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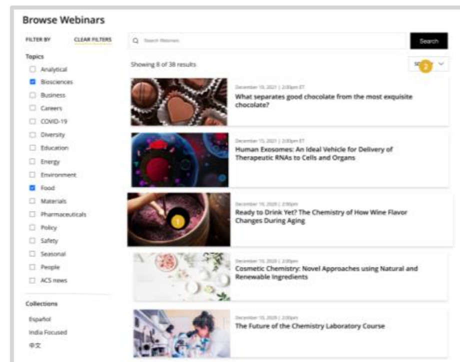


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## chemidp.acs.org/my-vitae

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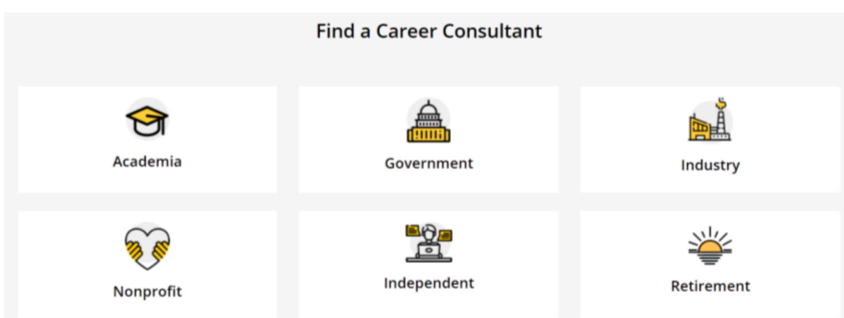


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*"Being a part of the ACS Bridge program has benefited me in several ways. I was able to pursue fully independent, fascinating research at a top institution, but even more importantly, I was exposed to a number of opportunities (such as conferences, career events, etc.) I never would have known about otherwise. The best thing about Bridge in my opinion, are the people at ACS who have worked to make it happen. Their dedication to helping me develop professionally and supporting me in good or bad times I will forever be grateful for."*

*Hanin Sarhan, Bridge Fellow at Indiana University*

Group picture from 2022 CKS at ACS HQ in Washington, DC



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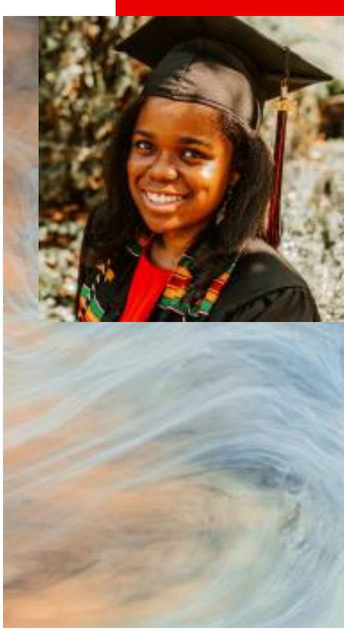
## ACS Scholar Adunoluwa Obisesan

BS, Massachusetts Institute of Technology, June 2021
(Chemical-biological Engineering, Computer Science & Molecular Biology)



*"The ACS Scholars Program provided me with monetary support as well as a valuable network of peers and mentors who have transformed my life and will help me in my future endeavors. The program enabled me to achieve more than I could have ever dreamed. Thank you so much!"*

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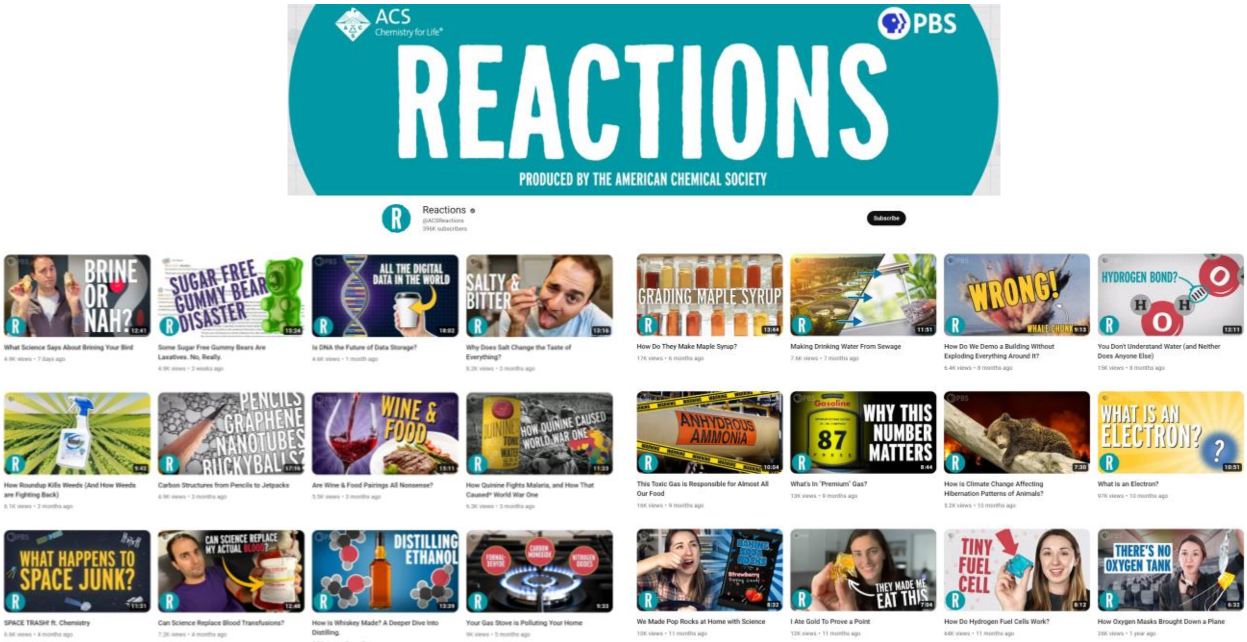


https://www.youtube.com/c/ACSReactions/videos

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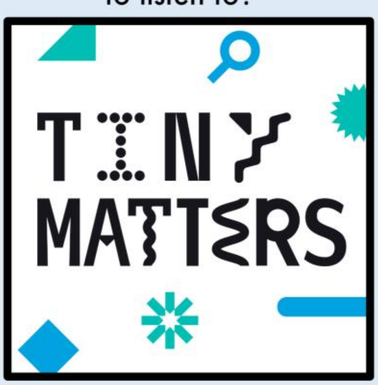
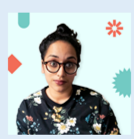



Check out Tiny Matters, from the American Chemical Society.

Sam Jones, PhD
*Science Writer & Exec Producer*



Deboki Chakravarti, PhD
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# ACS Industry Member Programs

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ACS member only content with exclusive insights from industry leaders to help you succeed in your career. #ACSIndustryMatters

**Preview Content:** **acs.org/indnl**

- **ACS Innovation Hub LinkedIn Group**

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**ACS on Campus** is the American Chemical Society's initiative dedicated to helping students advance their education and careers.

ACS ON CAMPUS


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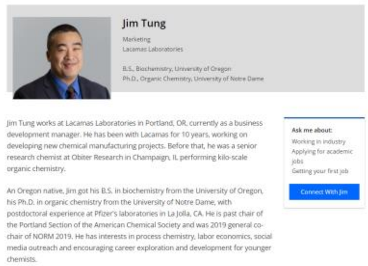
## ACS Career Resources

### Virtual Office Hours

https://www.acs.org/careerconsulting.html

### Personal Career Consultations



Jim Tung

Marketing
Lacamas Laboratories

B.S., Biochemistry, University of Oregon
Ph.D., Organic Chemistry, University of Notre Dame

Jim Tung works at Lacamas Laboratories in Portland, OR, currently as a business development manager. He has been with Lacamas for 10 years, working on developing new chemical manufacturing projects. Before that, he was a senior research chemist at Obiter Research in Champaign, IL performing kilo-scale organic chemistry.

An Oregon native, Jim got his B.S. in biochemistry from the University of Oregon, his Ph.D. in organic chemistry from the University of Notre Dame, with postdoctoral experience at Pfizer's laboratories in La Jolla, CA. He is past chair of the Portland Section of the American Chemical Society and was 2019 general co-chair of NORM 2019. He has interests in process chemistry, labor economics, social media outreach and encouraging career exploration and development for younger chemists.

Ask me about:
Working in industry
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Connect With Jim

https://www.acs.org/careerconsulting.html

### LinkedIn Learning


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## ACS Advocacy

*See your influence in action!*

The impact and results of **ACS member advocacy** outreach and efforts by the numbers!

| 2439+ | 1739+ | 49 | 2000 |
|---|---|---|---|
| Members participated In Act4Chemistry | ACS Advocacy Workshops participants or enrollees | Years of Public Policy Fellows | Letters sent to Congress |
| Get Involved | Enroll in a workshop | Become a Fellow | Take Action |

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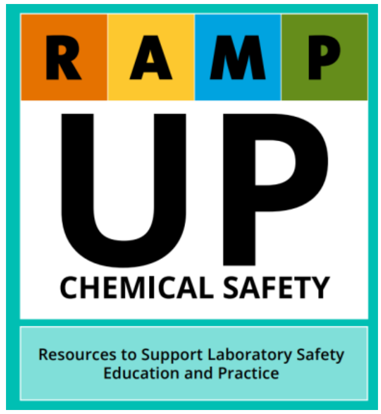
## A complete listing of ACS Safety Programs and Resources




Download it for free in the "Projects & Announcements" Section! www.acs.org/ccs

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# ACS OFFICE OF DEIR

*Advancing ACS' Core Value of Diversity, Equity, Inclusion and Respect*

## Resources

**Inclusivity Style Guide**
Designed to help staff and members use language and images that respect diversity in all its forms.

**ACS Webinars on Diversity**
Covering diversity and inclusion at the workplace

**ACS Publications DEIR Hub**
See what ACS Publications is doing for fostering inclusivity in scholarly publishing

**ACS Volunteer and ACS Meetings Code of Conduct**
Fostering a positive and welcoming environment for attendees, volunteers and staff.

**C&EN Trailblazers**
C&EN highlights scientists from different backgrounds who are making an impact in chemistry.

**NEW! Download DEIR Educational Resources**
Download this educational guide for additional recommendations on videos, articles, books, podcasts, and more on diversity, inclusion, and related topics.

**Quick Guide: Inclusion Moments**
Learn more about what Inclusion Moments are and see ideas to host them during your meetings.

**Quick Guide: How to host inclusive in-person events**
Recommendations and best practices to ensure that your events can accommodate everyone.

### Diversity, Equity, Inclusion, and Respect

**Adapted from definitions from the Ford Foundation Center for Social Justice:

**Equity****
Seeks to ensure fair treatment, equality of opportunity, and fairness in access to information and resources for all. We believe this is only possible in an environment built on respect and dignity. Equity requires the identification and elimination of barriers that have prevented the full participation of some groups.

**Diversity****
The representation of varied identities and differences (race, ethnicity, gender, disability, sexual orientation, gender identity, national origin, tribe, caste, socio-economic status, thinking and communication styles, etc.), collectively and as individuals. ACS seeks to proactively engage, understand, and draw on a variety of perspectives.

**Inclusion****
Builds a culture of belonging by actively inviting the contribution and participation of all people. Every person's voice adds value, and ACS strives to create balance in the face of power differences. In addition, no one person can or should be called upon to represent an entire community.

**Respect**
Ensures that each person is treated with professionalism, integrity, and ethics underpinning all interpersonal interactions.

https://www.acs.org/diversity

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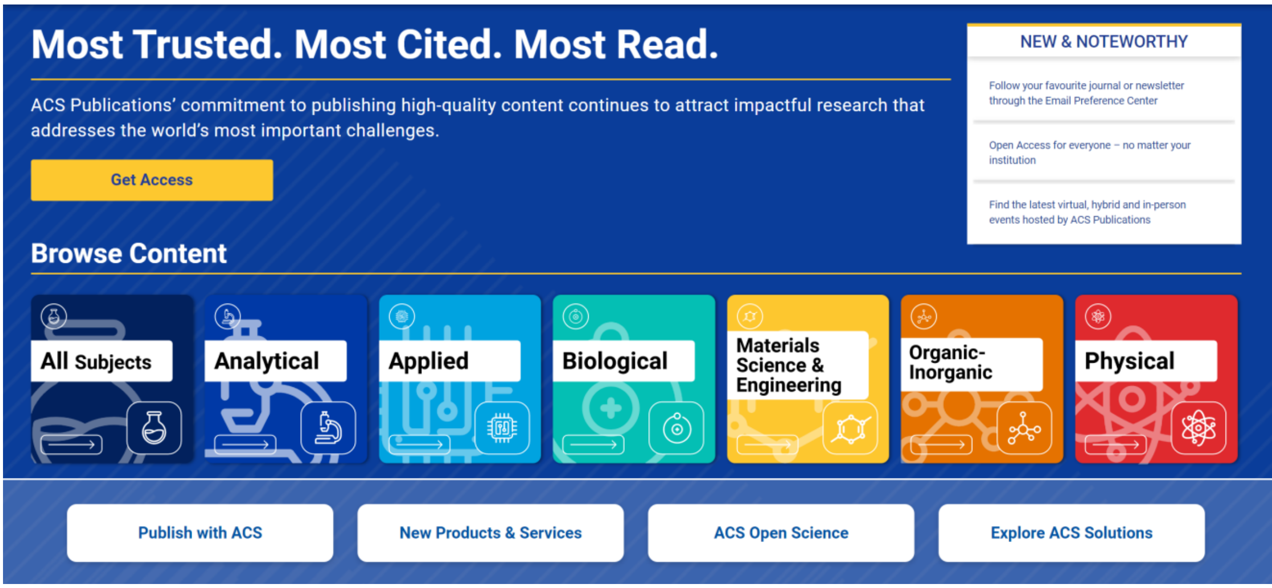


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- Sign up below to be notified when registration begins in August 2024

Go to www.acs.org/pib to pre-register for the event

American Chemical Society

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# THE BENEFITS OF PMSE MEMBERSHIP

100TH PMSE 1924 - 2024

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- Enjoy the technical programming at ACS National Meetings and support for regional meetings in polymer science and engineering
- Be eligible to be nominated and to nominate others for PMSE awards
- Take advantage of volunteer and leadership opportunities for both students and professionals (committees, governance, and award panels)
- Obtain support and networking for early career scientists through the local PMSE chapters
- Make use of educational, professional development resources, and polymer-specific techniques through the MACRO initiative
- Participate in expert-led technical webinars focusing on techniques and methods relevant to polymer materials
- Take part in professional development at a range of levels, from undergraduate students through early career independent scientists and engineers

https://pmsedivision.org

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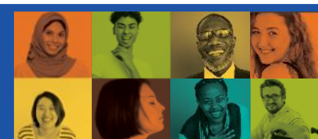
www.acs.org/membership



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Wednesday, May 29, 2024| 3pm-4pm ET

**Electrones en Movimiento: Efecto de los Campos Magnéticos sobre las Moléculas**

Co-produced with the Sociedad Quimica de Mexico

Wednesday, June 6, 2024| 2pm-3:15pm ET

**Pharmacology for Chemists**

Co-produced with ACS Office of Career and Professional Education

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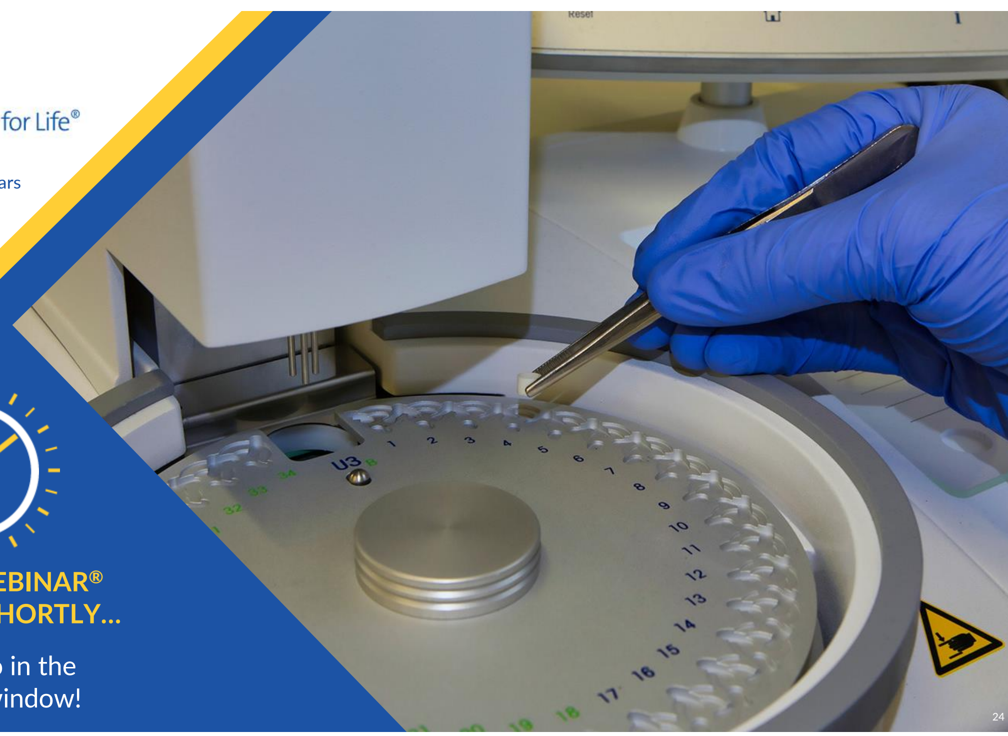

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Say hello in the questions window!

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**Exploring Thermal Mechanics in Polymeric Materials:**
Thermomechanical and Self-Healing Properties




**TIM WHITE, PhD**
Gallogly Professor of Engineering, Associate Director of Research at the Center for National Security Initiatives, and Graduate Director in Department of Chemical and Biological Engineering, University of Colorado

**DHRITI NEPAL, PhD**
Research Materials Engineer, Air Force Research Lab

**RACHEL LETTERI, PhD**
Assistant Professor, Department of Chemical Engineering, University of Virginia


*This ACS Webinar® is co-produced with ACS Division of Polymeric Materials: Science & Engineering (PMSE).*

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# Exploring Thermal Mechanics in Polymeric Materials:

## Thermomechanical and Self-Healing Properties

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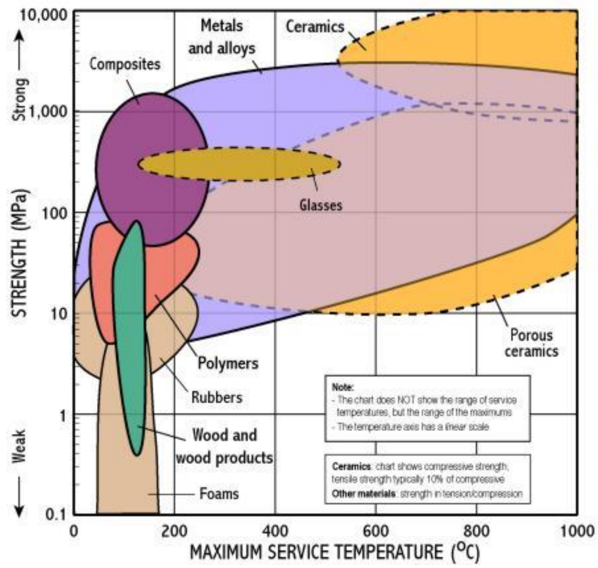
## Thermal Properties of Materials - Why Care?

- Consider: what structural or functional application of materials does not have to consider the use temperature?




http://www-materials.eng.cam.ac.uk/mpsite/interactive_charts/strength-temp/NS6Chart.html

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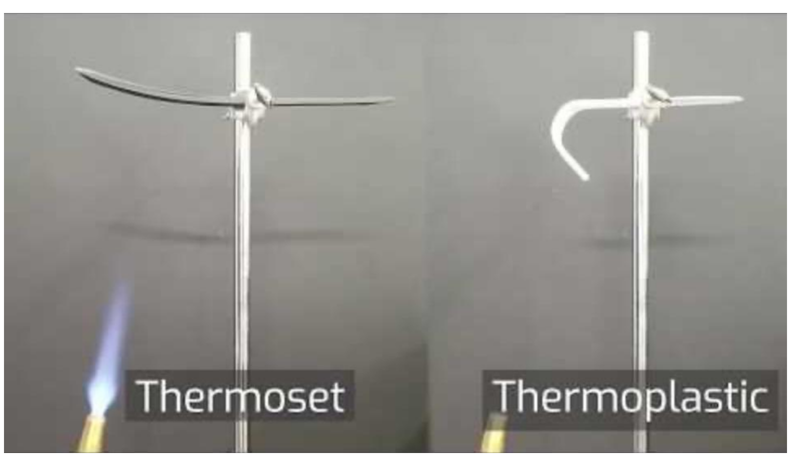
## Thermal Properties of Materials - Why Care?

- Consider: what structural or functional application of materials does not have to consider the use temperature?
- Further: what structural or functional application of materials is not subject to temperature change?




https://youtu.be/-WCNJNTSFMk

The thermal properties of materials are paramount in importance!

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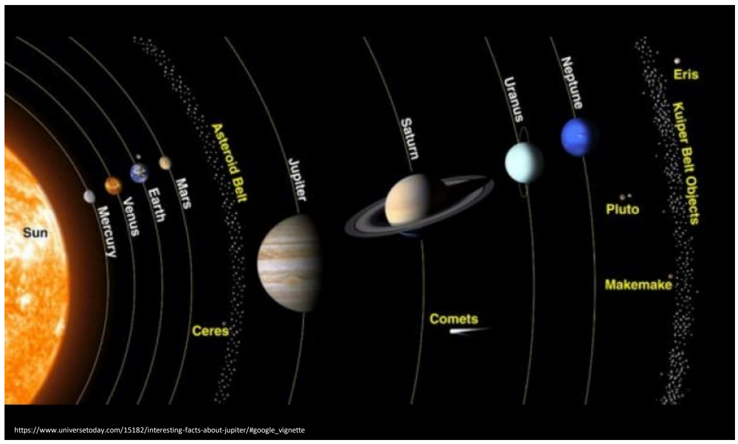
## Background: Heat and Temperature

- Although very elementary, it is critical to establish - are heat and temperature the same?
  - Temperature - measure of the average kinetic energy of particles in an object
  - Heat - form of energy, for which temperature is a measure of that energy, and is the “total” energy (kinetic and potential) of an object

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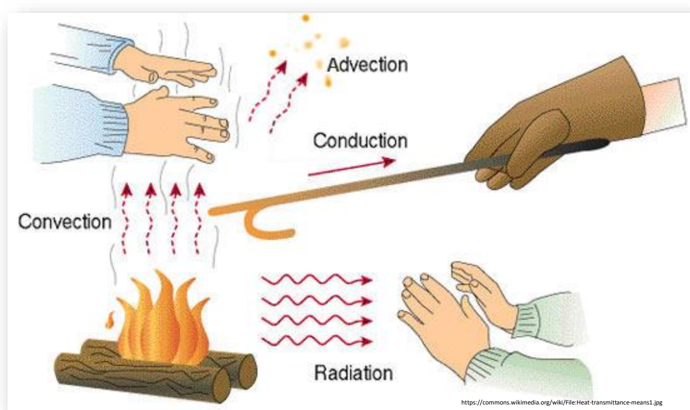
## Background: Modes of Heat Transfer

- Convection
  - Energy (heat) transfer between an object and its environment
- Conduction (diffusion)
  - Energy (heat) transfer between objects in conductivity
  - Property: thermal conductivity
  - Fourier’s law:
    - $q_x = -k\frac{dT}{dx}$
      - q is local heat flux density (W/m2)
      - k is conductivity of material (W/mK)
    - $Q = -k\frac{A\Delta t\Delta T}{L}$
      - Q is thermal power (in W)
- Radiation
  - Energy (heat) transfer via emission of electromagnetic radiation
- Advection
  - Transport of fluid from one location to another
  - Ex: warm/cold air in the atmosphere or a home

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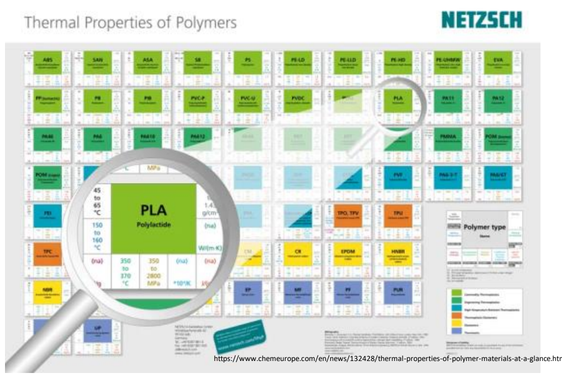
# Thermal Properties - What You May Want to Know?

- Constrained to polymeric materials and composites of them:
  - How does heat transfer in the material?
    - Properties: heat capacity, thermal conductivity
  - How do the material properties change as a function of temperature?
    - Properties: glass transition, phase transition, crystalline melting (as well as more beta transitions)
      - Secondary influence on modulus, optical properties, …
  - Does my material degrade and if so, at what temperature? In what environmental conditions?
    - Properties: mass loss



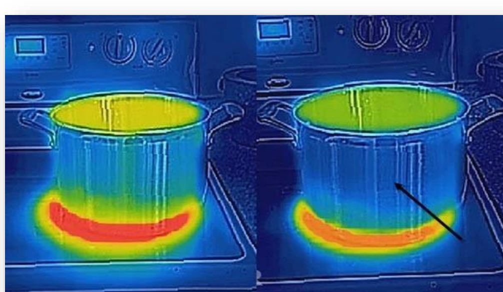

https://www.chemeurope.com/en/news/132428/thermal-properties-of-polymer-materials-at-a-glance.html





# Heat Capacity

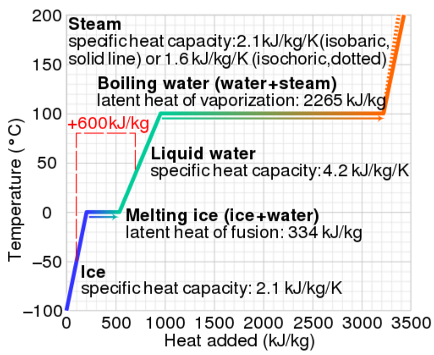
- An extensive property (e.g., dependent on quantity//mass)
  - Heat capacity is simply the amount of heat needed to raise the temperature of a material
  - C = $\frac{Q}{\Delta T}$
  - Heat capacity can be measured at constant volume ($C_v$) or constant pressure ($C_p$)
  - Physically, heat capacity can be thought of:



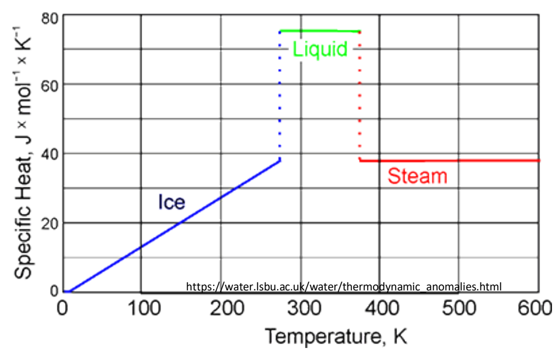
    - Water in a pot (amount, type of material)
    - Want to heat from room temperature to 100 C ($\Delta$T = 80 C)
    - Heat capacity indicates how much energy input (e.g., Q as heat) this temperature change requires
- Specific heat capacity (c) → J/g * K → intensive property
  - C = m c

## Thermodynamics of Heat Capacity

- Should heat capacity depend on the state of matter?
  - YES! But why…?
  - States of matter largely defined by variance in intermolecular forces
  - As a material transitions from gas to liquid and liquid to solid, intermolecular forces are increasing
  - Put simply: when a material is being converted from a higher energy state (e.g. solid to liquid) requires more energy to overcome those stronger forces
    - Accordingly, on melting heat capacity increases
    - On freezing, heat capacity decreases




https://commons.wikimedia.org/wiki/File:Water_temperature_vs_heat_added.svg

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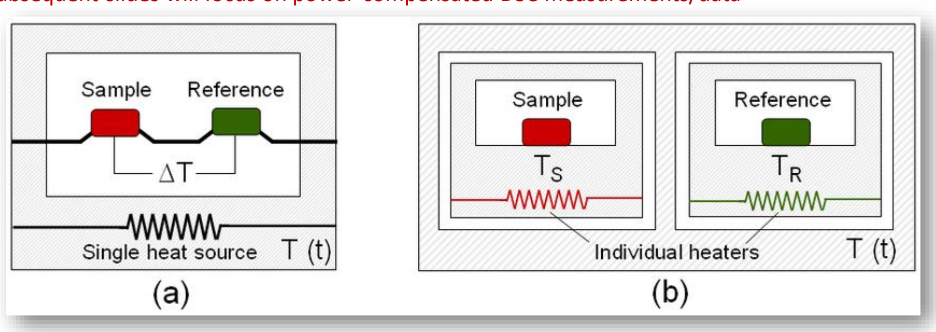
## Types of Differential Scanning Calorimeters

Subsequent slides will focus on power-compensated DSC measurements/data




- Two primary types of DSC
  - Power-Compensated (image in b, more popular)
    - Dual heaters allow for different heat fluxes at varied temperatures.
    - Difference in heat flow is recorded
  - Heat-flux (image in a, cheaper)
    - Heat flux is varied
    - Temperature difference is recorded
    - Calibration yields heat flow

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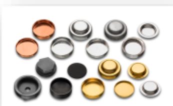
# The Practice of DSC

**$Q = m\,c\,\Delta T$**

**Q** = Heat (cal or J)
**m** = Mass (g)
**c** = Specific heat (J/g°K)
**ΔT** = Change in temperature


"The term DSC simply implies that during a linear temperature ramp, quantitative calorimetric information can be obtained on the sample. According to the ASTM standard E473, DSC is a technique in which the heat flow rate difference into a substance and a reference is measured as a function of temperature, while the sample is subjected to a controlled temperature program."

*Thermal Analysis of Polymers: Fundamentals and Applications, C.2*



**Sample prep:**
- The crucible (pan)
  - Pick crucible compatible with material/temperature range
  - Always use tweezers to avoid contamination or crucible deformation
- Crucible lid
  - Hermetic seal requires crucible press
  - Make sure sample material does not obstruct lid
- Precisely weigh sample

**Experimental Protocol:**
- Crucible must be in good contact with heating plate
- Pick acceptable temperature range
  - Use slower scanning rate to see subtle transitions
  - DSC can take anywhere from 30 min to 3+ hr. per cycle

**Hysteresis**
- Thermal history can skew measurement
- Run one slow heat cycle prior to measurement cycle

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# Beware: DSC Data and Heating Rate

Same sample subject to different heating rates - wide variance in transitions

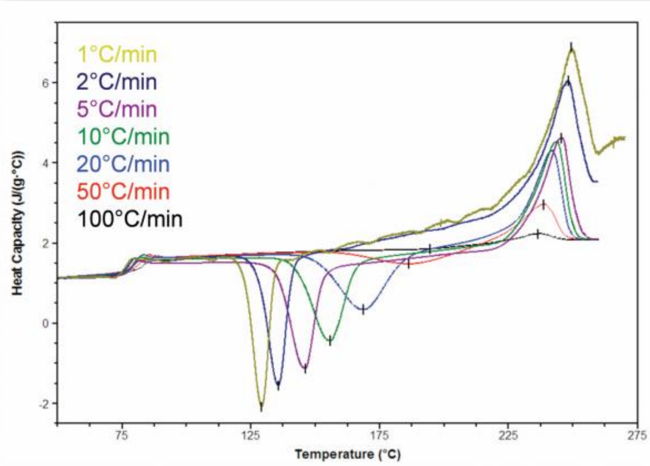


Figure 7: DSC thermal curves of PET at various scan rates, showing the glass transition, crystallisation and melting events.

https://www.europeanpharmaceuticalreview.com/article/1358/fast-scan-differential-scanning-calorimetry/

- Why does scanning rate matter?
  - Thermal lag
- New DSC techniques addressing for "rapid-scan" DSC (not discussed)
  - Enabling high throughput measurements

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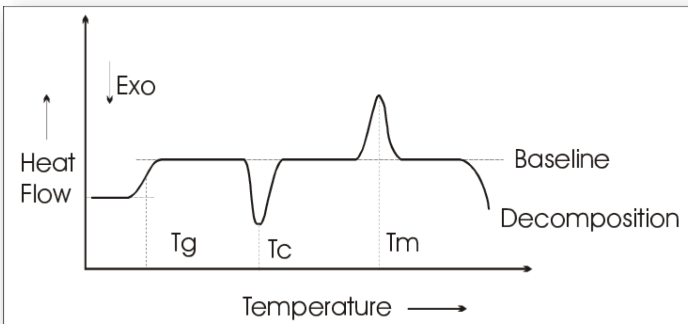
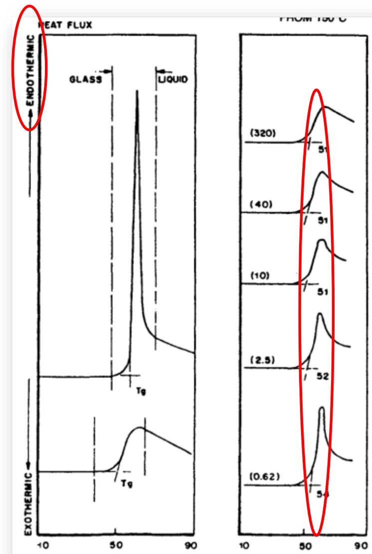
# DSC Curve Interpretation

- Interpretation of DSC curves is an art
  - Baseline ➔ very important
- Sign convention (typically labelled, “endo up”)
  - Endothermic processes ➔ positive peak
    - Melting and glass transition
  - Exothermic processes ➔ negative peak
    - Crystallization
- Glass transition temperatures ($T_g$)
  - Subtle change in DSC curve
  - Intersection of tangent line drawn from $T_g$ onset and 1st peak inflection point




*Thermal Analysis of Polymers: Fundamentals and Applications, C.2*

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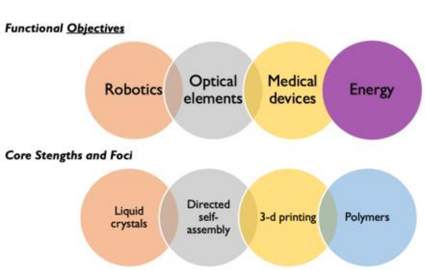
## Responsive and Programmable Materials Group
### *PI: Tim White*

***R+PM Group Snapshot***
- PI: Tim White
  - Moved to CU in July 2018
- Current state: 10 students, 3 post-doctoral associates
  - 5 PhD alumni

***Research Foci***
- Polymers and soft materials
- Material processing (self-assembly, 3-D printing)
- Enabling dynamic function

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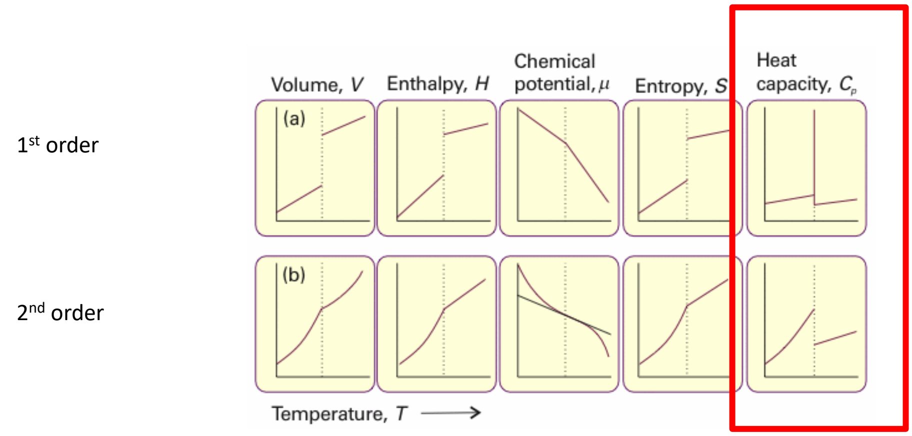
## Ehrenfest Classification of Phase Transitions

- 1st Order
  - Discontinuity in first derivative of free energy
  - In solid → liquid, liquid→gas: large change in density, results in large change in heat capacity
- 2nd Order
  - Continuous with the first derivative of free energy




39

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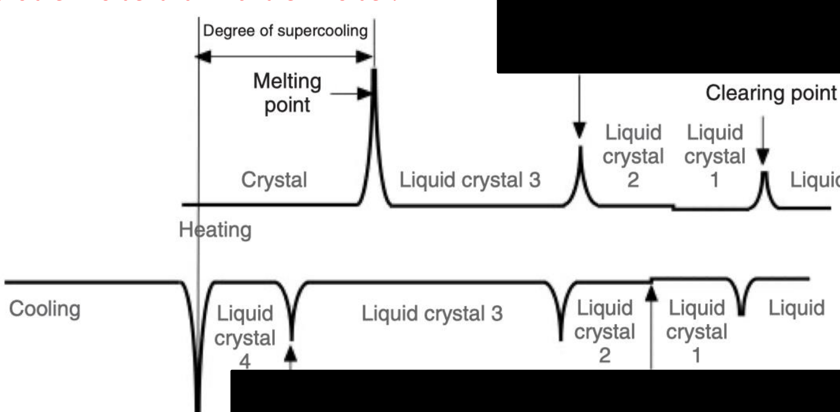
## Using DSC: Transition Temperatures of a Liquid Crystal

Which of these transitions are 1st order and which are 2nd order?




*Credit: Handbook of Liquid* [redacted]

40

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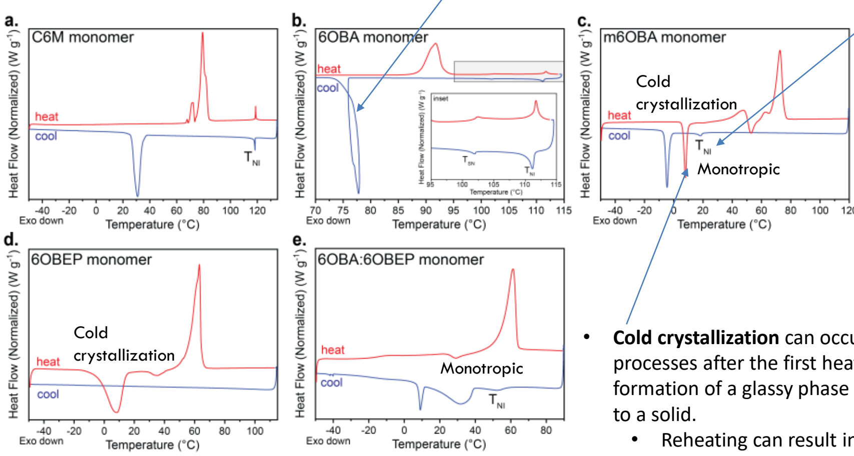
# Using DSC: Phase Behavior of Monomeric and Oligomeric Mixtures

- As shown in panel (b) high purity affects the crystalline transition on cooling

- LC transitions which appear only on cooling are termed **monotropic** (panel (c) and (e)) where at least one of the phases exists only at temperatures below the melting point and is revealed by supercooling of the material




- **Cold crystallization** can occur (panel (c) and (d)) during heating processes after the first heating cycle often associated with the formation of a glassy phase produced when a liquid crystal cools to a solid.
  - Reheating can result in molecular motions that reorganize the molecules in the glass, and recrystallization occurs, usually followed by a melting point in the reheating process

*R+PM data*

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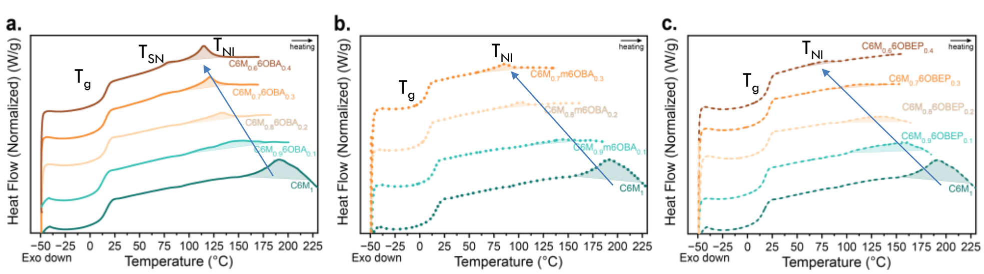
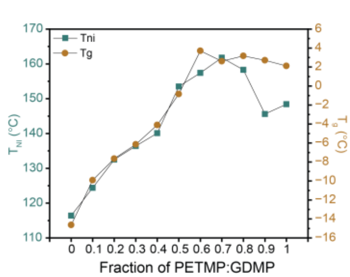
# Using DSC: $T_g$ and $T_{NI}$ of Liquid Crystalline Elastomers




- Formulations and mixtures of different LC mesogens can drastically impact phase behavior and temperatures of transitions




- Crosslinking density has a significant impact on glass transition ($T_g$) and the nematic to isotropic transition ($T_{NI}$)

Increasing crosslinking density

*R+PM*

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# Modulated DSC to Separate Transitions

$\frac{dH}{dt}$ = DSC heat flow signal (mW or $\frac{mJ}{s}$)

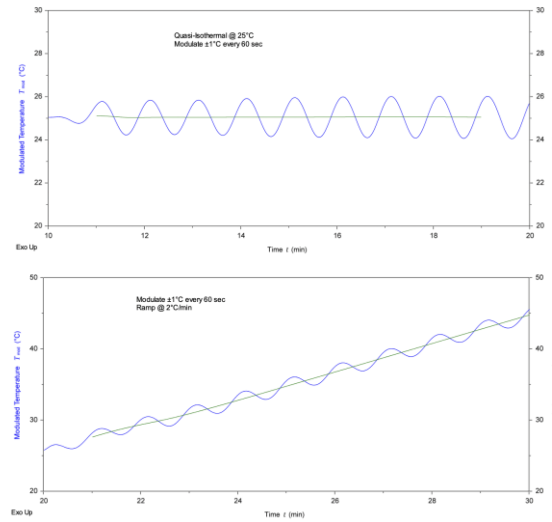
Cp = Sample Heat Capacity = Sample Specific Heat x Sample Weight

$$\frac{dH}{dt} = Cp\frac{dT}{dt} + f(T, t)$$

$\frac{dT}{dt}$ = Heating Rate (°C/min)

$f(T, t)$ = Heat flow that is function of time at an absolute temperature (kinetic)

| Total Heat Flow | Heat Capacity: Reversing Heat Flow | Kinetic: Non-Reversing Heat Flow |
|---|---|---|
| •All Transitions | •Heat Capacity<br>•Glass Transition<br>•Melting | •Enthalpic Recovery<br>•Evaporation<br>•Crystallization<br>•Thermoset Cure<br>•Denaturation<br>•Decomposition<br>•Some Melting<br>•Chemical Reactions |




Sinusoidal heating ramp overlaid on linear heating



# MDSC Example: Liquid Crystalline Elastomers

**MDSC to Separate Thermal Transitions**

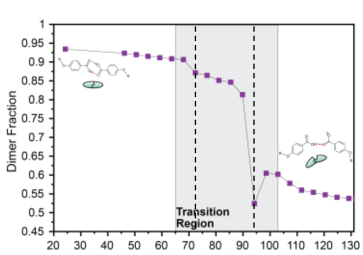
$$\frac{dQ}{dt} = C_p\frac{dT}{dt} + f(T,t)$$

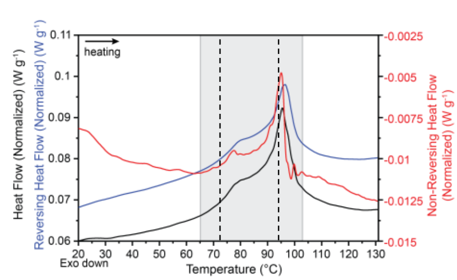
**Total Heat Flow**
- All transitions

**Reversing Heat Flow**
- Heat capacity events (phase transitions)
- Glass transition

**Non-Reversing Heat Flow**
- Enthalpy recovery
- Kinetic events (breaking/forming H-bonds) [3]

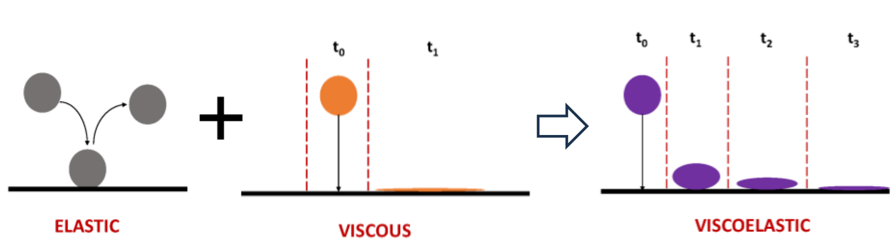
The contribution of hydrogen bond disruption on the total heat flow can be separated from the LC transition and paired with FTIR to track the associated heat flow change with dimer breakage




R+PM

# Polymers are Viscoelastic Materials




Like a rubber ball spring

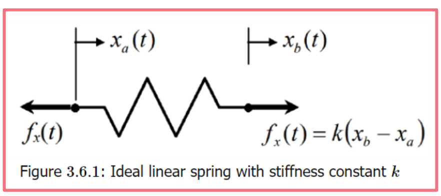



Figure 3.6.1: Ideal linear spring with stiffness constant $k$

Like honey dashpot

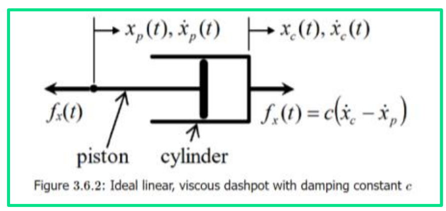



Figure 3.6.2: Ideal linear, viscous dashpot with damping constant $c$

G. M. Swallowe (ed.), Mechanical Properties and Testing of Polymers

TA Instruments: Rheology Theory and Applications



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# Audience Survey Question

ANSWER THE QUESTION ON THE INTERACTIVE SCREEN IN ONE MOMENT

**Dynamic mechanical analysis can be utilized to: ?** (Select all that apply)

- Determine storage and loss modulus in polymeric materials
- Determine the glass transition temperature in polymeric materials
- Can assess thermomechanical response of stimuli-responsive materials
- None of the above

*** If your answer is "Other" tell us in the questions window!**



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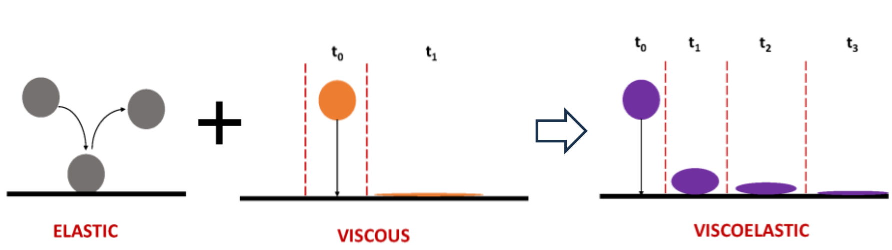
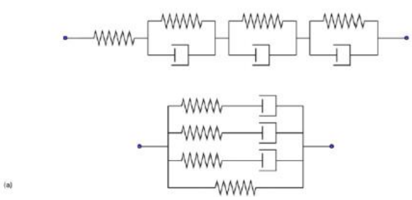
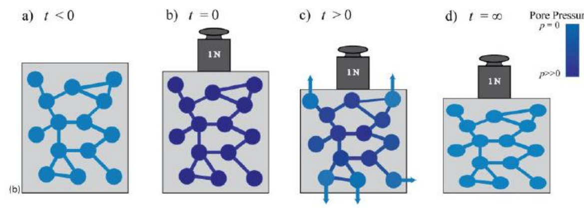
## Polymers are Viscoelastic Materials




Spring/dashpot models - “Maxwell model” (in series) or Voigt model (in parallel)




M. L. Oyen (2014) Mechanical characterisation of hydrogel materials, International Materials Reviews, 59:1, 44-59, DOI: 10.1179/1743280413Y.0000000022





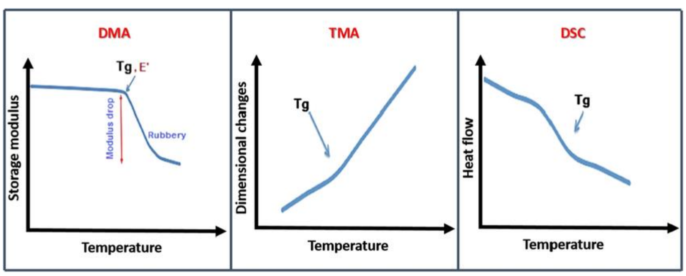
## Mechanical Characterization


The characterization of mechanical properties of materials is well-established and utilizes load cells to apply force and assess deformation.

These systems can be used to assess the mechanical properties of many polymers.

## Thermomechanical Characterization

Thermomechanical properties of polymers are well-characterized by dynamic mechanical analysis (DMA) and thermomechanical analysis (TMA). These instruments are related by distinct. DMA measures mechanical properties (e.g. deformation to force as a function of temperature) and TMA measures thermal expansion (e.g., sample dimensional changes as a function of temperature)




I will focus on DMA the remainder of my time; Dr. Nepal will talk about DMA and TMA.

https://link.springer.com/article/10.1007/s10570-021-03710-3

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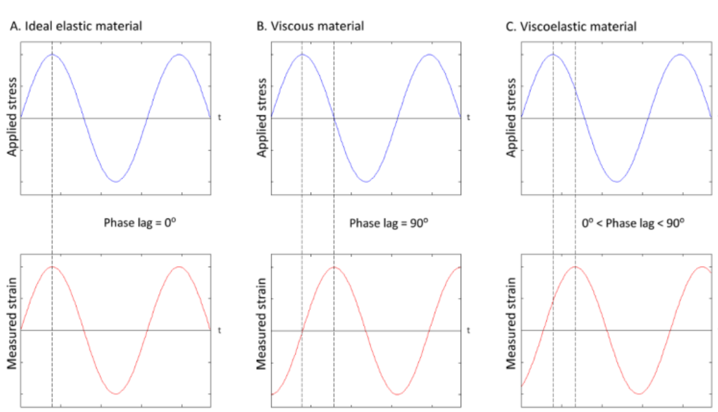
## DMA Can Apply an Oscillating Mechanical Stress

$$\sigma = \sigma_0 sin(\omega t + \delta)$$

Stress applied is described by a sine function
- $\sigma_o$ is the maximum stress applied
- $\omega$ is the frequency of applied stress
- t is time




(a) Stress and strain are in phase for an ideal elastic material

(b) Stress and strain are 90° out of phase for a purely viscous material

(c) Viscoelastic materials have a phase lag less than 90°.

https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Physical_Methods_in_Chemistry_and_Nano_Science_(Barron)

Image adapted from M. Sepe, Dynamic Mechanical Analysis for Plastics Engineering, Plastics Design Library: Norwich, NY (1998).

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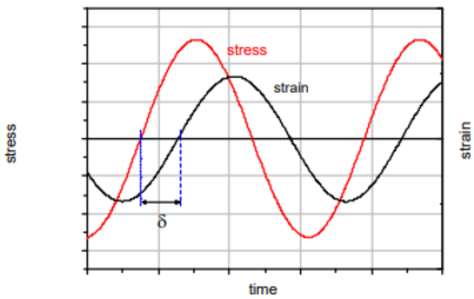
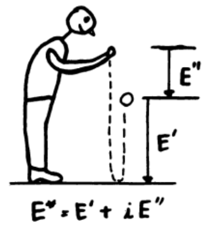
## DMA - Raw Data and Extension to Moduli and tan δ
### (and can do this as a function of temperature)

A viscoelastic response to oscillation




E'= STORAGE MODULUS
E"= LOSS MODULUS
E"/ E'= TAN δ

What this means for the network:

Storage modulus (E') → mechanical energy stored by the material during a loading cycle. Related to the stiffness and shape recovery of the polymer

Loss modulus (E'') → damping behavior. Indicates the polymer's ability to disperse mechanical energy through internal molecular motions.

Strain: $\varepsilon(t) = \varepsilon_0 \sin(\omega t)$

Stress: $\sigma(t) = \sigma_0 \sin(\omega t + \delta)$

Complex Modulus: $E^* = E' + iE''$

$$|E^*| = \sqrt{E'^2 + E''^2} = \frac{\sigma_A}{\varepsilon_A}$$

Loss factor: $tan\delta = \frac{E''}{E'}$

Sound and Vibration Damping with Polymers: Basic Viscoelastic Definitions and Concepts. L. H. Sperling

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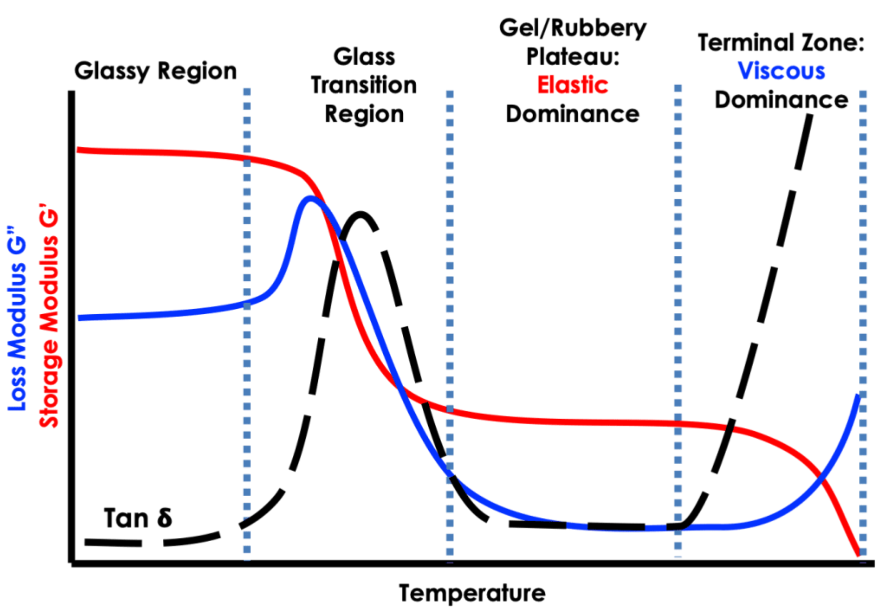
## DMA Data Examples




https://www.rheologylab.com/services/dynamic-mechanical-analysis-dma/

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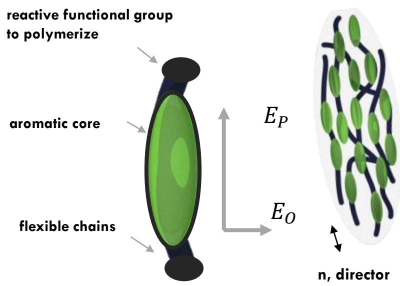
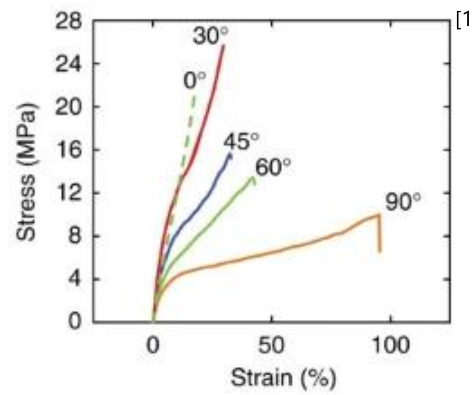
# DMA Use Cases: Assessment of Anisotropic Mechanical Properties of LCE

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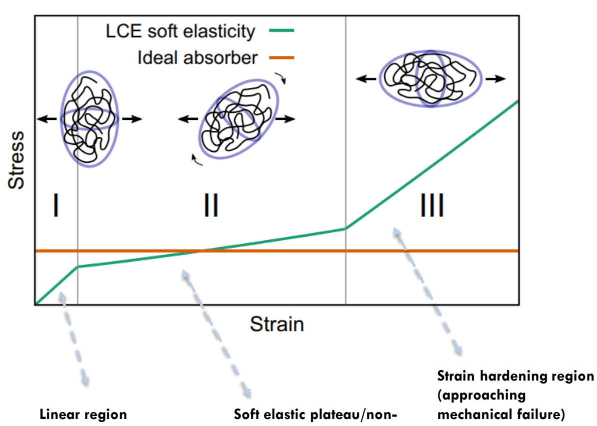
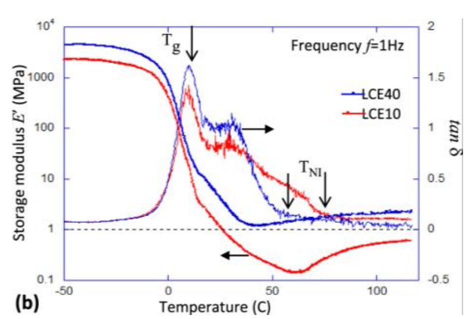
# DMA Uses Cases: Nonlinearity in LCE Mechanical Properties Potential for Dissipation








Mistry, D., Traugutt, N.A., Sanborn, B. et al. Soft elasticity optimises dissipation in 3D-printed liquid crystal elastomers. Nat Commun 12, 6677 (2021). https://doi.org/10.1038/s41467-021-27013-0

https://www.nature.com/articles/s41467-021-27012-1/figures/1

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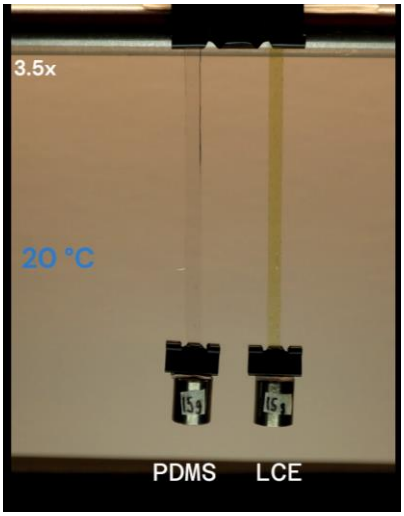
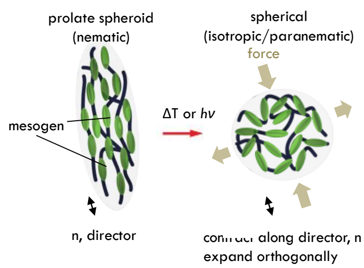
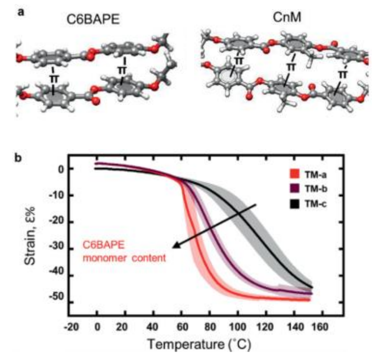
## DMA Use Cases: Characterizing Stimuli-response of LCE




- Thermotropic actuation of LCEs depends on intermolecular interaction within the network and crosslinking




Adv. Funct. Mater.2021, 31, 2100564

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## Summary

- The thermal properties of materials define and scope their use!
  - Characterizing thermal properties are critical to enabling functional and structural utility!
- Differential scanning calorimetry (DSC) is a powerful tool to:
  - Directly measure heat capacity of materials
  - Assess transitions in polymeric and liquid crystalline materials
- Dynamic mechanical analysis (DMA) is a complimentary and powerful tool that:
  - Directly assesses mechanical properties of materials as a function of temperature
    - Insight into viscoelastic character!
  - Can be utilized to assess the stimuli-response of materials

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# VITRIMER NANOCOMPOSITE: THERMOMECHANICAL AND SELF HEALING PROPERTIES

**Dhriti Nepal**
Materials & Manufacturing Directorate,
Air Force Research Lab, WPAFB, OH

May 22$^{nd}$, 2024

**Email: dhriti.nepal.1@afrl.af.mil**









## Motivation: Epoxy Resins in Extreme Environments

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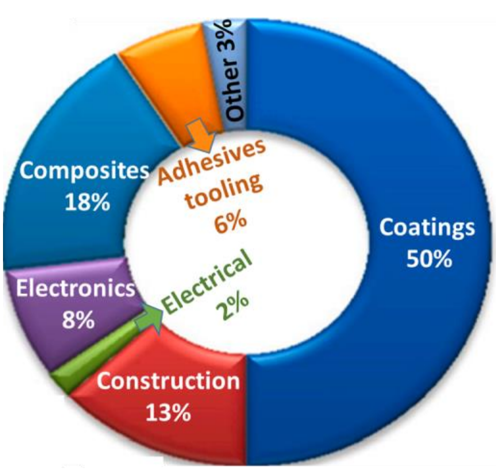
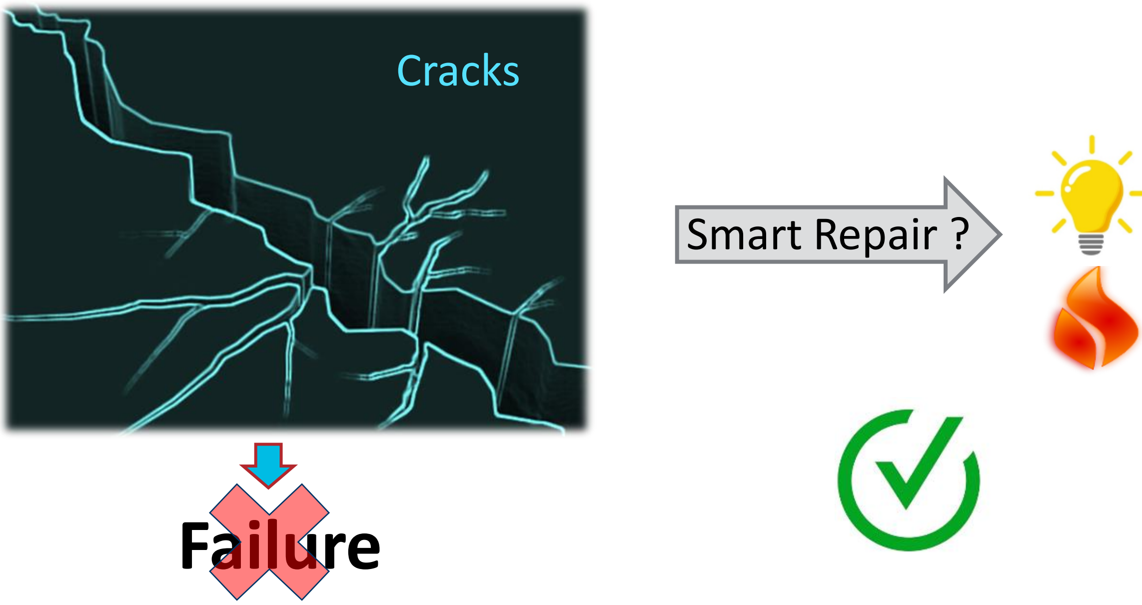



ACS Sustainable Chem. Eng. 2014, 2, 2217−2236

Sources: sicomin, promarinesupplies, pcimag

## Motivation: Epoxy Resins in Extreme Environments

AFRL

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## Audience Survey Question

ANSWER THE QUESTION ON THE INTERACTIVE SCREEN IN ONE MOMENT

**What is Tv?** (Select all that apply)

- Glass Transition Temperature
- Temperature below which material changes from a glassy state to a rubbery
- Vitrimer Transition Temperature
- Topology Freezing Transition Temperature
- None of the above

*** If your answer is “Other” tell us in the questions window!**

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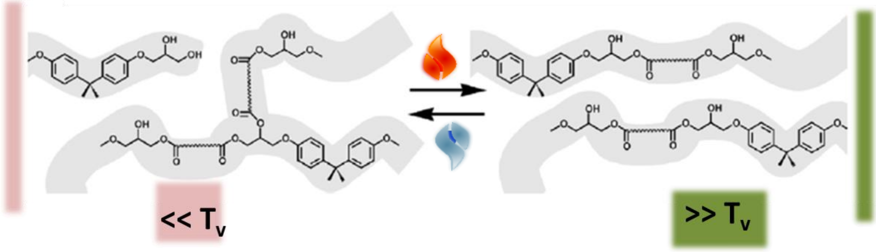
# Thermoset Vitrimer – New Class of Polymer

AFRL




$T_v$ – Vitrimer Transition Temp.
Transesterification Reaction Temp.

Montarnal et. al. Science, **2011**, *6058*, 965

| Thermoset | Vitrimer | Thermoplastic |
|---|---|---|
| ✓ Thermo-mechanically robust | ✓ Thermo-mechanically robust | ○ Thermo-mechanically weak |
| ✓ Chemically stable | ✓ Chemically stable | ○ Chemically unstable |
| ○ Non-processable | ✓ Processable | ✓ Processable |
| ○ Non-reformable | ✓ Reformable | ✓ Reformable |

Hubbard et. al. ACS Omega 2022, 7, 33, 29125–29134







# Epoxy Vitrimer Chemistry

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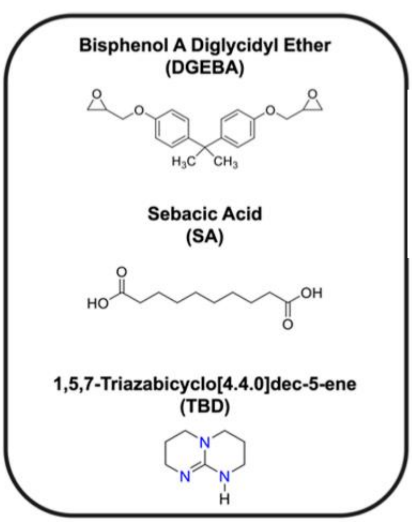
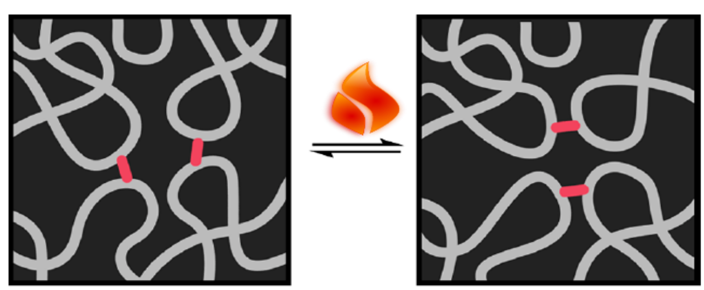
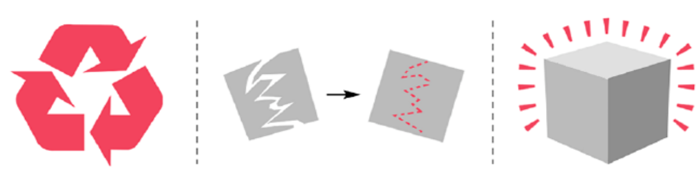


Dynamic Crosslink Exchange



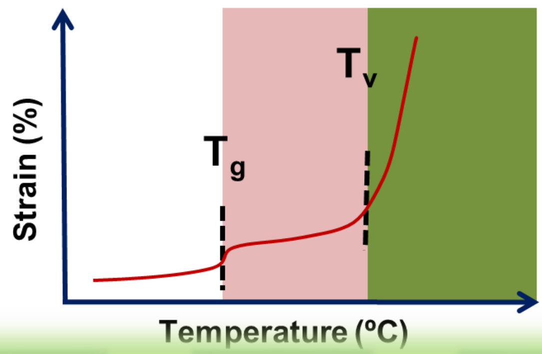

Hubbard et al., *ACS Omega* 2022, 15, 21-28.

Elling, Dichtel *ACS Cent Sci.* **2020** 3; 6, 1488–1496

## $T_v$ Drives Shape Reprograming / Healing

AFRL

Shape Memory
Shape Reprograming




$T_g$ - Glass Transition Temp.

$T_v$ – Vitrimer Transition Temp.

**How do we characterize Tv?**

Control Epoxy Vitrimer



Hubbard et. al. ACS Omega 2022, 7, 33, 29125–29134





## Major Methods for Tv Characterization

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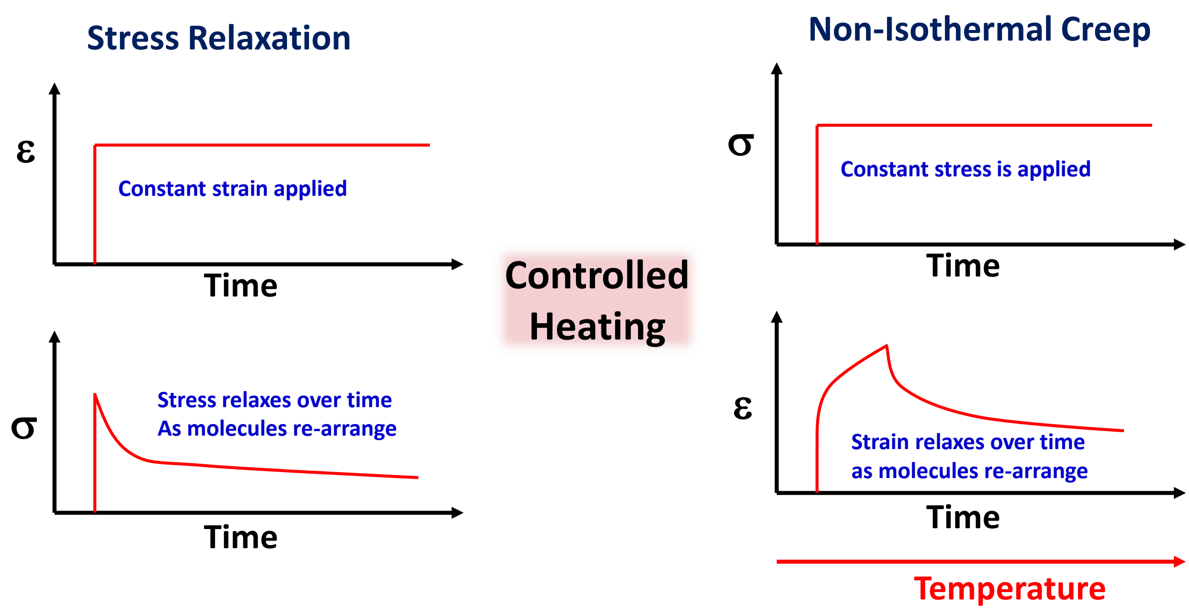
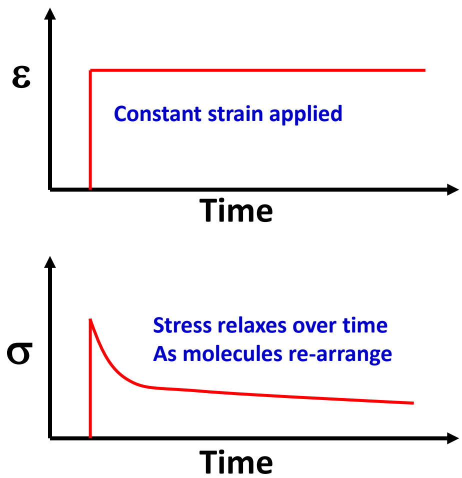
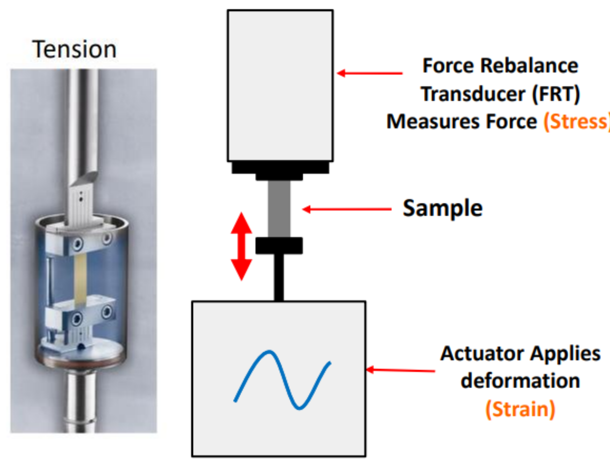


## Stress Relaxation




https://www.tainstruments.com/wp-content/uploads/2020_DMA_Online_Training_Part_1.pdf



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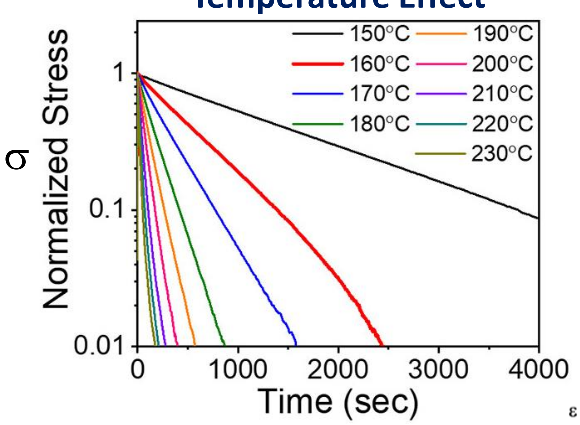
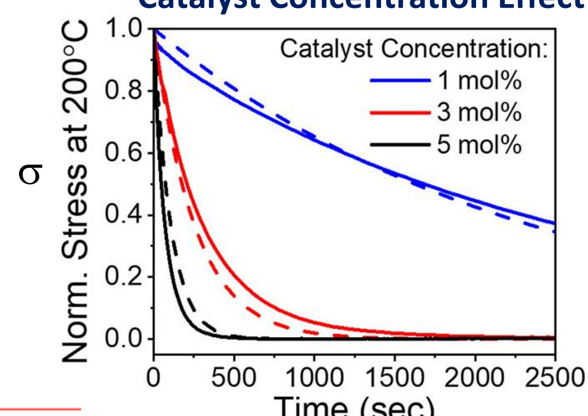
## Stress Relaxation

### Temperature Effect

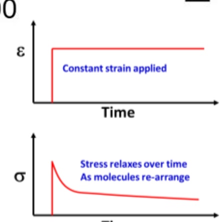



### Catalyst Concentration Effect




**Stress Relaxation Time Constant**

$$\sigma = \sigma_0 e^{-(t/\tau_1)}$$




**Takeaways:** Stress relaxation increases with temperature and catalyst concentration.



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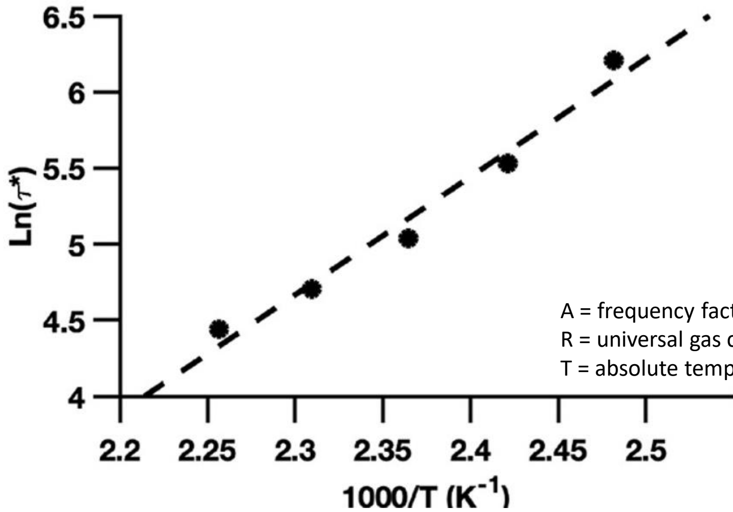
# Arrhenius Plot






A = frequency factor
R = universal gas constant
T = absolute temperature

$$\tau = \frac{1}{A}\exp\left(\frac{E_A}{RT}\right)$$

Arrhenius plot of the characteristic relaxation time (τ*) against inverse temperature.

$T > T_g$, where flow is limited by the bond exchange, the primary contribution to $E_a$ is the **activation energy required** for the bond exchange reaction

Elling, Dichtel *ACS Cent Sci.* **2020** 3; 6, 1488–1496





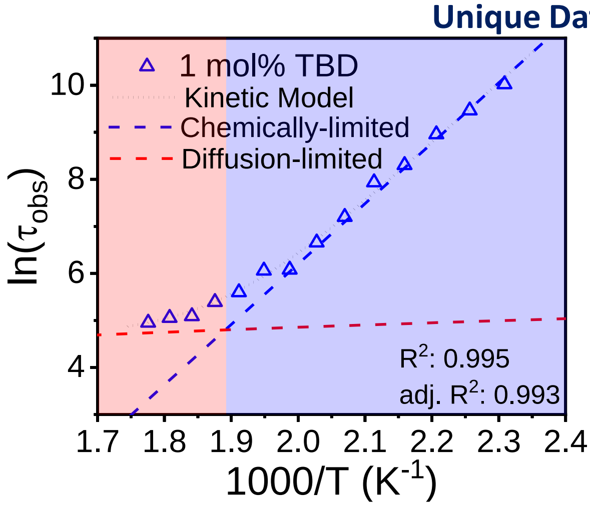


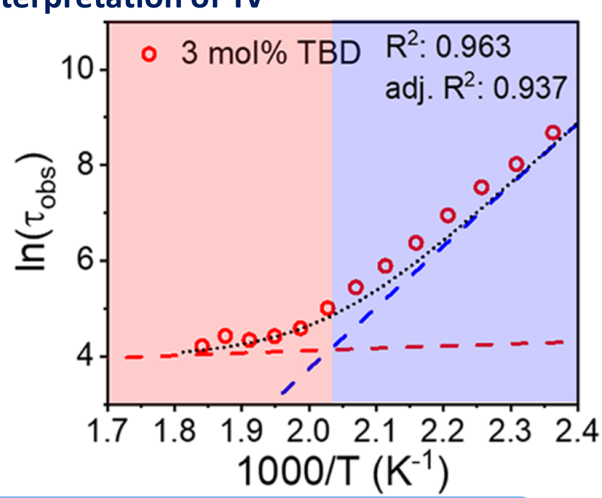


# Tv Calculation from Stress Relaxation



## Unique Data Interpretation of Tv



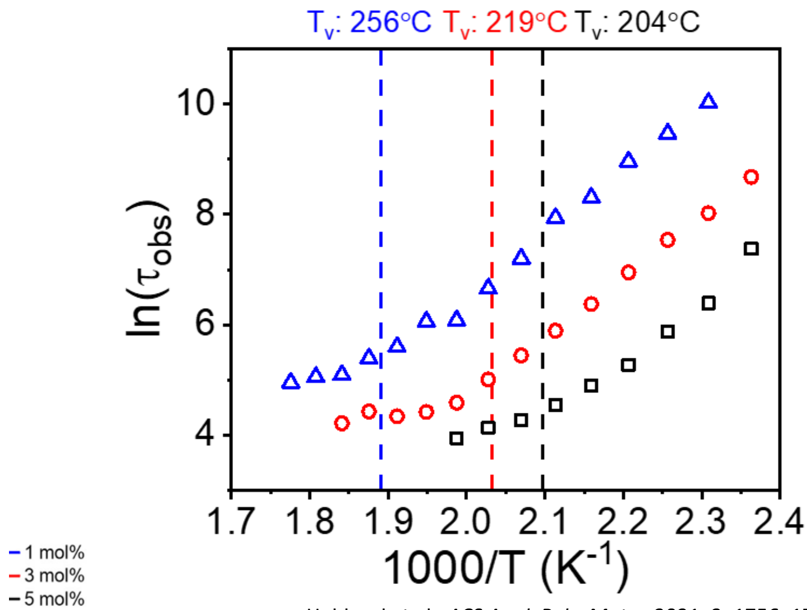



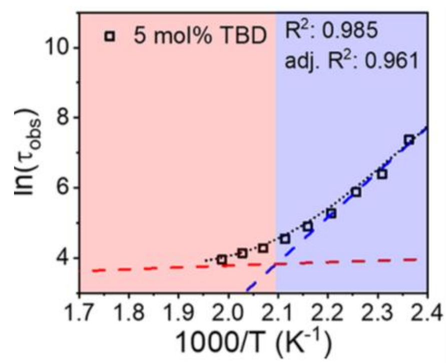

– 1 mol%
– 3 mol%
– 5 mol%

- **Takeaways:** A change in slope of the Arrhenius plot indicates the Tv as the dynamic reaction transitions from being chemically-limited to diffusion-limited

Hubbard et al., *ACS Appl. Poly. Mater.* 2021, 3, 1756–1766

# Tv Calculation from Stress Relaxation




- **Takeaways:** A change in slope of the Arrhenius plot indicates the Tv as the dynamic reaction transitions from being chemically-limited to diffusion-limited

Hubbard et al., *ACS Appl. Poly. Mater.* 2021, 3, 1756–1766



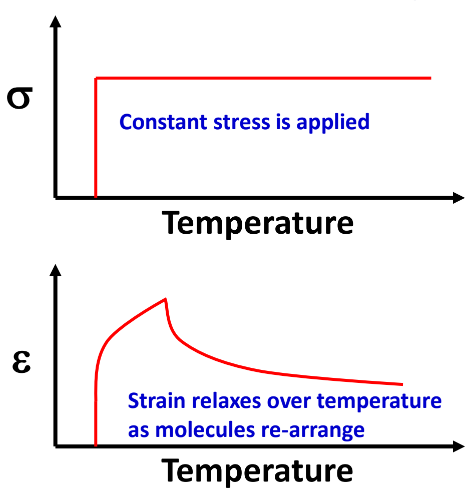


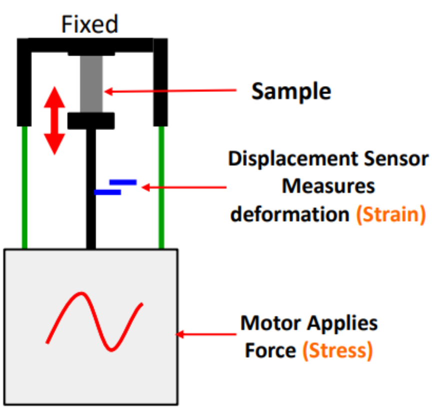






## Non-Isothermal Creep



## Tv Calculation from Non-Isothermal Creep

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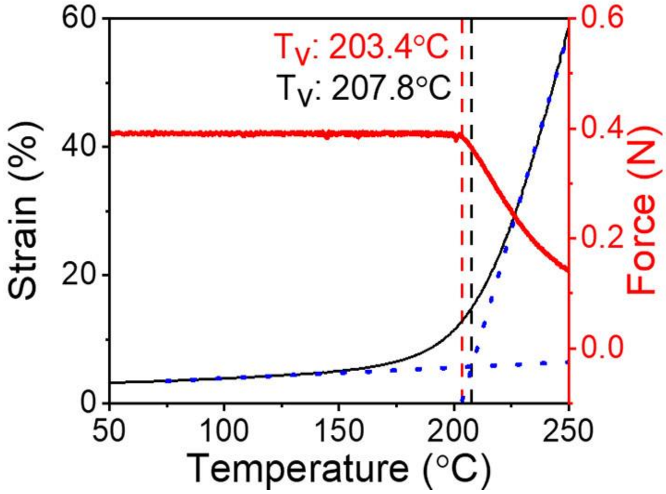


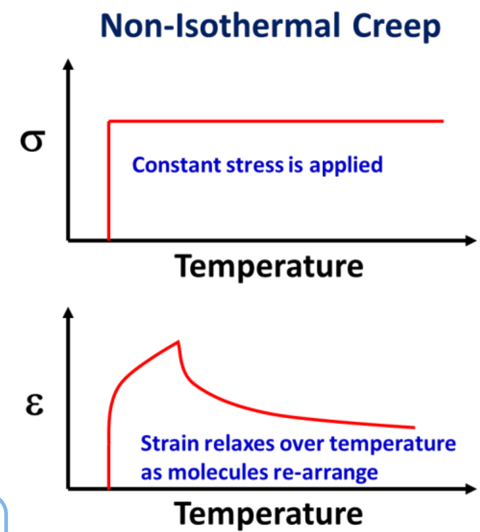


**Takeaways:**
- **Strain-temperature curve reaches an inflection point**
- **Force-temperature slope changes**



## Tv Calculation from Non-Isothermal Creep

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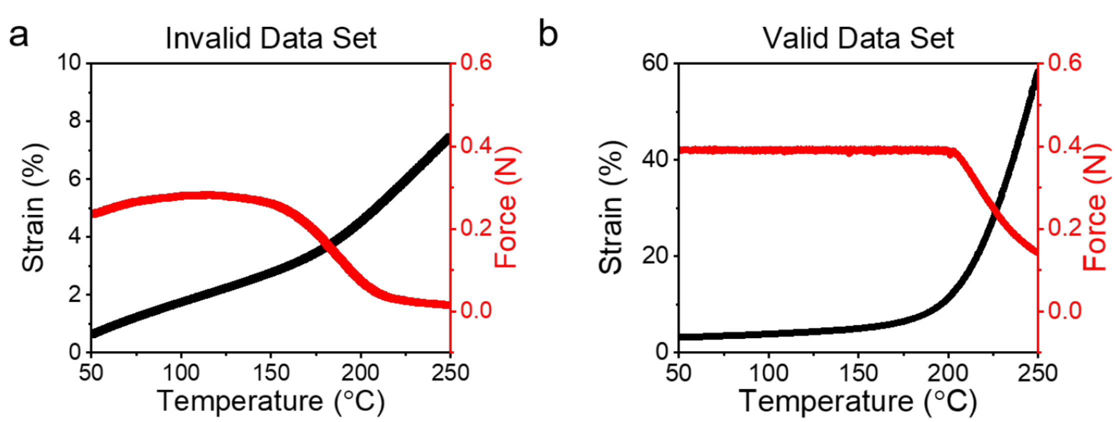


- **Takeaways:** Identify invalid data set – Force curve

## Tv Calculation from Non-Isothermal Creep

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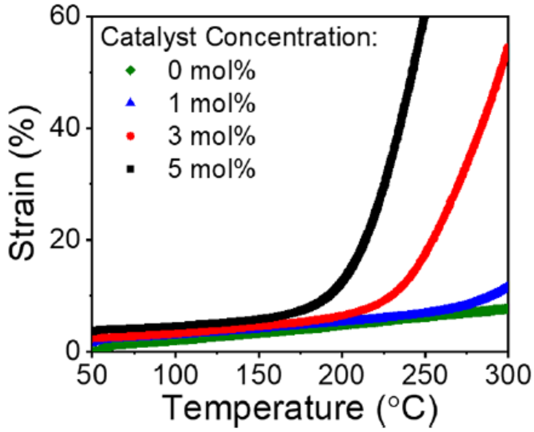


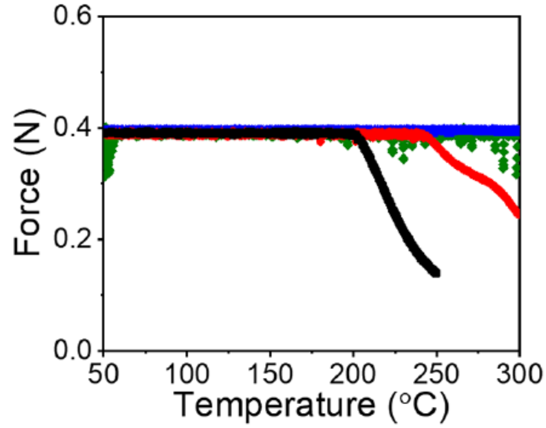


- **Takeaways:** Tv decreases with increasing catalyst concentration









## Tv from Stress Relaxation & Non-Isothermal Creep

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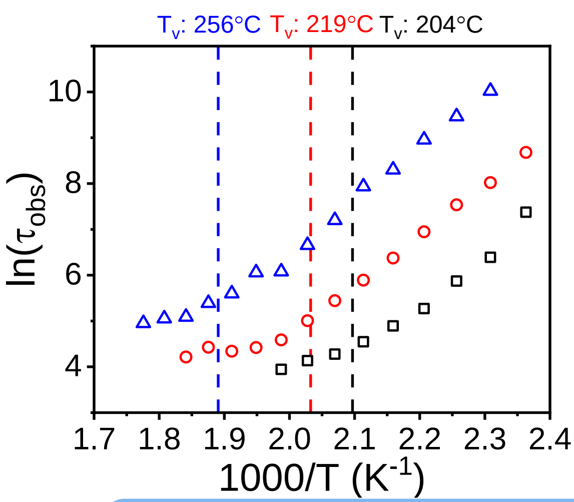


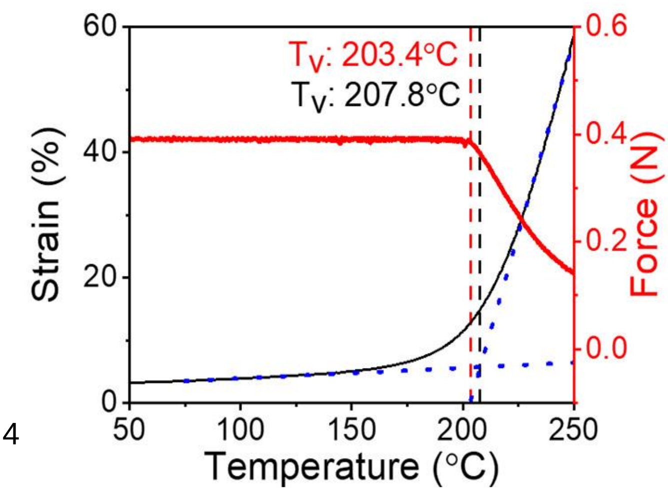


- Arrhenius slope changes (stress relaxation)
- **Strain-temperature curve reaches an inflection point (non-isothermal creep)**
- **Force-temperature slope changes (non-isothermal creep)**

# Thermomechanical Analysis (TMA) of Vitrimers

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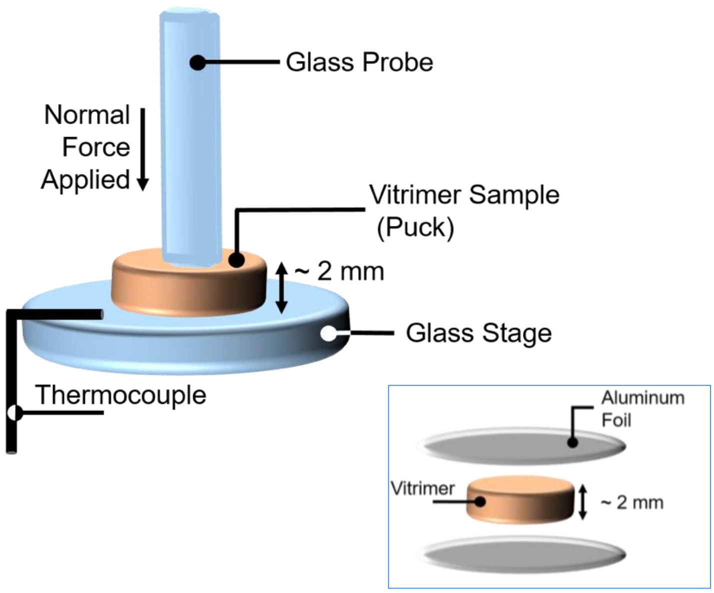


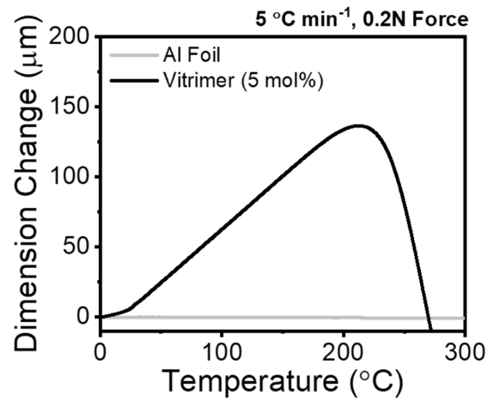




# Tv from TMA

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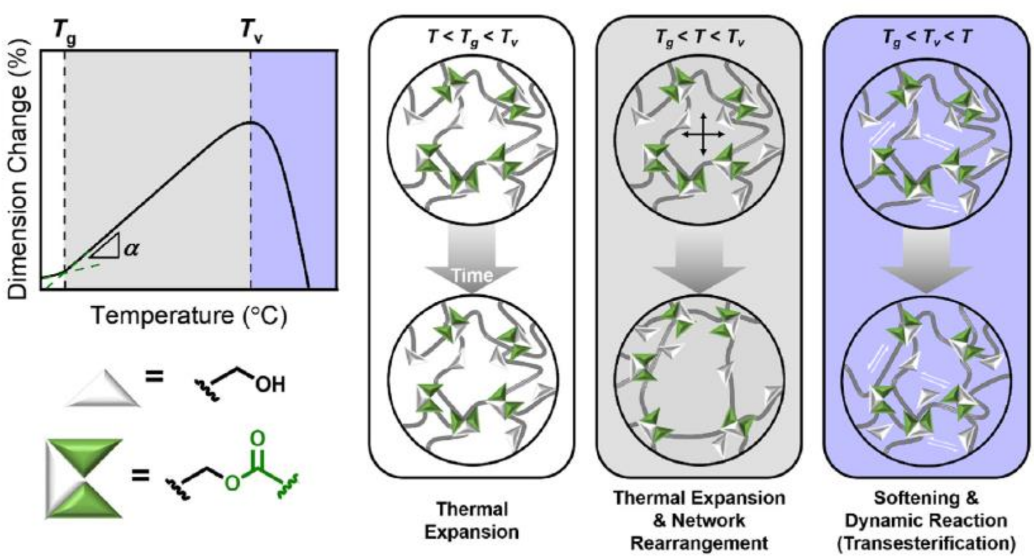
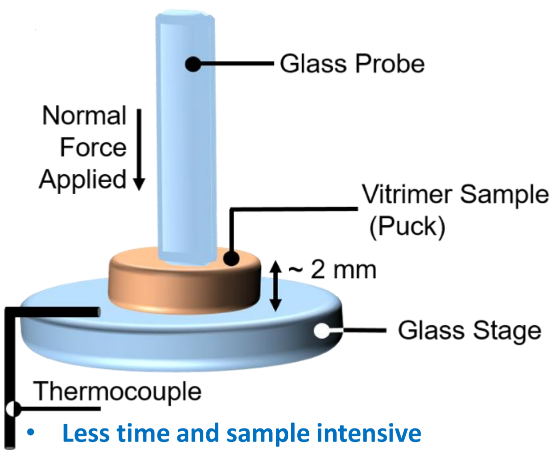
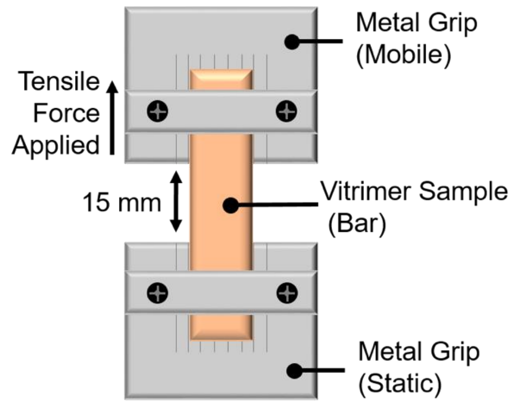



Hubbard et al., *Polymer Testing,* 2023, *118,* 107877

# TMA vs DMA for Tv Characterization




- Less time and sample intensive
  - High-throughput measurement
- Compression Mode - more representative
- – often needed for healing




- Stress Relaxation
- Iso-thermal Creep
  - Larger sample sizes

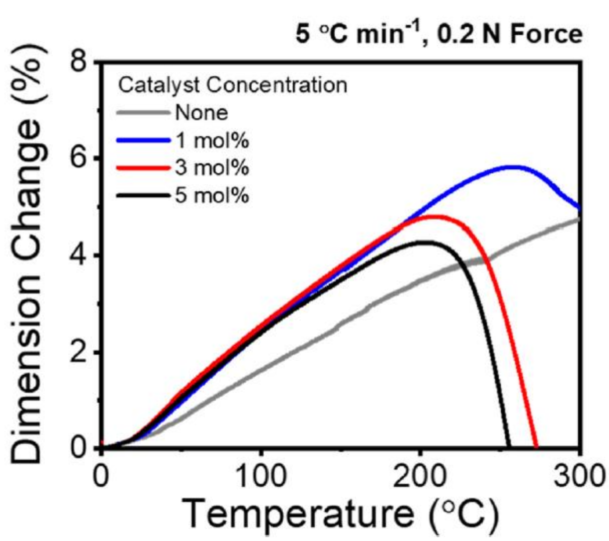






# TMA of Vitrimers

## Influence of Catalyst Concentration on Tv

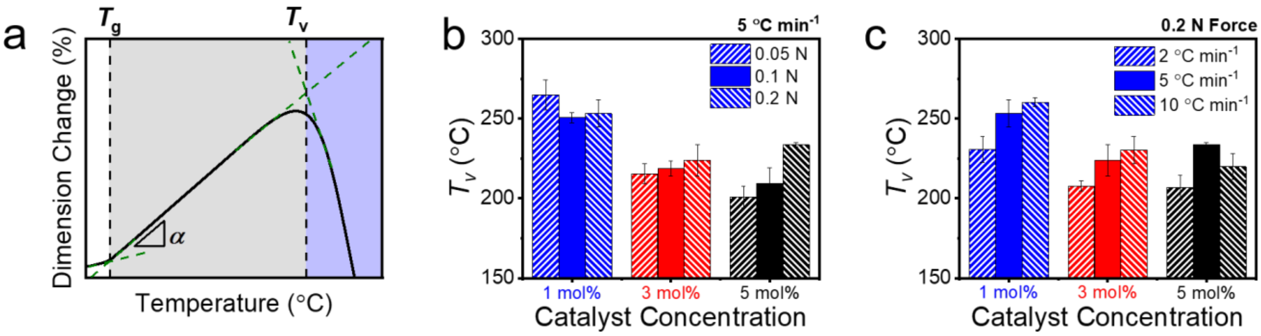



- **Takeaways:** Tv decreases with increasing catalyst concentration, and no reported Tv is identified for samples with no catalyst

Hubbard et al., *Polymer Testing,* 2023, *118,* 107877

# TMA of Vitrimers






- **Takeaways:** Influence of Force, Heating Rate and Catalyst Concentration on Tv

Hubbard et al., *Polymer Testing,* 2023, *118,* 107877



# Tv of Vitrimers – Comparison of 3 Methods

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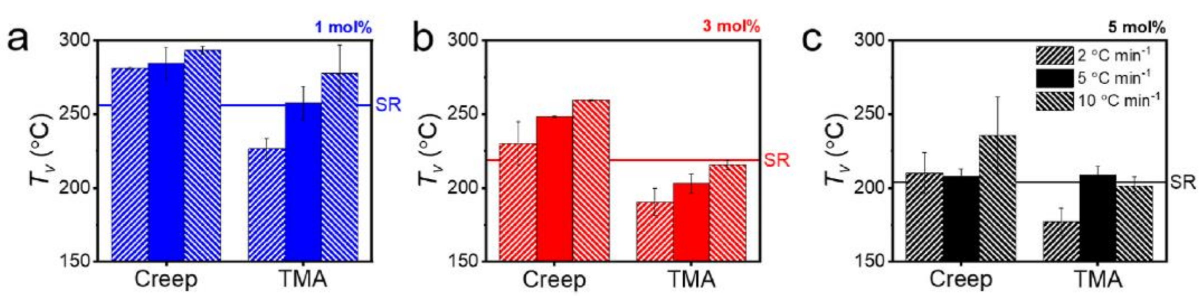
**SR – Stress Relaxation; Creep – Non-Isothermal Creep; TMA**




- **Takeaways:** Tv as measured via stress relaxation is closer to the value recorded via TMA.

Hubbard et al., *Polymer Testing,* 2023, *118,* 107877

# Summary

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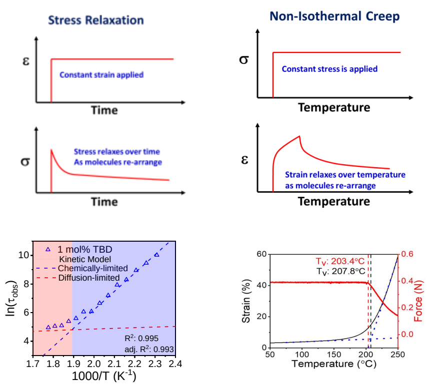
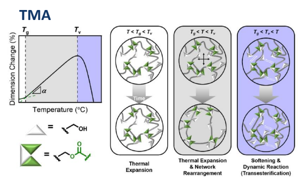
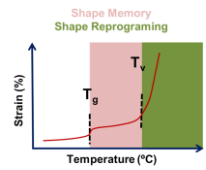
**Tv can be measured via variety of thermo-mechanical methods**

- Stress Relaxation
- Non-Isothermal Creep
- TMA

- Identification of Tv is important for healing
- Experimental parameters (e.g., heating rate and applied force) & catalyst concentration are crucial in dictating the Tv range




## Future Outlook

- Tv - Range of values when measured due to mesoscale physics (e.g., heterogeneity in the material, varying catalyst concentration, thermal expansion, etc.)
- Further theoretical studies w/ advanced characterizations are required to provide a complete understanding of this phenomenon



# Acknowledgement

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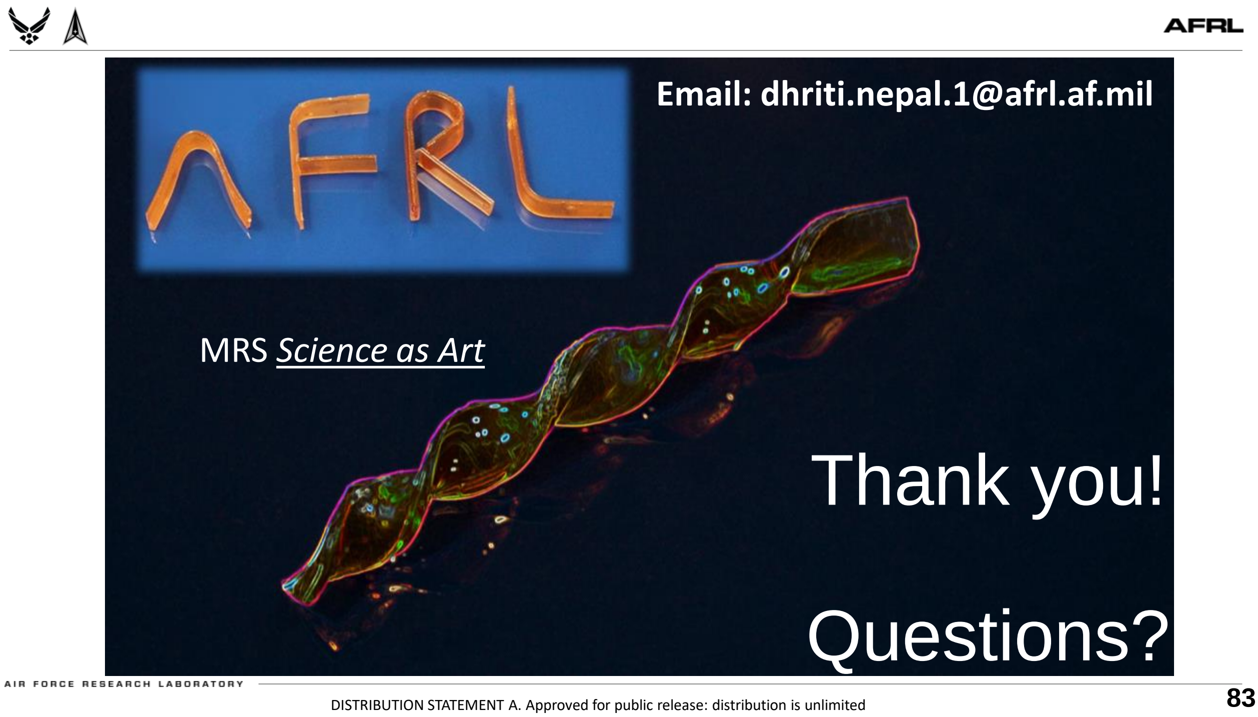
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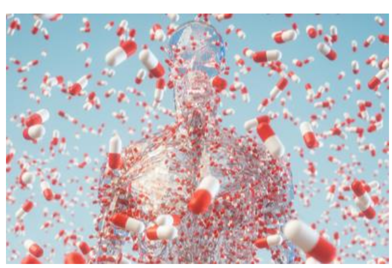

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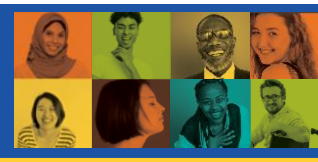

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