

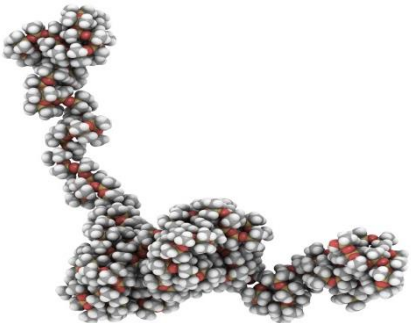
REACTIVE SILICONES HOMOPOLYMERIZED AND COPOLYMERIZED WITH ORGANIC POLYMERS

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Siltech Corporation
Toronto, ON Canada

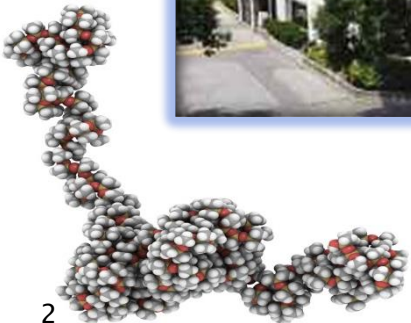


Siltech Background

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



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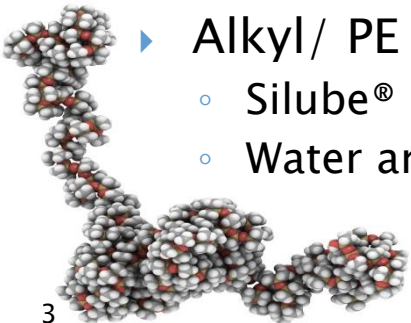
Chemically Modified Silicones

Silicone w/ Organic Nature offer improved solubility

- ▶ Polyether
 - Silsurf®
 - Soluble in water, ketones, aromatics, halides, esters.
- ▶ Alkyl, Aryl
 - Silwax®
 - Silube®
 - Soluble in hydrocarbons
- ▶ Fluorocarbon
 - Fluorosil®
 - Soluble in fluoro materials
- ▶ Alkyl/ PE
 - Silube®
 - Water and Oil Emulsifiers

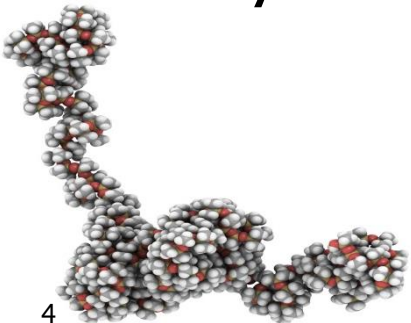
Silicone w/ Special Groups

- ▶ Primary, tertiary and PE Amines
 - Silamine®
- ▶ Quaternary amines
 - Silquat®
- ▶ Phosphate, carboxylates
 - Silphos®
- ▶ Anionic/Cationic Complexes
 - SilPlex®
- ▶ Reactive Silicones
 - Silmer®

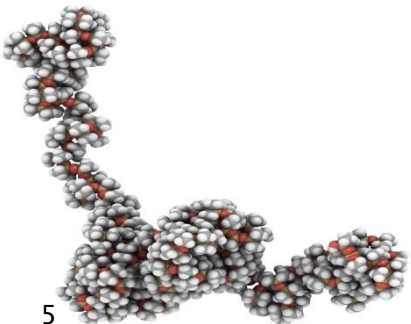
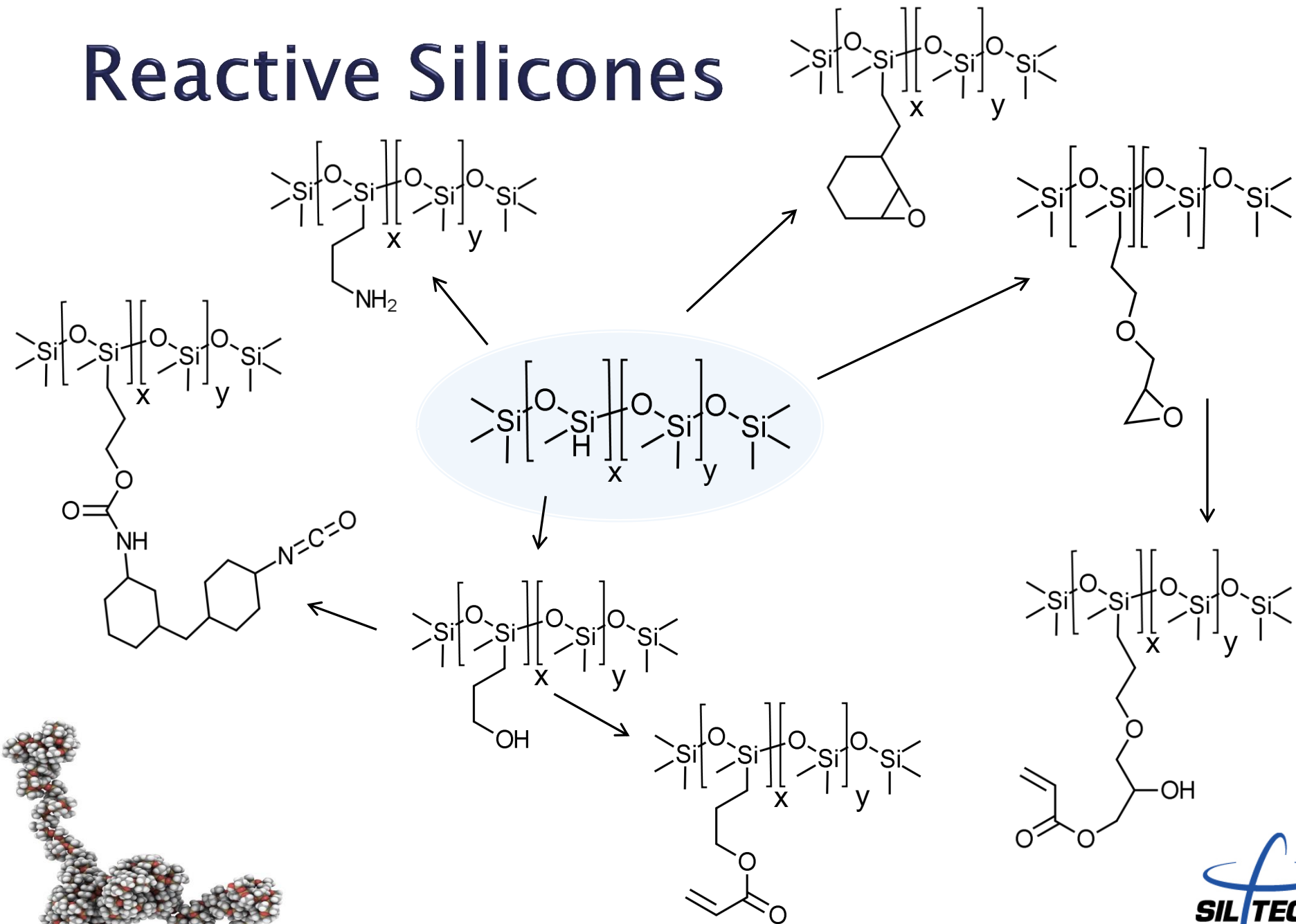


Agenda

- ▶ An Overview Of Reactive Silicones Examining Use Level, Compatibilizer, Silicone Backbone And Cross-Link Density
- ▶ UV Cured Acrylated Silicones
- ▶ Epoxy Silicones
 - Thermally Cured
 - UV Cured
 - OH and NH₂ Silicones With Epoxy Resins
- ▶ Hydroxyl Silicones in Polyurethane



Reactive Silicones



Acrylate Silicone Organic Hybrid

0-80% CN 104 C75 (Epoxy Acrylate)

13% CN 386 (Synergist)

5% Esacure TzT

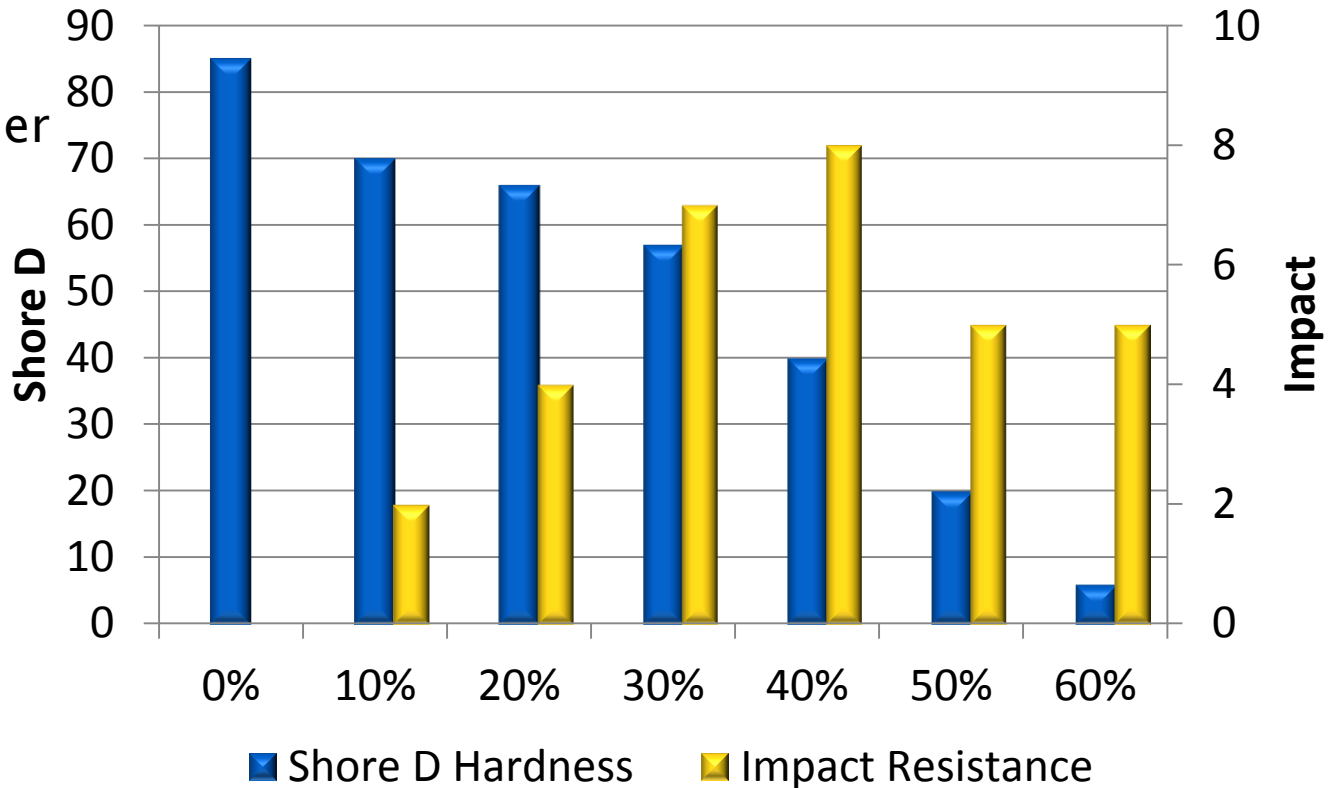
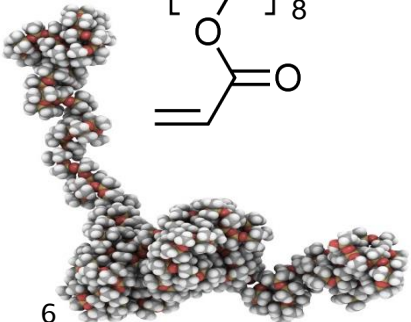
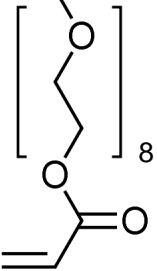
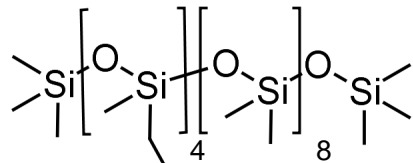
1.5% Irgacure 184

0.5% reactive defoamer

UV light, RT



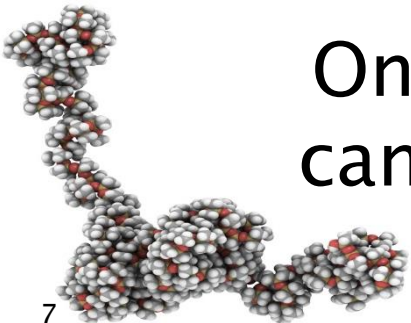
0-80% silicone



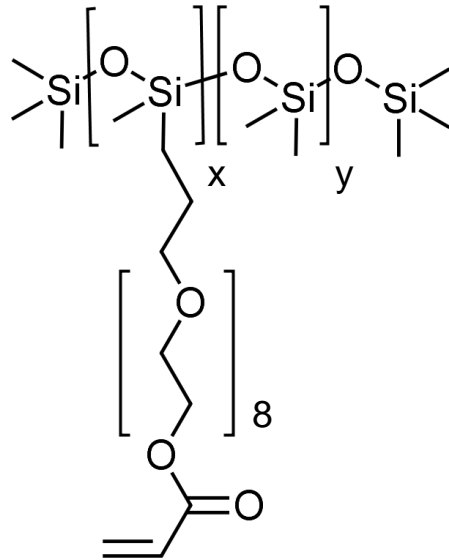
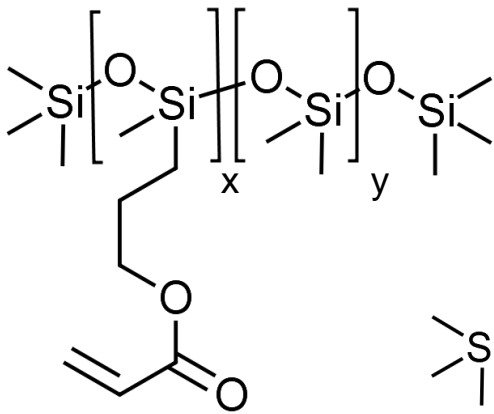
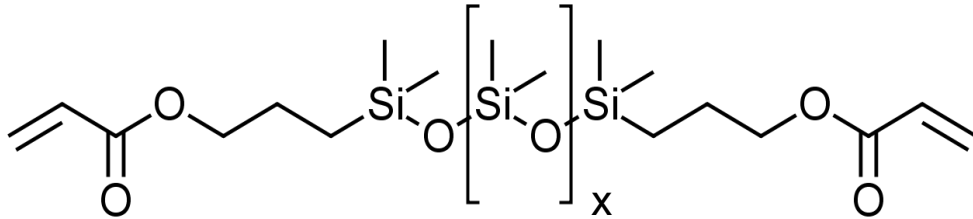
The Effect of Use Level

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



Acrylated Silicone Types



22% silicone



40% CN 102Z (epoxy acrylate)

15% CN 386 (Synergist)

5% Esacure TzT

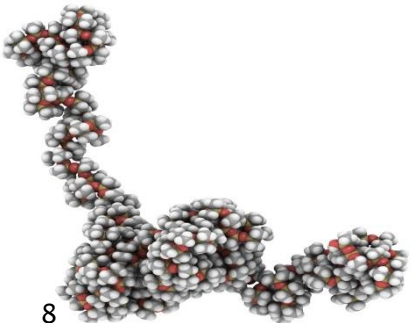
1.5% Darocur 1173

0.5% reactive defoamer

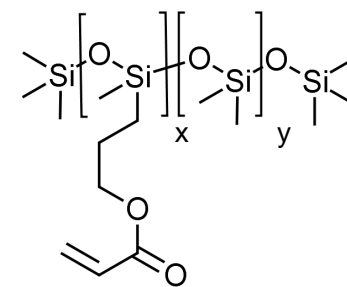
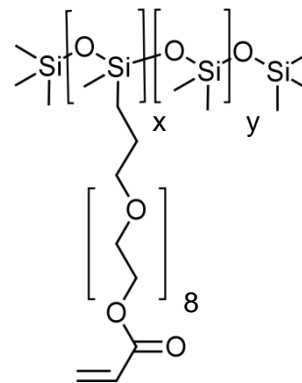
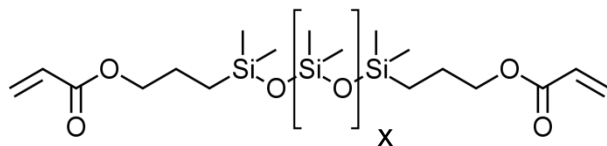
10% DTPTA

6% TRPGDA

UV light, RT

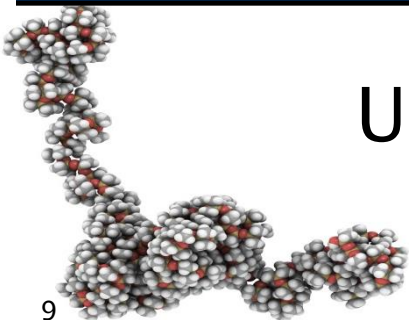


Results

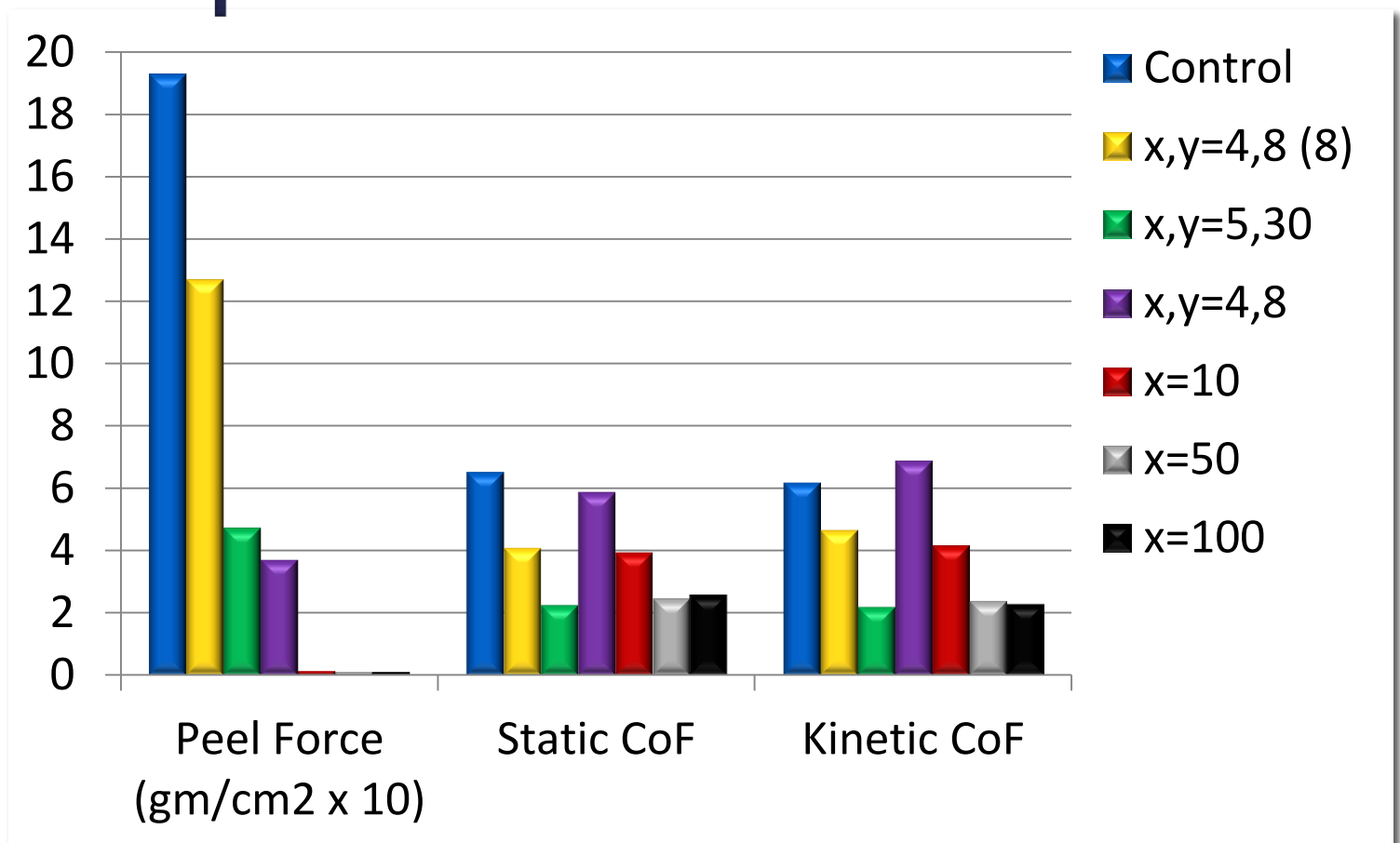


	X=10	X=50	X=100	x, y =4,8	x, y =5,30	x, y = 4,8	Control
Polyether	None	None	None	EO	EO	None	NA
G' (MPa)	8.3	18.5	11.91	9.71	11.64	20.06	20.1
G'' (MPa/10)	0.71	3.19	1.88	0.82	0.91	1.42	1.56
Condition & Appearance	oily	oily, defects	oily	Cured	Cured	Sl. Tacky	Cured

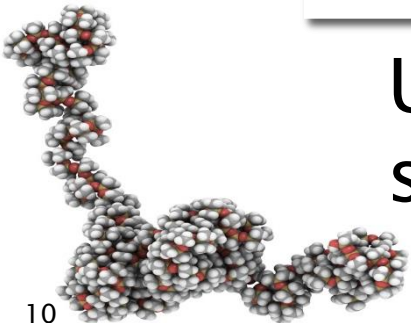
Uncured Silicone from Insolubility



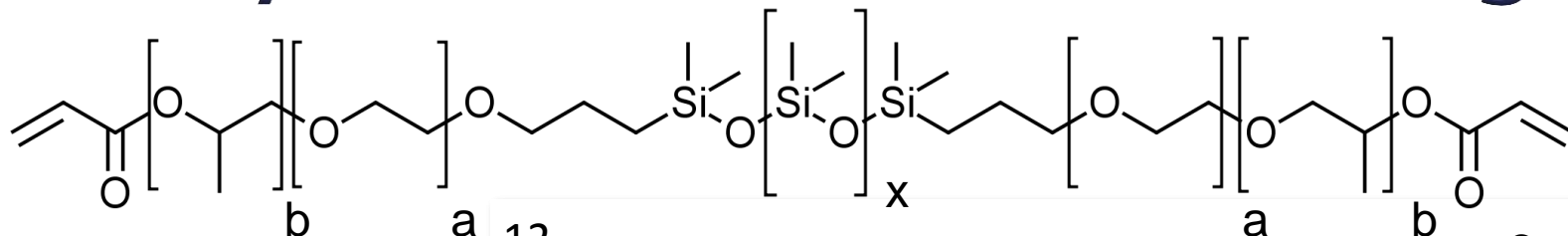
Slip Properties



Unreacted silicone is probably skewing the results



Acrylate Silicone UV coating



10% silicone



67% CN 104 C75

(epoxy acrylate)

10% CN 386 (Synergist)

5% Esacure TZT

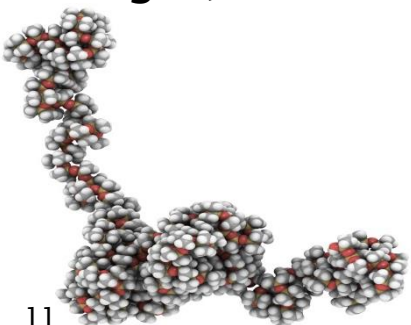
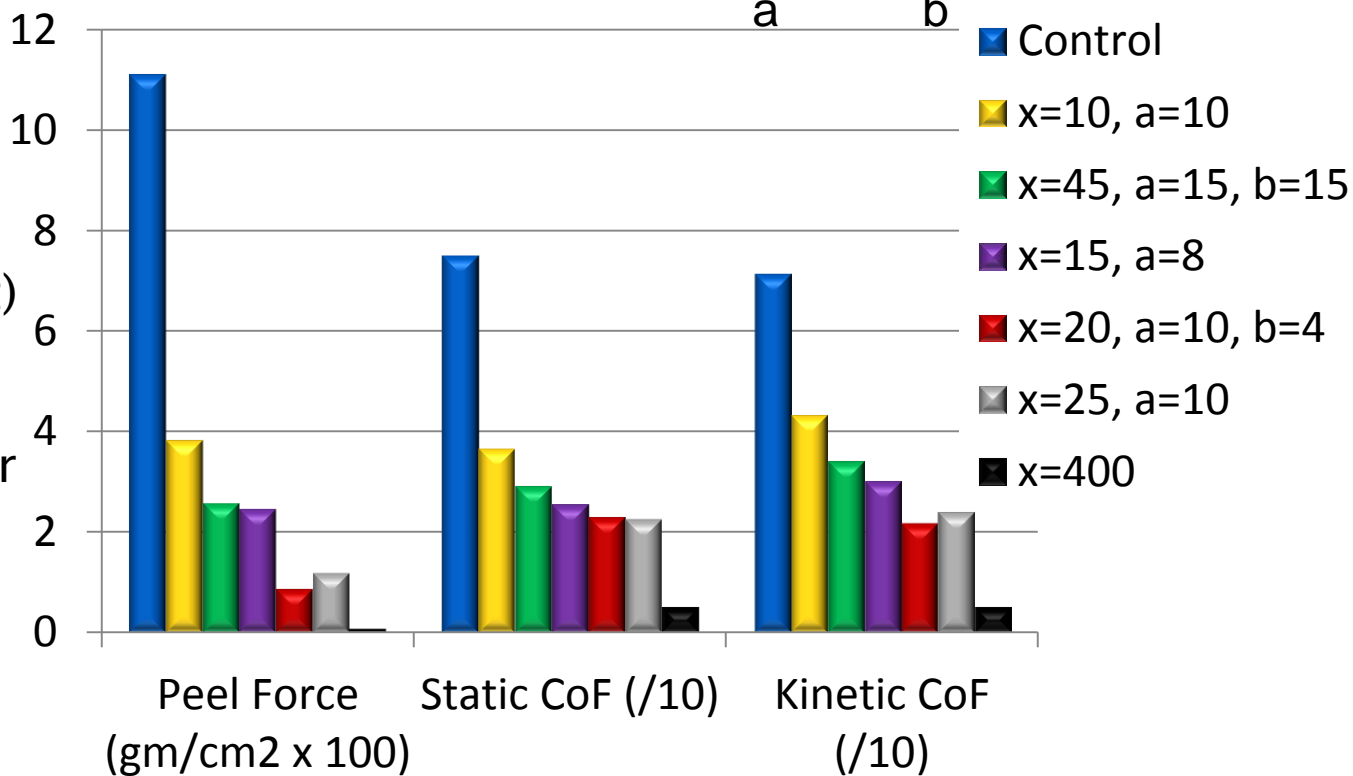
1.5% Darocur 1173

0.5% reactive defoamer

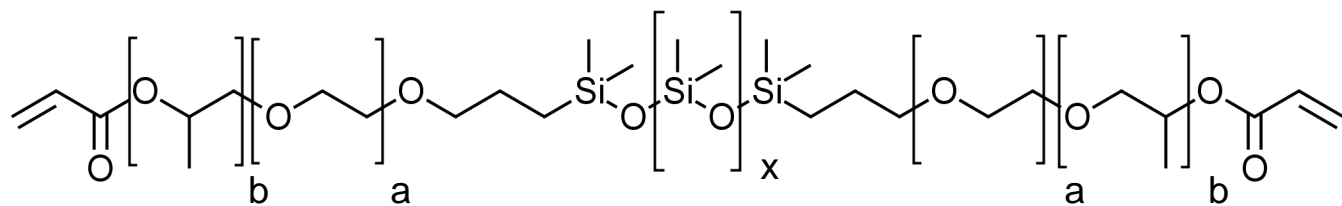
1% DTPTA

5% TRPGDA

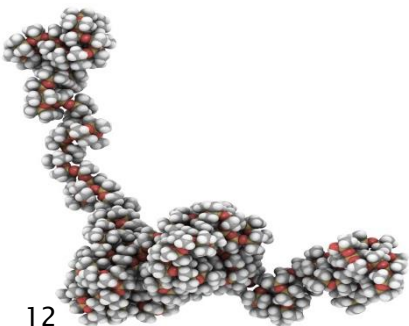
UV light, RT



Results

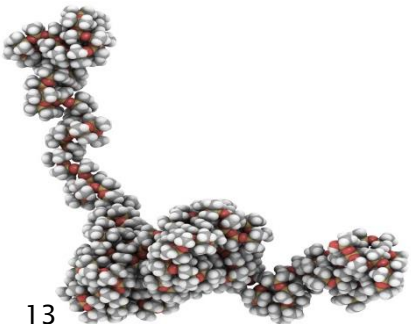


	x=15 a=8 b=0	x=45 a=15 b=15	x=400, a, b=0	x=10 a=10 b=0	x=20 a=10 b=4	x=25 a=10 b=0	Control
G' (MPa)	16.5	11.6	14	17	17	16.3	17
G'' (MPa/10)	14.8	10.2	14.1	52.9	7.5	10.3	34.5
tan(delta)/(100)	9	8.8	10.19	31.1	4.51	6.35	20.3
Condition & Appearance	Cured		Un-cured	Cured			

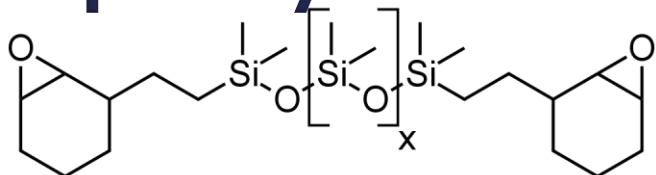


Compatibility is Important

- ▶ Outcomes of incompatibility can be unstable formulas, slow reaction, oily films, defects and very low CoF
- ▶ A modified silicone with organic groups can solubilize the silicone
- ▶ Chain length is important for slip
 - Silicone larger
 - Compatibilizer smaller



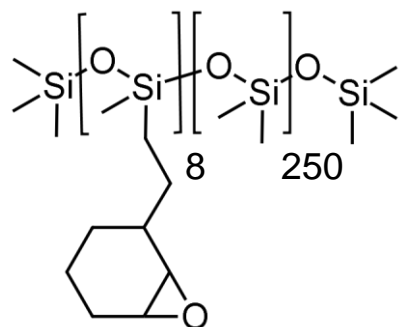
Epoxy Silicone Homopolymer



Linears

X=575 (45-76%)

X=10 (10-35%)



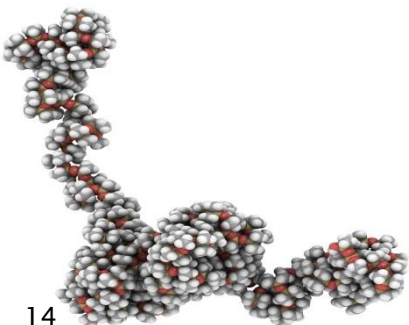
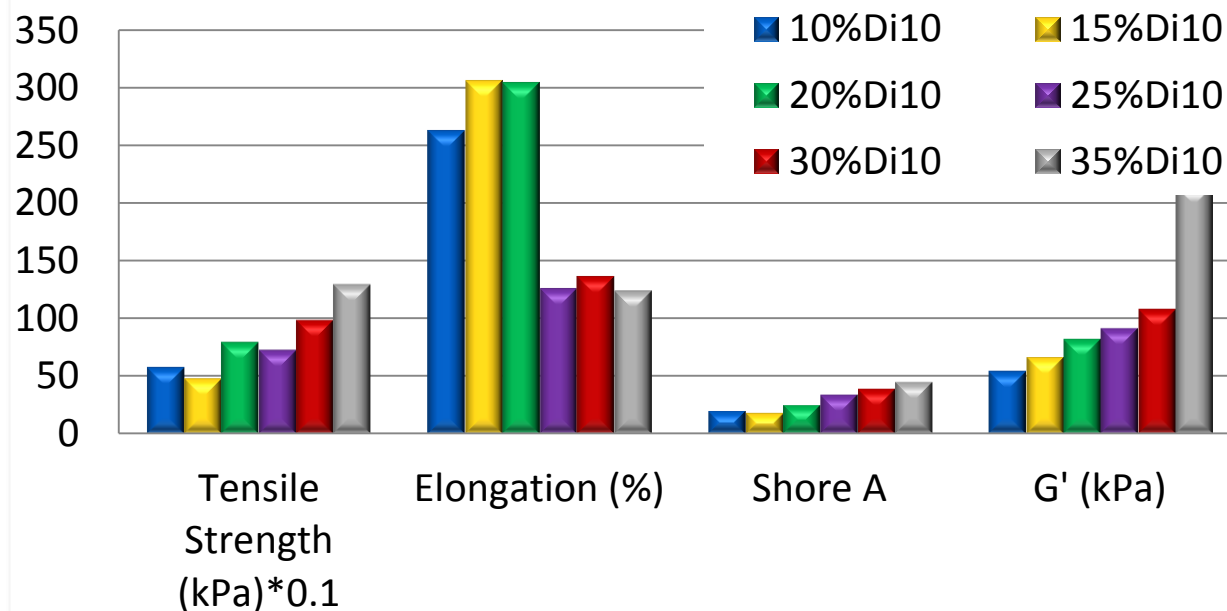
X-linker (8 wt%)



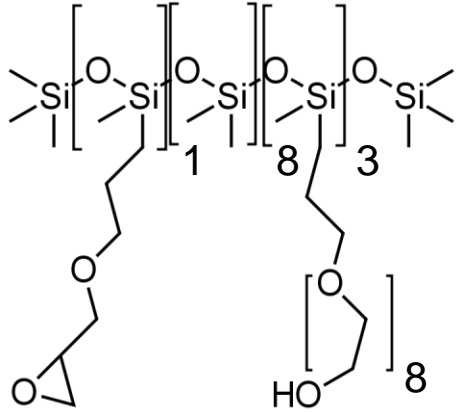
5-11% MHHPA (0.9 mole ratio)

AMI-1

110°C, 8-16 hours



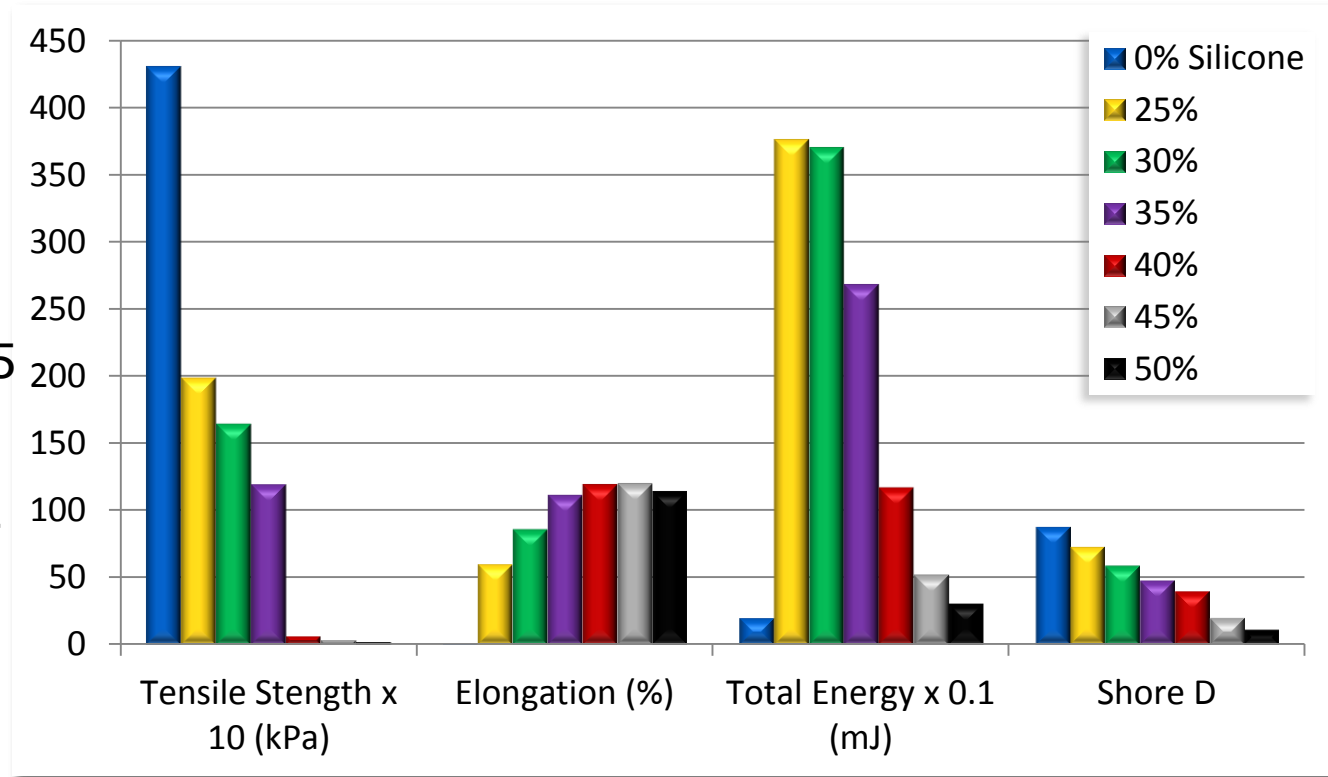
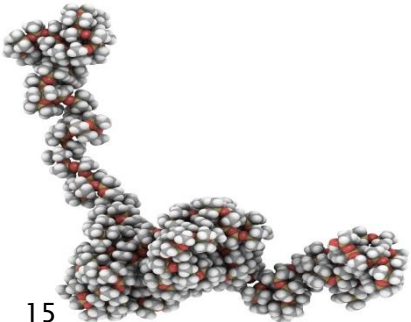
Silicone/ Hard Glycidyl Epoxy



0-50%

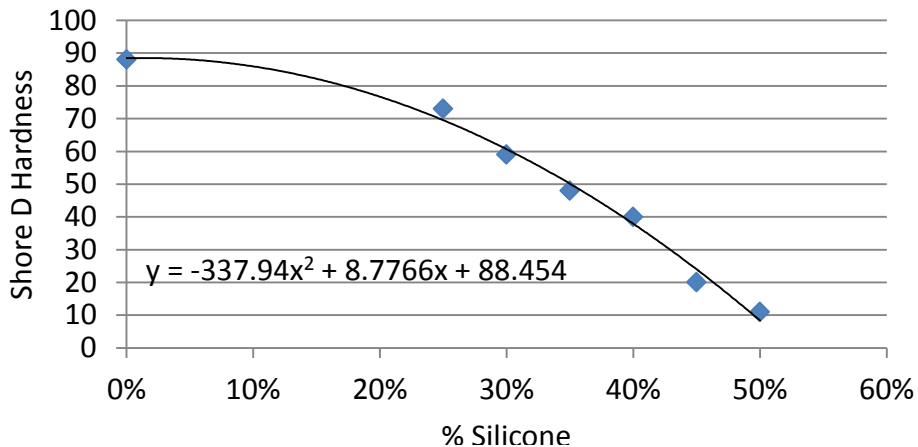


32-53% D.E.R. 671-X75
 17-23% MHHPA
 0.1% AMI-1
 0.2% reactive defoamer
 110°C, 4 hours

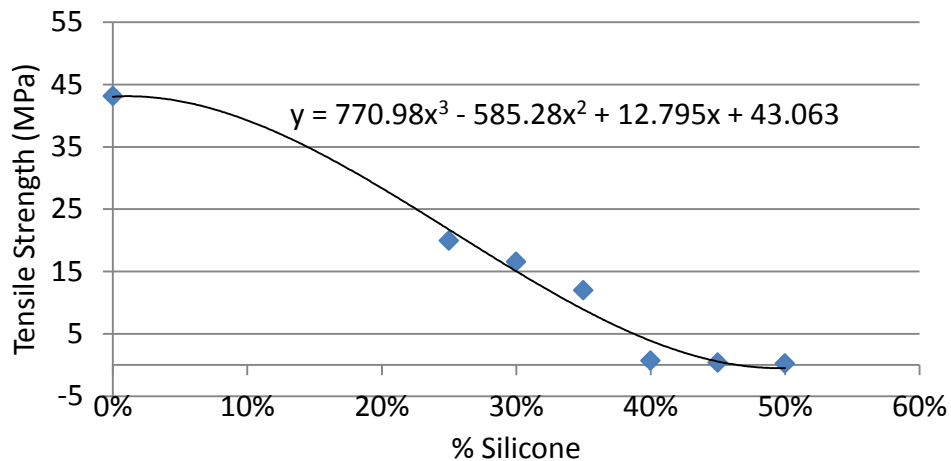


Properties

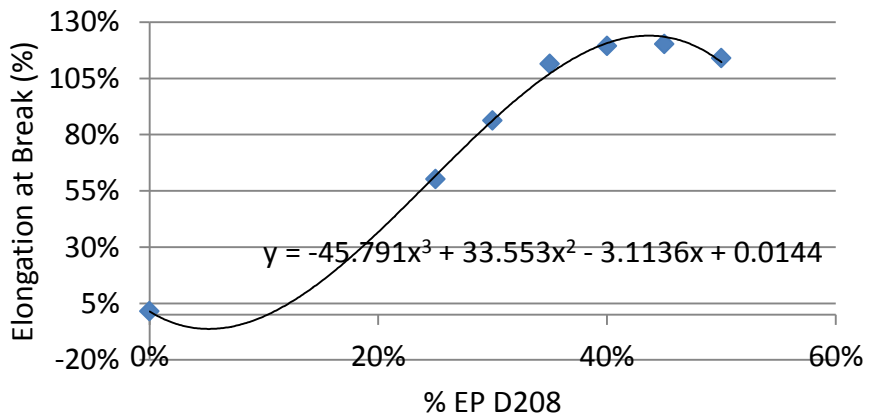
Shore D Hardness



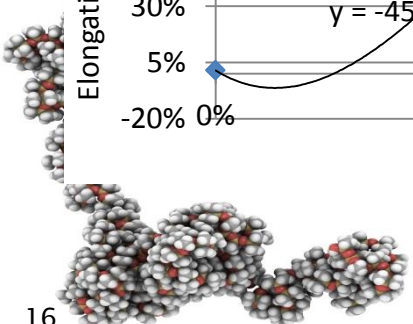
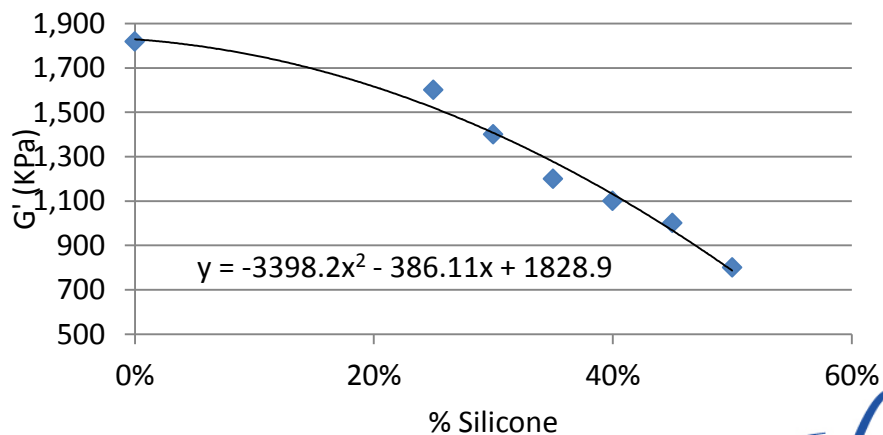
Tensile Strength



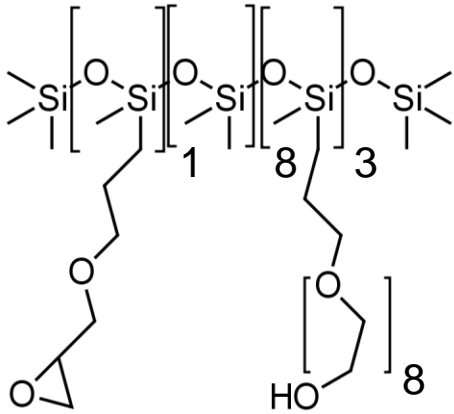
Elongation at Break



Storage Modulus G'



Silicone/ Soft Epoxy Hybrid



25-50%



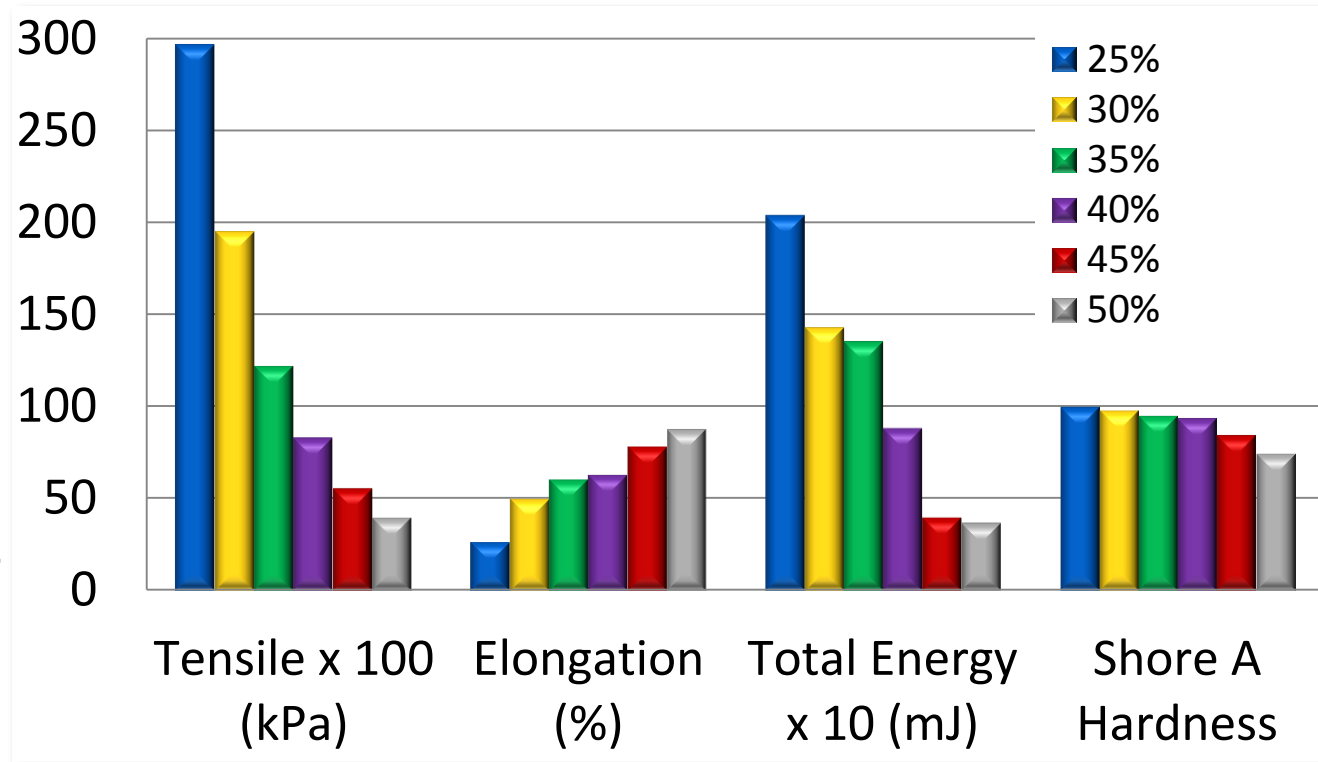
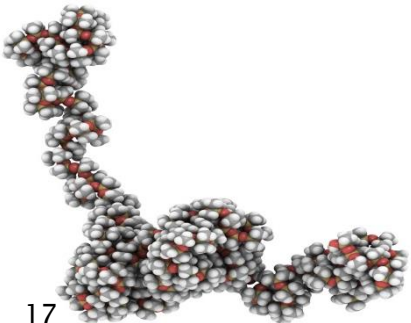
25-37% D.E.R. 331

25-37% MHHPA

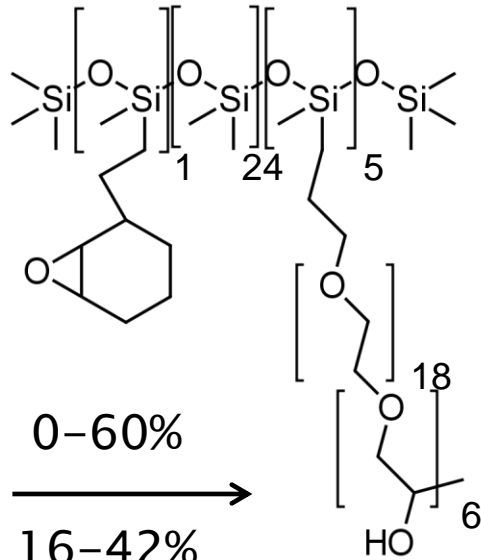
0.1% AMI-1

0.2% reactive defoamer

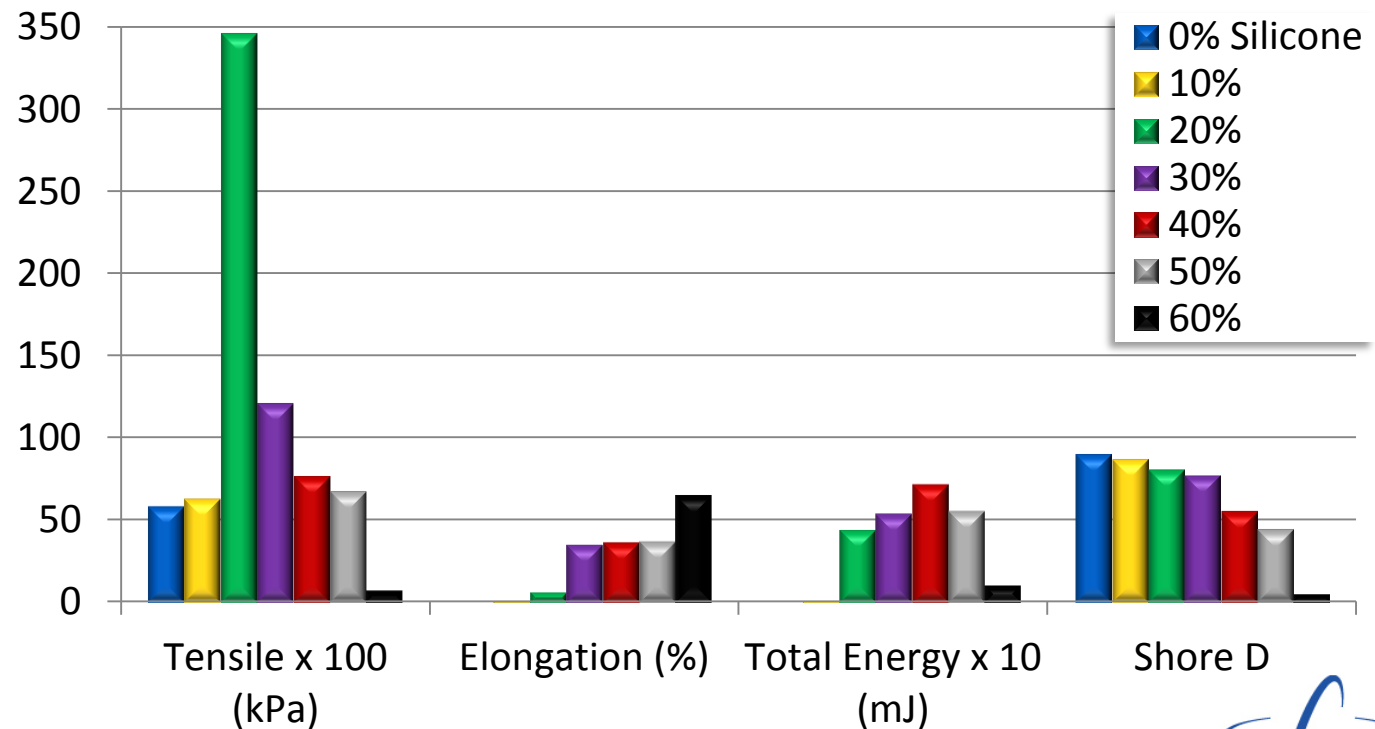
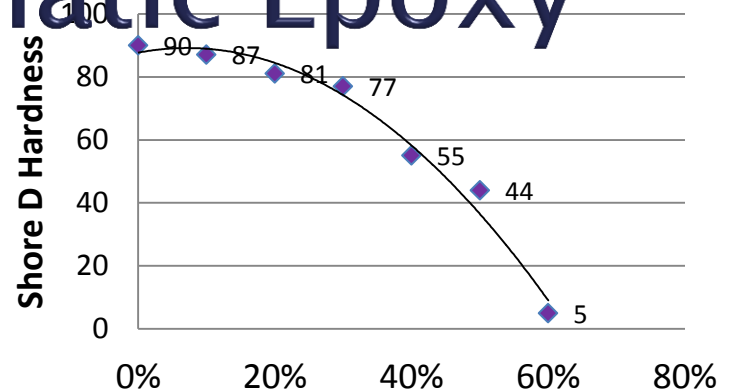
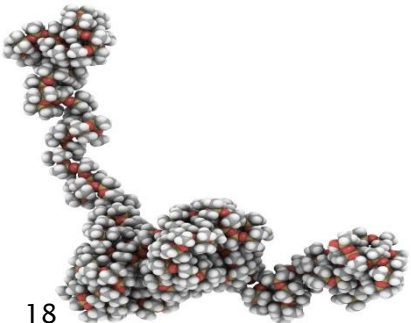
110°C, 4 hours



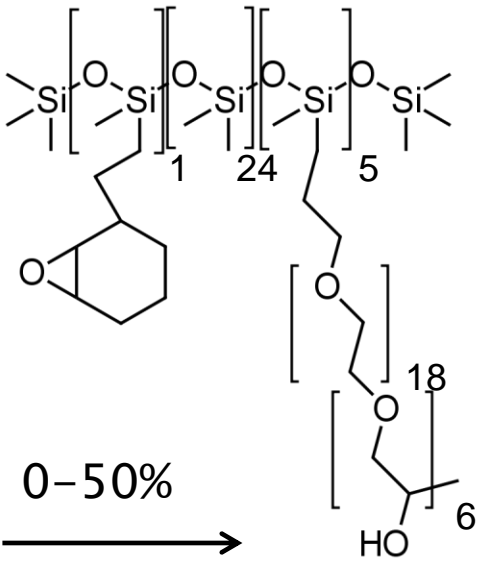
Silicone/ Cycloaliphatic Epoxy



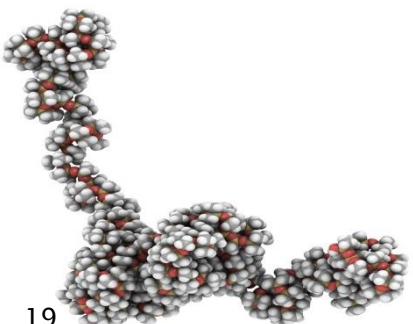
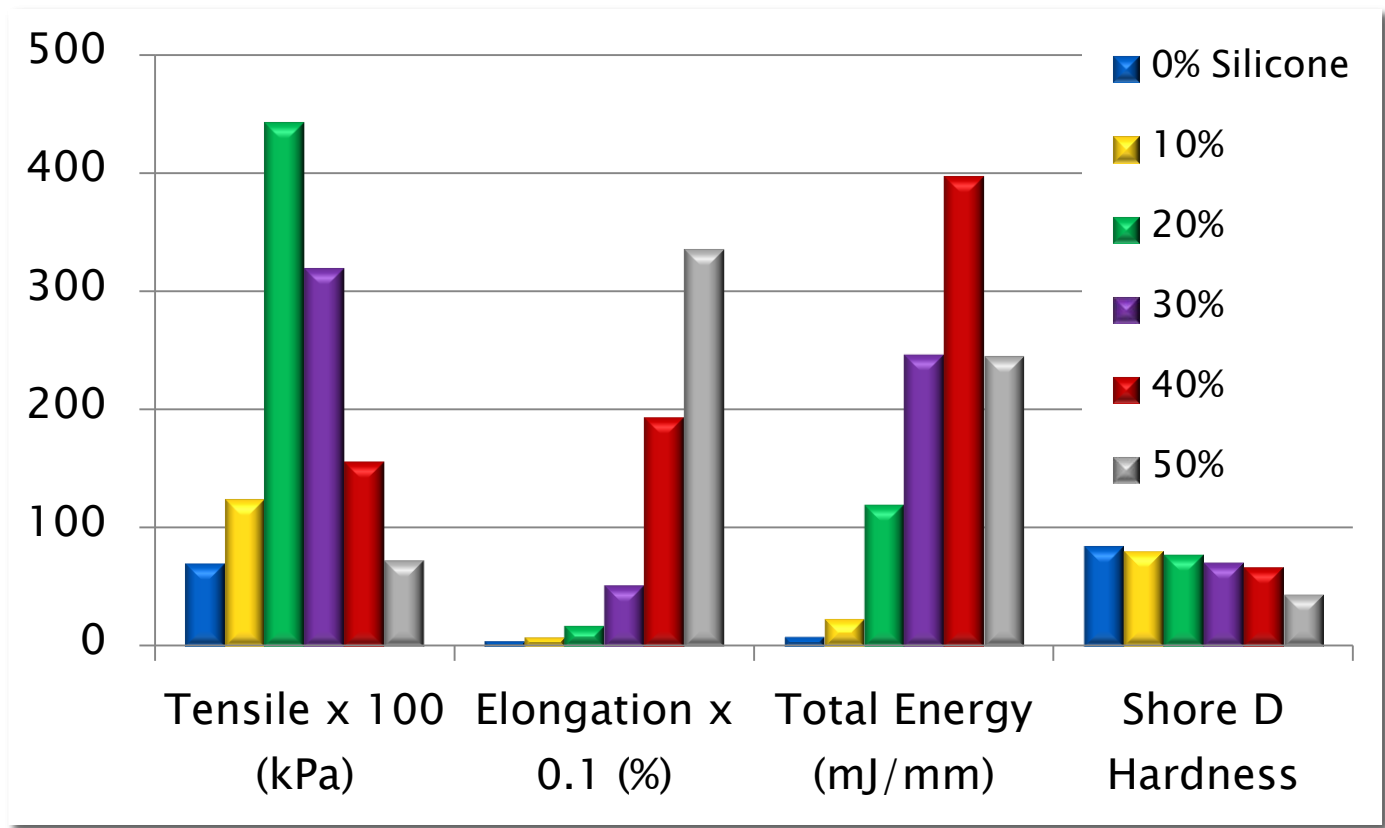
UVACURE 1500
24-58% MHHPA
0.1% AMI-1
110°C, 4 hours



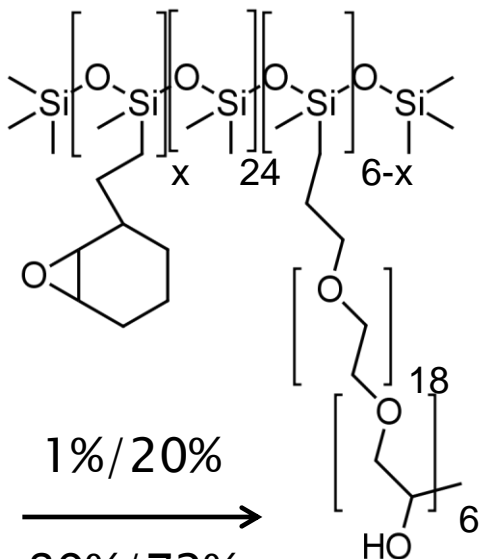
Silicone/ Epoxy UV Cured



0-50%
 →
 50-99 %
 UVACURE 1500
 1% UV 9380
 365nm, RT



Effect of X-Link



1%/20%

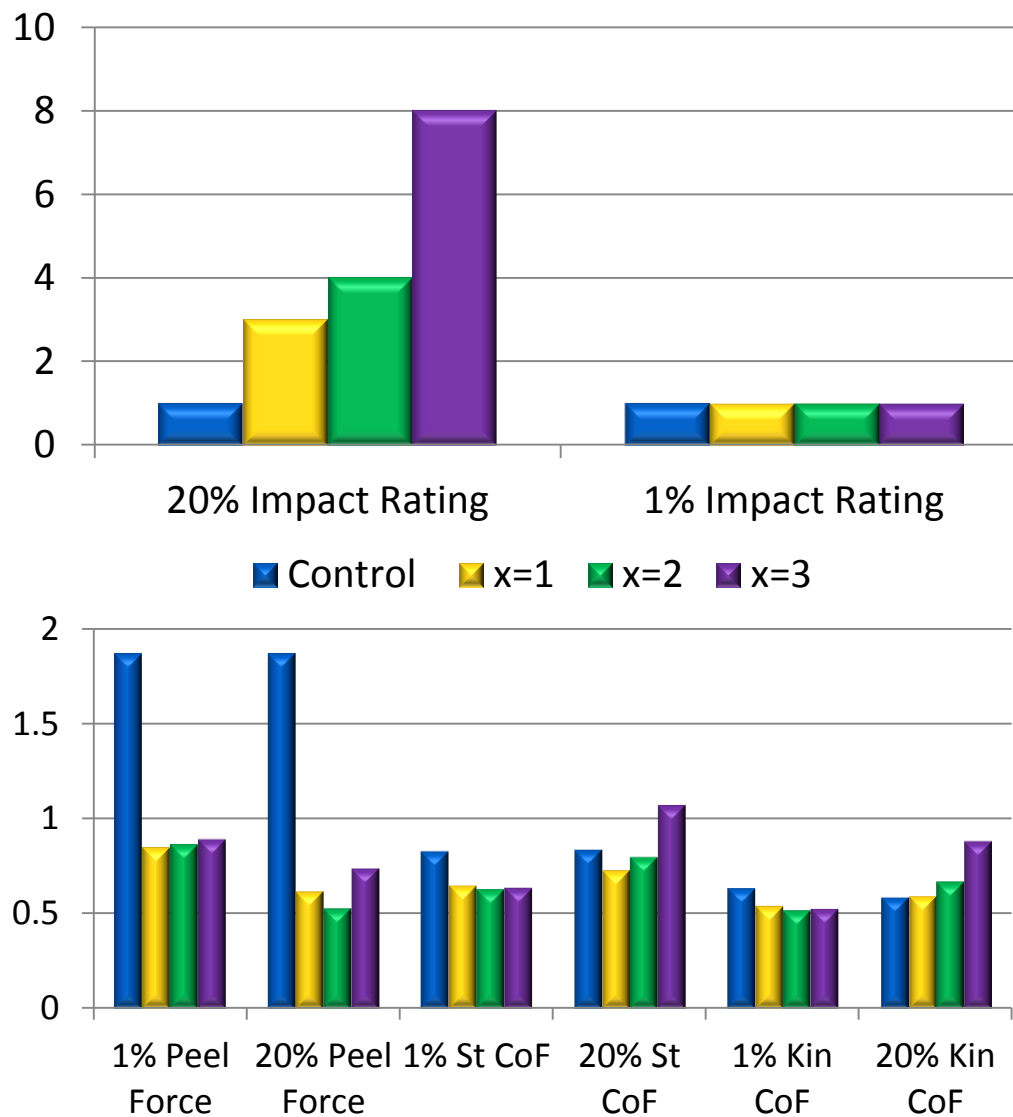
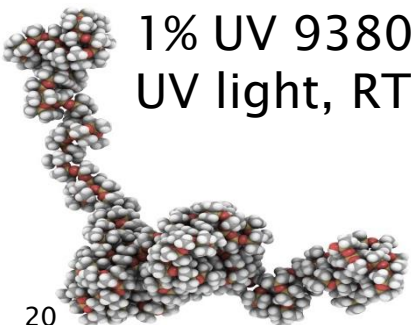
89%/72%

UVACURE 1500

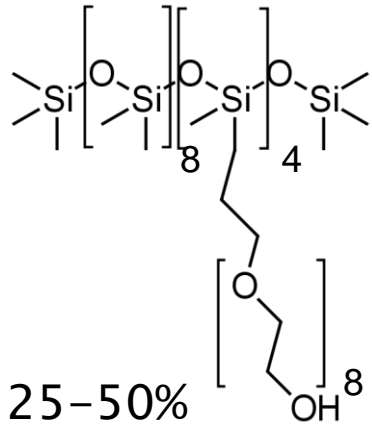
9%/7% CAPA A polyol

1% UV 9380C

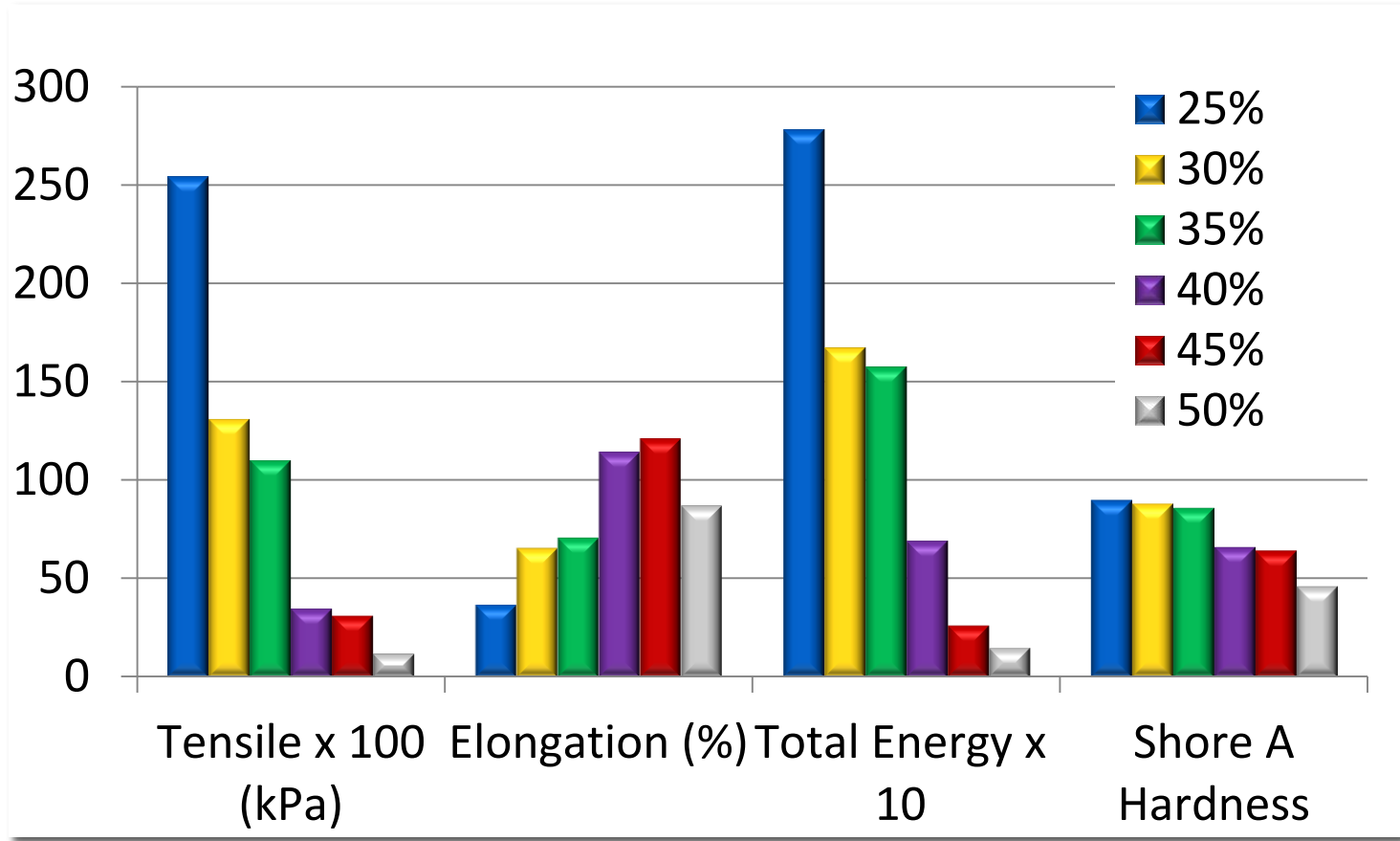
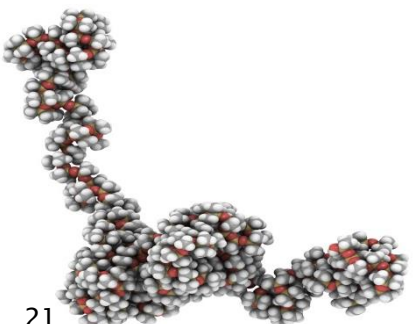
UV light, RT



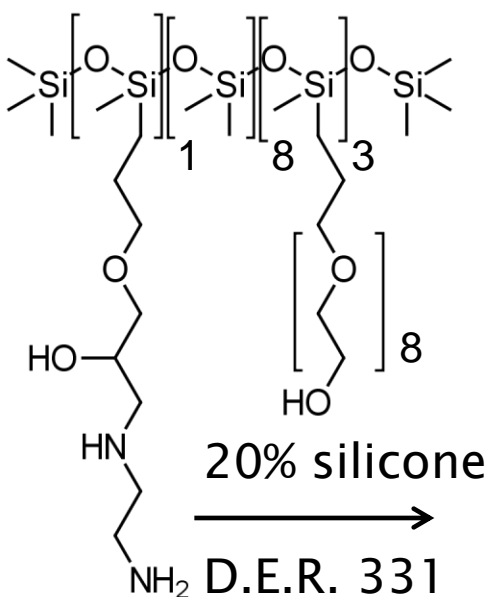
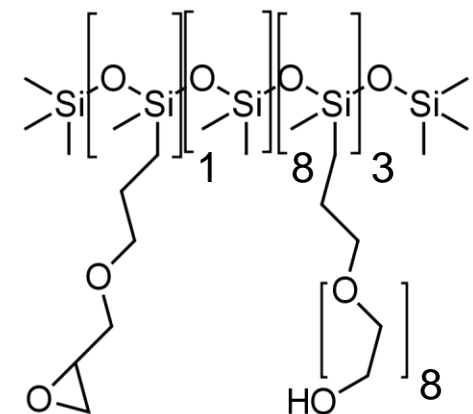
OH Silicone / Glycidyl Epoxy



→
 25-37%
 D.E.R. 331
 25-38% MHHPA
 0.1% AMI-1
 110°C, 4 hours



NH₂ Silicone/Glycidyl Epoxy Hybrid



20% silicone

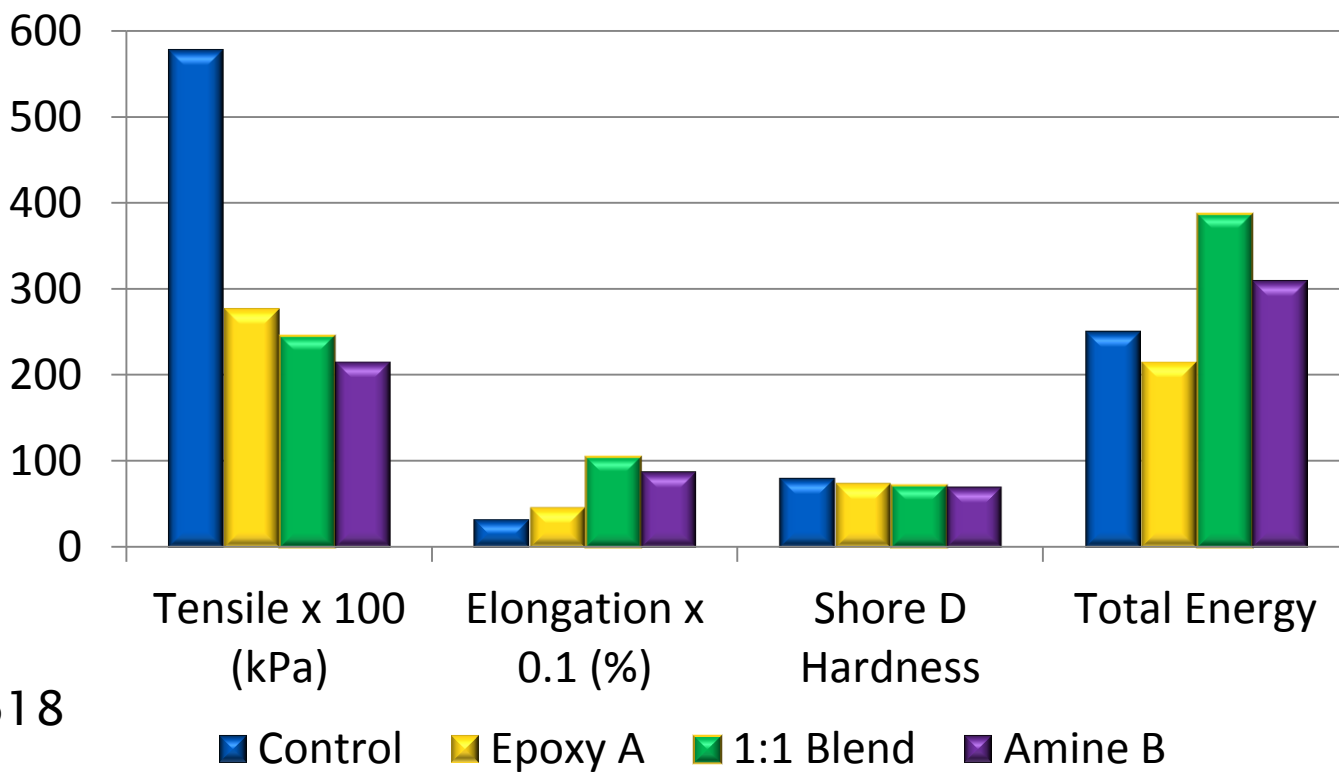
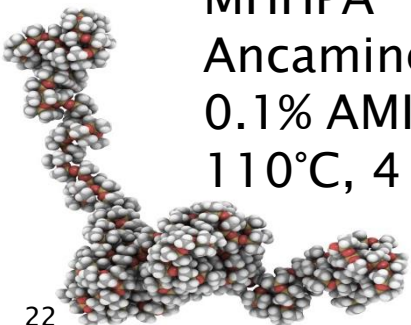
D.E.R. 331

MHHPA

Ancamine 1618

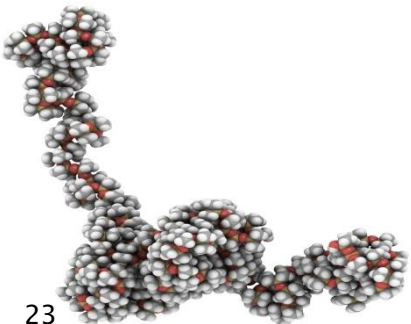
0.1% AMI-1

110°C, 4 hours

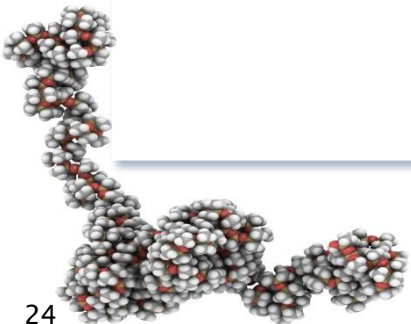
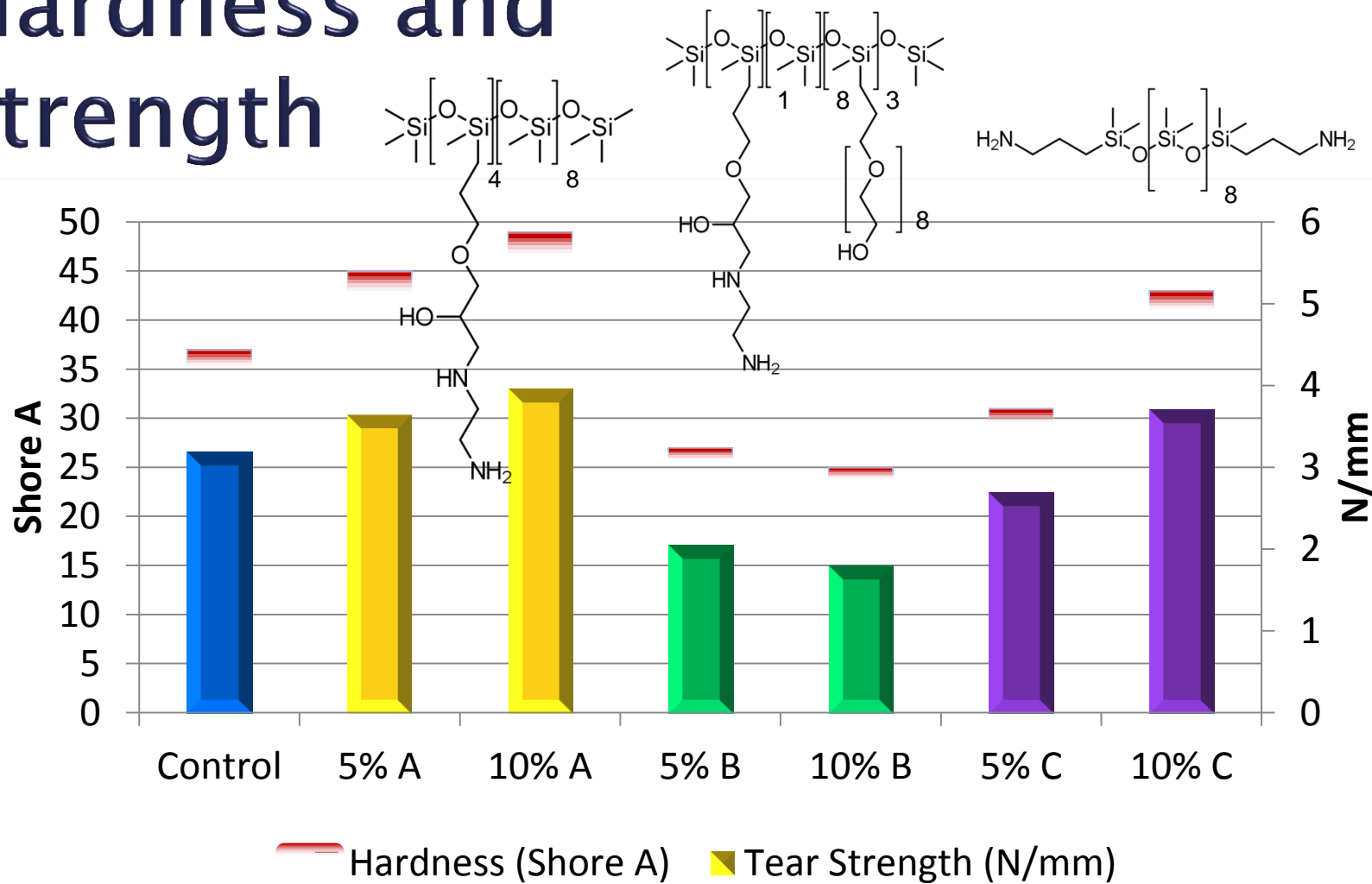


Rubber Filled Epoxy with Silicone Hardener

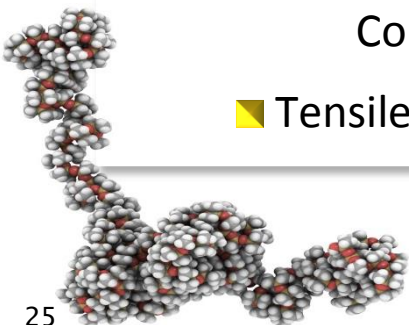
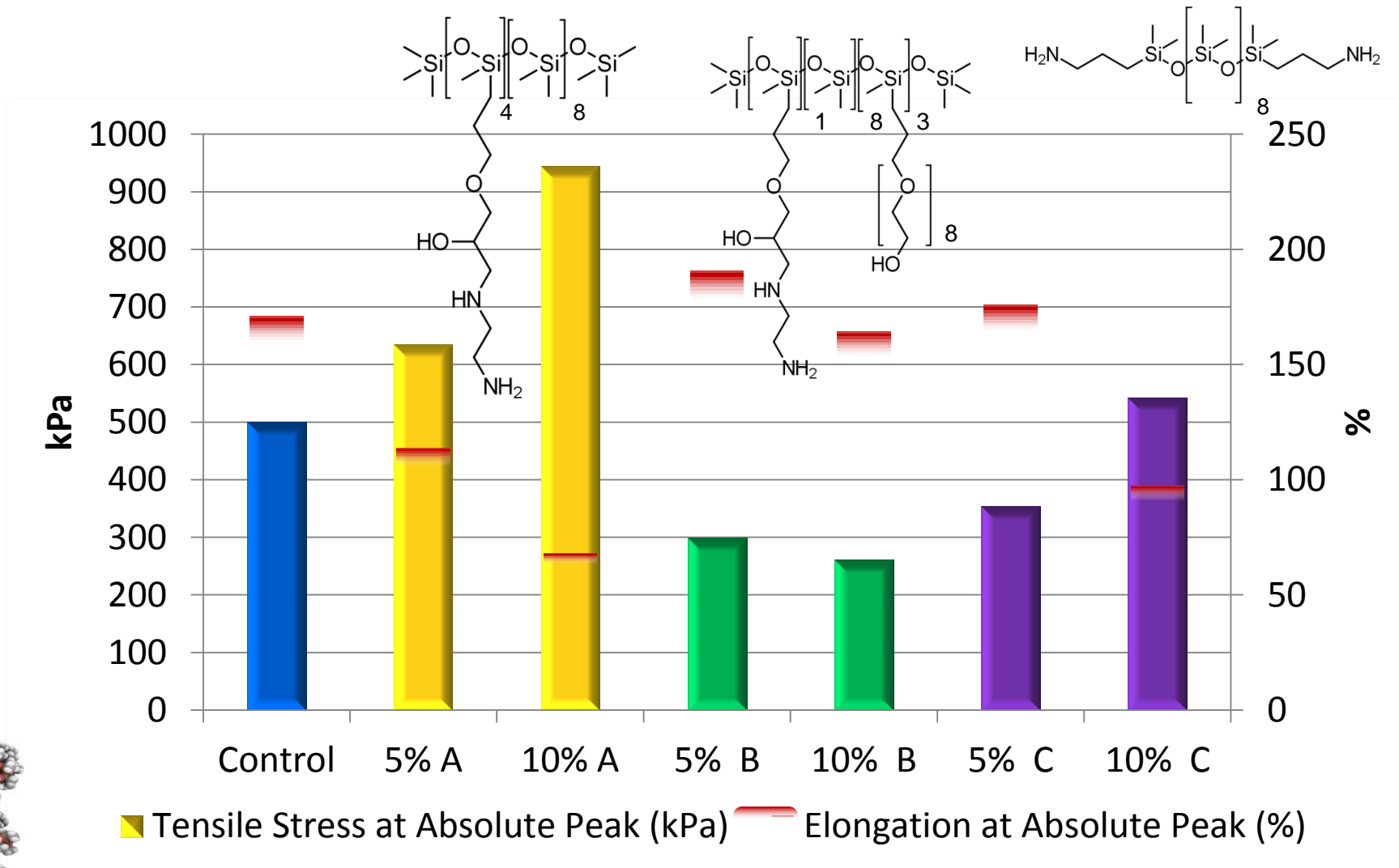
- ▶ Proprietary epoxy with 5–10% reactive silicones and rubber crumbs
- ▶ Mold and cure at ambient for 7 days
- ▶ -15°C and -30°C impact resistance measured with a steel ball drop
- ▶ Severity of fracture rated 1–10 (best)



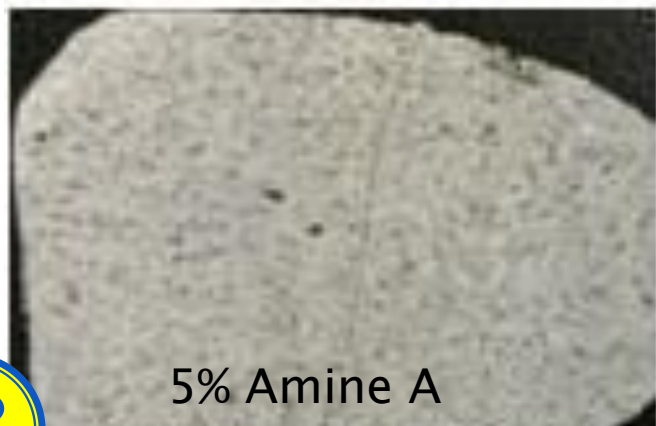
Hardness and Strength



Tensile Stress and Elongation



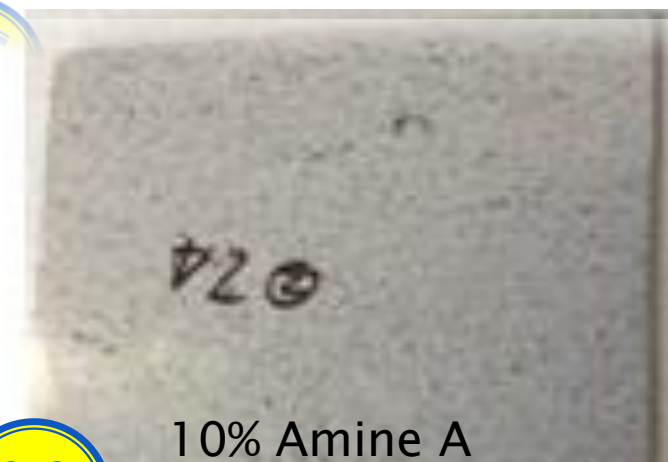
-15°C
Fracture



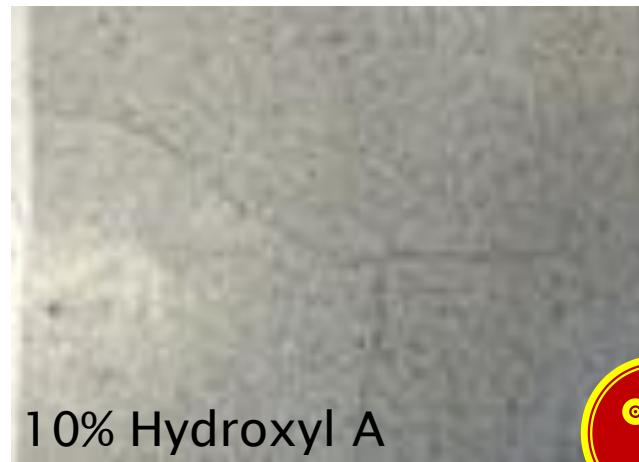
5% Amine A



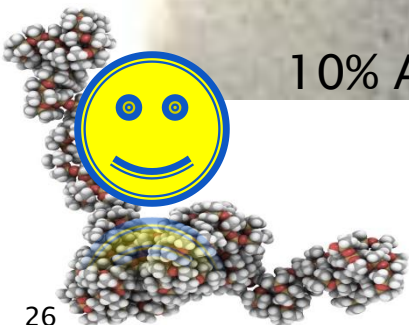
Control



10% Amine A

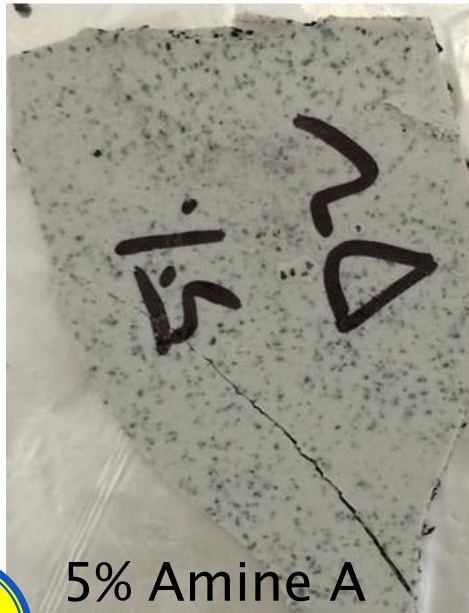


10% Hydroxyl A

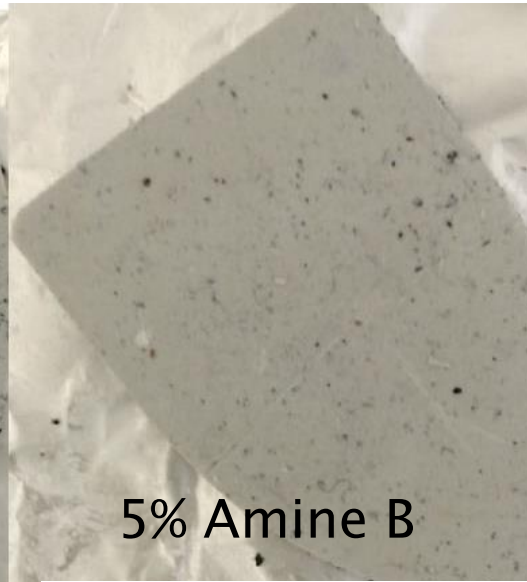




Control



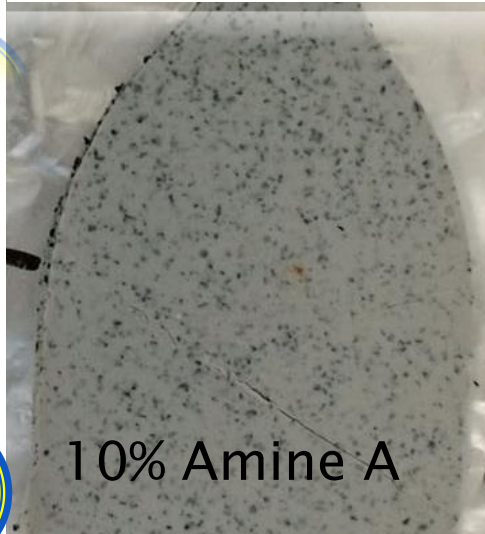
5% Amine A



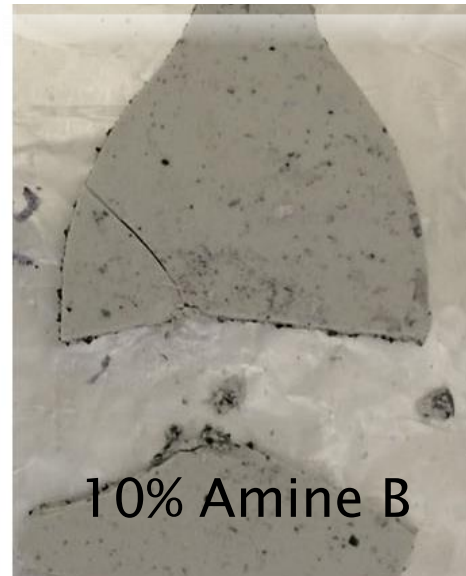
5% Amine B



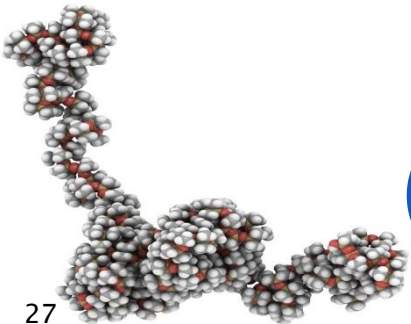
-30°C
Fracture



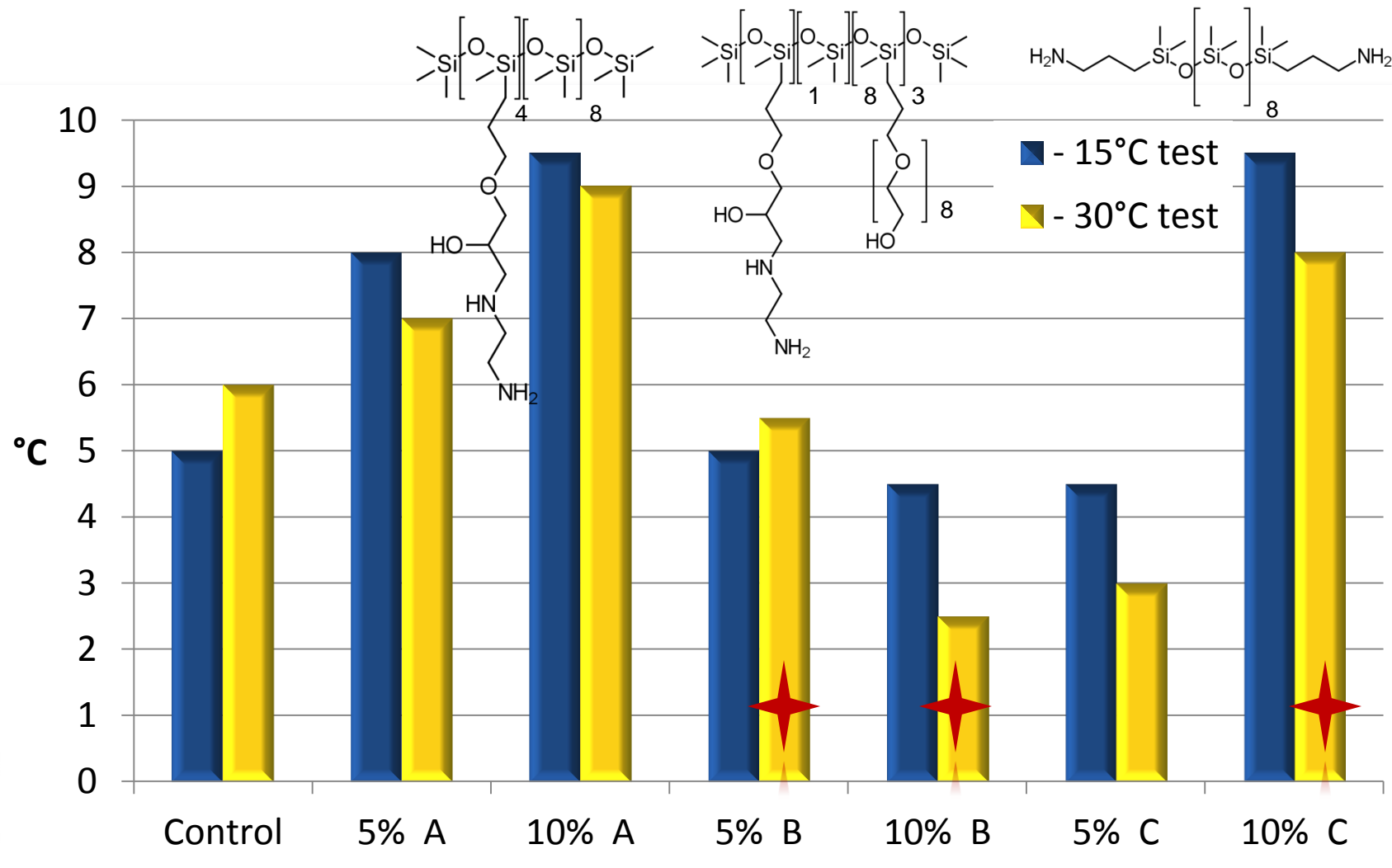
10% Amine A



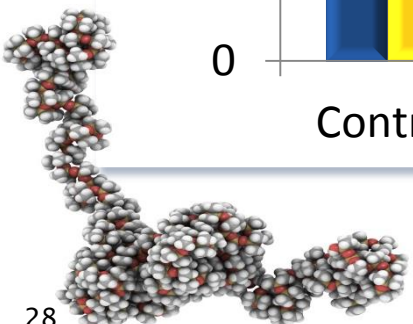
10% Amine B



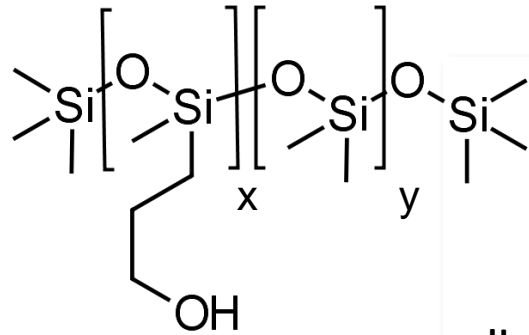
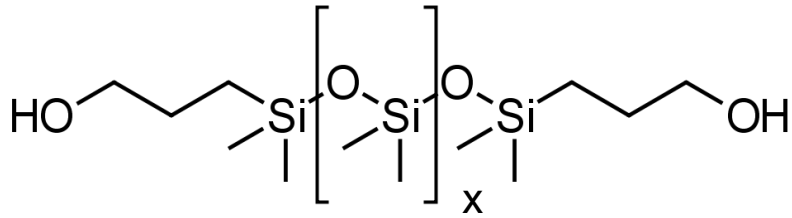
Low Temperature Impact



★ Fractured on second of two impacts

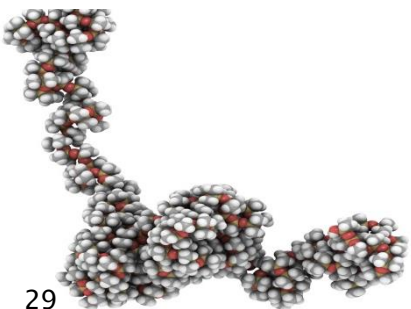
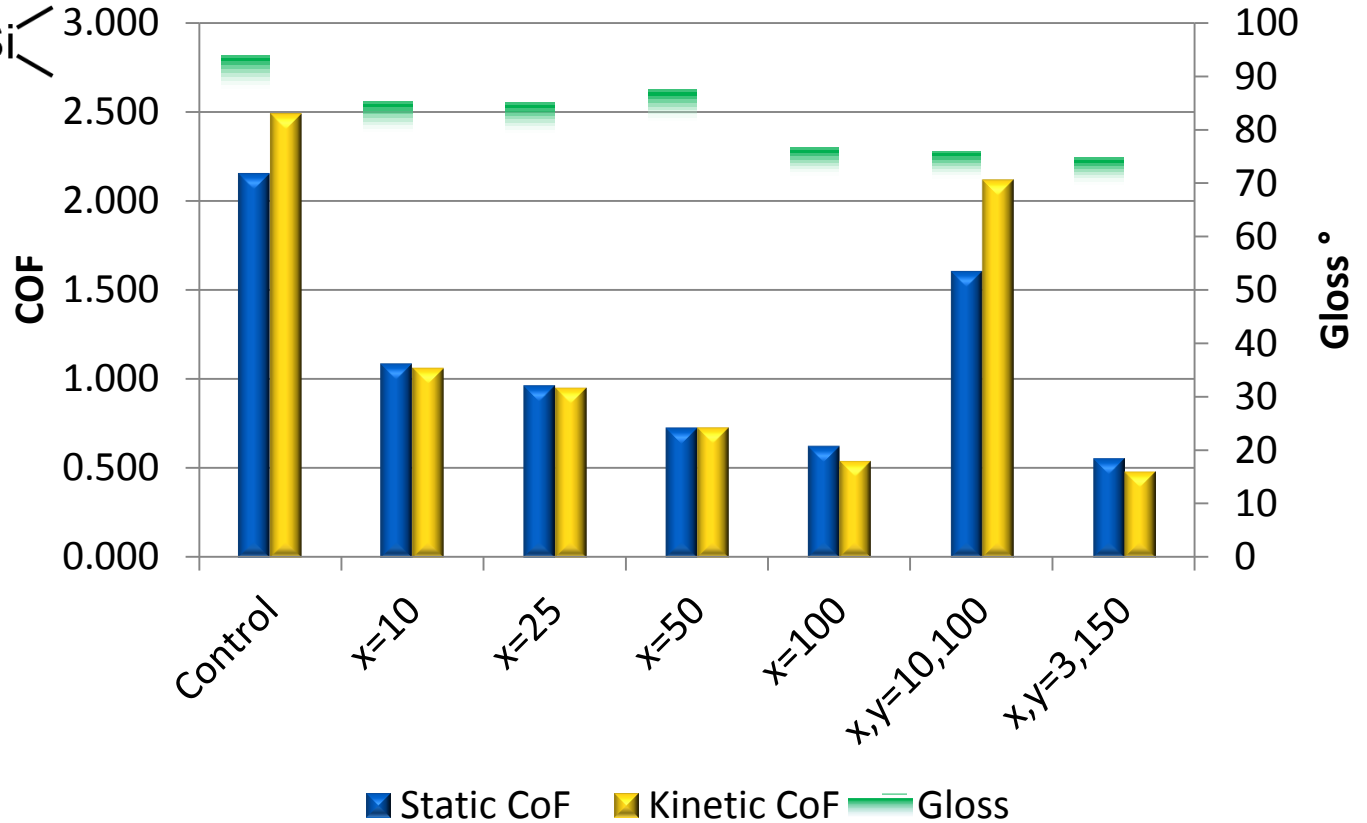


OH Silicone/ SB Polyurethane

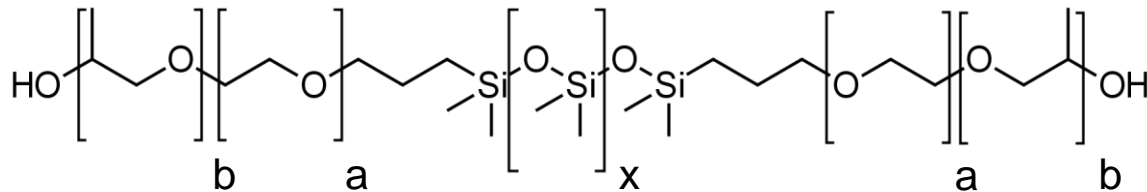


10% in part A

Part A:
 43% A870 BA
 28% 670A-80
 0.1% Dabco T-12
 20% Solvents
 Part B: N-3390 BA/SN
 1:1 polyol/NCO

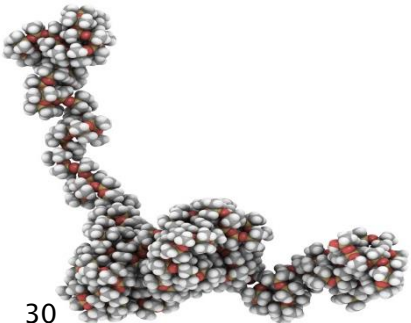
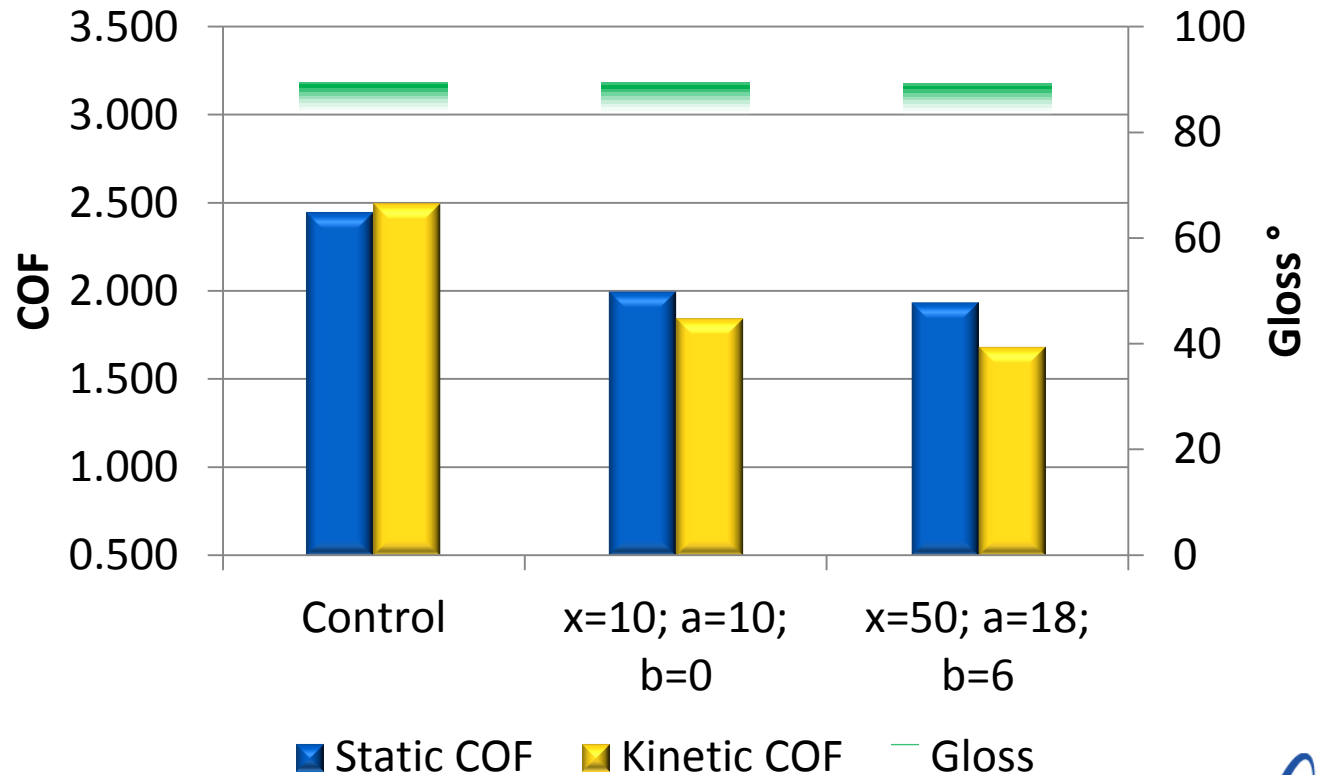


OH Silicone/ WB Polyurethane



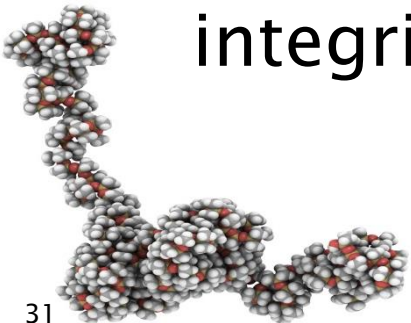
1 %
→

Part A:
76% Bayhydrol A145
2% Surfynol 104 DPM
1% Borchigel PW25
20% Water
Part B: (1.5:1 OH/NCO)
64% Bayhydur XP7165
23% XPLS2150/1
13% Exxate 600



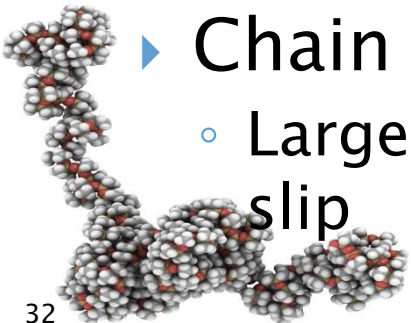
Conclusions

- ▶ One can react acrylate, epoxy, amino, hydroxyl silicones with themselves or resins with corresponding reactive groups.
- ▶ Outcomes of incompatibility can be unstable formulas, slow reaction, oily films, defects and very low CoF
 - A modified silicone with organic groups can solubilize the silicone
- ▶ One can go very high in use level, but film integrity can be lost



Conclusions

- ▶ For some properties 1% is adequate.
 - Slip
 - Release
 - Mar Resistance
- ▶ Other properties require more silicone
 - Impact Resistance
 - Stain Resistance
- ▶ More reactive groups on the silicone has a minor affect on stain and slip properties
- ▶ Chain length is important for slip
 - Larger silicone or smaller compatibilizer gives more slip



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