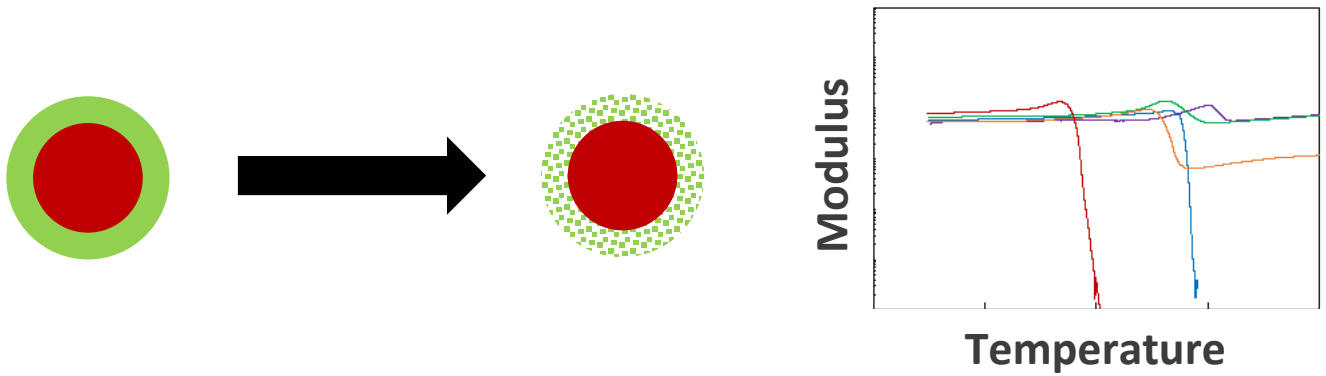
SAND2022-16383C

Sandia National Laboratories

Polybutadiene Elastomers with Degradation Profiles Programmed by Microencapsulation and Controlled Release of Metathesis Catalysts



Brad H. Jones and Matthew J. Warner

6 December, 2022

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

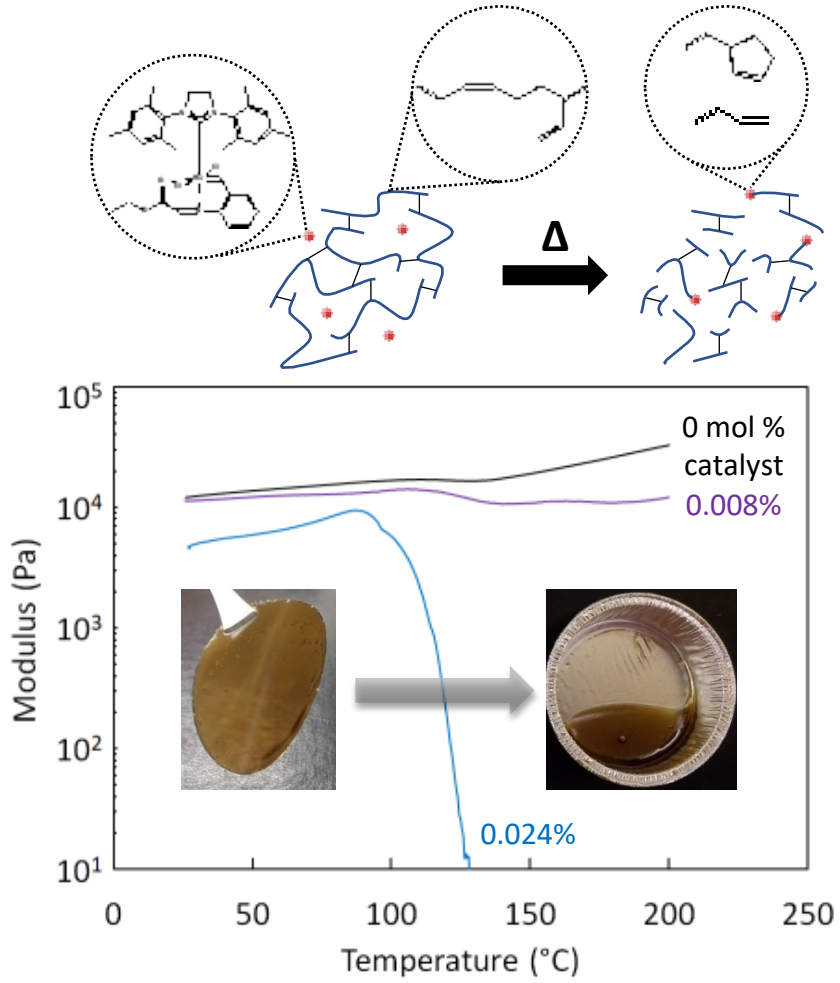
SAND2022-xxxxC

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

In Situ Degradation

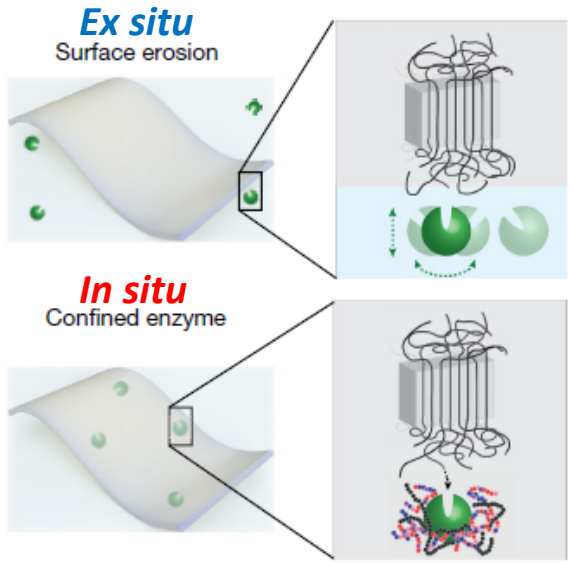
In situ degradation may improve efficiency in waste remediation with greater control over degradation profiles

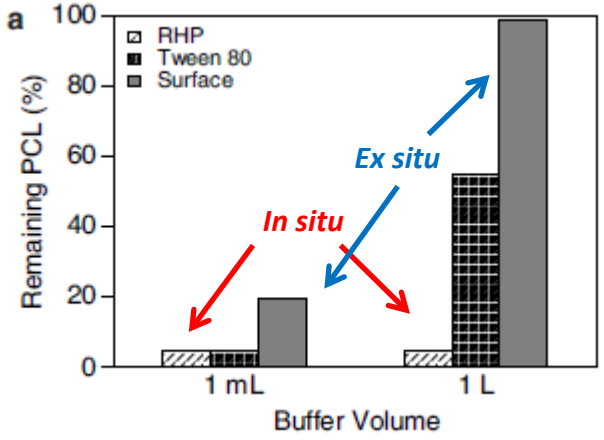
PB elastomer degradation with latent metathesis catalysts

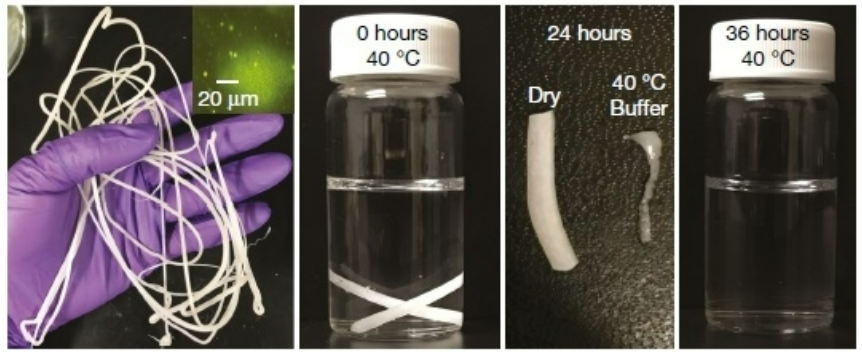


Herman, J.A.; Jones, B.H.; *et al. ACS Appl. Polym. Mater.* **2019**, *1*, 2177-2188.

Polyester degradation with protected, nano-dispersed enzymes





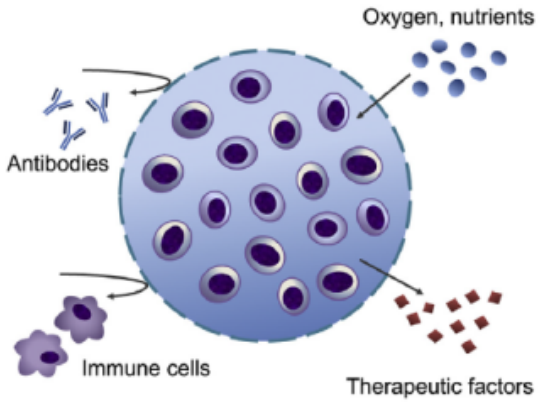


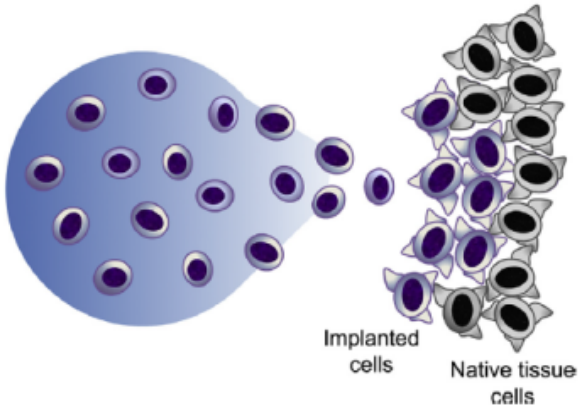
DelRe, C.; *et al. Nature* **2021**, *592*, 558-563.

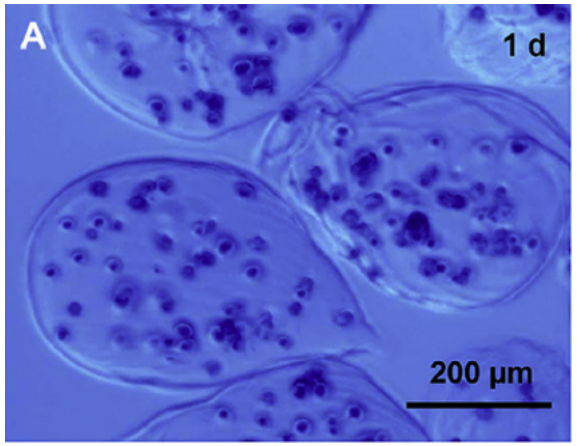
Inspiration from Therapeutics and Self-Healing Materials

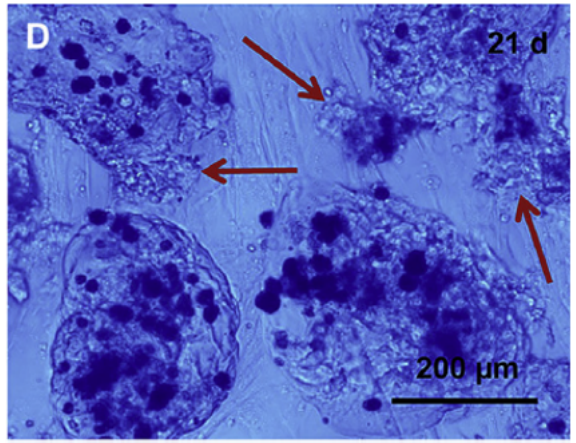
Microencapsulation can be used to program *in situ* physical and chemical processes

Therapeutic delivery with microencapsulated stem cells



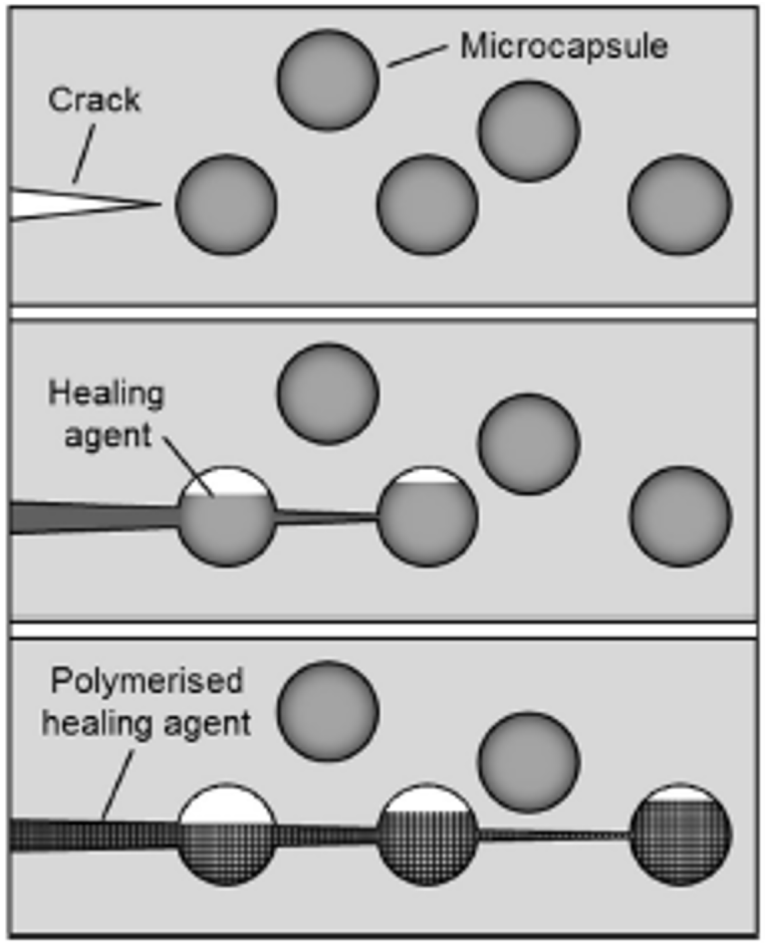


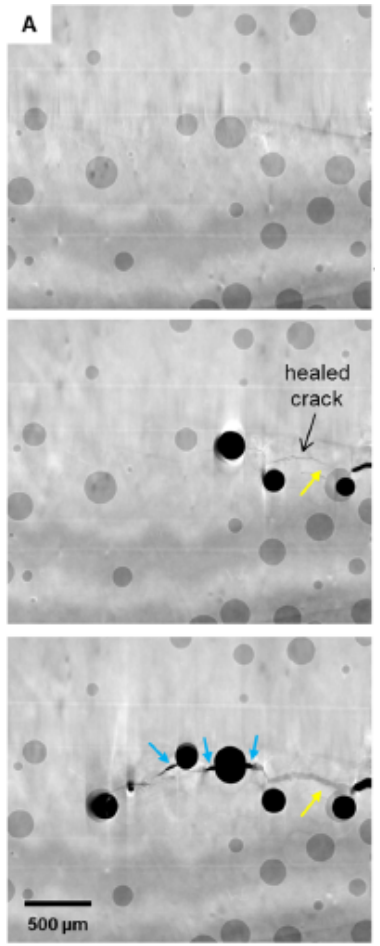




Gonzalez-Pujana, A.; *et al. J. Drug Deliv. Sci. Technol.* **2017**, *42*, 49-62.

Self-healing epoxy with microencapsulated resin



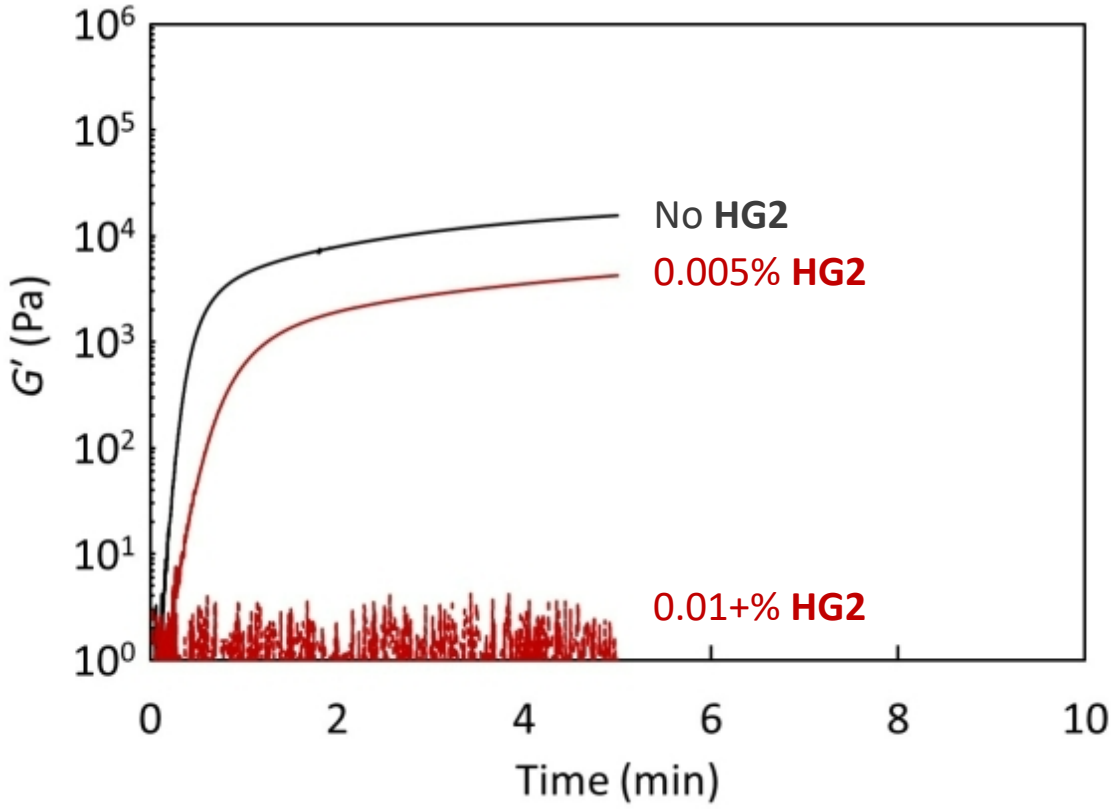


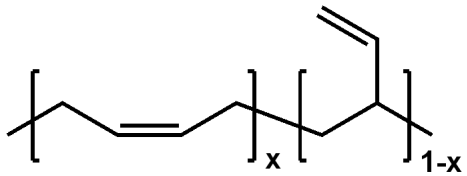
McDonald, S.A.; *et al. Sci. Rep.* **2019**, *9*, 17773.

Goal: Controlled Release for Elastomer Degradation

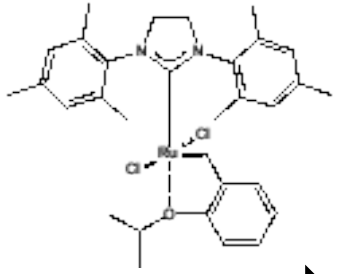
This work explores microencapsulation of metathesis catalysts for polybutadiene (PB) elastomer degradation

PB resin pre-loaded with **HG2** does not crosslink to a proper elastomer

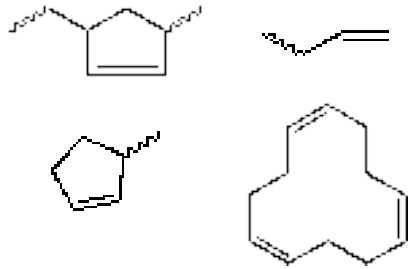




PB resin

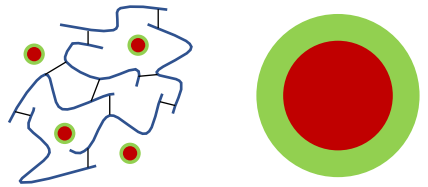


HG2
(2nd gen. Hoveyda-Grubbs catalyst)

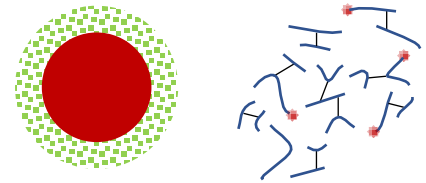


typical metathesis products

How to protect catalyst?



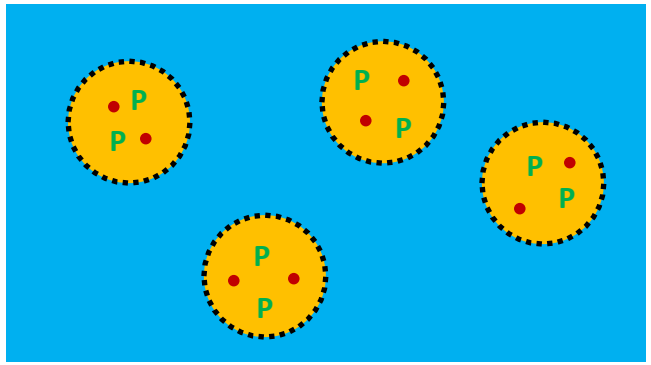
How to release catalyst?



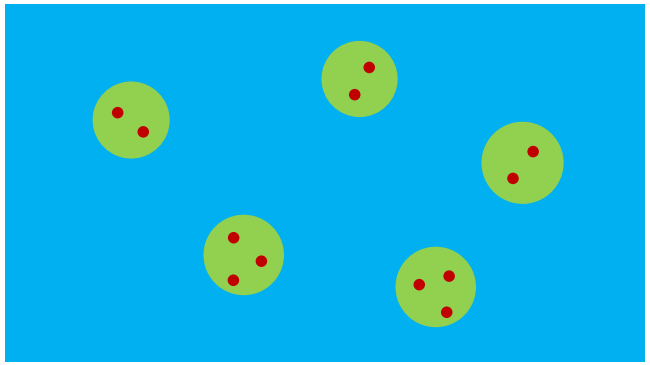
Herman, J.A.; Jones, B.H.; *et al. ACS Appl. Polym. Mater.* **2019**, *1*, 2177-2188.

Microencapsulation *via* Emulsion Templating

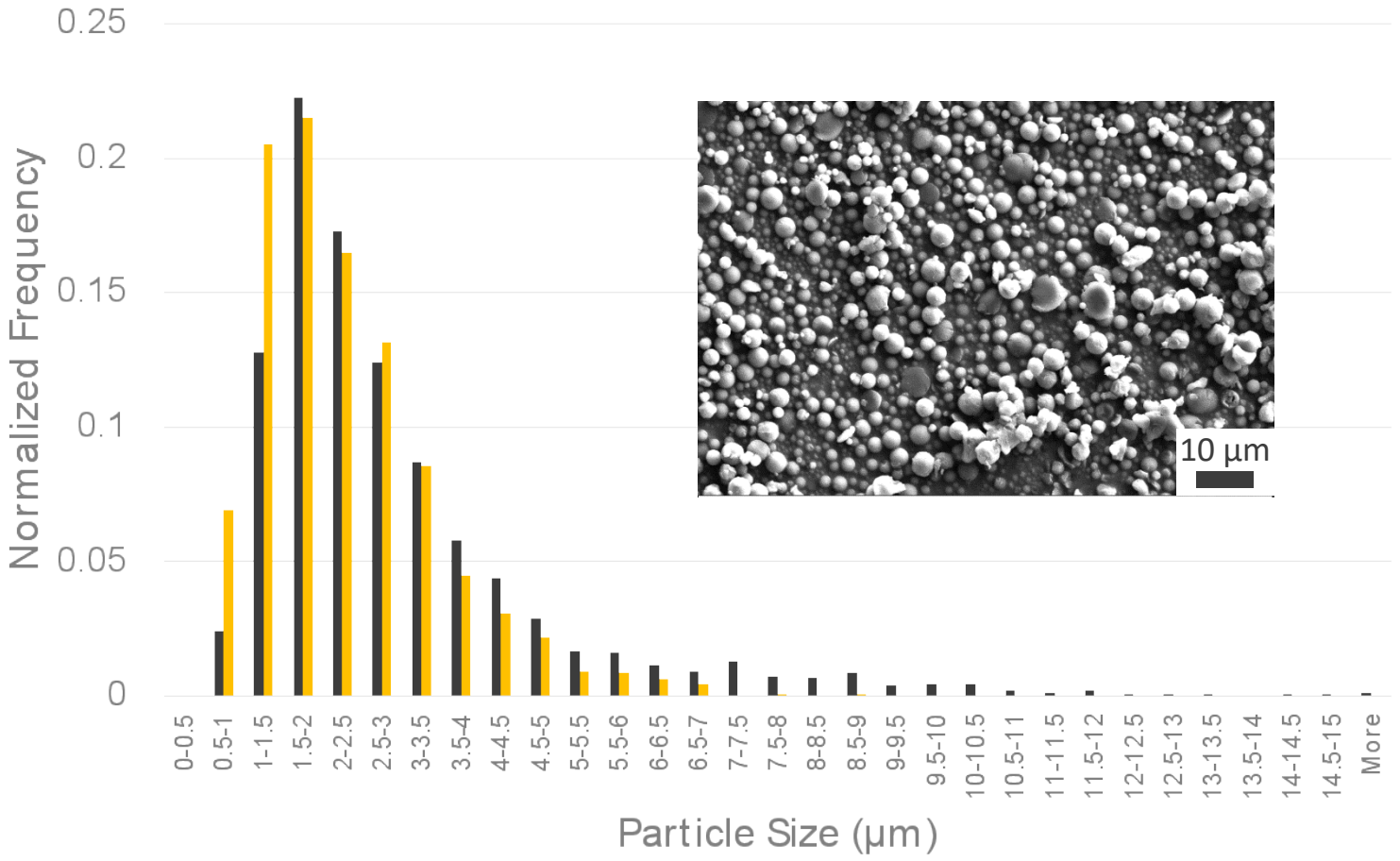
Co-solubilization of polymer (encapsulant) and catalyst in dispersed phase of emulsion is a simple route to microencapsulation



P polymer
• HG2
····· surfactant
water
immiscible solvent
(*e.g.*, CH_2Cl_2)



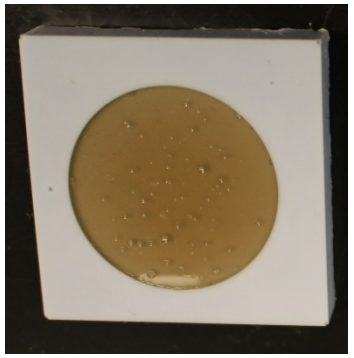
solid polymer



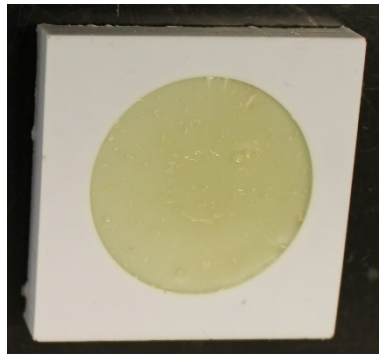
Importance of Glass Transition Temperature (T_g)

T_g of encapsulant needs to be above processing temperature of elastomer for catalyst protection

$T_g < T_{x\text{-}link}$



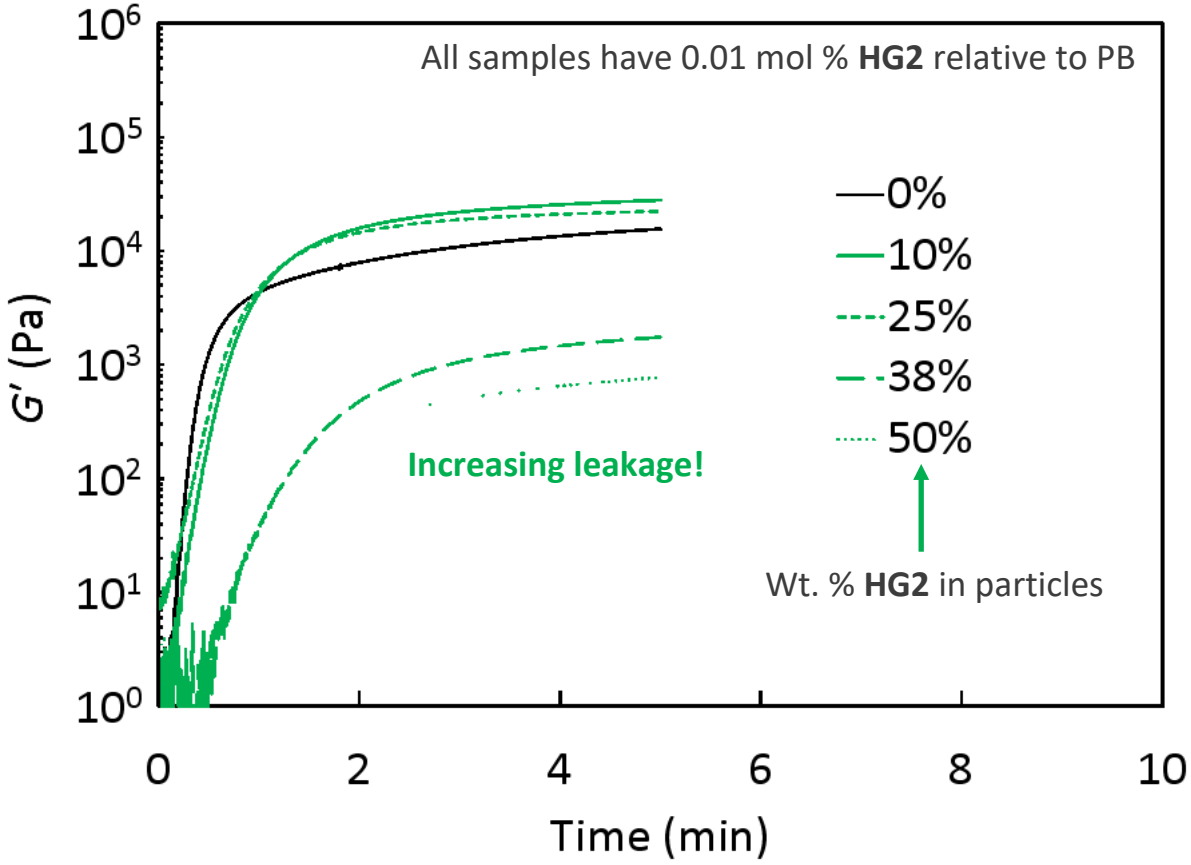
$T_g > T_{x\text{-}link}$



No catalyst release
(Aside from leakage)
Can make a proper elastomer!

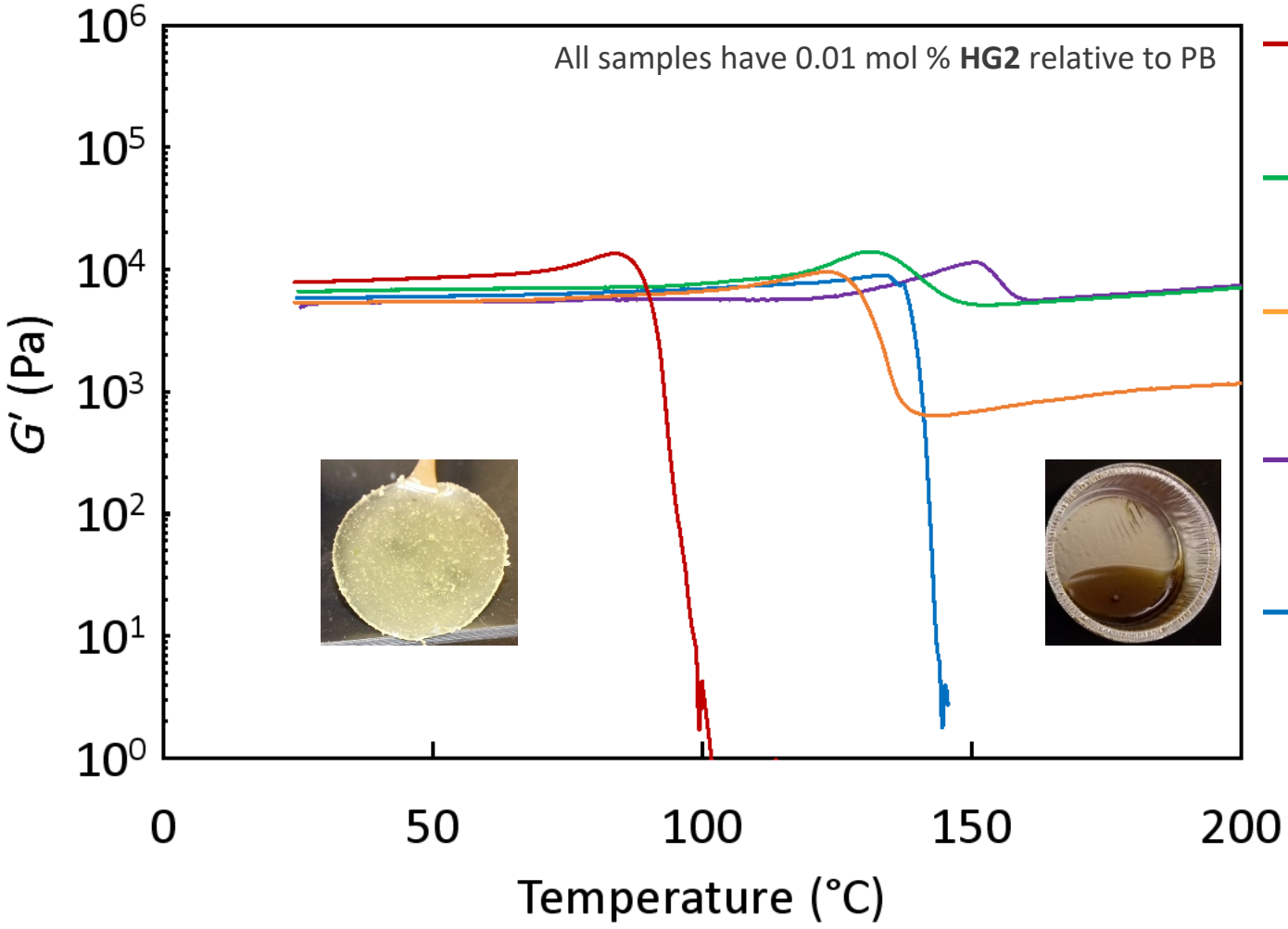
Rapid catalyst release & PB resin degradation
Cannot make a proper elastomer!

Crosslinking of PB resin with encapsulated **HG2** particles of varied **HG2**:encapsulant composition

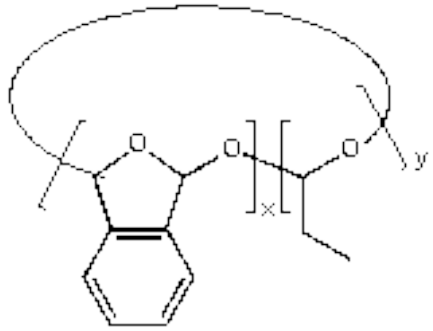


Importance of Glass Transition Temperature (T_g)

Catalyst is released and elastomers degrade with an onset temperature that trends with encapsulant T_g



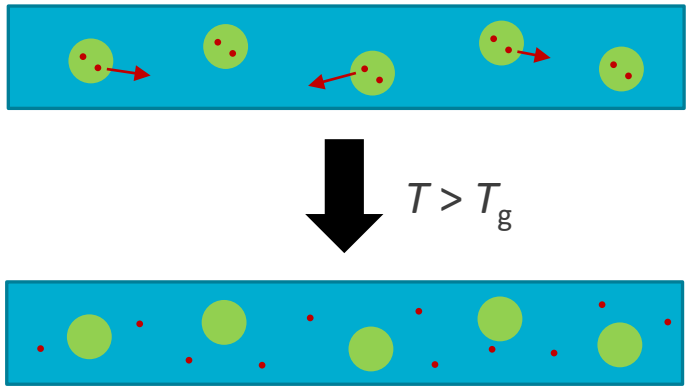
- Polylactide
  T_g = 60 °C
- Poly(methyl methacrylate)
  T_g = 92 °C
- Polystyrene
  T_g = 104 °C
- Poly(bisphenol A carbonate)
  T_g = 140 °C
- Cyclic copolymer of pthalaldehyde and propanal
  T_c = 110 °C



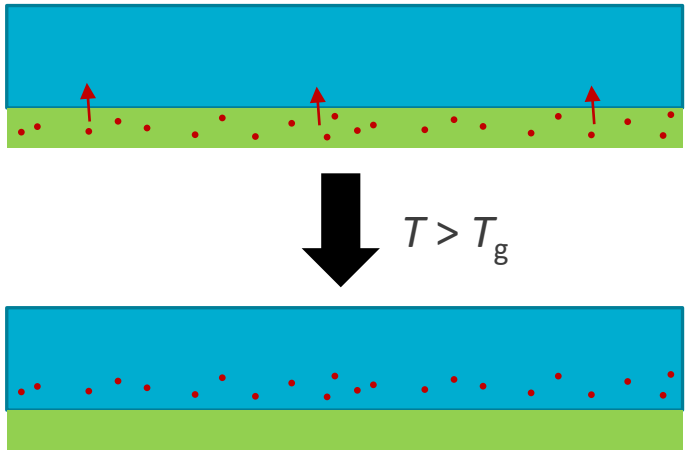
In Situ is Better than *Ex Situ*

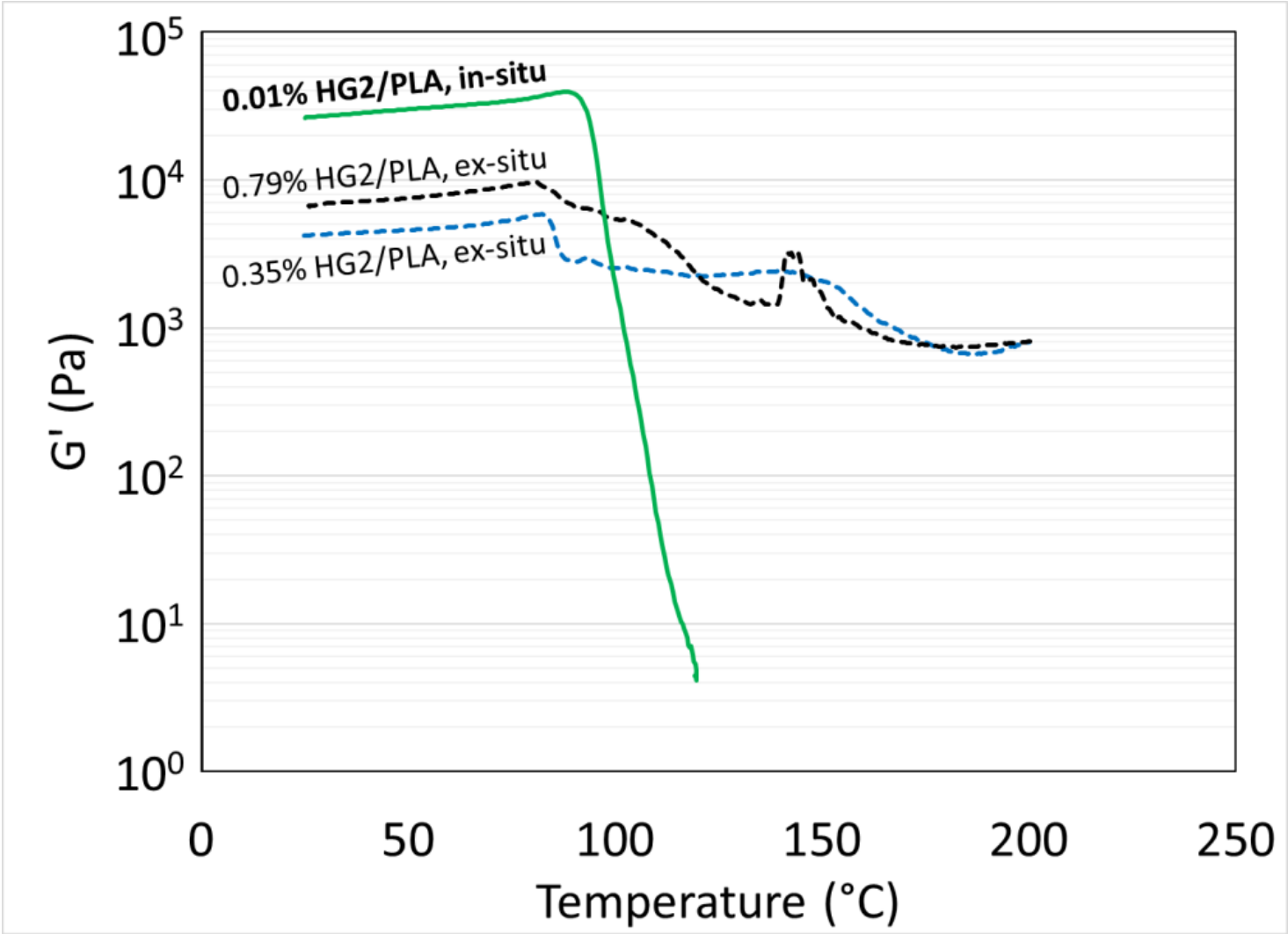
Degradation is far more efficient from inside out rather than outside in

In situ experiment



Ex situ experiment

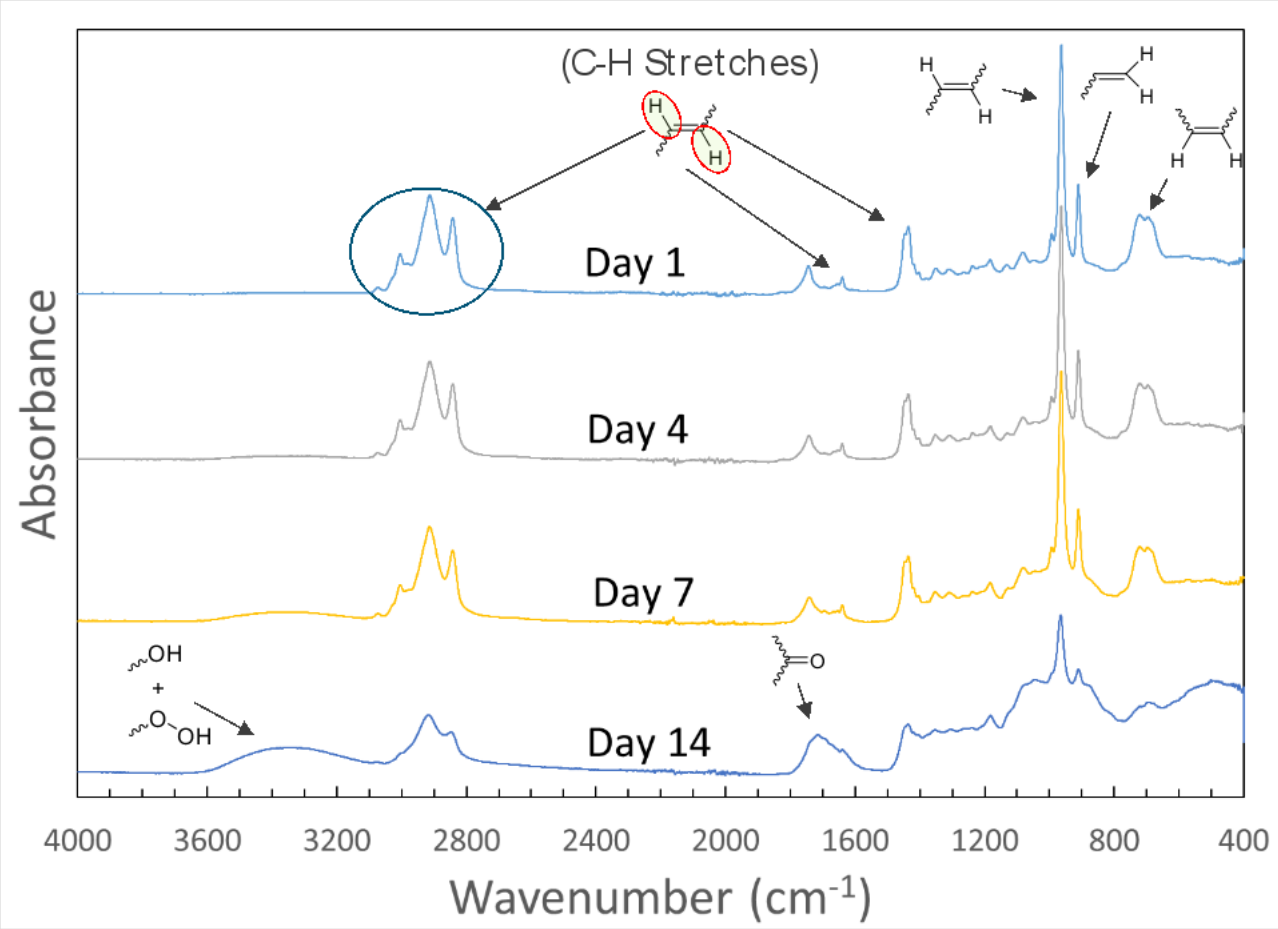


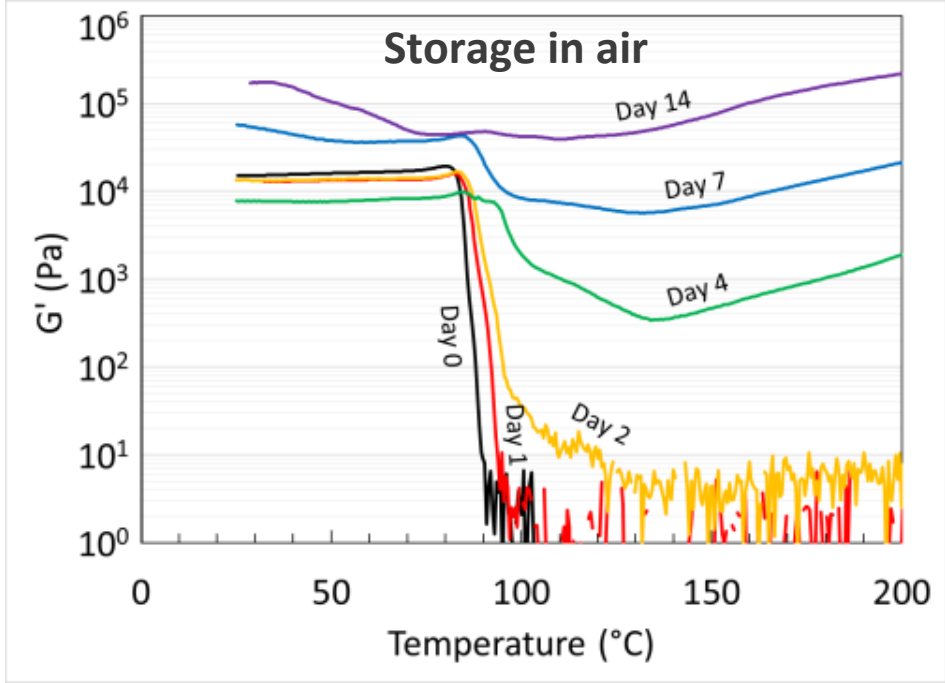


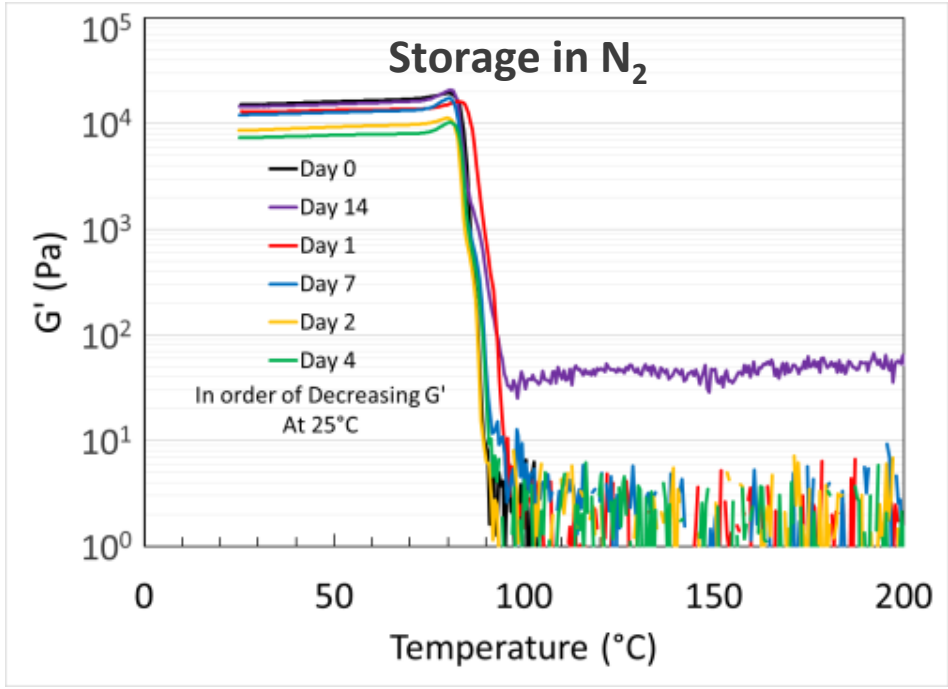
Stability and Efficacy with Time

Oxidation of PB network decreases efficacy with storage

FTIR spectra, elastomers stored in air







Summary

1. Microencapsulated catalyst particles enable *in situ* degradation of elastomers for waste remediation
2. Glassy encapsulants protect catalyst from interaction with elastomer during crosslinking
3. Catalyst release/elastomer degradation temperature correlates with encapsulant T_g or T_c
4. Currently requires inert storage conditions for extended stability

Acknowledgements

Paul Kohl, Jared Schwartz, Anthony Engler (Georgia Tech) – collaborators for stimuli-responsive encapsulants

Koushik Ghosh, James Lassa, Sam Leguizamon, Hannah Narcross (Sandia) – discussion and experimental support

Sandia's Laboratory Directed Research and Development Program – financial support