UV REACTIVE SILICONES FOR 3D PRINTING

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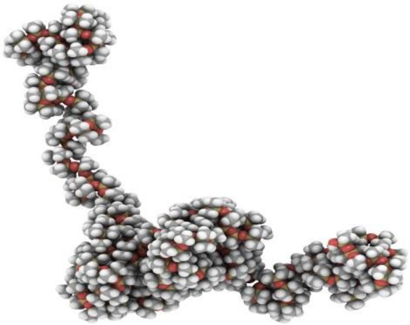

Siltech Background

- Family owned/operated
- 120 Employees
- Focus on modified silicones
- 20 kg to 30,000 kg reactors in two modern plants

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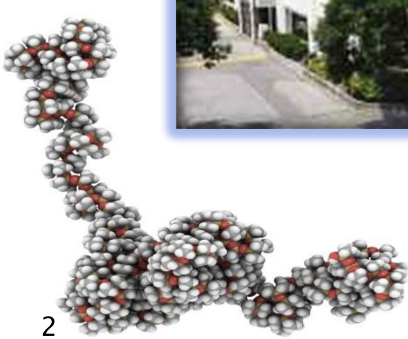
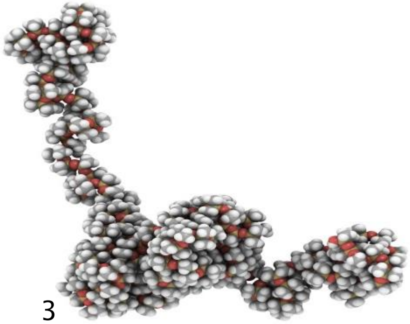
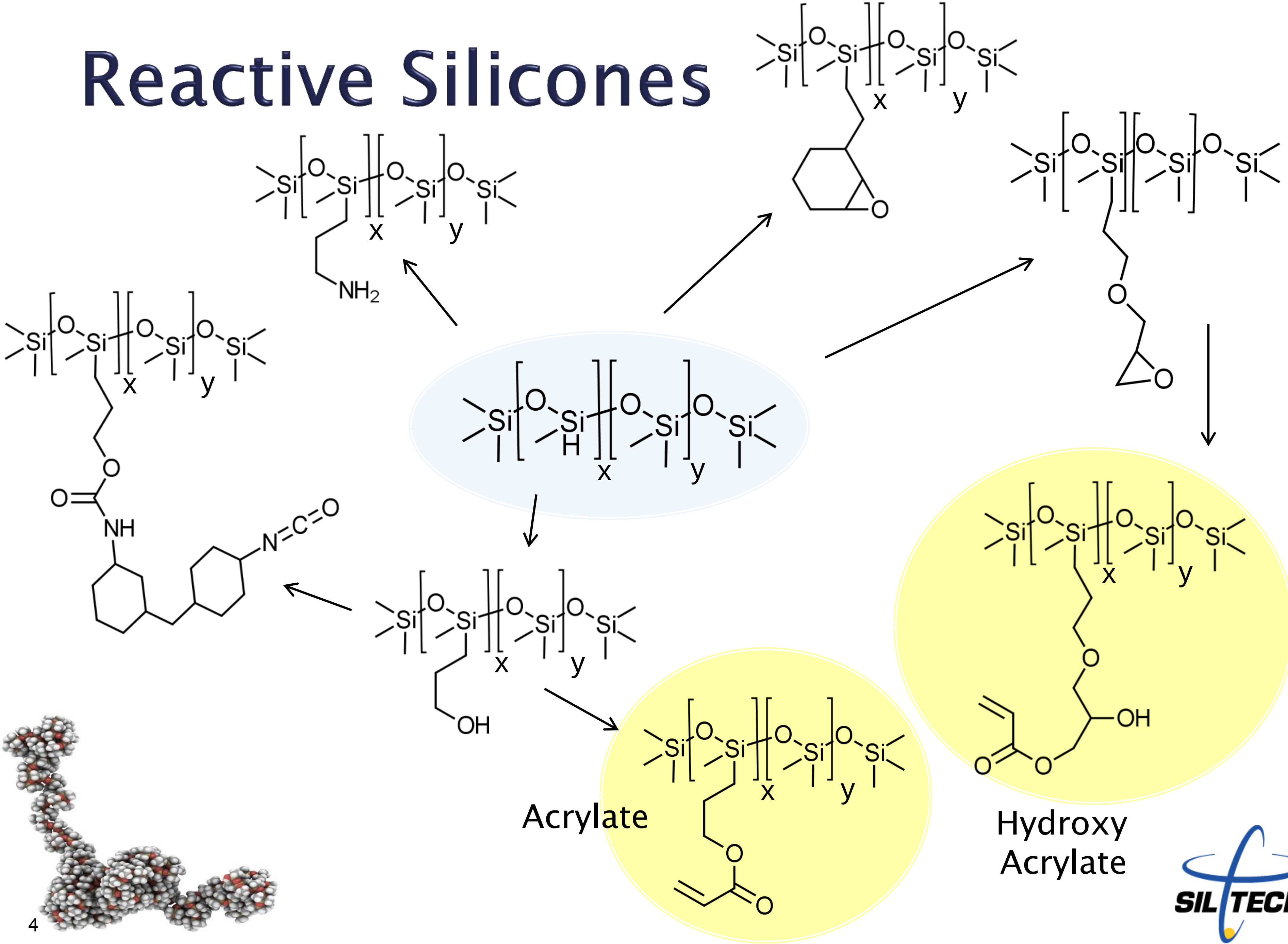


Agenda

- Overview. Reactive silicones
- Silicones reacted with themselves.
  - Structure Property/ Formulating.
- Silicones reacted with other resins.
- 3D printed examples

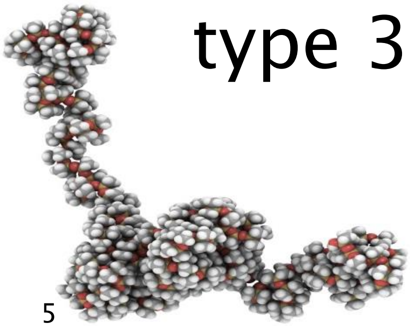


Reactive Silicones

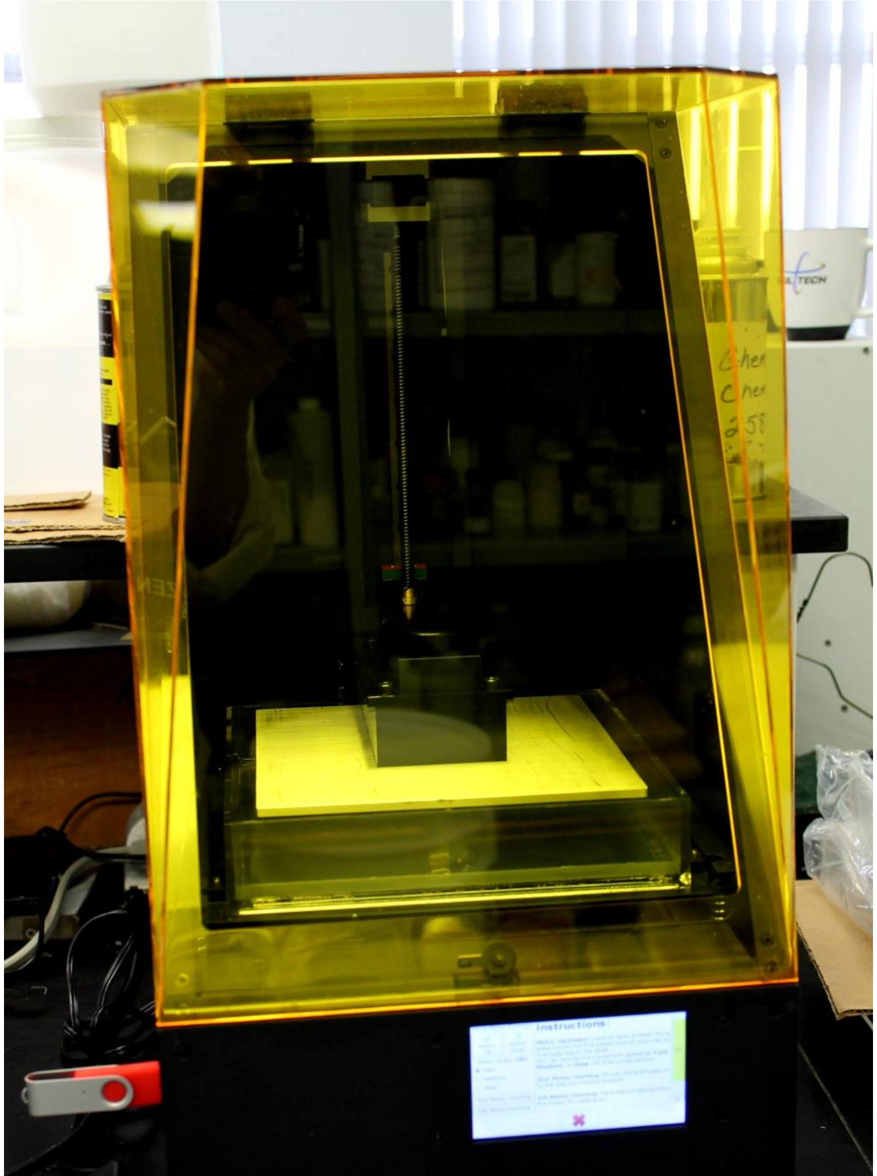


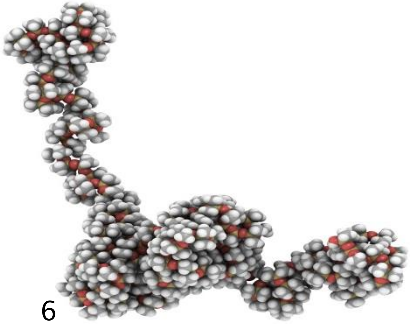
Experimental

- Materials are cured in a TA Instrument AR-G2 Rheometer using:
  - 150 mW/cm^2 LCD UV lamp at 365nm
  - UV lamp turned on at 300 sec. for 600 sec.
  - Strain Set at 0.05% with normal force control
- Properties measured with an Instron 1122 according to ASTM D412 using separately cured dumbbells.
- Some dumbbells were 3D printed with a SLA type 3D printer from Full Spectrum Laser



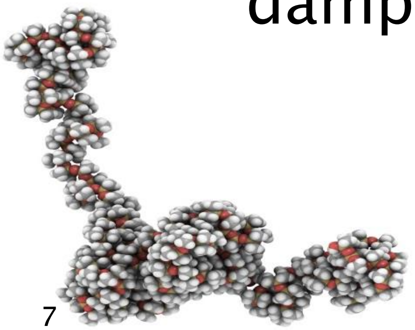
Pegasus Touch from FSL3D





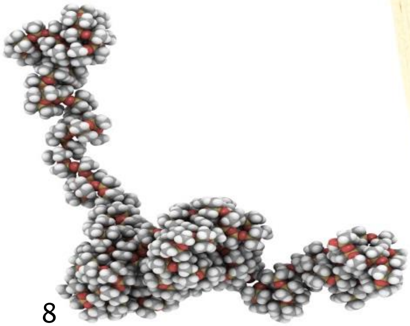
Definitions and Experimental

- G' is the storage modulus
  - The ***storage modulus*** measures the stored energy, representing the elastic portion. Similar to Young's Modulus
- G" is the loss modulus
  - The ***loss modulus*** measures the energy dissipated as heat, representing the viscous portion.
- Tan(delta)
  - Tangent of the phase angle. Also G"/G'. Measures dampening.

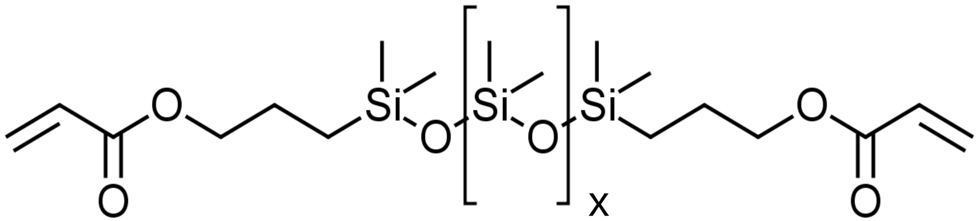


Silicone as the Resin

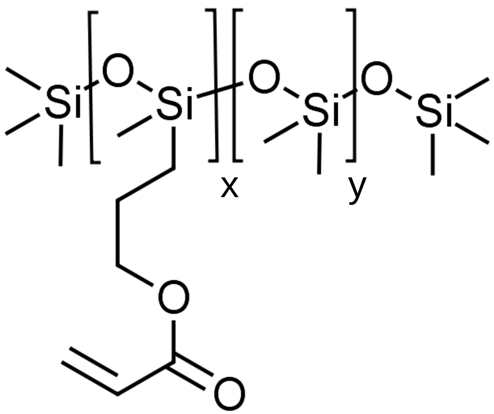
- Cured Acrylated Silicones provide soft and flexible elastomer with excellent release, impact resistance, elongation, temperature tolerance and feel properties.



Acrylated Silicone Types

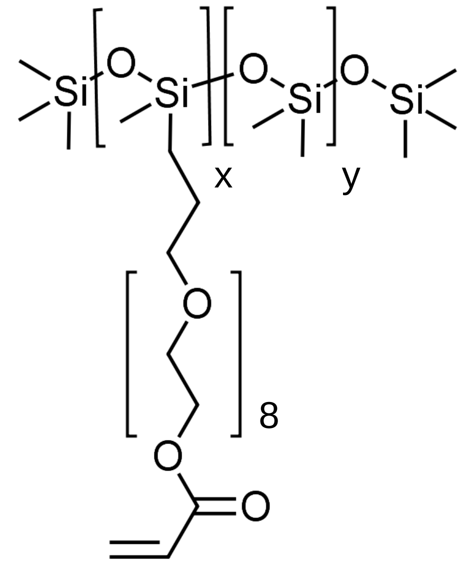


Linear, Di-functional
Extender

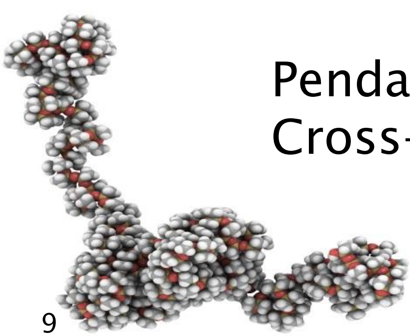


Pendant, Multi-functional
Cross-Linker

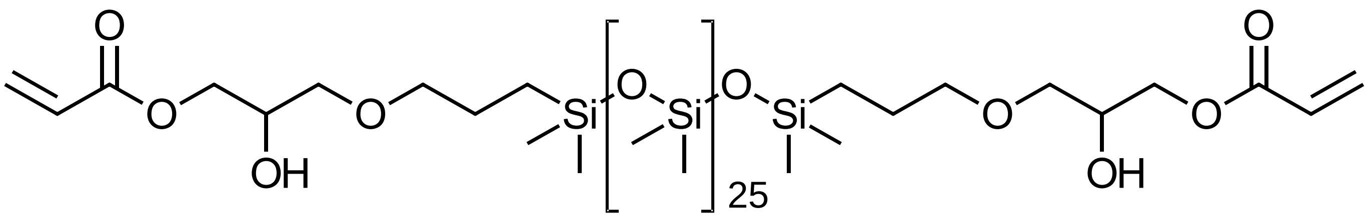
Illustrated with
Acrylate Type

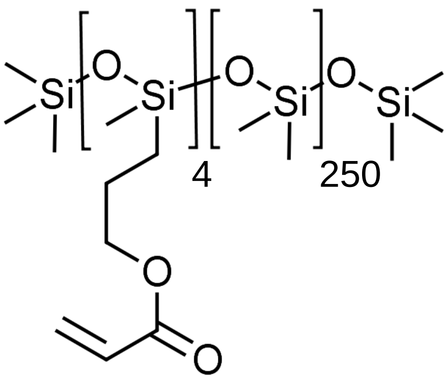


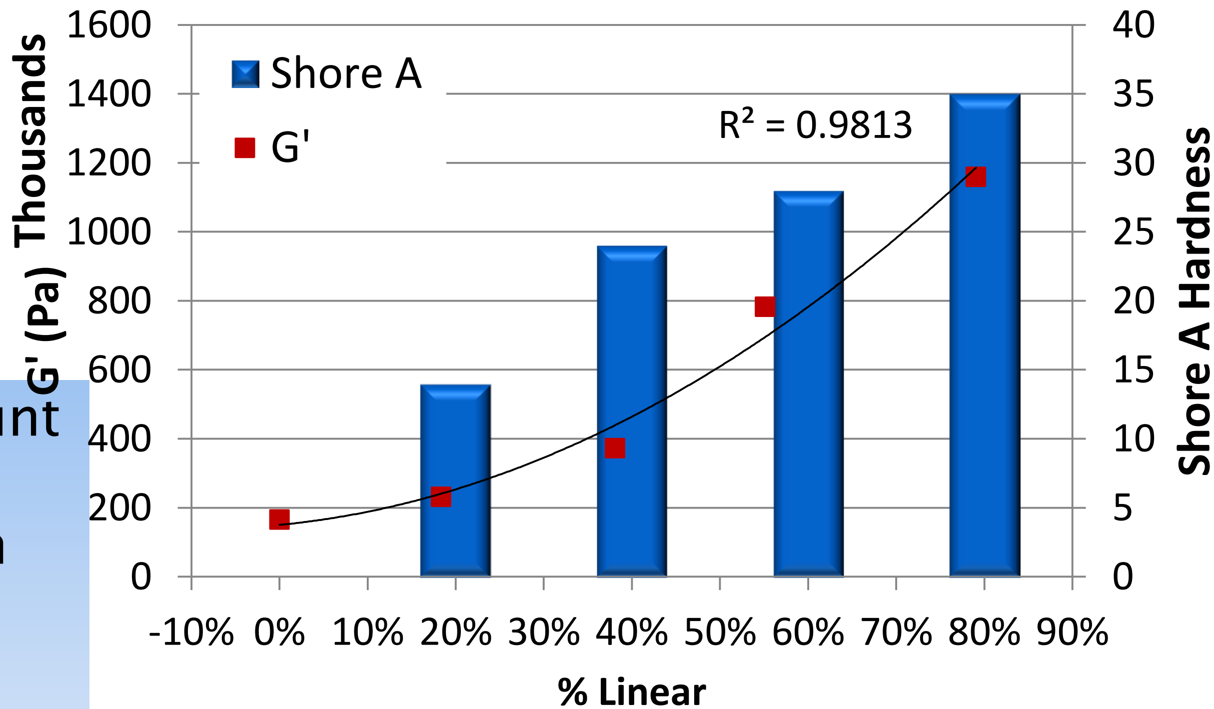
Pendant, Compatibilized



Effect of Extender Concentration







As you increase the amount of a short extender the average distance between cross-links decreases.

The Storage modulus (G') increases and the hardness increases.

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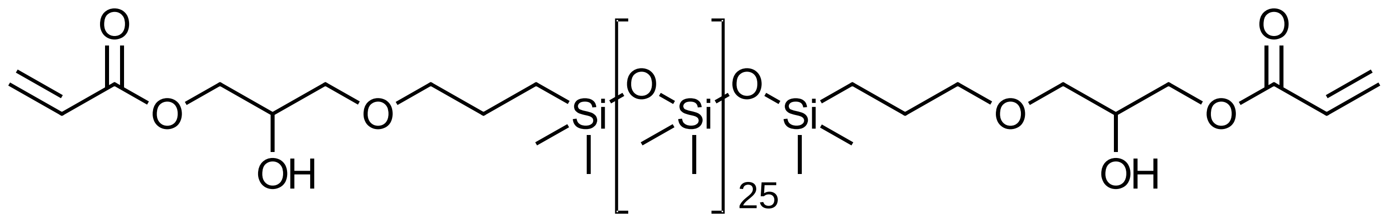
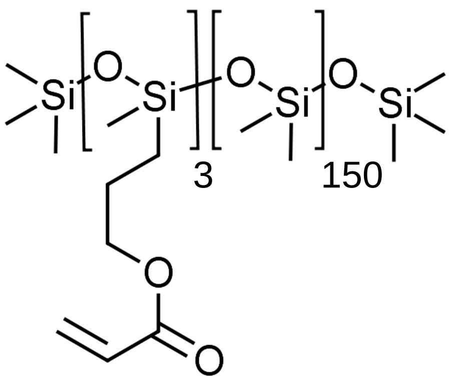
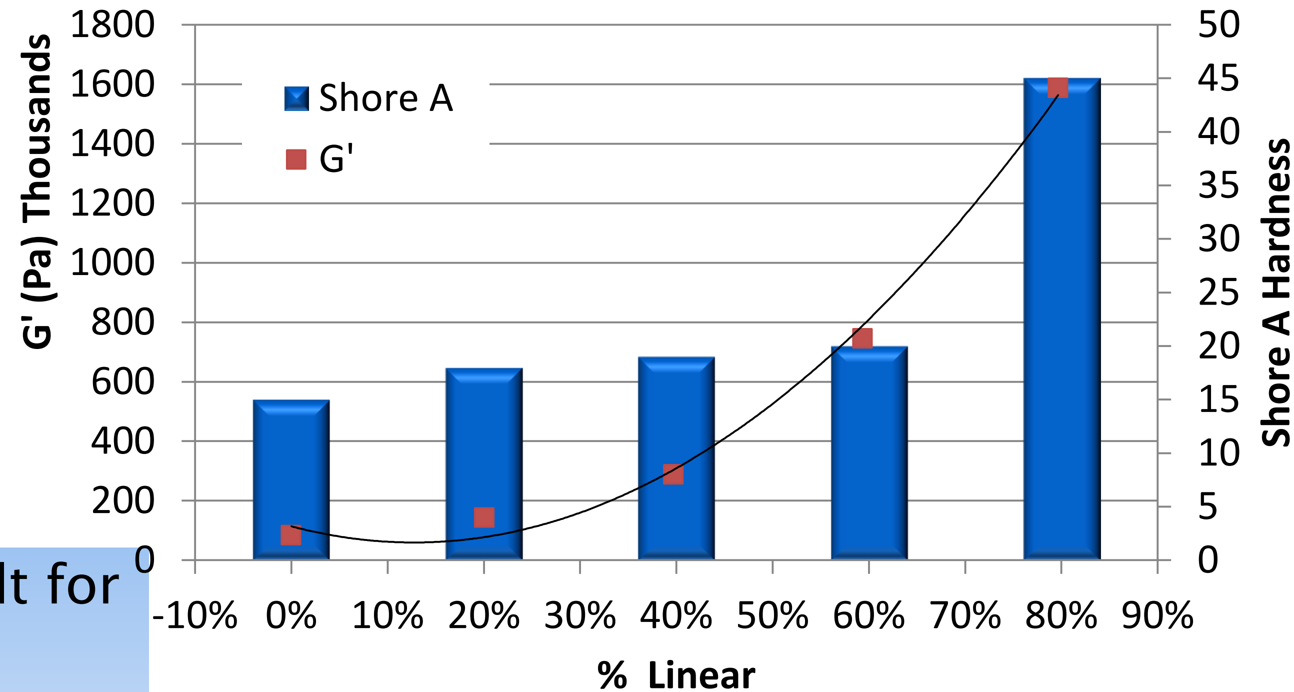
Effect of Extender Concentration



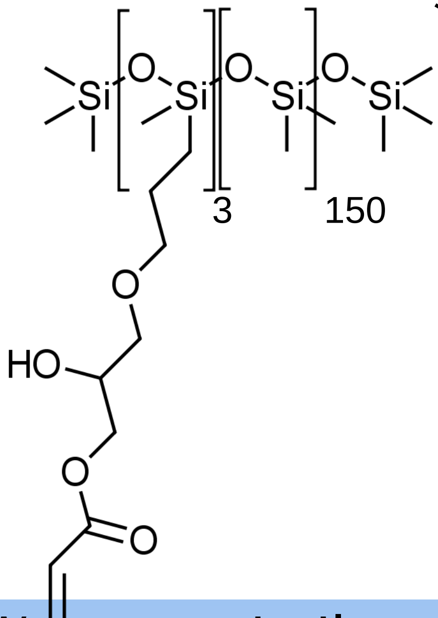


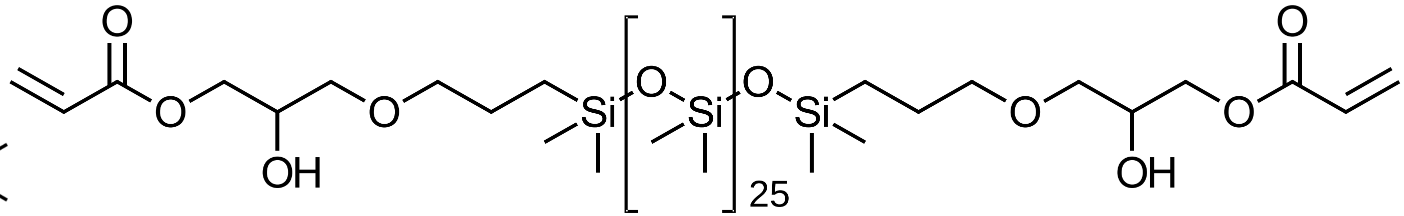


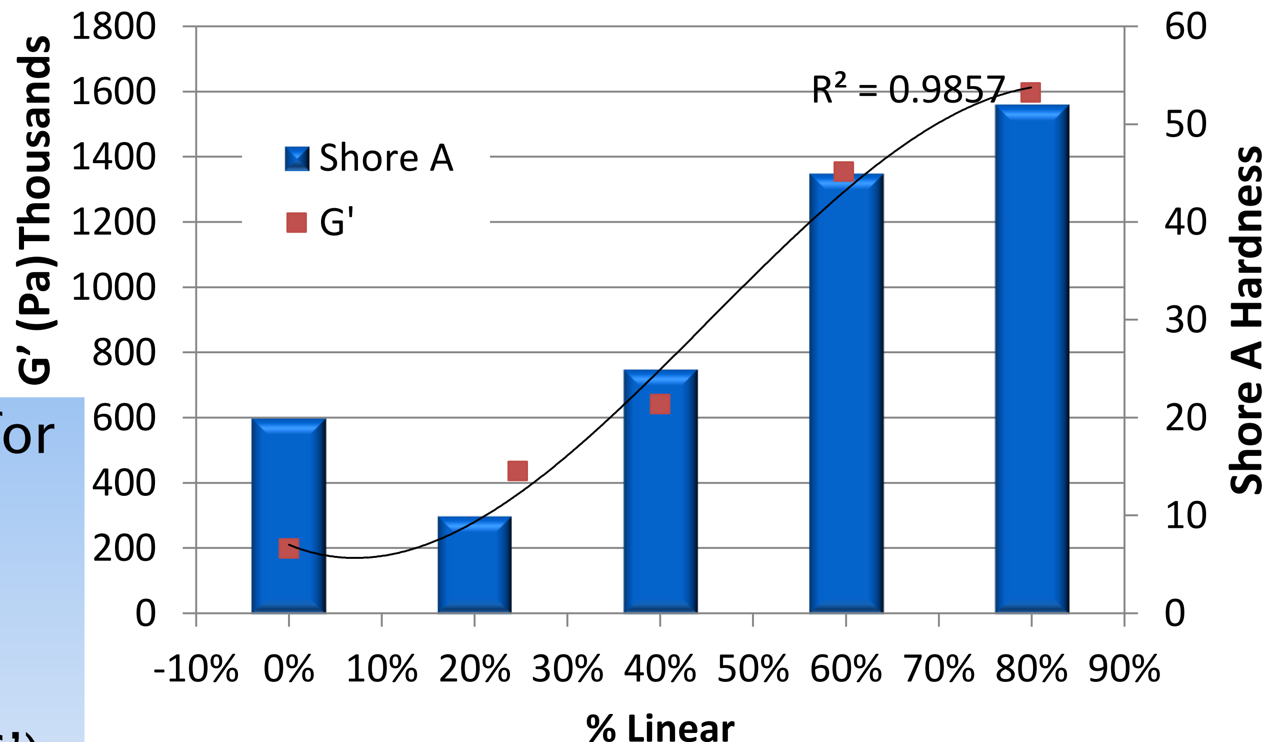
We see a similar result for this smaller X-linker.

The Storage modulus (G') increases and the hardness increases.

Effect of Extender Concentration



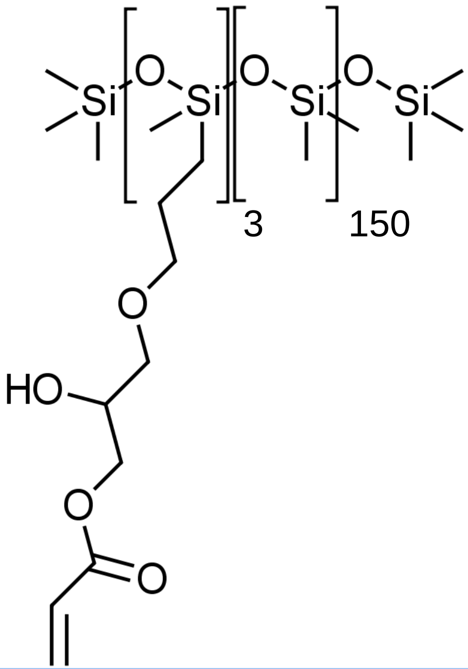


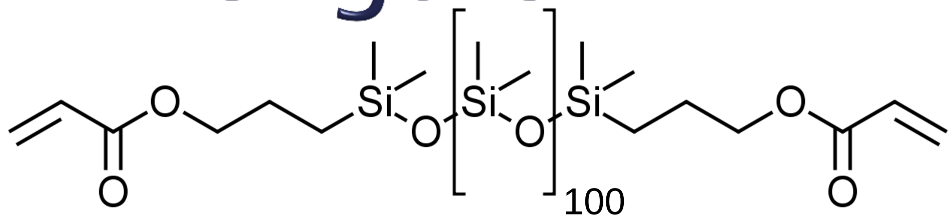


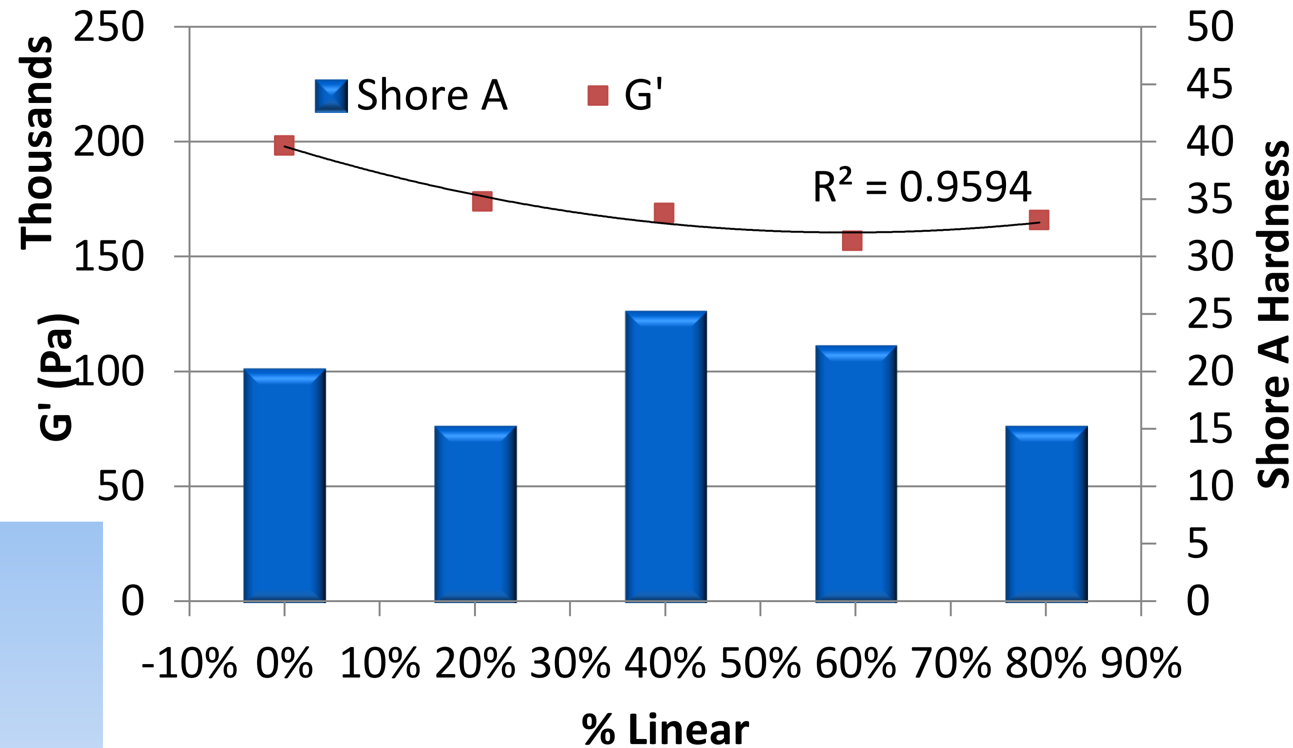
We see a similar result for the corresponding hydroxy acrylate cross-linker.

The Storage modulus (G') increases and the hardness increases.

Similar Chain Lengths

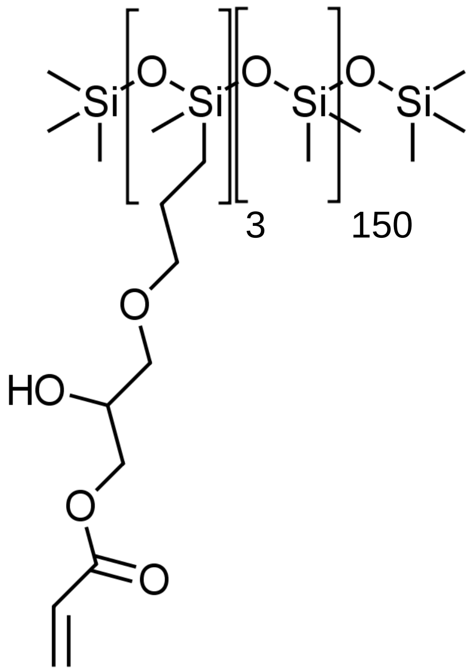


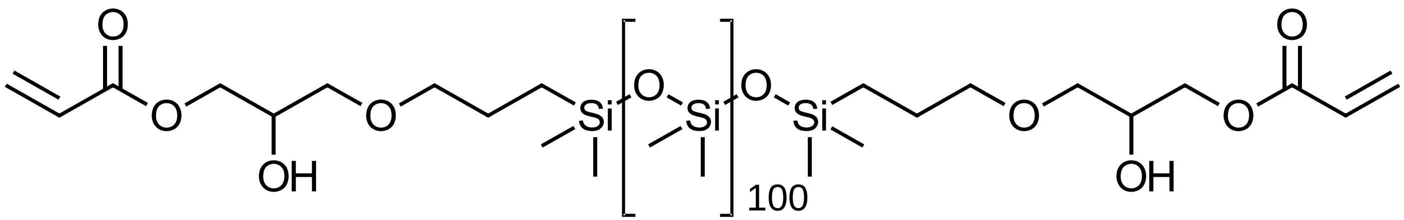


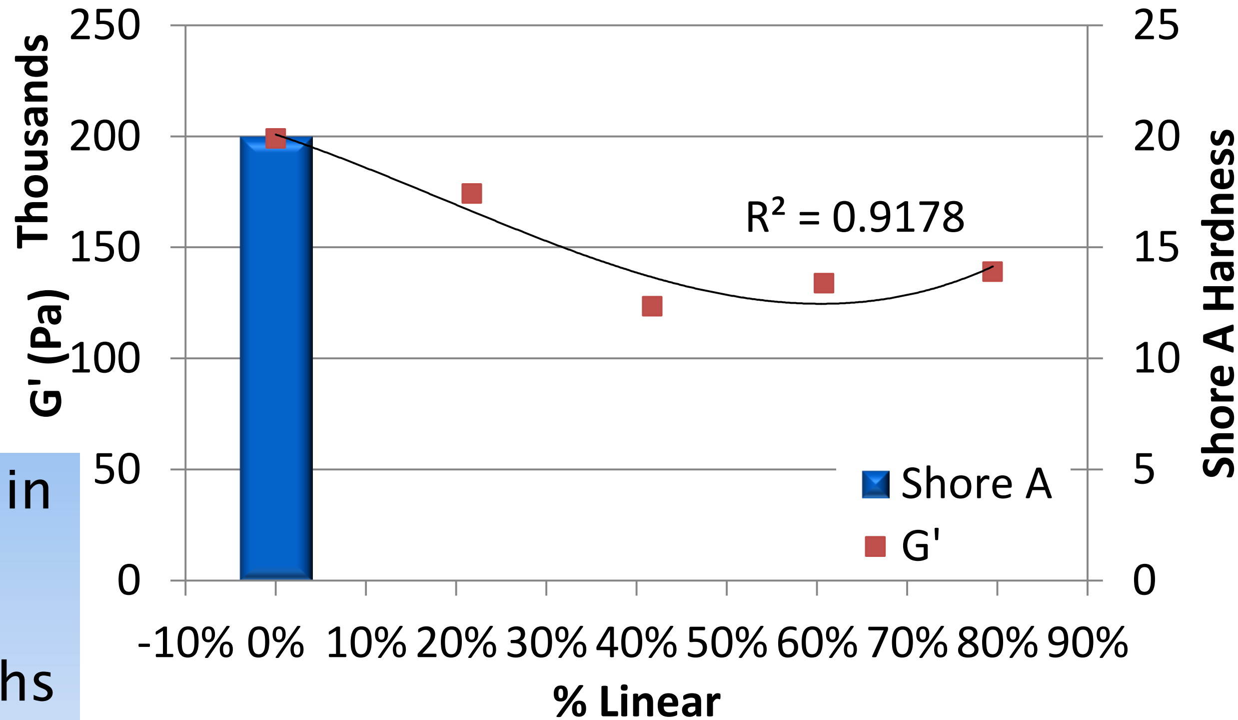


When the extender and cross-linker chain lengths are similar, there is little or no change in properties.

Similar Chain Lengths

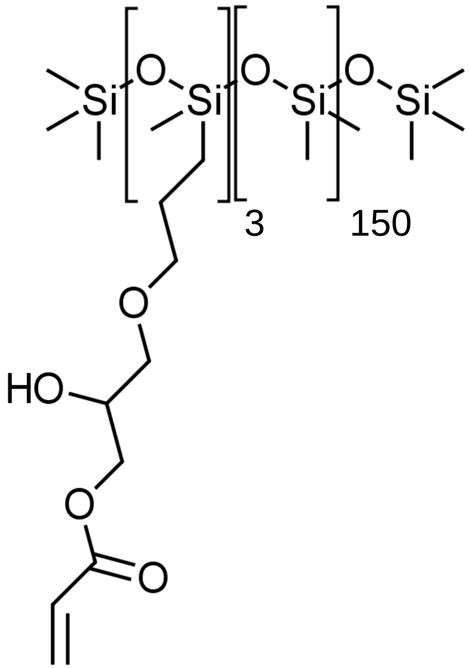


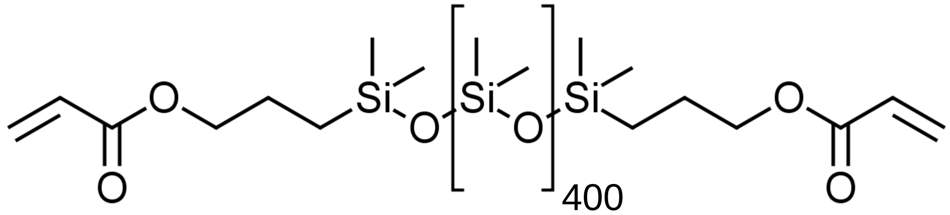


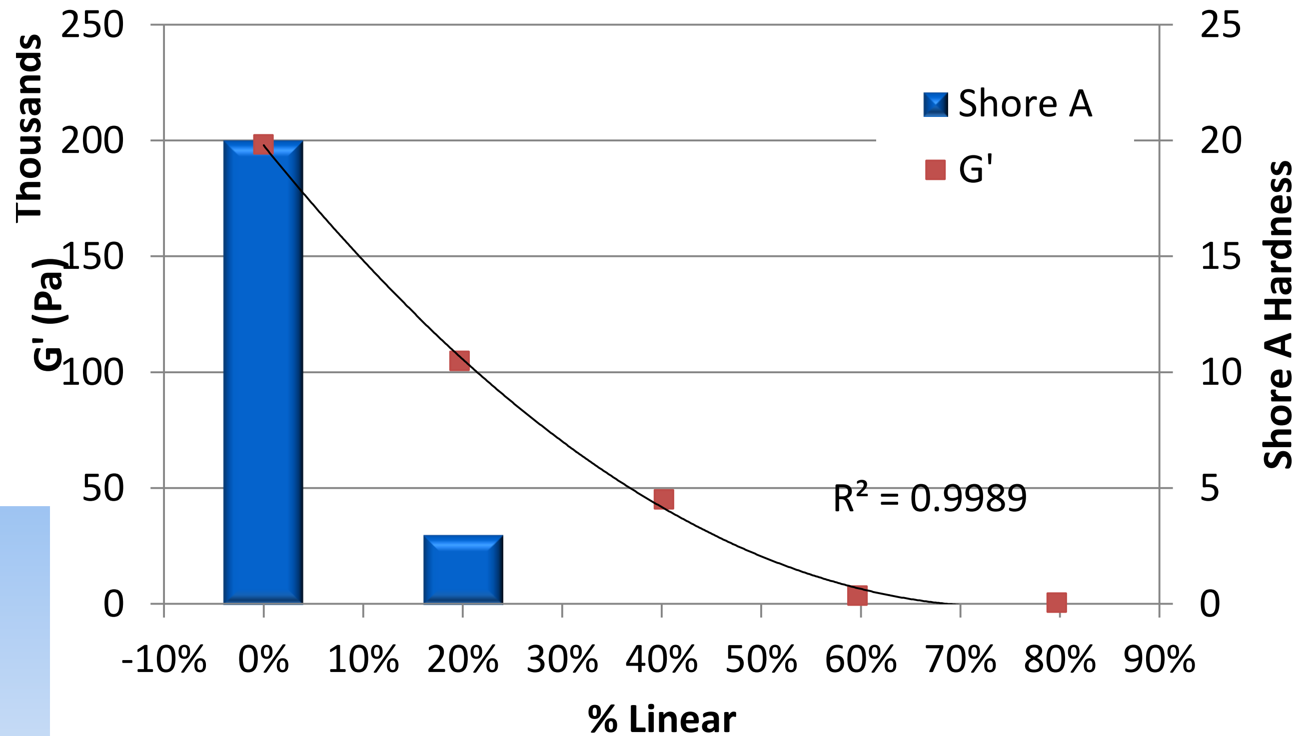


The same effect is seen in both connection types. When the extender and cross-linker chain lengths are similar, little impact is seen on G'. The hardness could not be measured.

Extender Chain Length

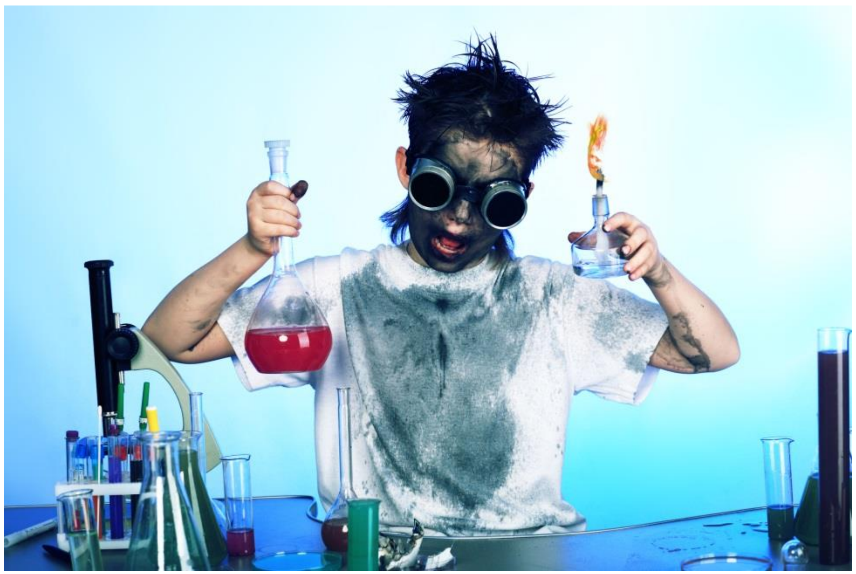




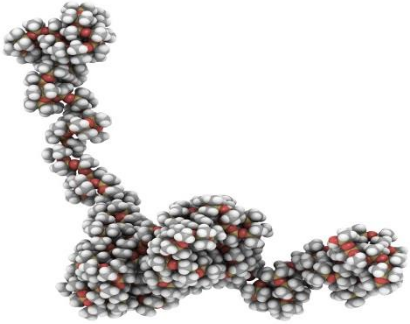


When the extender is larger then the cross-linker chain; G' and Hardness decrease as the distance between cross-linkers is too great.

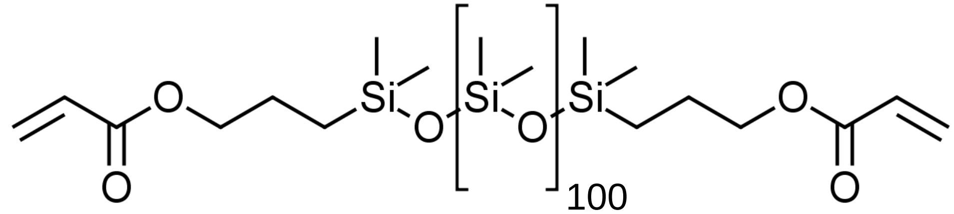
Optimized Blend



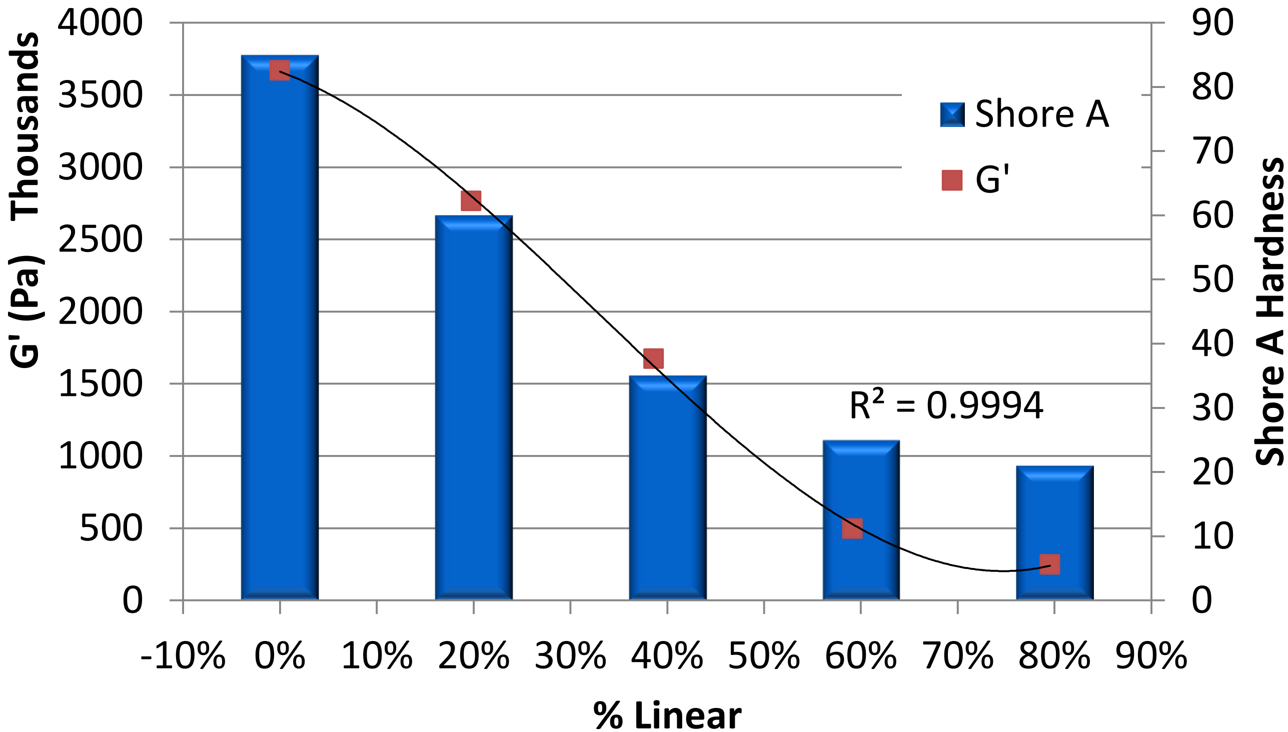
- By combining a cross-linker with higher functionality and MW with a small MW extender we can get a much better basic formulation.

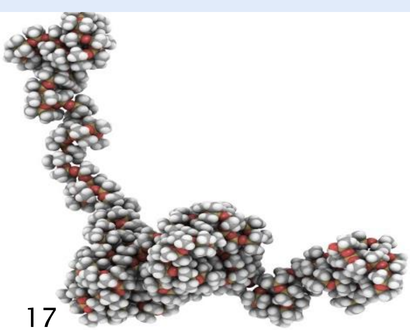


Optimized Blend



With this somewhat optimized formula, the addition of a similar MW extender, lowers G’ and hardness less substantially.





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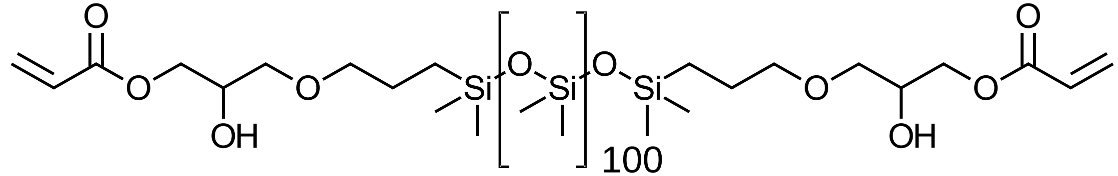
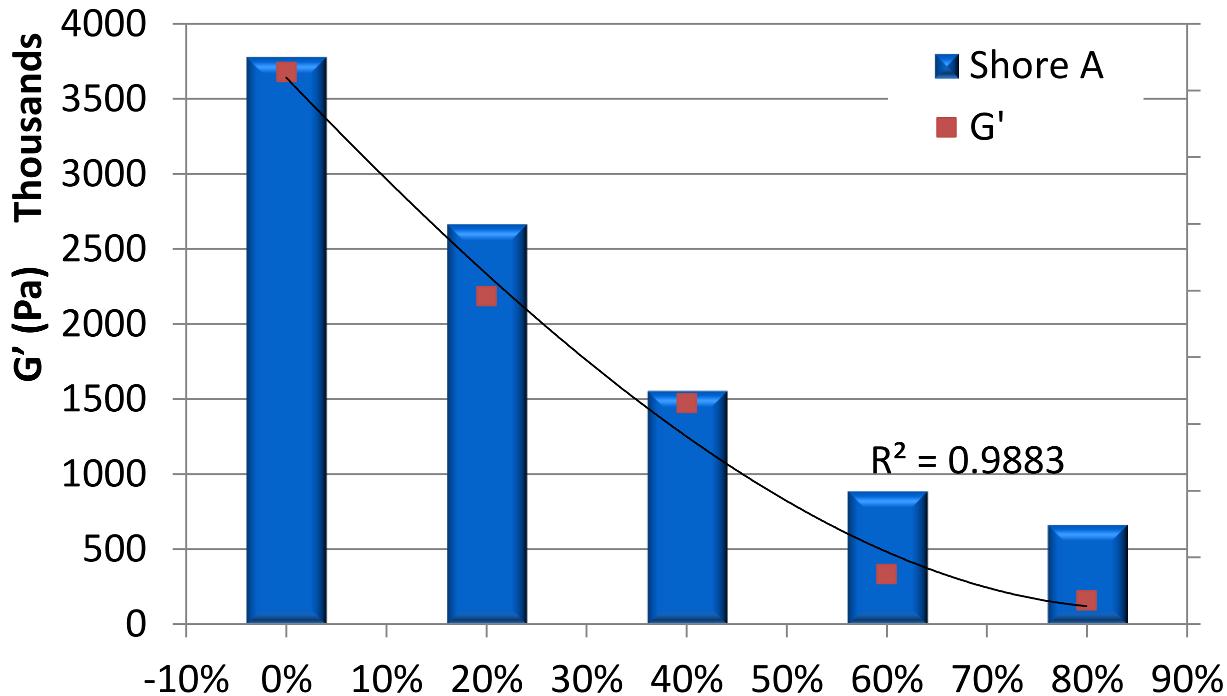
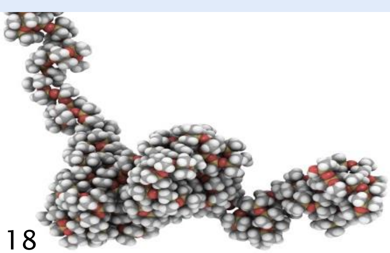
Optimized Blend

We see a similar result for the hydroxy acrylate type extender.

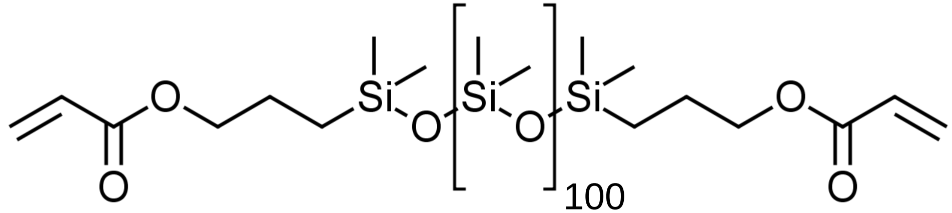
The Storage modulus (G') and the hardness decreases with more x=100 extender.



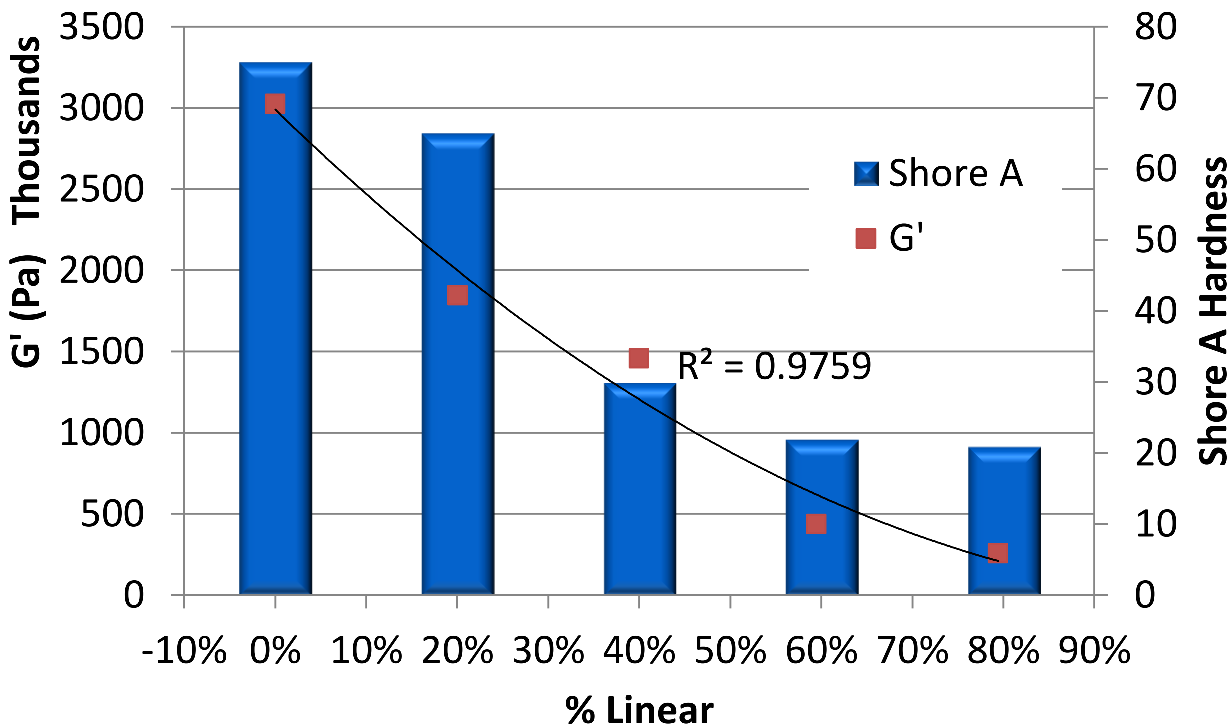


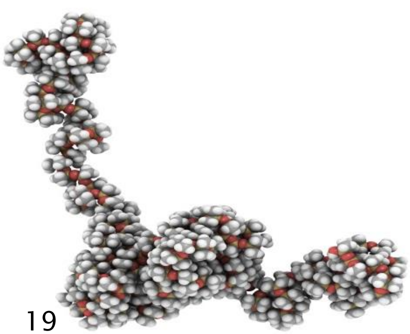


Optimized Blend Higher MW

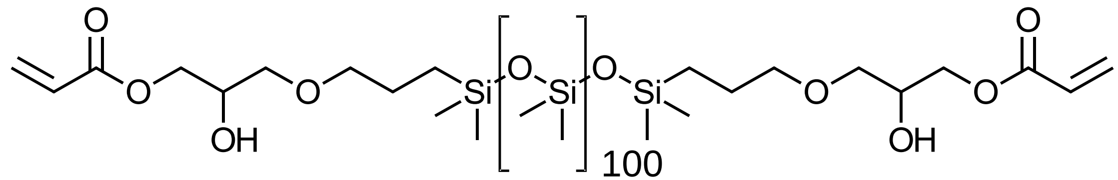


With this higher MW X-linker, the addition of the similar MW extender, lowers G' and hardness even less substantially.

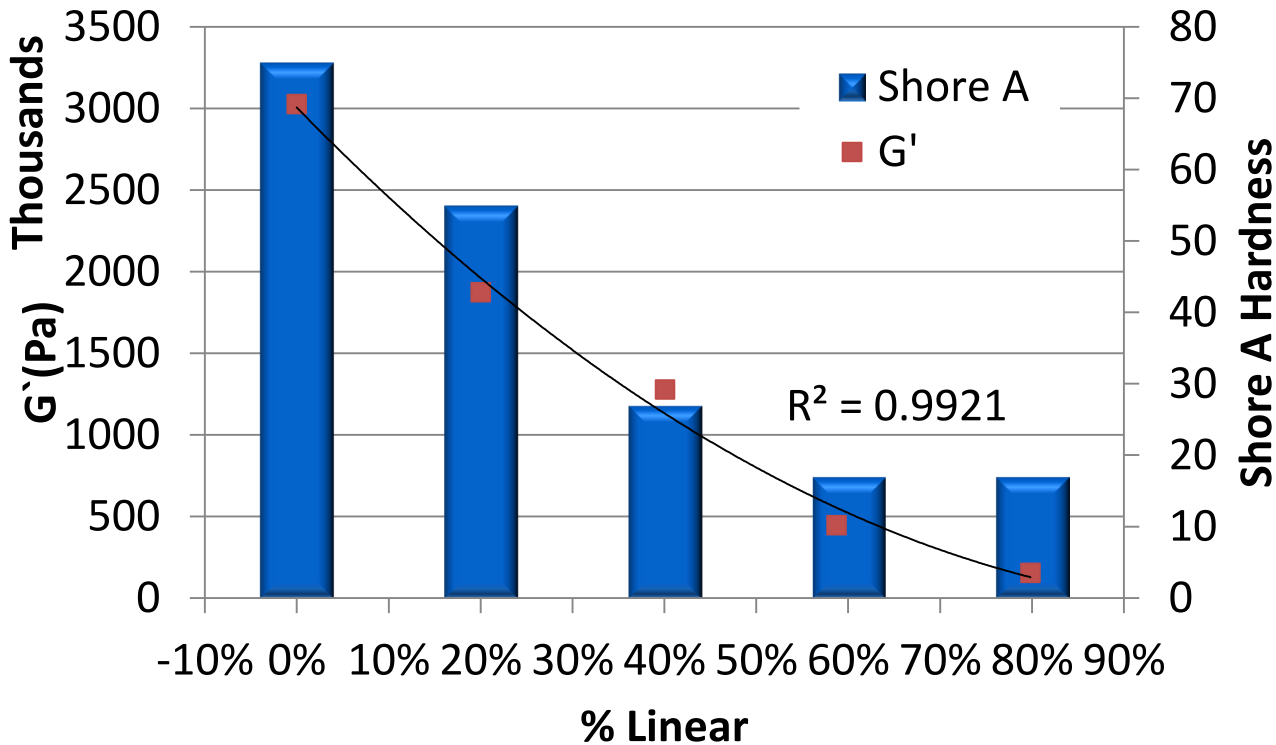


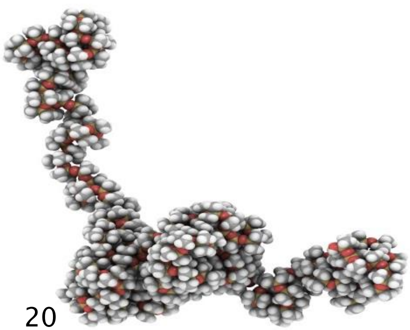


Optimized Blend Higher MW

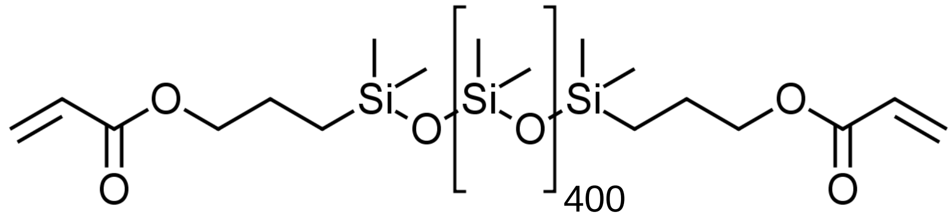


Similar results with Hydroxy Acrylate type

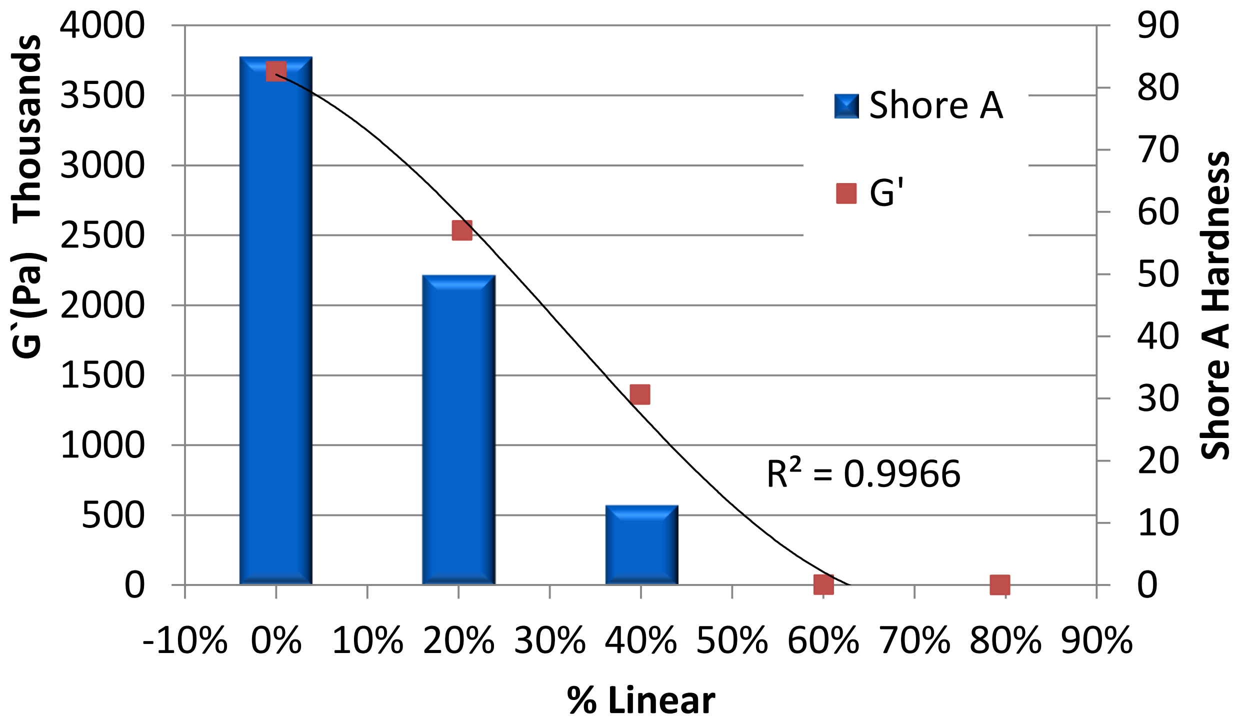


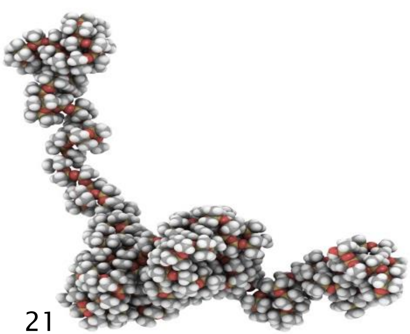


Optimized Blend



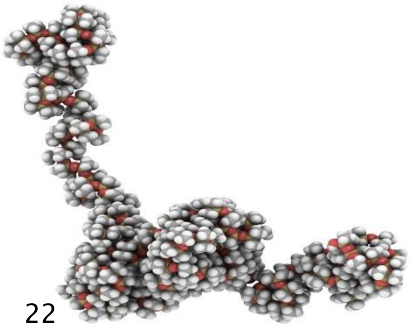
Even in the optimized system, when the extender is much larger then the cross-linker chain; G’ and Hardness are lost.





Summary

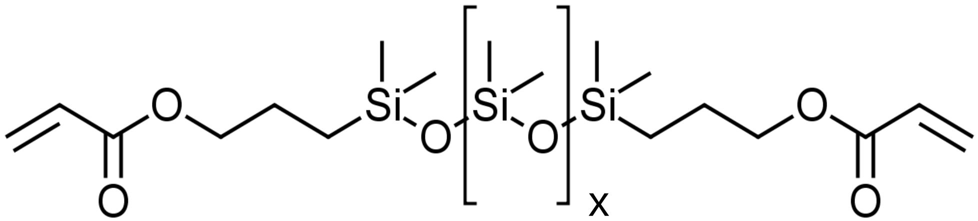
- The best formulation contains, a cross-linker with a high number of cross-link sites and higher molecular weight.
- Small MW extender is needed.
- With this base higher MW extenders will lower Storage and Loss Moduli, adding flexibility.

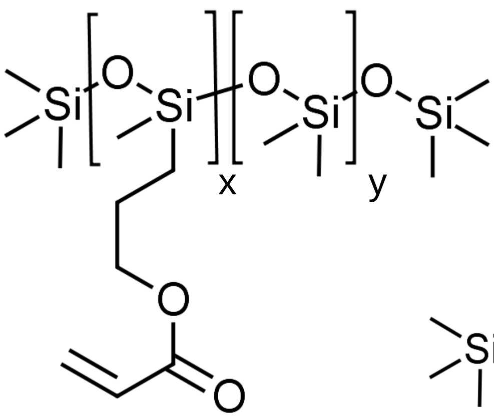


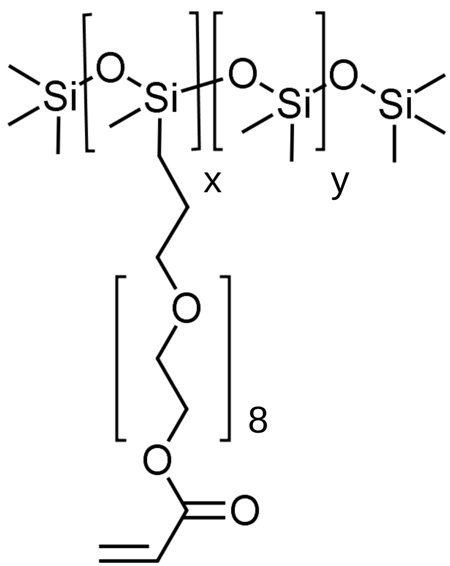
Modifying Organic Resins

- Silicone/Organic Hybrids can give the best compromise

Compatibilizer Often Needed



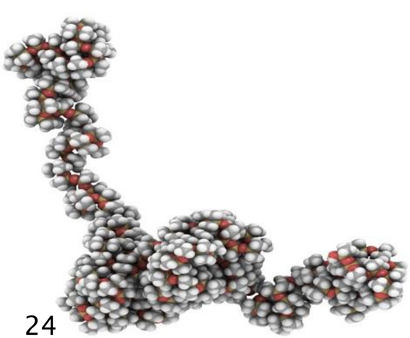




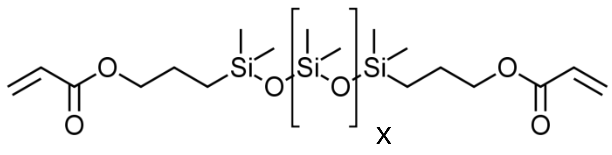
22% silicone

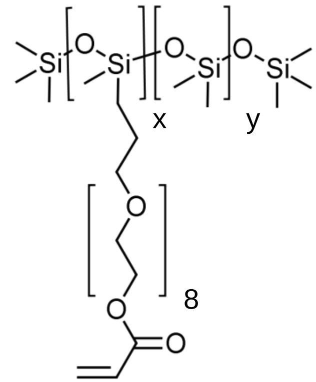
→

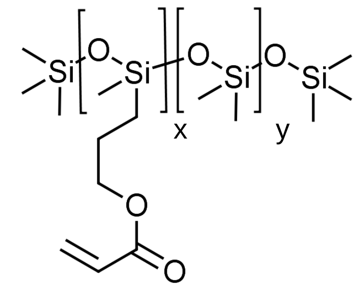
40% CN 102Z (epoxy acrylate)
15% CN 386 (Synergist)
5% Esacure TZT
1.5% Darocur 1173
0.5% reactive defoamer
10% DTPTA
6% TRPGDA
UV light, RT



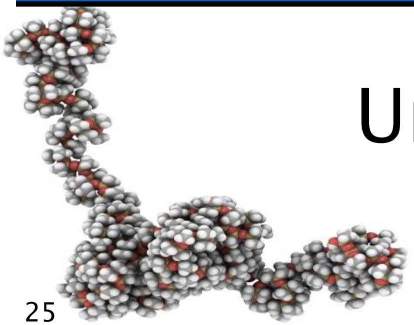
Imperfect Cure





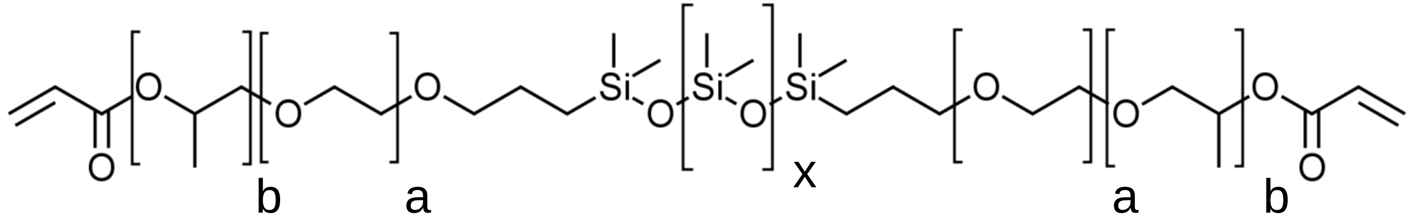


	X=10	X=50	X=100	x, y =4,8	x, y =5,30	x, y = 4,8	Control
Polyether	None	None	None	EO	EO	None	NA
G' (MPa)	8.3	18.5	11.91	9.71	11.64	20.06	20.1
G" (MPa/10)	0.71	3.19	1.88	0.82	0.91	1.42	1.56
Condition & Appearance	oily	oily, defects	oily	Cured	Cured	Sl. Tacky	Cured



Uncured Silicone from Insolubility

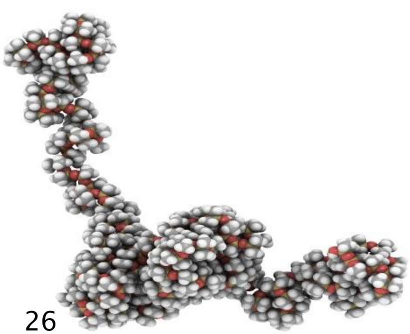
Silicone/Epoxy Hybrid



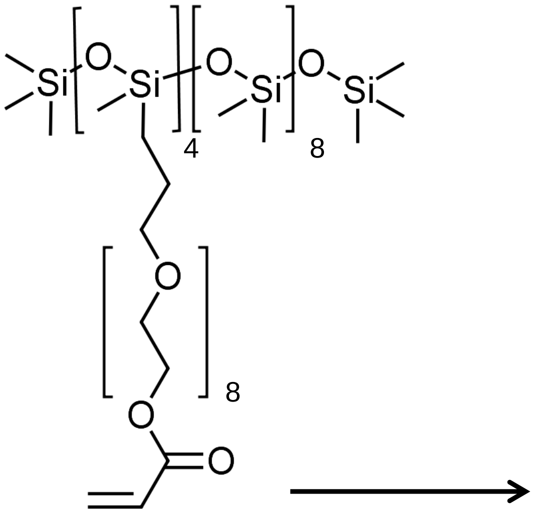
10% silicone →

67% CN 104 C75 (epoxy acrylate)
10% CN 386
5% Esacure TZT
1.5% Darocur 1173
0.5% reactive defoamer
1% DTPTA
5% TRPGDA
UV light, RT

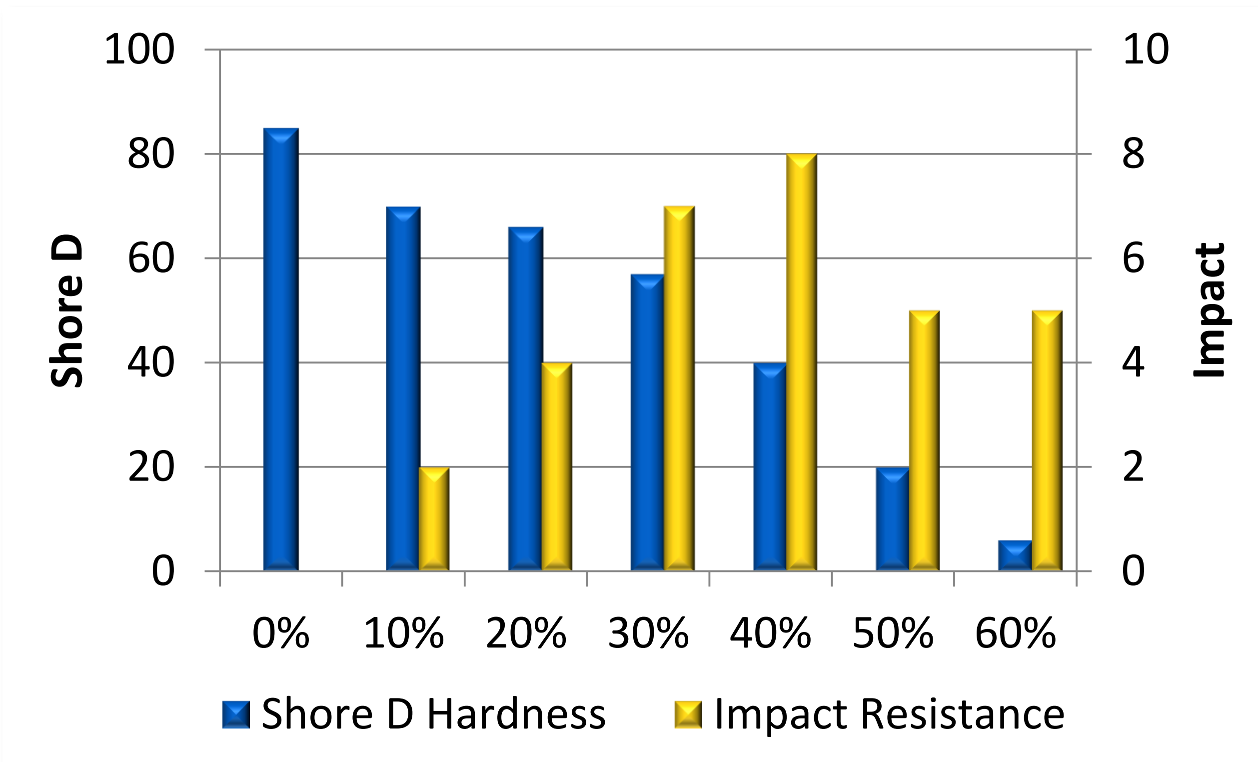
	x=15 a=8 b=0	x=45 a=15 b=15	x=400, a, b=0	x=10 a=10 b=0	x=20 a=10 b=4	x=25 a=10 b=0	Control
G' (MPa)	16.5	11.6	14	17	17	16.3	17
G" (MPa/10)	14.8	10.2	14.1	52.9	7.5	10.3	34.5
tan(delta)(/100)	9	8.8	10.2	31.1	4.51	6.35	20.3
Condition & Appearance	Cured		Un-cured	Cured			

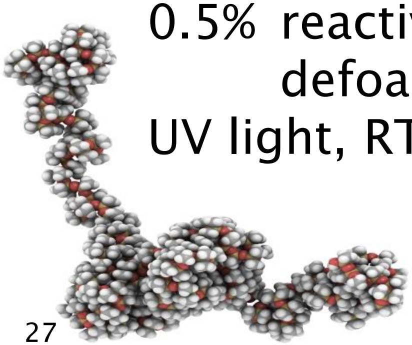


Silicone/Epoxy Hybrid



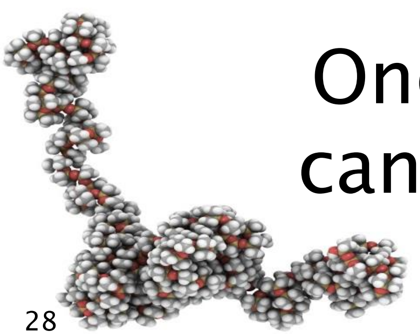
0-80% silicone
0-80% CN 104 C75
13% CN 386
5% Esacure TZT
1.5% Irgacure 184
0.5% reactive defoamer
UV light, RT





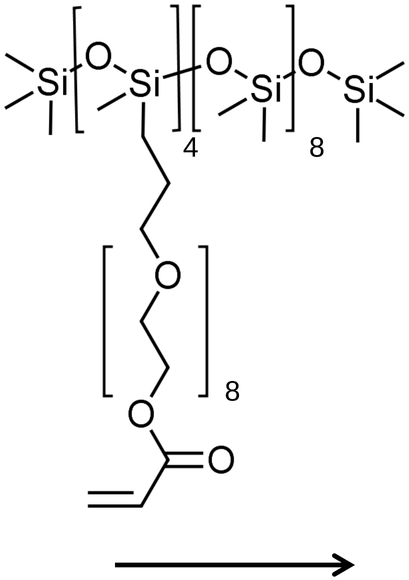
The Effect of Use Level

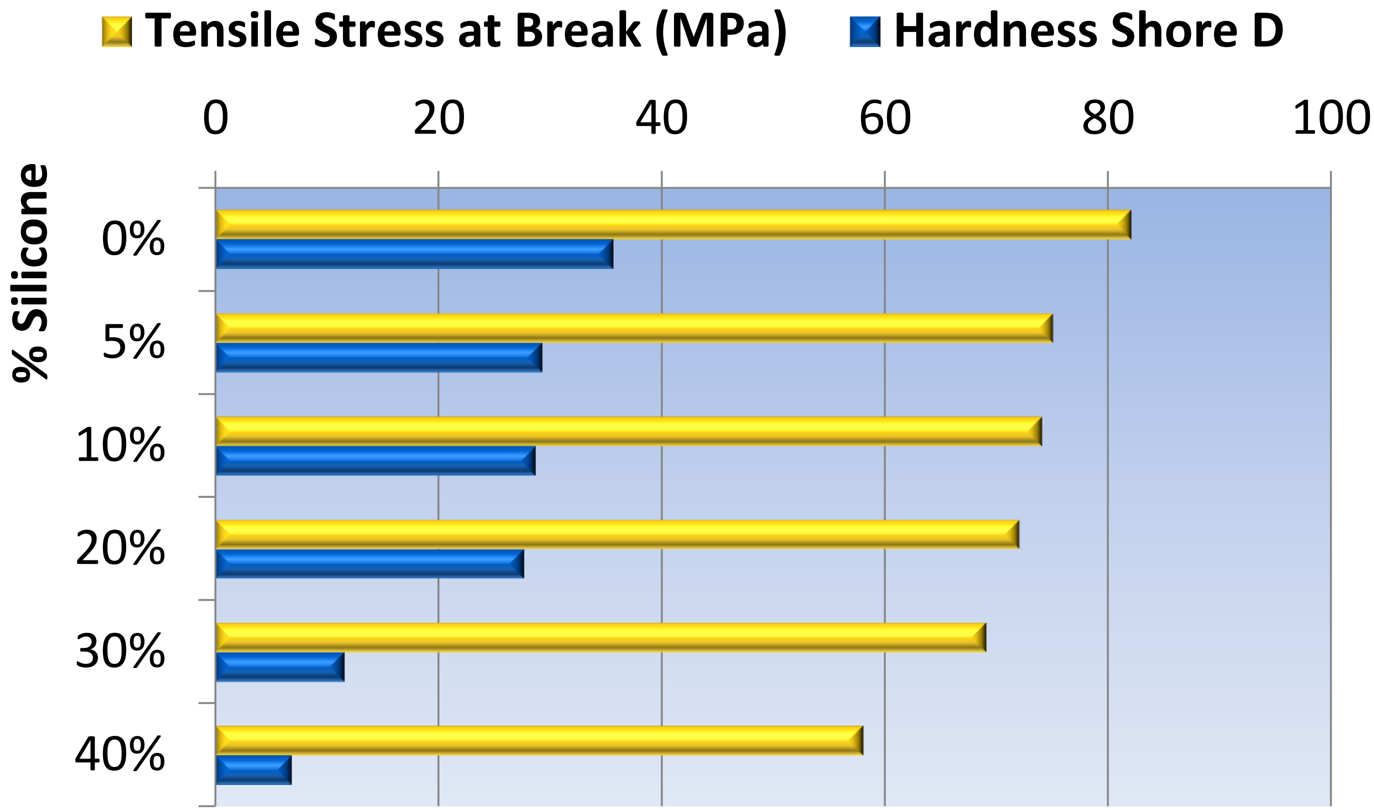
Silicone	0%	10%	20%	30%	40%	50%	60%	70%	80%
Tensile (kPa)	8335	7300	6900	6675	3435	1465	978	347	197
Elongation (%)	0.04	0.13	0.14	2.65	5.44	5.61	6.18	5.37	5.01
G' (MPa)	22.3	19.9	19.9	16.6	12.6	6.94	3.44	1.63	0.83
G" (MPa)	1.3	1.65	1.87	1.64	1.26	0.67	0.15	0.017	0.0063
tan(delta)	0.059	0.083	0.094	0.099	0.10	0.097	0.044	0.010	0.008
Film	very brittle		Sl. flex.	more flexible		flexible		no integrity	
Shore D Hardness	85	70	66	57	40	20	6	2	1
Impact Resistance	0	2	4	7	8	5	5	not measured	



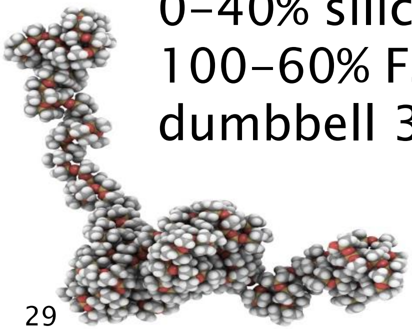
One can go very high, but film integrity can be lost. 20-30% often a good range

3D Printed Data

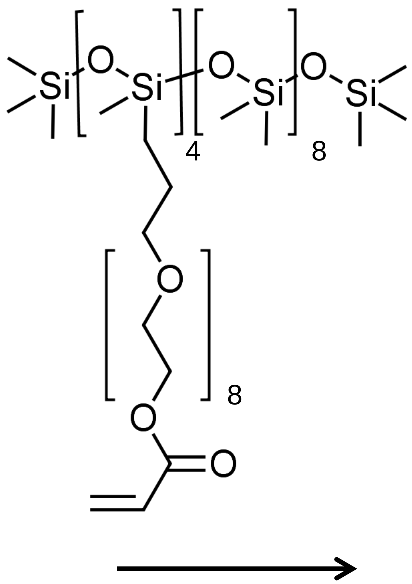


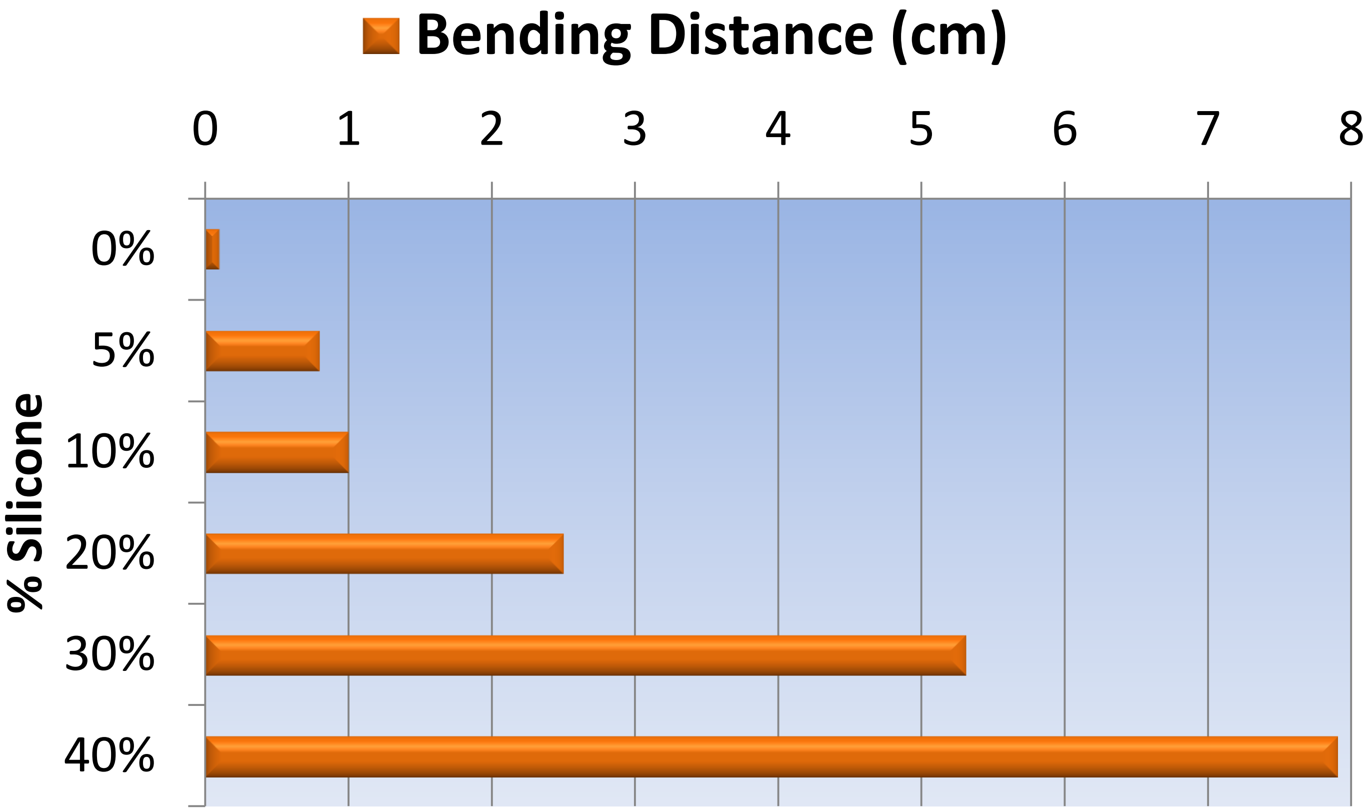


0–40% silicone
100–60% FSL3D resin
dumbbell 3D printed with ASTMD638_specimen.stl



3D Printed Data





0–40% silicone
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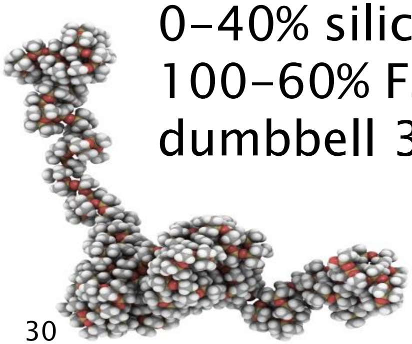
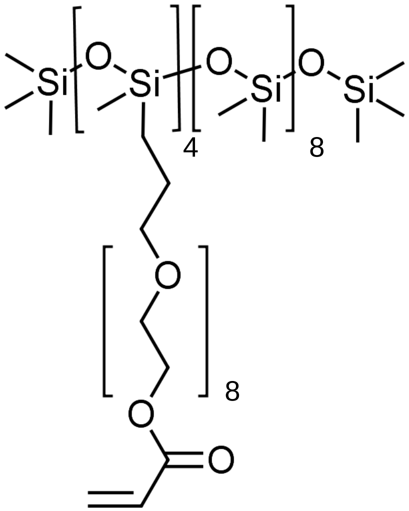
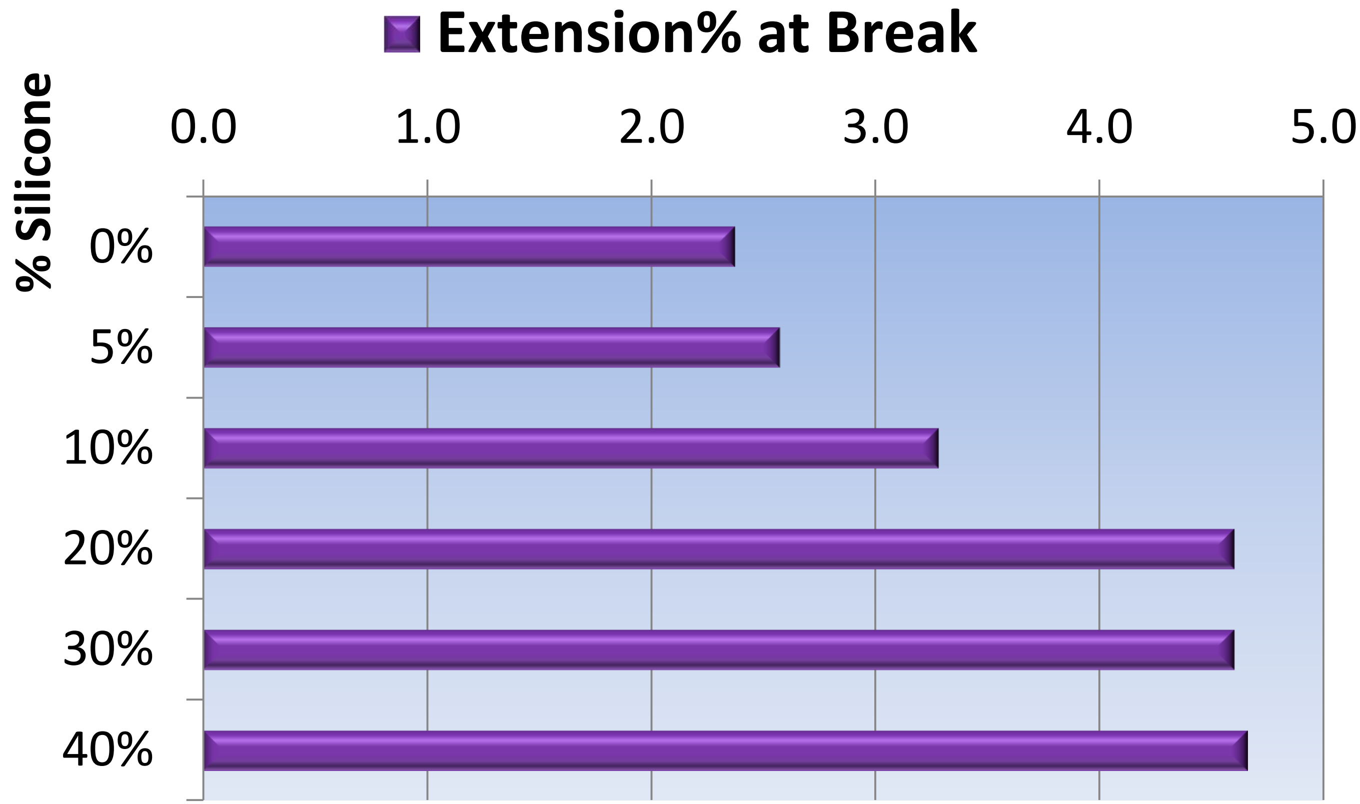
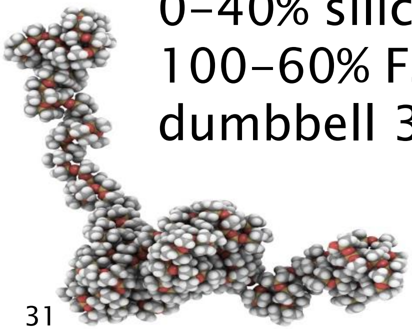


3D Printed Data







0–40% silicone
100–60% FSL3D resin
dumbbell 3D printed with ASTMD638_specimen.stl

Conclusions

- Acrylated Silicones can be cured to give soft elastomers
- Or…
- Cured with Organic Acrylates to give hard elastomers with improved flexibility