Computationally Guided Design of Polymer-Coated Microparticles as Reusable Materials

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Materials innovation needed for sustainable exploration

- Long-duration human exploration necessitates a reduced dependency on Earth supply
- Reusable and in-situ materials are critical for sustainability

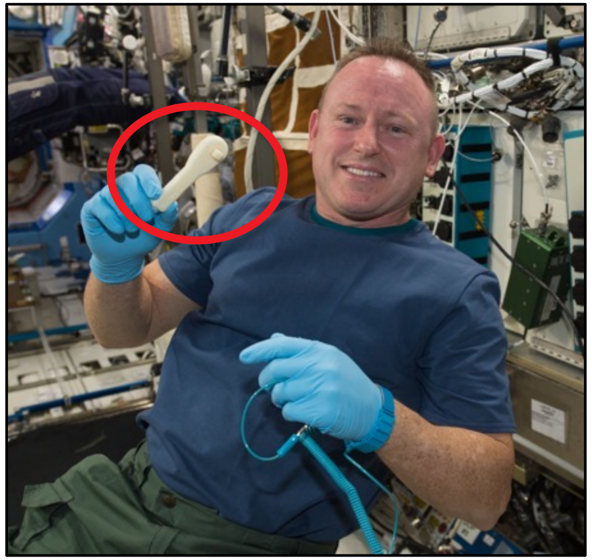
Transit time:
~6 months

Mission duration:
~2-3 years

Image credit: NASA

Additive manufacturing capabilities enhanced by recycling

- In-space manufacturing (ISM) allows for on-demand fabrication of articles to reduce mission mass and risk
- Enabling Sustained Presence Using Recyclables (ESPUR) project focuses on development of reusable feedstocks



3D-printed ratchet wrench

3D-printed sample container

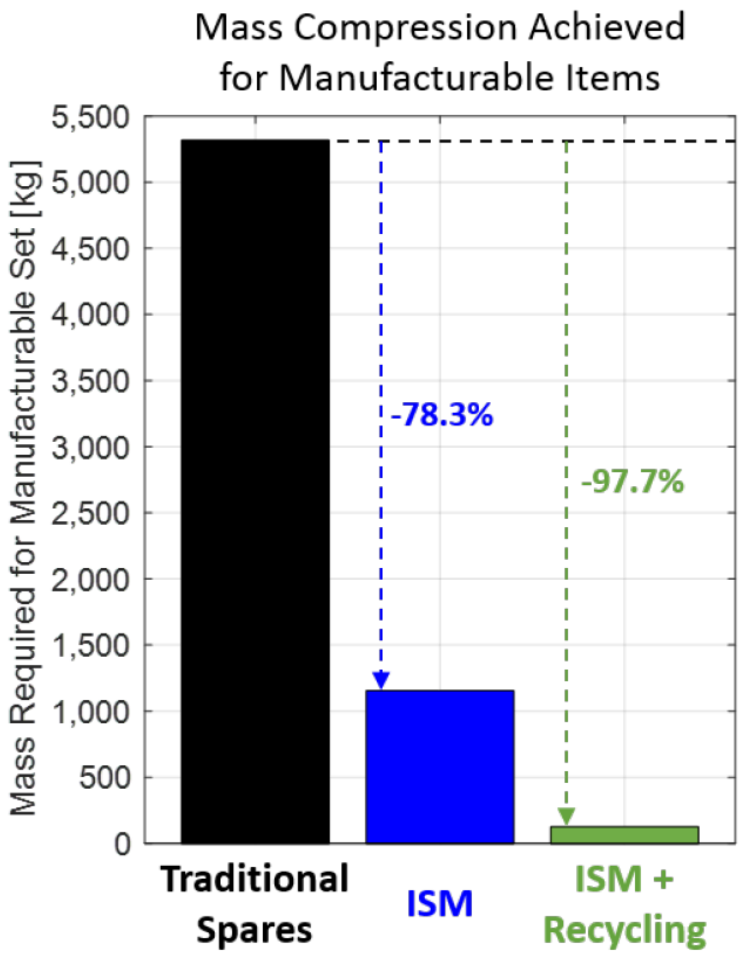
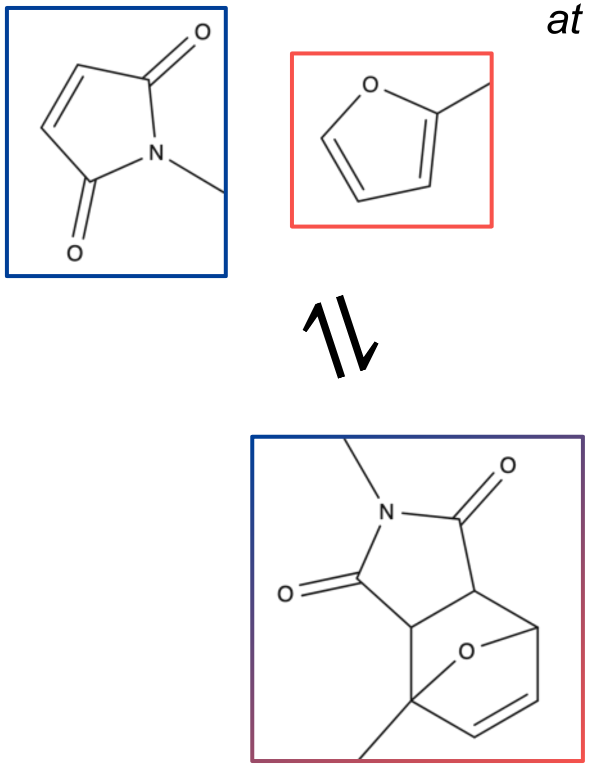


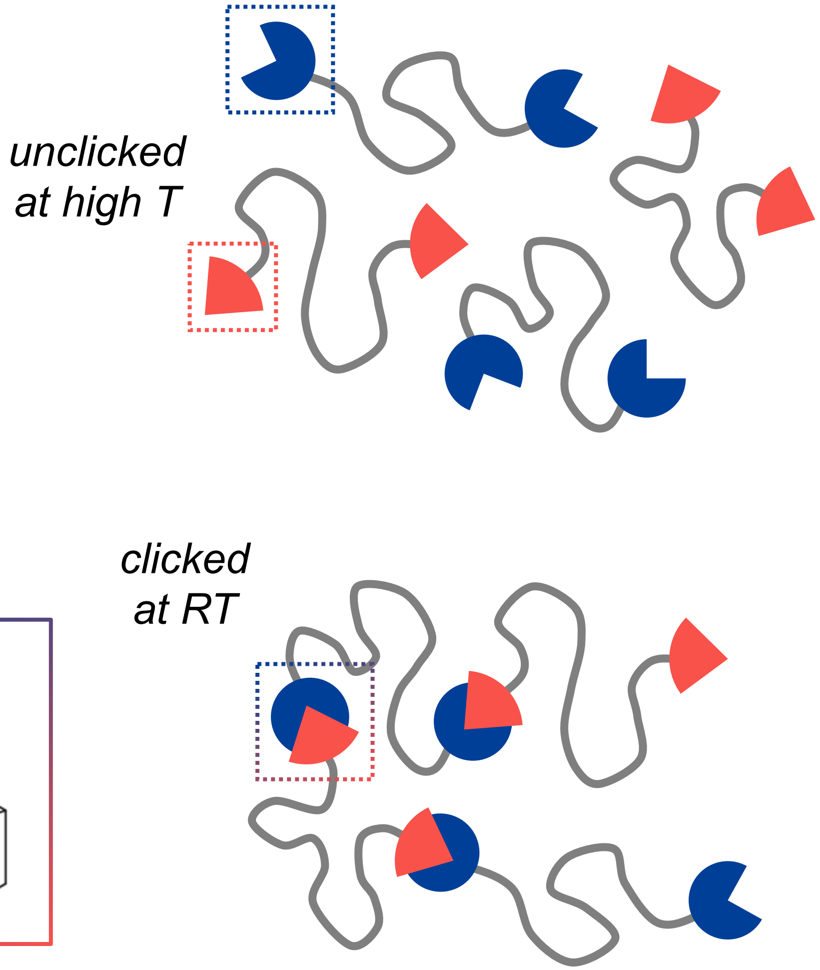
Image credits: NASA

Owens and Weck, AIAA SPACE 2016

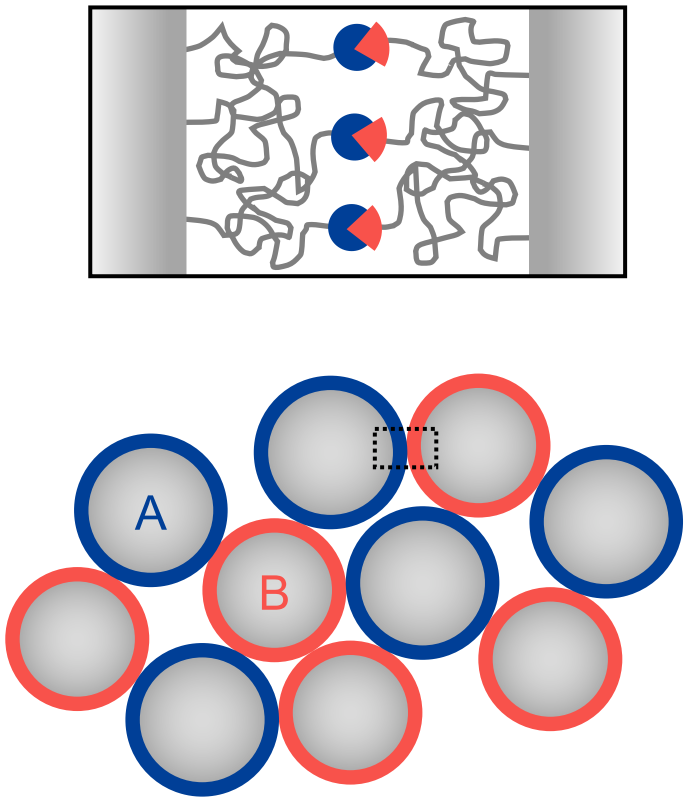
Reusable material concept via reversible click chemistry

ESPUR materials incorporate thermoreversible Diels-Alder reactions





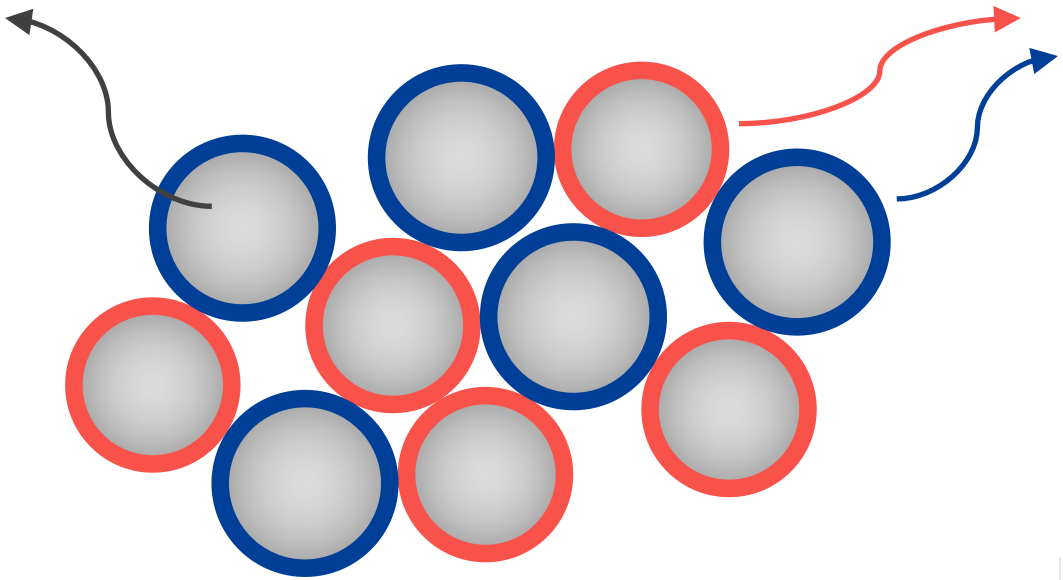
Microparticle building blocks feature complementary polymer coatings

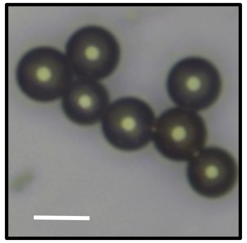


Tunability possible within the large design space

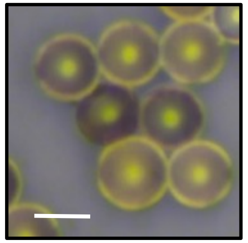
Epoxy Microparticles

- Epoxy chemistry
- Microparticle size
- Coating thickness





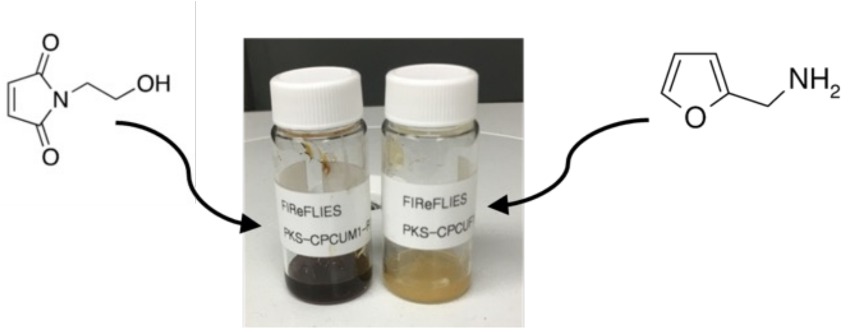
Uncoated



Coated

Polymer Coatings

- Polymer chemistry
- Molecular weight
- Reversible chemistry



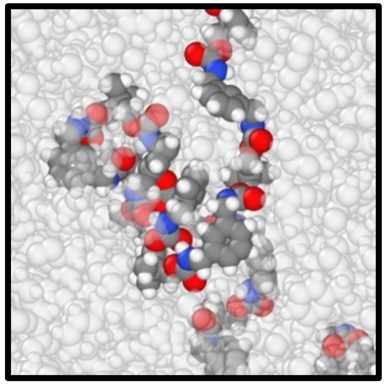
Today at 2:25 pm…

***M. Beaudry et al.** Recent advances of the ESPUR reversibly assembling materials project.*

Materials characterization undertaken across scales

Molecular models for molecular interactions

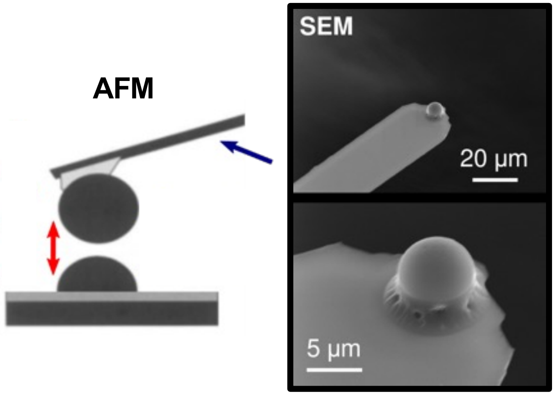
NASA Ames



10^{-9} m

Atomic force microscopy for microparticle interactions

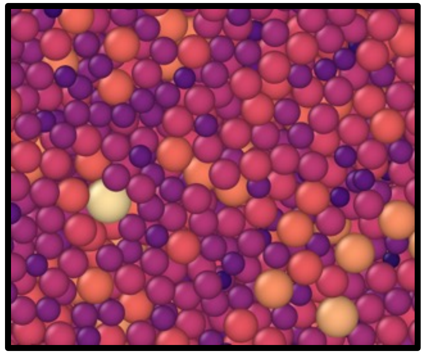
William & Mary



10^{-6} m

Discrete element models for microparticle packing

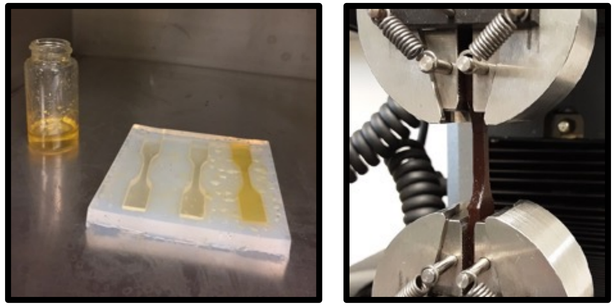
NASA Ames



10^{-3} m

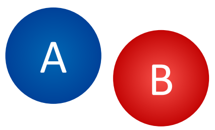
Mechanical testing for material property calculation

NASA Langley, William & Mary

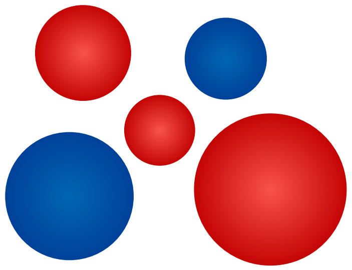


10^{-1} m

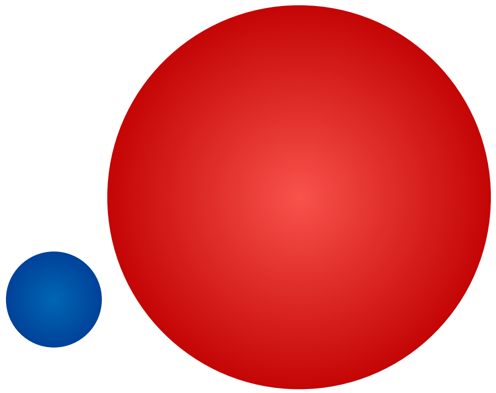
Influence of microparticle size dispersity on packing



monodisperse



polydisperse



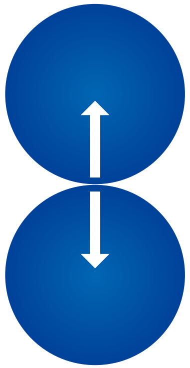
bidisperse

Can we tune particle sizes to:

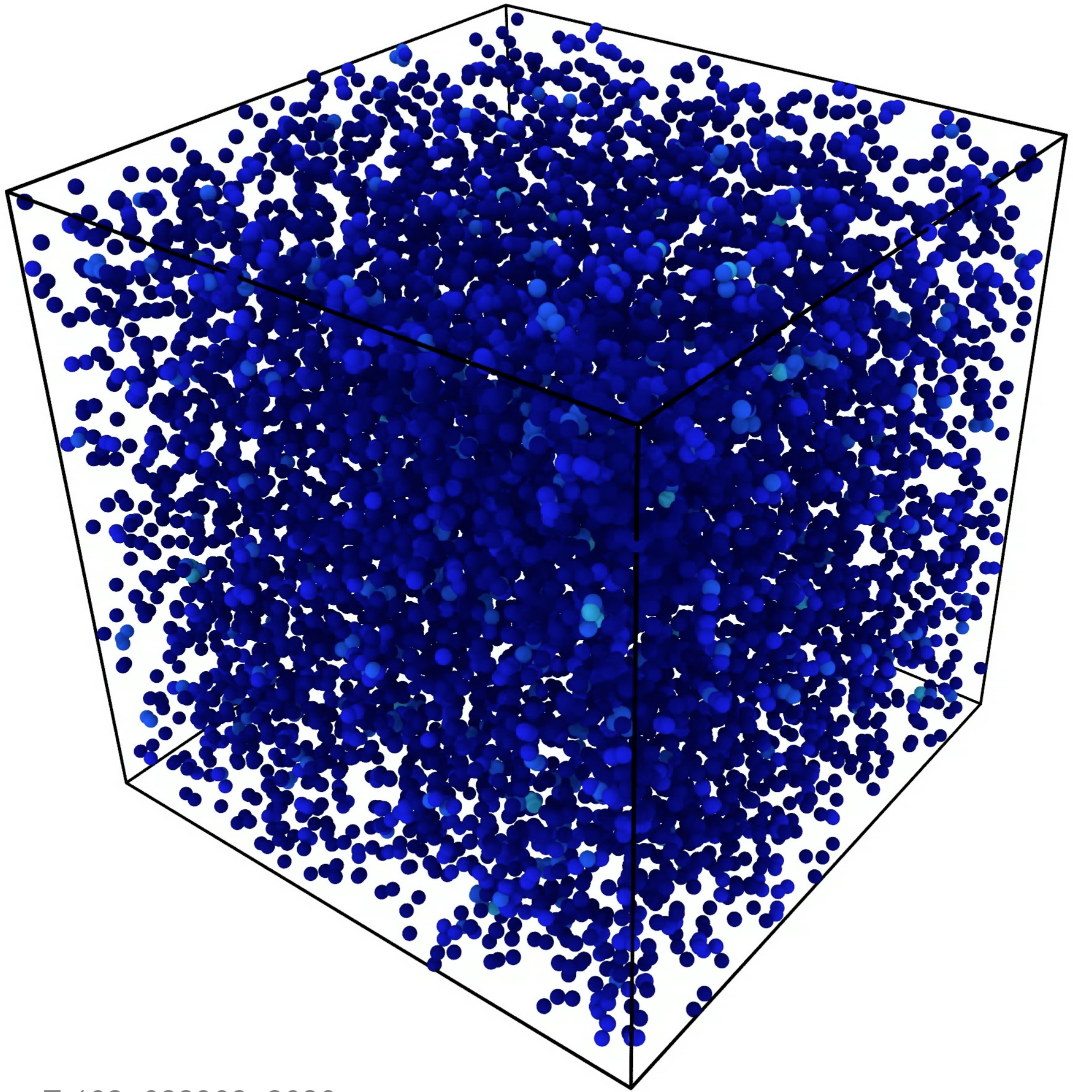
Maximize A-B contacts + Minimize void volume → Increase mechanical strength

Discrete element method (DEM) simulations

- Box contains at least 1000 each of type A and B particles, up to 10 million total
- Contact mechanics described with Hertzian model, experimentally relevant parameters
- Compress dilute to dense final packing
- Periodic boundary conditions
- LAMMPS



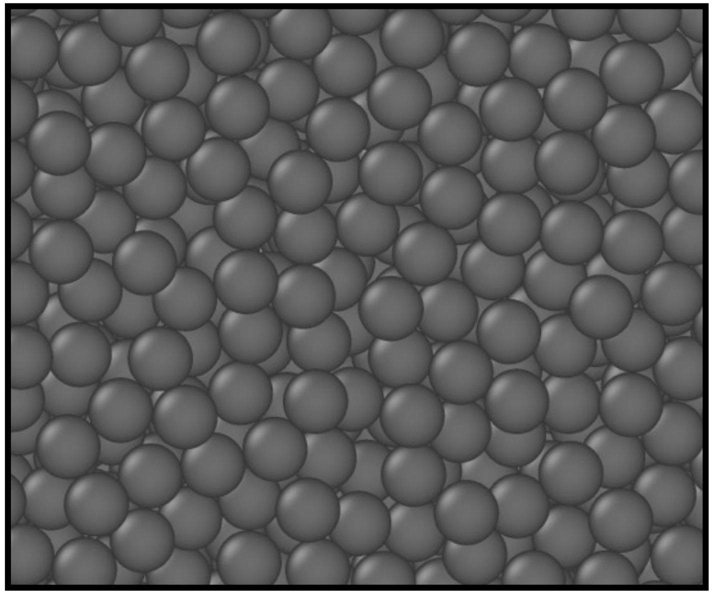
Property	Model parameter	
Young's modulus	k_n	4.808 GPa
Poisson's ratio	k_s	4.345 GPa
Coeff. of restitution	γ_n	0.009404 μm^{-1} ns^{-1}
Density	m_{eff}	1.1 pg μm^{-3}
Diameter	R_{eff}	10 μm



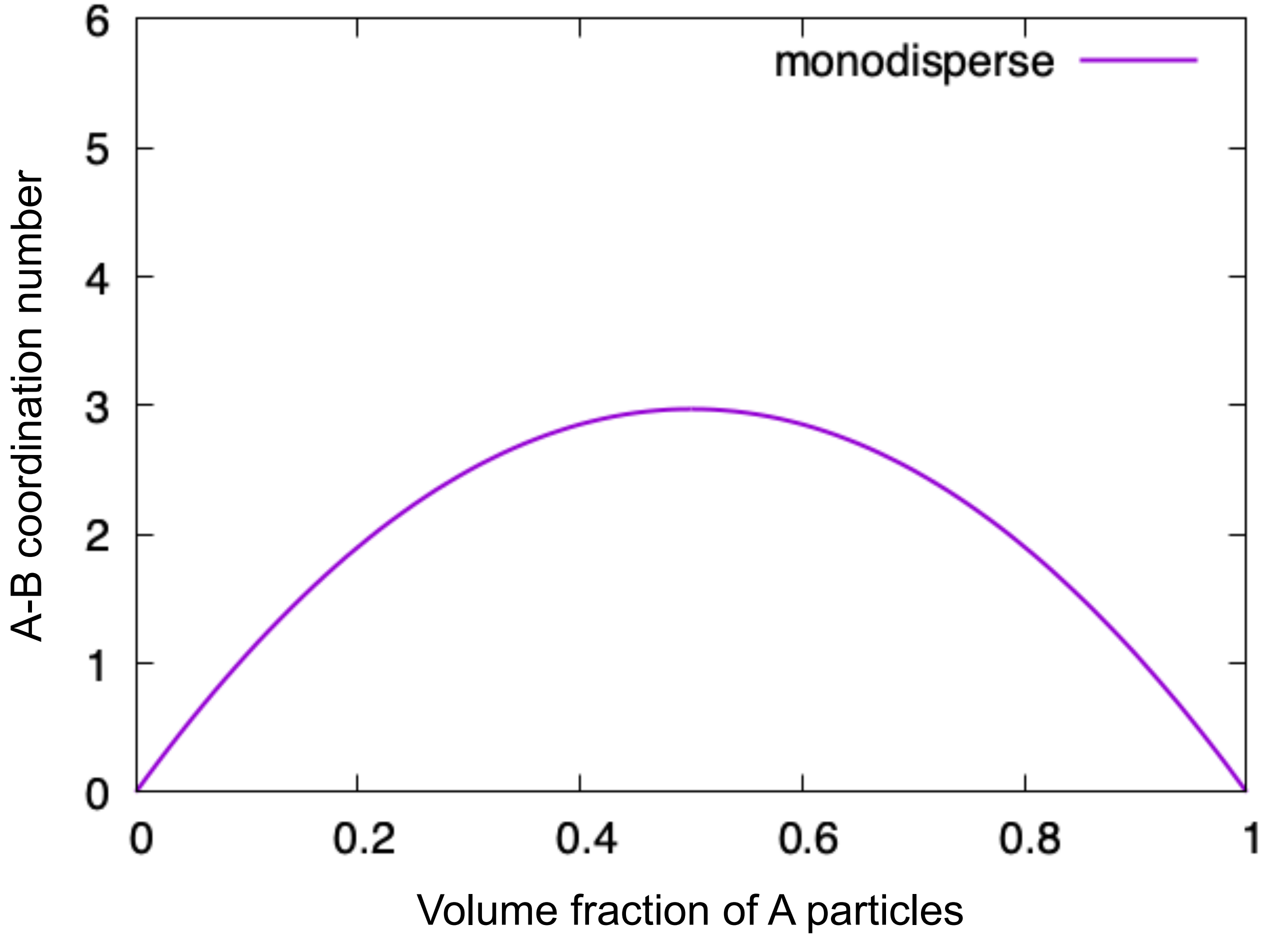
Plimpton et al, Com. Phys. Comm. 271, 10817, 2022; Santos et al, Phys. Rev. E 102, 032903, 2020

Monodisperse microparticles: the baseline case

- Maximum A-B contacts with 50:50 mix of A and B
- Packing density of ~64%

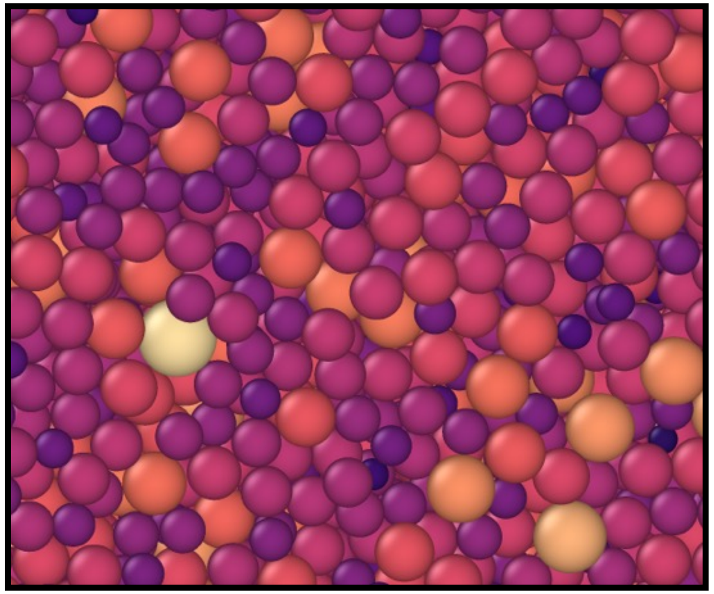


$D_A = D_B = 10\ \mu m$

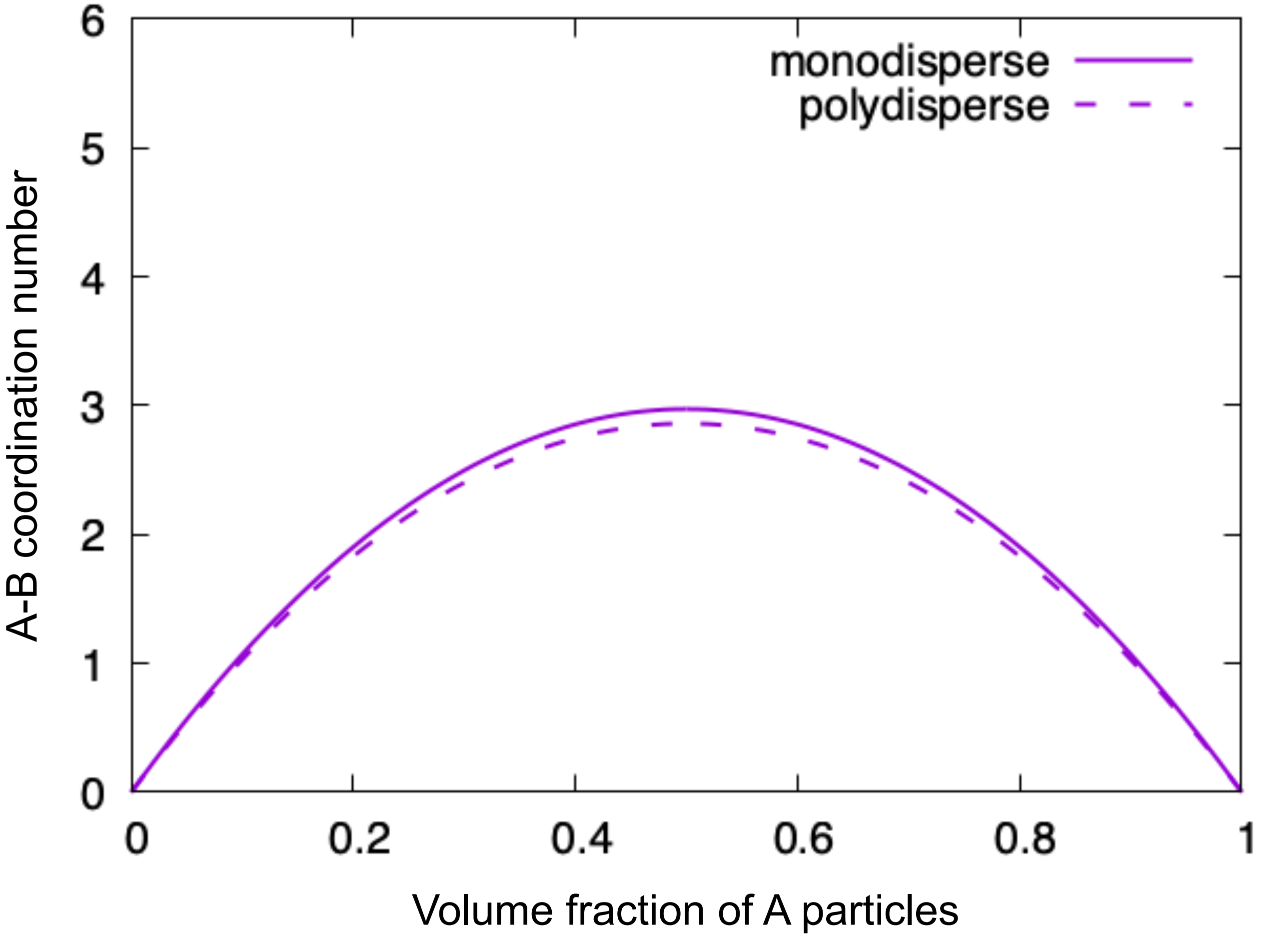


Polydisperse microparticles: experimentally informed

- Slight decrease in contacts, still maximum at 50:50 mix
- Slight increase in packing density

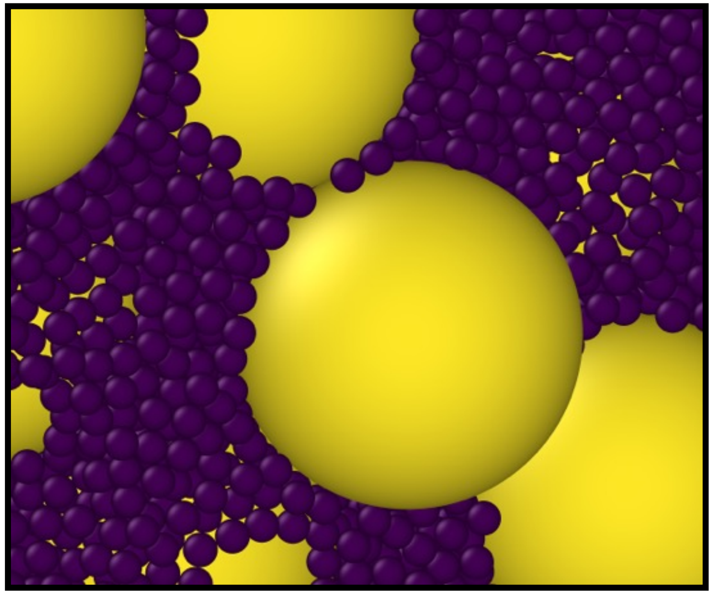


D_A, D_B ~ N(10 μm, 1.5 μm)

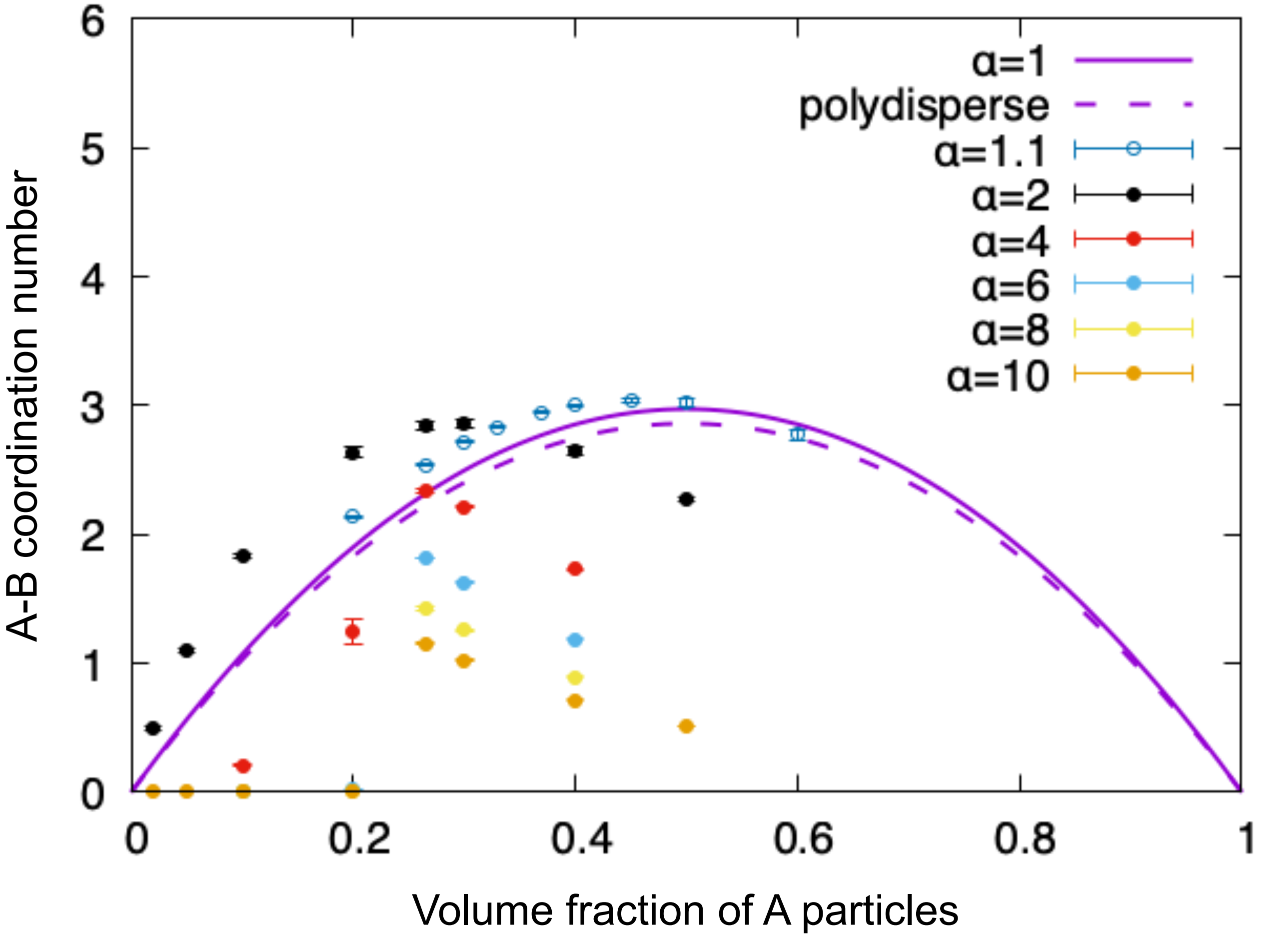


Bidisperse microparticles: guiding future design

- Shift of maximum to lower volume fractions of A particles
- Smaller size ratios ➔ more contacts

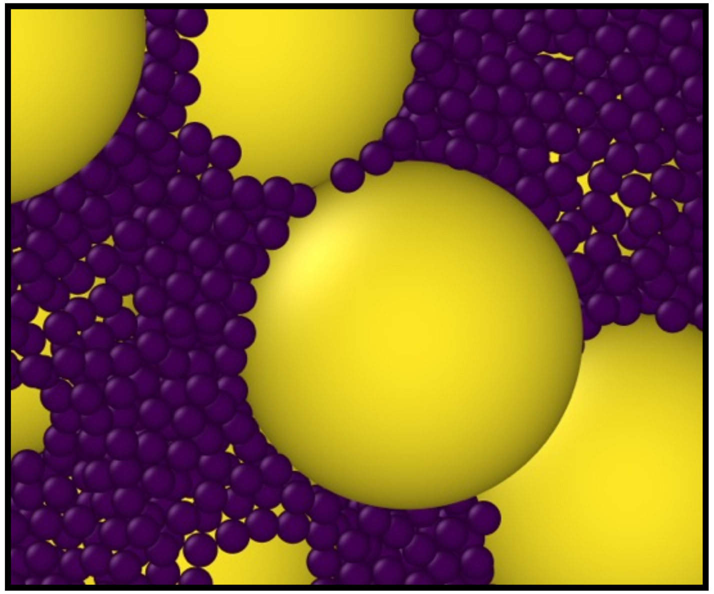


D_A = 10 μm, $D_B = \alpha D_A$

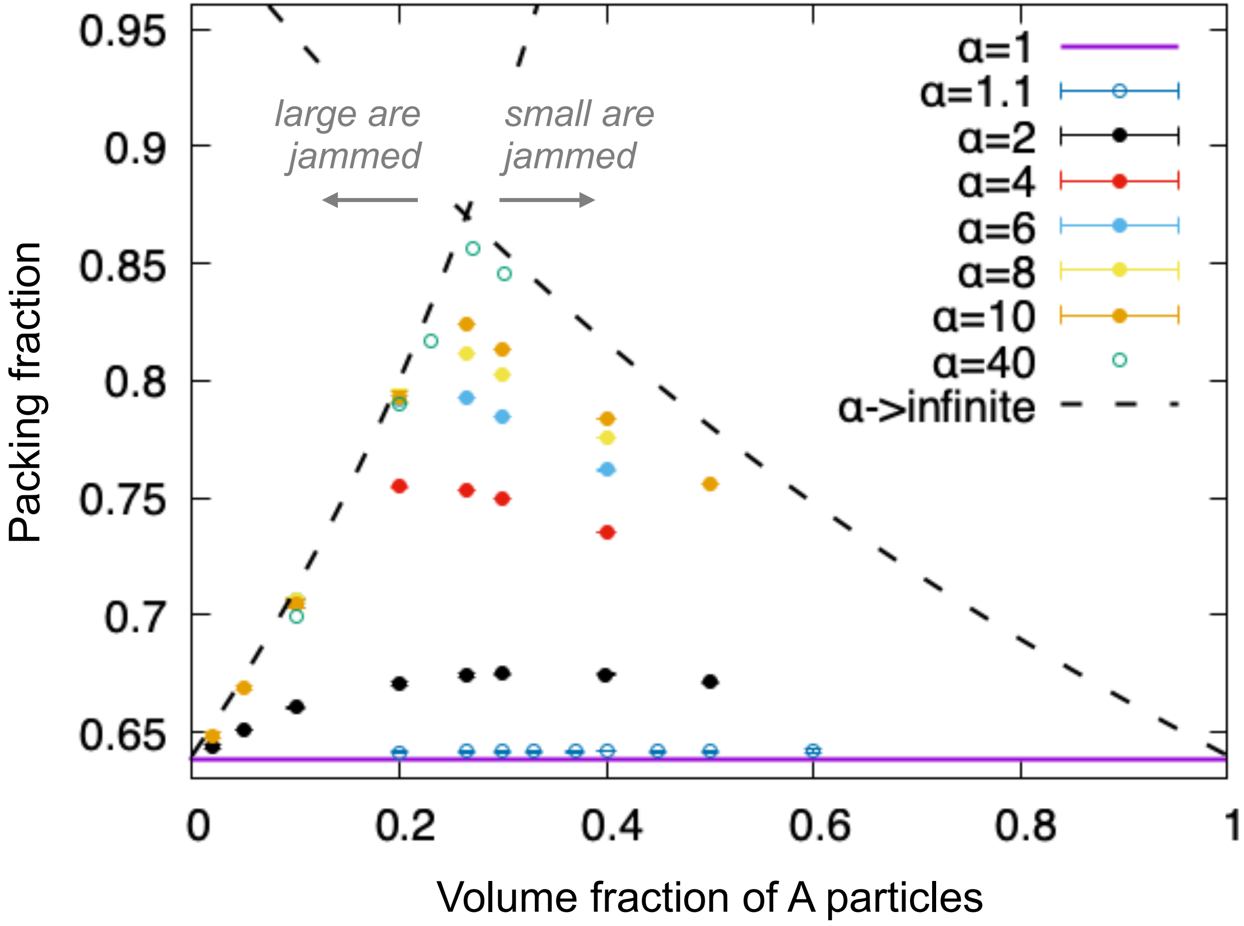


Bidisperse microparticles: guiding future design

- Maximum contacts consistent with maximum packing fraction
- Larger size ratios ➔ fewer voids



D_A = 10 μm, D_B = αD_A



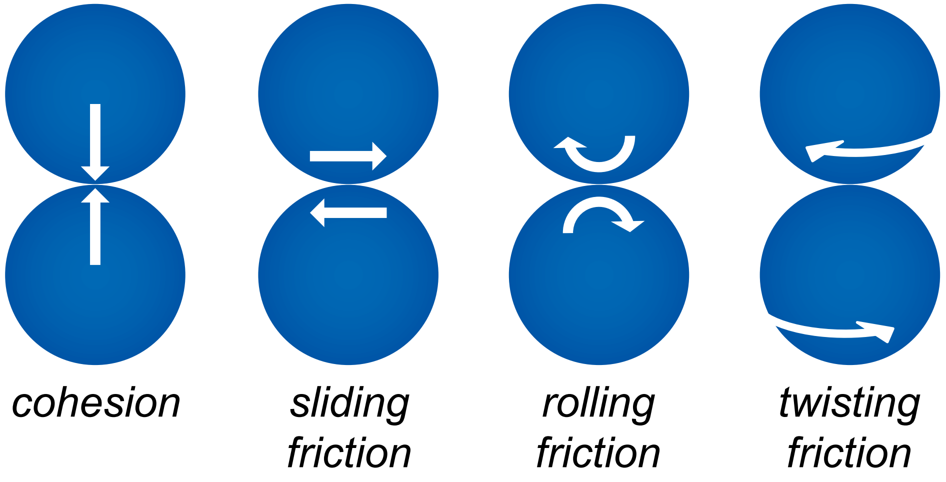
Furnas, Ind Eng Chem, 1931, 23, 1052; Srivastava et al, Phys Rev Research, 2021, 3, L032042

Key takeaways from the microparticle simulations

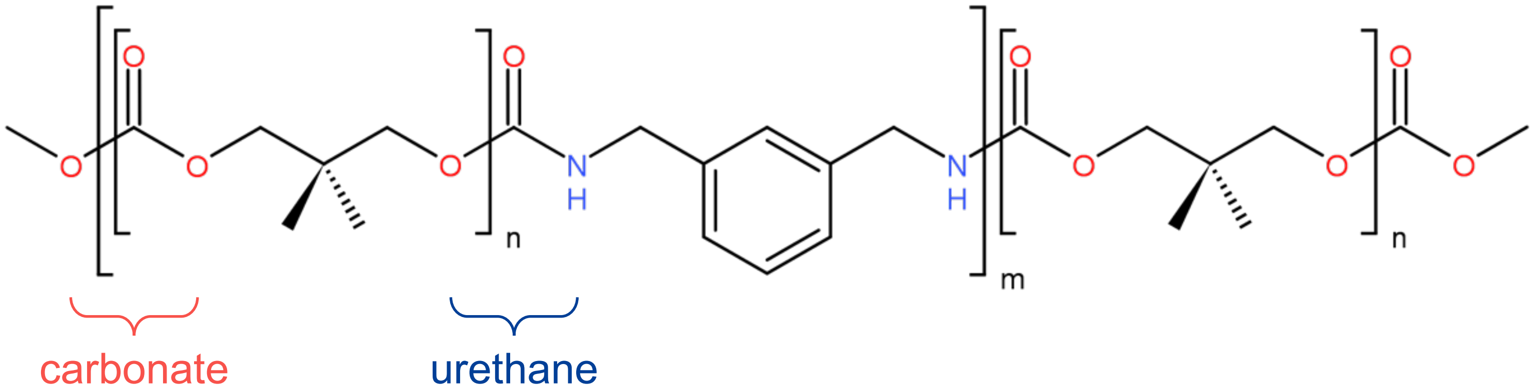
- The optimal A:B mixture depends on the particle size distribution
- The peak volume fraction corresponds with a peak in A-B contacts for bidisperse packings
- Increasing the A:B size ratio causes the volume fraction to increase and A-B contacts to decrease ➔ an expected trade-off for mechanical properties

Next steps:

- Improve discrete element model with addition of cohesion and friction
- Leverage atomic force microscopy data to refine model parameters for microparticle interactions
- Calculate mechanical properties to elucidate expected trade-off behavior for bidisperse packings



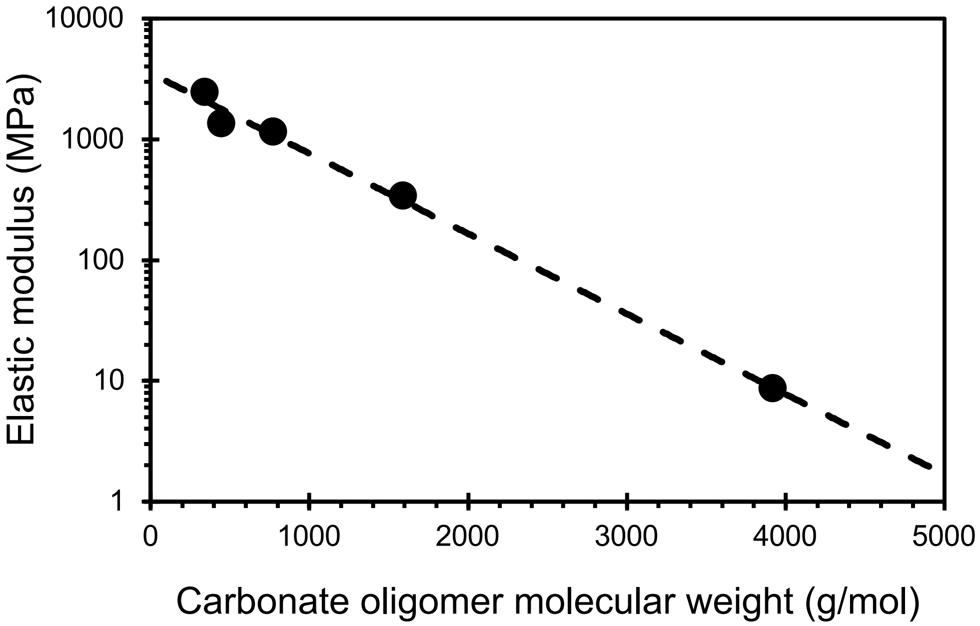
Influence of polymer chemistry on properties



Copoly(carbonate urethane)
(CPCU)

How does copolymer composition affect:

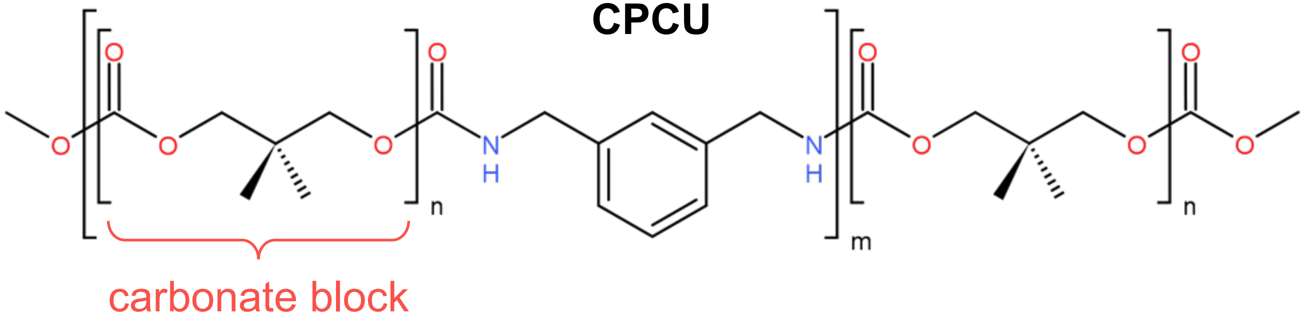
- Molecular interactions
- Polymer properties



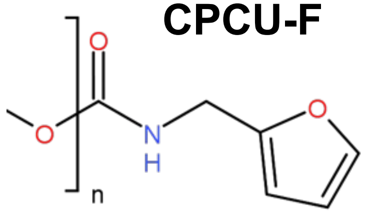
Molecular dynamics (MD) simulations

- Varying the carbonate block (*n* = 1 or *n* = 4), similar polymer backbone length
- Varying the end-group functionalization
- Simulations contain ~17-20K atoms
- Polymer interactions described with polymer consistent force field (PCFF)
- Periodic boundary conditions
- LAMMPS

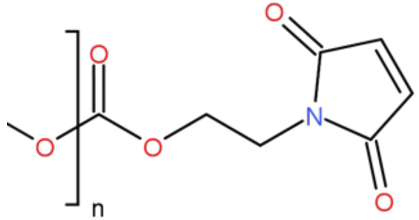
CPCU



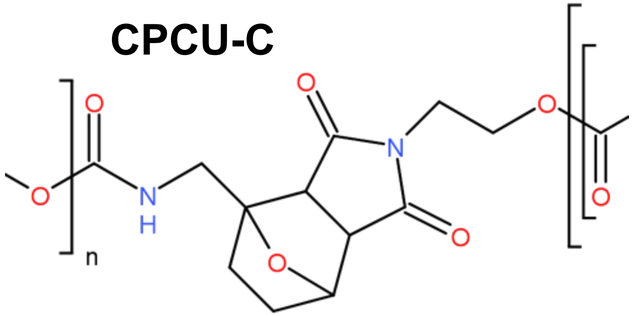
CPCU-F

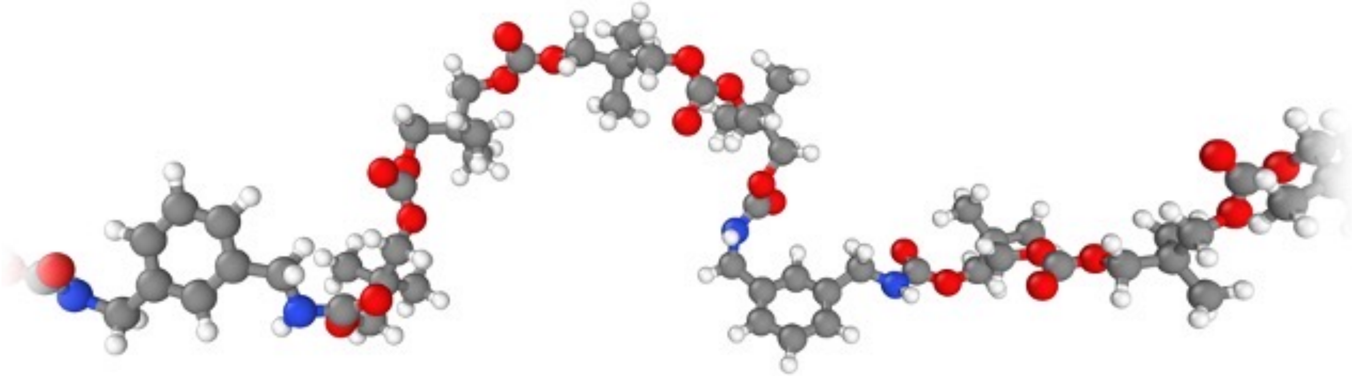


CPCU-M

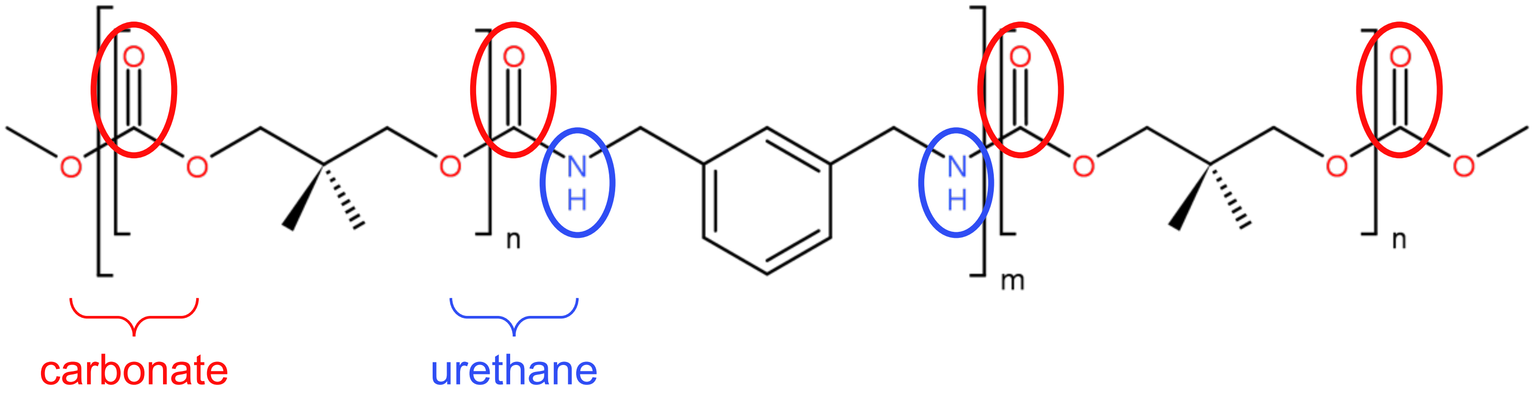


CPCU-C

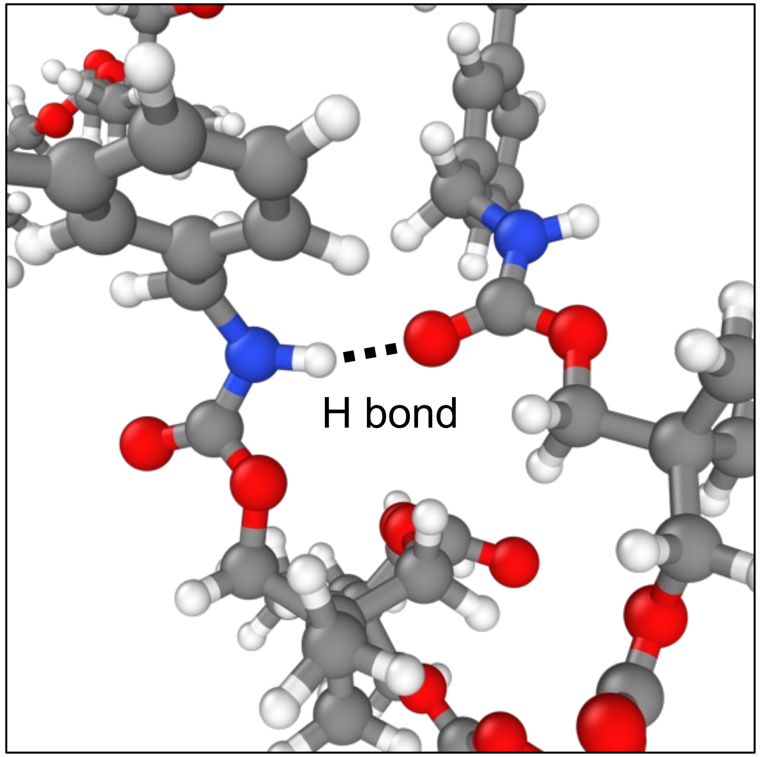




Hydrogen bonds play a key role in polymer interactions

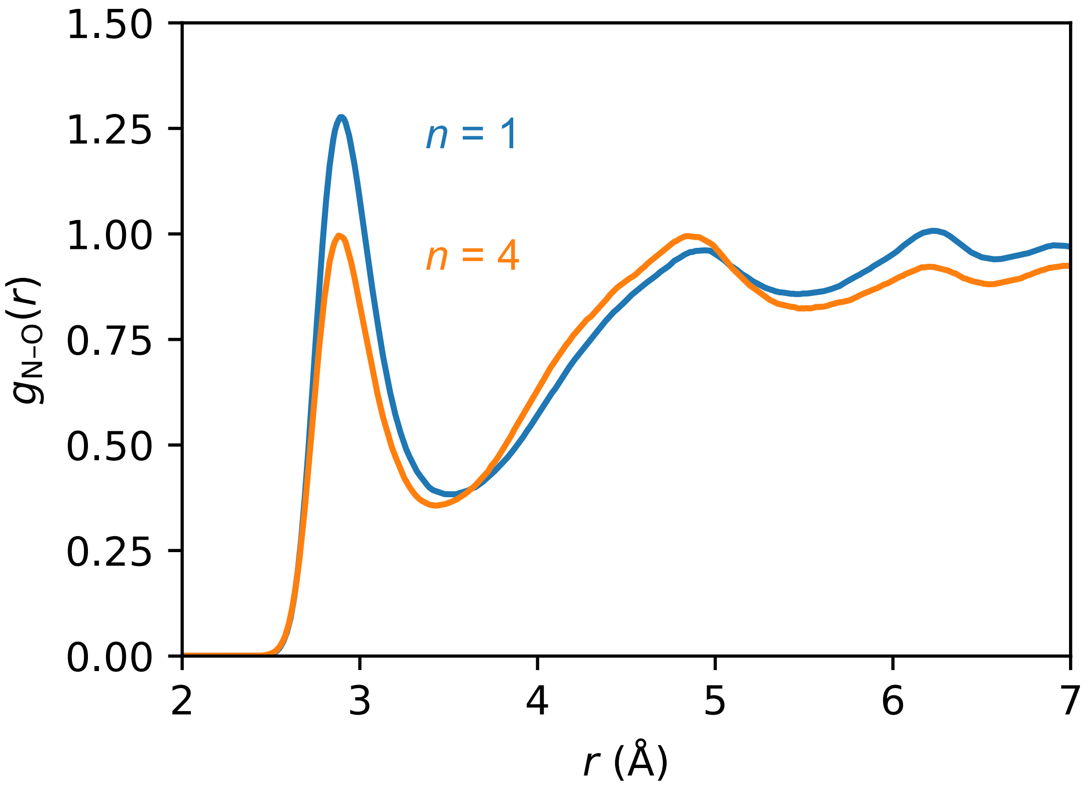


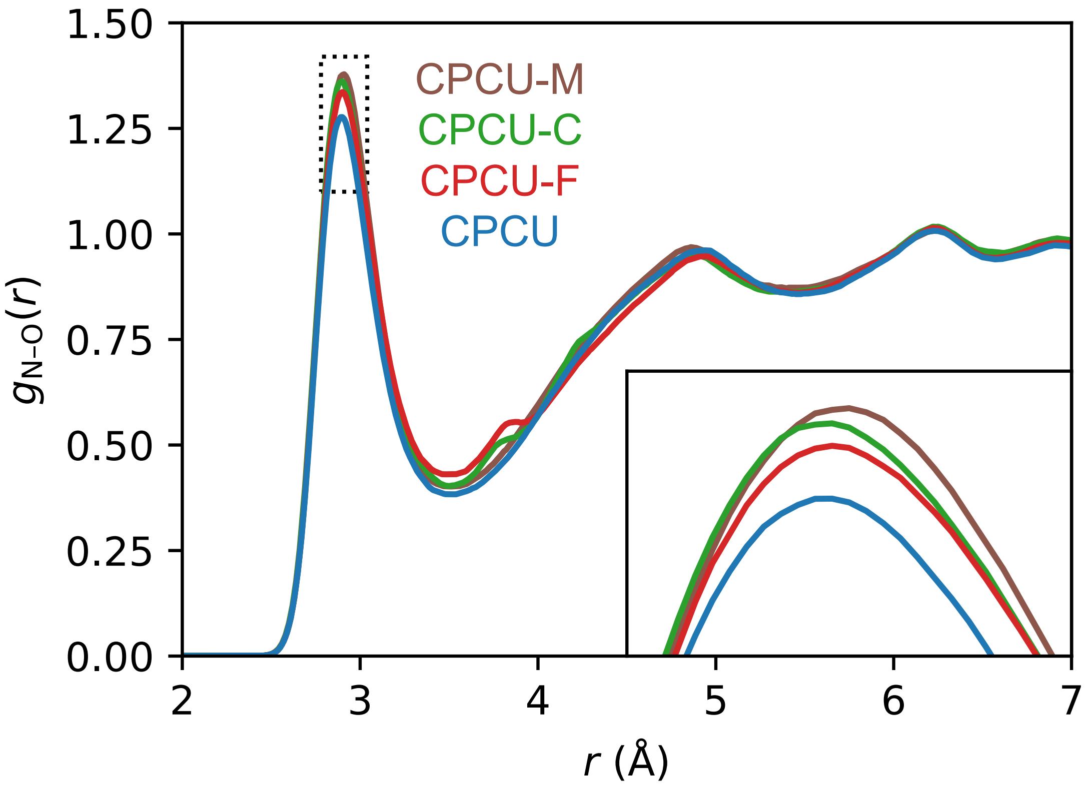
- Hydrogen bonding C=O groups in both carbonate and urethane linkages
- Hydrogen bonding NH groups in urethane linkage only
- Increasing the carbonate block length decreases the frequency of NH groups along the backbone



Copolymer composition affects H-bond interactions

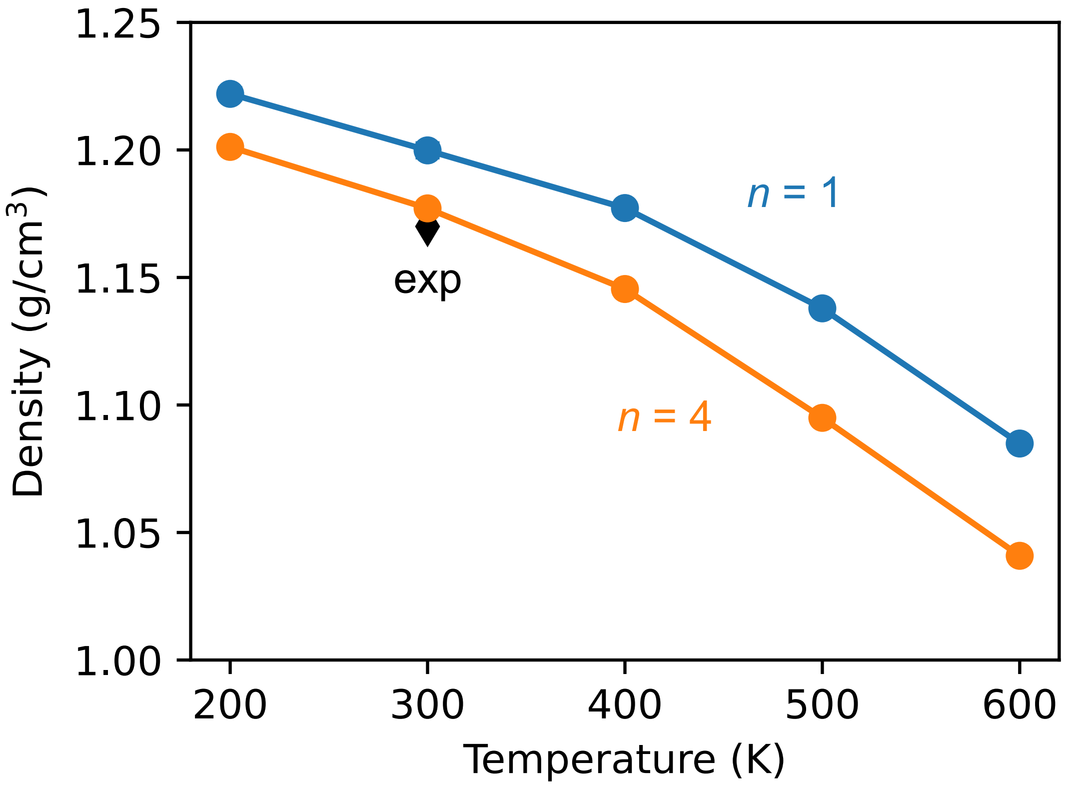
- The first peak in the N-O radial distribution function arises from O···HN hydrogen bonds
- Increasing the carbonate molecular weight reduces the extent of hydrogen bonding
- End functionalization increases the extent of hydrogen bonding

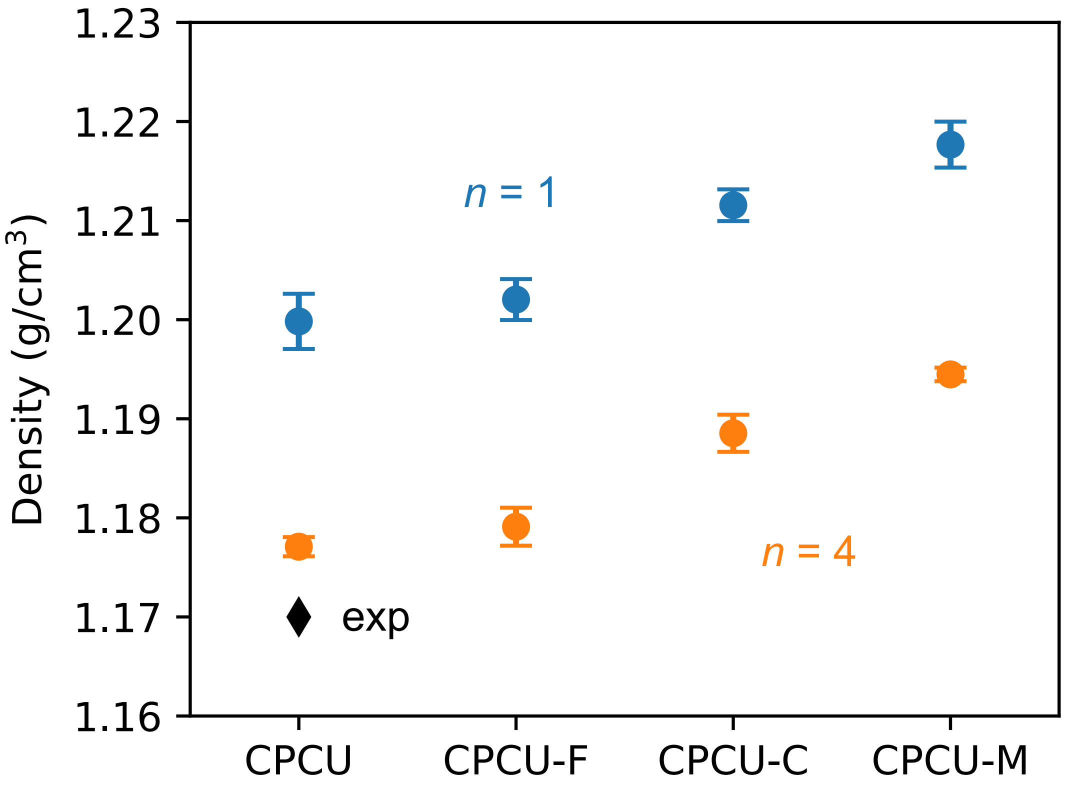




Increased H-bond interactions yield higher densities

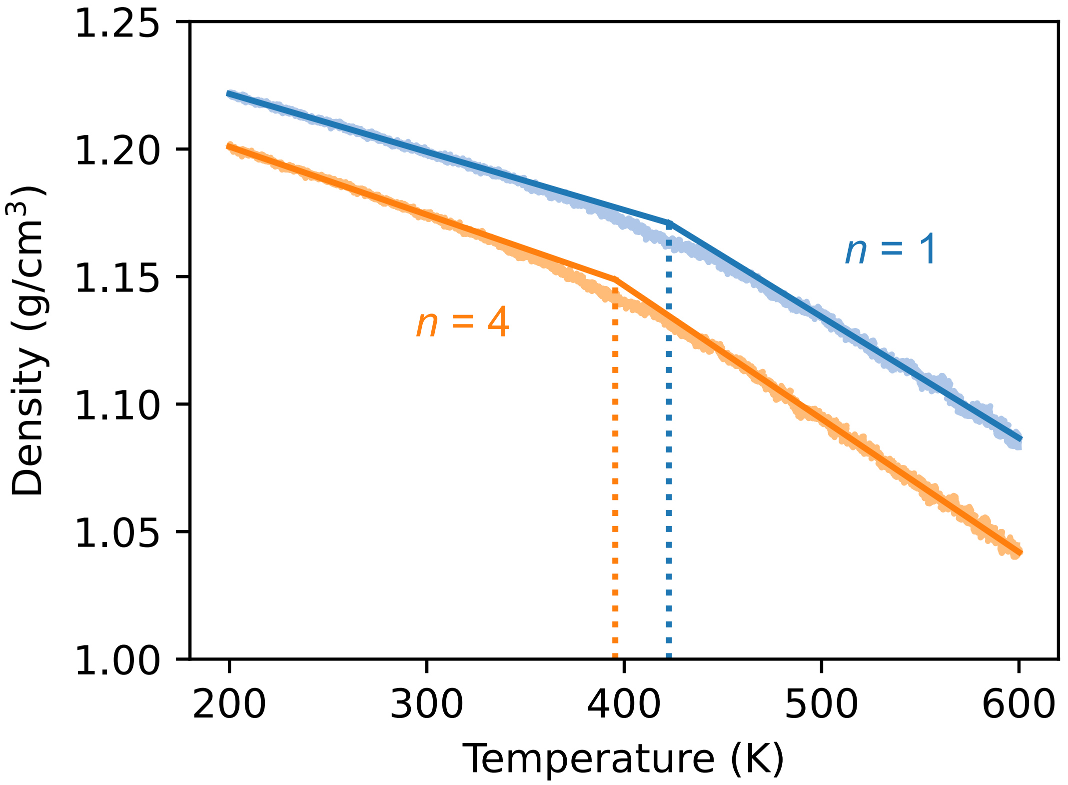
- CPCUs with a greater extent of hydrogen bonding tend to have higher densities
- The experimentally measured density of a CPCU ($n \approx$ 3-4) is consistent with the simulations

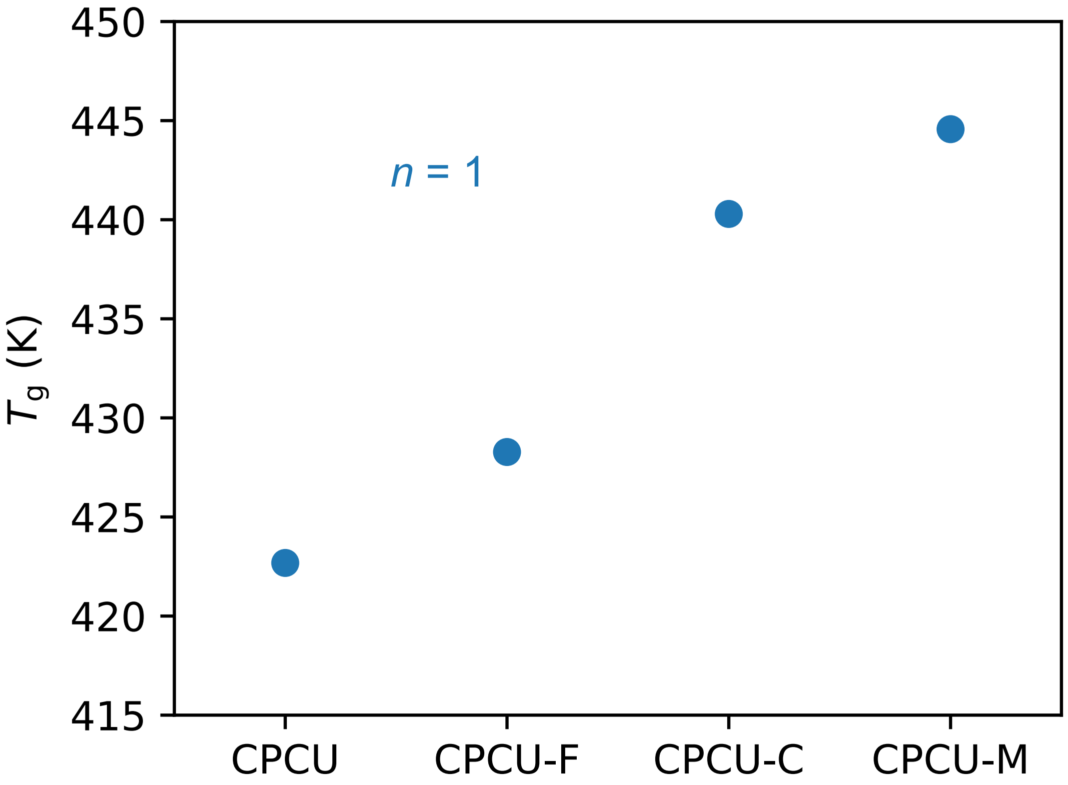




Increased H-bond interactions yield higher glass transitions

- CPCUs with a greater extent of hydrogen bonding tend to have higher glass transition temperatures
- The glass transition is observed at high temperatures in the simulations due to the fast heating rate



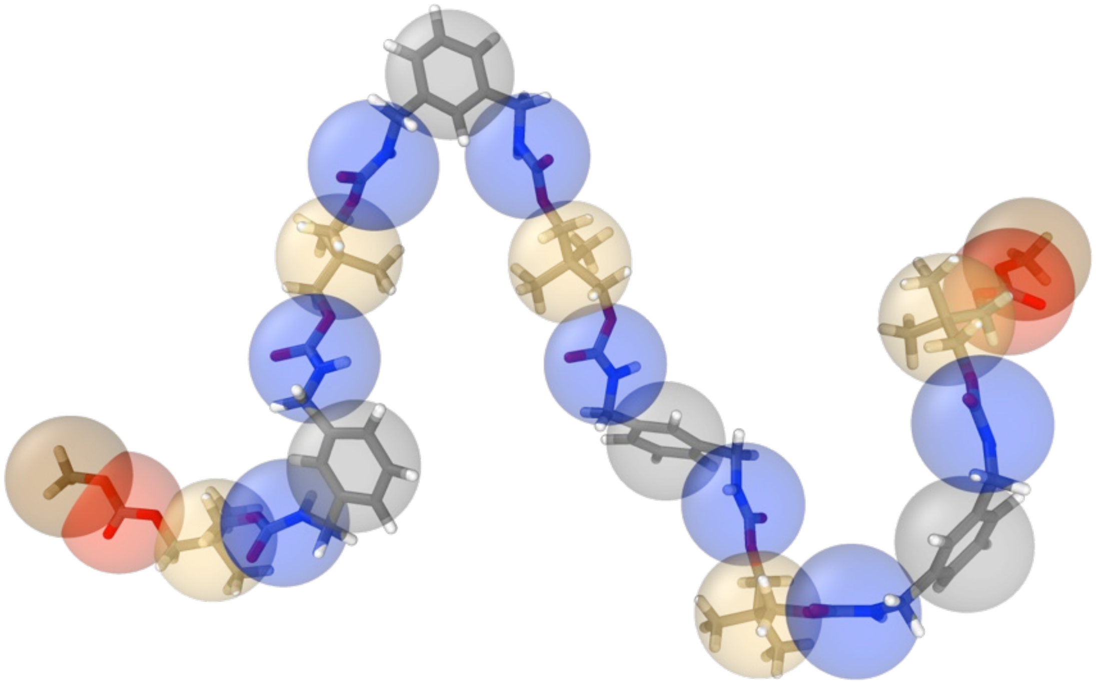


Key takeaways from the polymer simulations

- The CPCU chemistry can be tailored to adjust the hydrogen bonding interactions
- Increasing the extent of hydrogen bonding results in increased densities and higher glass transition temperatures

Next steps:

- Use coarse-grained models to run larger and longer simulations
- Investigate influence of copolymer composition on mechanical properties
- Incorporate click chemistry reactions



Summary

- Computational materials modeling provides important insights to guide materials design, limiting unnecessary experimental efforts
- Discrete element simulations pinpoint the optimal mixtures of functionalized microparticles to increase the mechanical properties
- Molecular dynamics simulations elucidate the extent of hydrogen bonds and their affect on the properties of the CPCU polymer coatings