3-9-2019

New developments in dual cure epoxies

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Innovative Materials for Additive Manufacturing 2020
Santa Ana Pueblo, NM, USA
March 9th, 2020

New Developments in Dual Cure Epoxies

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(since September 2017)

LUXEMBOURG INSTITUTE OF SCIENCE AND TECHNOLOGY

LIST

- Formed from public research centers Lippmann and Tudor (2015)
- ~600 people (~75% researchers, 45 nationalities)
- 350 publications, 50 patent families
- Nearly 300 research projects (30% EU; ~11 M€ contract, ~15 M€ competitive, ~64 M€ total budget)

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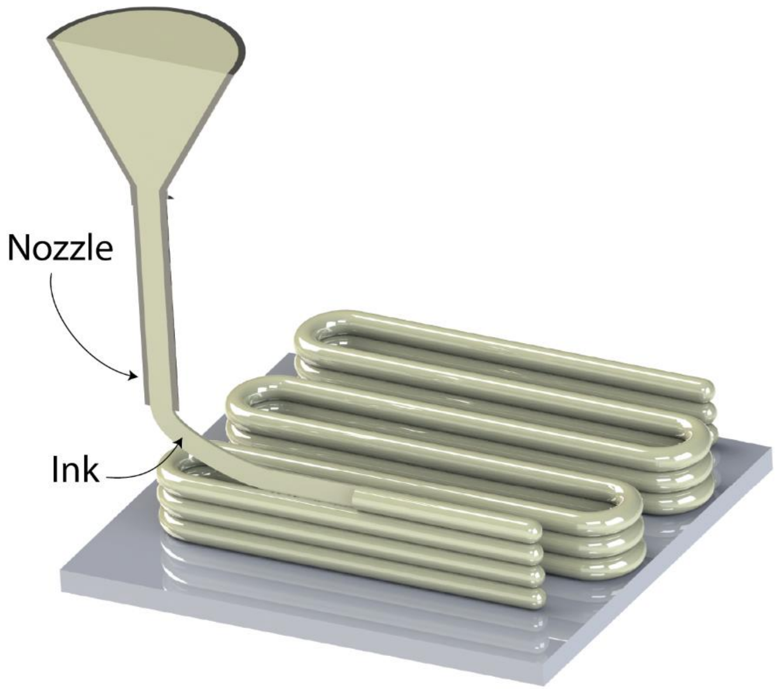
Introduction

- In theory, AM promises a convenient route functionally graded materials (FGMs)
- In practice…
  - In polymer AM, we still have trouble achieving bulk properties in homogeneous parts
  - To realize FGMs, we tend to focus on process innovation (i.e. complex co-deposition systems)
  - This makes the realization of high quality parts even harder and further limits materials choices

Introduction

- Much progress has been made in the area of direct ink write (DIW) AM of thermosets

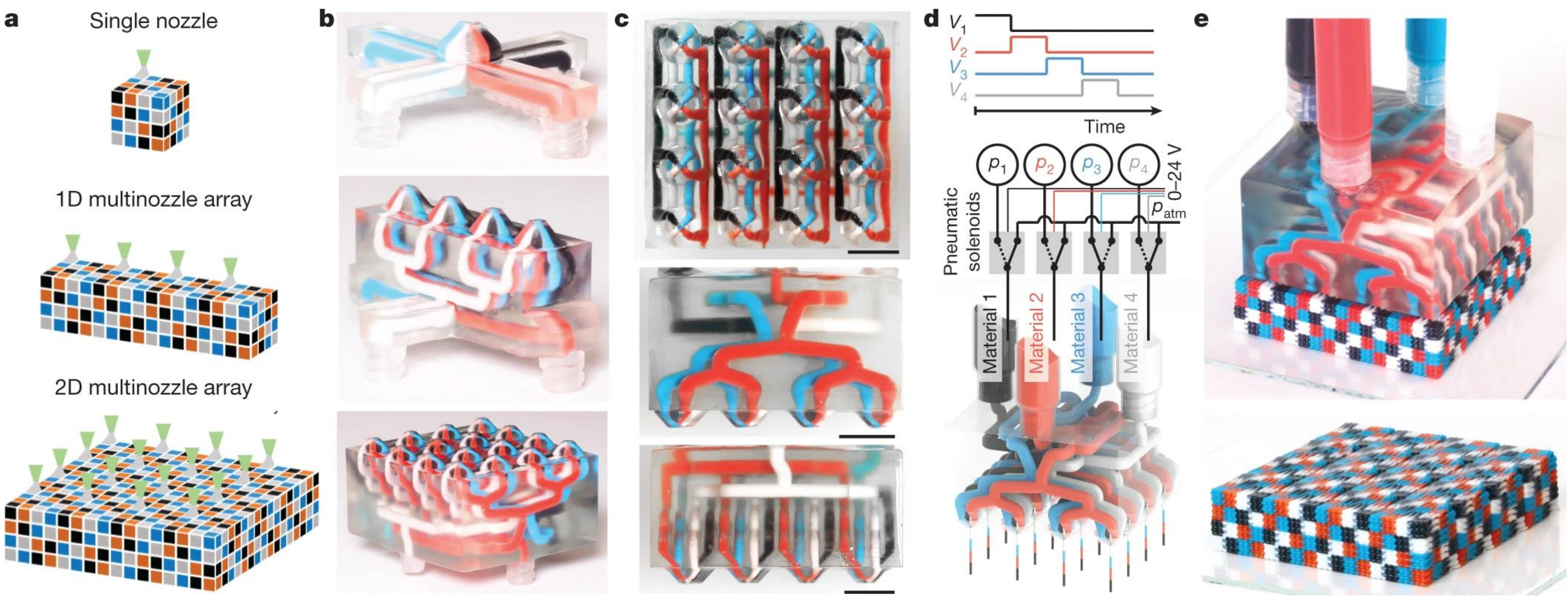


https://labs.wsu.edu/mpml/projects/

  - Can print a range of thermosets and (nano)composites
  - Can align fillers via the application of a variety of fields
  - Can realize excellent performance in the resultant materials

Introduction

- Recently, multi-material DIW has been convincingly demonstrated as well



Skylar-Scott, M.A., Mueller, J., Visser, C.W. *et al.* [Voxelated soft matter via multimaterial multinozzle 3D printing](). *Nature* **575**, 330–335 (2019).

Introduction

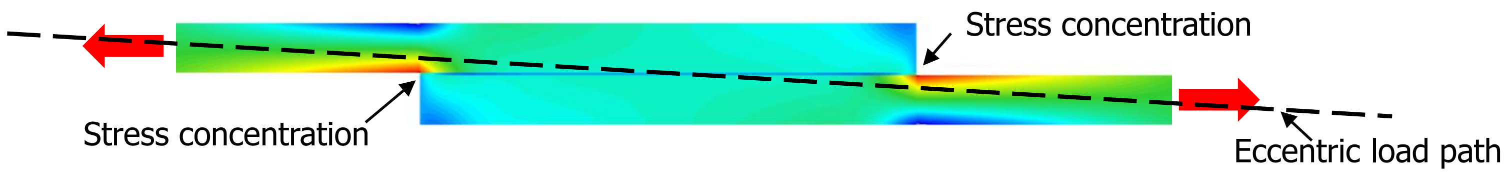
- The previous examples highlight process innovation in the field of thermoset AM
  - Here, careful control of ink rheology enables these processes to work
  - Variations in structure, composition and properties, while significant, remain bounded by process requirements

Q: Is there anything we can do on the materials side to provide additional freedom?

Proposition

- Process-lead innovation is sure to continue, with a host of exciting results anticipated
- Complementing such efforts would be the ability to tune local properties post-printing
- This may be achieved via dual-cure behavior
  - Conventional solidification process enables formation of part
  - Use of high energy radiation post-printing gives localized crosslinking
  - Can be used alone or in tandem with AM

Example: Functionally Graded Adhesives (FGAs)



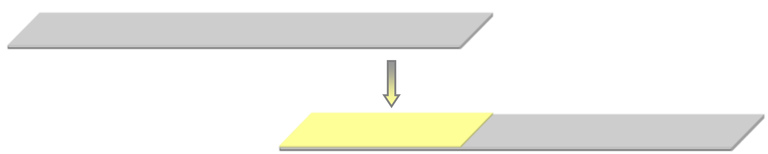
REMINDER: Stress distribution in a normal adhesive bond line

- Advantages of FGAs
  - Stress can be distributed throughout the joint
  - All of the adhesive contributes to joint strength
  - Expectation is that joint is less flaw-sensitive as well
  - Theory predicts 50+% increases in joint strength
  - Confirmed experimentally (+25-60% in practice)
- Hard to make, unstable / inconsistent in practice

Example: Functionally Graded Adhesives (FGAs)

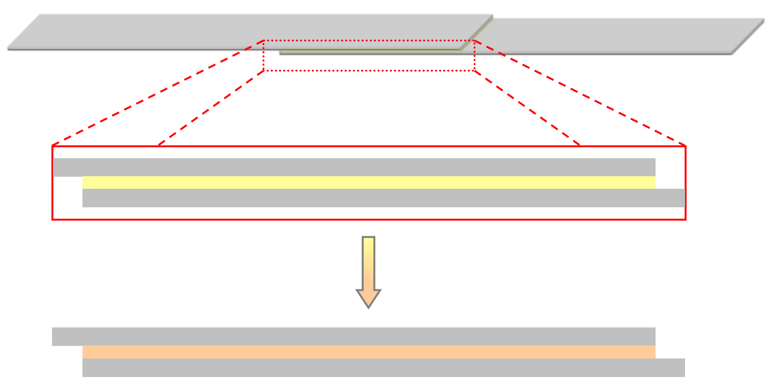
Dual-cure Approach

a)



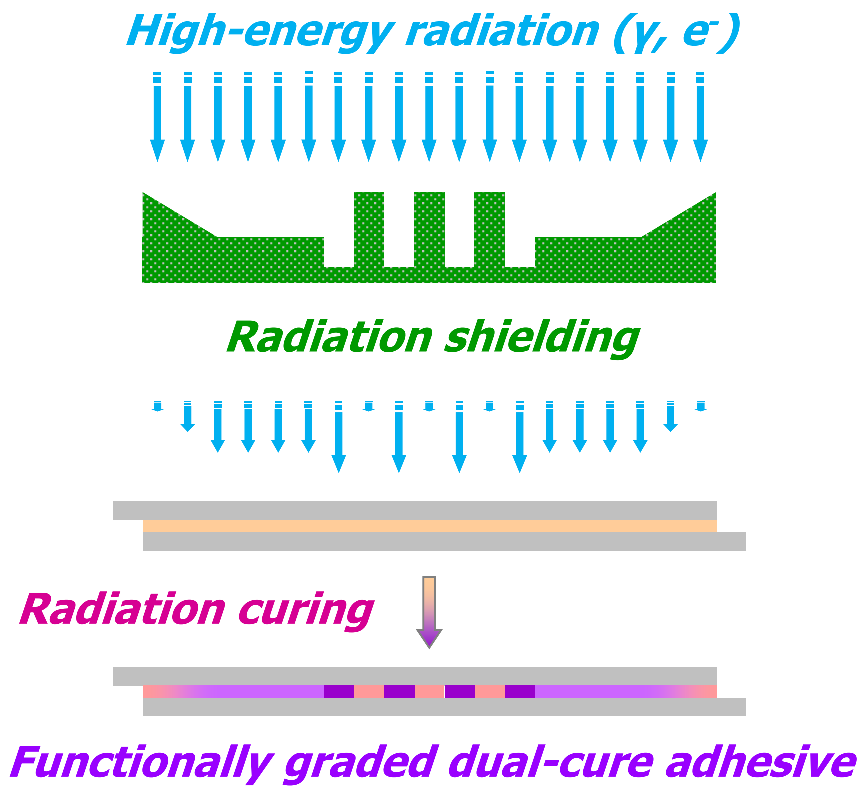
Adhesive application

b)



Conventional (RT, thermal) curing

c)

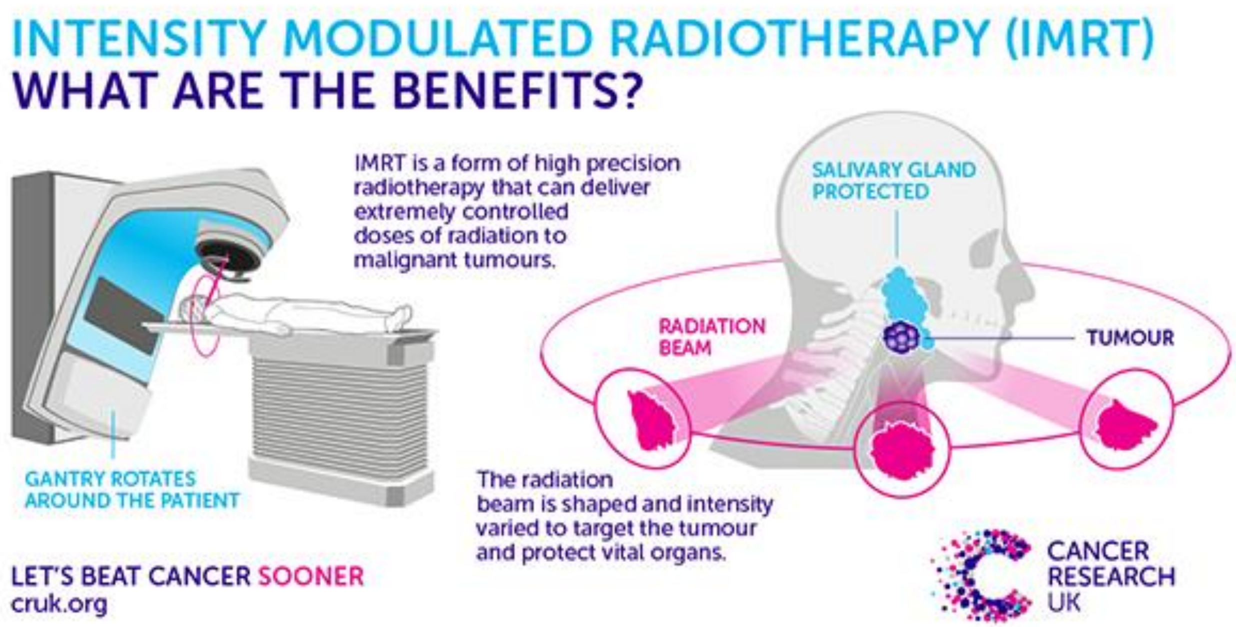


→ ***Easy to manufacture***

→ ***Stable, consistent properties***

Extrapolating to Applications in AM

- For FGAs, only need 1- or 2D control of dose; for AM, would like full 3D control
- Luckily, this technology already exists:



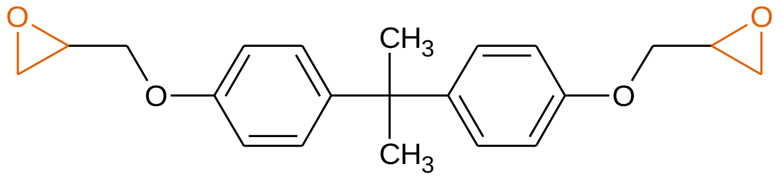
https://scienceblog.cancerresearchuk.org/2017/07/31/imrt-bending-radiotherapy-beams-to-spare-healthy-cells/

Designing a dual cure thermoset

- High energy radiation can give the crosslinking we want – <u>but</u> it can also cause degradation, which must be avoided
  - Need base network with desirable properties, radiation resistance
  - Need to be able to incorporate functional groups that favor radiation-induced crosslinking
  - Need to be able to utilize in the context of an AM process
- Epoxy resins stand out
  - Can be formulated for RT or thermal cure with different hardeners
  - Well-known process characteristics and materials performance
  - Demonstrated to possess excellent radiation resistance
  - Many unsaturated resins, hardeners and modifiers are available
  - Materials class of choice for many DIW AM technologies

Proof-of-concept formulations

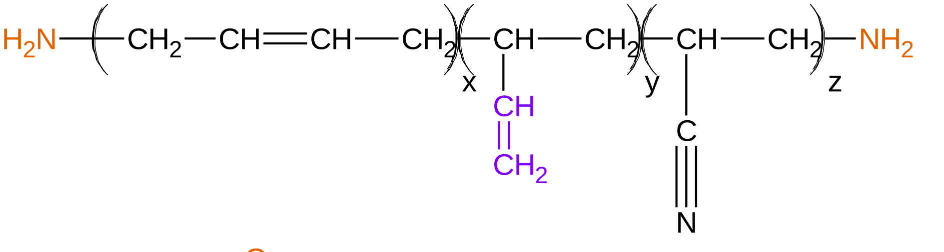
- Using DGEBA base resin
  - Readily available
  - Used in many adhesives
  - Good baseline properties

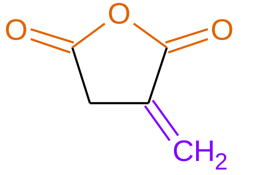


Diglycidyl ether of bisphenol A (DGEBA)

- Two hardeners studied
  - Elastomeric, RT-cured formulation
  - Rigid, thermally cured formulation

Amine-terminated butadiene-nitrile (ATBN)

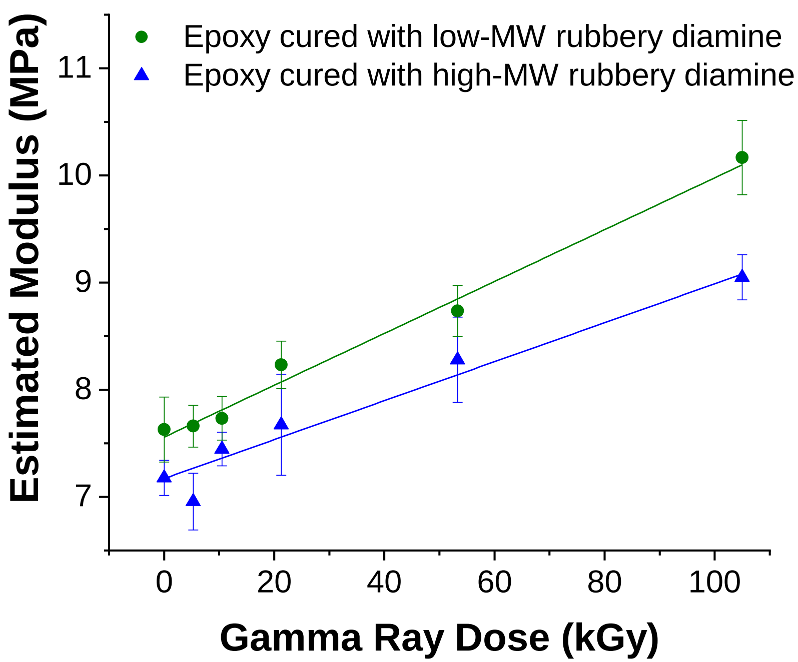


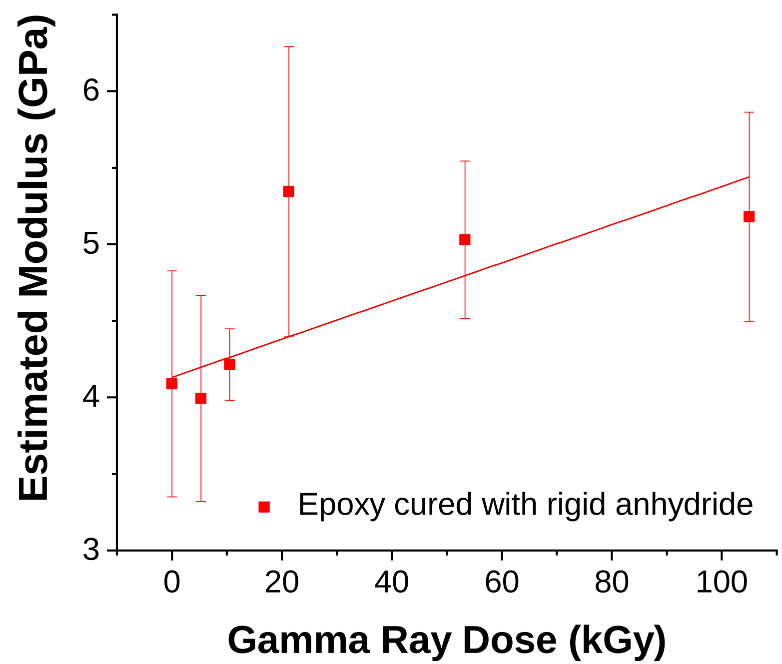


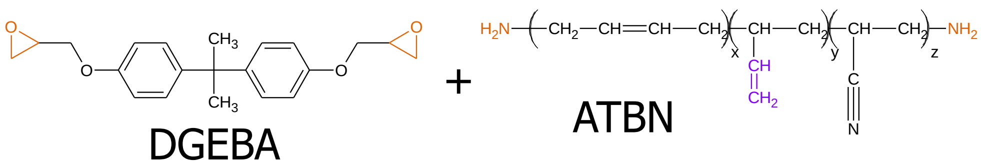
Itaconic anhydride (IA)

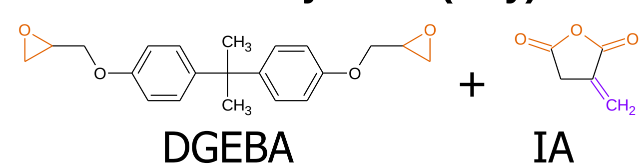
Proof-of-concept formulations

- Small samples cured then irradiated at various doses using ^{60}Co γ-rays
- Hardness measured, converted to modulus via Mix & Giacomin model



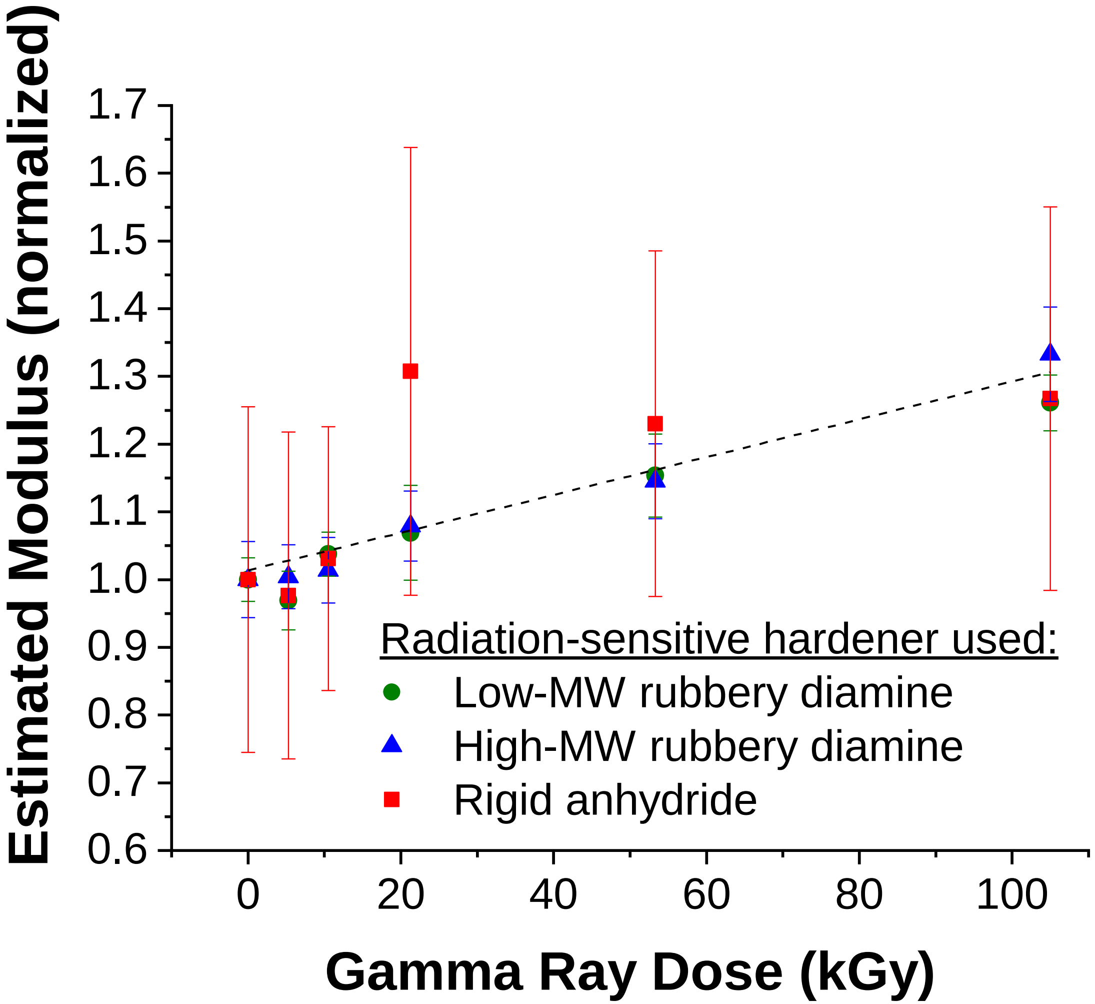






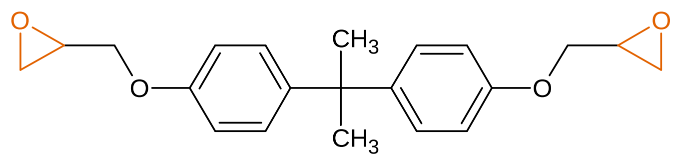
Proof-of-concept formulations

- Post-cure irradiation increases estimated modulus regardless of crosslinking chemistry, T_g
- Similar increases in all cases (+30% @ 100 kGy)
- Minimal shrinkage observed (<0.15%)
- (For reference, this should reduce stress conc. by up to ~40% in an FGA)

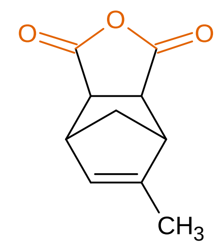


2nd generation dual cure epoxy formulations

Diglycidyl ether of bisphenol A (DGEBA)



+



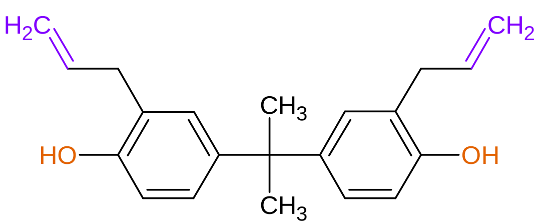
Nadic methyl anhydride (NMA)

<u>Baseline high-performance epoxy</u>

(~1:2 DGEBA:NMA with DBU catalysis)

+

Rigid radiation sensitizer



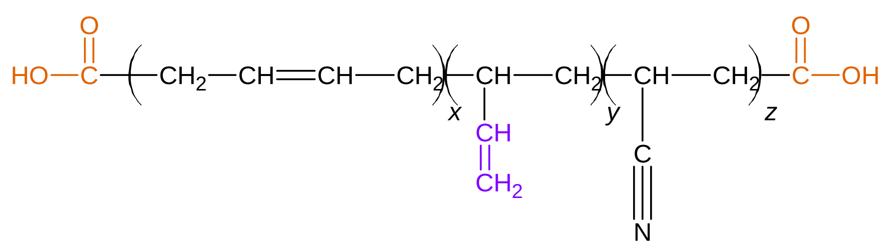
Diallyl bisphenol A (DBPA)

(replaces ~⅓ of NMA)

OR

+

Flexible radiation sensitizer



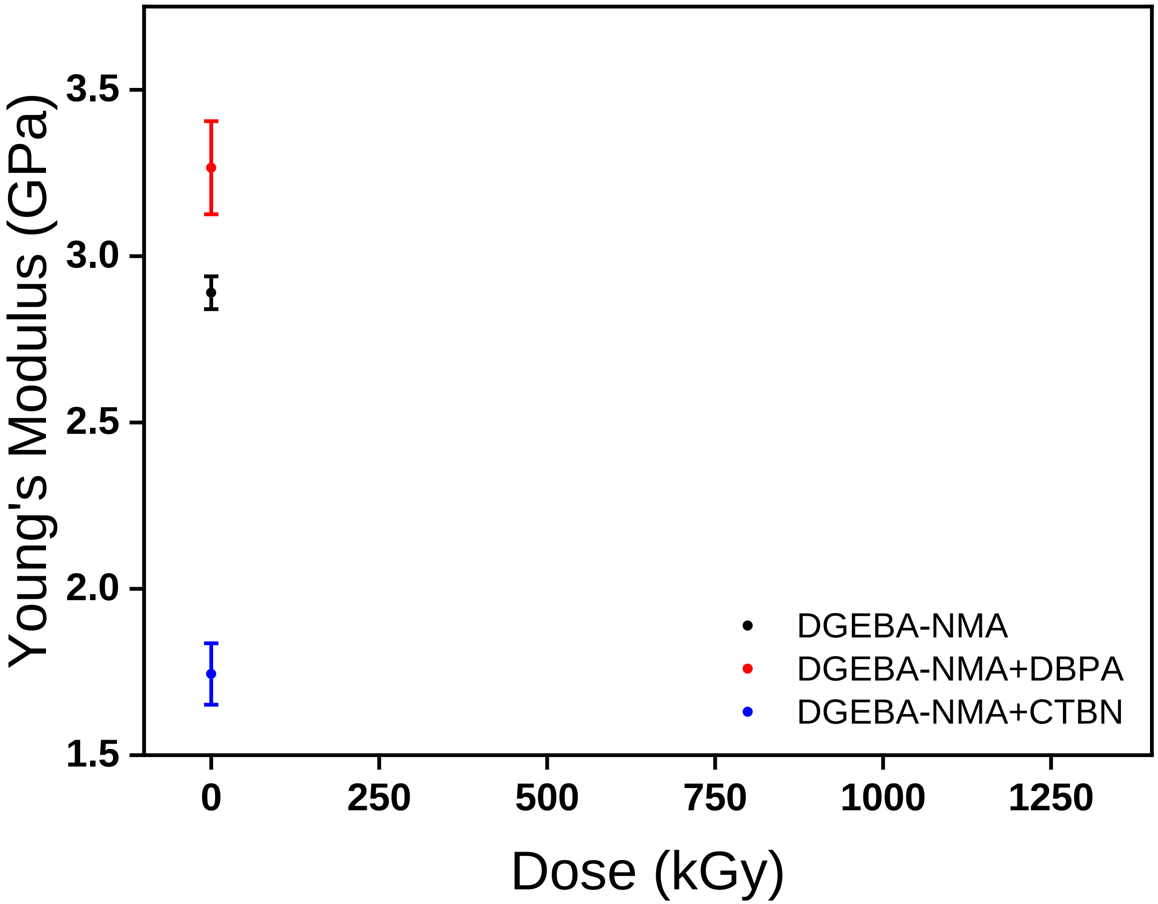
Carboxy-terminated butadiene-nitrile (CTBN)

(15 wt%)

- Samples cured, then irradiated at various doses using ^{60}Co γ-rays
- Analyzed via FTIR, TGA, DSC, DMA, TMA & tensile testing vs. composition & dose (ongoing)

2G dual cure epoxies:
Tensile testing

- Sensitizers behave as expected prior to irradiation
  - DBPA → E↑
  - CTBN → E↓
- Irradiation effects are interesting



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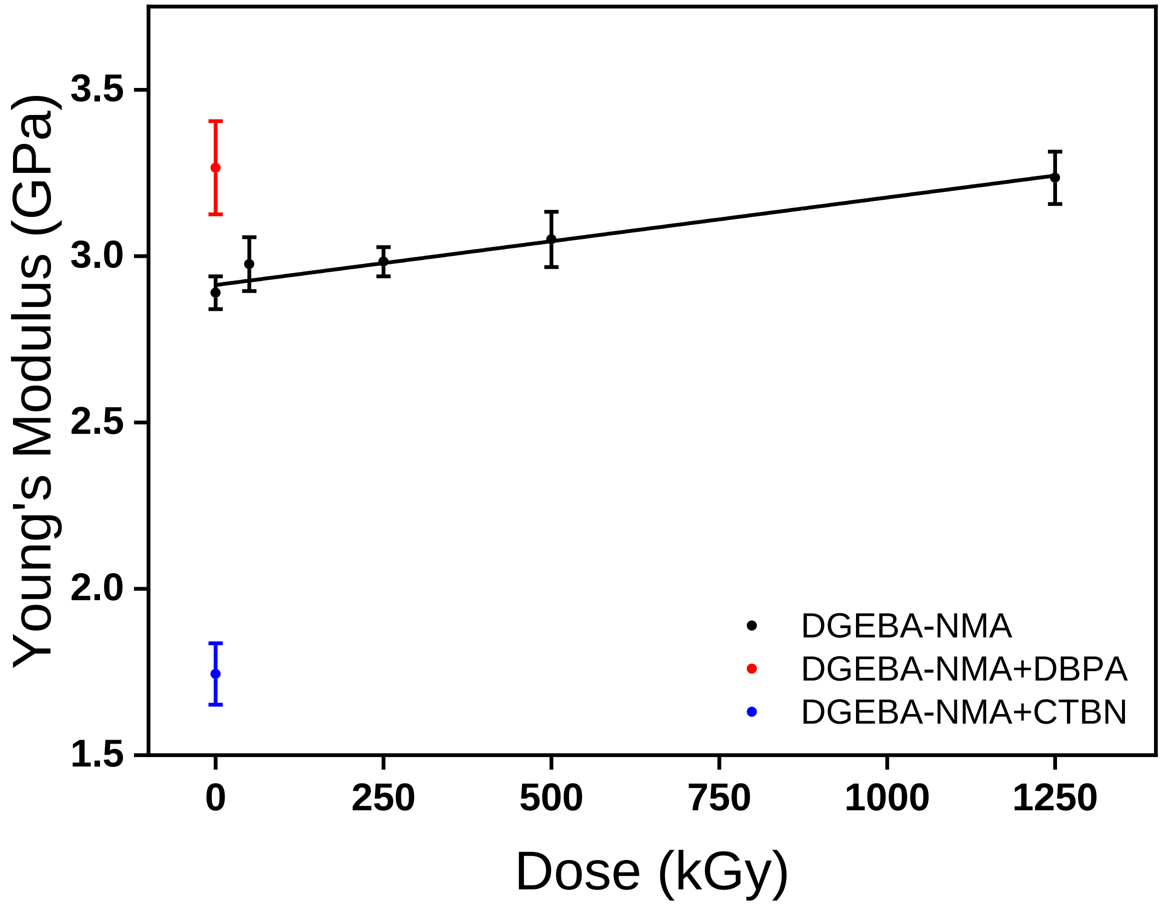

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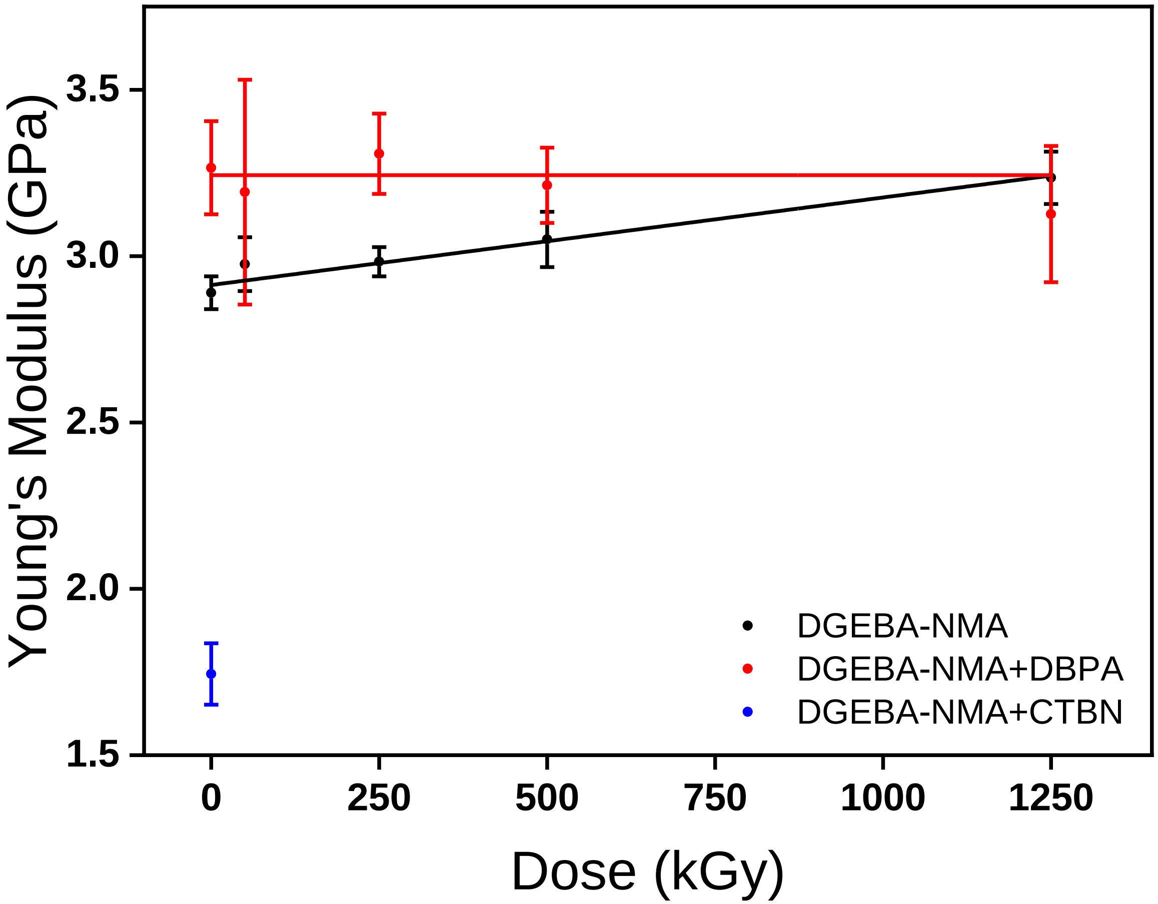

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  - DBPA → E↑
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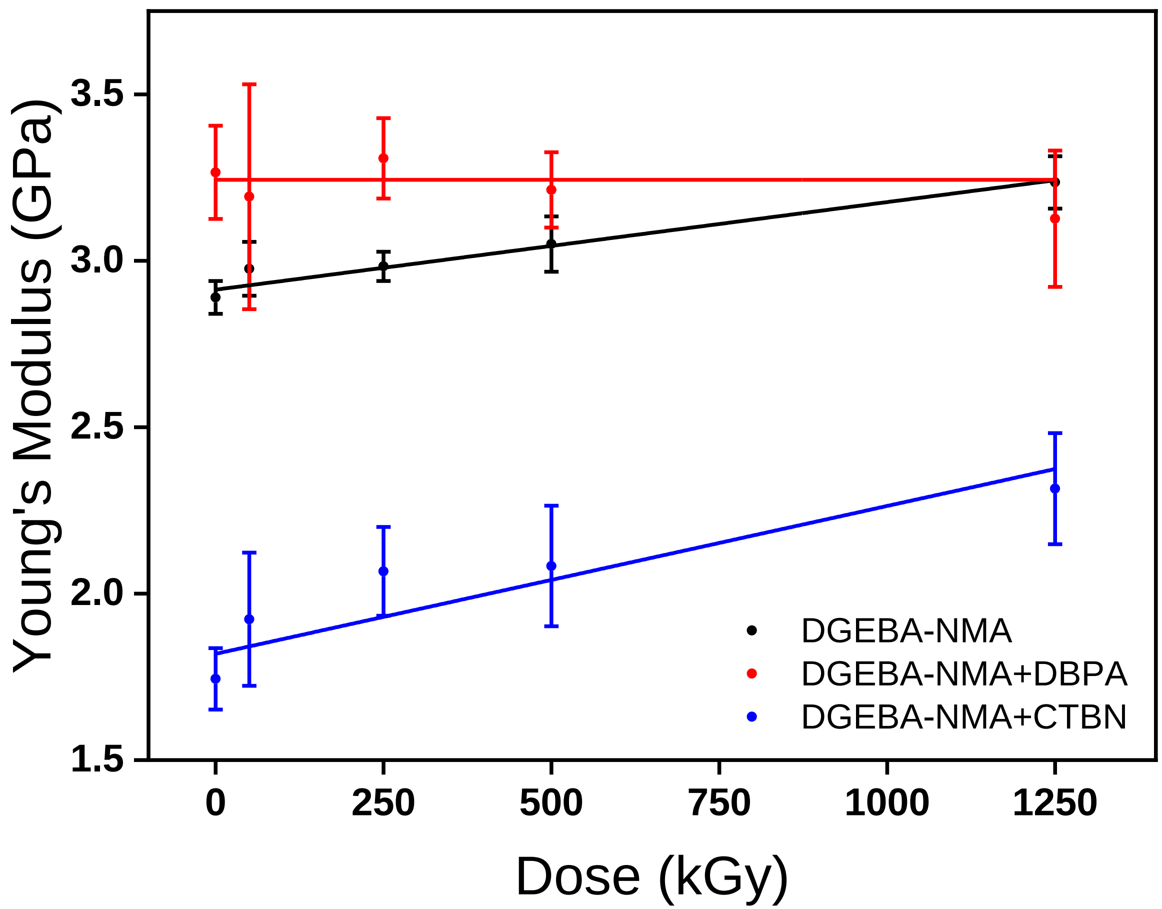
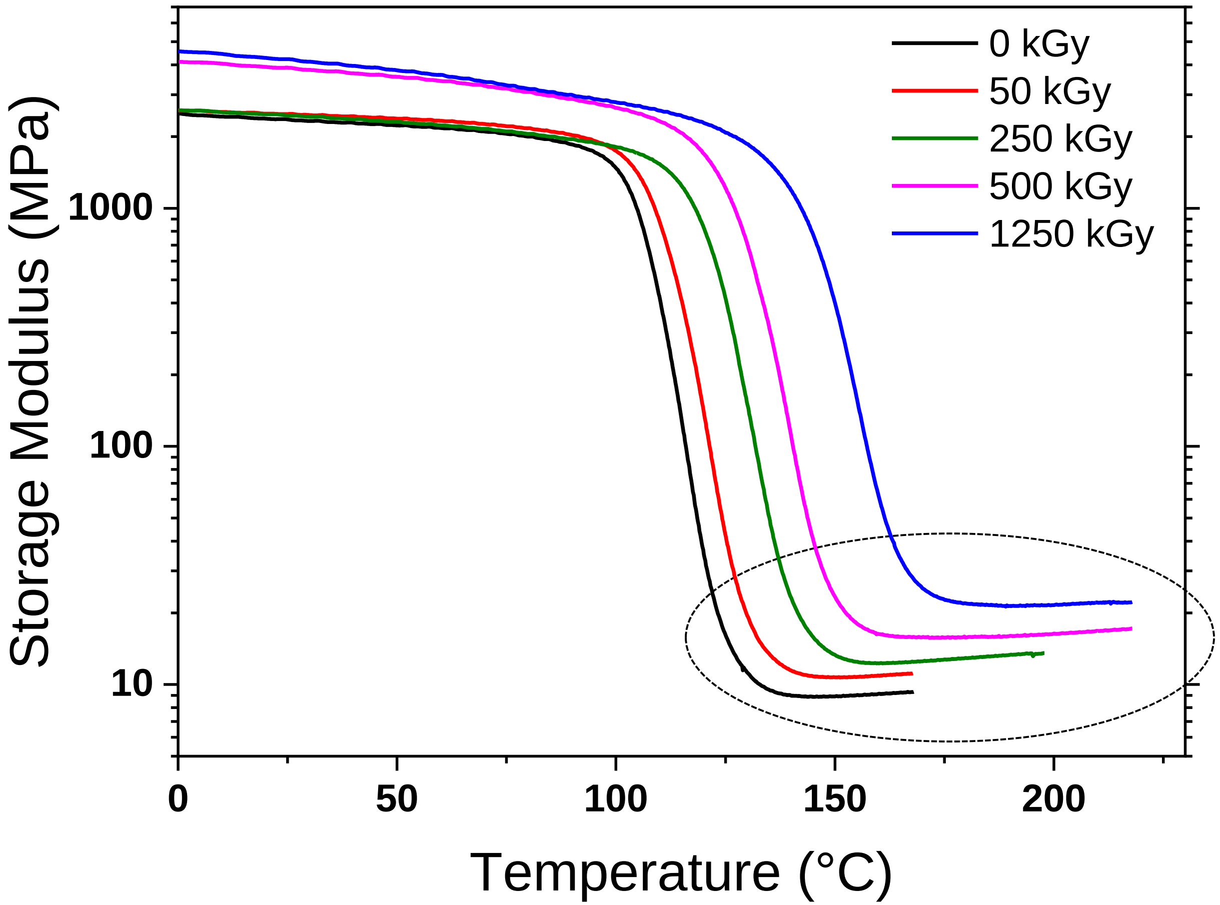
- Irradiation effects are interesting
  - E↑ in baseline system
  - DBPA addition stabilizes E(!)
  - E↑ with CTBN
- Break stress, strain unaffected



2G dual cure epoxies: Crosslink density via DMA

- Tensile DMA performed vs. composition, dose (1 Hz)
- Crosslink density (n) estimated as

$$n = \frac{E'(T_\alpha + 50°C)}{3RT}$$



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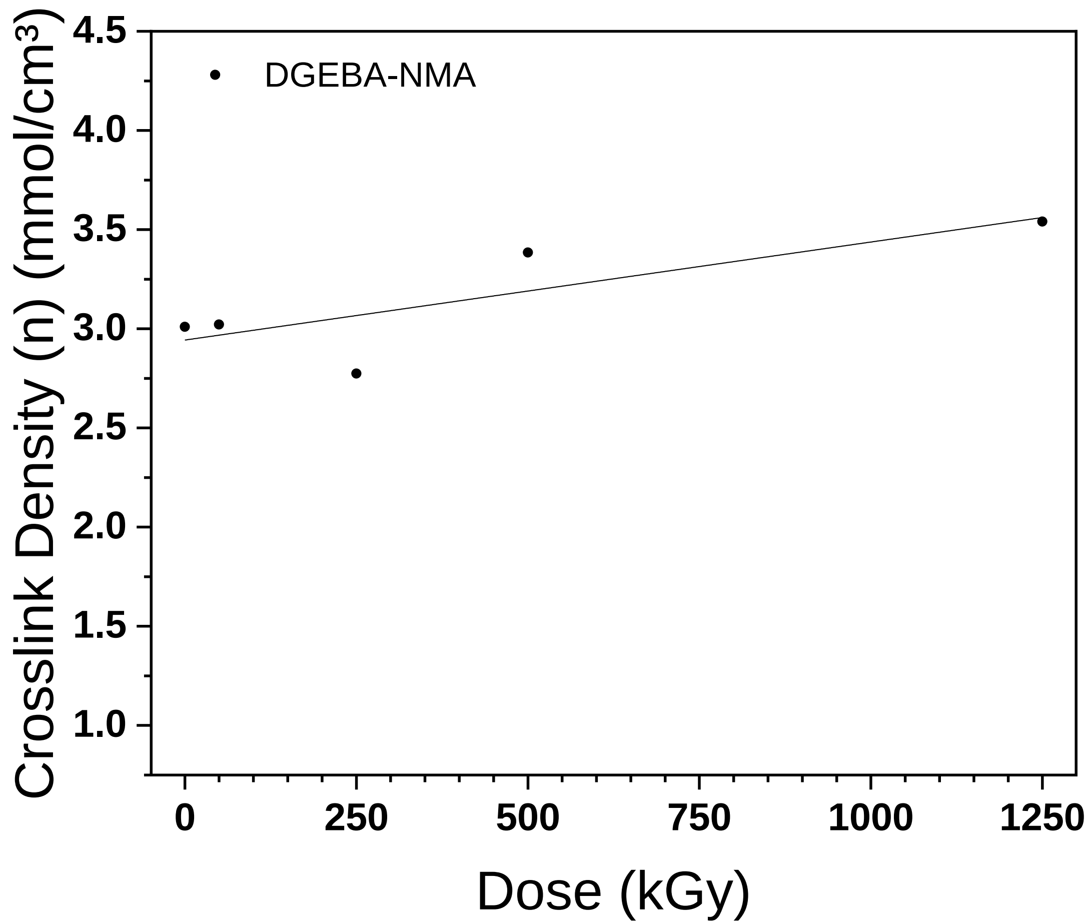

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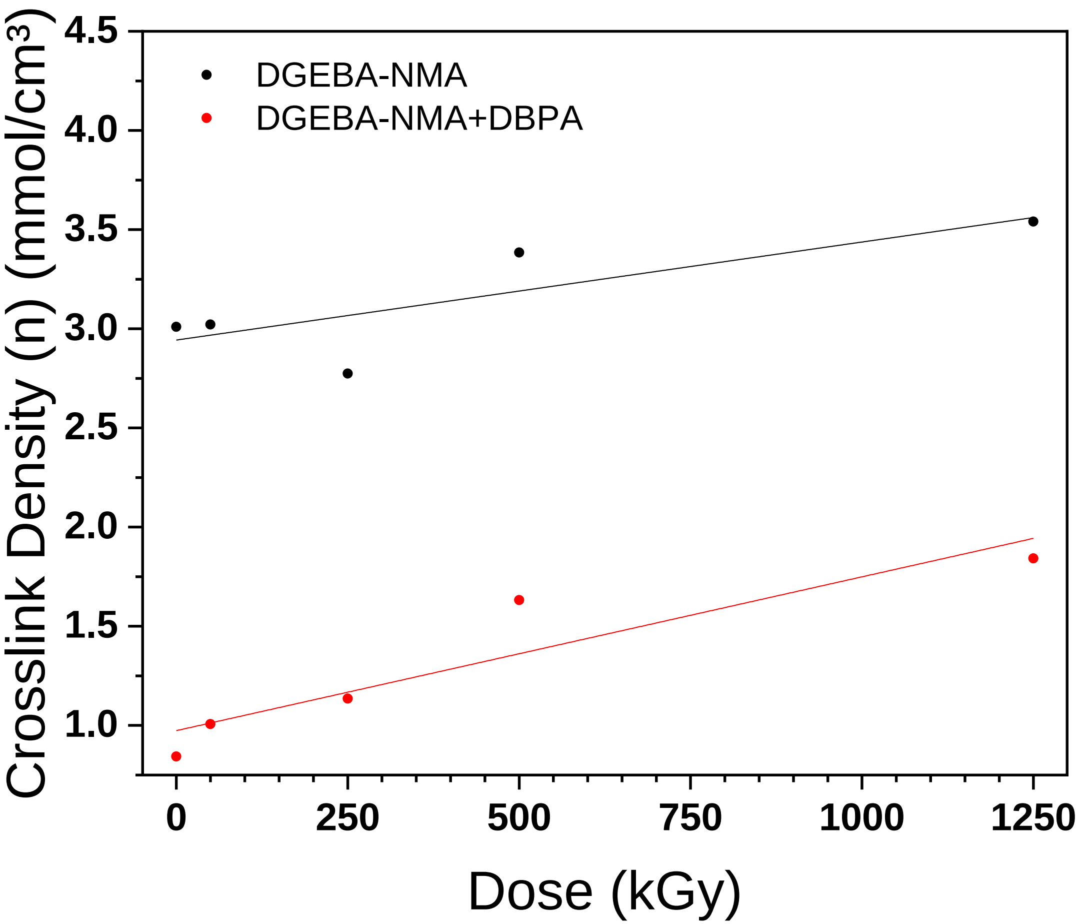

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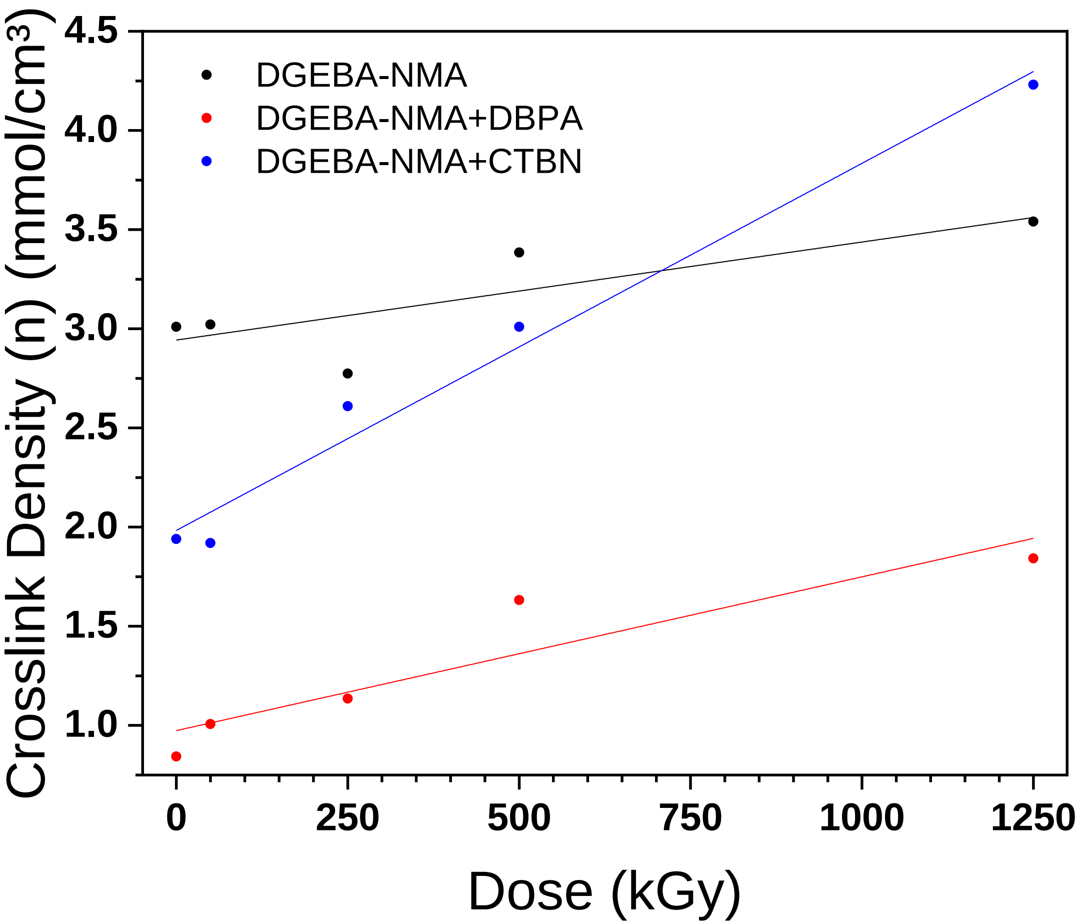
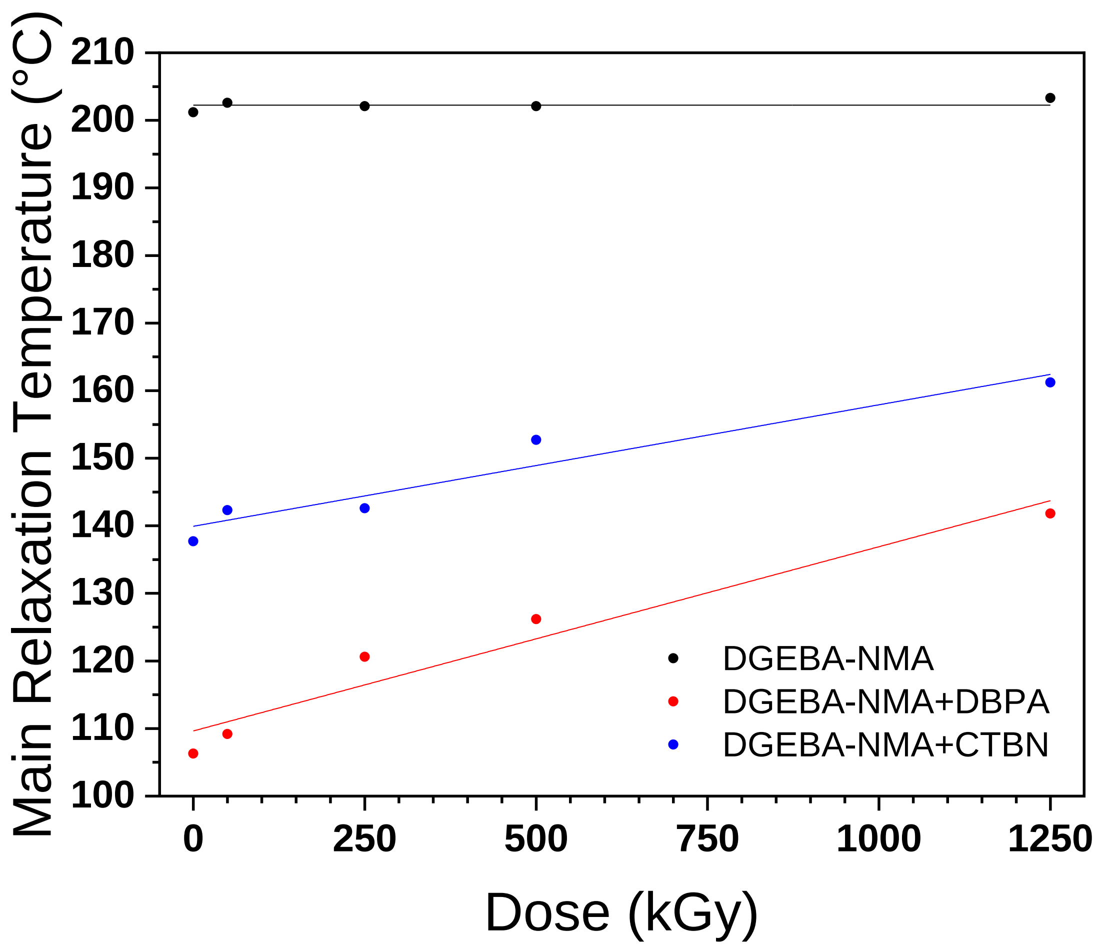
- Baseline system shows some crosslinking
- Addition of DBPA reduces n, increases sensitivity somewhat
- CTBN provides highest sensitivity, explaining larger modulus rise



2G dual cure epoxies: Glass transition via DMA

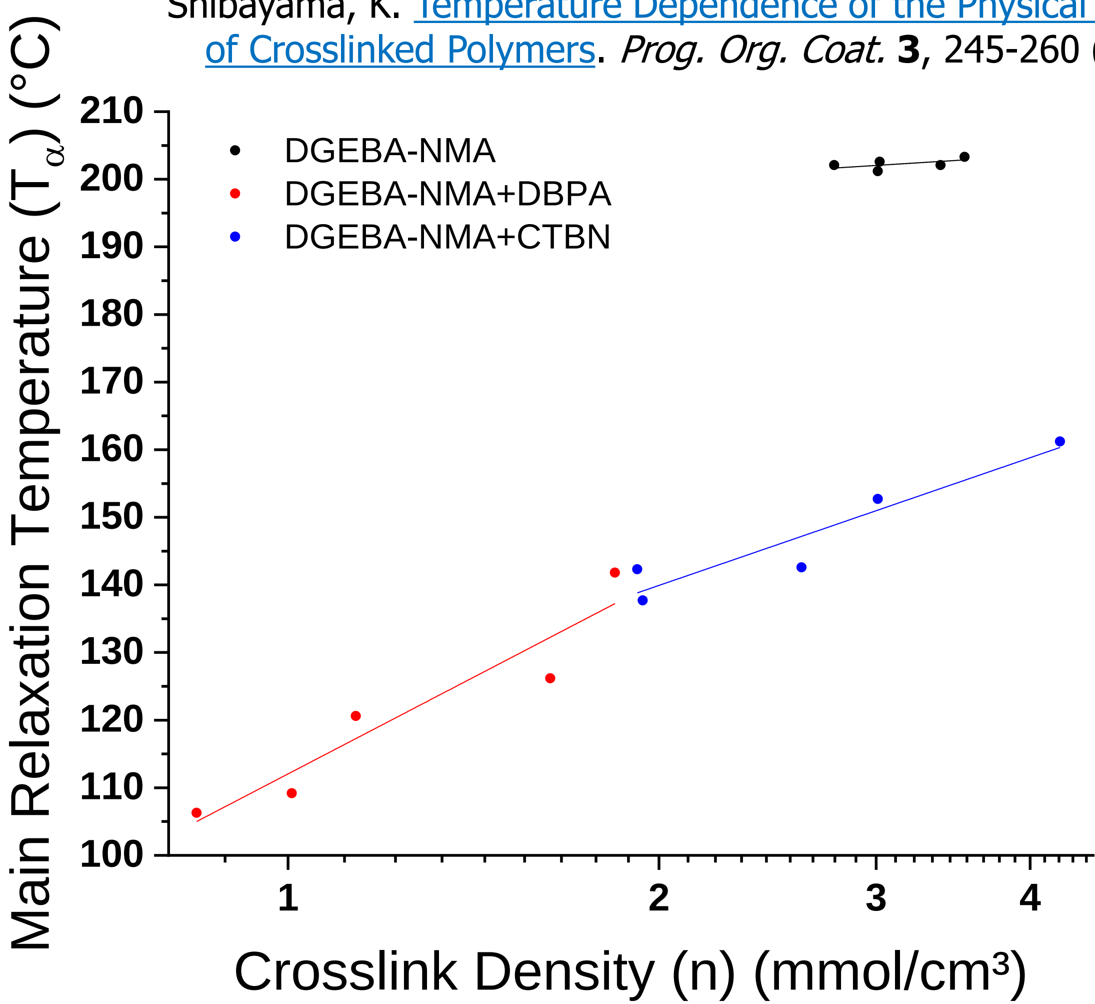
- T_{α} from E” peak → glass transition
- DBPA, CTBN reduce T_{α} vs. baseline, but irradiation causes major increases
- T_{α} of baseline system is nearly unchanged(!)
- How can we understand various dose effects?
  - Baseline: n,E↑; T_{α}~
  - +DBPA: n,T_{α}↑; E~
  - +CTBN: n,T_{α},E↑



2G dual cure epoxies: Insights via Shibayama model

- Shibayama* shows that, for a range of thermosets, $T_g = K_1 \cdot \log(K_2 \cdot n)$
  - $K_1\downarrow$ with more restraint around crosslinks
  - $\log K_2\uparrow$ with rigidity, interactions of chains between crosslinks

*Shibayama, K. Temperature Dependence of the Physical Properties of Crosslinked Polymers. *Prog. Org. Coat.* **3**, 245-260 (1975).



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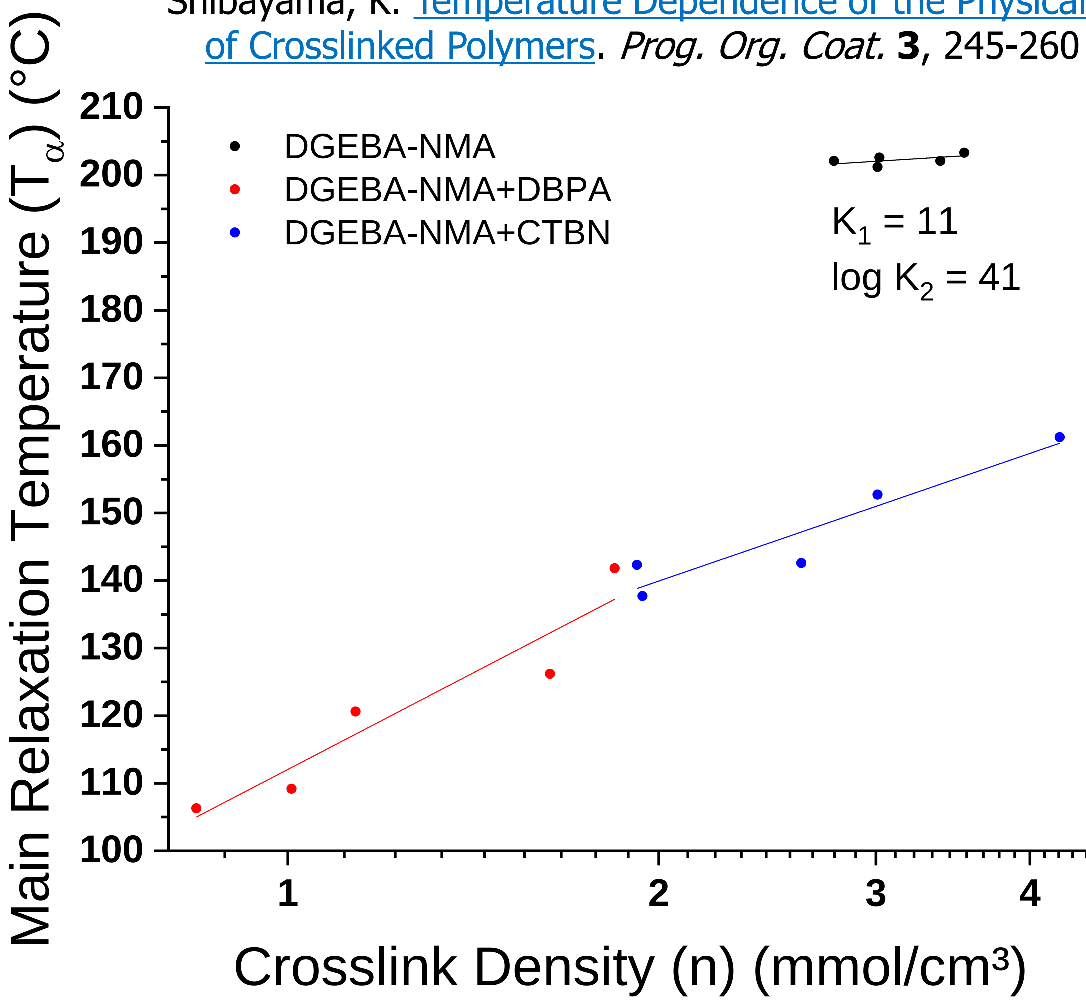

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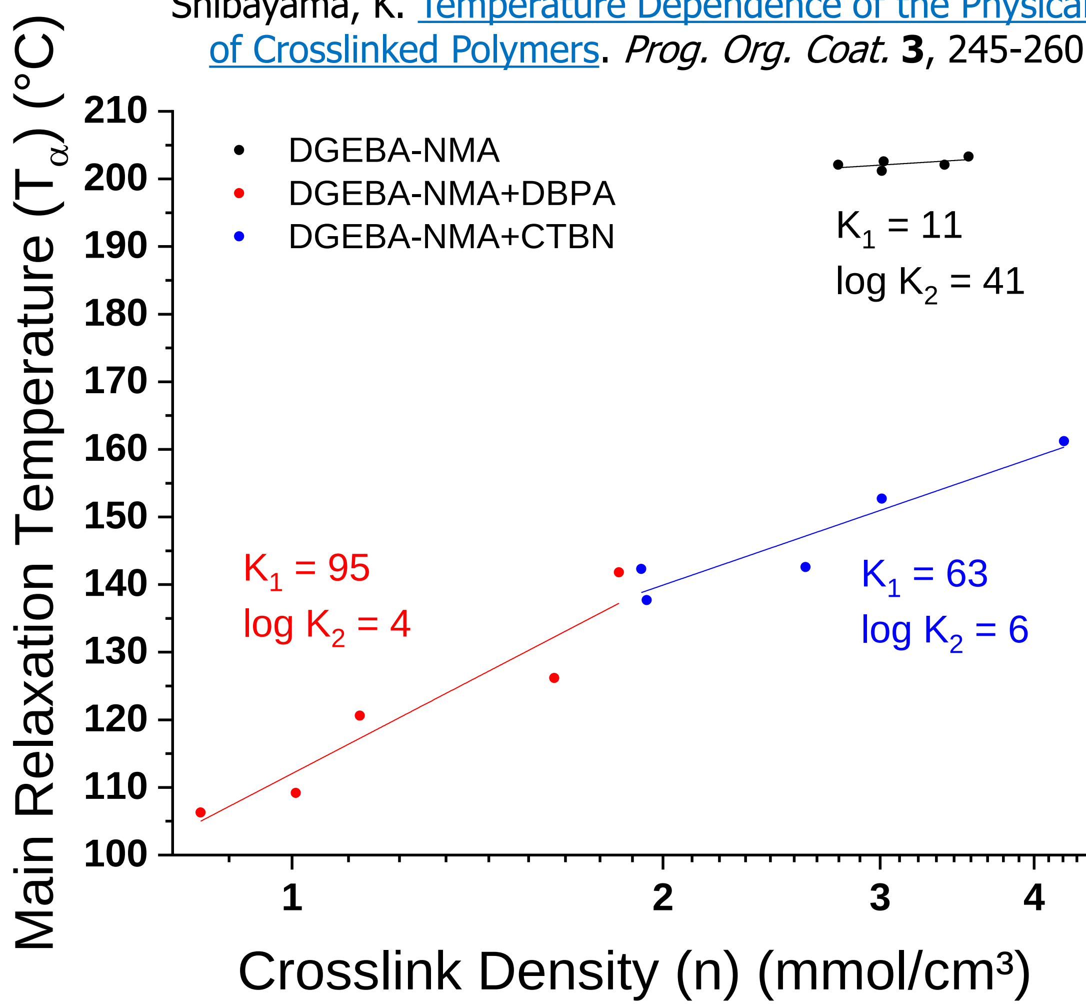
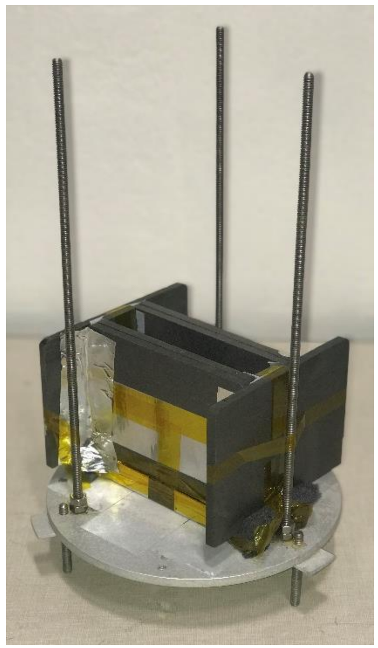
  - K_1↓ with more restraint around crosslinks
  - Log K_2↑ with rigidity, interactions of chains between crosslinks
- In baseline, chain rigidity already high, crosslinking provides little added restraint
- With DBPA & CTBN, more chain flexibility, crosslinking increases local restraint

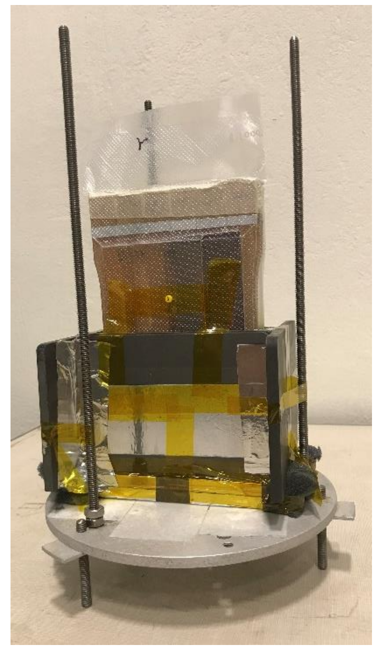


2G dual cure epoxies:
Functionally graded specimens

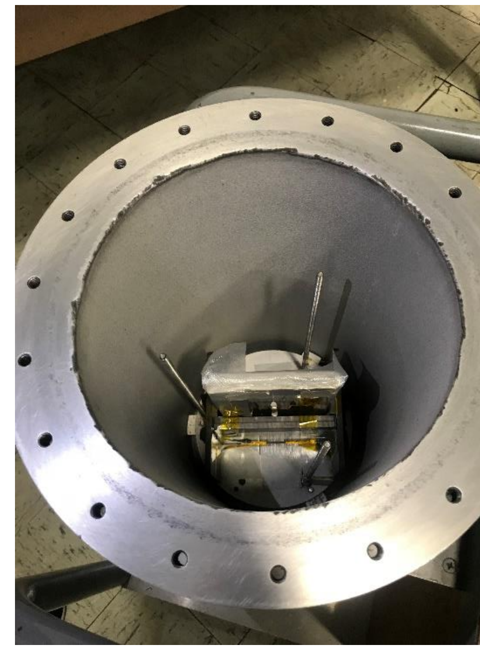
Specimens are vacuum-sealed to minimize oxidation during exposure



Desired shielding (PA12+W) is formed and assembled



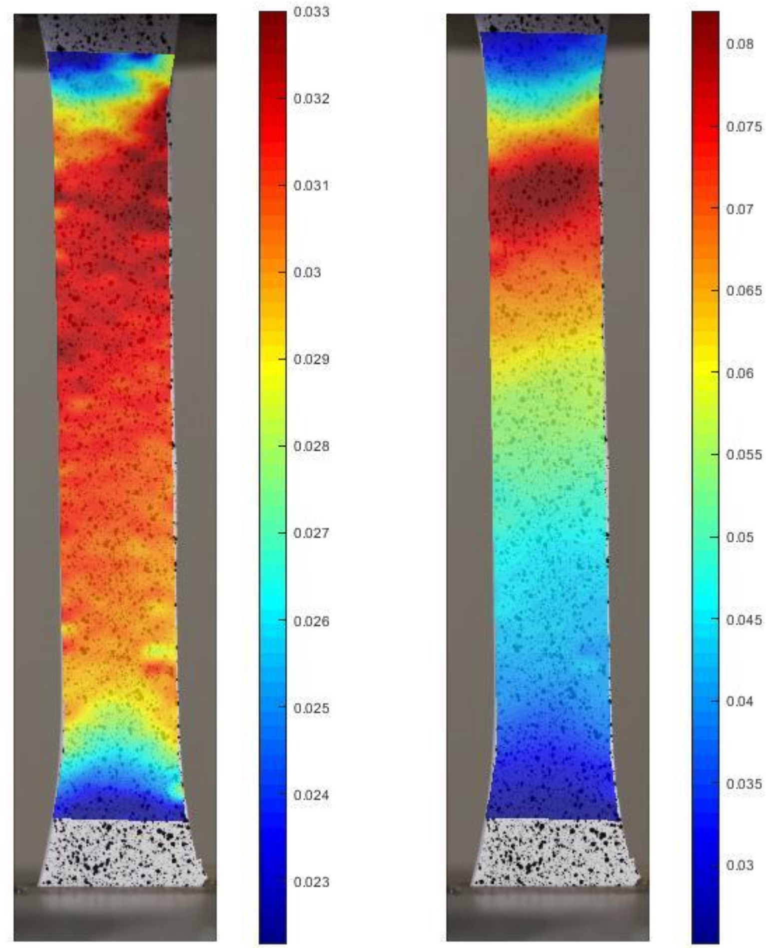
Specimens are mounted behind shielding (ex. half-shielded)



Assembly is sealed in "submersion can" prior to underwater γ-ray exposure with ^{60}Co

2G dual cure epoxies:
Functionally graded specimens

- Mechanical testing of functionally graded specimens requires digital image correlation (DIC)
- Strain localization already observed at low strains
- Trend becomes more apparent at high strains
- Confirms the creation of a gradient in modulus!



THANK YOU FOR YOUR ATTENTION!

Summary & Conclusions

- Significant process-lead innovations in AM may be complemented by additional post-printing control of materials properties in 3D
- Novel materials promise a path towards realization of such control
  - Solidification via conventional means (crosslinking, cooling, etc.)
  - Subsequent modulation of properties via crosslinking induced by precisely localized doses of high energy radiation (γ, e^-, etc.)
- Dual-cure epoxies provide proof-of-concept of this approach
  - Processed in an identical fashion to conventional epoxies
  - Dosed with γ-rays to induce additional crosslinking
- Mechanical and thermal properties studied vs. dose
  - Increases in modulus and / or T_g observed with increasing dose
  - Shibayama model may help us to understand these changes
- Production of graded structures demonstrated via DIC
- Work ongoing, publication(s) coming soon!

This material is based upon work supported by the National Science Foundation under Award # CMMI-1663502. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.