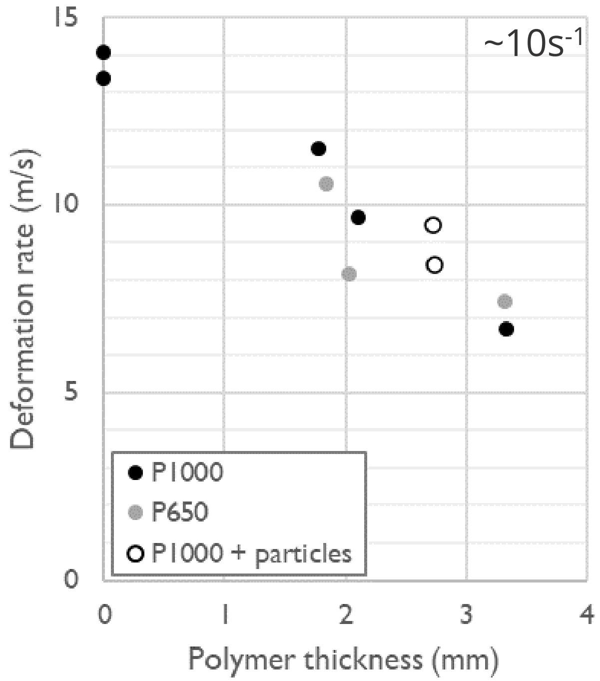
MATERIAL DYNAMICS- SHOCK TUBE

Shock tube & digital image correlation (DIC) experiments credit: Justin Wagner & Elizabeth Jones





Shock tube imposes a mach 2.5 blast of air on a 3x3 inch, 1 mm thick plate of aluminum, covered with polyurea and deflection is measured using DIC.



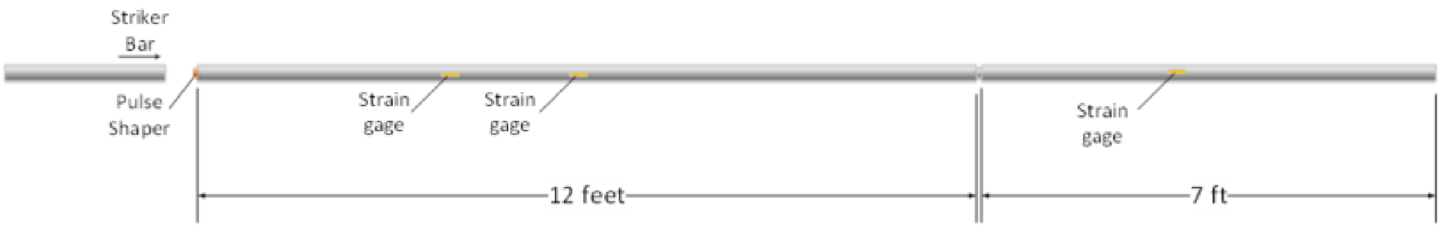
The bare aluminum plate has the highest deformation rate, whereas polyurea composites damp the impact.

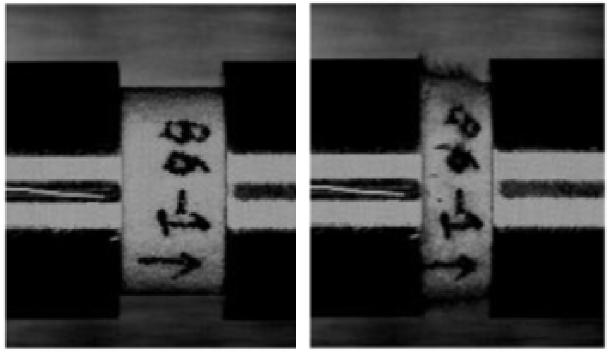
In this specific environment, polyurea chemistry and the addition of nanoparticles do not significantly affect the shock tube behavior.

Still under investigation

MATERIAL DYNAMICS-SPLIT HOPKINSON BAR

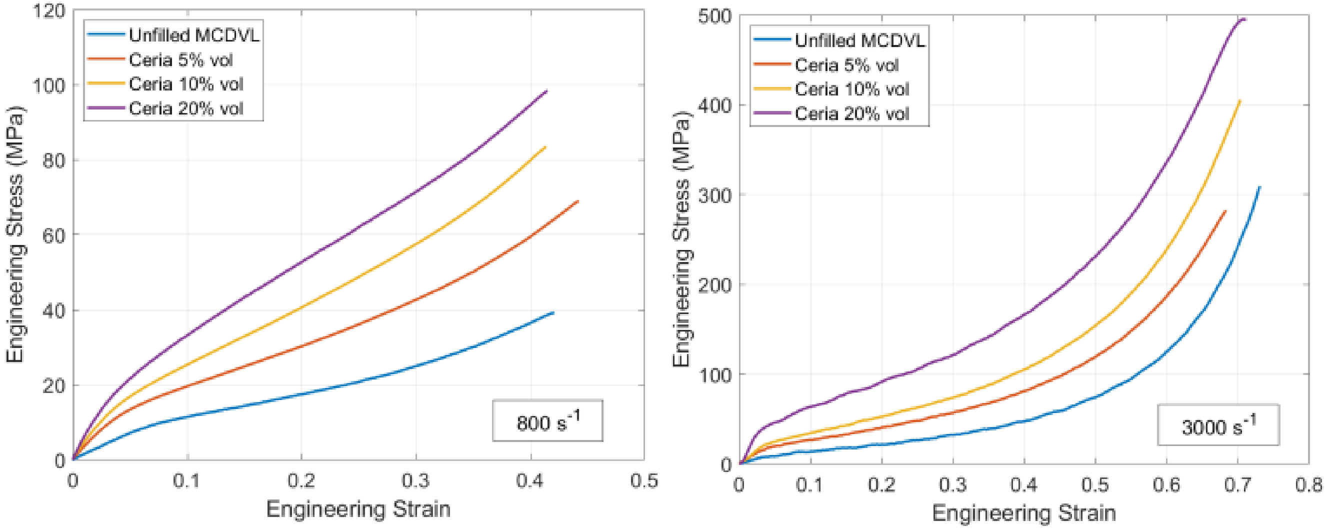
Split Hopkinson bar experiments credit: Brett Sanborn & Colin Loeffler



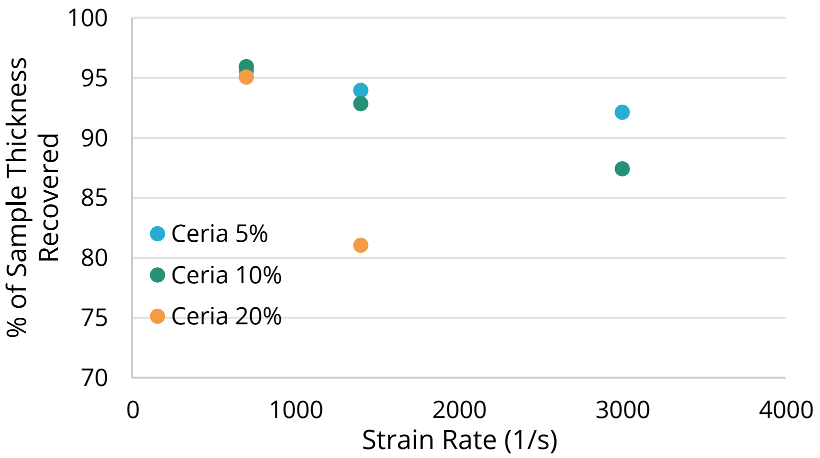


Before strike *After strike*

Polyurethane foams deform irreversibly in the Hopkinson bar



Addition of ceria increased stiffness, yield and plateau stress, but had insignificant effect on hardening behavior



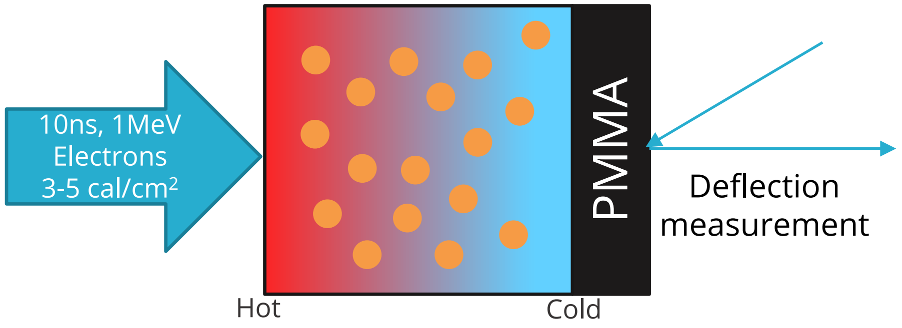
Permanent deformation increased with increased strain rate and higher fill volumes

20 vol% PVP CeO_2 sample became more brittle and failed during the test

EXTREME ENVIRONMENT TESTING

SPHINX: E-beam impulse

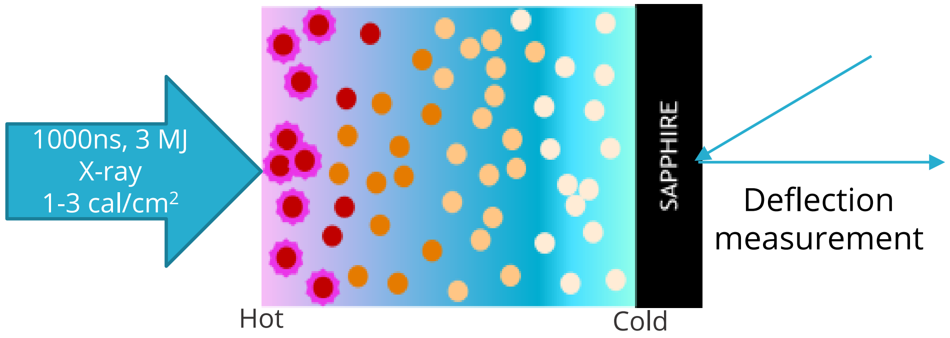
Experiments credit: Cody Kunka



- Electron beam has high pulse that **interacts with/heats up polymer** causing coefficient of thermal expansion mismatch
- Thermo-mechanical shock is generated
- Deflection of front is measured on back-side

Z-machine: X-ray impulse

Experiments credit: Chad McCoy



Temperature increase of agglomerated particles >> dispersed

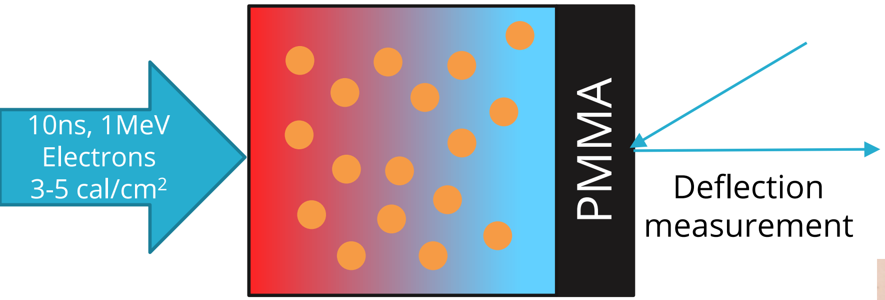
- X-ray has high pulse that interacts with and **heats up particles** that dissipate heat to polymer, causing coefficient of thermal expansion mismatch
- Thermo-mechanical shock is generated
- Deflection of front is measured on back-side

Goals:
Gain mechanical damping from polymer
Thermal/shock dissipation from particles

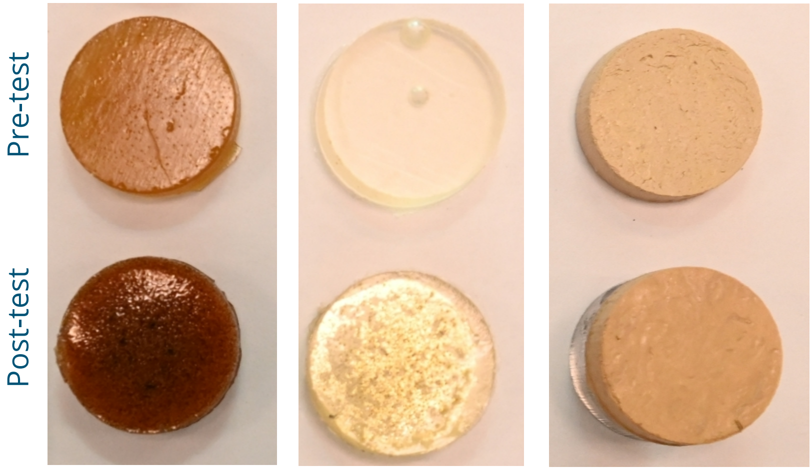
EXTREME ENVIRONMENT TESTING- SPHINX

E-beam causes thermomechanical shock, polymer sensitive

Experiments credit: Cody Kunka



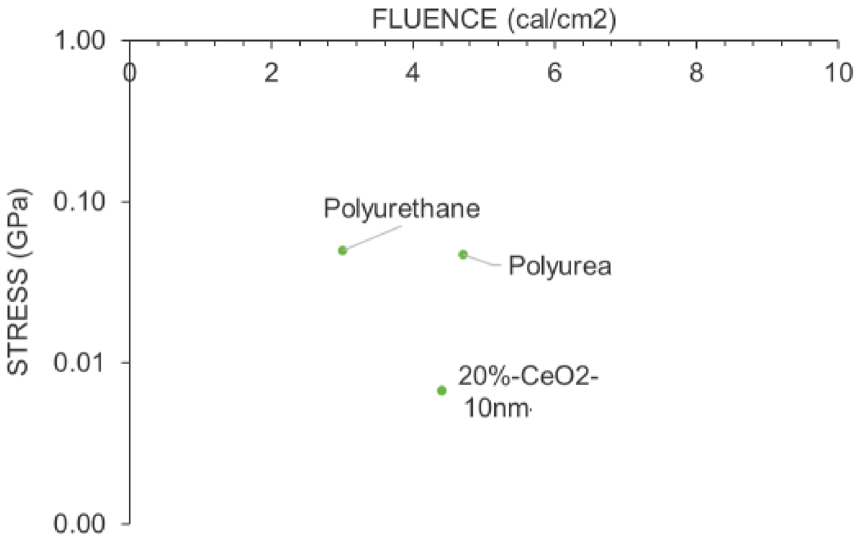
Rate similar to Shock Tube ($10s^{-1}$)



Polyurethane | P1000 Polyurea | P1000 + 5vol% PVPCeO_2

Polyurea samples withstand SPHINX shots showing minimal degradation via optical/color changes

Want: **high** fluence & **low** stress



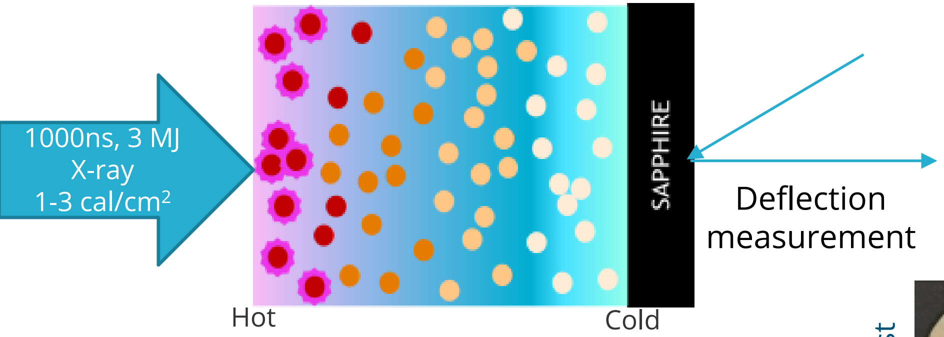
- **Fluence**: total energy per area
- **Stress:** Material response, lower stress is less likely to break

Good particle-matrix adhesion is needed for withstanding thermomechanical shock
Particle aggregates behave as stress points & result in local heat fluctuations, degrading thermomechanical shock properties

EXTREME ENVIRONMENT TESTING- Z-MACHINE

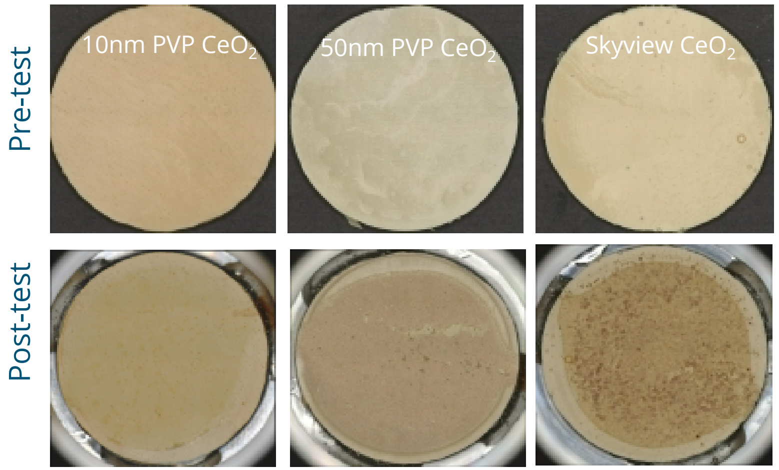
X-ray causes thermomechanical shock, particle sensitive

Experiments credit: Chad McCoy

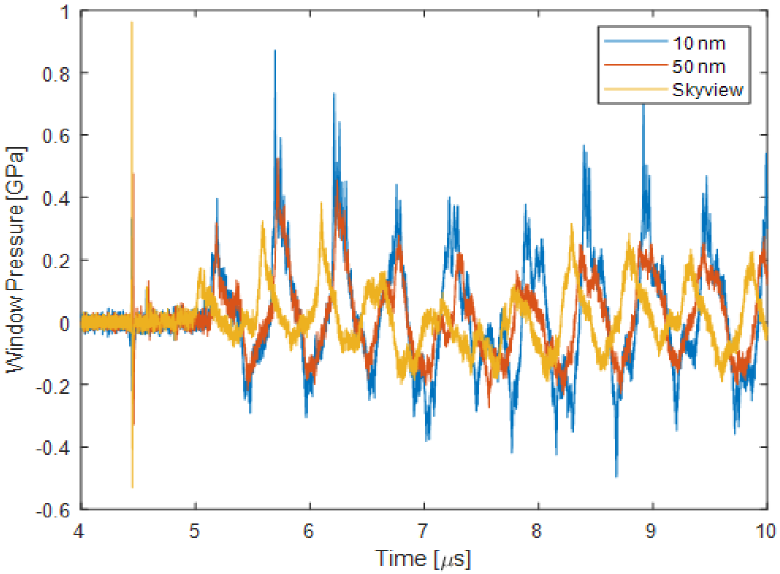


agglomerated particles >> dispersed

20vol% loading



Weight Loss:
10 nm PVP CeO_2 lost 16 mg
50 nm PVP CeO_2 lost 8 mg
Skyview CeO_2 lost 4 mg



Performance: Skyview >> 50nm >> 10nm
Skyview has tri-modal distribution
10nm believed to be agglomerated

Good particle-matrix adhesion is needed for withstanding thermomechanical shock
Particle aggregates behave as stress points & result in local heat fluctuations, degrading thermomechanical shock properties

CONCLUSIONS

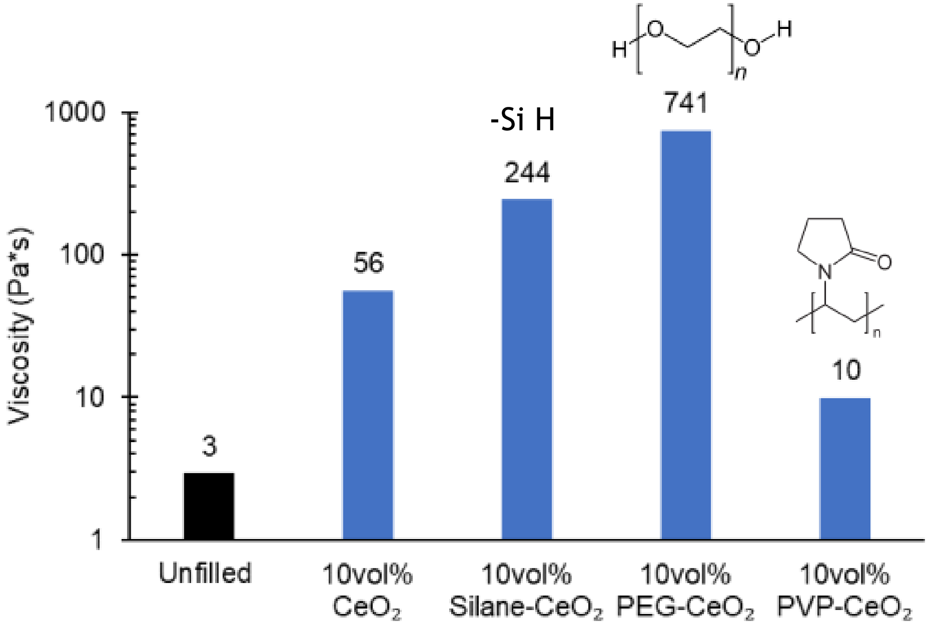
- Surface functionalization of cerium oxide using polyvinylpyrrolidone (PVP) aids in dispersion & results in best thermomechanical properties
  - Attributed to similar polarity of PVP-coating and polyurea matrix
- Addition of nanoparticles:
  - Stabilized newtork during temperature sweeps
  - Decreased toughness and strain-at-failure due to nanoparticles impeding polymer chain mobility at low strain rates in tension
  - Outperformed unfilled polyurea under extreme strain rates (SPHINX/Z-machine)
    - Agglomerates degrade the thermoemcahnical properties

These composites are regarded a novel materials for determining compatible surface chemistries between nanoparticles and urea-containing polymers

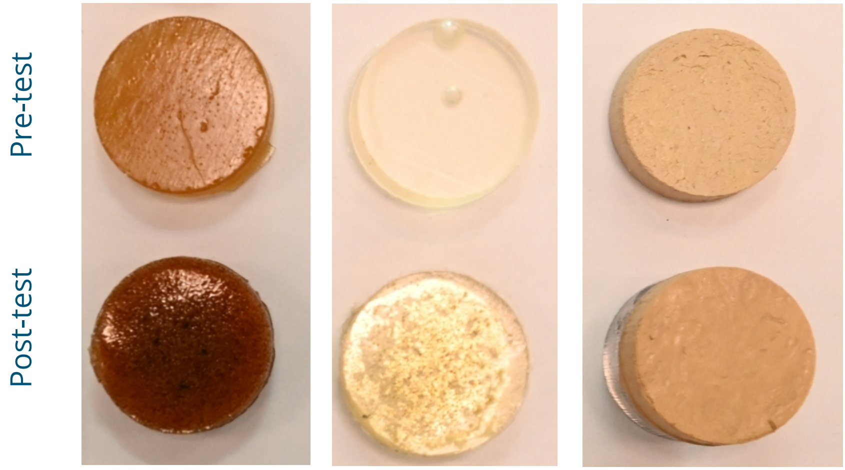
Gained understanding of filler-surface/polymer-matrix compatibility on mechanical properties

THANK YOU

Credit: Dragonshield polyurea (TDI)



SPHINX E-Beam

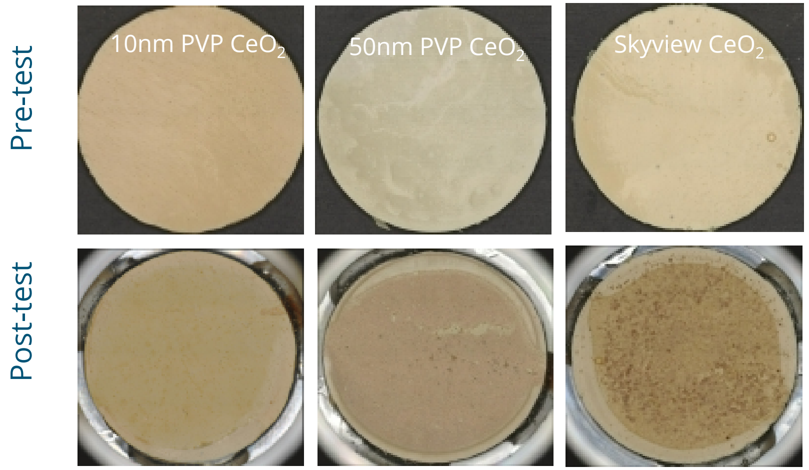


Polyurethane

P1000 Polyurea

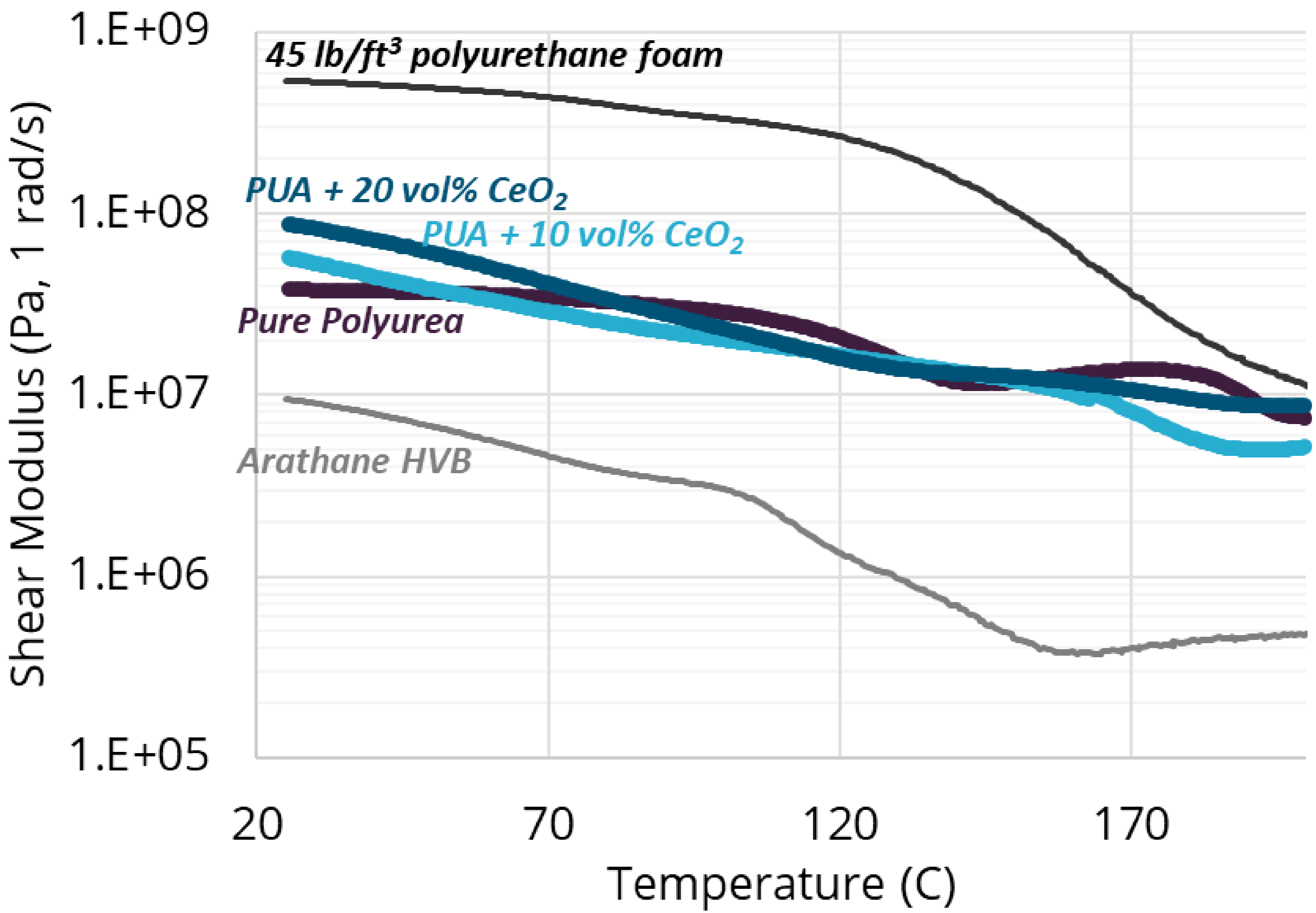
P1000 + 5vol% PVPCeO_2

Z-machine X-ray

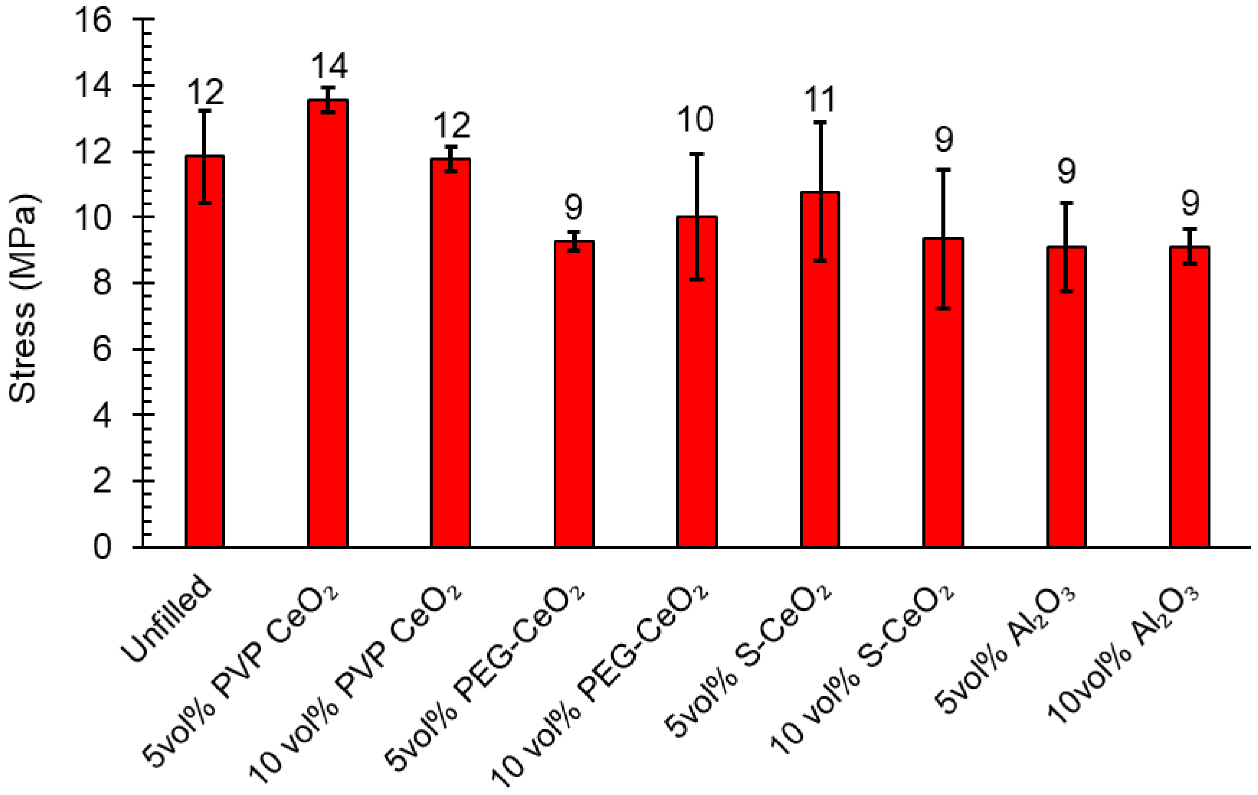


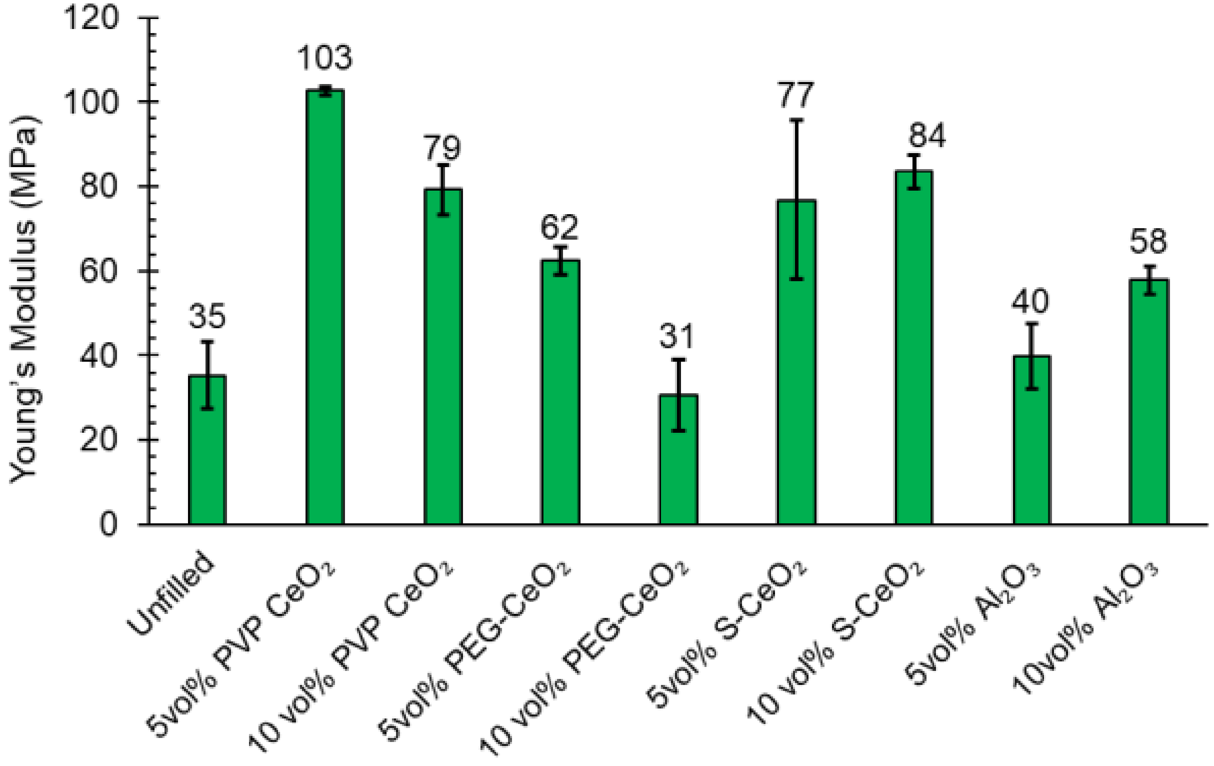
BACKUP

POLYURETHANE VS POLYUREA MODULUS



MATERIAL PROPERTIES – TENSILE TESTING





- Addition of particles did not influence ultimate tensile stress
  - Lack of percolation

- Particles increased Young's modulus
  - Particles had greater modulus than the polyurea matrix
  - PVP had greatest impact indicating increased particle-matrix adhesion