Environmental Effects on the Toughness of Photopolymerizable Acrylate Networks for Biomedical Applications

Kathryn Smith[1]
Ken Gall[1, 2]
[1]Woodruff School of Mechanical Engineering
[2]School of Materials Science and Engineering
Georgia Institute of Technology
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Georgia Tech

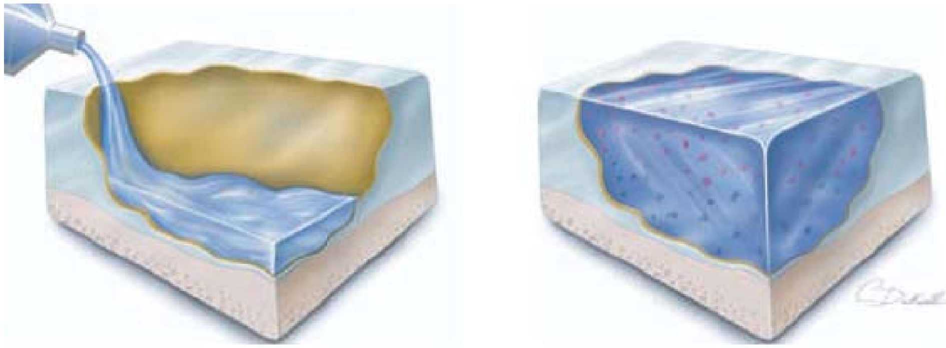
Overview

- Photopolymerization and its uses
- Limitations due to mechanical properties
- Temperature effect on network toughness
- Network toughness under aqueous conditions
- Networks toughness versus modulus
- Conclusions

UV-Curable Acrylate Networks

Advantages/Uses

- *In situ* formation
  - dental resins (Bowman et al)
- Cell Encapsulation
  - tissue engineering scaffolds and drug delivery (Anseth, West, Elisseeff)
- Complex geometries
  - actuated fixation devices, stents (Gall et al)



Elisseeff et al

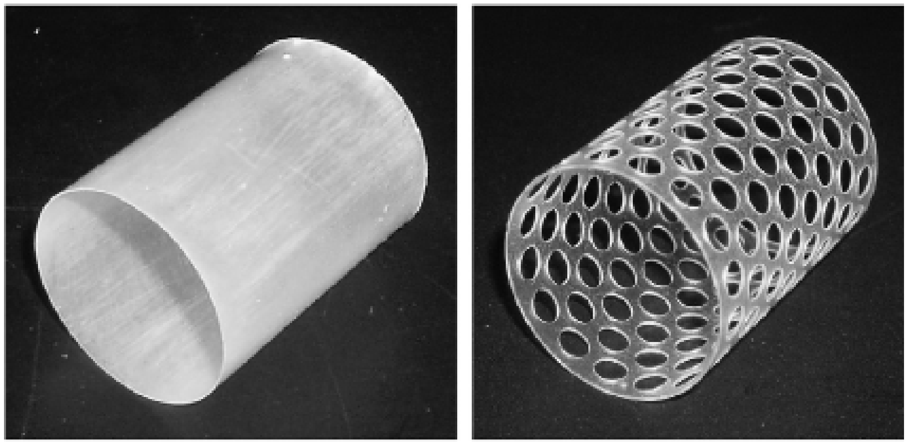
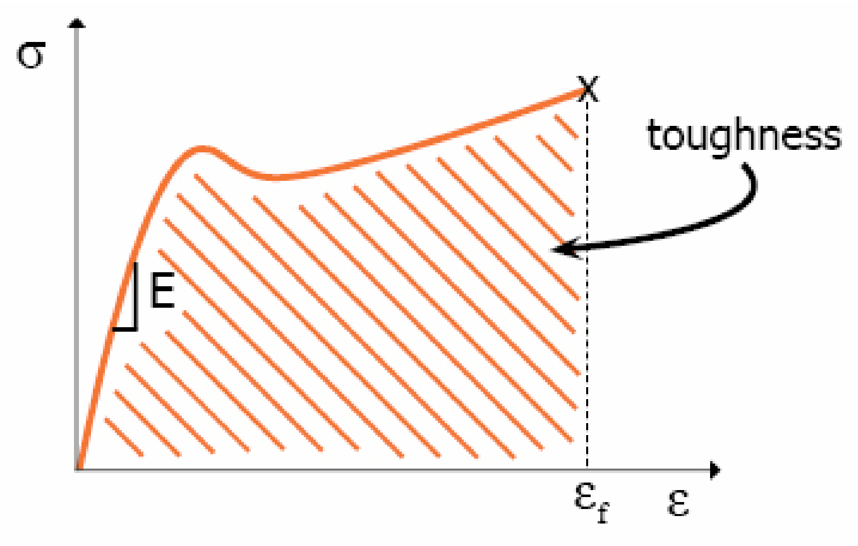


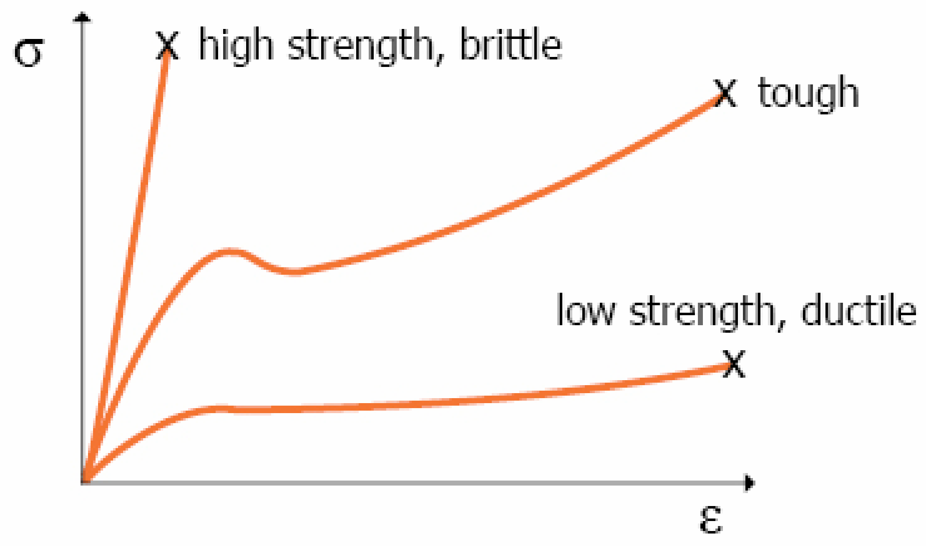
Fig. 3. Design of solid and 50% perforated shape-memory polymer stents.

Yakacki et al

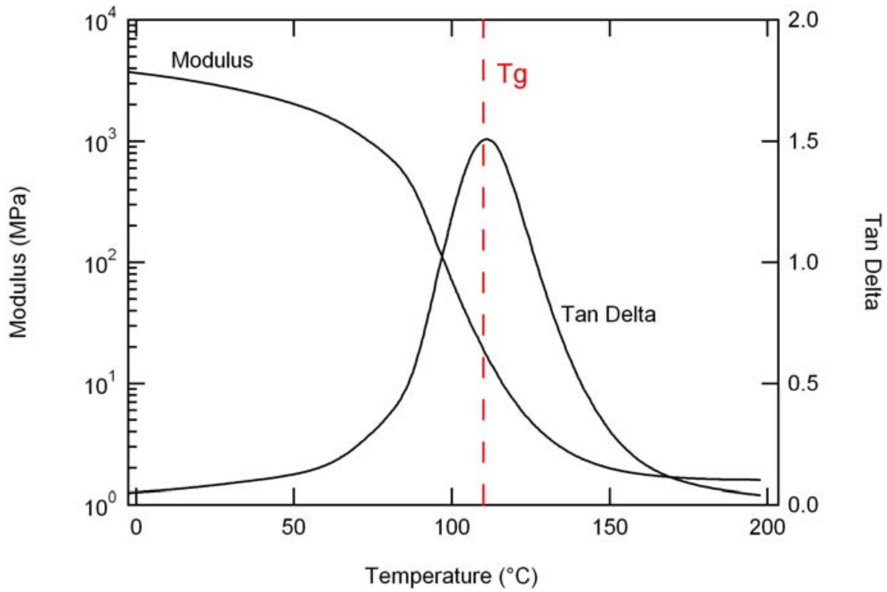
UV-Curable Acrylate Networks

- Lack durability for long term implantation
- Limited function in large load bearing applications
- Related to network toughness (energy required to break)

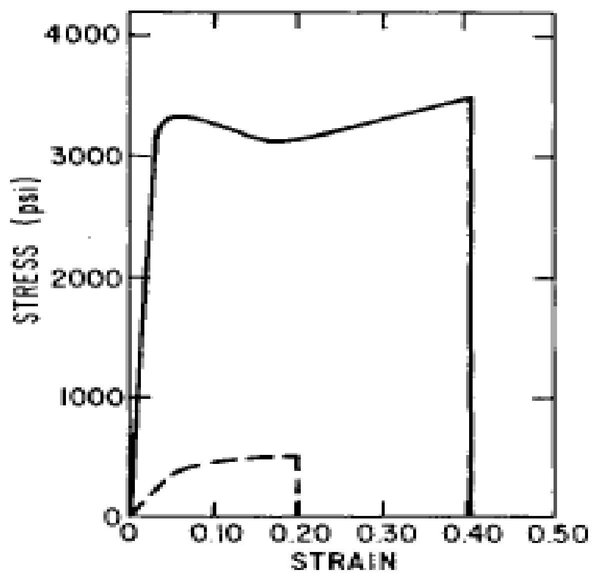




UV-Curable Acrylate Networks



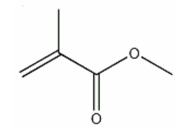
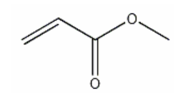
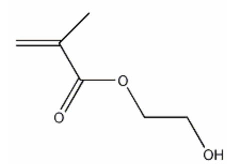
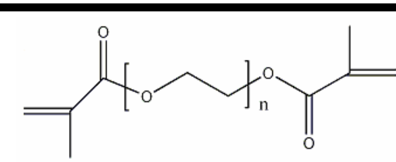
Mechanical properties dictated by glass transition region (Tg)

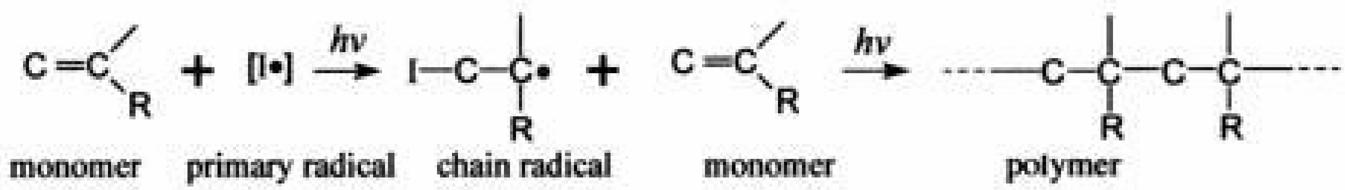


Water alters mechanical properties (Bolon et al)

What is the combinatorial effect of temperature and water on network toughness?

Monomer Components

Name	Abbreviation	Chemical Structure
Methyl Methacrylate	MMA	
Methacrylate	MA	
2-hydroxyethyl methacrylate	2HEMA	
Poly(ethylene glycol) dimethacrylate	PEGDMA	



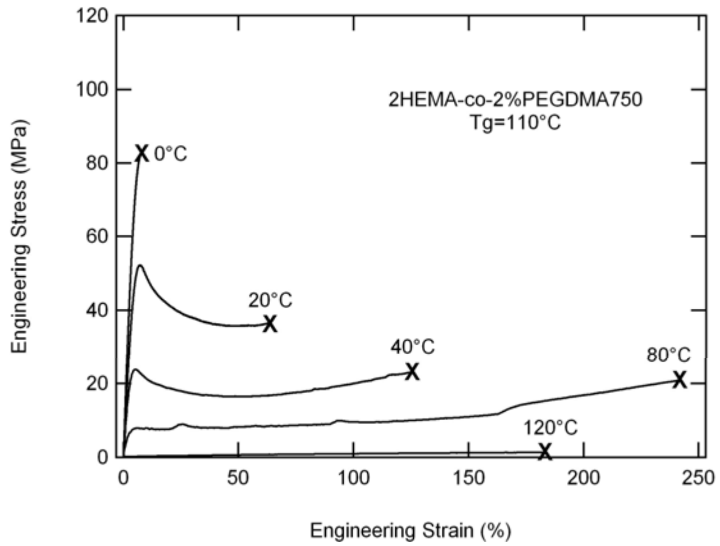
Eq. 2 Photopolymerization of vinyl monomers.

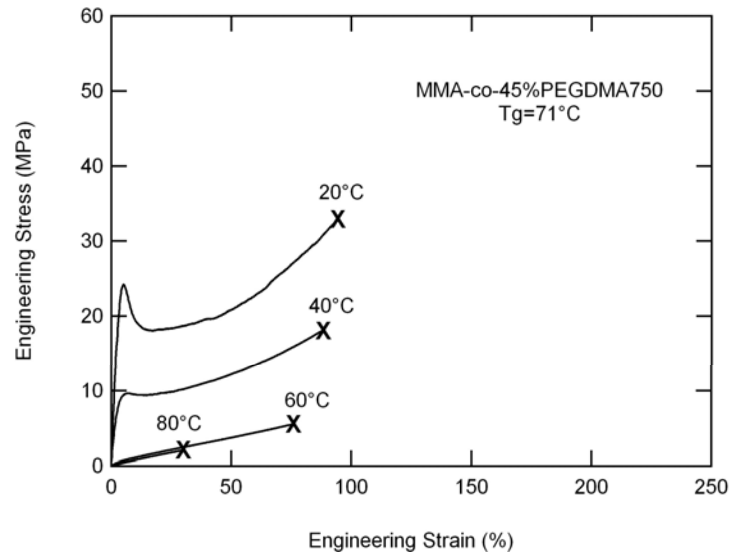
Elisseeff et al

Network Formulations

Name	Monomer Wt. %	Tg(ºC)	$q=W_s/W_i$	Application
MMA-co-PEGDMA	55 MMA 45 PEGDMA	71	1.14	High force shape memory applications
2HEMA-co-PEGDMA	98 2HEMA 2 PEGDMA	110	1.58	Hydrogels, Soft contact lens
MA-co-MMA-co-PEGDMA	52 MA 46MMA 2 PEGDMA	58	1.02	Large deformation shape memory applications

Stress Strain Behavior

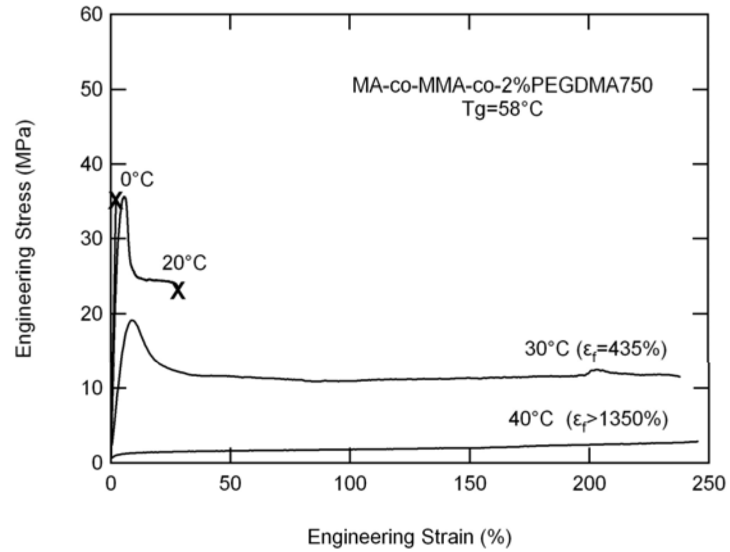




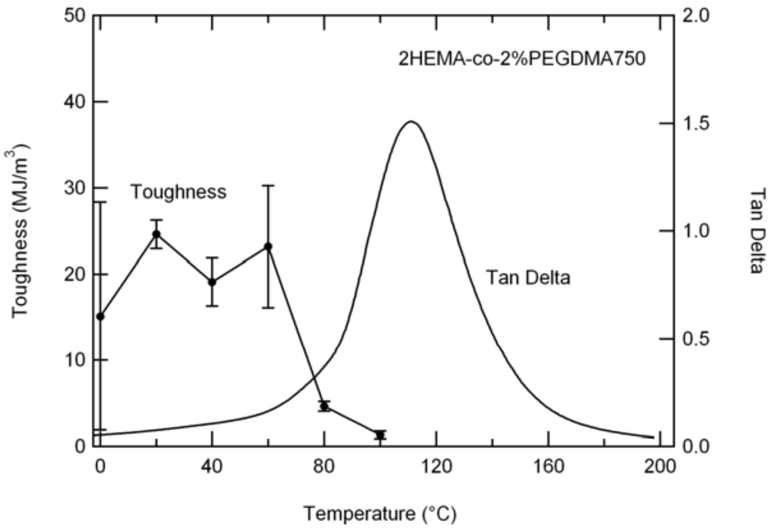
T < Tg
Modulus decreases and failure strains increase

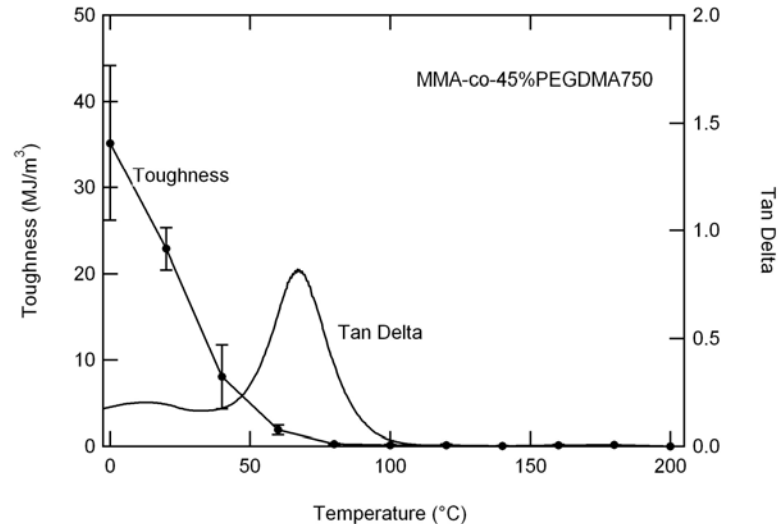
T>=Tg
Failure strains decrease and modulus plateaus

Ultimate stresses and strains dependent on chemical structure of network

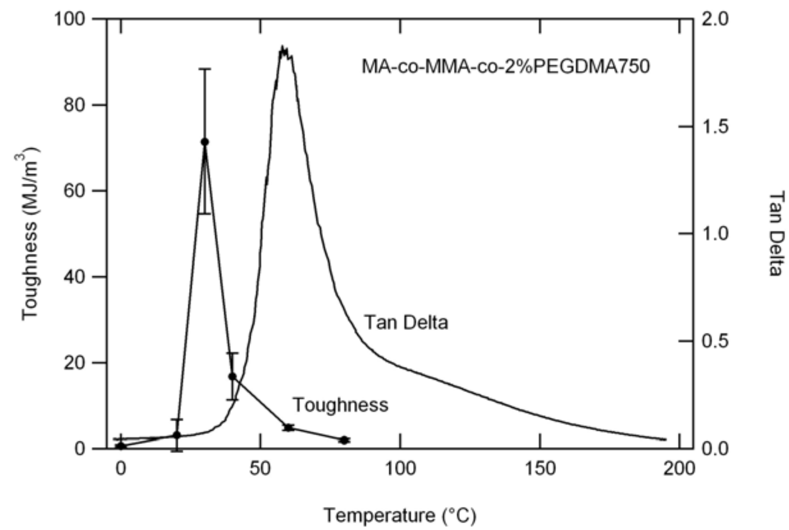


Toughness vs. Temperature

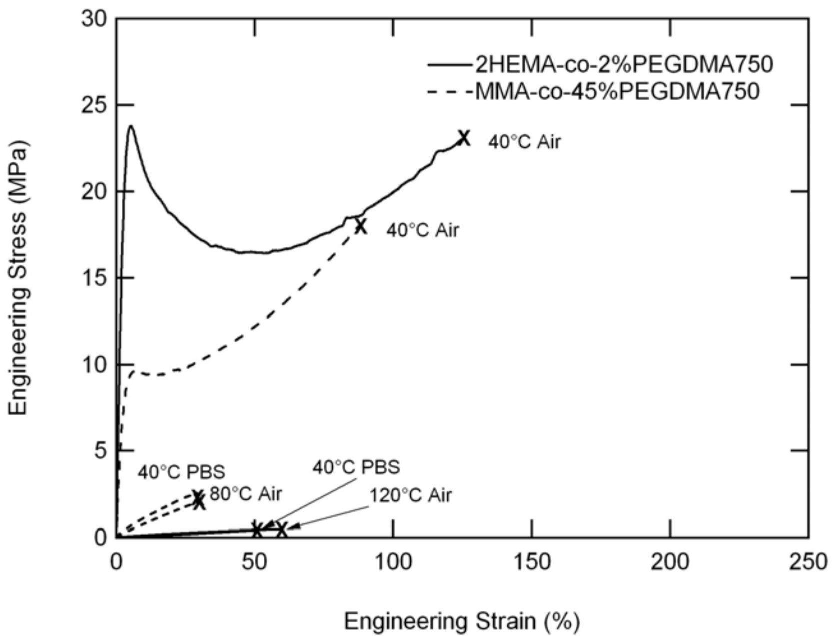


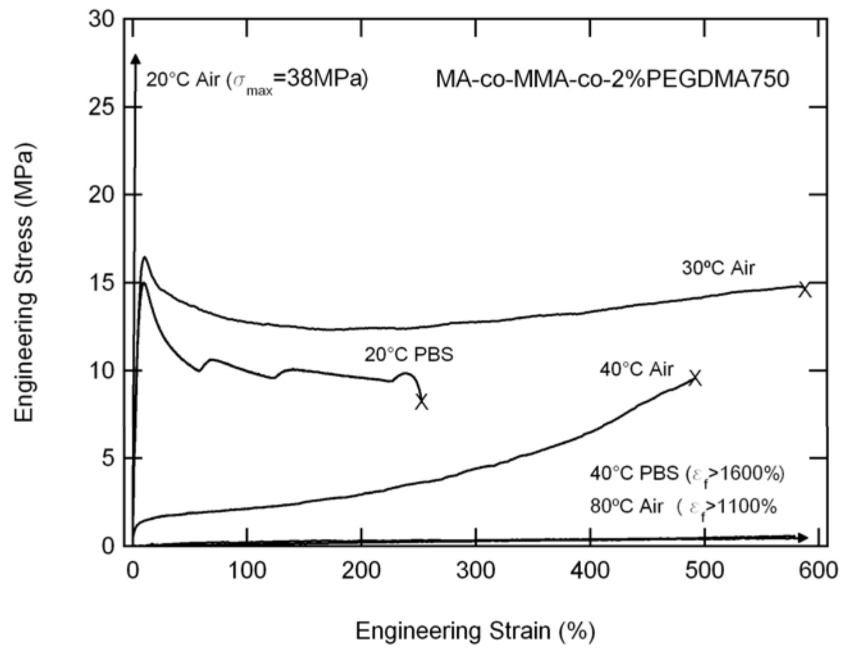


- Peak in toughness occurs below Tg
- Distance between two peaks and breath of peaks correlated to chemical and network structure
- 2HEMA network relatively tough near body temperature



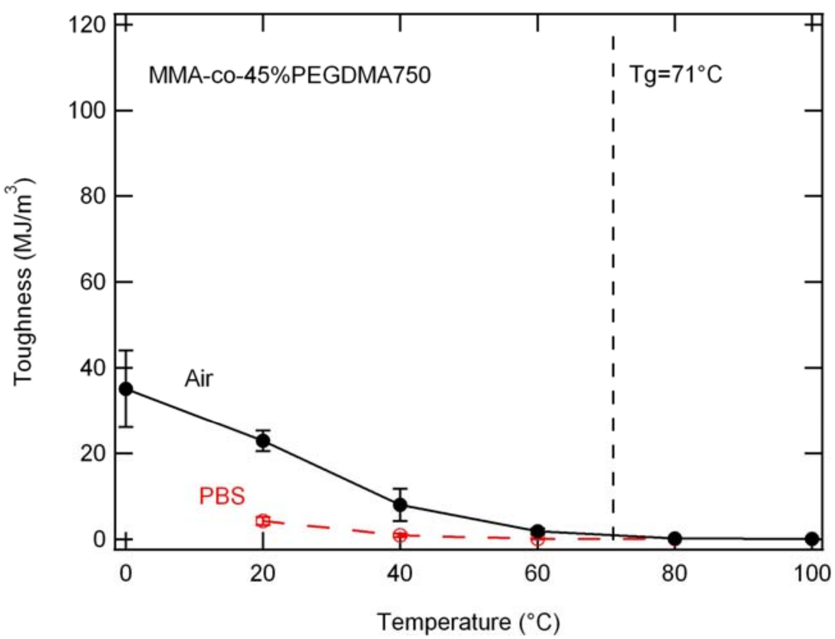
Toughness in PBS

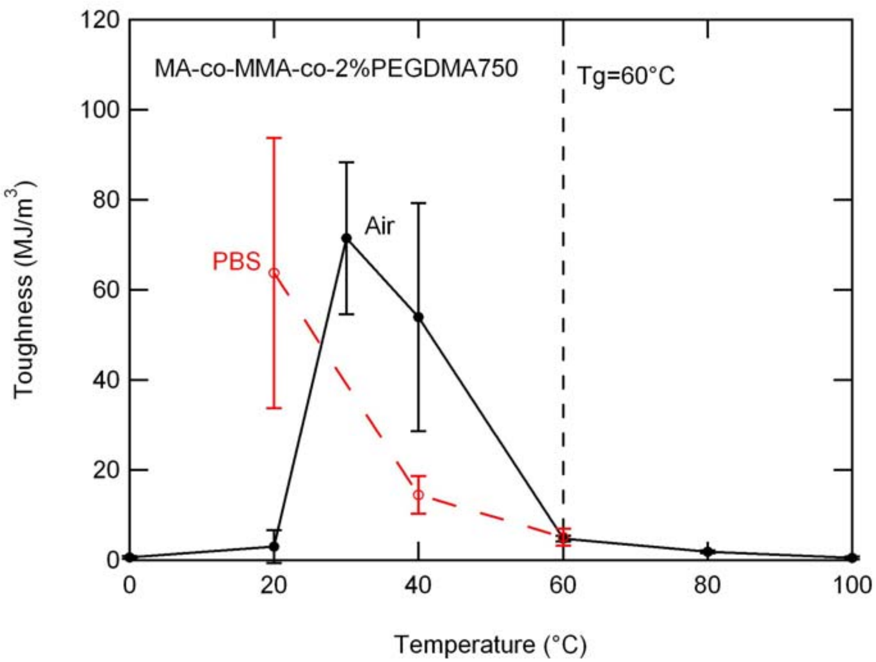




Stress strain behavior in PBS at lower temperatures matches the behavior of the same system at temperatures above Tg in air

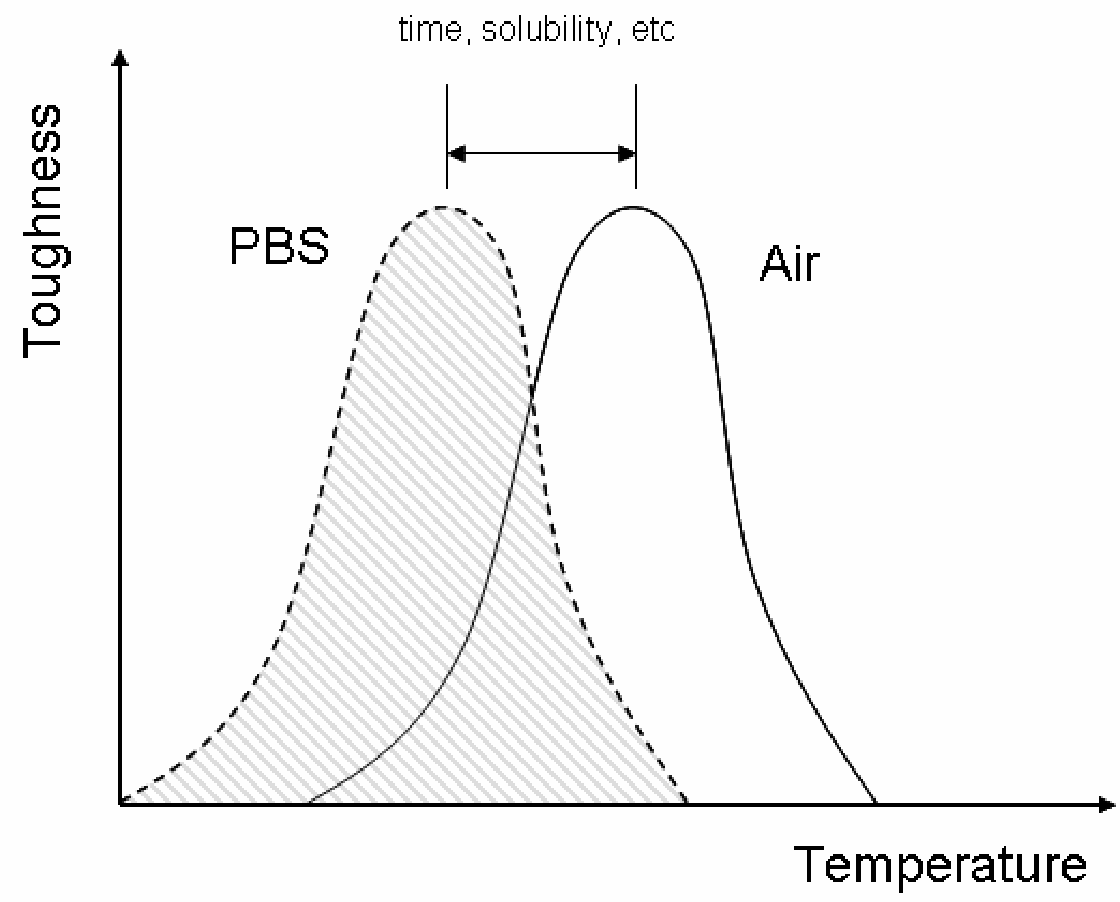
Toughness in PBS





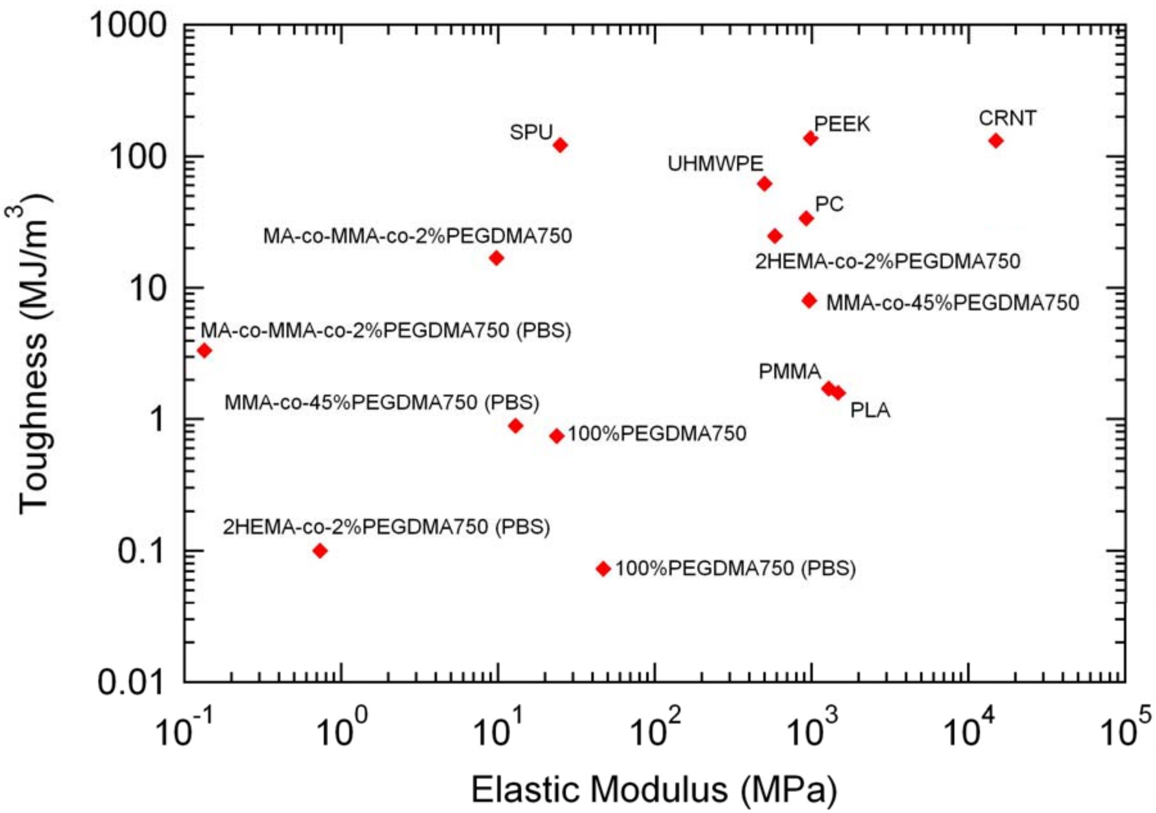
- Temperature of peak toughness decreases in PBS
- Dependent on relative position of toughness peak to Tg

Toughness in PBS



Toughness increase or decrease dependent upon testing temperature and how far the toughness peak shifts

Toughness vs. Modulus



SPU: segmented polyurethane

UHMWPE: Ultra-high molecular weight polyethylene

CRNT: carbon reinforced nanotubes

- At 40C, polymers with similar moduli have different toughness values from over 100 MJ/m^3 to approximately 0.1 MJ/m^3.
- Photopolymerized acrylate networks possess less toughness than current biomedical polymers (PC, PEEK, UHMWPE, SPU)

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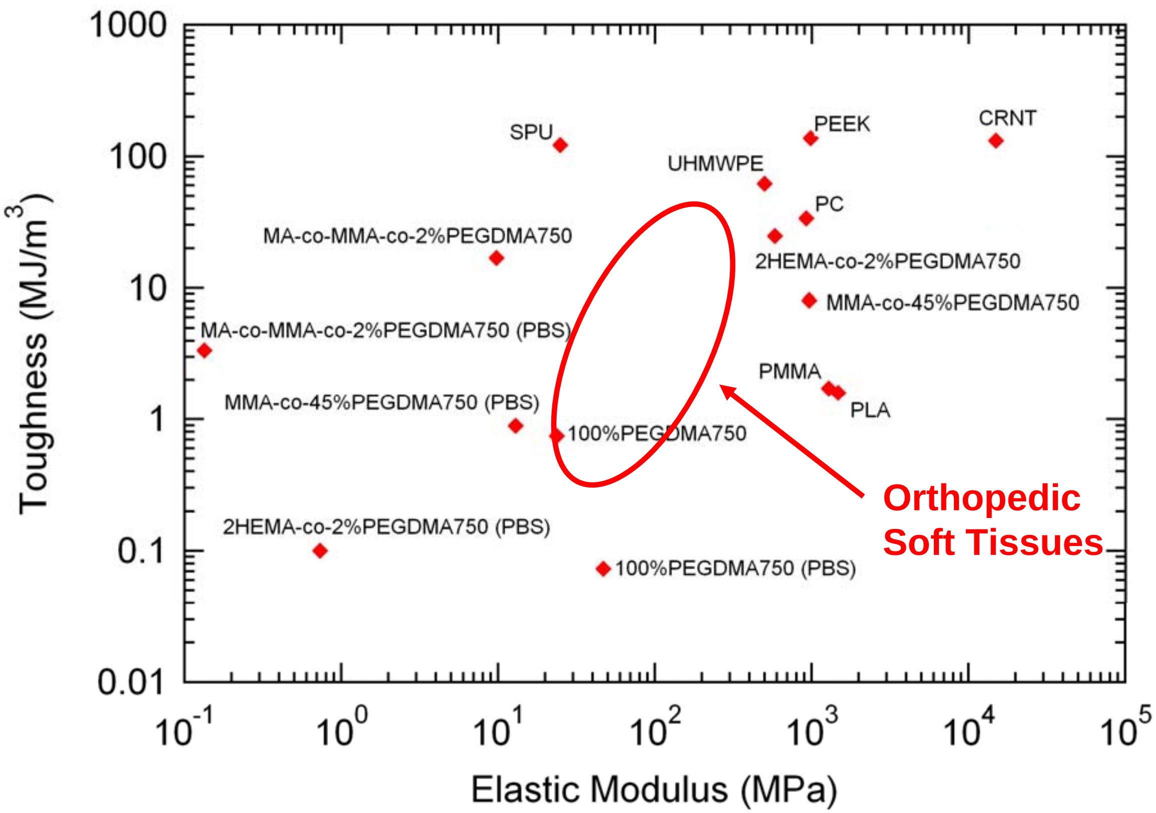

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- At 40C, polymers with similar moduli have different toughness values from over 100 MJ/m^3 to approximately 0.1 MJ/m^3.
- Photopolymerized acrylate networks possess less toughness than current “tough” biomedical polymers (PC, PEEK, UHMWPE, SPU)

Conclusions

- Toughness peaks at a temperature below the glass transition temperature.
- The location and breadth of the toughness peak depended strongly on the nature of the glass transition in the network (breadth, number of peaks).
- For equivalent glass transition temperature network structure (crosslink density) and chemistry is shown to impact toughness.
- Apparent toughness is significantly altered in water driven by changes in the test temperature relative to the glass transition temperature.

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Questions?