Novel Acrylated Urethane Silicone Polymers and Formulations to Increase Elongation in 3D Printing Resins.

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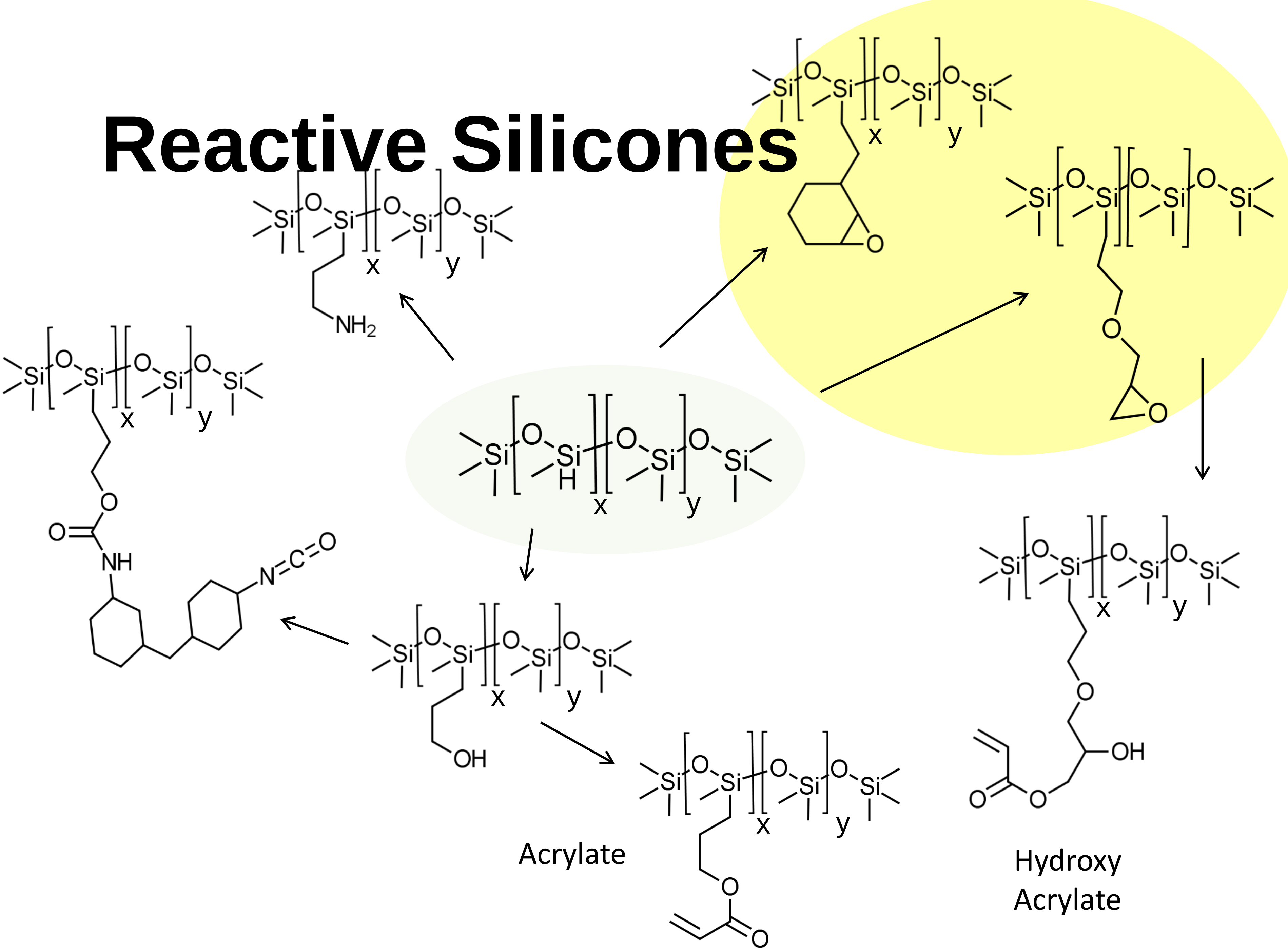
Abstract

- To increase the flexibility and elongation of silicone acrylate resins, we have explored both a formulated and modified polymer approach to include both urethane and silicone polymers into the matrix. These will be cured under UV and SLA 3D printed (UV Laser) conditions and their physical and mechanical properties will be evaluated in the context of SLA 3D printing.

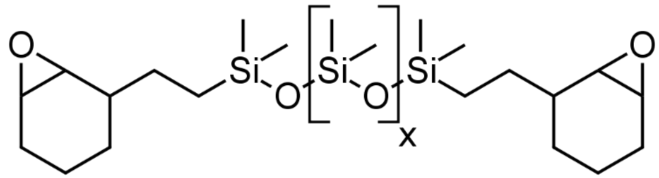
Elongation

- In condensation cured systems, reactive silicones provide up to 300 % elongation, but in energy cured acrylate systems, the reactive silicones typically give low elongation of around 5%. The new materials have shown elongation as high as 45%.

Reactive Silicones

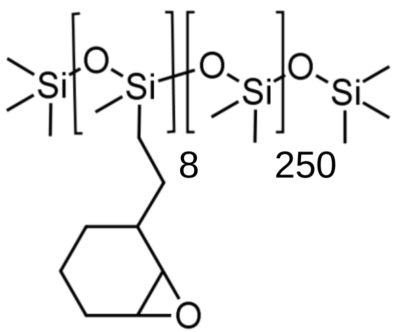


Epoxy Silicone System

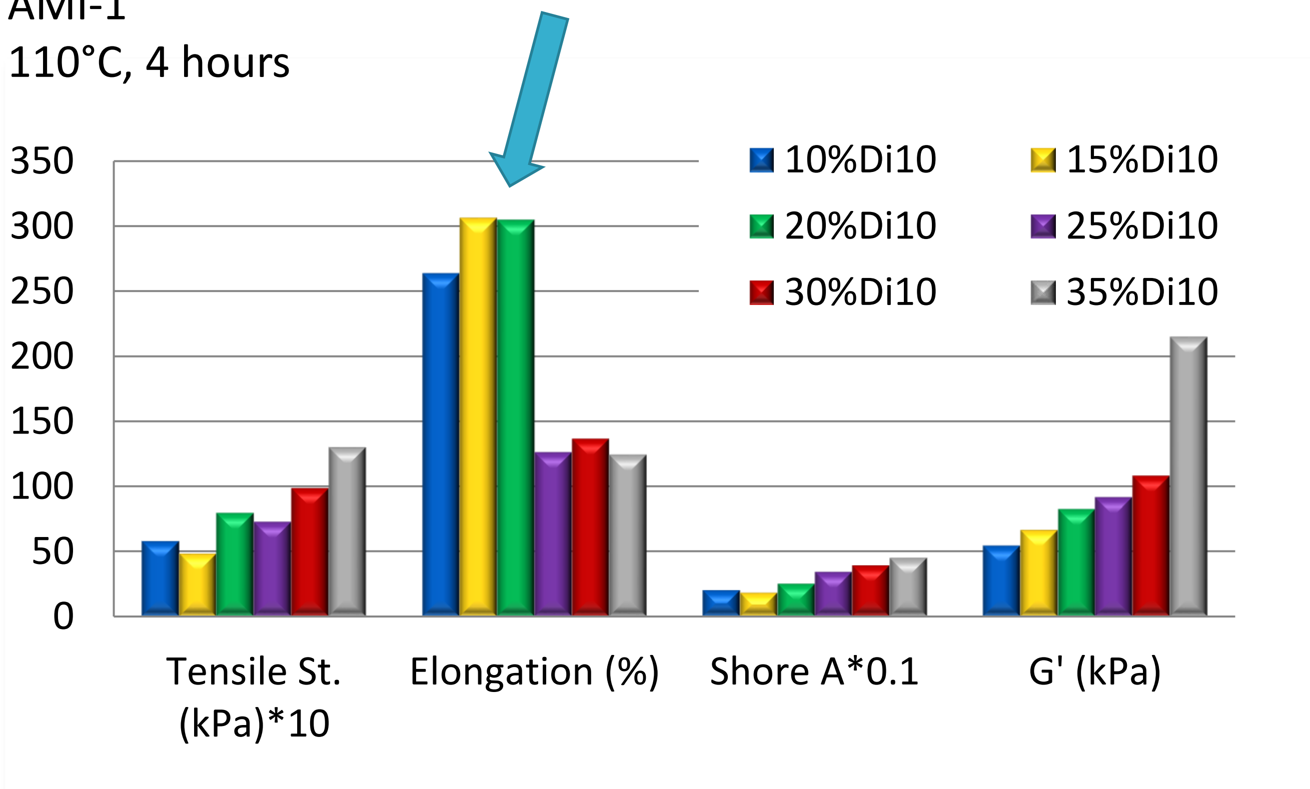


5-11% MHHPA
AMI-1
110°C, 4 hours

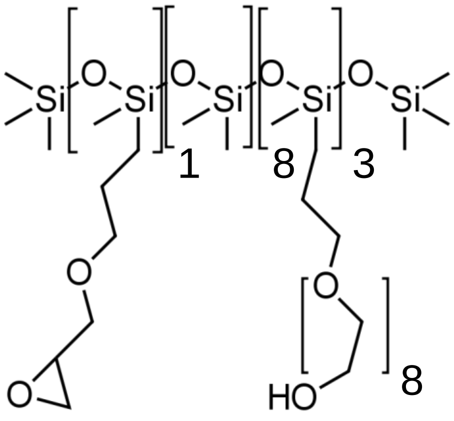
Linears
X=400 (20-34%)
X=10 (10-35%)



X-linker (8%)



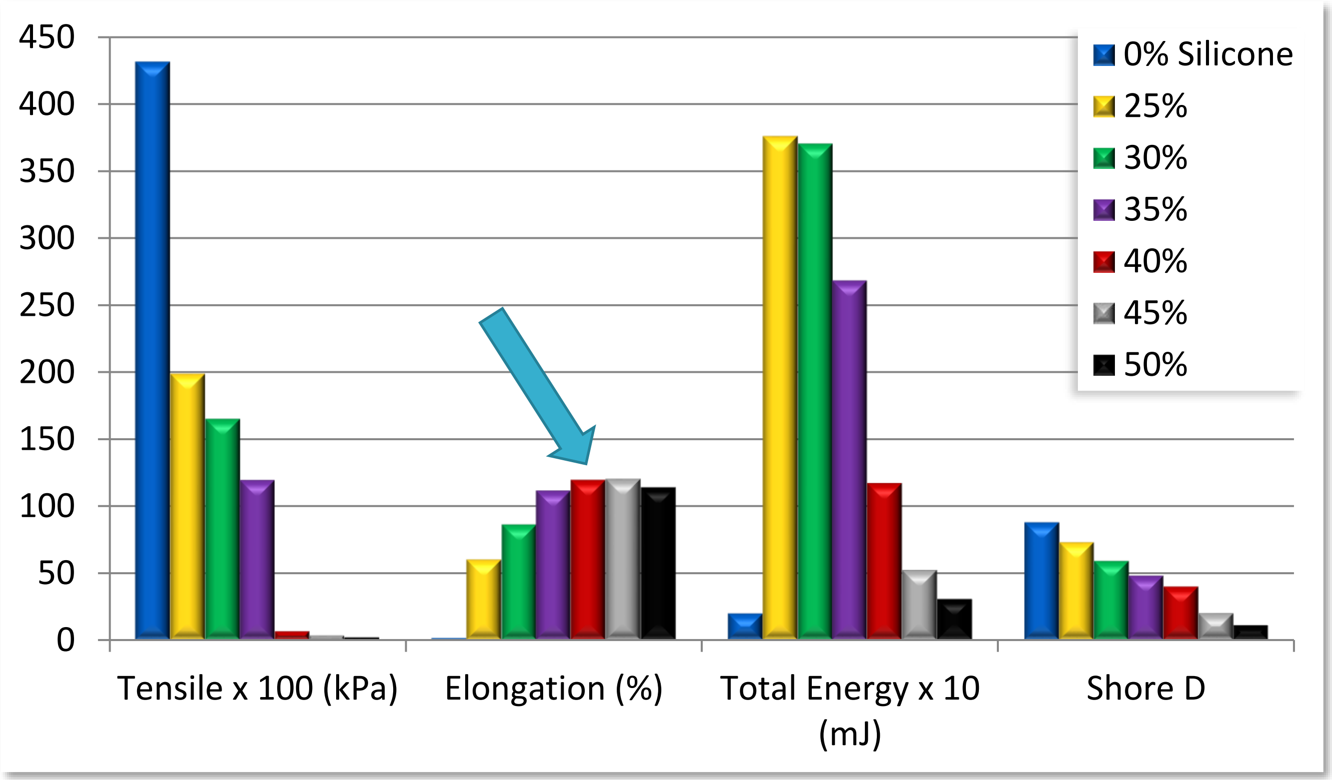
Silicone/ Organic Epoxy Hybrid System



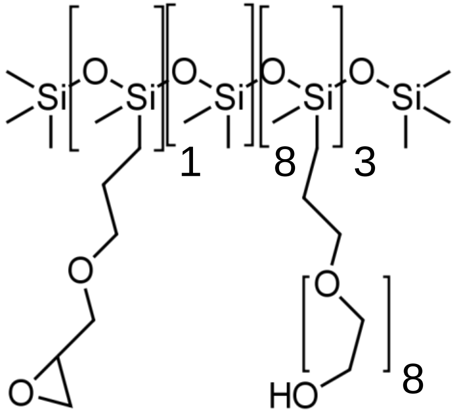
0-50%

→

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

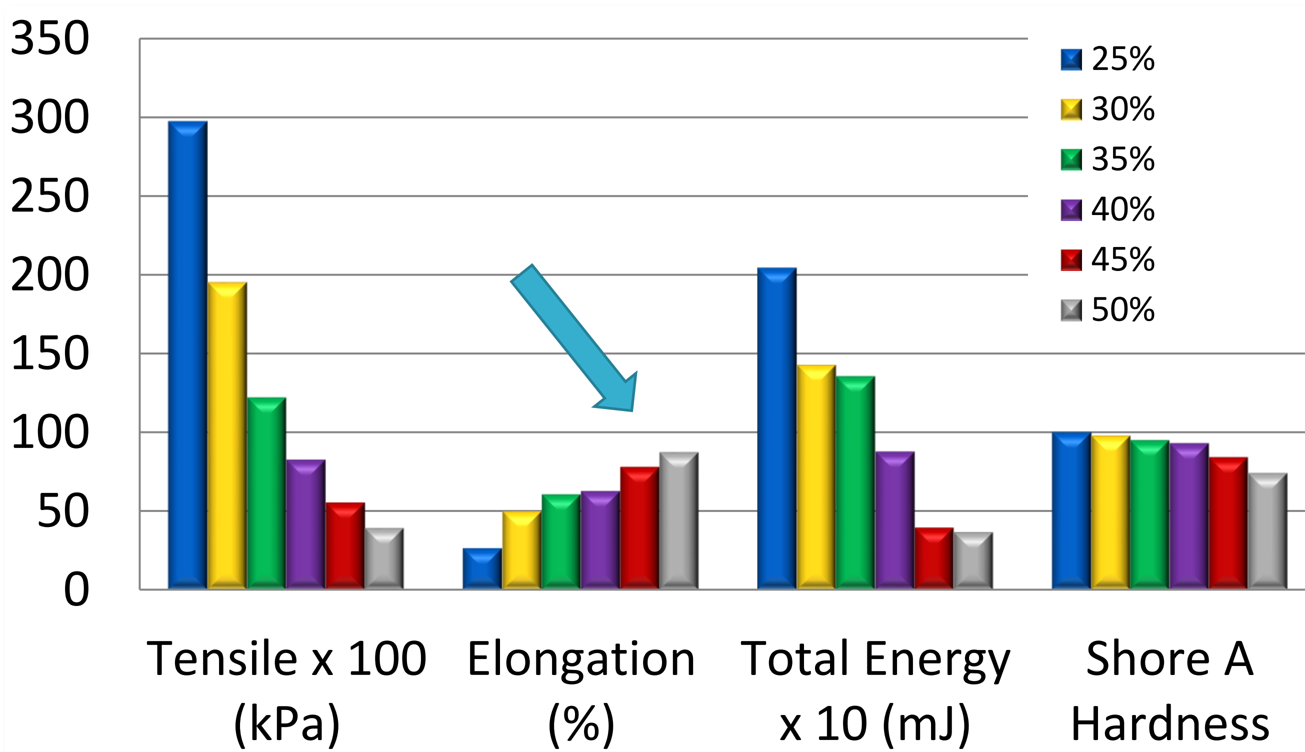


Silicone/ Organic Epoxy Hybrid System

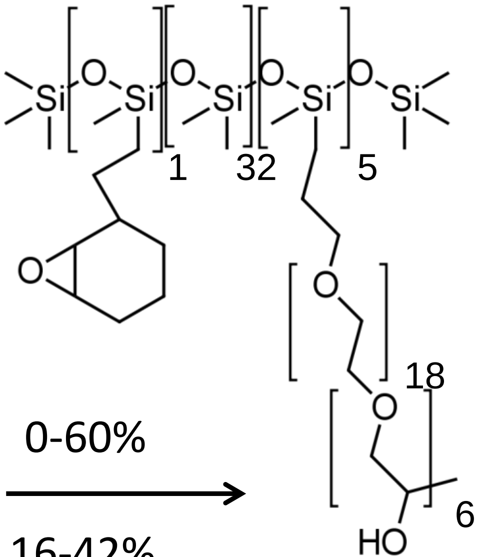


25-50%

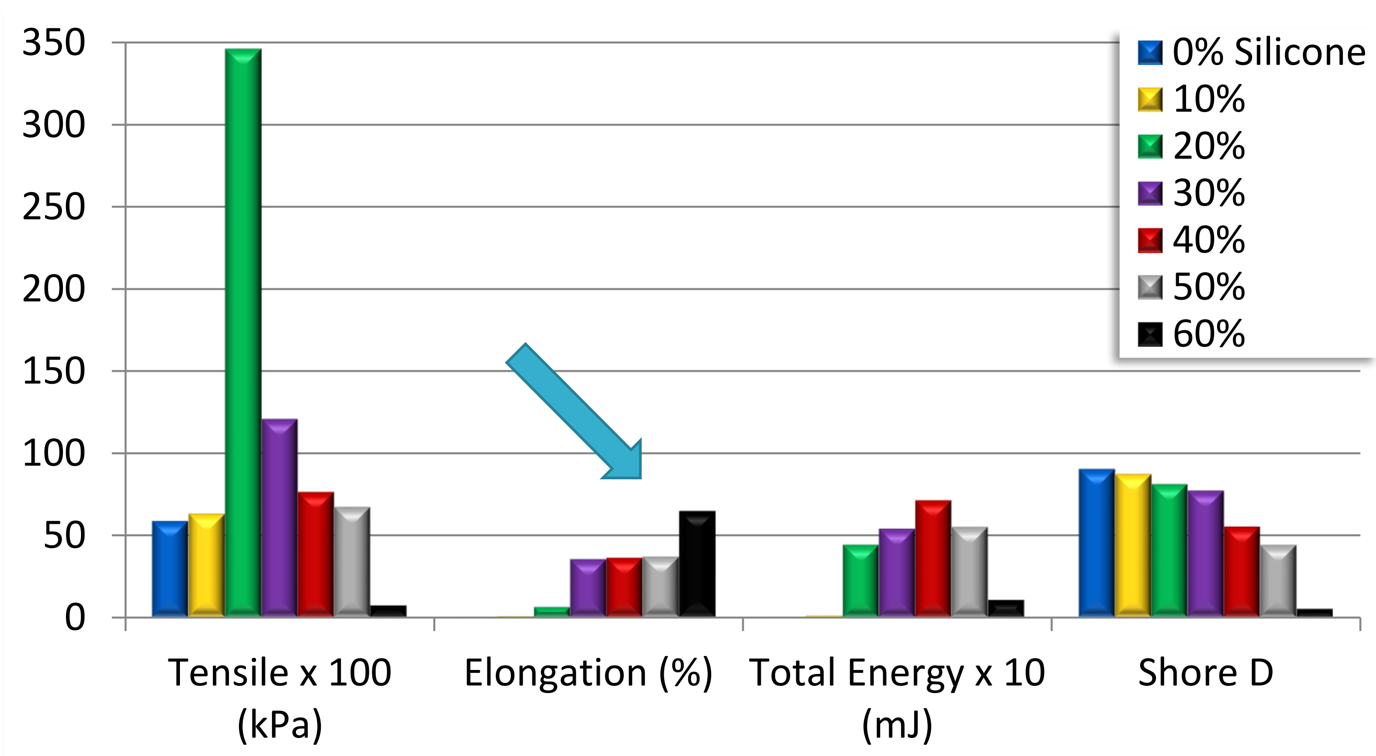
25-37% D.E.R. 331
25-37% MHHPA
1% AMI-1
0.2% reactive defoamer
110°C, 4 hours



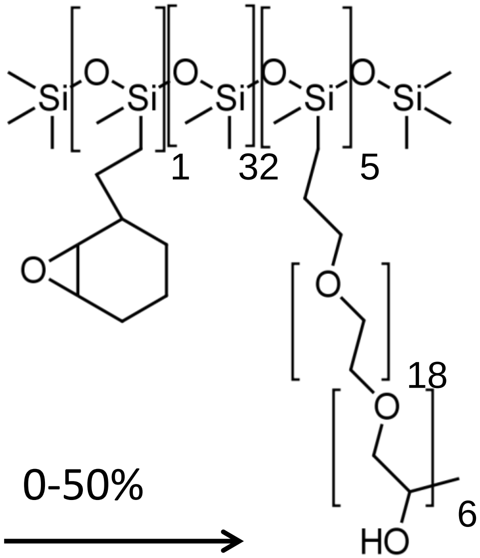
Silicone/ Organic Epoxy Hybrid System



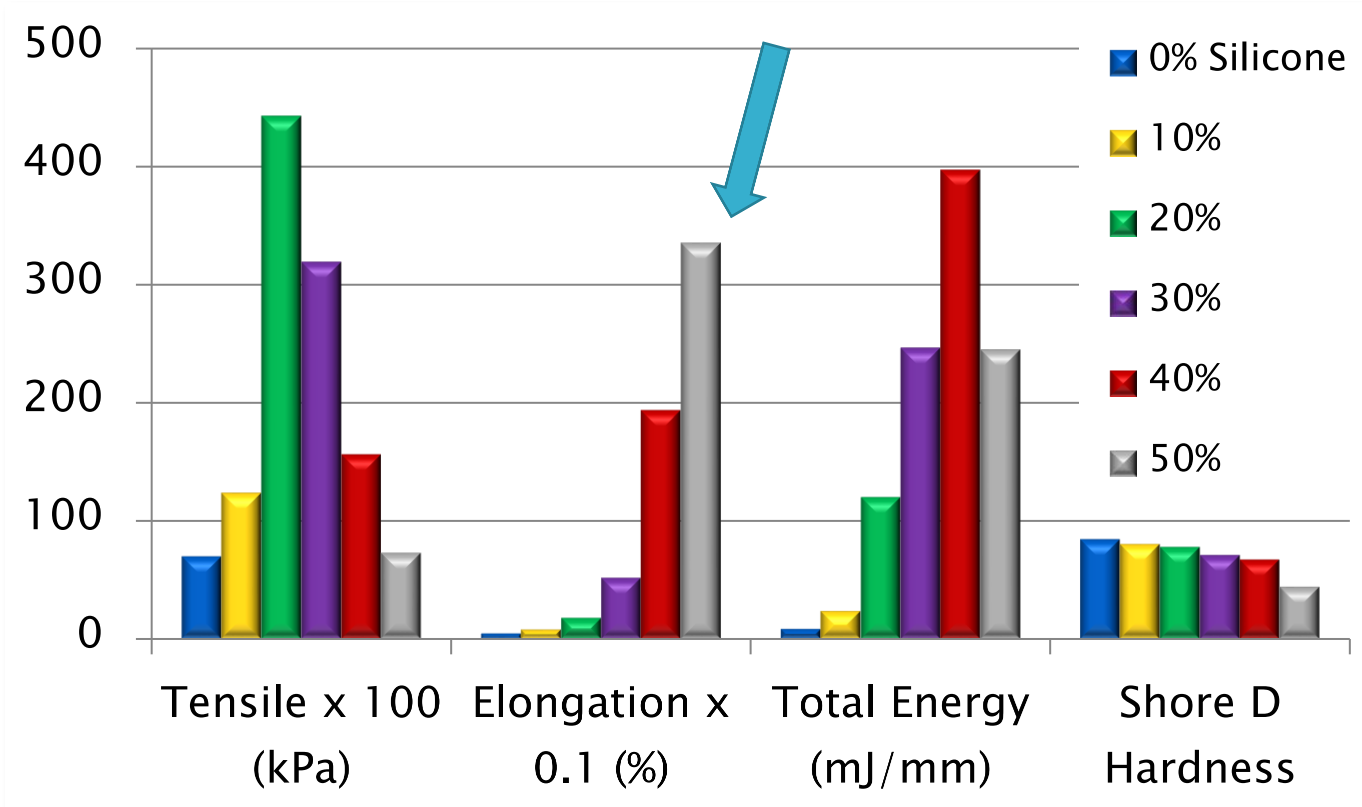
16-42% UVACURE 1500
24-58% MHHPA
1% AMI-1
110°C, 4 hours



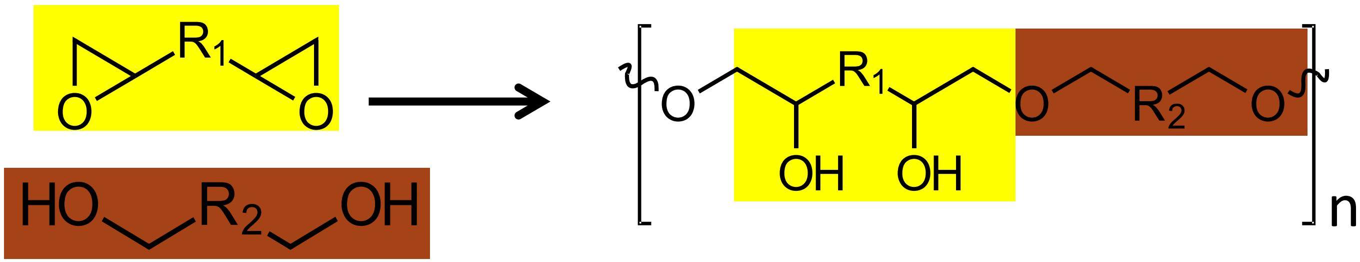
Silicone/ Organic UV Cured Epoxy Hybrid System

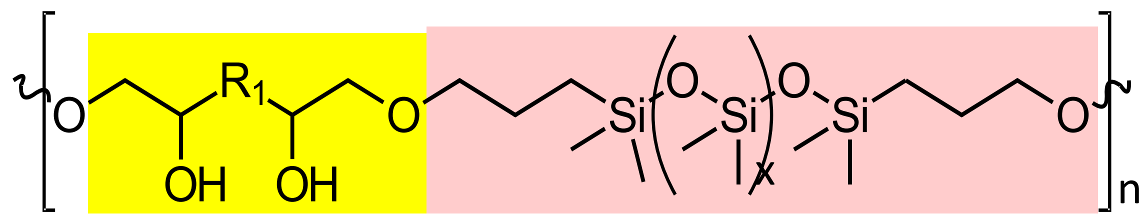


50-100 %
UVACURE 1500
UV 9380
UV light, RT



Polymers from Condensation Reactions

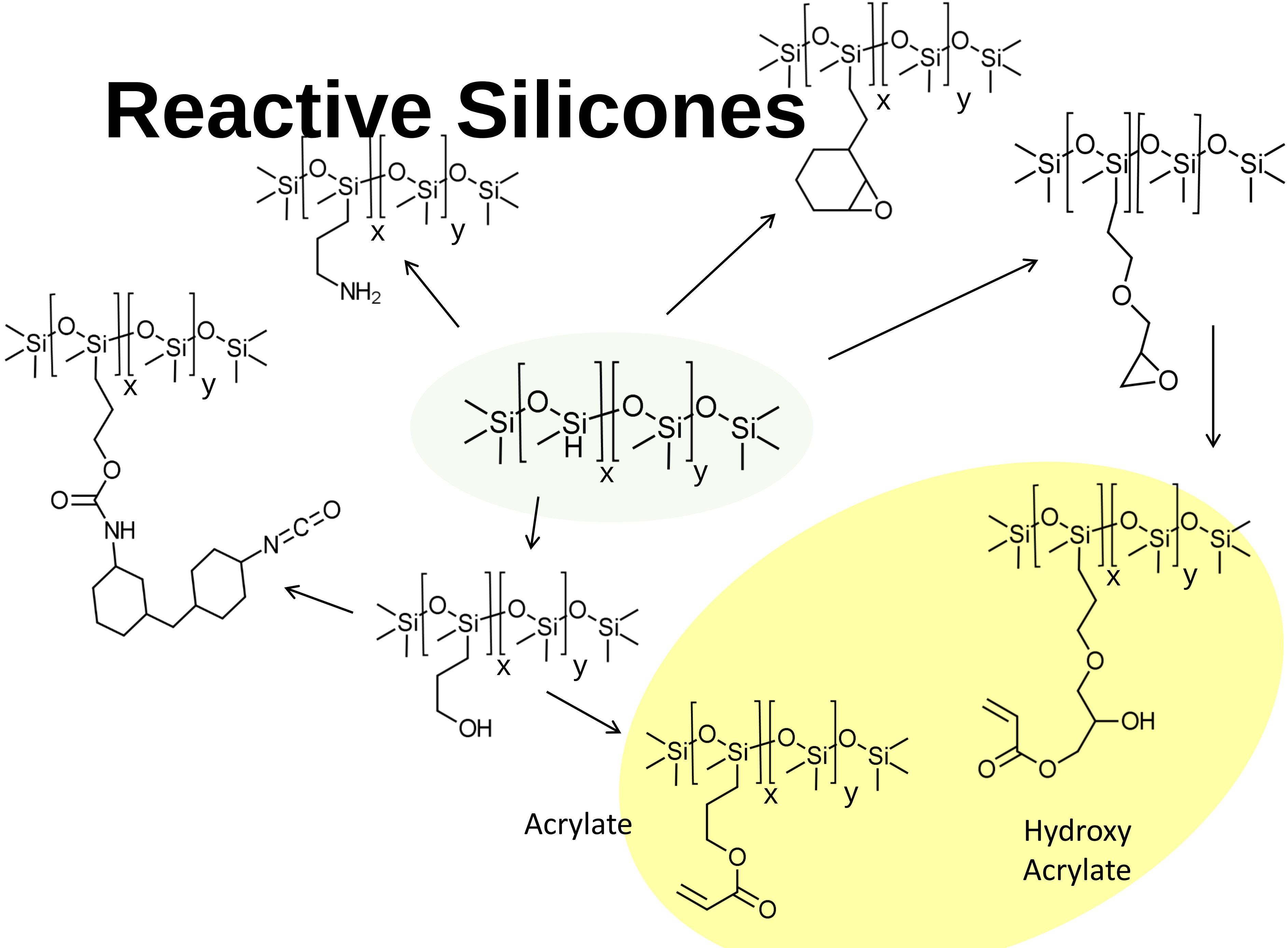




R_2 = hydroxyalkyl silicone

The flexible silicone is in the backbone

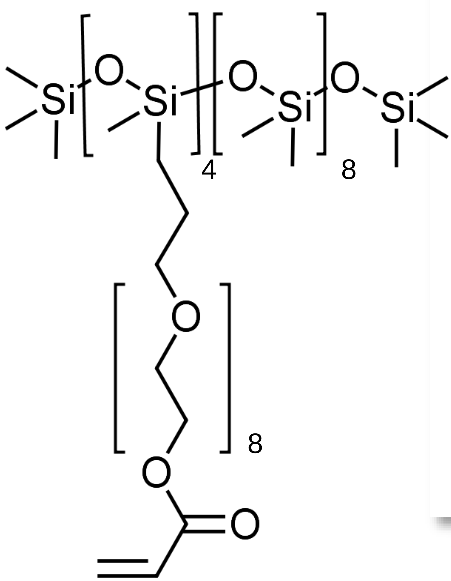
Reactive Silicones

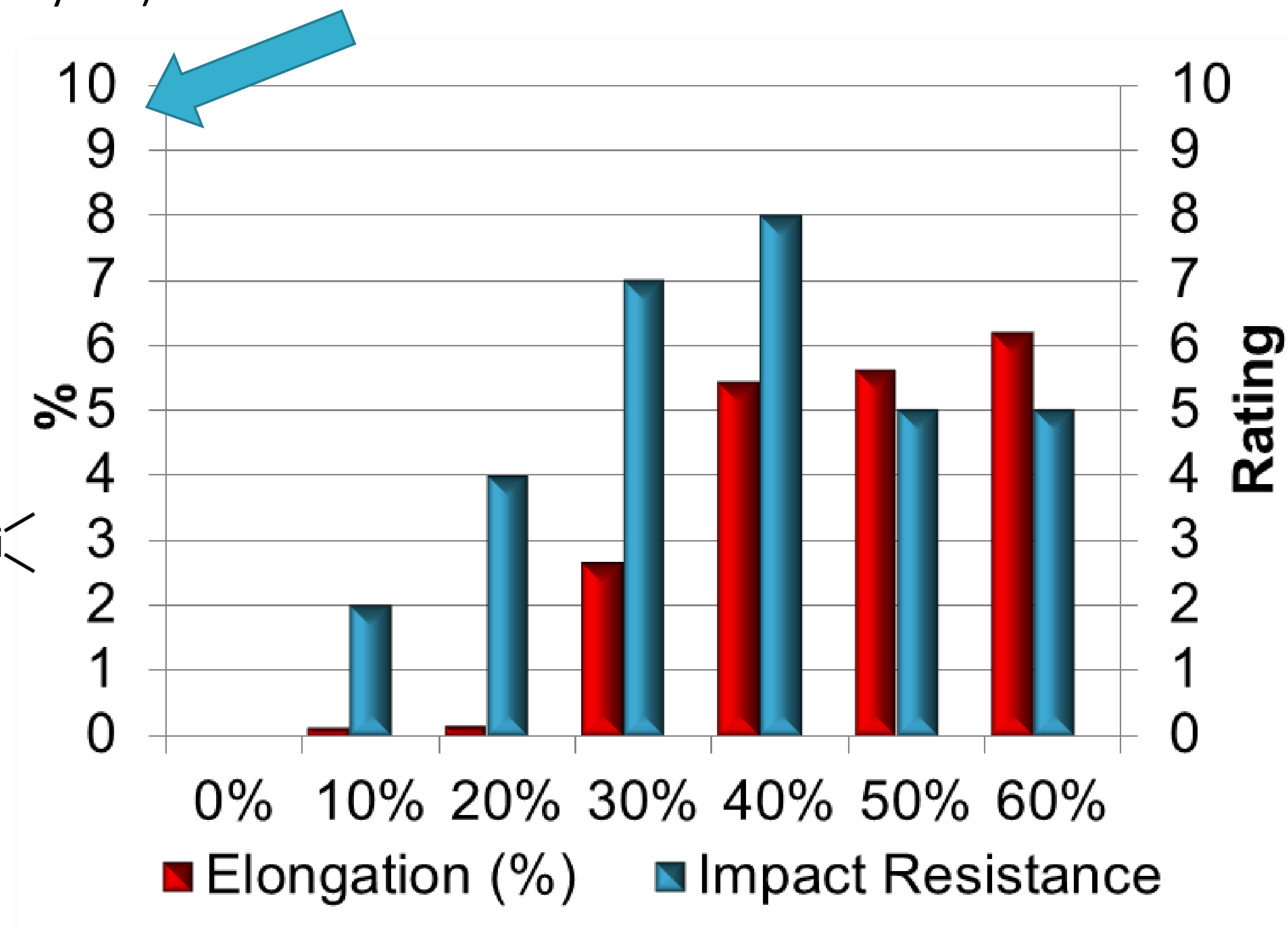


Acrylate Silicone UV coating

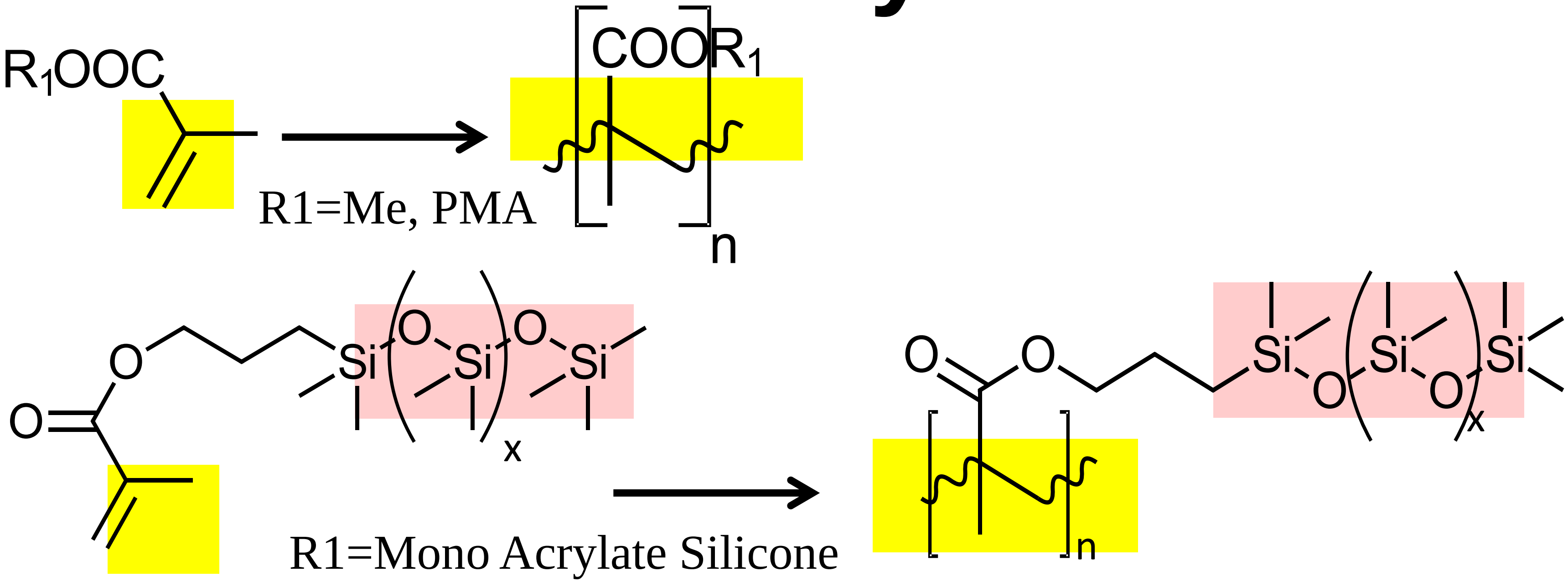
0-80% CN 102Z (Epoxy Acrylate)
13% CN 386 (Synergist)
5% Esacure TZT
1.5% Darocur 1173
0.5% reactive defoamer
UV light, RT

0-80% silicone



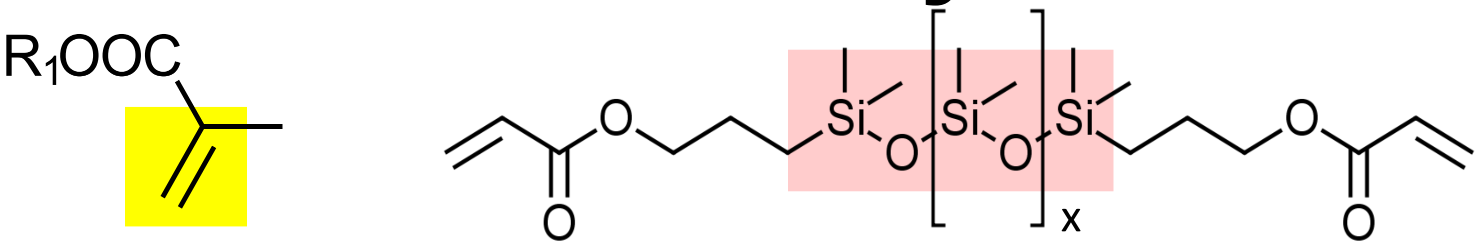


Free Radical Polymerization

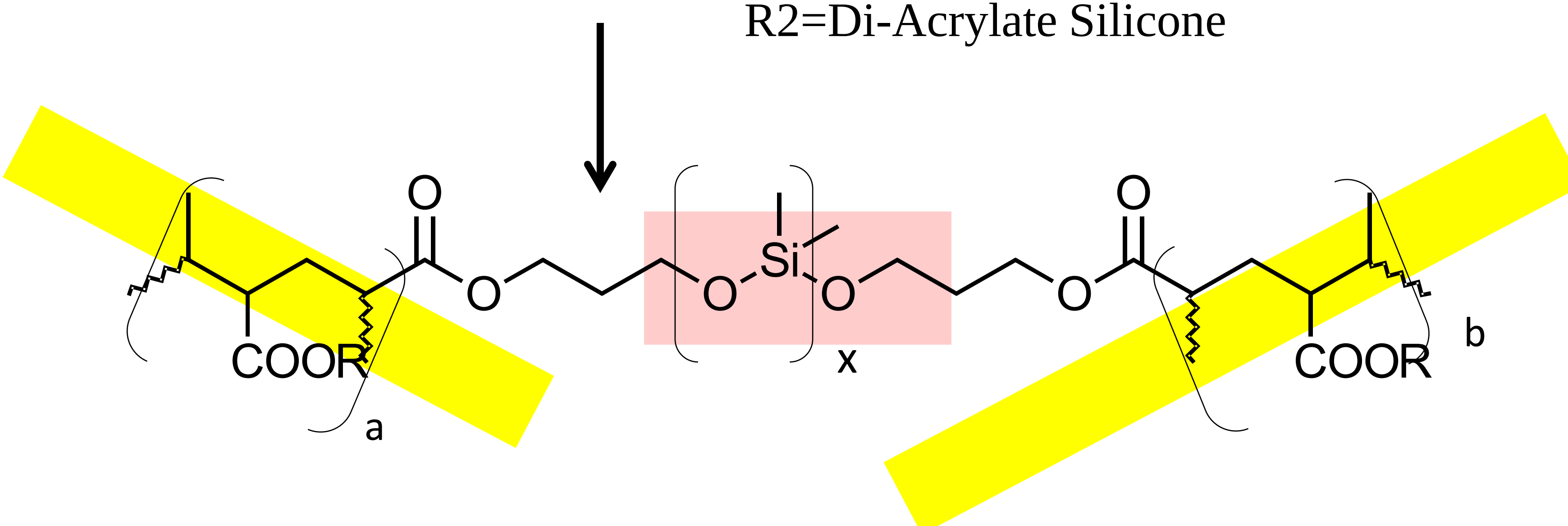


The flexible silicone is NOT in the backbone

Free Radical Polymerization

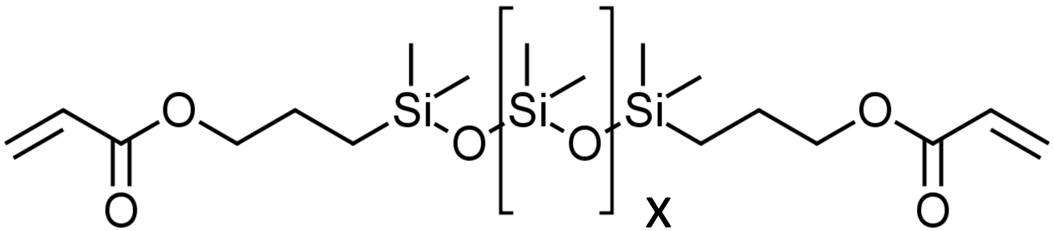


R2=Di-Acrylate Silicone



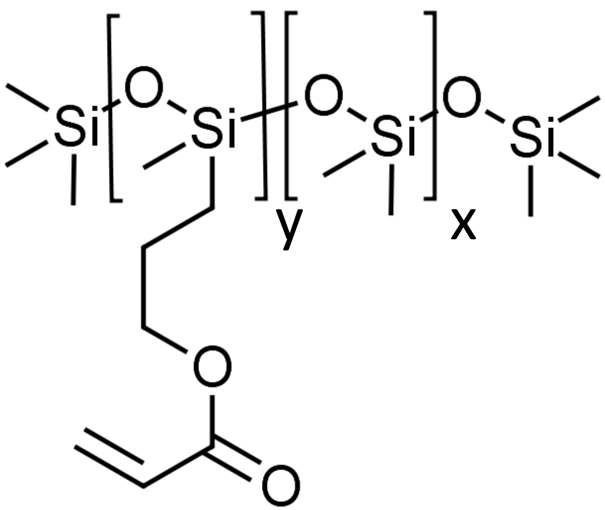
The flexible silicone is in the side chains

Silicone Structures Explored



Linear
(Extension)

Silmer ACR	Di-1010	Di-2010-D	Di-4515-O	Di-1018-F	D208	E608
Arch.	Linear				Pendant	
# ACR	2				2	3
MW	1300	2500	5000	2000	1000	3000



Pendant
(Cross-link)

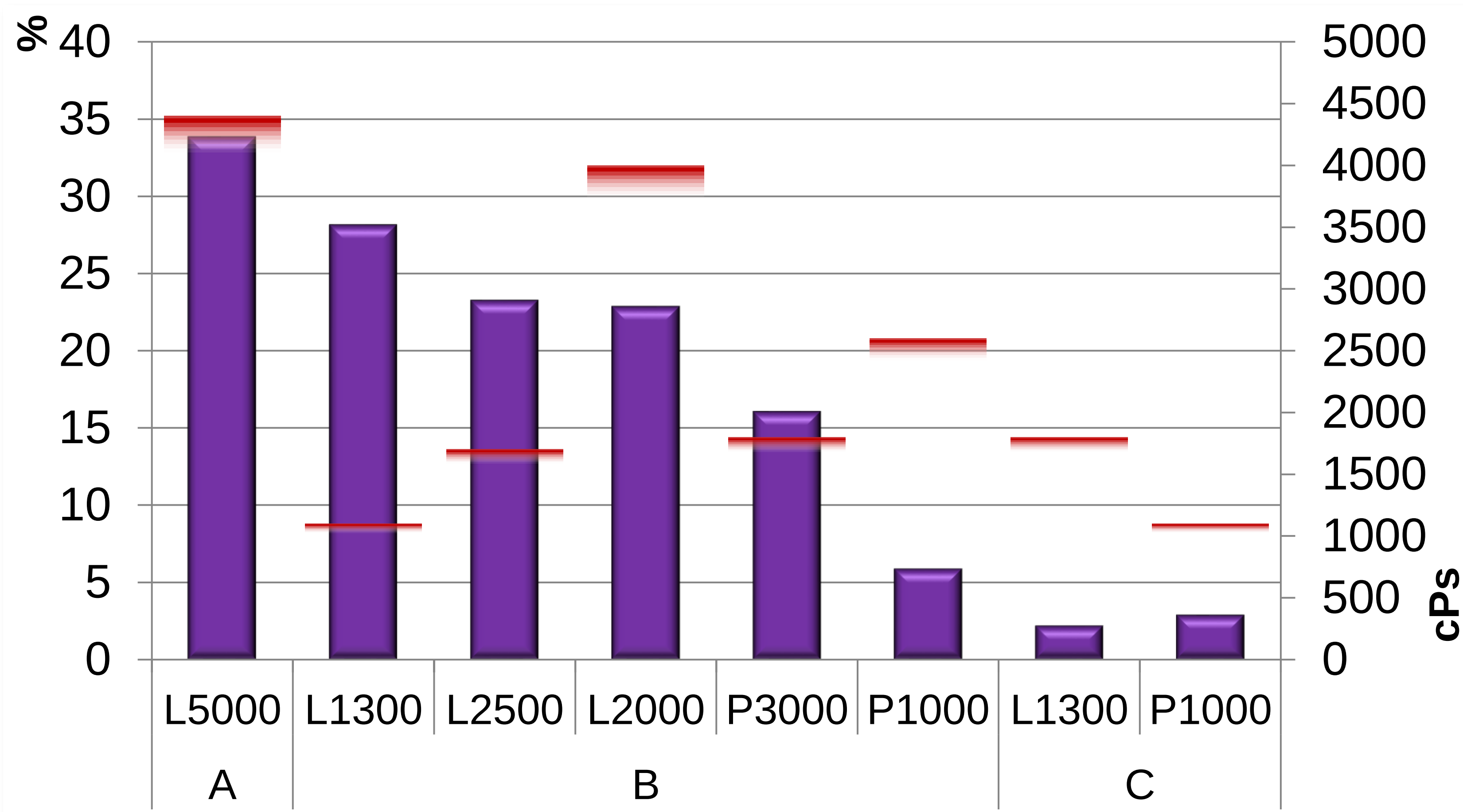
Formulation Approach

Component\Wt%	A	B	C
Laromer UA-9072	43%	43%	38%
Sartomer CN133	0%	0%	7.5%
Laromer LR-8887	14.36%	34.88%	6.5%
Laromer TBCH	20.52%	0%	16.5%
Silicone Additive	20%	20%	30%
TPO-L	1.22%	1.22%	1.0%
TZT	0%	0%	0.5%

Results

	20%						30%	
Silmer ACR	Di-4515-O	Di-1010	Di-2010-D	Di-1018-F	E608	D208	Di-1010	D208
Formulation	A	B					C	
Viscosity, cPs	4400	1100	1700	4000	1800	2600	1800	1100
G‘, Pa	9.72 E+5	1.45 E+6	7.48 E+5	5.57 E+5	1.62 E+6	1.04 E+6	2.06 E+6	2.30 E+6
G''‘, Pa	5.76 E+5	6.94 E+5	3.43 E+5	2.77 E+5	6.20 E+5	3.01 E+5	7.56 E+5	8.13 E+5
Tan Delta	0.591	0.478	0.451	0.488	0.386	0.288	0.370	0.464
Hardness, A	59	63	60	54	75	62	70	77
Peak Tens. Str., kPa	1748	1984	1566	1015	2113	1248	2193	1414
Elongation at Peak, %	33.9	28.2	23.3	22.9	16.1	5.9	2.2	2.9

Elongation and Viscosity



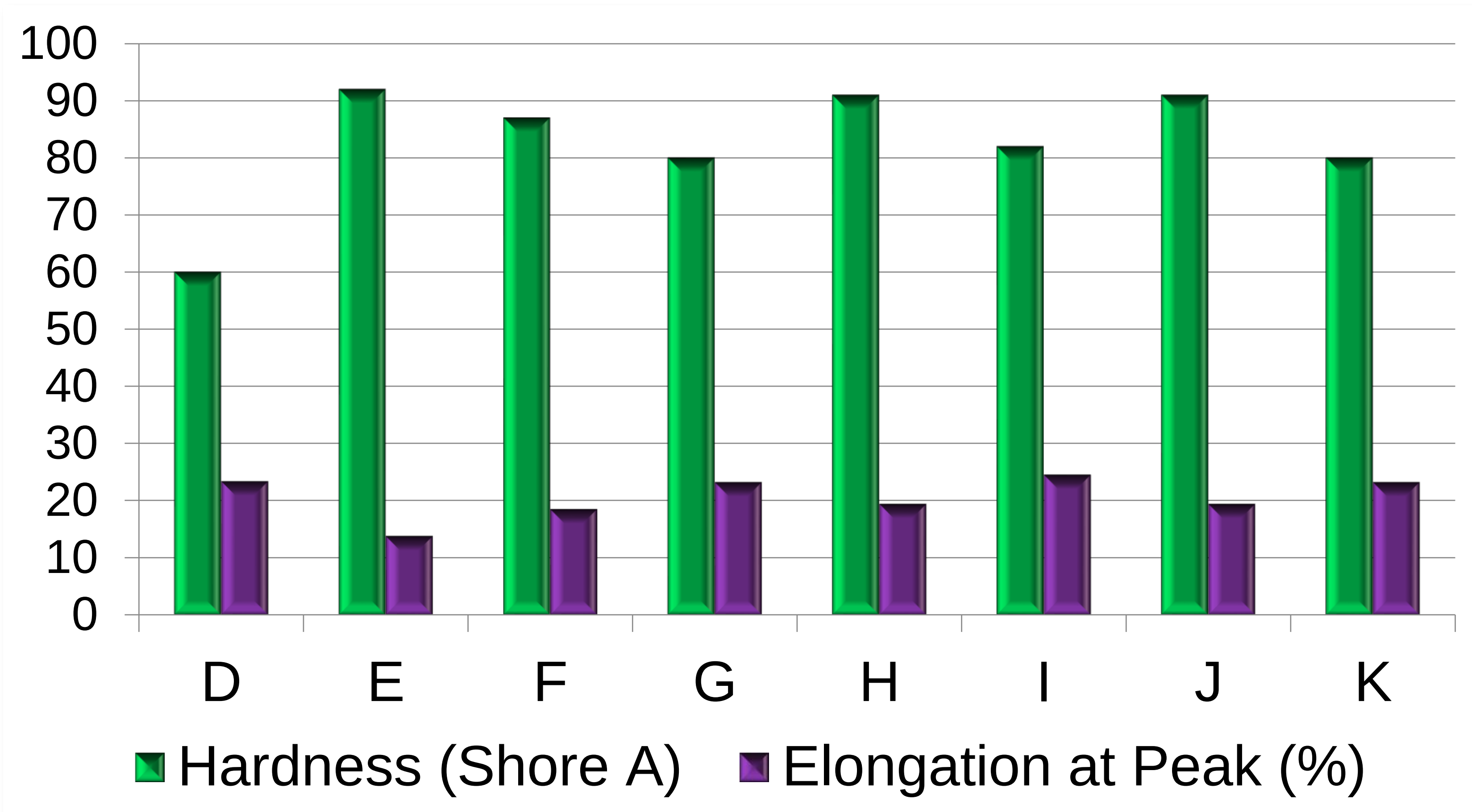
Optimize Formulation: ACR Di-2010-D

Component\Wt%	D	E	F	G	H	I	J	K
Laromer UA-9072	43.90%	43.90%	43.88%	34.33%	11.45%	22.89%	11.45%	34.33%
Sartomer CN991	0.00%	0.00%	0.00%	11.45%	34.33%	22.89%	34.33%	11.45%
Laromer LR-8887	34.88%	23.25%	26.15%	29.00%	29.00%	29.00%	29.00%	29.00%
SR833S	0.00%	11.63%	8.75%	4.00%	4.00%	4.00%	4.00%	4.00%
TPO-L	1.22%	1.22%	1.22%	1.22%	1.22%	1.22%	1.22%	1.22%
ACR Di-2010-D	20.00%	20.00%	20.00%	20.00%	20.00%	20.00%	20.00%	20.00%

ACR Di-2010-D Results

Properties	D	E	F	G	H	I	J	K
Viscosity	1700	2200	1800	2800	1000	3000	1000	2800
G`, Pa	7.48 E+5	1.31 E+7	7.47 E+6	1.28 E+6	1.21 E+6	2.95 E+6	1.21 E+6	1.28 E+6
G``, Pa	3.43 E+5	7.54 E+6	2.30 E+6	6.88 E+5	1.54 E+5	2.28 E+6	1.54 E+5	6.88 E+5
Tan Delta	0.451	0.245	0.318	0.290	0.121	0.443	0.121	0.290
Hardness, Shore A	60	92	87	80	91	82	91	80
Peak Tens. Str., kPa	1566	6791	6295	3474	5092	5081	5092	3473
Elongation at Peak, %	23.3	13.7	18.4	23.1	19.3	24.4	19.3	

Elongation and Hardness



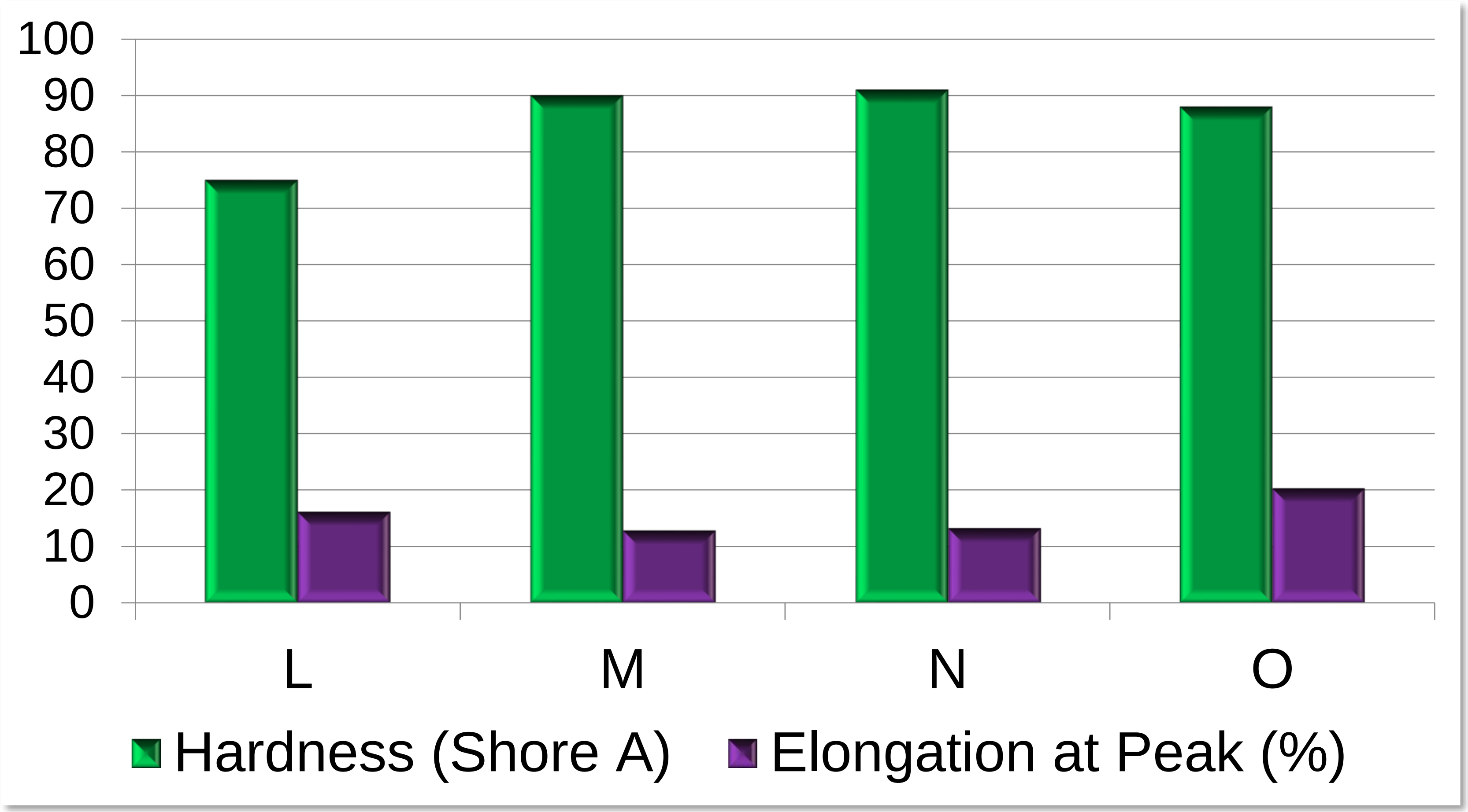
Optimize Formulation: ACR E608

Breakdown	L	M	N	O
Laromer UA-9072	43.90%	43.88%	0.00%	22.89%
CN991	0.00%	0.00%	45.78%	22.89%
Laromer LR-8887	34.88%	26.15%	29.00%	29.00%
SR833S	0.00%	8.75%	4.00%	4.00%
TPO-L	1.22%	1.22%	1.22%	1.22%
P3000	20.00%	20.00%	20.00%	20.00%

Results ACR E608

Properties	L	M	N	O
Viscosity, cPs	1800	1700	700	2200
G‘, Pa	1.62 E+6	1.29 E+5	6.84 E+6	1.33 E+6
G'‘, Pa	6.20 E+5	1.27 E+4	3.14 E+6	2.31 E+5
Tan Delta	0.386	0.102	0.537	0.176
Hardness, A	75	90	91	88
Peak Tens. Str., kPa	2113	4953	5707	7057
Peak Elongation, %	16.1	12.8	13.2	20.2

Elongation and Hardness



Summary to this point

- Within the viscosity range of 3D printing, our current silicones can provide elongation in the low 20%.
- Outside of the viscosity concerns we have achieved 33%.

Formulation Design of Experiments Approach

	UA9072	UA19T	P3000
P	29 (high)	26(Mid2)	17(low)
Q	29(high)	23(Low)	20(Mid)
R	26(mid2)	29(High)	17(Low)
S	23(low)	29(High)	20(Mid)
T	24(Mid1)	23(Low)	25(High)
U	23(Low)	24(Mid1)	25(High)
V	29(High)	26(Mid2)	17(Low)

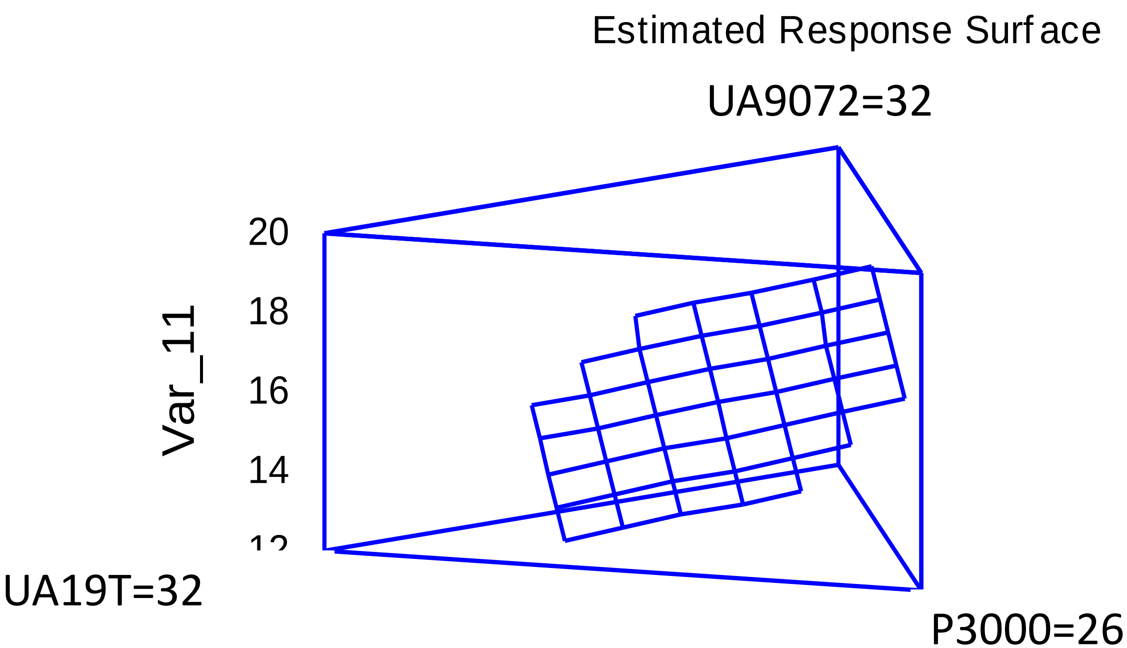
Formulations

	P,Q,R,S,T,U,V
UA9072	22.9-29.2%
UA19T	22.9-29.2%
P3000	16.7-25.0%
TBCH	19.8%
SR833S	5.2%
TPO-L	2.1%

Results

	P	Q	R	S	T	U	V
Viscosity, cPs	1400	1236	1417	1318	1207	1120	1374
G‘, (Pa)	1.11 E+7	8.30 E+6	9.39 E+6	1.08 E+7	6.86 E+6	9.35 E+6	1.40 E+7
G" (Pa)	1.90 E+6	2.04 E+6	1.46 E+6	2.05 E+6	1.55 E+6	2.55 E+6	2.32 E+6
Tan Delta	0.171	0.245	0.65	0.190	0.226	0.273	0.165
Cure Rate (Pa/s)	7.73 E+4	4.97 E+4	7.43 E+4	7.83 E+4	4.17 E+4	6.99 E+4	8.66 E+4
Hardness, (D)	40	35	34	34	38	34	37
Av. Tear Str. , N/mm	31.3	23.2	29.4	23.8	22.2	19.5	28.1
Max Tear Str., N/mm	31.3	23.2	29.4	23.8	22.2	19.5	28.1
Av. Tens. Str., kPa	9450	6588	8989	5627	5145	4584.	6947
Max Tens. Str., kPa	9450	6588	9627	6007	5497	4962	7154
Avg. Elong, %	18.9	19.7	16.7	12.4	15.3	14.6	11.8
Max Elong, %	18.9	19.7	18.5	13.5	16.0	15.9	14.2
Avg.Energy, J/m	22[illegible]	164	189	84	93	86	110
Max Energy, J/m	224	164	221	94	97	101	140

Results: Linear Models Fit to Elongation



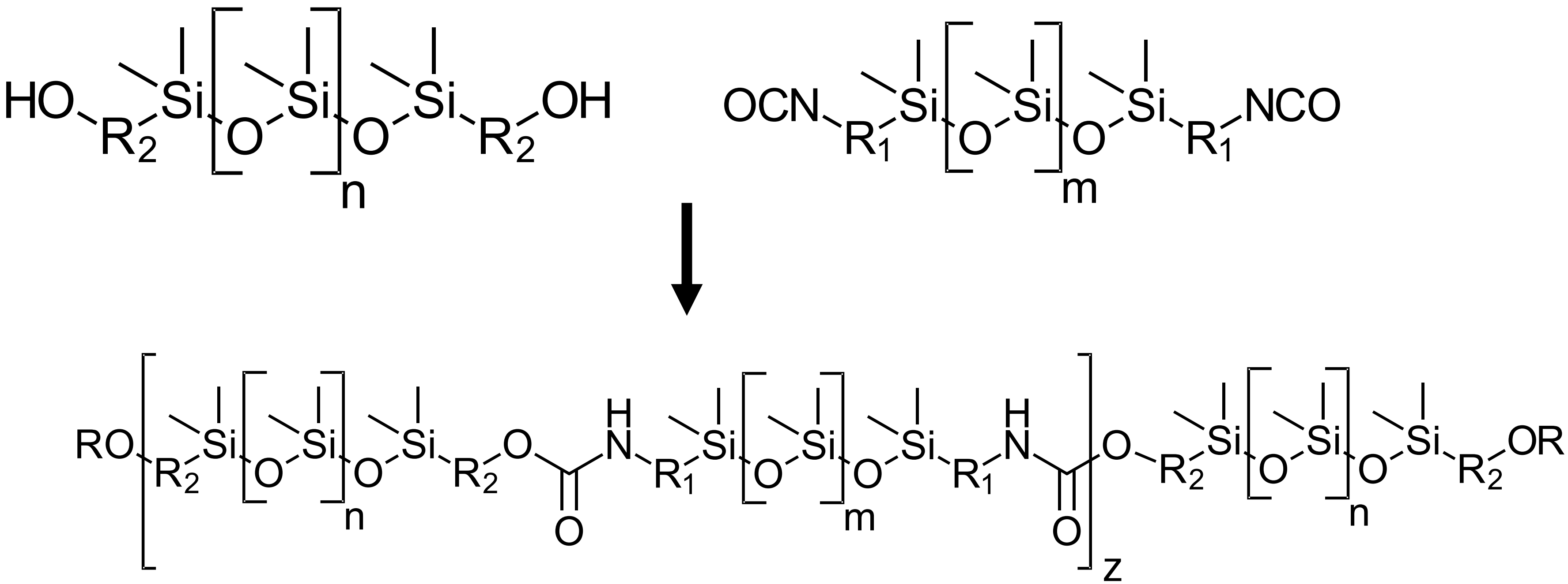
Correlations

Correlation with	ACR E608	UA9072	UA19T
Viscosity	-ve	null	null
G’	-ve	null	+ve
G”	+ve	-ve	null
Tan Delta	+ve	null	-ve
Hardness	null	+ve	null
Tear Strength	-ve	null	null
Tensile Strength	-ve	null	null
Elongation	**null**	+ve	-ve
Energy/thickness	-ve	+ve	null
Cure Rate	-ve	null	+ve

Summary of DOE

- UA9072 gives higher hardness, elongation, and toughness (total energy to break) and lowers G'' (Flexibility).
- UA 19T increases cure rate and G', lowers elongation and tan delta
- ACR E608 increases G" and tan delta. Flexibility. It does not strongly impact Elongation

Silicone Urethane Hybrid



New Silicone Properties

Silmer UACR	Di-10	Di-50	Di- 1010
Appearance	Waxy, melts at 40°C	Clear to hazy liquid	White pasty liquid
Viscosity, cPs	Solid	65,500	125,000

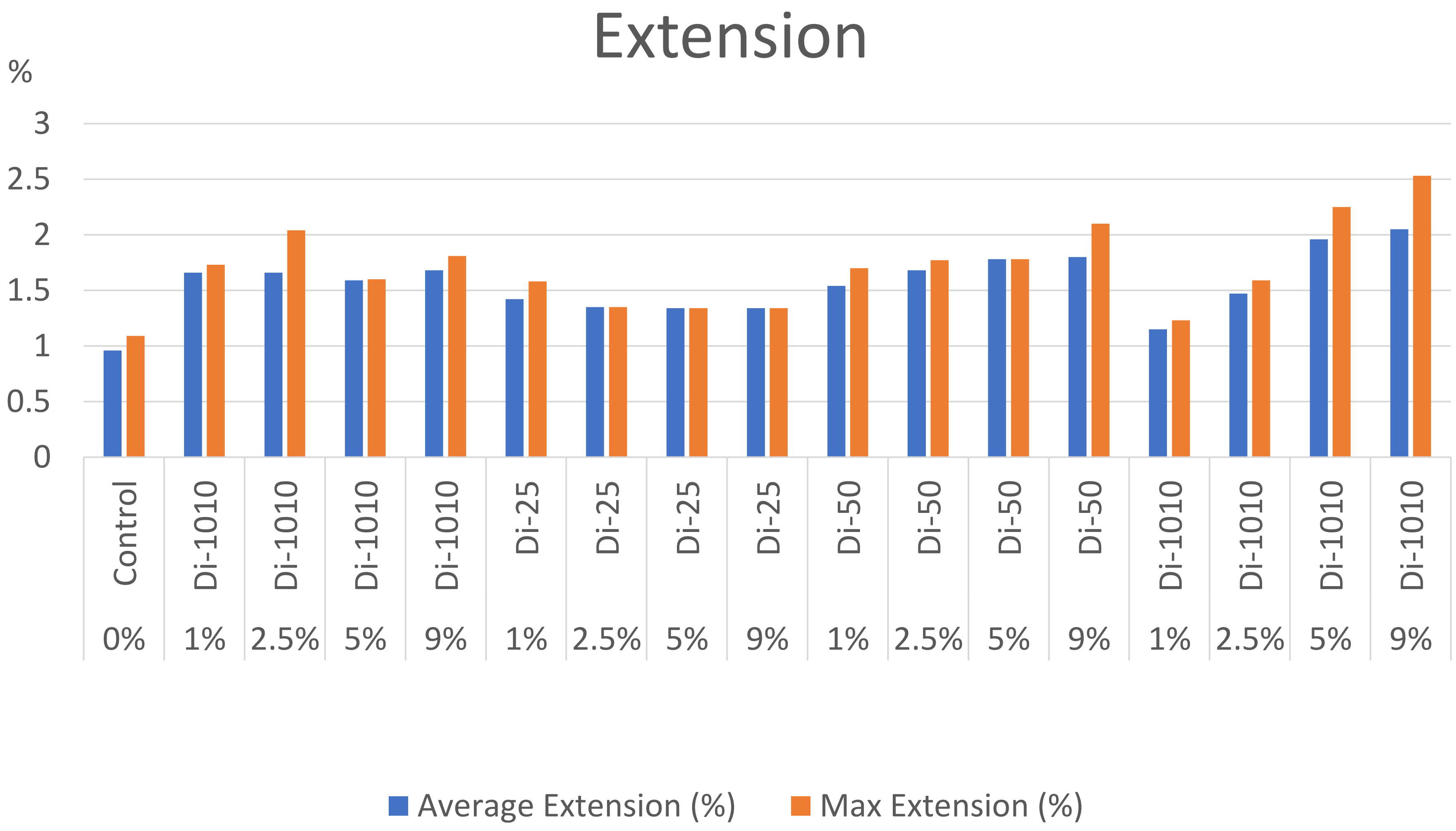
Test Formulation (A and B)

Ingredient	Control	1%	2.5%	5%	9%
Silmer UACR	0.00%	0.97%	2.40%	4.69%	8.96%
Acrylate Resin	98.36%	97.40%	96.00%	93.75%	89.55%
DMA	0.15%	0.15%	0.14%	0.14%	0.13%
MEKP	1.48%	1.46%	1.44%	1.41%	1.34%
Dabco T-12	0.02%	0.02%	0.01%	0.01%	0.01%

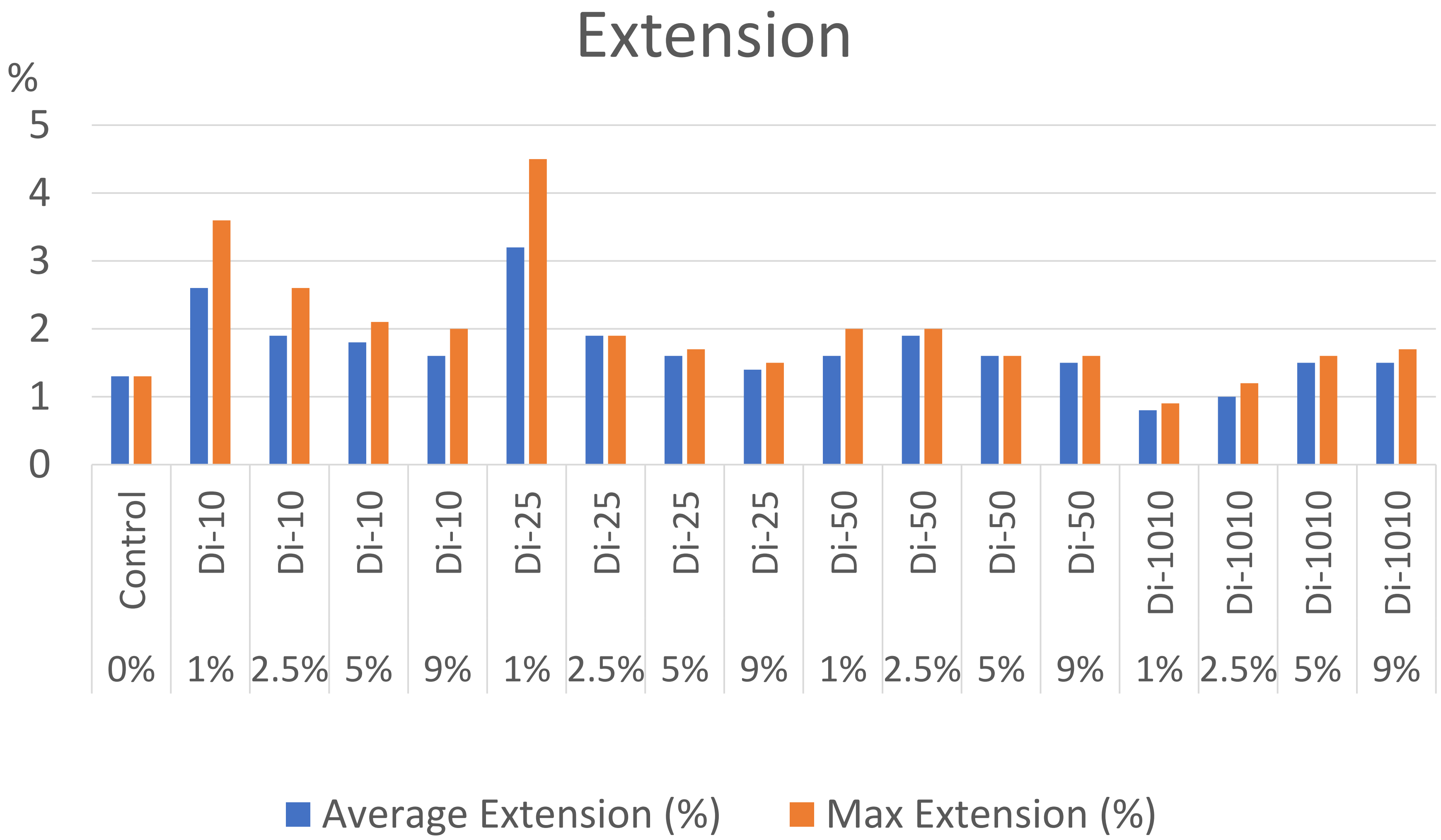
		Average Tensile Strength (kPa)	Max Tensile Strength (kPa)	Average Extension (%)	Max Extension (%)	Average Energy/ Thickness (J/m)	Tear Strength (N/M)	Flexure Stress (mPa)	Flexure Strain (%)	Bending Modulus (mPa)	Hardness (Shore D)
Control		8129	10773	1.3	1.3	very low	12.9	35.2	4.5	2130	48
UACR 50	1%	13794	22621	1.6	2.0	very low	23.2	55.2	4.9	2154	45
	2.5%	12705	12808	1.9	2.0	very low	53.2	52.5	5.2	1730	46
	5%	11058	12338	1.6	1.6	very low	52.7	51.3	5.3	1431	48
	9%	10190	10607	1.5	1.6	very low	50.6	50.8	5.6	1340	50
UACR 1010	1%	3874	4962	0.8	0.9	very low	20.4	48.9	4.8	1243	46
	2.5%	5001	6765	1.0	1.2	very low	36.3	88.3	8.6	1625	49
	5%	5134	6935	1.5	1.6	very low	25.9	90.8	8.2	1664	52
	9%	6963	8142	1.5	1.7	very low	22.8	91.3	7.4	1793	53

		Average Tensile Strength (kPa)	Max Tensile Strength (kPa)	Average Extension (%)	Max Extension (%)	Average Energy/ Thickness (J/m)	Tear Strength (N/M)	Flexure Stress (mPa)	Flexure Strain (%)	Bending Modulus (mPa)	Hardness (Shore D)
Control		8129	10773	1.3	1.3	very low	12.9	35.2	4.5	2130	48
UACR 10	1%	11700	12523	2.6	3.6	very low	26.0	58.4	3.9	1739	48
	2.5%	10482	10878	1.9	2.6	very low	29.3	64.9	7.0	1786	52
	5%	9797	10185	1.8	2.1	very low	29.8	69.3	6.0	1719	55
	9%	9028	10071	1.6	2.0	very low	29.7	77.0	5.5	1700	55
UACR 25	1%	13775	17026	3.2	4.5	very low	19.8	64.6	5.3	1569	52
	2.5%	10189	13189	1.9	1.9	very low	31.9	85.3	5.5	1893	55
	5%	9428	12365	1.6	1.7	very low	26.7	73.5	6.0	2122	58
	9%	7251	9045	1.4	1.5	very low	24.7	59.6	6.6	1340	60

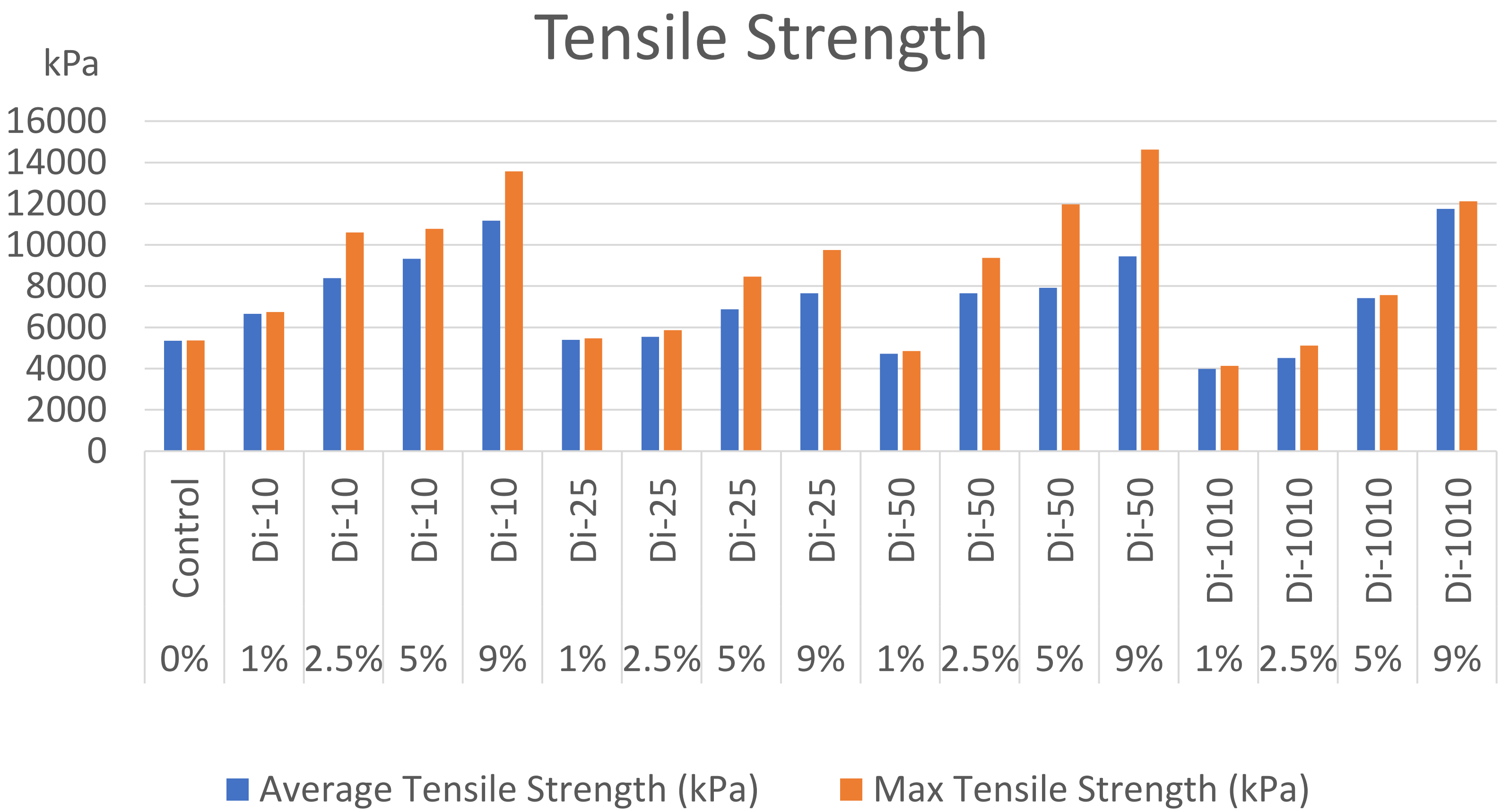
Acryate Resin A



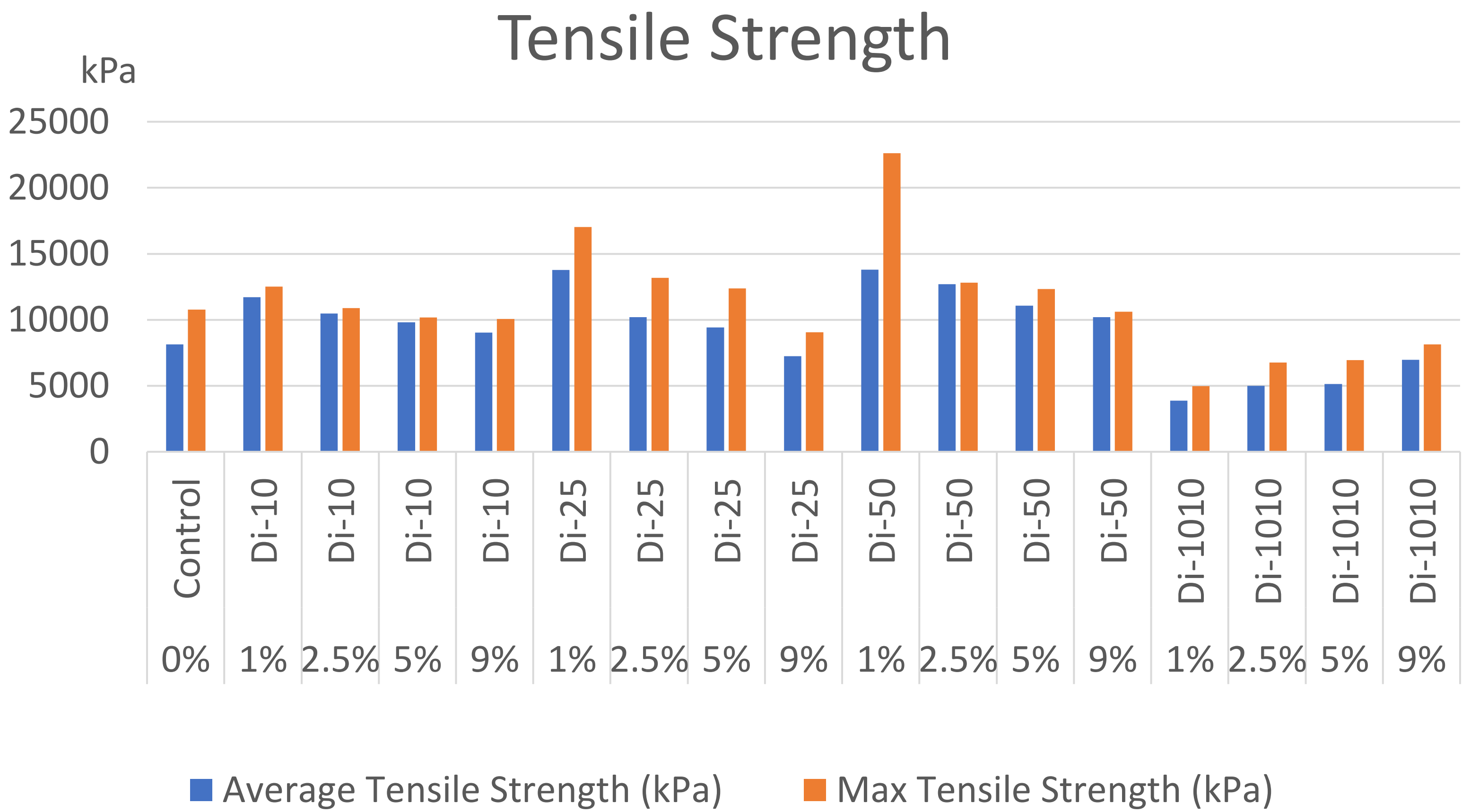
Acryate Resin B



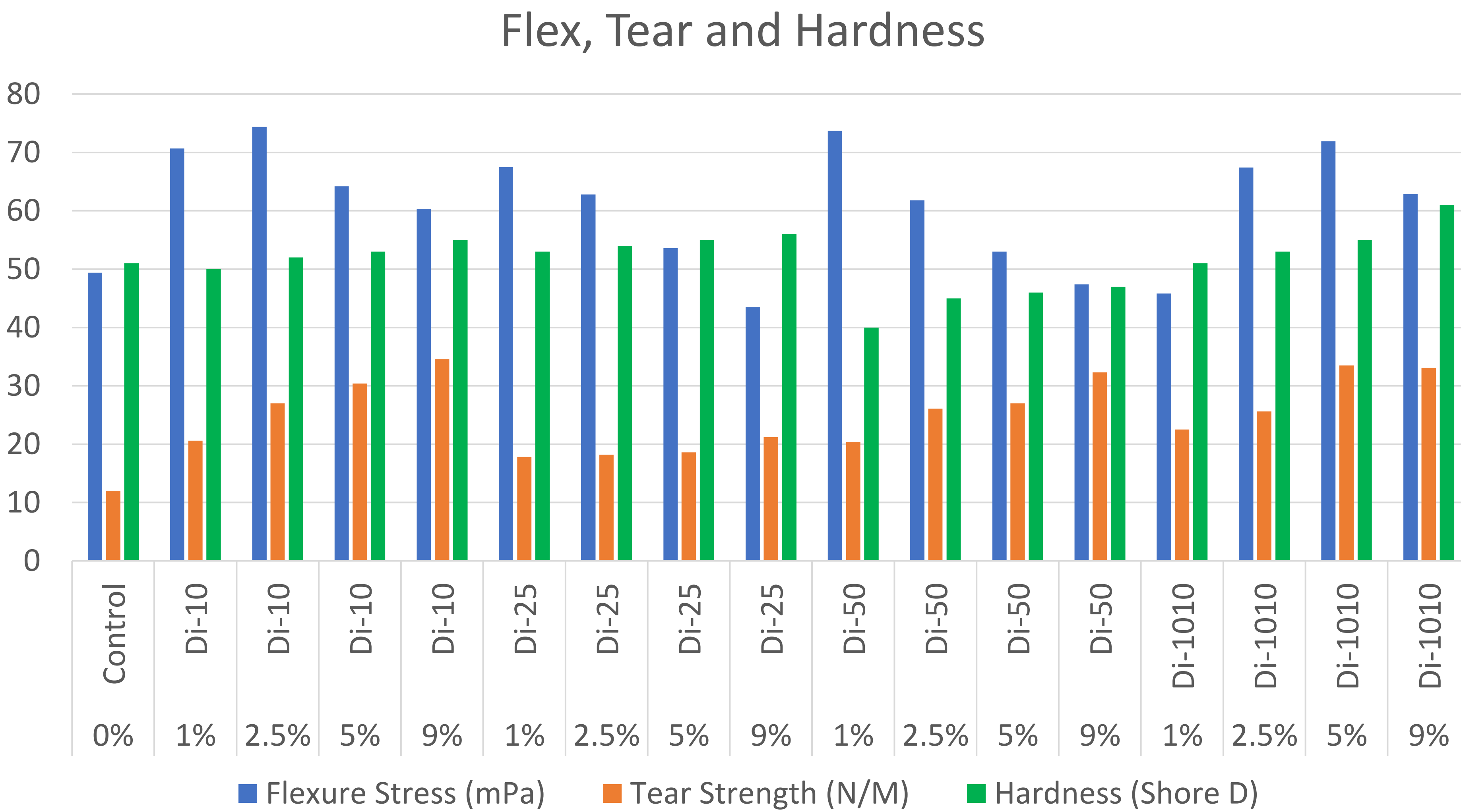
Acryate Resin A



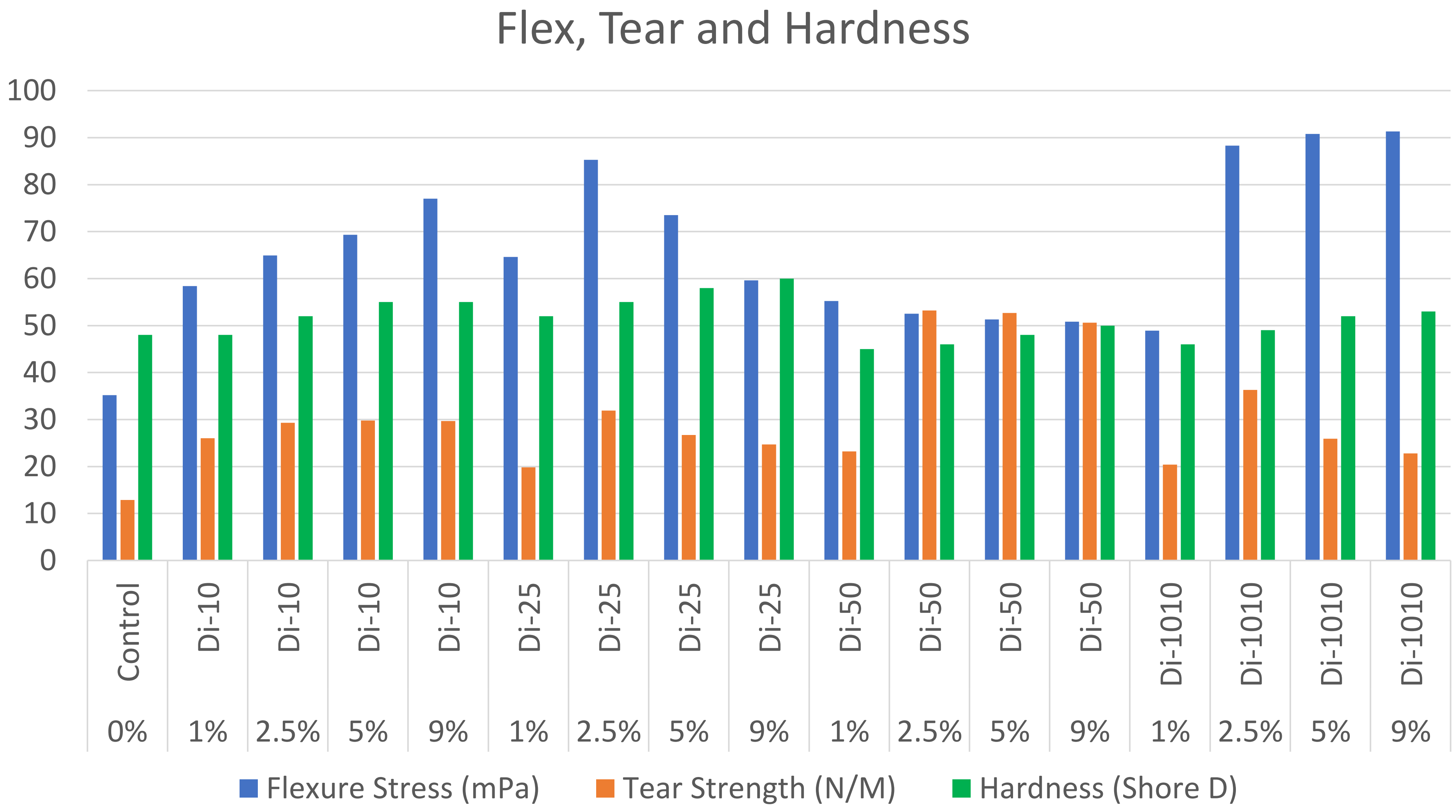
Acryate Resin B



Acryate Resin A



Acryate Resin B



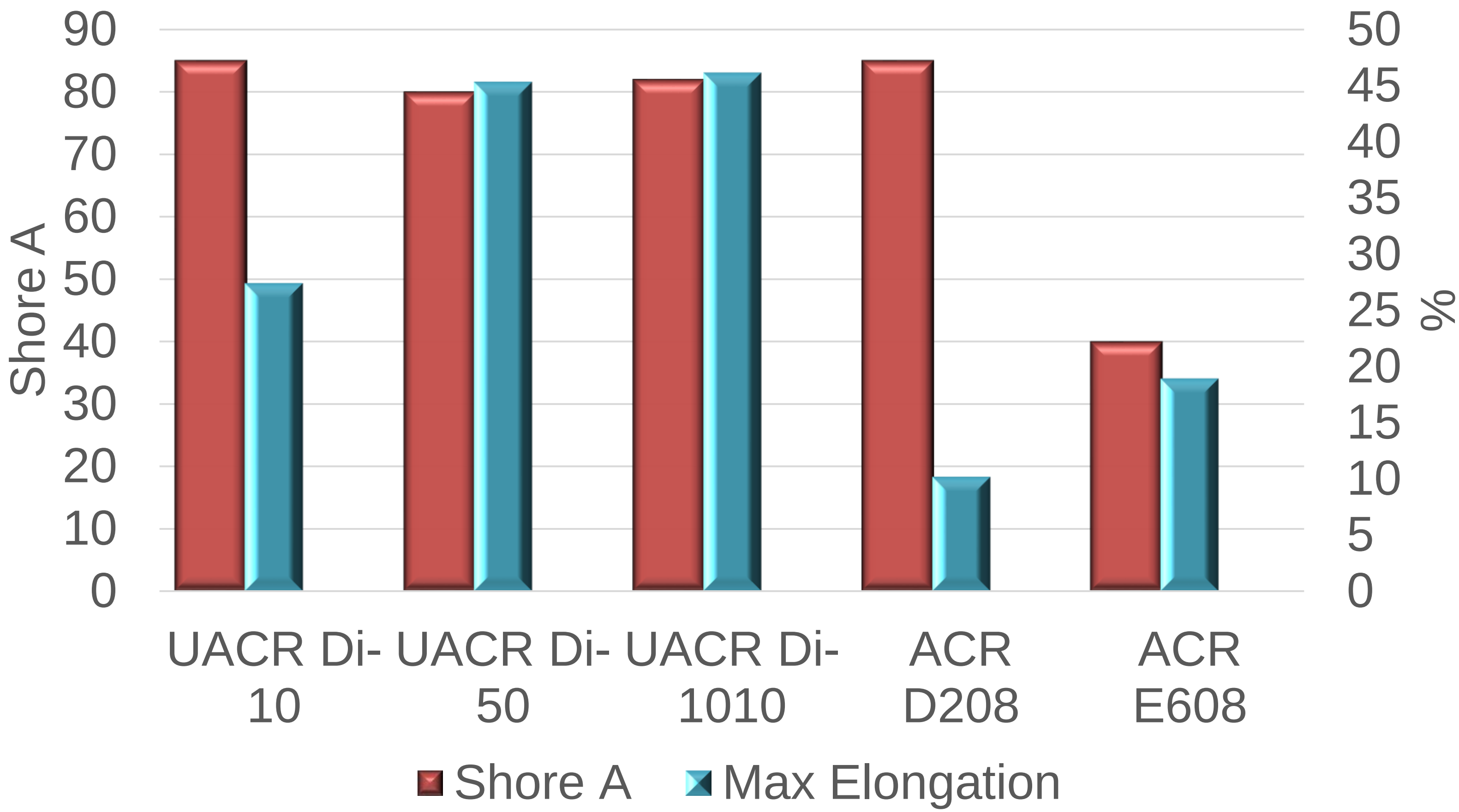
3D Printing Formulation

Ingredient	Level
Silicone	17.62%
UA 9072	30.84%
UA 9033	28.63%
V-Cap	20.93%
TPO-L	1.98%
Total	100.00%

Results

Silmer	UACR Di-10	UACR Di-50	UACR Di-1010	ACR D208	ACR E608
Viscosity, cps	4333	5700	4710	1095	1400
G‘, Mpa	8.13	5.02	6.05	18.76	11.12
G"‘, Mpa	3.21	1.67	2.10	7.02	1.90
Tan Delta	0.39	0.33	0.35	0.37	0.17
Cure Rate, kPa/s	51.5	33.9	44.3	197.1	77.3
Hardness, A	85	80	82	85	40
Avg. Tens. Str, kPa	7599	6211	5512	2837	9450
Max Tens. Str, kPa	8695	6620	5512	2837	9450
Avg Elongation, %	27.3	37.6	46.1	10.2	18.9
Max Elongation	27.4	45.3	46.1	10.2	18.9
Avg Unit Energy, J/m	292.53	320.90	308.71	39.18	224.28
Max Unit Energy, J/m	311.01	355.61	308.71	39.18	224.28
Tear Str., N/mm	35.2	48.3	26.1	31.6	31.3
Clarity, 1-10	9	2	5	9	6

Results



Shore A
90
80
70
60
50
40
30
20
10
0
50
45
40
35
30
25
20
15
10
5
0
%
UACR Di-10
UACR Di-50
UACR Di-1010
ACR D208
ACR E608
Shore A
Max Elongation

Conclusions on Hybrid

- The new products are high in molecular weight and not entirely soluble in the systems, as shown by the clarity results. While some interesting results are shown, the materials are difficult to work with in normal coatings systems.
- The tensile strength of the acrylate resin A is significantly improved with the hybrid silicone urethane materials.
- Both of these resins also show a significant increase in tear strength. In resin A there is a clear dose response, but in the B the effect is seen at low levels and holds as usage level is increased. The hybrid polymers all work similarly with the exception that the UACR Di-50 shows a strong advantage in tear strength with the B resin.

Conclusions on Hybrid

- Surprisingly, hardness seems to be increased with the use of the hybrid polymers which is the opposite of what is normally seen. The magnitude of the effect is small enough that it may not be significantly different from the control. However, another and perhaps more interesting way to state this is that hardness is not reduced as it is with other reactive silicones.
- Elongation appears to be improved with the new polymers and shows a dose response. However, these resins are designed to minimize extension and the effect is again so small that it is unconvincing.

Conclusions on Hybrid

- Finally examining the 3D printed formulation, which we spent significant effort optimizing for maximum elongation achieving 10-20. All three of the hybrid polymers evaluated in this system showed much higher elongation than the reactive silicone controls. The UACR Di-1010 gave 46% elongation which is great for a free-radical system.
- Hardness and strength seem to be retained with these new products in this system as well.

Conclusions

- Formulation Variations can get us to 33% elongation
- A new class can deliver 45%


Thank
You