Electron Beam Crosslinked Polyurethane Shape Memory Polymers With Tunable Mechanical Properties

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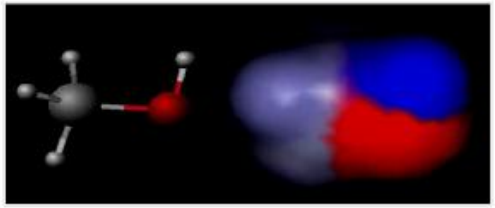
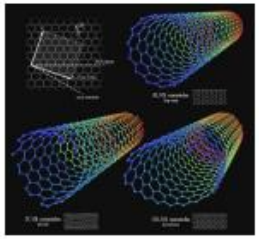
Radiation & Mechanical Properties



CHEMISTRY



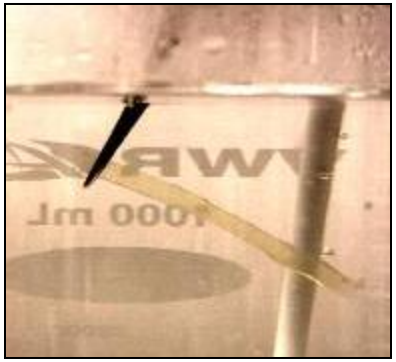
MATERIALS SCIENCE

INDUSTRY

…via e-beam

Shape Memory Polymers

Shape memory polymers (SMPs) have the ability to remain in a deformed shape and then recover their original shape after introduction to a stimulus.



Primary geometry (strip-like)

1. Heat
2. Deform
3. Cool

Secondary geometry (coiled)

4. Reheat

Primary geometry (strip-like)

Thermally actuated shape recovery from coiled (secondary) geometry to strip-like (primary) geometry for polyurethane SMP in water at 70 C

SMPs in the Biomedical Industry

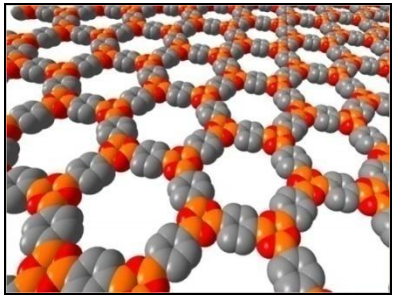
- May 2009 marked the first-ever FDA approval for an SMP-based biomedical implant device
- This device, a suture anchor device called Morphix©, was developed by MedShape Solutions® in Atlanta, GA, and has recently been implanted into humans for the first time.

Morphix: An SMP-based suture anchor device, which received FDA approval in May 2009

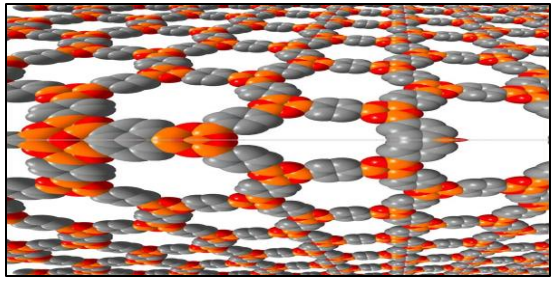
source: medshapesolutions.com

SMP Processing Limitations

- Many applications require SMP-based components with complex geometries.
- Covalently crosslinked SMPs are produced by one-step polymerization
- This process does not allow for processing by injection molding.



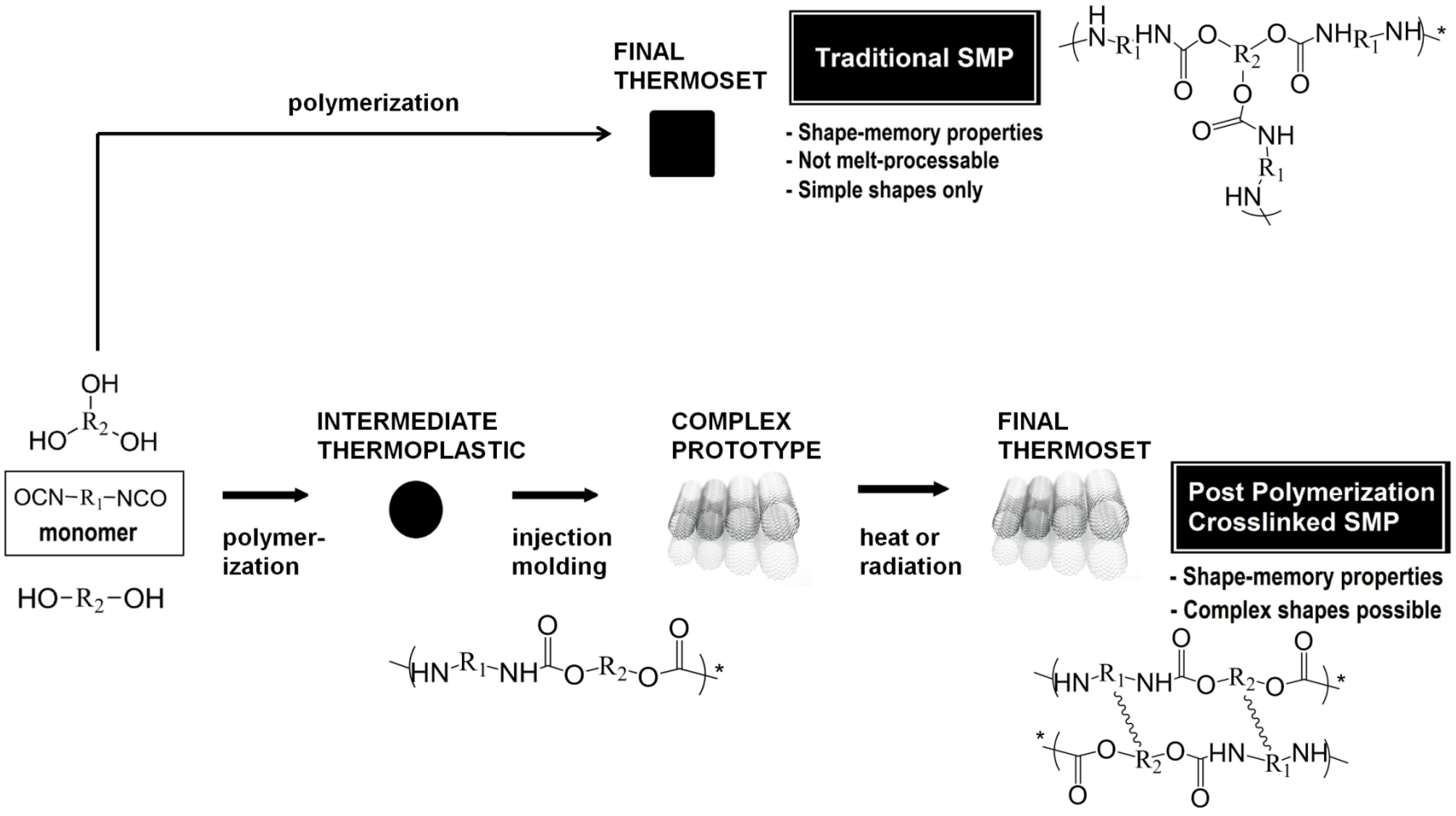
High T, P



Covalently Crosslinked SMP

Does not flow → NO injection molding

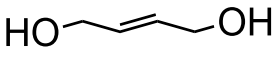
Objectives



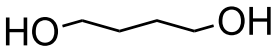
source: Hearon 2010

Sample Preparation

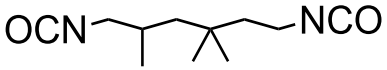
I. Linear, olefinic polyurethanes were prepared from the following monomers:



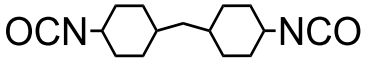
2-butene-1,4-diol



1,4-butanediol

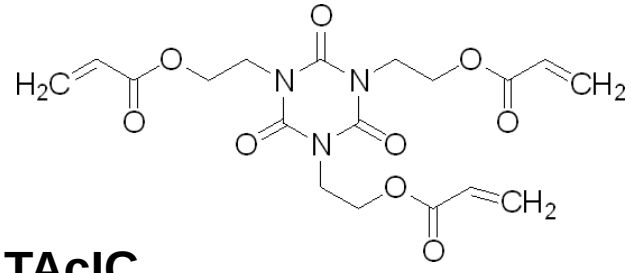


TMHDI

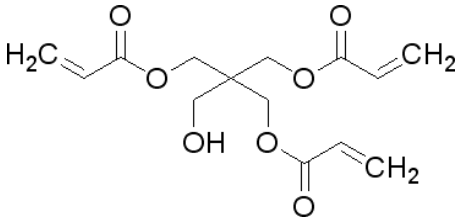


DCHMDI

II. Radiation sensitizers were solution blended (THF)



TAcIC



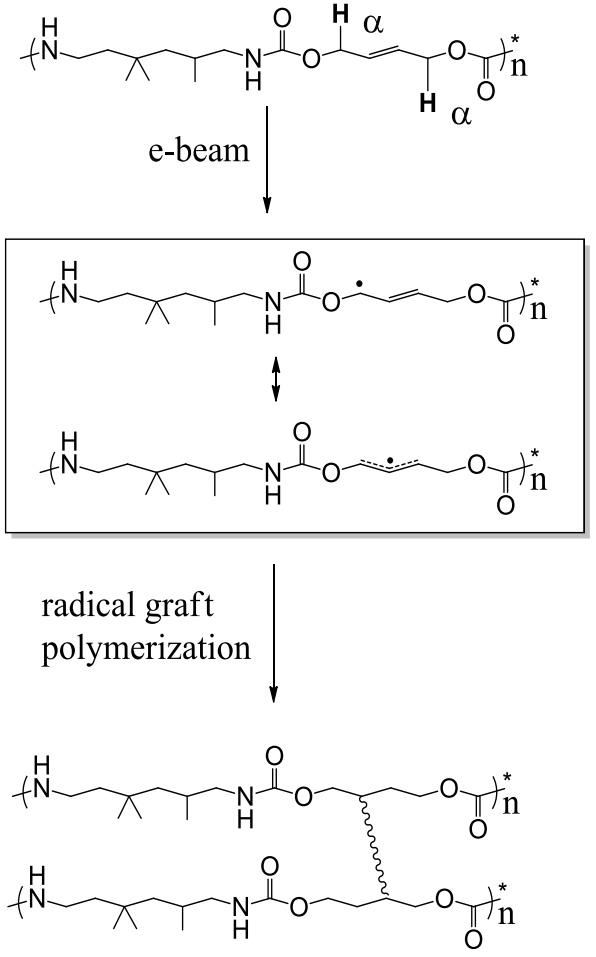
PETA

III. Crosslinking was attempted by irradiating samples (1-100 kGy, 1.8 MeV, 0.25 kGy/min, Van de Graaff)

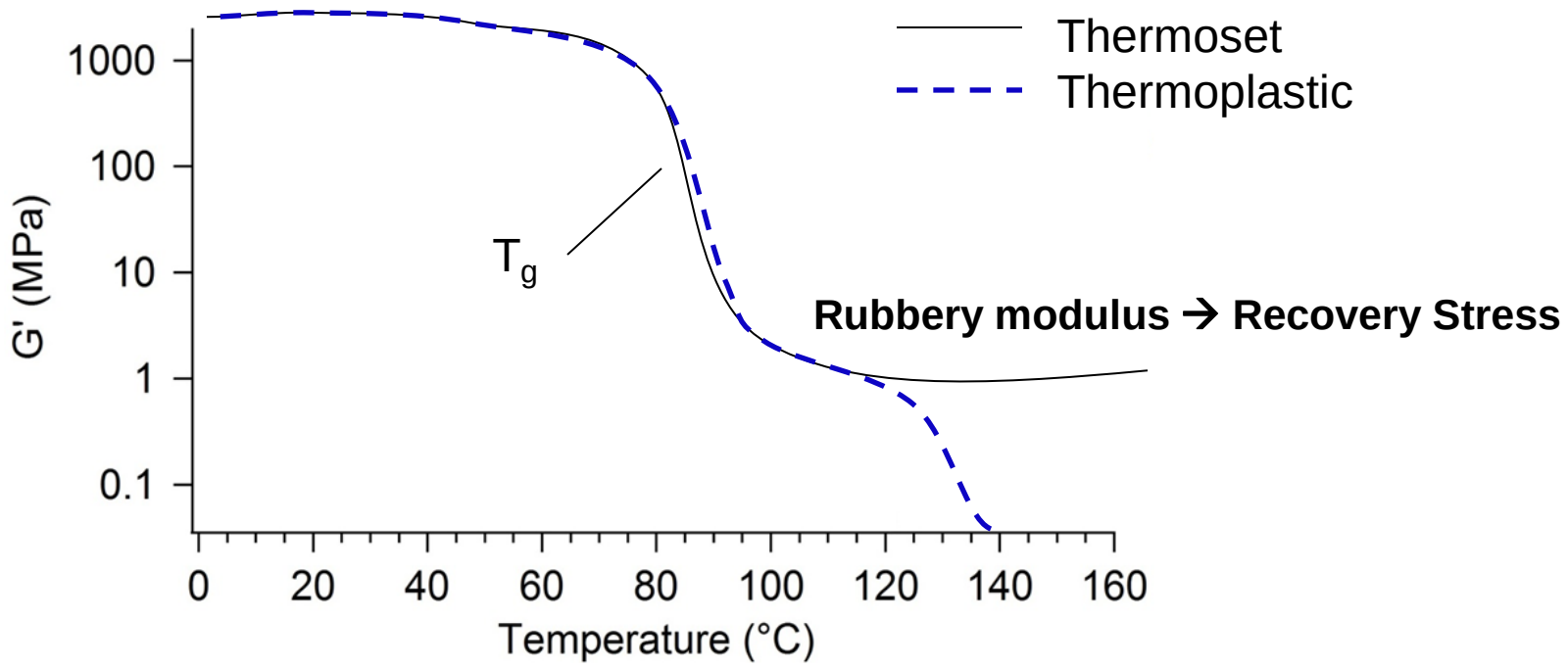
Hypothesis

E-beam is predicted to generate radicals by extracting α-carbamate hydrogens

The unique structure of 2-butene-1,4-diol provides resonance stabilization for radicals



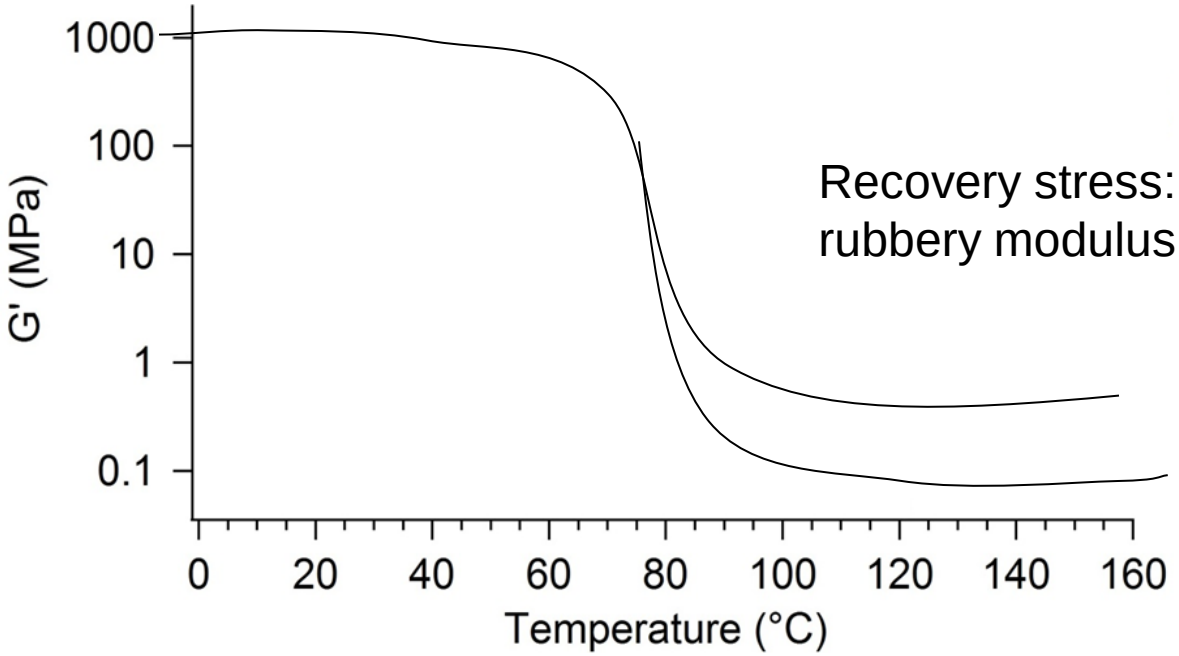
Background: Storage Modulus & DMA



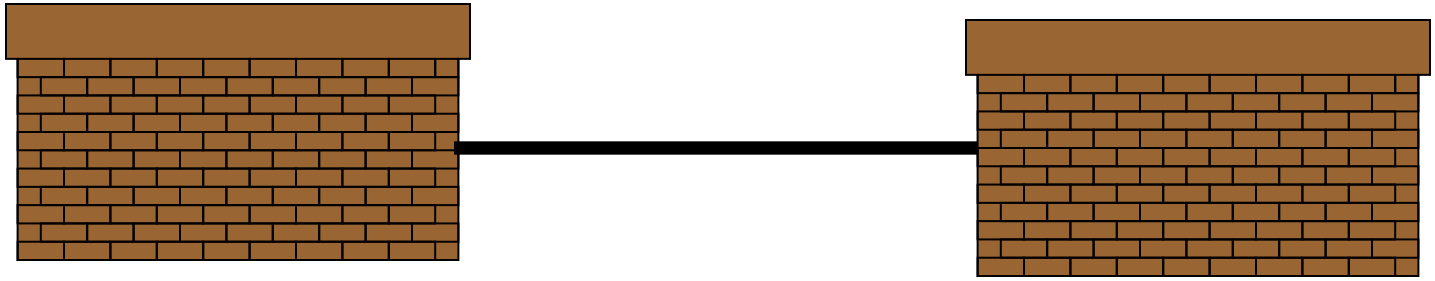
- Stainless Steel ~ 155 GPa
- Polycarbonate ~ 3.0 GPa
- Rubber Band ~ 0.2 MPa

} room temperature

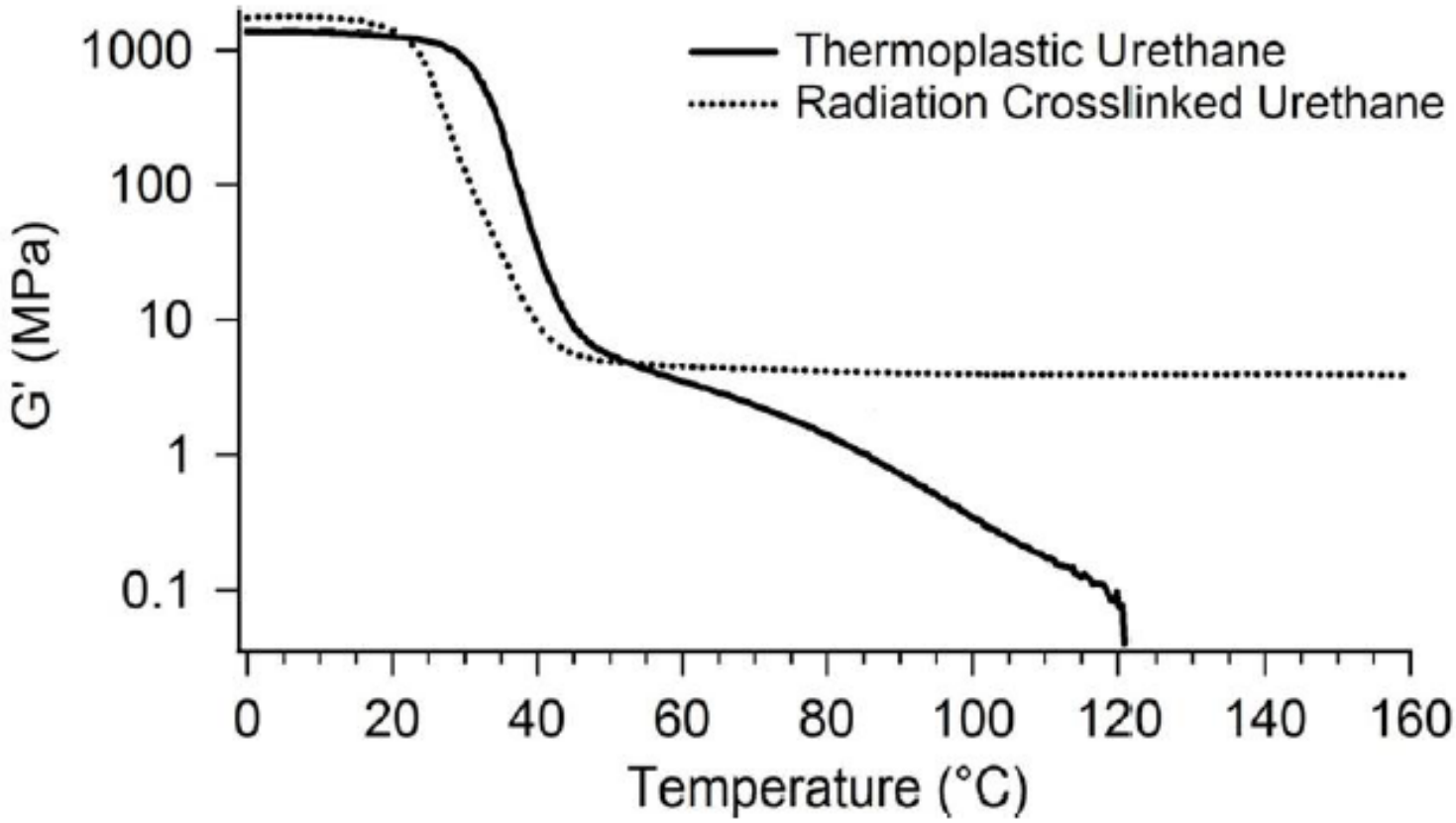
Rubbery Modulus



Recovery stress: proportional to rubbery modulus

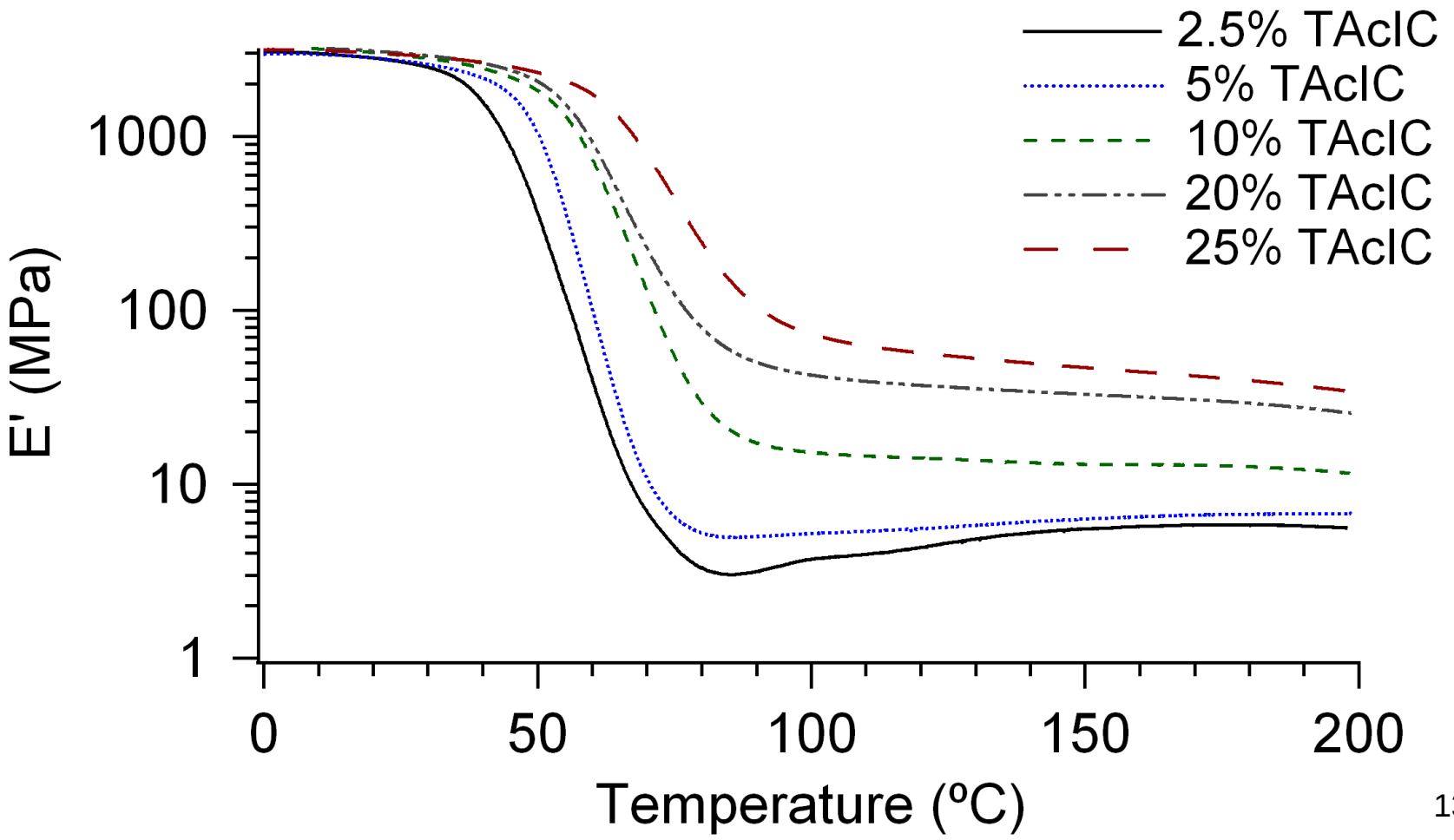


Confirmation of Chemical Crosslinking

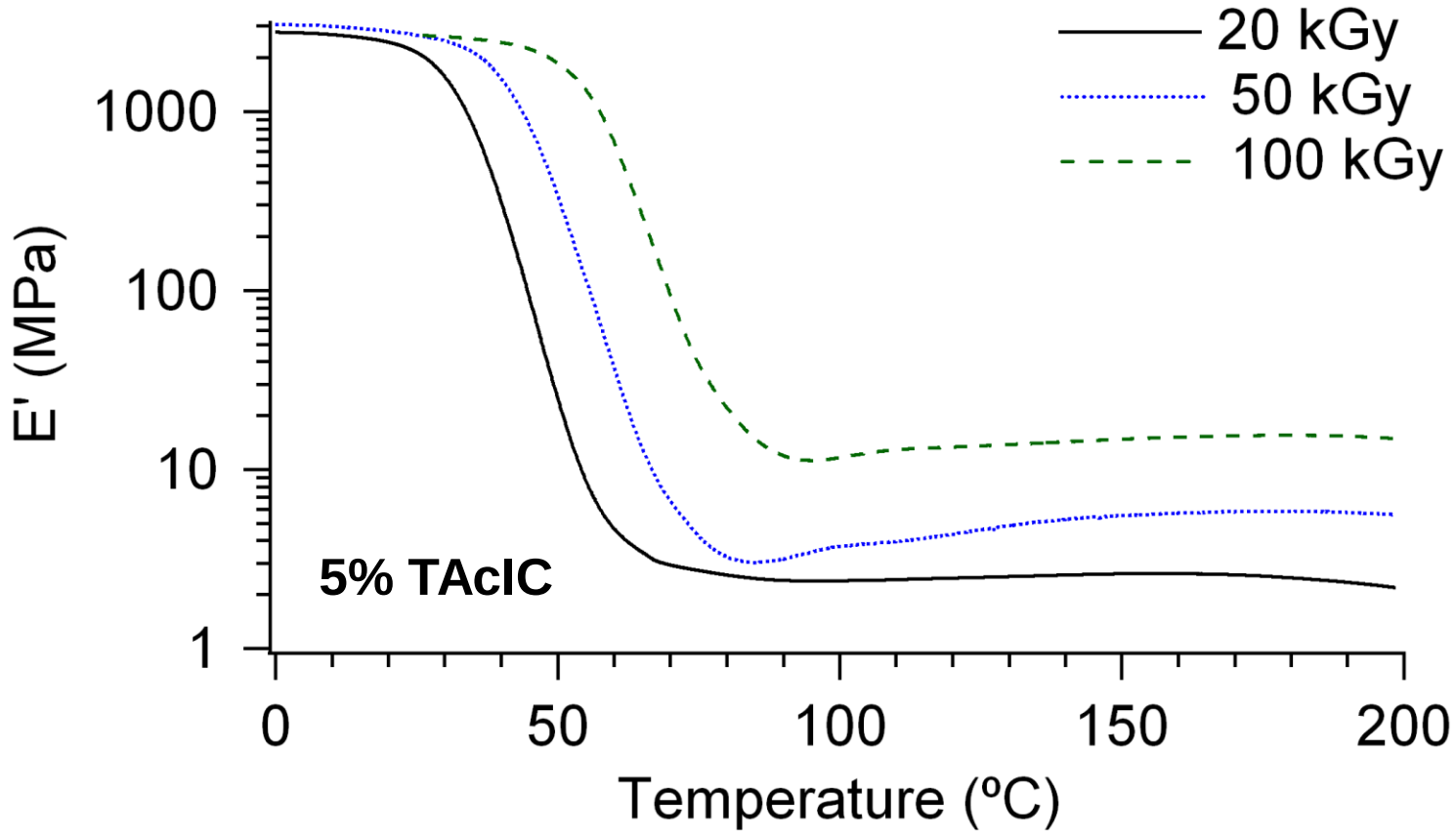


source: Hearon 2010

Tailoring Rubbery Modulus by Sensitizer Content



Tailoring Rubbery Modulus by Radiation Dose



Summary

1. PU SMPs were developed that can be first made into thermoplastic precursors and later crosslinked via electron beam irradiation.

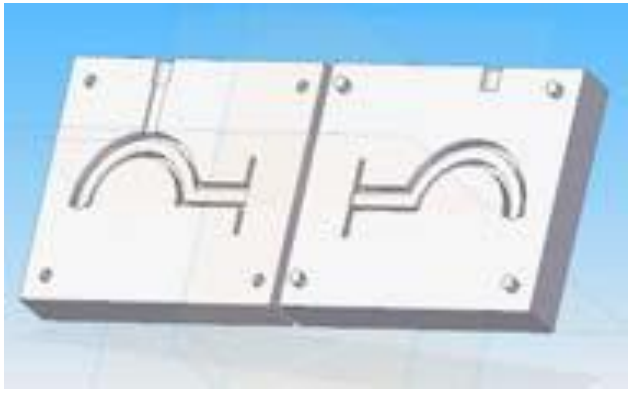
2. These materials appear to have potential use in a variety of industrial applications.

3. Rubbery modulus can be controlled by varying either radiation dose or radiation sensitizer content

Conclusions

1. PU SMP-based devices with complex geometries can now be mass-produced

2. These devices have an extended application range because of the high recovery stress of these SMPs



injection molding possible

broadened application range

Acknowledgements

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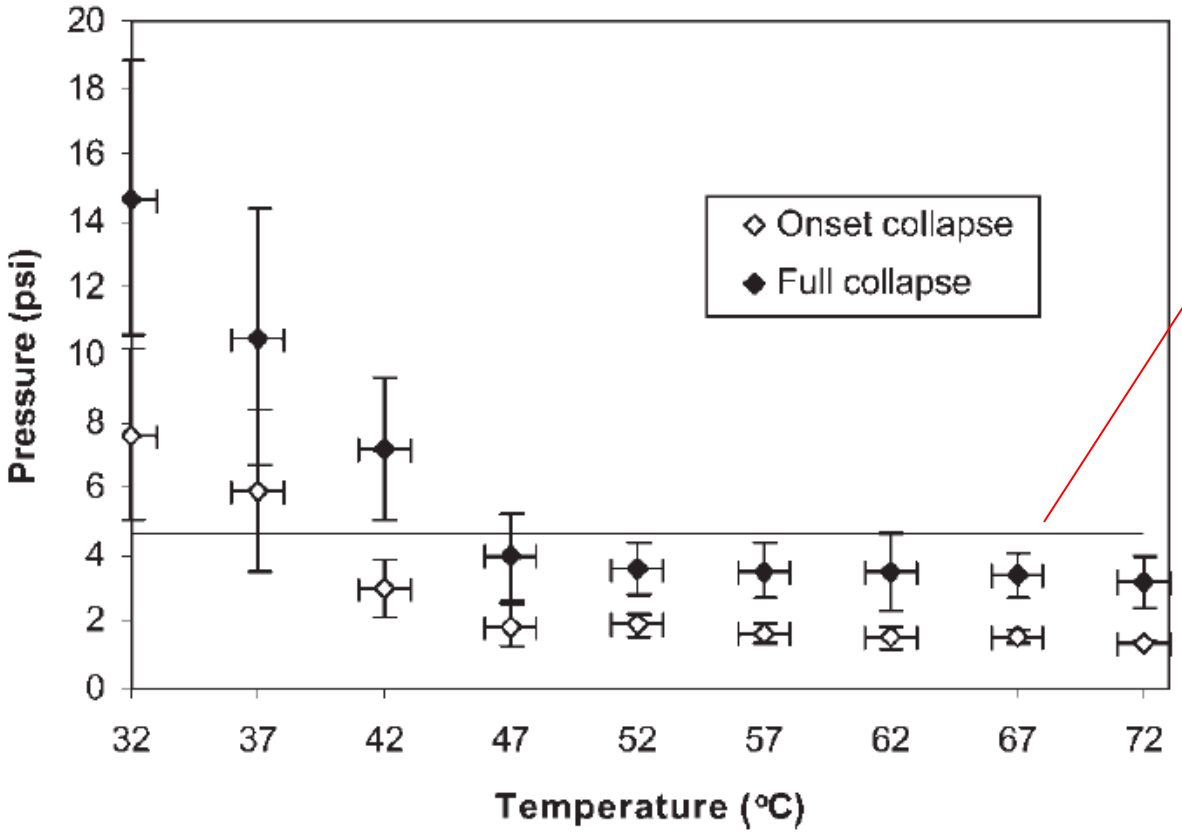
Questions?

Supplementary Slides

Collapse Pressure of Laser Etched SMP (Mitsubishi) Stent



4.7 psi = max pressure exerted by a vasospastic artery

source: Baer 2009

Commercially Available Stents

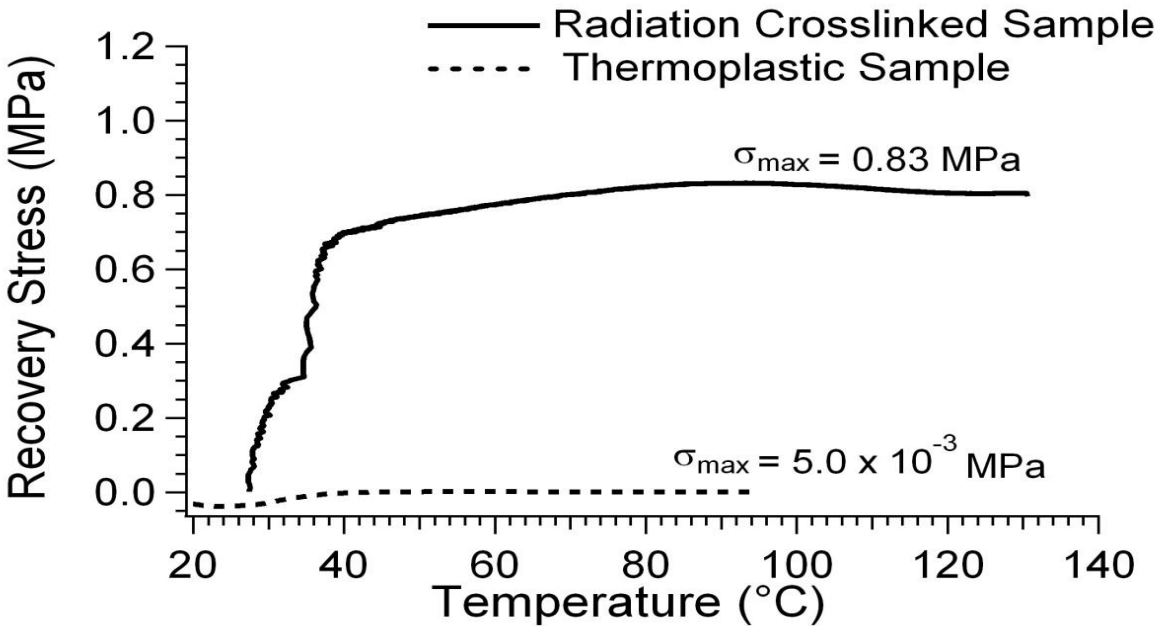
TABLE II. Collected Data on Collapse Pressure of Commercially Available and Prototype Stents

Stent Type	Manufacturer	Material	Diameter (mm)	Length (mm)	Thickness (mm)	Collapse Pressure (psi)		Ref.
						Onset	Full	
Solid tubular	LLNL	Polyurethane	4	18	0.25	15.5	23	
Laser etched	LLNL	Polyurethane	4	18	0.25	5.9	10.5	
Multi-link Vision	Guidant	Cobalt Chromium	4	15	0.1	10.8	13.6	
BxVelocity	Cordis	Steel 316L	4	13	0.22	26.3	36.4	
Wiktor	Medtronic	Tantalum	3.5	16			10.1	30
Tenax Complete	Biotronik	Steel 316L	3.5	15			7.7	30
NIR Primo	Scimed	Steel 316L	3.5	16			>21.8	30
Crossflex	Cordis	Stainless steel	3.5	15			8.7	31
BeStent Brava	Medtronic	Stainless steel	3.5	15			14.5	31
Tenax XR	Biotronik	Steel 316L	3.5	15			8.7	31
Wiktor	Medtronic	Tantalum	3	15		<4.3[a]	11.6	29
Crossflex	Cordis	Stainless steel	3	15		15.9[a]	31.9	29
GFX stent	AVE	Steel 316L	3	18		<10.1[a]	29	29
PLLA 2.4 helical		PLLA	3	32?[b]		26.1–36.2		35
Multi-link Tetra	Guidant	Stainless steel	3?	?		29–31.9		35
PLLA mesh	PLLA*	PLLA	4	?			23.8–39.7	28

[a] Pressure taken at 2% change in diameter.
[b] Evaluated from picture.

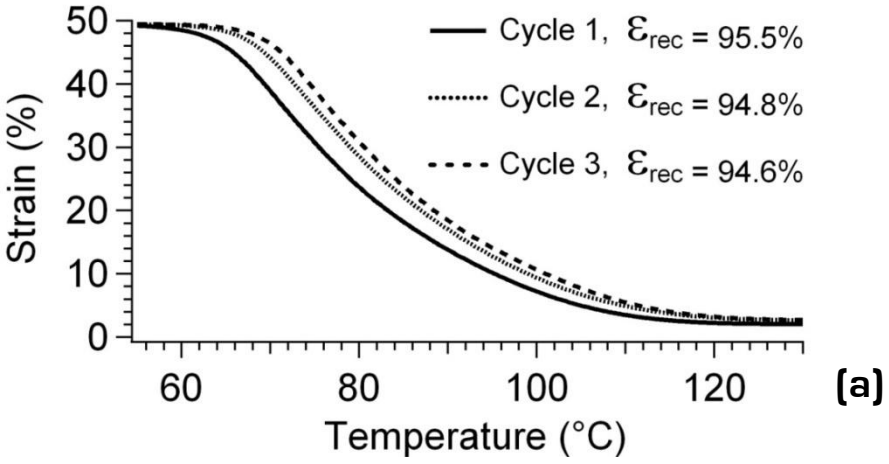
source: Baer 2009

Constrained Recovery Results

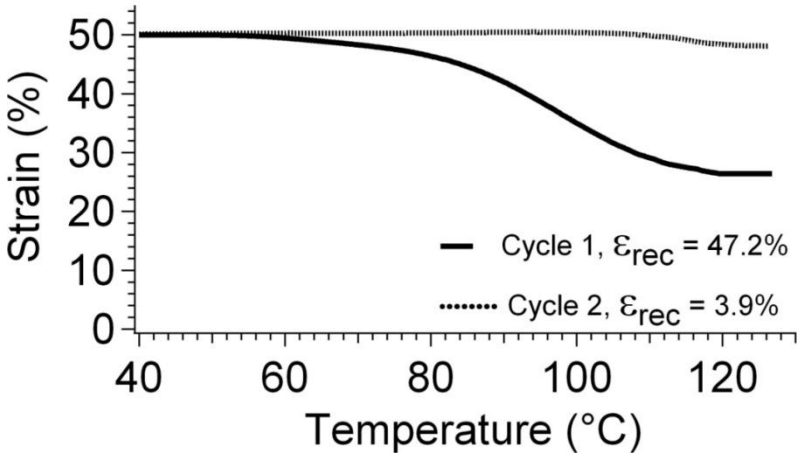


Constrained recovery results for radiation crosslinked and thermoplastic samples

Cyclic Free Strain Recovery Results



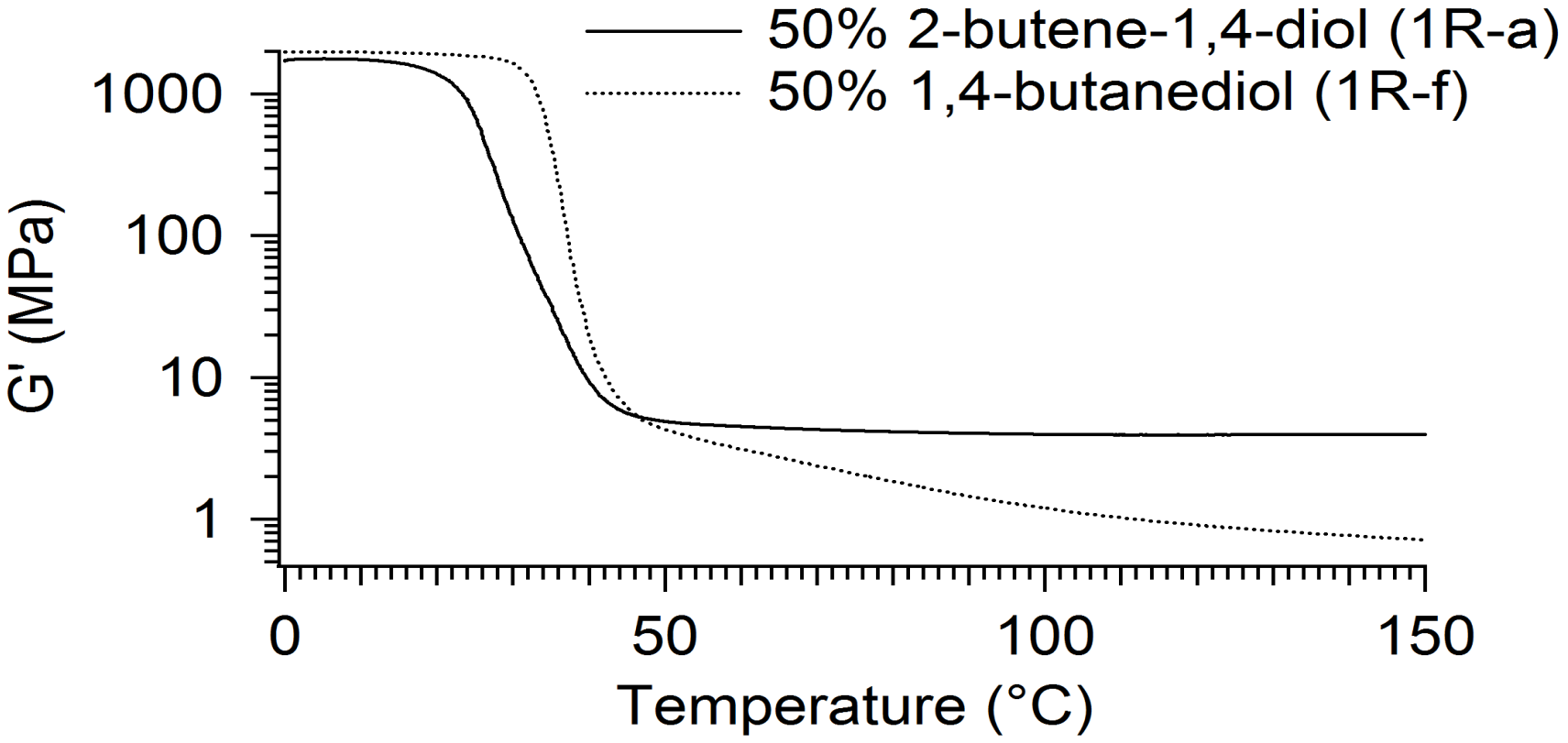
(a)



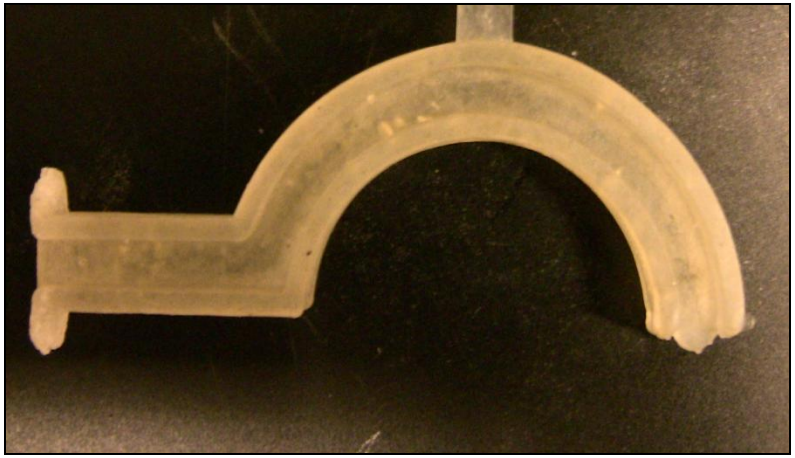
(b)

Cyclic free strain recovery data for thermally crosslinked **(a)** and thermoplastic **(b)** 20% DCHMDI samples

Resonance Stabilization of β-Unsaturated Group



Prototype Synthesis



- The radiation crosslinked 0% DCHMDI sample was selected for use in the design of a complex medical device.
- Oropharyngeal airway devices keep patients' airways open during medical procedures requiring sedation.
- This device utilizes SMP technology to conform precisely to patients' throats to reduce trauma.
- An SMP-based airway could potentially reduce the number of standard airway device sizes from 12 to 5 or fewer standard sizes.

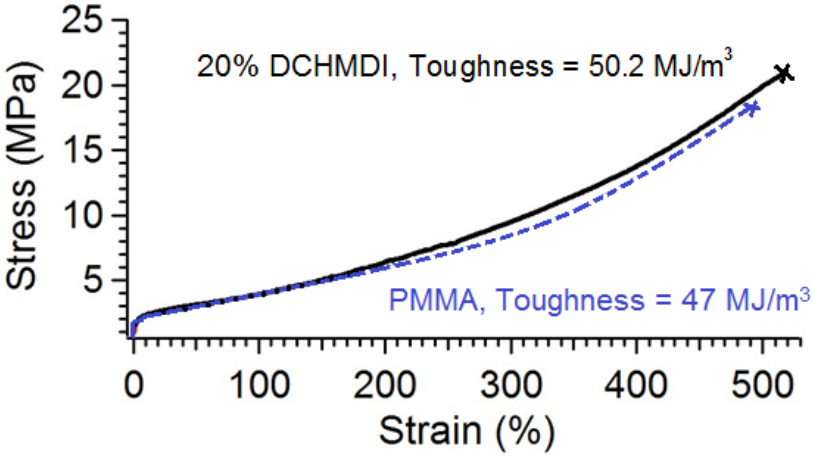
Characterization Methods

- DMA, sol/gel analysis to evaluate extent of crosslinking in samples
- DSC to determine T_g and % crystallinity
- Further DMA, tensile testing, and shape-recovery analysis to evaluate biomedical relevance of SMPs

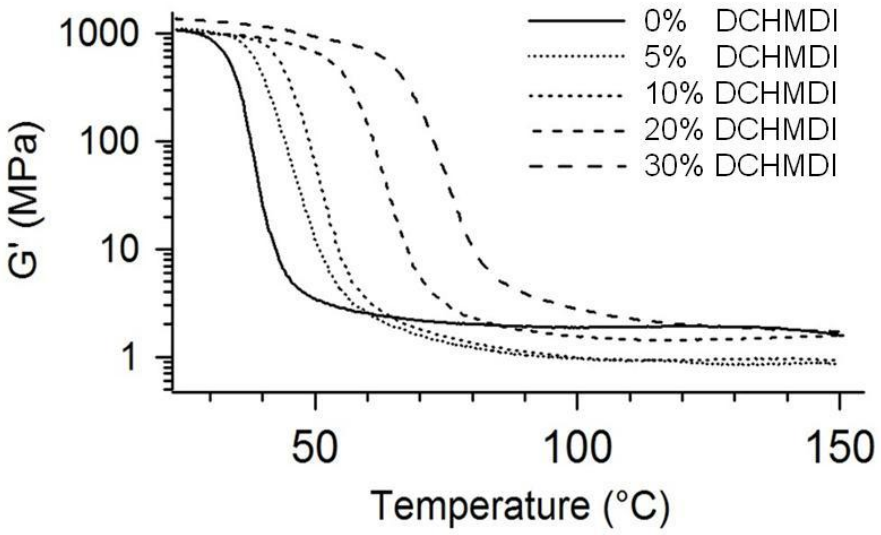
TA Instruments QSeries Q800 DMA

MTS Systems Insight 2 Tensile Testing Apparatus

Mechanical Characterization: To Evaluate Biomedical Relevance



Strain to failure



Glass transitions between 37 and 80 C

source: Hearon 2010