NOVEL ENERGY CURED MERCAPTO FUNCTIONAL SILICON Q RESIN MATERIALS FOR 3D PRINTING

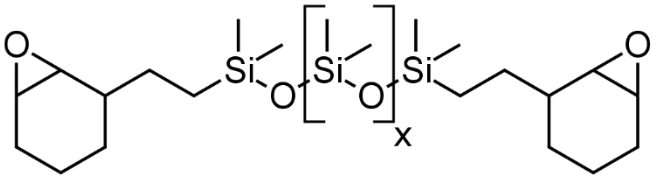
Bob, Ruckle; Tom-Seung, Cheung; John Grande; & Yanjun Luo

Siltech Corporation
Toronto, ON Canada
Robert@siltech.com, Tom@siltech.com

Problem: Elongation

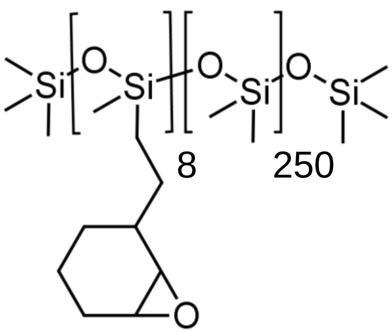
- Silicones routinely provide up to 300% elongation in homopolymers or organic/ silicone hybrid copolymers
- UV cured acrylate silicones do not do this elongation is typically under 10%.
- The mercapto/vinyl systems bring elongation back to >100% as high as 200% in one.

Epoxy Silicone System

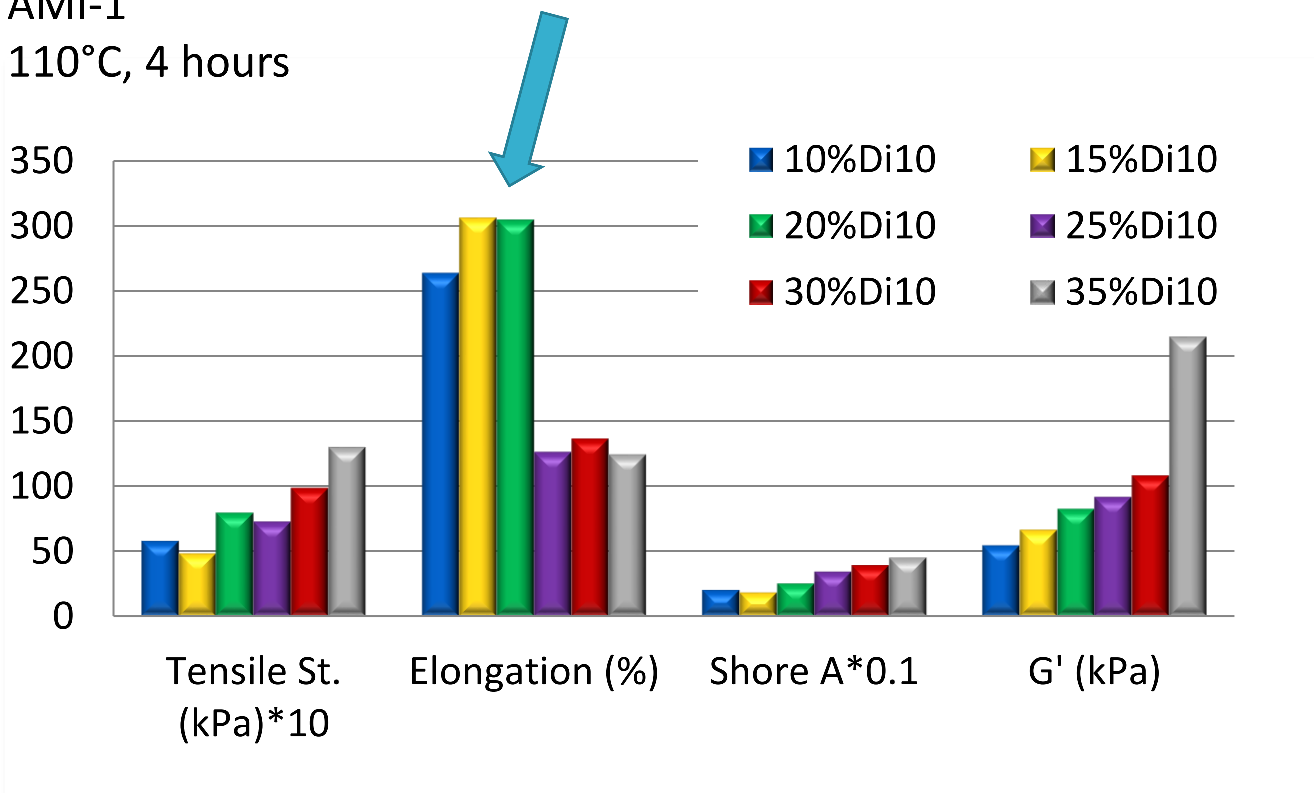


Linears
X=400 (20-34%)
X=10 (10-35%)

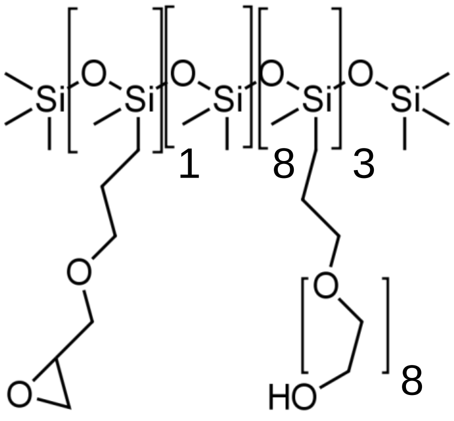
5-11% MHHPA
AMI-1
110°C, 4 hours



X-linker (8%)

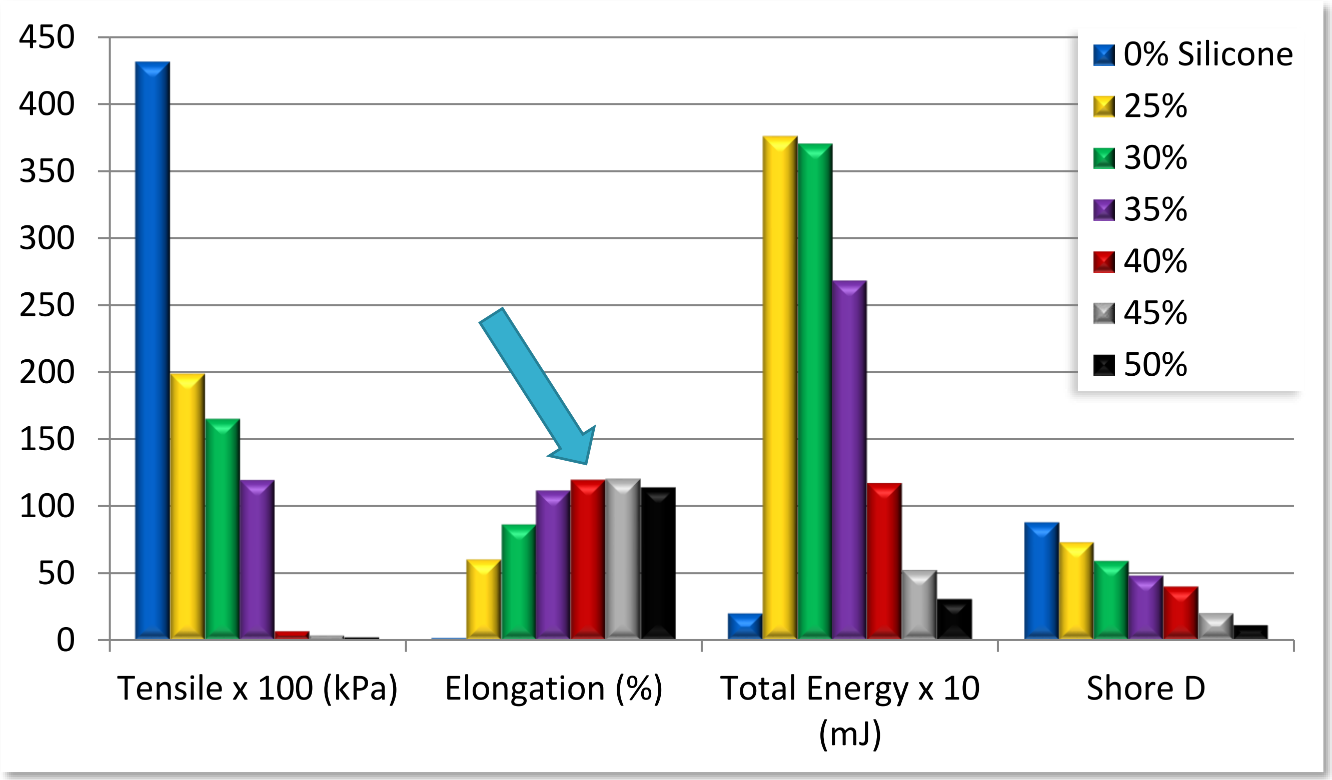


Silicone/ Organic Epoxy Hybrid System

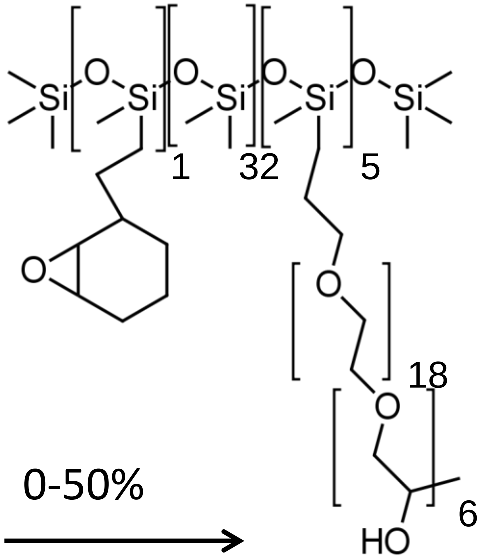


0-50%

32-53% D.E.R. 671-X75
17-23% MHHPA
1% AMI-1
0.2% reactive defoamer
110°C, 4 hours



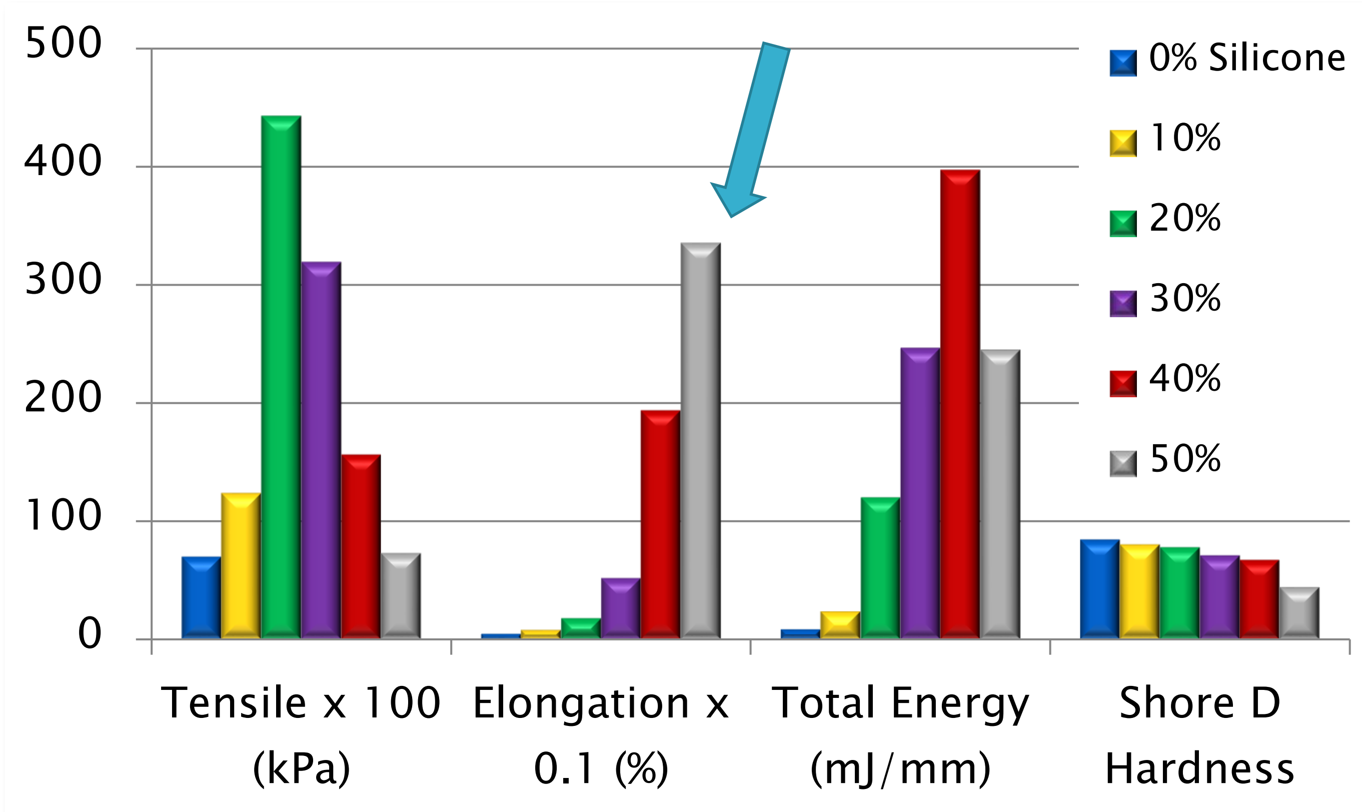
Silicone/ Organic UV Cured Epoxy Hybrid System



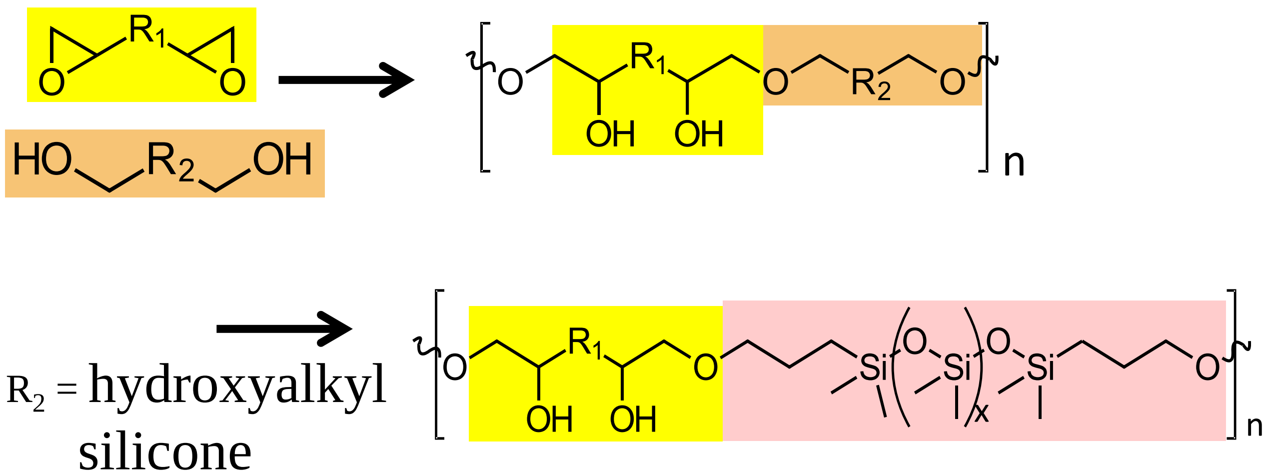
0-50%

→

50-100 %
UVACURE 1500
UV 9380
UV light, RT



Polymers from Condensation Reactions

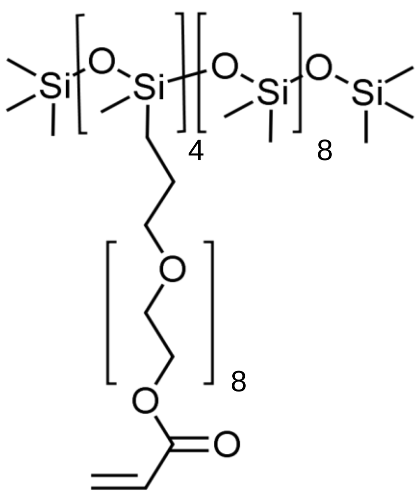


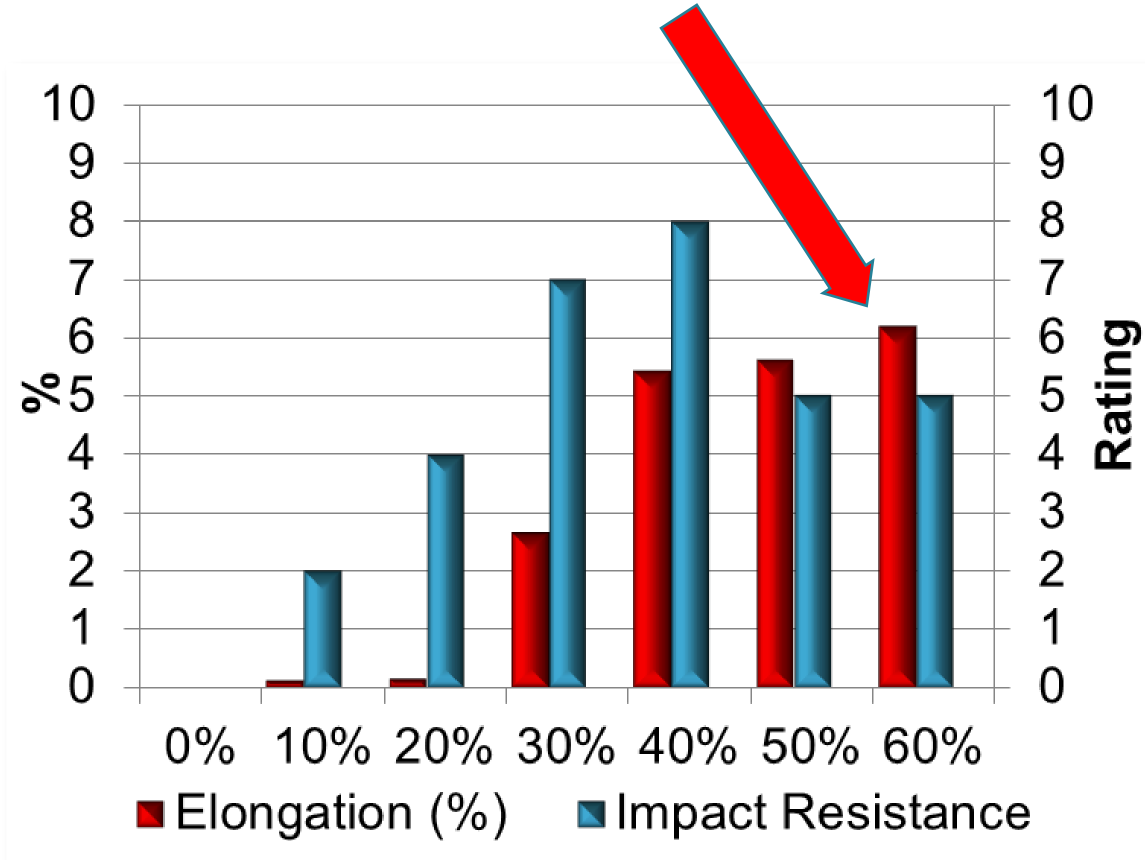
The flexible silicone is in the backbone elongation is high

Acrylate Silicone UV coating

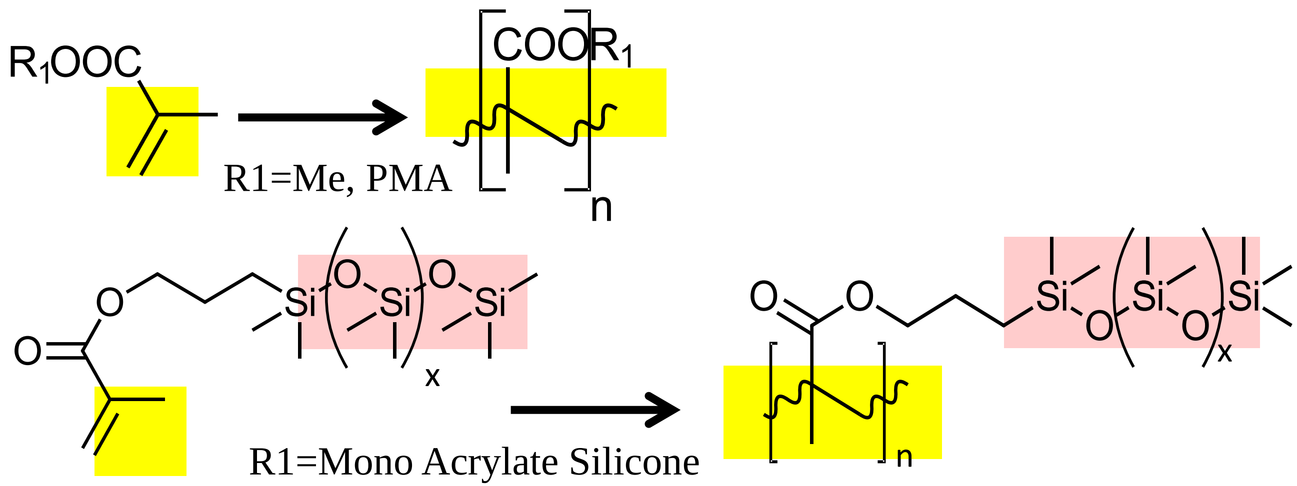
0-80% CN 102Z (Epoxy Acrylate)
13% CN 386 (Synergist)
5% Esacure TZT
1.5% Darocur 1173
0.5% reactive defoamer
→
UV light, RT

0-80% silicone



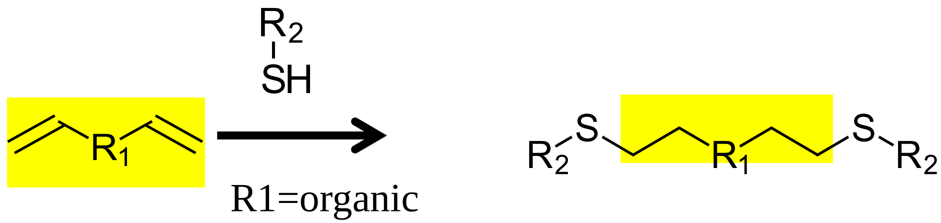


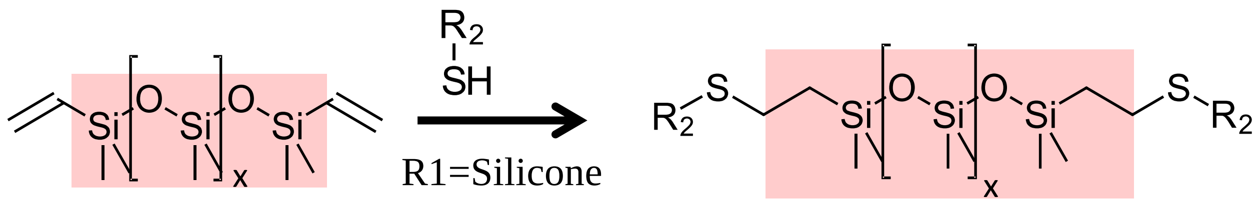
Free Radical Polymerization

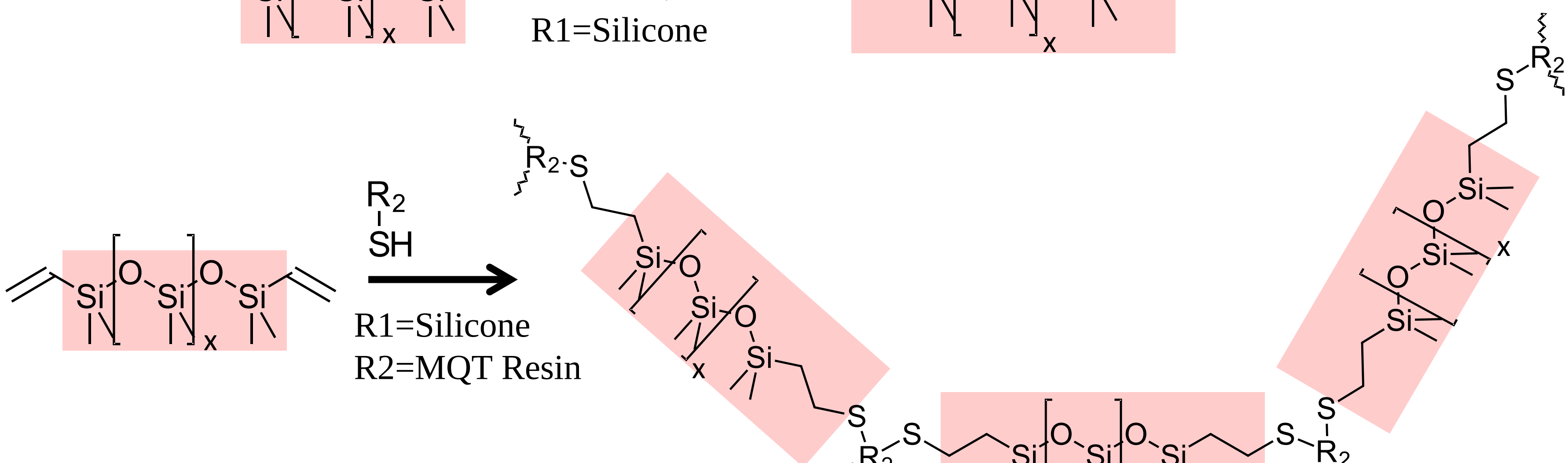


The flexible silicone is NOT
in the backbone.

Polymers from Thiol Ene Reaction

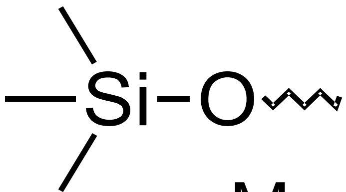




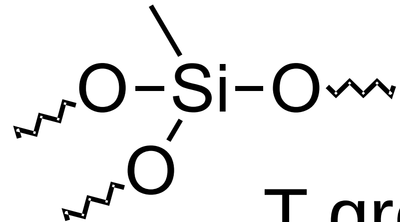


The flexible silicone is in the backbone.

Silicon Nomenclature

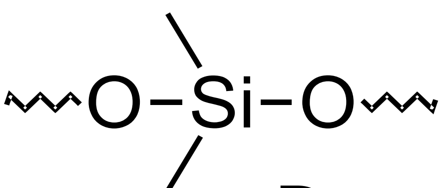


M group

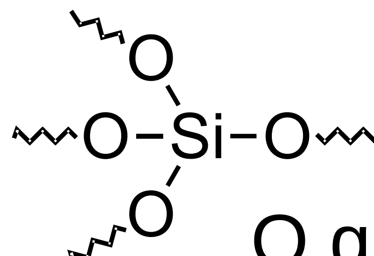


T group

Trialkoxy silanes are T groups



D group



Q group

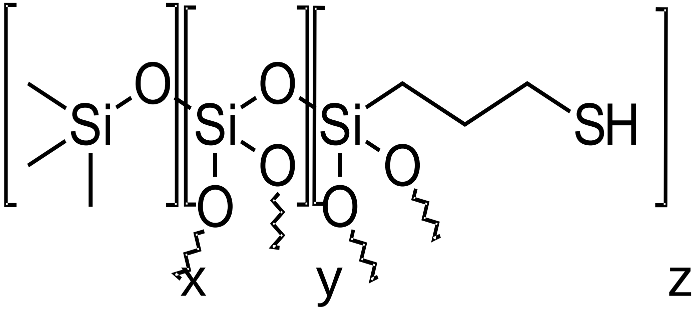
MD_xM is the standard formula for silicone

Formulation

Ingredient	Amount (wt %)	Purpose
Mercaptosilicon Resin	5-40%	Cross-linker
65K	50-70%	Extender
Vinyl Silicon Resin	15-25%	Softer Cross-Linker
TP0-L	0.6-0.7%	Photoinitiator

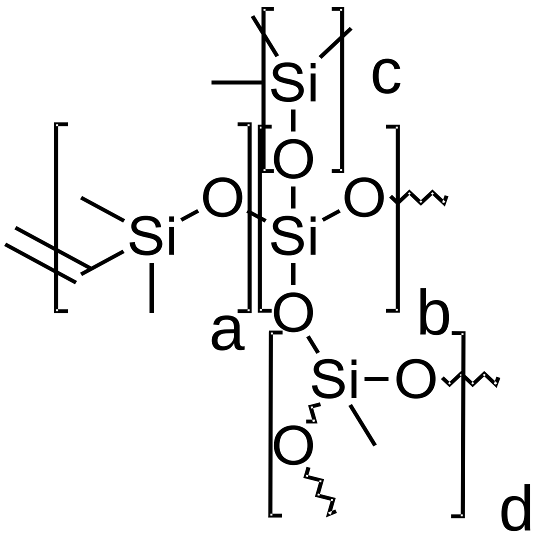
MQT(SH) Silicon Resins

Designation	Q / T (y/z)	Equivalent Weight	Viscosity (cPs)
SH 208	0%	208.0	215
SH208-10Q	10%	217.0	530
SH208-20Q	20%	220.3	1,350
SH208-30Q	30%	226.3	2,325
SH208-40Q	40%	231.6	12,300
SH208-50Q	50%	237.5	228,000



M(vinyl)QT Silicon Resins

Designation	a/b/c/d	Vinyl %	Viscosity (cPs)
Q83T30	25/100/55/30	1.84%	25,500
Q91T30	10/100/80/30	0.63%	16,200
Q92T30	20/100/70/30	1.33%	18,000
Q93T30	30/100/60/30	1.88%	14,600
Q94T30	40/100/50/30	2.49%	14,000
Q92T50	20/100/70/50	1.41%	5,300
Q92	20/100/70/0	1.07%	55,000
Q93	30/100/60/0	1.62%	NA
Q94	40/100/50/0	2.15%	64,500



Experimental

These experiments were conducted in a TA Instruments AR-G2 SN 10G4421 Rheometer with a UV reactive chamber.

The rheological properties including G’, G’’, tan (δ) and cure rate are analyzed and obtained by the TA Rheology Advantage software.

The reactions were repeated on the benchtop with a benchtop UV light and cut into shapes for mechanical property measurement on an Instron.

3D Printing

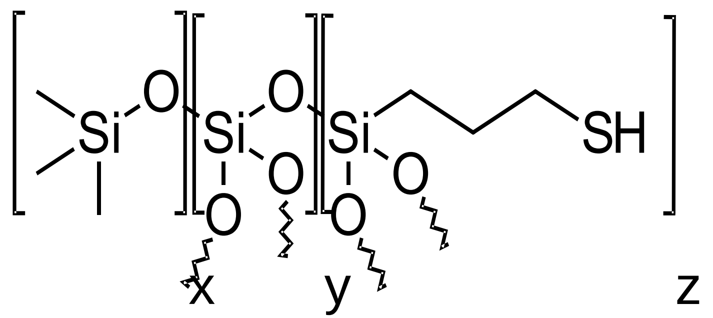
We used an UltiMaker 2+ FMD from Sturctra3D for 3D printing of the SH formulations due to the relatively high viscosity.

This is a thermal cured printer so we attached a UV lamp to the print head to effect UV curing or held the light by hand.

SH/Vinyl Ratio

	SH 208	SH 208-10Q	SH 208-20Q	SH 208-30Q	SH 208-40Q	SH 208-50Q
SH/vinyl	2.33	2.46	3.05	4.44	6.75	6.85

We determined the optimum SH/Vinyl ratio for each Q/T ratio



Example SH208 (0Q)

Component	YL3-128A	YL3-128B	YL3-127F	YL3-128C	YL3-127E	YL3-127A	YL3-127B	YL3-127C
SH 208	11.41%	12.61%	13.77%	14.88%	16.97%	19.89%	21.48%	23.54%
65K	47.71%	47.07%	46.44%	45.84%	44.71%	43.15%	42.29%	41.18%
Q93T30	40.19%	39.65%	39.12%	38.62%	37.67%	36.35%	35.62%	34.69%
TPO-L	0.69%	0.67%	0.67%	0.65%	0.65%	0.62%	0.62%	0.60%
SH/VINYL ratio	1.88	2.11	2.34	2.56	2.99	3.63	4.00	4.50
G' (Pa)	5.08E+05	5.70E+05	6.20E+05	5.31E+05	4.35E+05	2.96E+05	2.70E+05	2.09E+05
G" (Pa)	4.18E+04	4.55E+04	4.62E+04	4.03E+04	3.64E+04	2.95E+04	2.69E+04	2.44E+04
tan (delta)	0.082	0.080	0.074	0.076	0.084	0.099	0.100	0.117
Cure rate (Pa/s)	9.48E+04	1.48E+05	5.20E+05	2.88E+05	2.05E+05	1.14E+05	1.34E+05	1.38E+05
Appearance	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white

Amount of Q in MQT(SH)

	SH 208	SH 208-10Q	SH 208-20Q	SH 208-30Q	SH 208-40Q	SH 208-50Q
SH/vinyl	2.33	2.46	3.05	4.44	6.75	6.85

The higher the Q ratio, the more SH was needed to effect cure. Above 30% Q, the formulations were unworkable and not testable

Adjusted SiH/Vinyl

	-10Q	delta	-20Q	delta	-30Q	delta.	-40Q	delta	-50Q	delta
SH/VINYL ratio	2.46	5%	3.05	30%	4.44	90%	6.75	189%	6.85	193%
Tensile Strength (kPa)	3167	-3%	3006	-8%	Not Measured					
Elongation (%)	85	0%	87	9%	Not Measured					
Total Energy (J/m)	171	-16%	173	4%	Not Measured					
Tear Strength (N/mm)	3.2	6%	1.96	-45%	Not Measured					
Shore A Hardness	50	-4%	49	-6%	Not Measured					
G' (Pa)	7.11E+05	3%	8.43E+05	12%	7.36E+05	69%	5.18E+05	507%	2.11E+05	762%
G" (Pa)	5.14E+04	0%	5.95E+04	10%	5.97E+04	32%	4.67E+04	114%	6.48E+04	546%
tan delta	0.072	-3%	0.071	-2%	0.081	-22%	0.09	-65%	0.308	-25%
Cure rate (Pa/s)	1.79E+05	42%	2.47E+05	93%	1.51E+05	4%	8.24E+04	544%	2.89E+04	612%
Note	poor tear strength									

Effect of Changing Ratio

	SH 208-10Q	delta	-20Q	delta	-30Q	delta.
SH/vinyl ratio	2.46	5%	3.05	30%	4.44	90%
Tensile Strength (kPa)	3167.24	-3%	3006.54	-8%	Not Measured	
Elongation (%)	84.78	0%	87	9%		
Total Energy (J/m)	170.76	-16%	172.77	4%		
Tear Strength (N/mm)	3.2	6%	1.96	-45%		
Shore A Hardness	50	-4%	49	-6%		
G' (Pa)	7.11E+05	3%	8.43E+05	12%	7.36E+05	69%
G" (Pa)	5.14E+04	0%	5.95E+04	10%	5.97E+04	32%
tan delta	0.072	-3%	0.071	-2%	0.081	-22%
Cure rate (Pa/s)	1.79E+05	42%	2.47E+05	93%	1.51E+05	4%

G’, G” and Cure Rate increase

Many Mechanical Properties do not

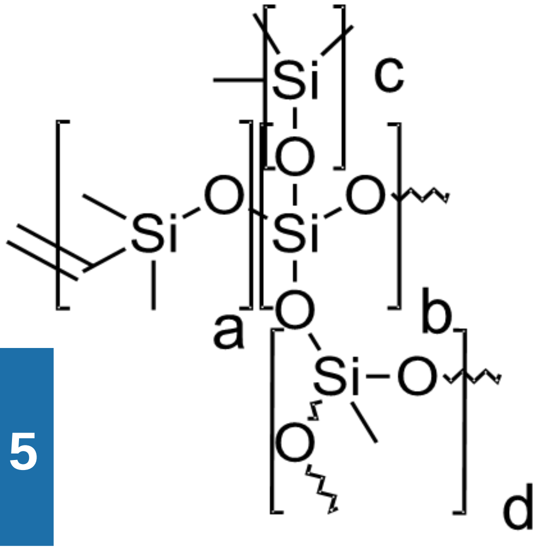
Adding more Reactive Diluent

Component	-10Q w/+10% 65K		-20Qw/+5% 65K		-30Q w/+5% 65K	
SH 208-xQ	12.24%		16.44%		17.96%	
65K	55.81%		49.23%		51.71%	
VQ93T30/VIN65K	31.26%		33.67%		29.84%	
TPO-L	0.69%		0.67%		0.49%	
SH/vinyl ratio	2.46		3.05		3.63	
Property		delta		delta		delta
Tensile Strength (kPa)	2495.98	-21%	2450.47	-18%	2898.85	14%
Elongation (%)	122.1	44%	97.1	12%	130.64	40%
Total Energy (J/m)	209.75	23%	162.97	-6%	283.56	76%
Tear Strength (N/mm)	3.27	2%	2.67	36%	3.92	39%
Shore A Hardness	38	-24%	42	-14%	40	-2%
G' (Pa)	3.62E+05	-49%	5.40E+05	-36%	4.70E+05	-25%
G" (Pa)	2.49E+04	-52%	3.76E+04	-37%	3.66E+04	-26%
tan delta	0.069	-4%	0.07	-1%	0.078	0%
Cure rate (Pa/s)	1.35E+05	-25%	5.54E+04	-78%	1.21E+05	-22%
Appearance			more flexible			

Elongation, Flex and Tear Strength Increase

Strength, Hardness, Moduli and Cure Rate decrease

Impact of M(Vinyl)/Q



(a+c)/b

Component	M/Q=0.9	M/Q=0.8	M/Q=0.8 + 5 wt% 65K
SH 208-30Q	18%	18%	16%
65K	52%	52%	57%
VQT83-30		30%	27%
VQ93T-30	30%		
TPO-L	0.5%	0.5%	0.6%

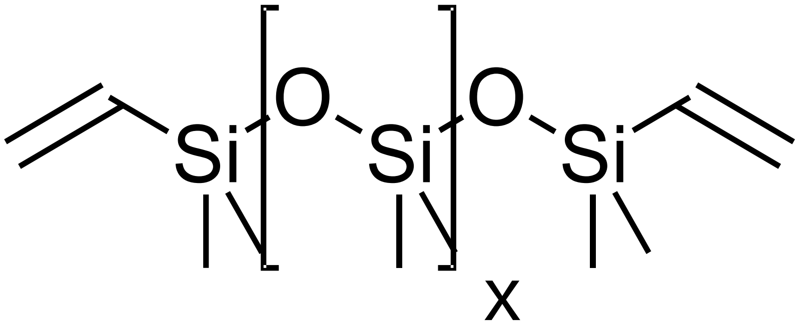
SH 208-30Q	M/Q=0.9	M/Q=0.8	M/Q=0.8 + 5 wt% 65K	
Property				Delta
SH/vinyl ratio	3.63	3.63	3.62	0%
Tensile Strength (kPa)	2898.85	2587.3	3186.03	-23%
Elongation (%)	130.64	85.5	148.51	-74%
Total Energy (J/m)	283.56	149.77	387.83	-159%
Tear Strength (N/mm)	3.92	4.32	4.63	-7%
Shore A Hardness	40	49	42	14%
G' (Pa)	4.70E+05	5.97E+05	4.39E+05	26%
G" (Pa)	3.66E+04	3.60E+04	2.82E+04	22%
tan delta	0.078	0.06	0.064	-7%
Cure rate (Pa/s)	1.21E+05	1.73E+05	4.04E+04	77%
Appearance	very flexible, leaves no marks after twisting.		very flexible, maybe marks after twisting	

M/Q=0.8 more crosslinked and tougher

less tensile strength, elongation, total energy

Impact of Diluent Vinyl Content

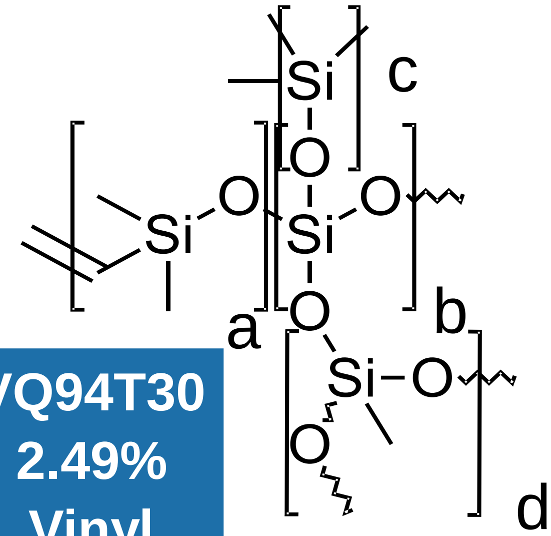
Component	0.060% vinyl	0.078% vinyl
SH 208-30Q	20.8%	21.0%
65K (0.060% vinyl)	42.6%	
65K (0.078% vinyl)		42.5%
VQT83-30/65K	35.9%	35.9%
TPO-L	0.6%	0.6%



SH 208-30Q	0.060% vinyl	0.078% vinyl
SH/vinyl ratio	3.63	3.63
Tensile Strength (kPa)	3571.56	4037.85
Elongation (%)	73.71	84.8
Total Energy (J/m)	209.13	238.75
Tear Strength (N/mm)	3.46	5.11
Shore A Hardness	59	57
G' (Pa)	1.05E+06	1.09E+06
G" (Pa)	7.46E+04	6.54E+04
tan delta	0.071	0.06
Cure rate (Pa/s)	1.83E+05	1.76E+05
Appearance	tears easily	very flexible, good twist

higher vinyl = better tensile strength, tear strength and twist

Vinyl in VQ Resin



Component	VQ91T30 0.63% Vinyl	VQ92T30 1.33% Vinyl	VQ93T30 1.88% Vinyl	VQ94T30 2.49% Vinyl
SH 208-20Q	8.12%	12.44%	14.43%	16.53%
65K	25.87%	39.67%	46.07%	49.09%
VQxT30	65.31%	47.20%	38.80%	33.75%
TPO-L	0.71%	0.70%	0.69%	0.63%
SH/vinyl ratio	2.35	2.34	2.34	2.33

a/c

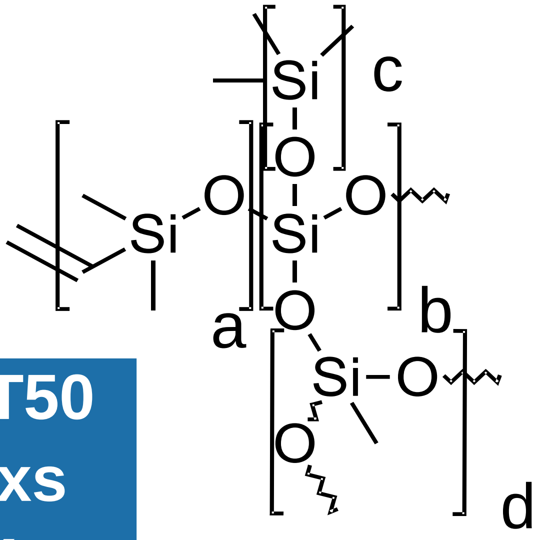
SH 208-20Q	VQ91T30 0.63%	VQ92T30 1.33%	VQ93T30 1.88%	VQ94T30 2.49%
SH/vinyl ratio	2.35	2.34	2.34	2.33
Tensile Strength (kPa)	1924.43	4923.25	3278.78	not measured
Elongation (%)	113.88	95.8	79.65	
Total Energy (J/m)	115.58	248.89	166.22	
Tear Strength (N/mm)	3.12	3.54	3.59	
Shore A Hardness	27	46	52	
G' (Pa)	1.63E+05	4.61E+05	7.53E+05	7.73E+05
G" (Pa)	2.70E+04	4.67E+04	5.42E+04	4.47E+04
tan delta	0.166	0.101	0.072	0.058
Cure rate (Pa/s)	3.57E+04	8.04E+04	1.28E+05	2.79E+05

storage modulus, tear strength, hardness and cure rate increase whereas elongation decreases

More Diluent for Tear Strength

SH 208-20Q	VQ91T30 0.626%	VQ92T30 1.33%	VQ93T30 1.88%	VQ94T30 2.49%
SH/vinyl ratio	2.35	2.34	2.34	2.29
Tensile Strength (kPa)	1924.43	4923.25	3594.64	2861.09
Elongation (%)	113.88	95.8	108.63	128.49
Total Energy (J/m)	115.58	248.89	288.86	301.43
Tear Strength (N/mm)	3.12	3.54	5.26	4.54
Shore A Hardness	27	46	48	45
G' (Pa)	1.63E+05	4.61E+05	4.83E+05	5.11E+05
G" (Pa)	2.70E+04	4.67E+04	3.65E+04	3.00E+04
tan delta	0.166	0.101	0.076	0.059
Cure rate (Pa/s)	3.57E+04	8.04E+04	8.33E+04	2.30E+05
Appearance	soft	firm with okay tear	firm with good tear	firm with okay tear

Impact of T Groups



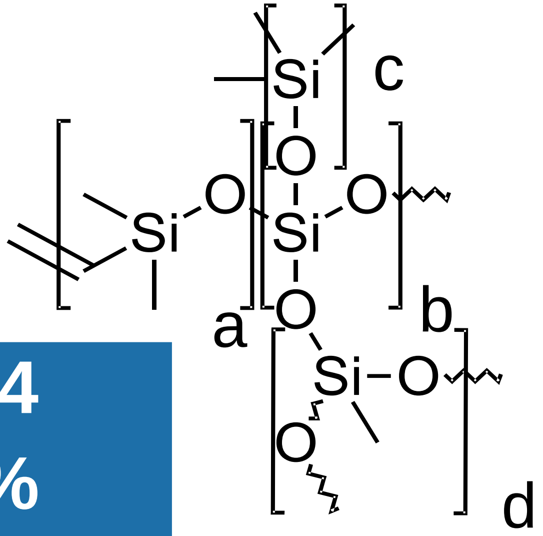
d/b

Component	VQ92T0	VQ92T30	VQ92T50 +5% xs 65K
SH 208-20Q	10%	12%	12%
65K	41%	40%	47%
VQ92Tx	48%	47%	41%
TPO-L	0.7%	0.7%	0.7%

SH 208-20Q	VQ92T0	VQ92T30	VQ92T30 +5% xs 65K	VQ92T50 +5% xs 65K
SH/vinyl ratio	2.32	2.34	2.32	2.33
Tensile Strength (kPa)	5524.11	4923.25	4293.6	2816.47
Elongation (%)	87	95.8	111.49	105.43
Total Energy (J/m)	284.75	248.89	288.53	163.51
Tear Strength (N/mm)	4.9	3.54	3.46	3.17
Shore A Hardness	58	46	44	31
G' (Pa)	9.14E+05	4.61E+05	4.25E+05	2.22E+05
G" (Pa)	7.28E+04	4.67E+04	3.56E+04	1.68E+04
tan delta	0.08	0.101	0.084	0.076
Cure rate (Pa/s)	3.19E+05	8.04E+04	1.06E+05	5.27E+04
Appearance	Tough. Can be twisted.	Firm, can be twisted without break	Break after twisting	Soft, break upon twisting

T groups lowers mechanical and rheological properties

Vinyl Content VQ Resins (T=0)



Component	VQ 92 1.07% vinyl	VQ 93 1.62% vinyl	VQ 94 2.15% vinyl
SH 208-30Q	11%	15%	19%
65K	55%	52%	50%
VQx	34%	32%	31%
TPO-L	0.8%	0.8%	0.8%

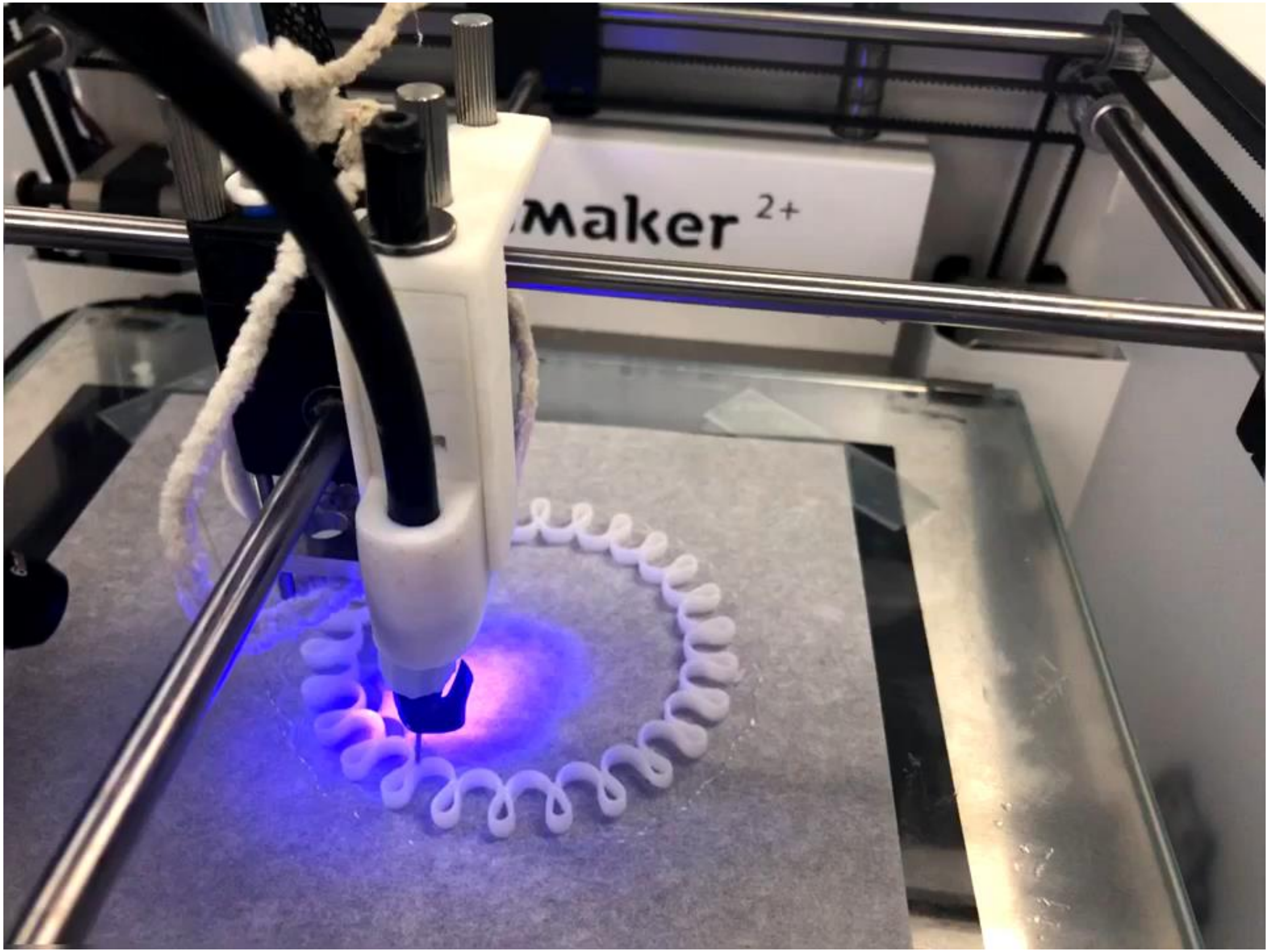
d=0

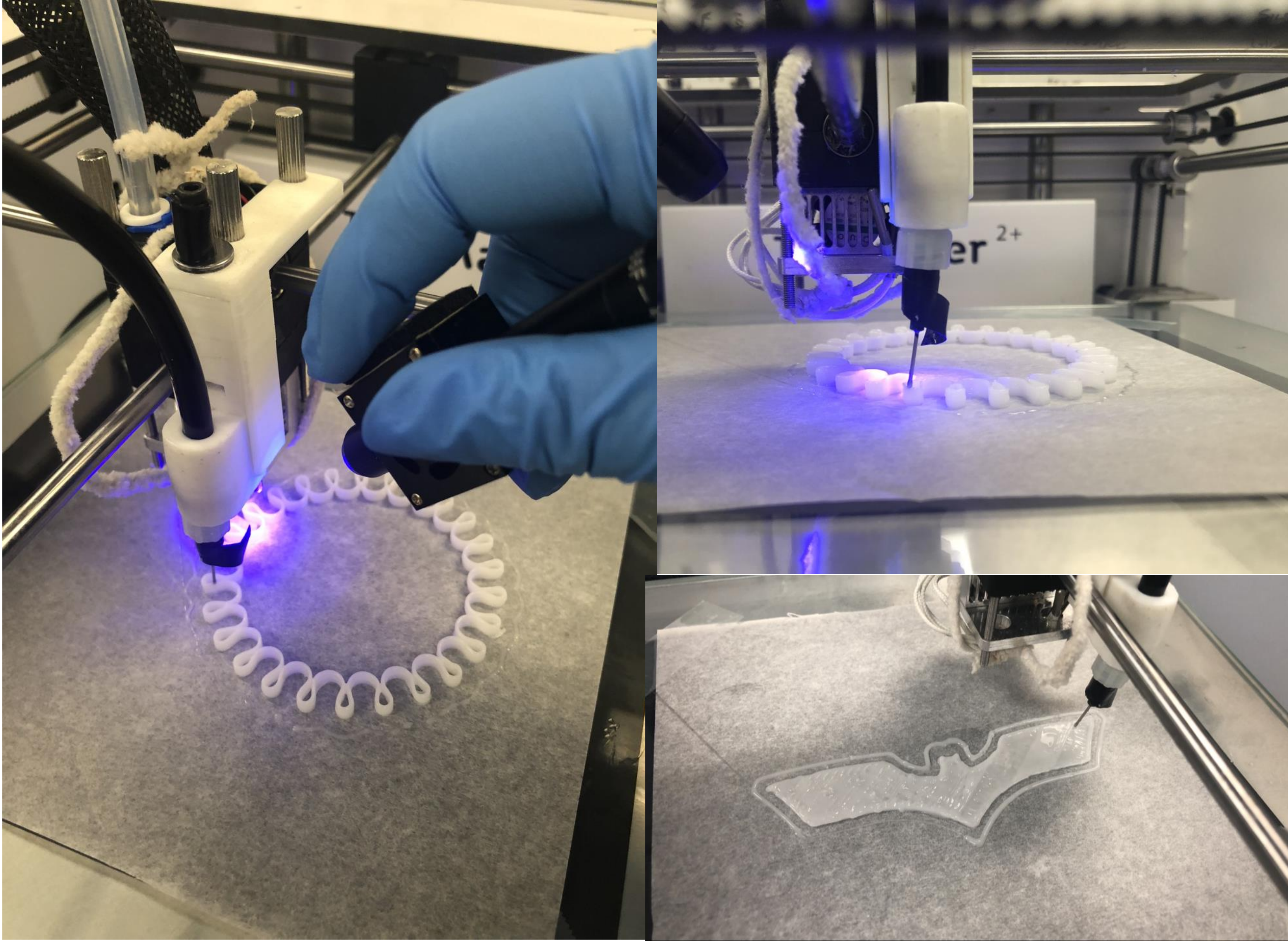
a/c

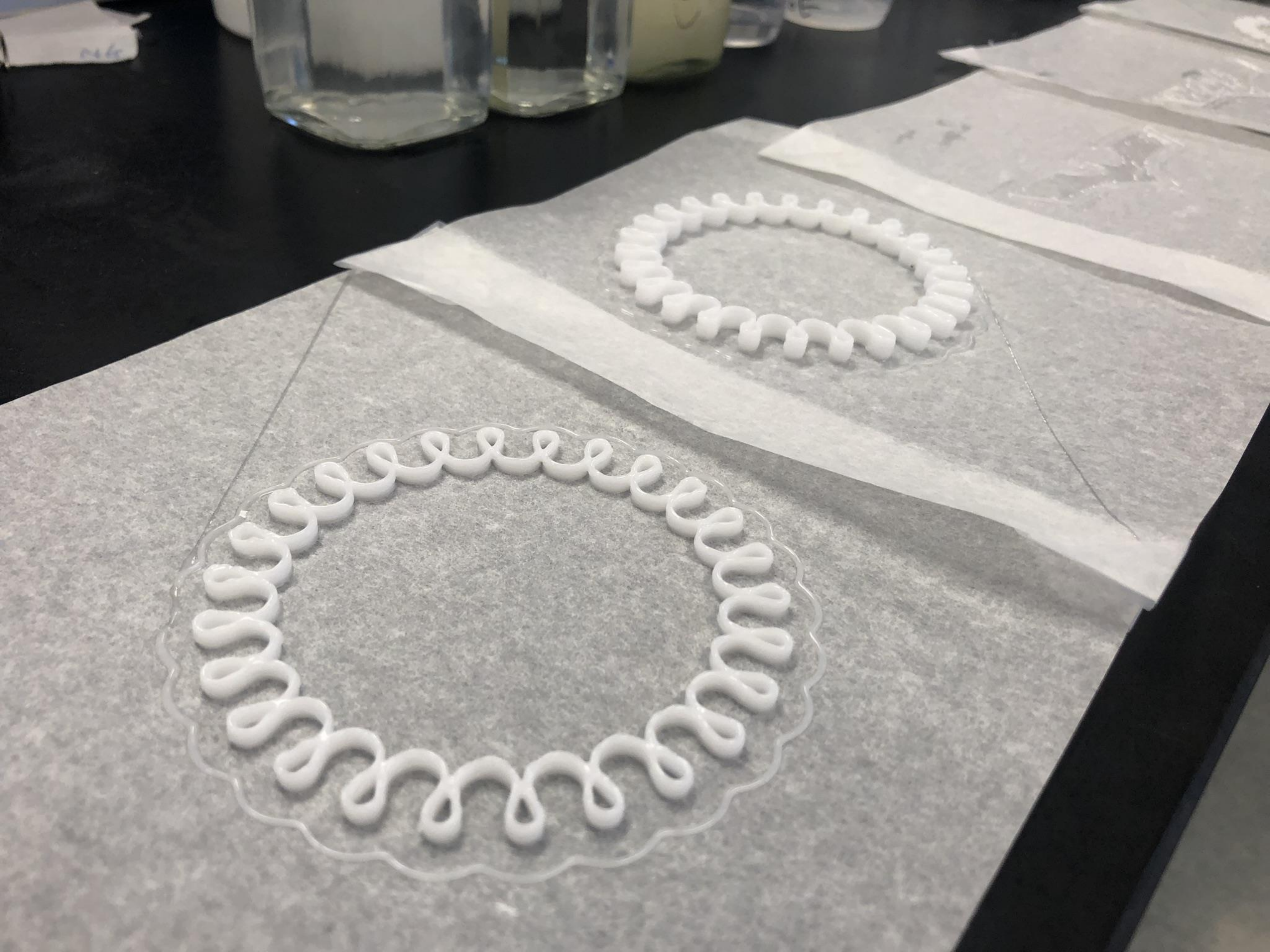
SH 208-30Q	VQ 92 (1.07%)	VQ 93 (1.62%)	VQ94 (2.15%)
SH/vinyl ratio	3.21	3.23	3.21
Tensile Strength (kPa)	3957.38	1642.08	2907.32
Elongation (%)	156.51	65.09	75.2
Total Energy (J/m)	550.25	79.41	185.8
Tear Strength (N/mm)	6.95	3.8	4.84
Shore A Hardness	44	50	56
G' (Pa)	4.71E+05	7.20E+05	1.26E+06
G" (Pa)	3.47E+04	4.35E+04	6.90E+04
tan delta	0.074	0.06	0.055
Cure rate (Pa/s)	1.21E+05	1.70E+05	1.84E+05
Appearance	Very tough flexible, white opaque	breaks upon twisting	

3D Printing

Component	YL2-153A	YL2-153B	YL4-10A
Proprietary MQT(SH)	21.5%	15.1%	15.6%
65K	42.3%	45.8%	51.7%
VQT83-30	35.6%	38.6%	0
VQ92	0	0	32.0%
TPO-L	0.6%	0.6%	0.7%
SH/vinyl	3.63	3.63	4.88
Tensile Strength (kPa)	3,495.98	2,303.68	4027.13
Elongation (%)	99.07	55.87	202.96
Total Energy (J/m)	262.95	104.34	762.75
Tear Strength (N/mm)	6.81	5.33	8.19
Shore A Hardness	55.00	53.00	46
G' (Pa)	6.41E+05	1.20E+06	4.73E+05
G" (Pa)	1.14E+05	5.23E+04	5.26E+04
tan delta	0.18	0.04	0.1112
Cure rate (Pa/s)	8.65E+04	2.87E+05	7.62E+04


Maker 2+





Conclusions

- MQT(SH) resin: more than -30Q unusable. T groups lower viscosity, but hardness and toughness suffer quickly.
- VTQ resin: M/Q ratios of 0.8 are best.
- SH/vinyl: is critical. Up to 17% VQ resin is ok.
- 65K: gives elongation and tear strength but a large reduction of hardness and tensile strength. 5% or less excess.
- Increasing the vinyl content of 65K improved tensile strength, tear strength and flexibility.

Conclusions

- We developed formulations which were:
  - up to 200% elongation
  - Shore A hardness of 59
  - Tear Strength of 8
- Further optimization of this work into a commercial product will be guided by the conclusions on this report and customer's needs.


Thank
You