Recyclable polymers with reversible click-chemistry for in space manufacturing applications

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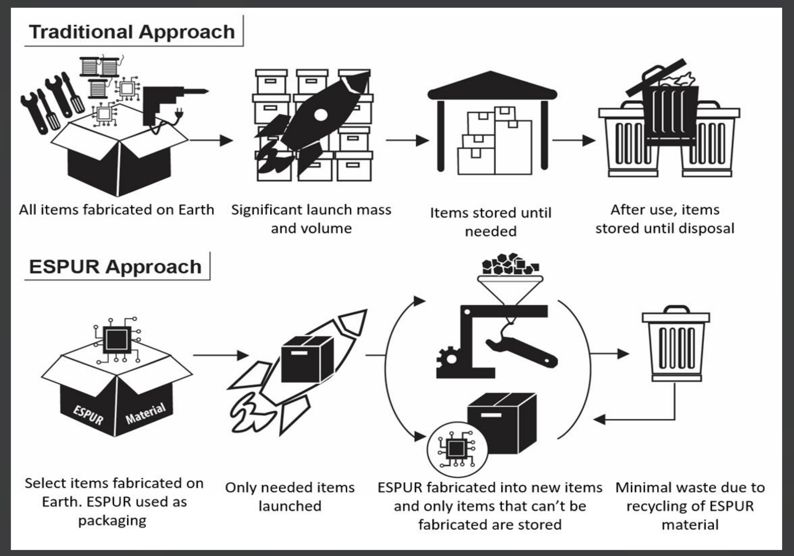
PURPOSE

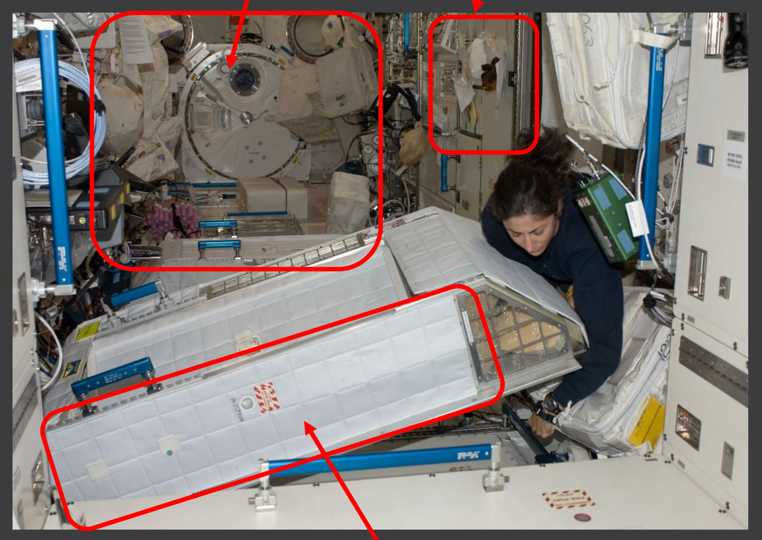


By Enabling a Sustained Presence Using Recyclable (ESPUR) chemistry, longer duration extra-terrestrial missions can be optimized.

APPLICATIONS

Recyclable packaging and storage

Clips, brackets, mounts



Feedstock stored as dual-purpose shielding

The International Space Station (ISS) offers opportunities to use ESPUR materials for part replacement and to provide radiation protection while in feedstock storage form.

APPROACH

Phase 1
Generate epoxy microparticles (EMPs) via precipitation polymerization.

Phase 3
Bond coated EMPs in click-chemistry reaction.

Phase 2
Generate a Copoly(carbonate urethane) to mobilize click-chemistry functions.

Phase 4
De-bond particles to revert to reusable feedstock.

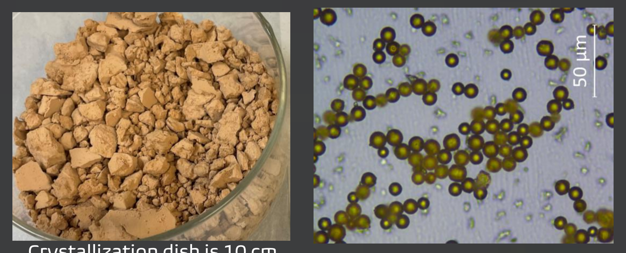
Experimental effort discussed here

Computational effort discussed here

Simultaneous experimental and computational efforts will enable rapid elucidation of the most promising polymer composition, EMP mixture formulations, and how best to evaluate these materials across several length scales.

EXPERIMENTAL EFFORTS

Phase 1



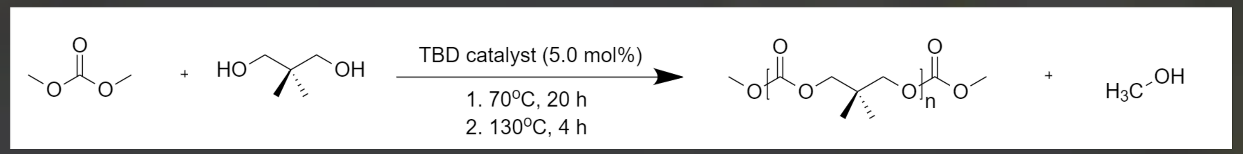
Crystallization dish is 10 cm

- Phase 1: EMPs are generated via precipitation polymerization.

Phase 2

- Phase 2: Materials to be utilized in EMP coatings are prepared.

Polycarbonate Synthesis

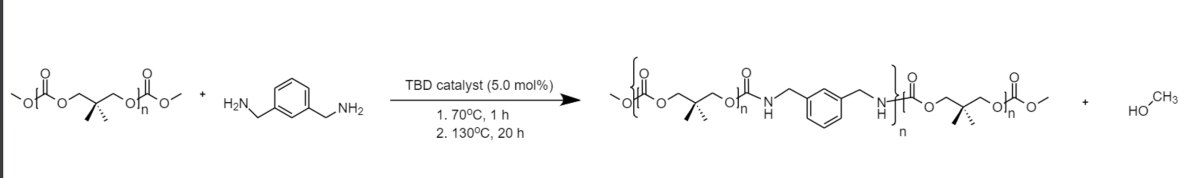


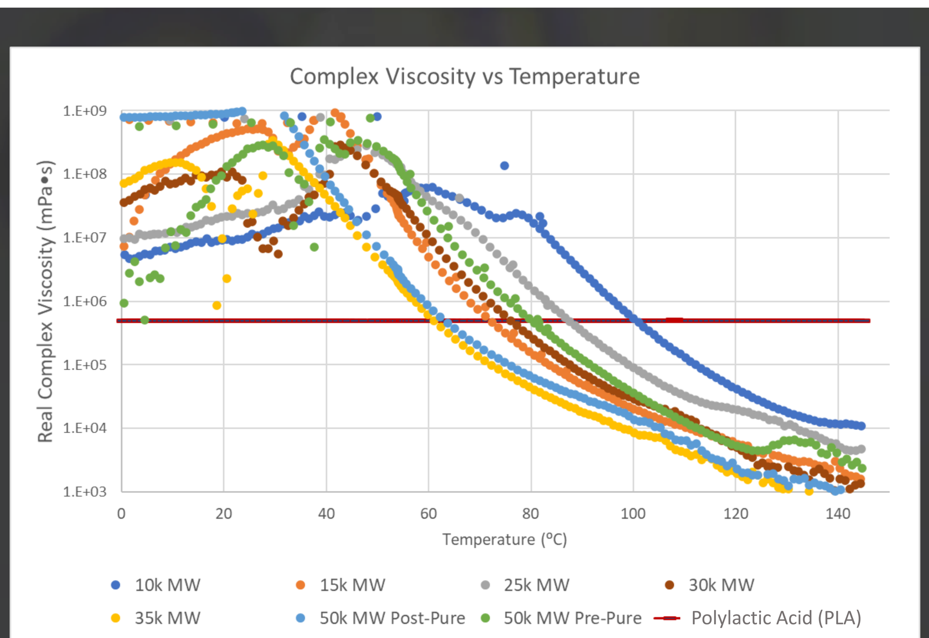
Polycarbonate	DMC:NPG ratio	TBD* (mol%)	Molecular Weight	Ether peaks
PC 9 pure	3.1	5	550	No

*1,5,7 Triazabicyclo[4.4.0]decene

- Reaction stoichiometry impacts molecular weight and polymer purity.

Copoly(carbonate) Urethane (CPCU) Synthesis





- Generation of the Polycarbonate and Copoly(carbonate) Urethane is the main objective of Phase 2.
- These polymers are used as bulk recyclable material to be functionalized with reversibly bonded end groups.

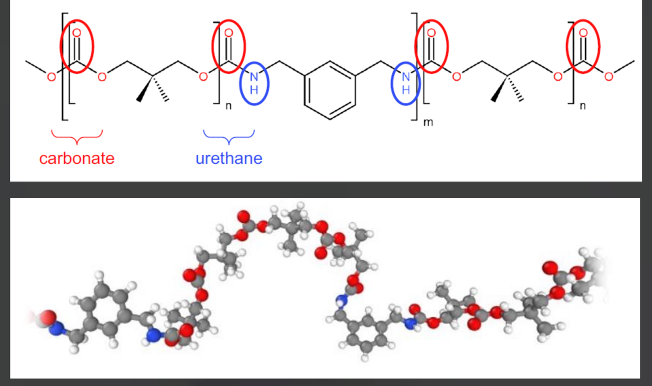
Material	Glass Transition Temperature (°C)	Temperature (°C) to Reach Viscosity of 5x10⁵ mPa•s
10k MW	96	100
15k MW	58	72
25k MW	61	87
30k MW	49	74
35k MW	52	62
50k MW	48	64
PLA	55-60	260

Viscosity of PLA filament from: Zhu, Pu, "Polymer Materials Via Melt Based 3D Printing: Fabrication and Characterization" (2018) 2895. https://tigerprints.clemson.edu/all_theses/2895

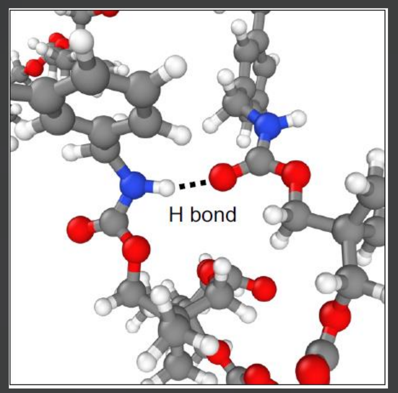
COMPUTATIONAL EFFORTS

Phase 2

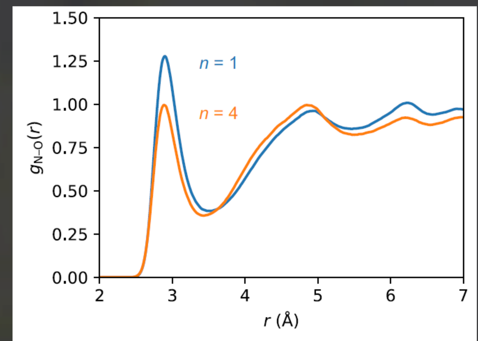
- Phase 2: Materials to be utilized in EMP coatings are prepared.



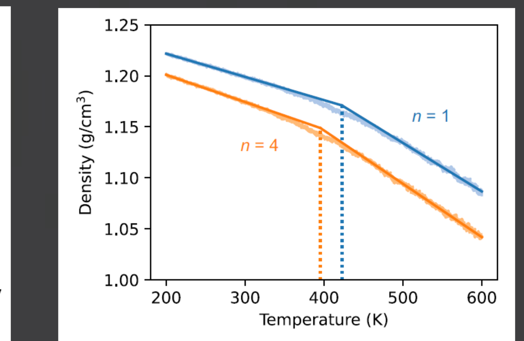
CPCU chemical structure and simulation configuration with a 4 unit carbonate block



Intermolecular hydrogen bonding



Radial distribution functions for 1 and 4 unit carbonate block CPCUs



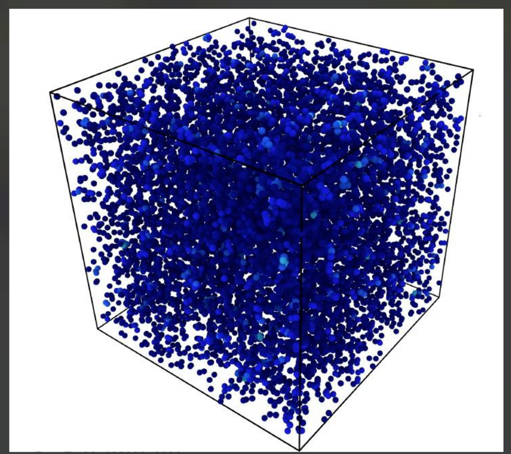
Glass transition temperature determination

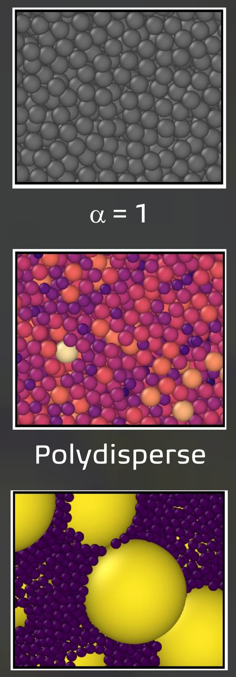
- Hydrogen bonding interactions have a significant impact on resultant material properties. Higher molecular weight, less hydrogen bonding, lowers glass transition temperature.

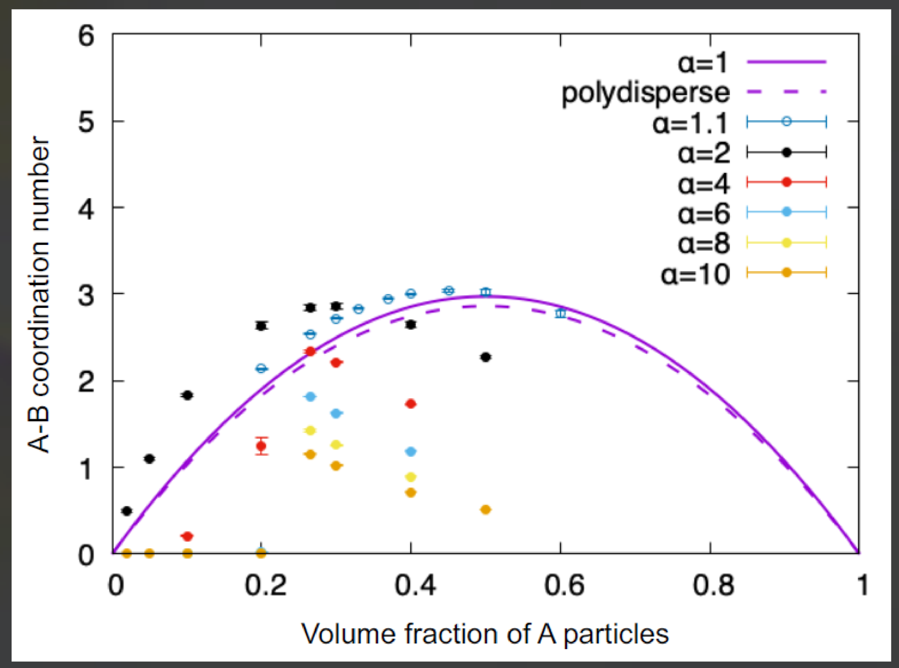
Phase 3

- Phase 3: Random packings generated with contact mechanics-informed interactions to represent a 'real' system.

- 2000 to 1 million particles
- Mixture of two particle types (A and B)
- α: multiplier for particle size difference
- Contact mechanics described by Hertzian model
- Compress dilute to dense final packing
- Periodic boundary conditions
- LAMMPS: large scale atomic/molecular massively parallel simulator



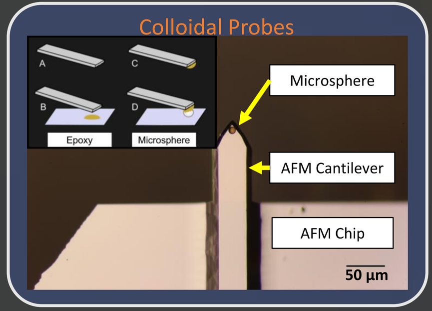




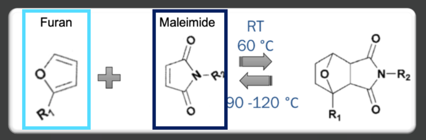
- A size ratio (α) of 2 and a volume fraction of the smaller (A) particles of approximately 25% will have the number of A-B particle interactions and a reduced void volume, relative to an α of 1, based on these results.

SINGLE PARTICLE CHARACTERIZATION

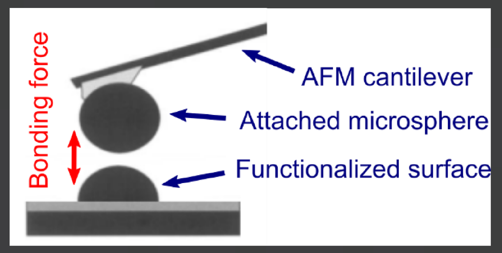
- Single particle interactions will be determined using atomic force microscopy (AFM) techniques.



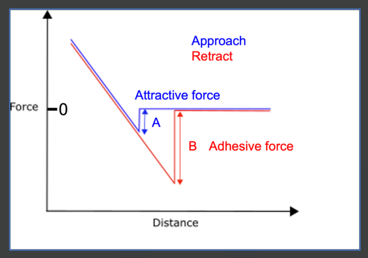
Generation of functionalized cantilevers



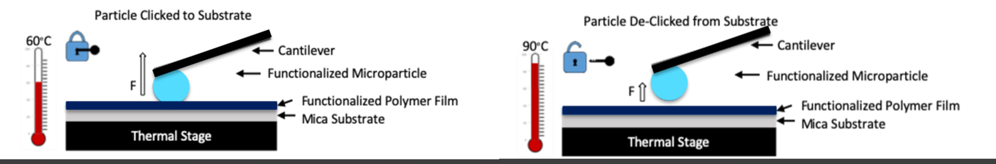
Reversible click-chemistry reaction



Schematic for adhesion force experiment



Representative adhesion force experiment data



- AFM will elucidate single particle interaction strengths to improve computational model fidelity, the onset temperature of the click reaction between furan and maleimide functionalities, and clicking and unclicking efficiency.

FUTURE WORK

Phase 3

- Phase 3: Functionalized end groups are attached to enable click-chemistry bonding and interactions are characterized.

Phase 4

- Phase 4: Functionalized end groups are reversed into original Copoly(carbonate) Urethane compositions and re-characterized for recyclability over time.

CONCLUSIONS

- Epoxy Microparticle size distribution can be tailored to influence polymer characteristics in final materials.
- Molecular weight of polycarbonate plays significant role in determining material toughness.
- Polycarbonate purity and molecular weight is dictated by well-defined boundaries in stoichiometric ratios.
- Copoly(carbonate) Urethanes can likely be processed into functional materials at approachable reaction temperatures around 90°C.
- Recyclable click-chemistry polymers can be applied via slurry extrusion and filament extrusion printing processes.

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