

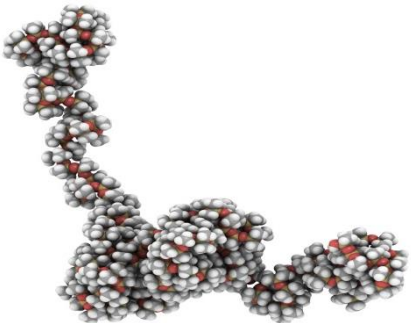
REACTIVE SILICONES HOMOPOLYMERIZED AND COPOLYMERIZED WITH ORGANIC POLYMERS

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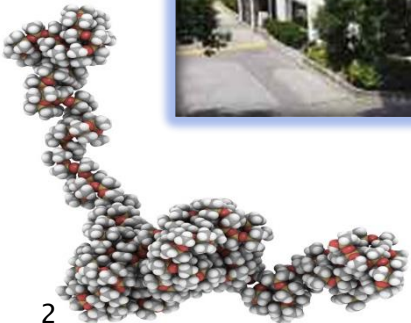


Siltech Background

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



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225 Wicksteed Avenue
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www.siltech.com



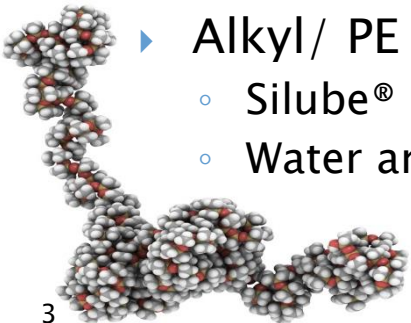
Chemically Modified Silicones

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

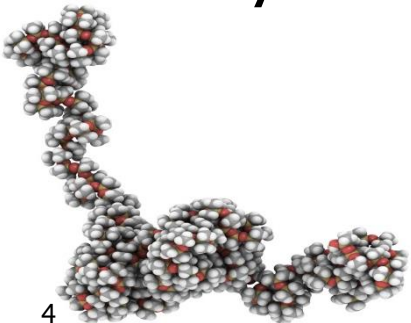
Silicone w/ Special Groups

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

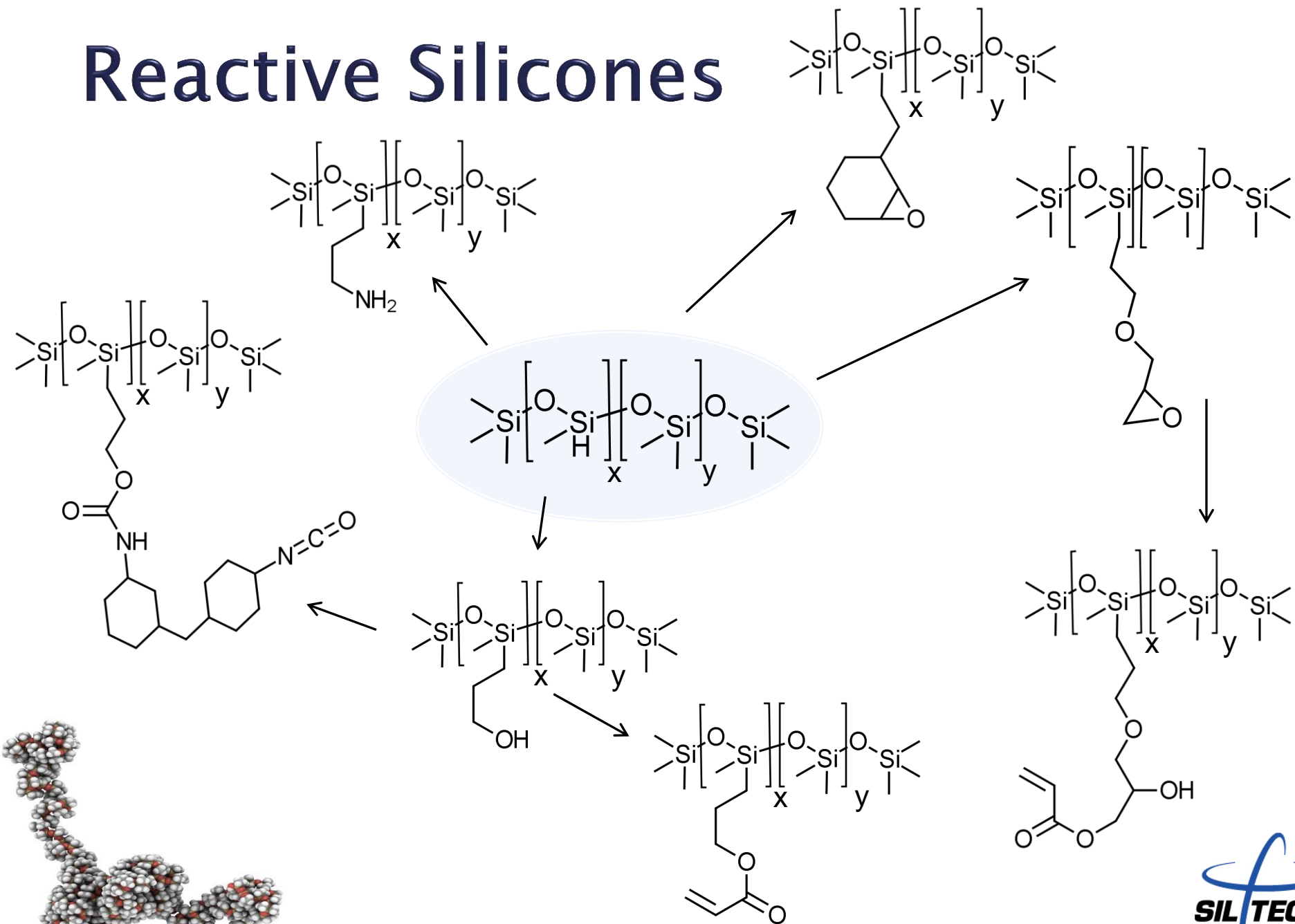


Agenda

- ▶ 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

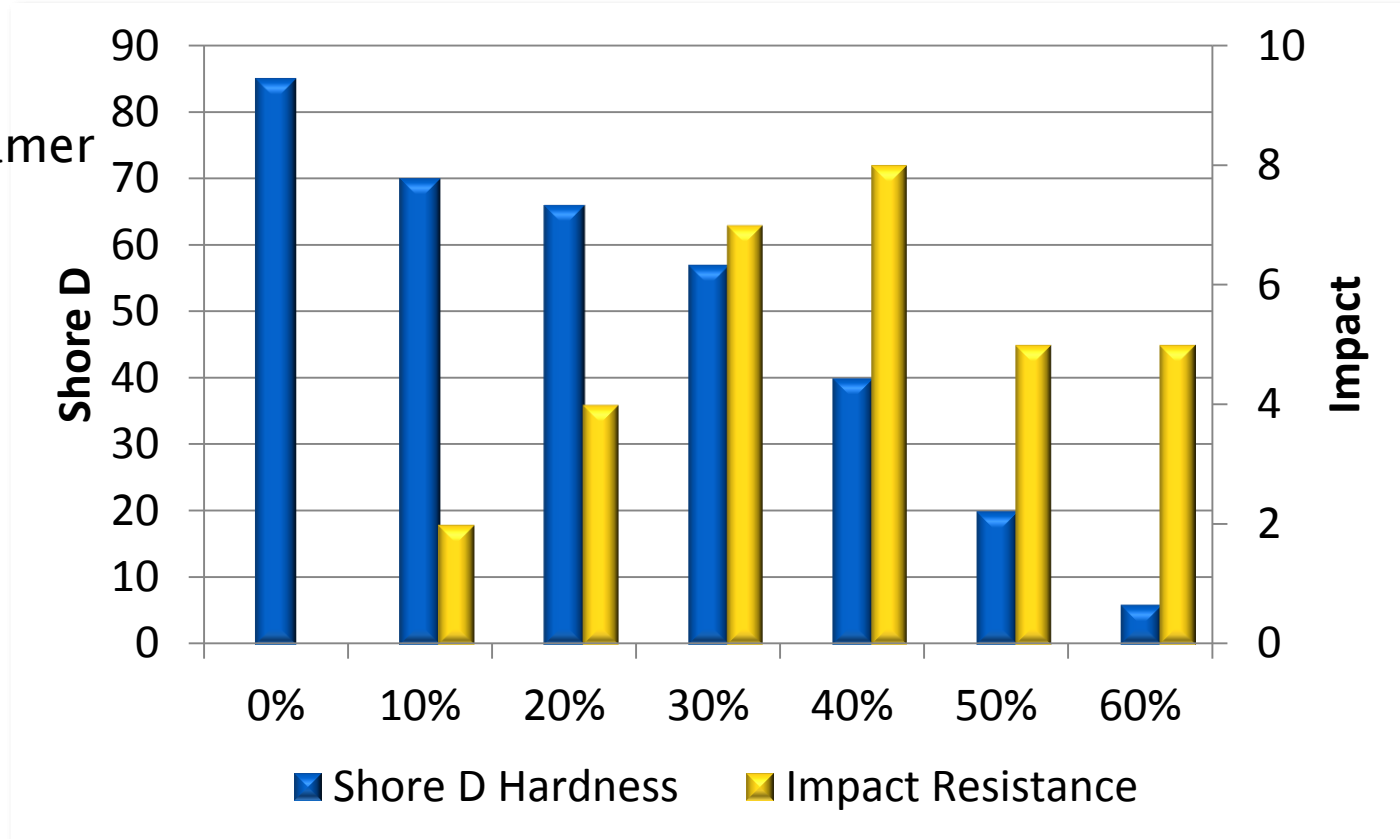
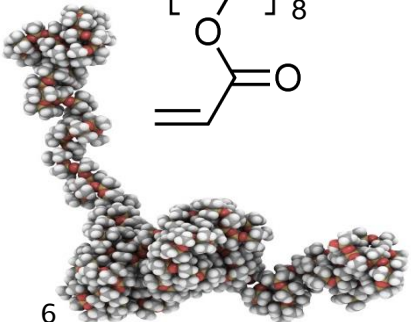
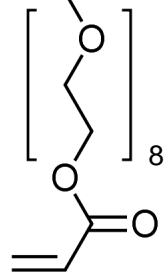
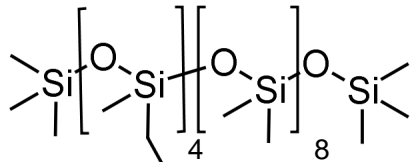
1.5% Irgacure 184

0.5% reactive defoamer

UV light, RT



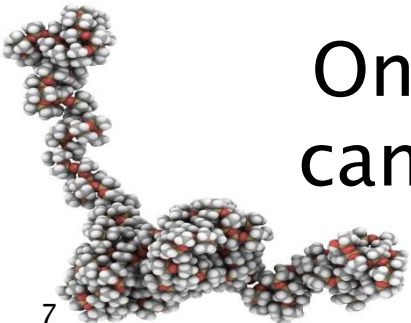
0–80% silicone



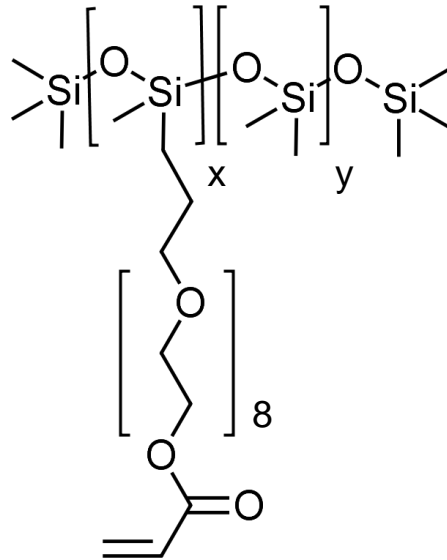
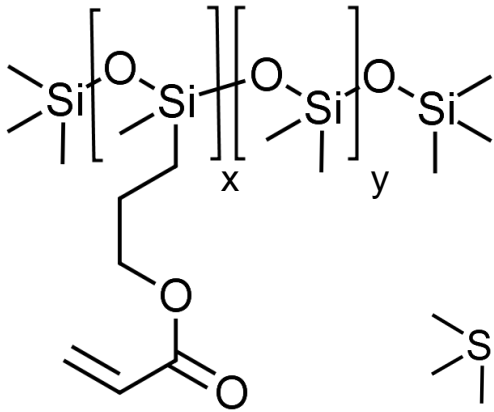
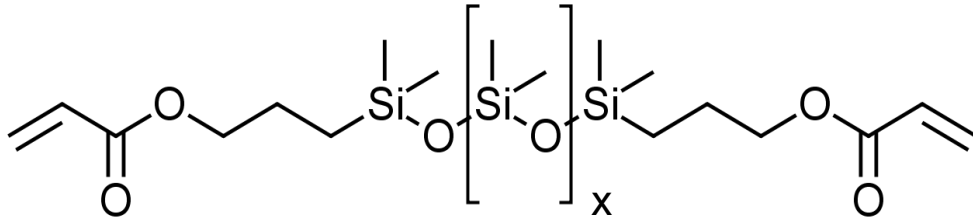
The Effect of Use Level

| 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 T2T

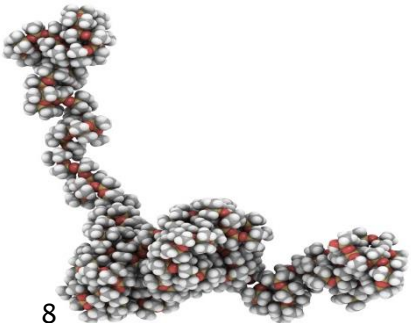
1.5% Darocur 1173

0.5% reactive defoamer

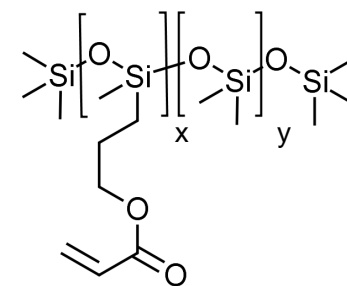
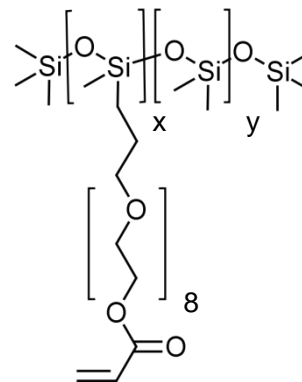
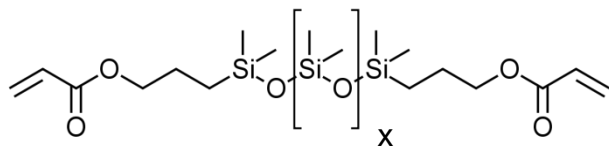
10% DTPTA

6% TRPGDA

UV light, RT

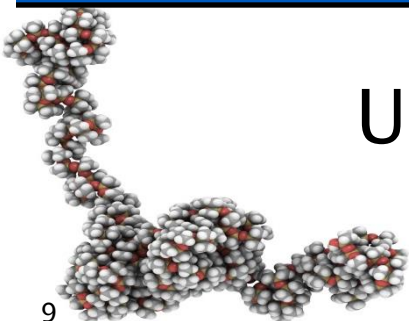


Results

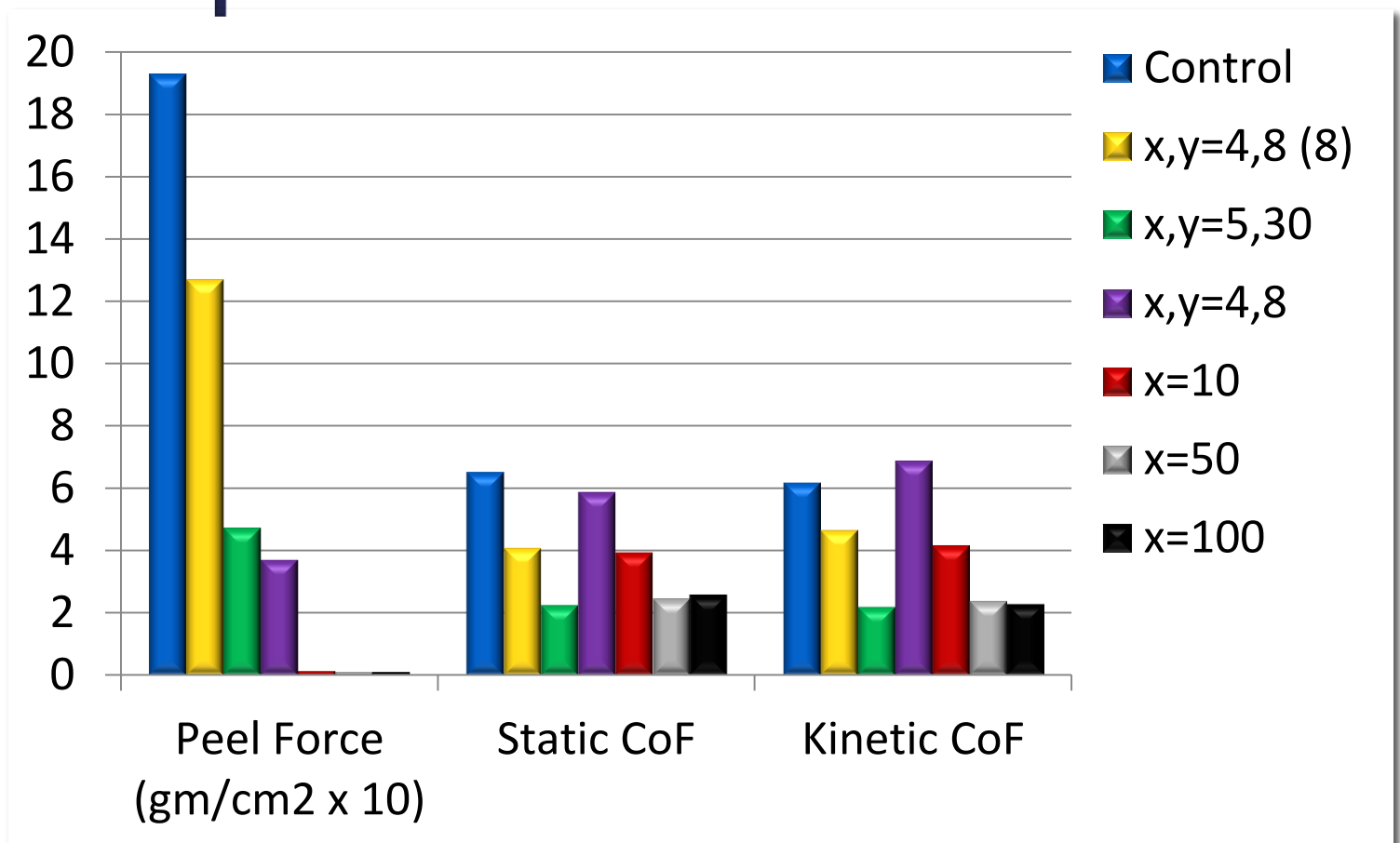


| | X=10 | X=50 | X=100 | x, y =4,8 | x, y =5,30 | x, y = 4,8 | Control |
|------------------------|------|---------------|-------|--------------|---------------|---------------|---------|
| Polyether | None | None | None | EO | EO | None | NA |
| G' (MPa) | 8.3 | 18.5 | 11.91 | 9.71 | 11.64 | 20.06 | 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 |

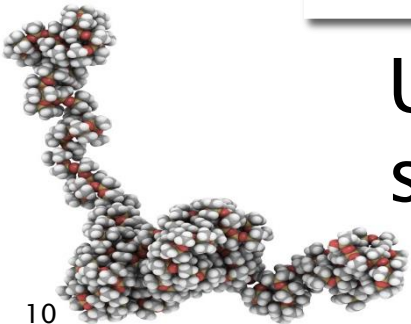
Uncured Silicone from Insolubility



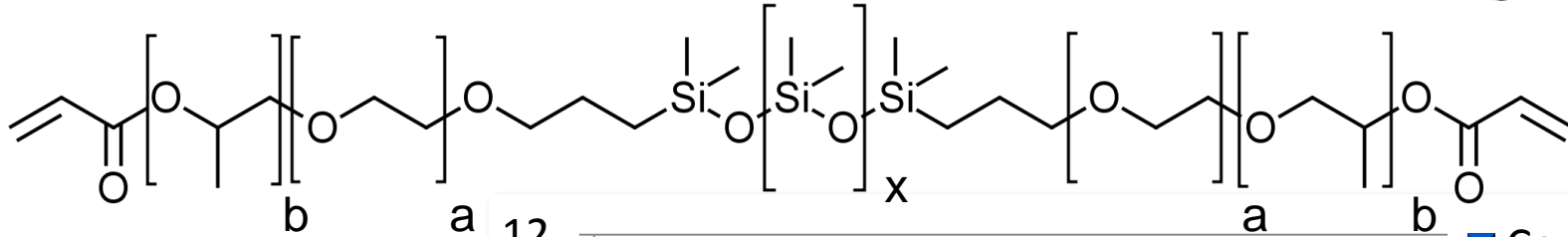
Slip Properties



Unreacted silicone is probably skewing the results



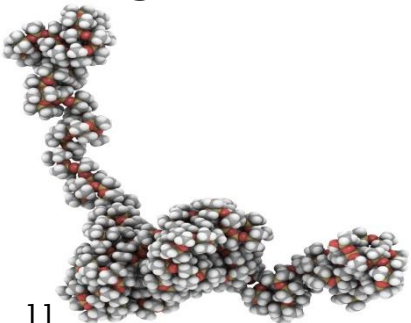
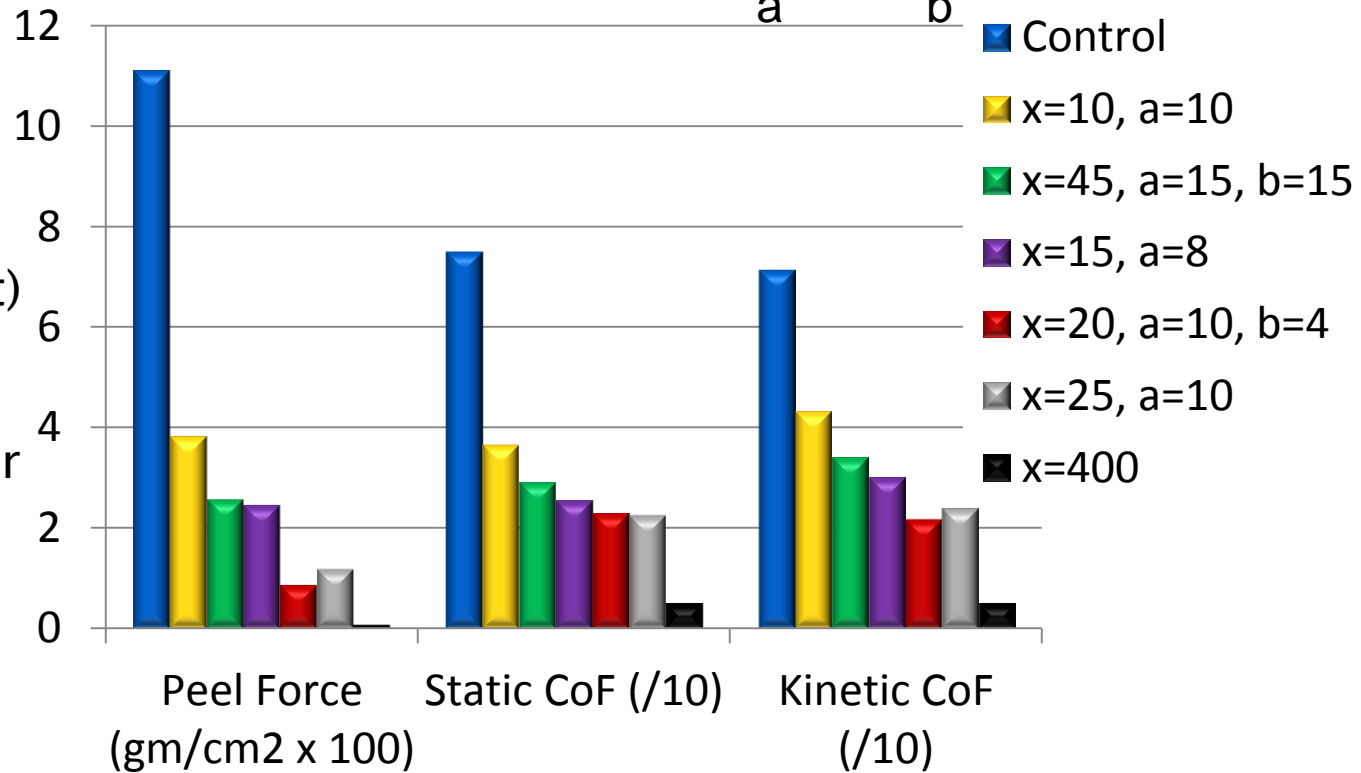
Acrylate Silicone UV coating



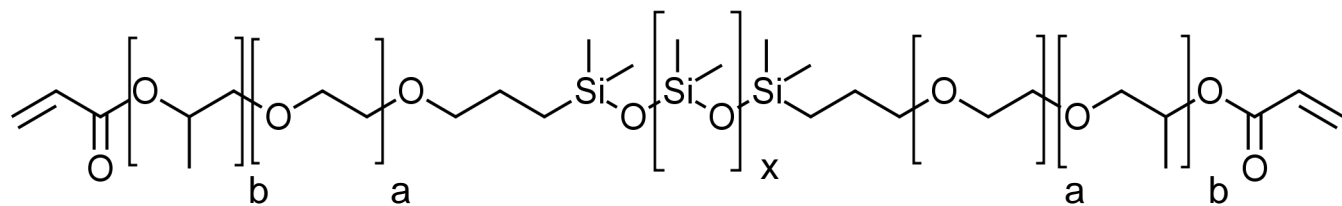
10% silicone



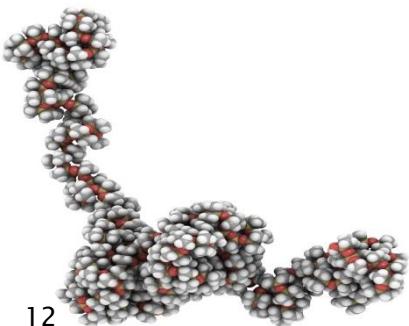
67% CN 104 C75
(epoxy acrylate)
10% CN 386 (Synergist)
5% Esacure TZT
1.5% Darocur 1173
0.5% reactive defoamer
1% DTPTA
5% TRPGDA
UV light, RT



Results

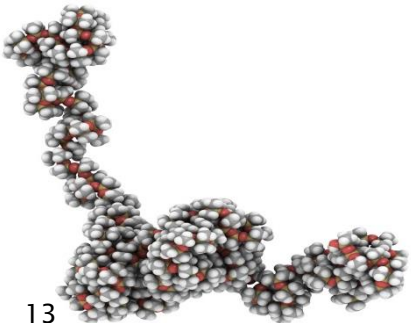


| | x=15 a=8 b=0 | x=45 a=15 b=15 | x=400, a, b=0 | x=10 a=10 b=0 | x=20 a=10 b=4 | x=25 a=10 b=0 | Control |
|------------------------|--------------------|----------------------|------------------|---------------------|---------------------|---------------------|---------|
| G' (MPa) | 16.5 | 11.6 | 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 | | | |

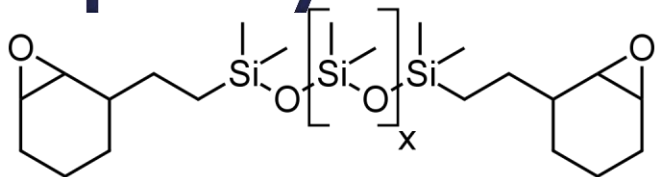


Compatibility is Important

- ▶ 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



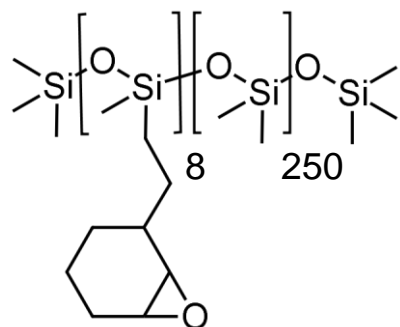
Epoxy Silicone Homopolymer



Linears

X=575 (45-76%)

X=10 (10-35%)



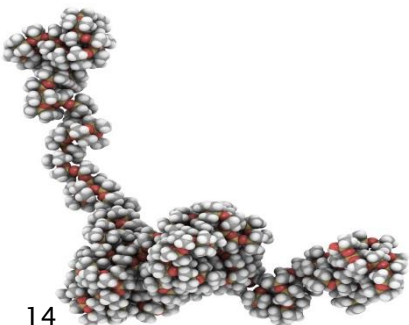
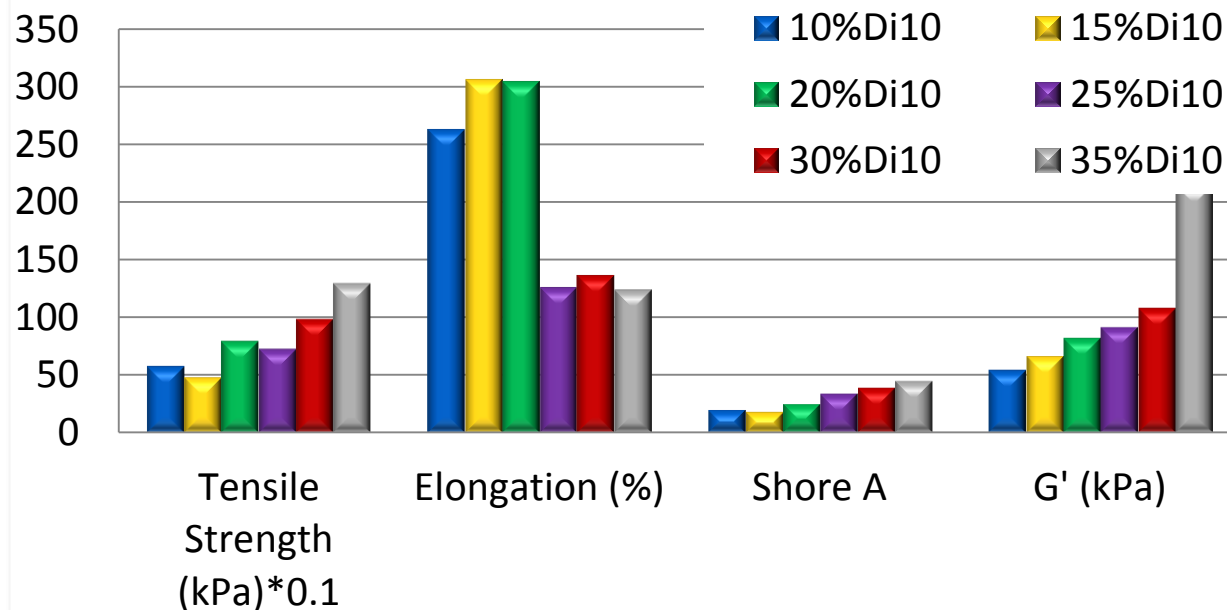
X-linker (8 wt%)



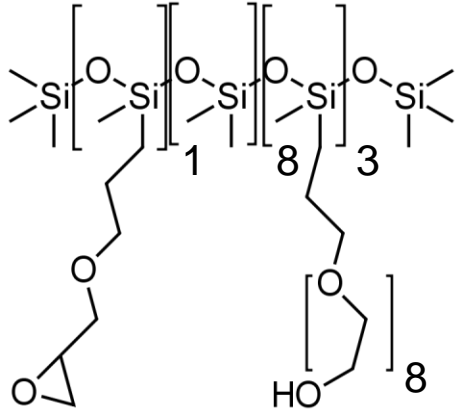
5-11% MHHPA (0.9 mole ratio)

AMI-1

110°C, 8-16 hours



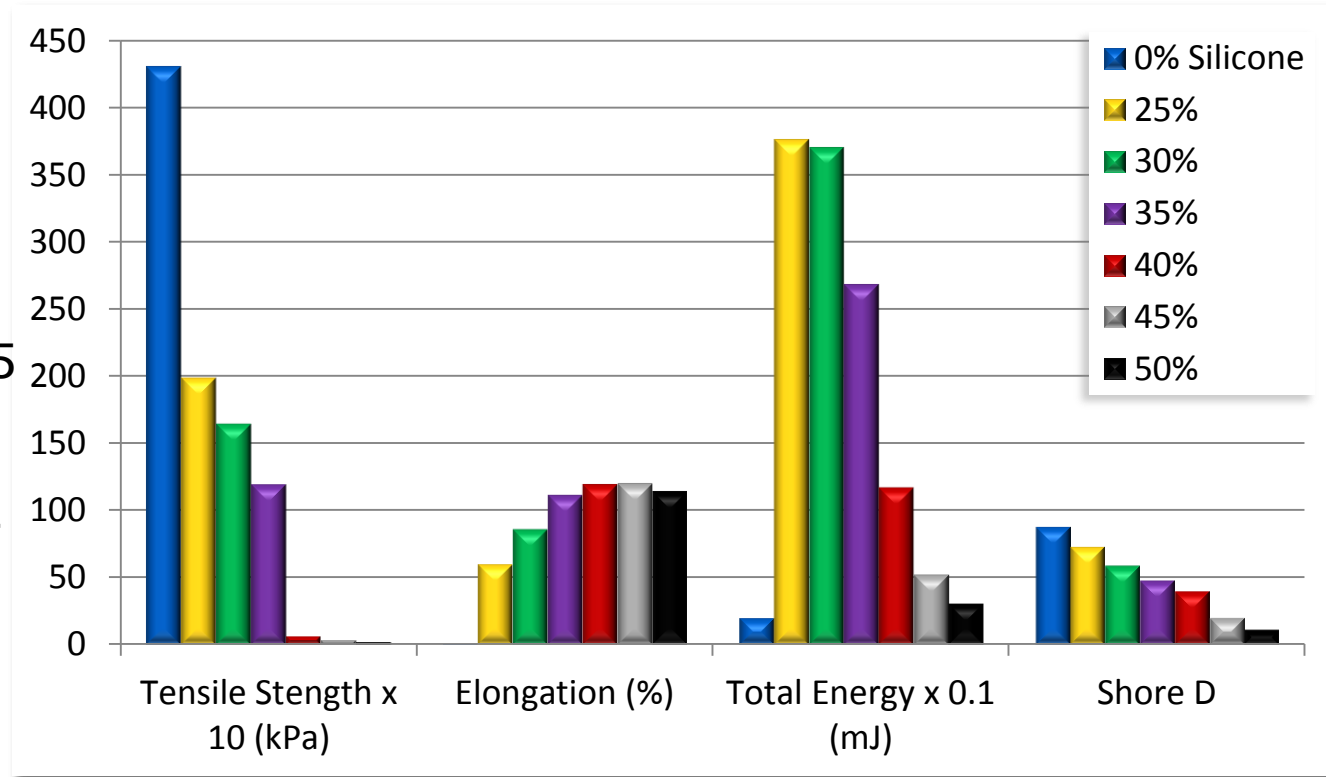
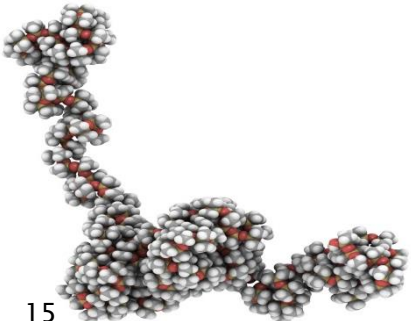
Silicone/ Hard Glycidyl Epoxy



0-50%

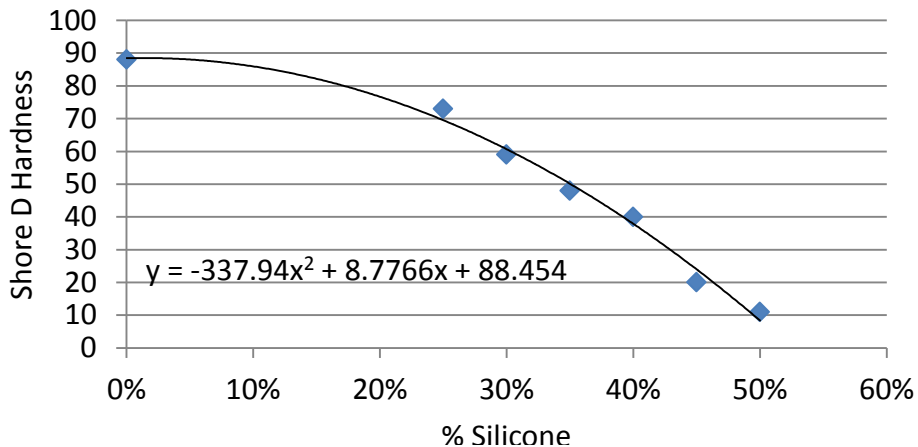


32-53% D.E.R. 671-X75
 17-23% MHHPA
 0.1% AMI-1
 0.2% reactive defoamer
 110°C, 4 hours

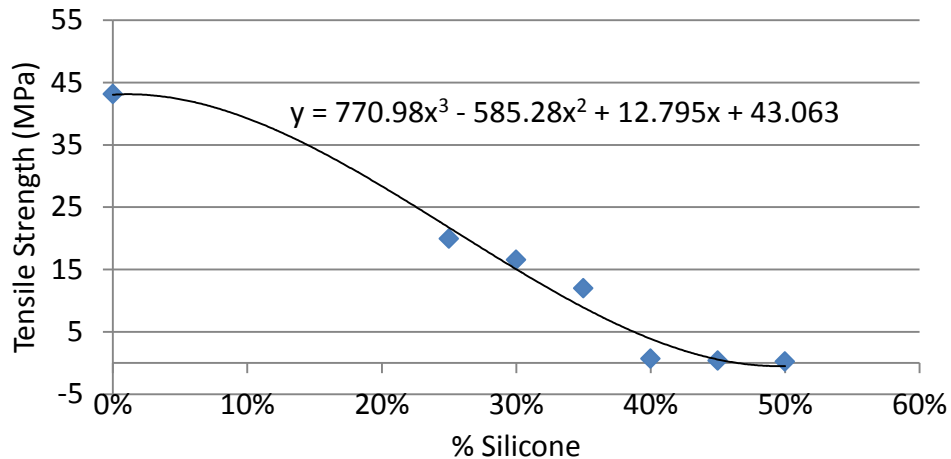


Properties

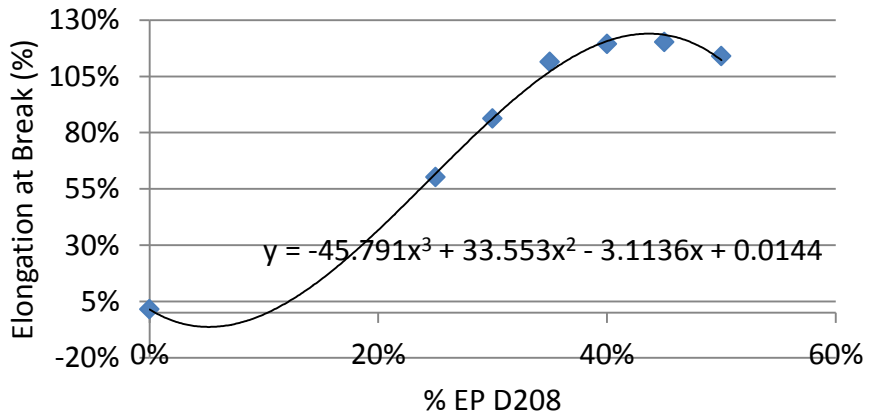
Shore D Hardness



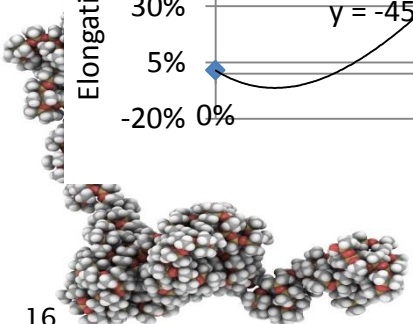
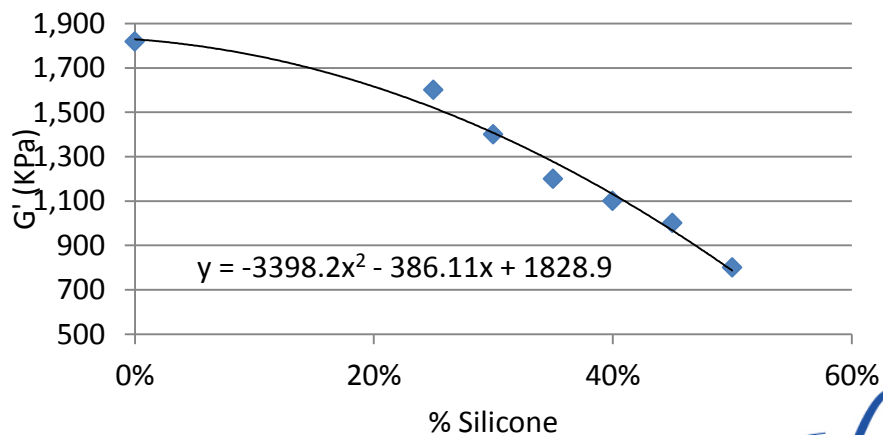
Tensile Strength



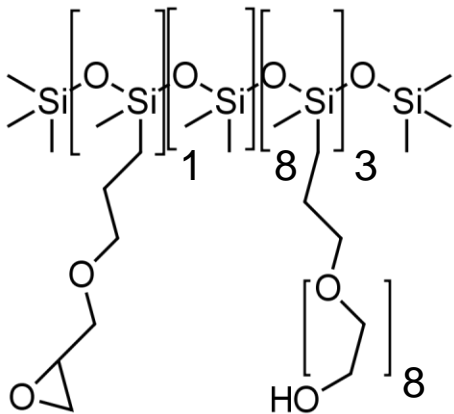
Elongation at Break



Storage Modulus G'



Silicone/ Soft Epoxy Hybrid



25-50%



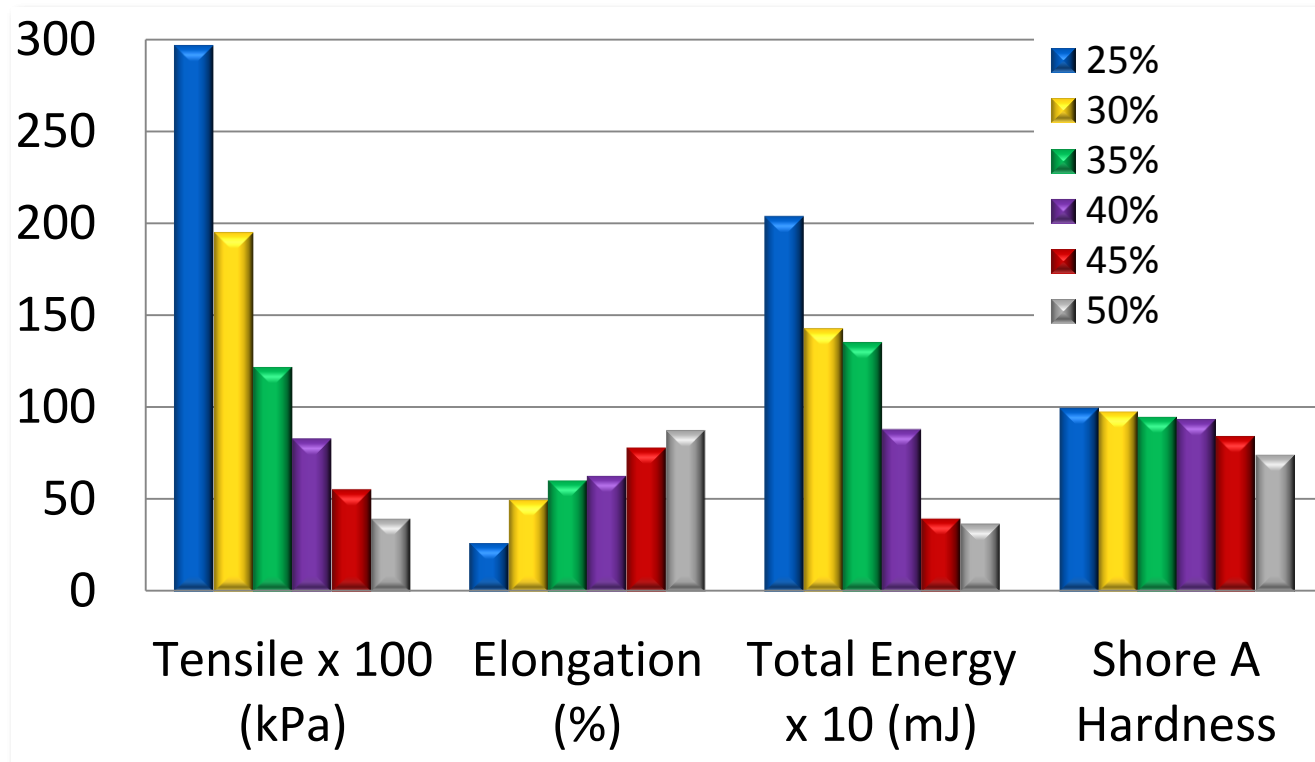
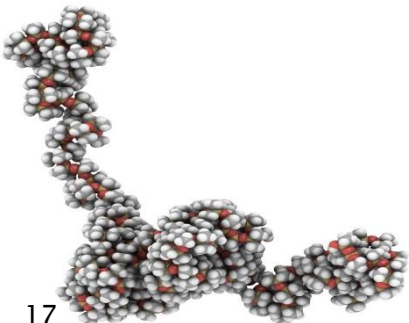
25-37% D.E.R. 331

25-37% MHHPA

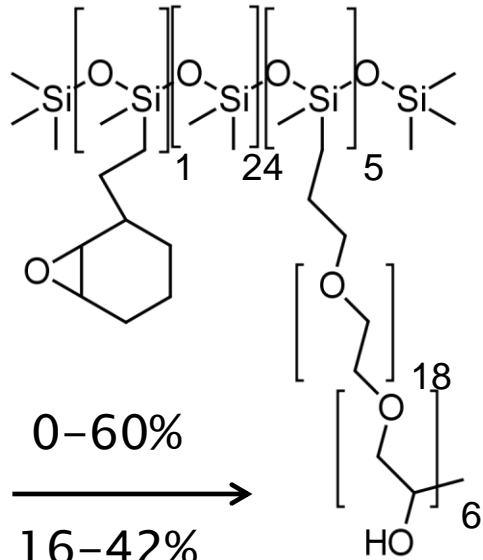
0.1% AMI-1

0.2% reactive defoamer

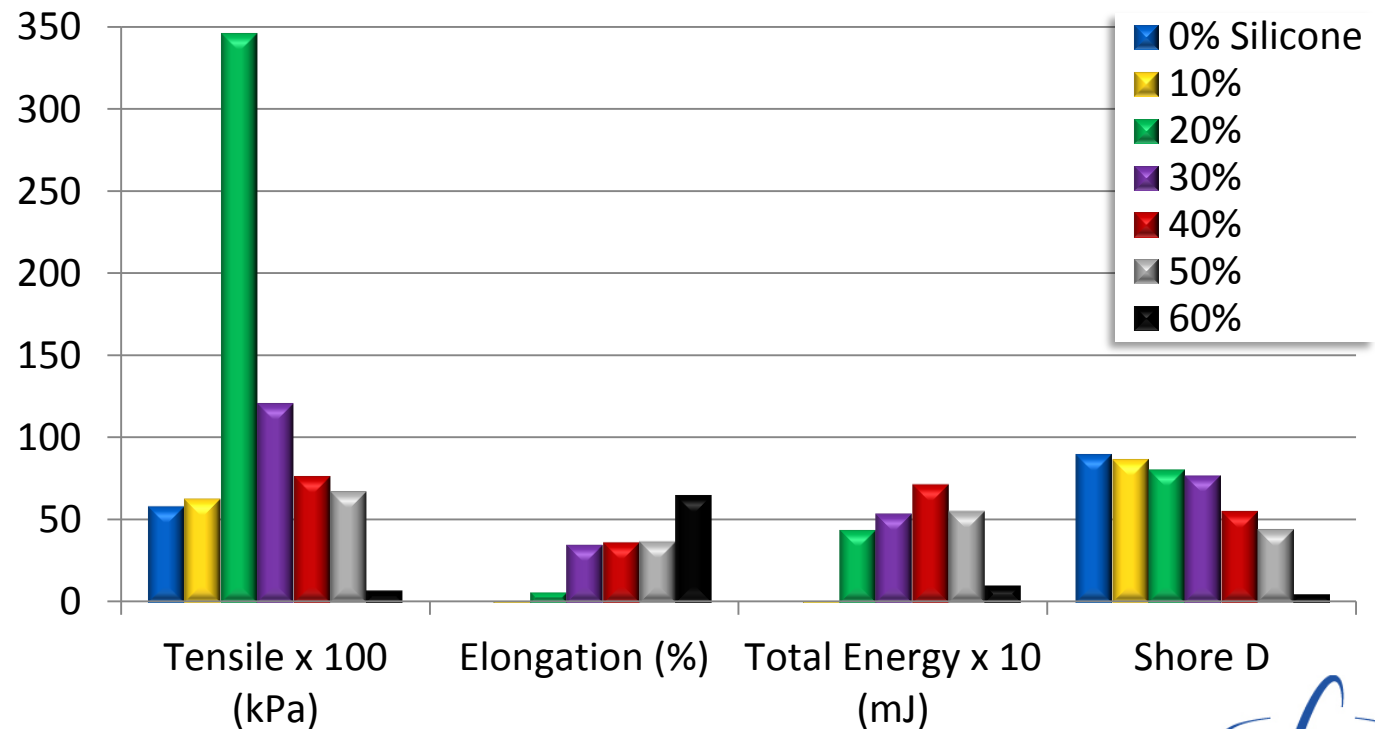
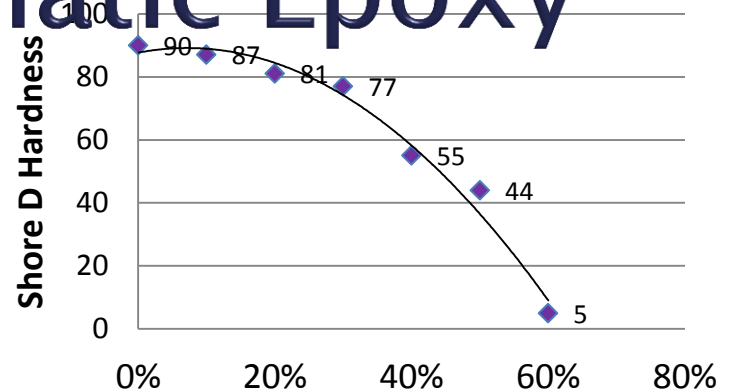
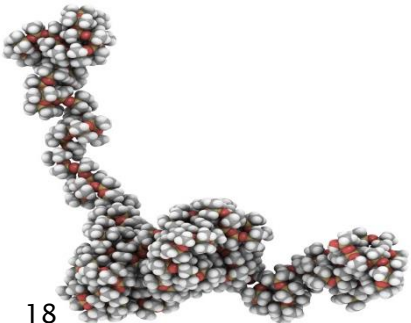
110°C, 4 hours



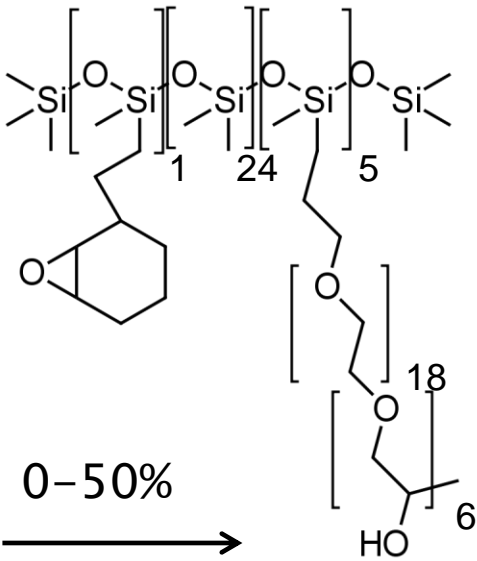
Silicone/ Cycloaliphatic Epoxy



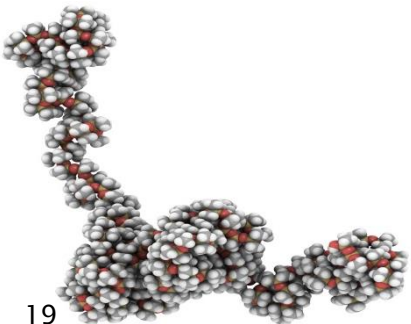
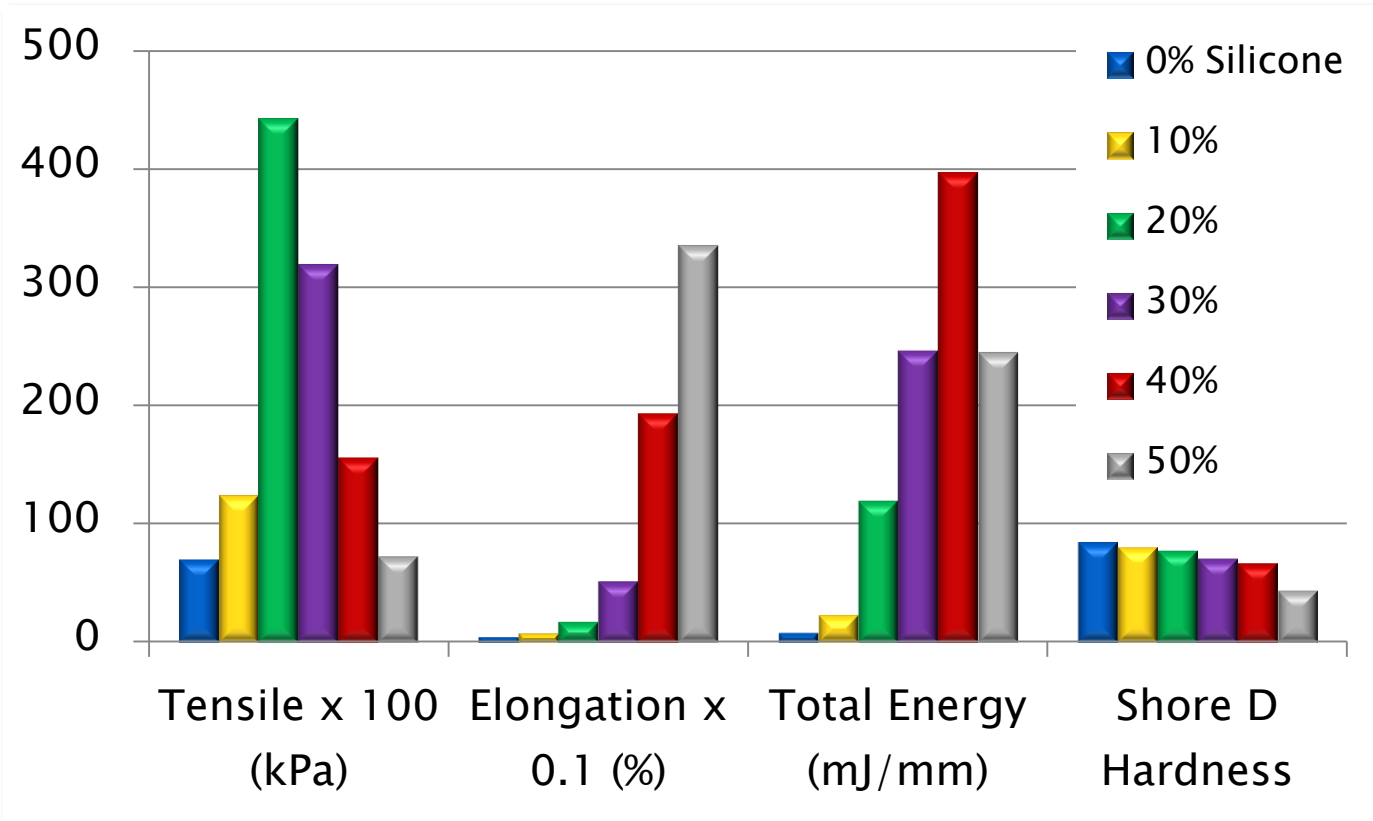
UVACURE 1500
24-58% MHHPA
0.1% AMI-1
110°C, 4 hours



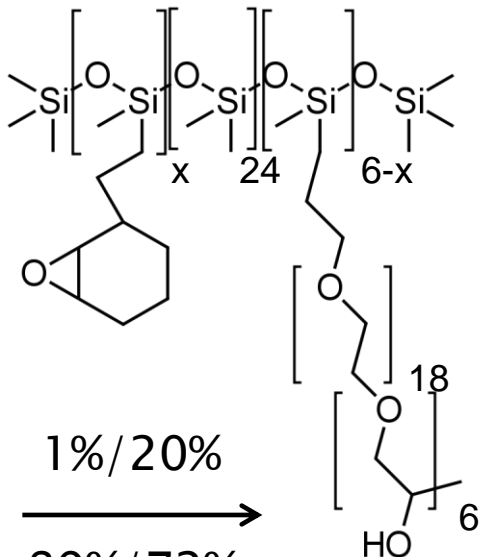
Silicone/ Epoxy UV Cured



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



Effect of X-Link



1%/20%

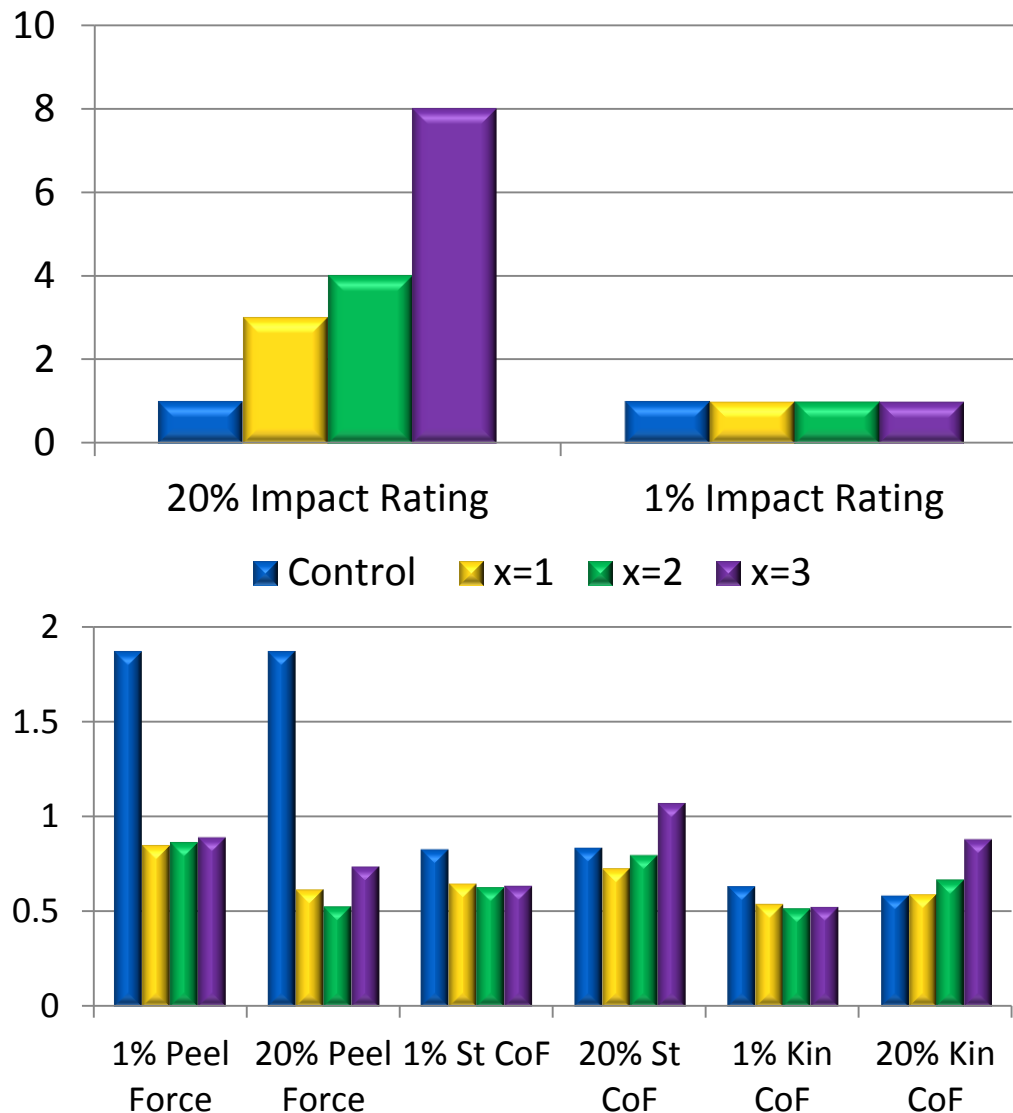
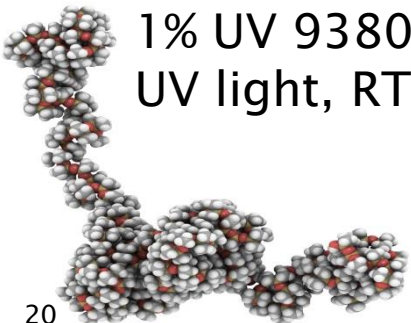
89%/72%

UVACURE 1500

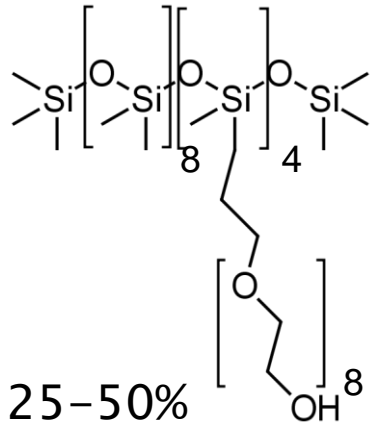
9%/7% CAPA A polyol

1% UV 9380C

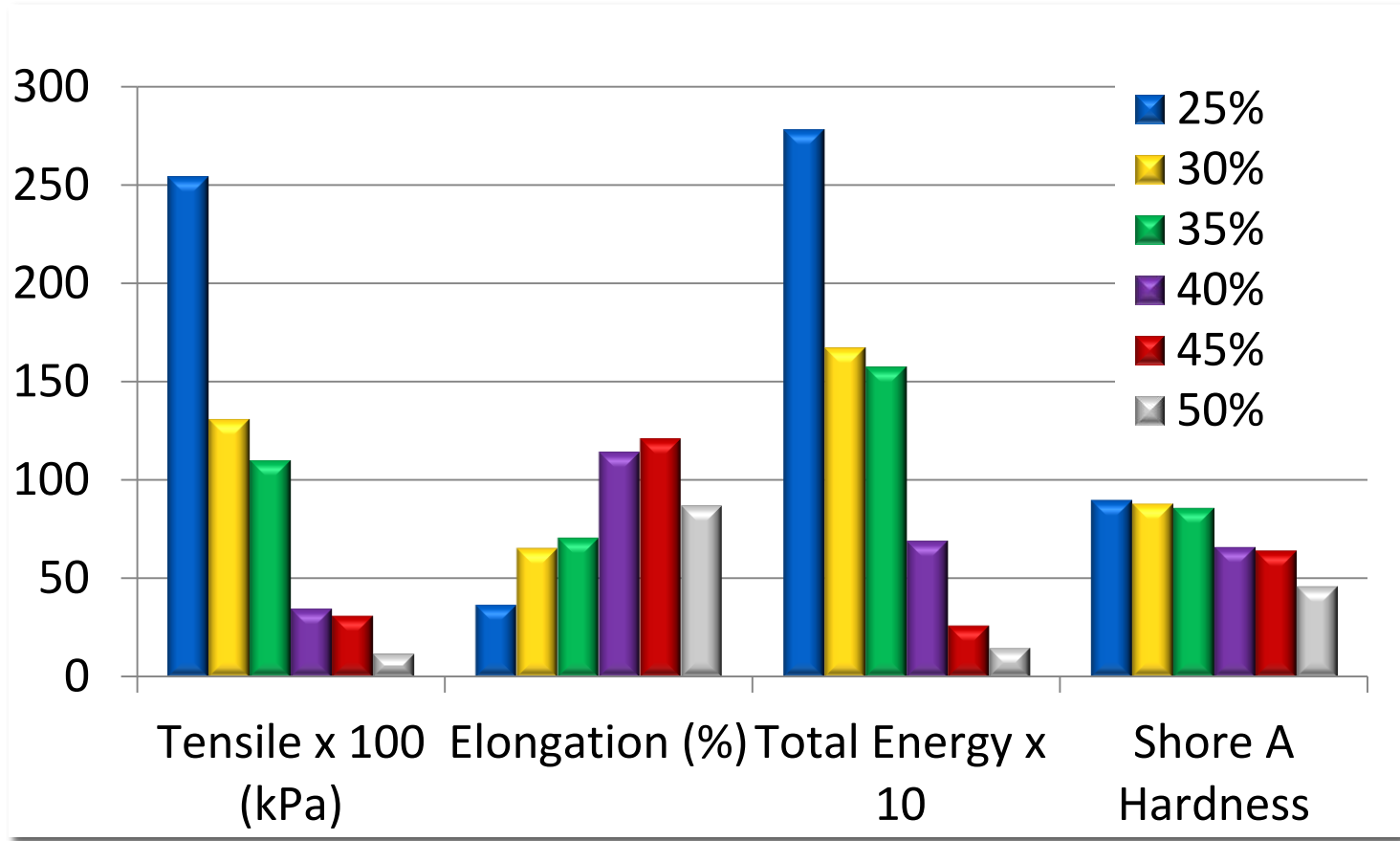
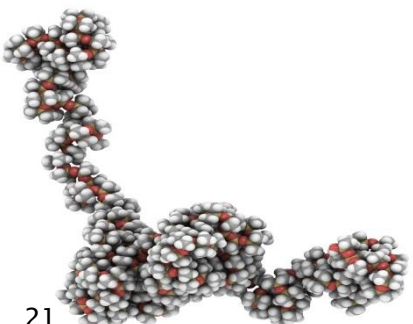
UV light, RT



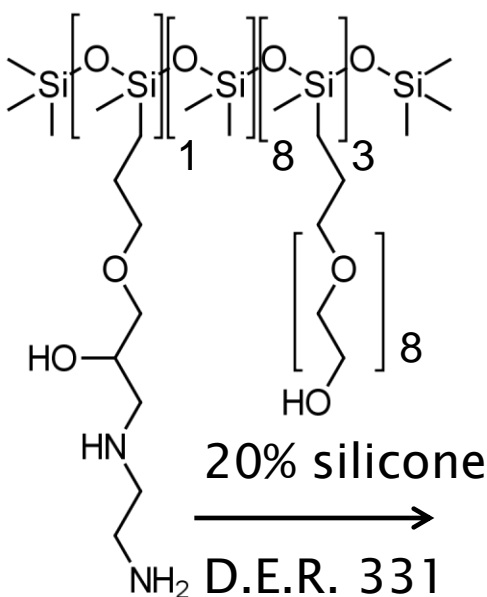
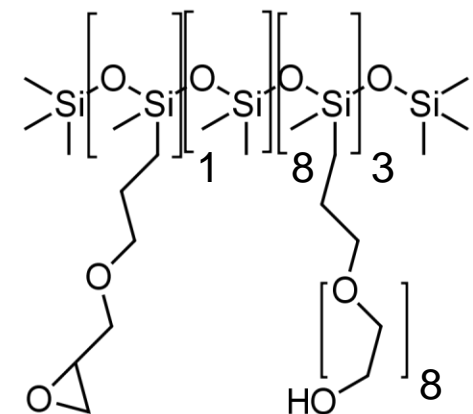
OH Silicone / Glycidyl Epoxy



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



NH₂ Silicone/Glycidyl Epoxy Hybrid



20% silicone

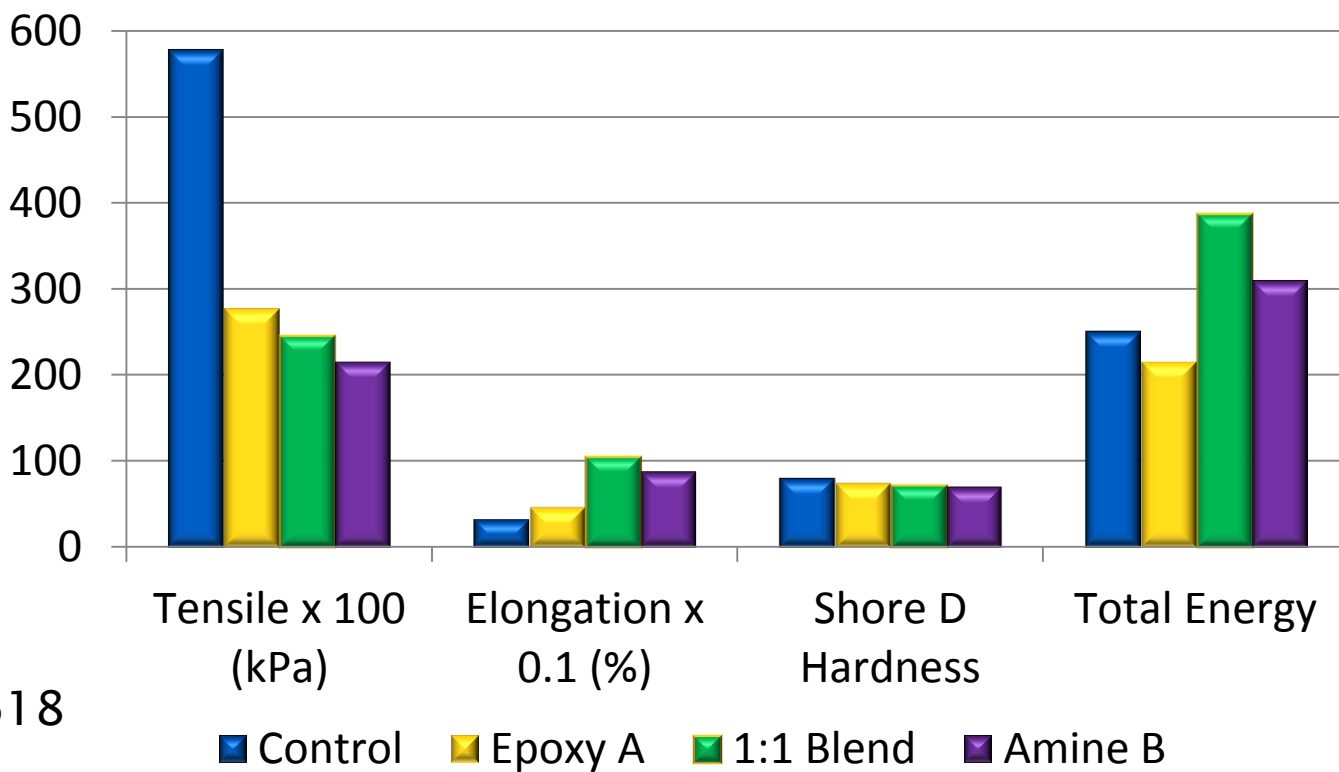
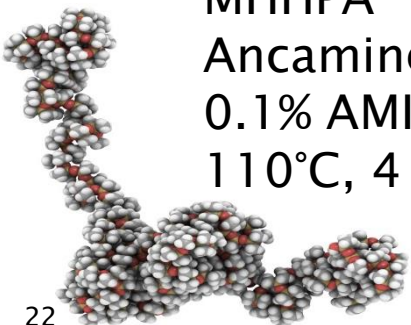
D.E.R. 331

MHHPA

Ancamine 1618

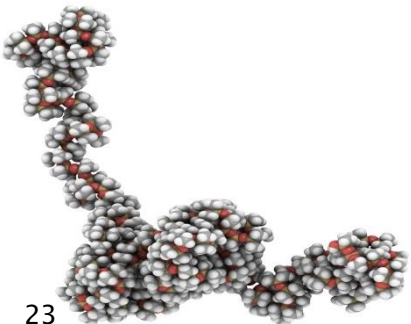
0.1% AMI-1

110°C, 4 hours

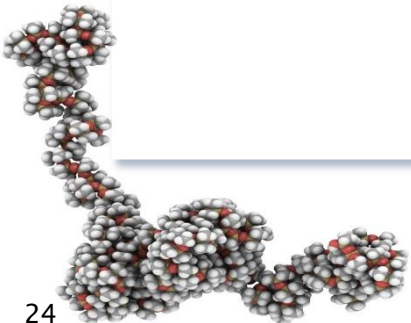
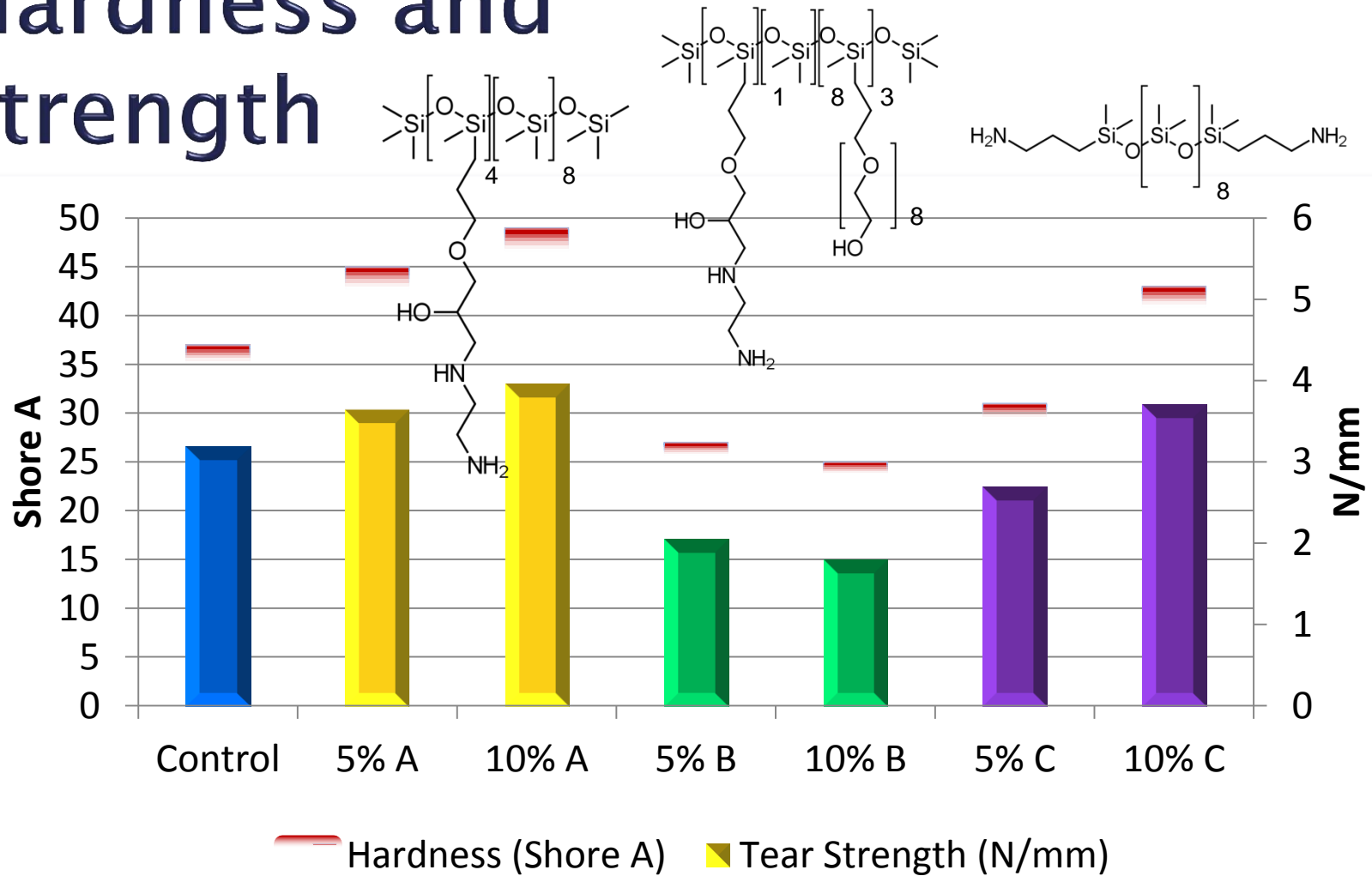


Rubber Filled Epoxy with Silicone Hardener

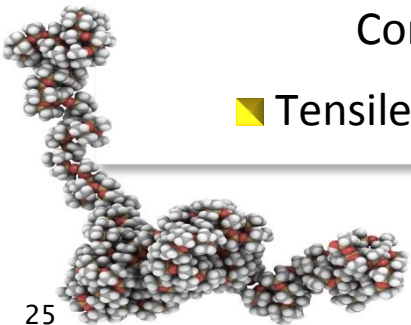
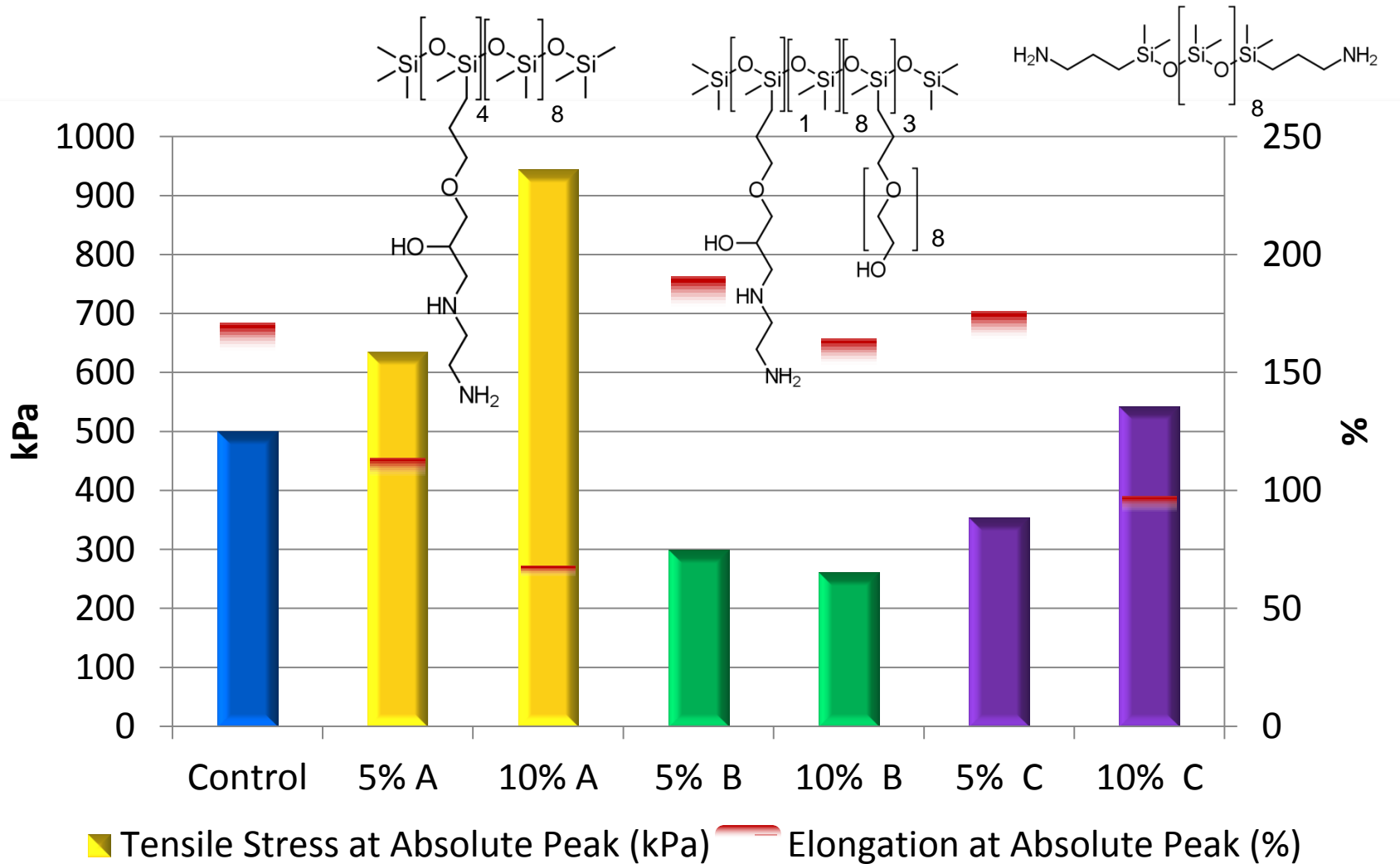
- ▶ Proprietary epoxy with 5–10% reactive silicones and rubber crumbs
- ▶ Mold and cure at ambient for 7 days
- ▶ -15°C and -30°C impact resistance measured with a steel ball drop
- ▶ Severity of fracture rated 1–10 (best)



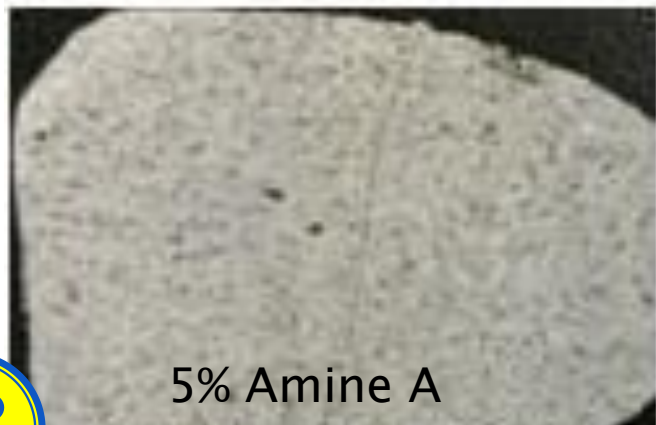
Hardness and Strength



Tensile Stress and Elongation



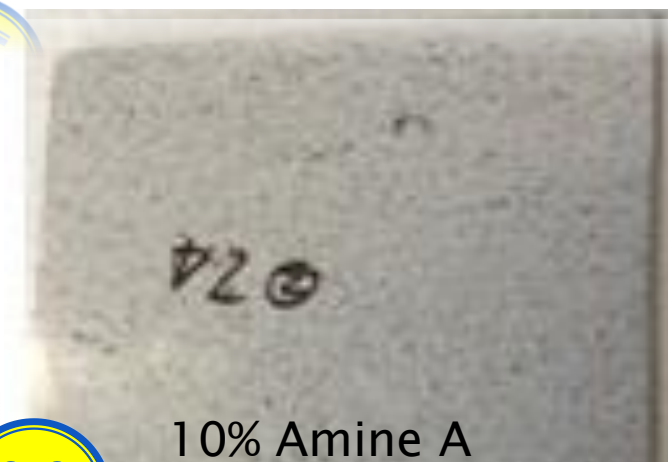
-15°C
Fracture



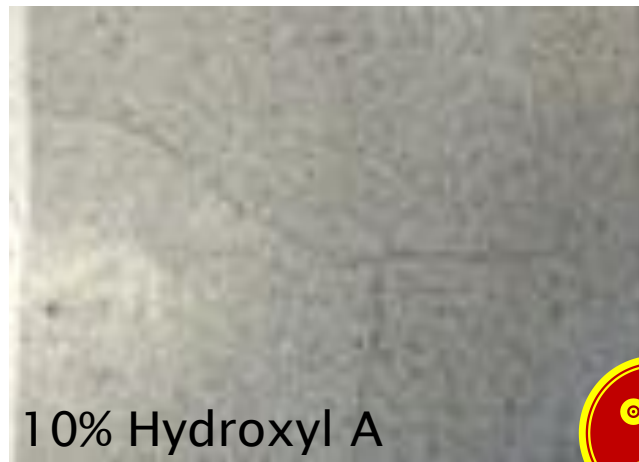
5% Amine A



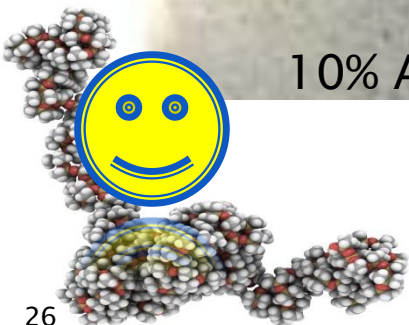
Control



10% Amine A

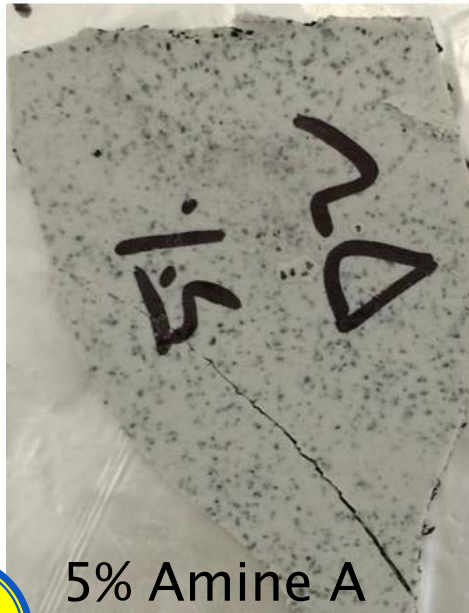


10% Hydroxyl A

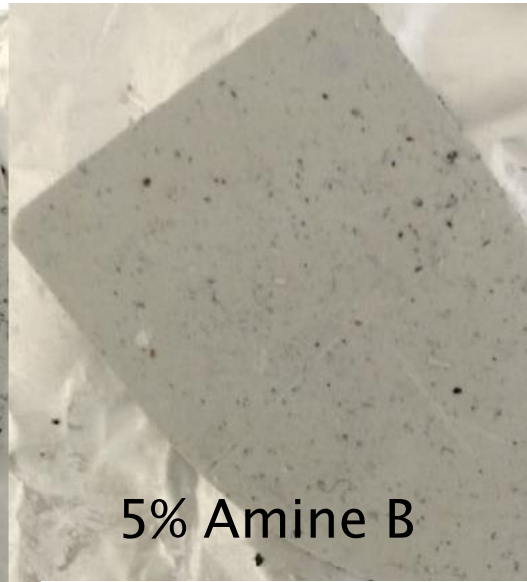




Control



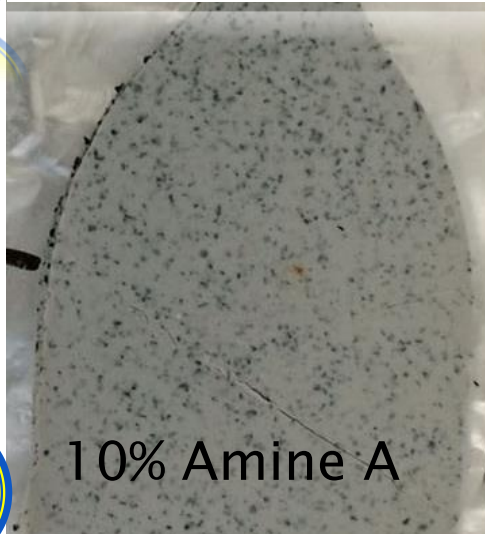
5% Amine A



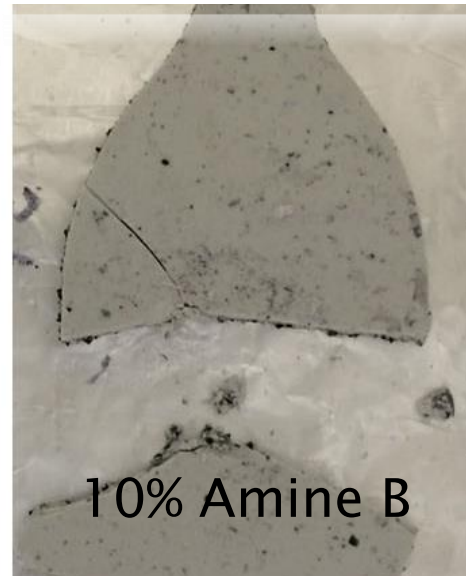
5% Amine B



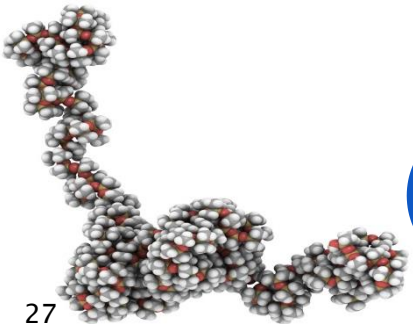
-30°C
Fracture



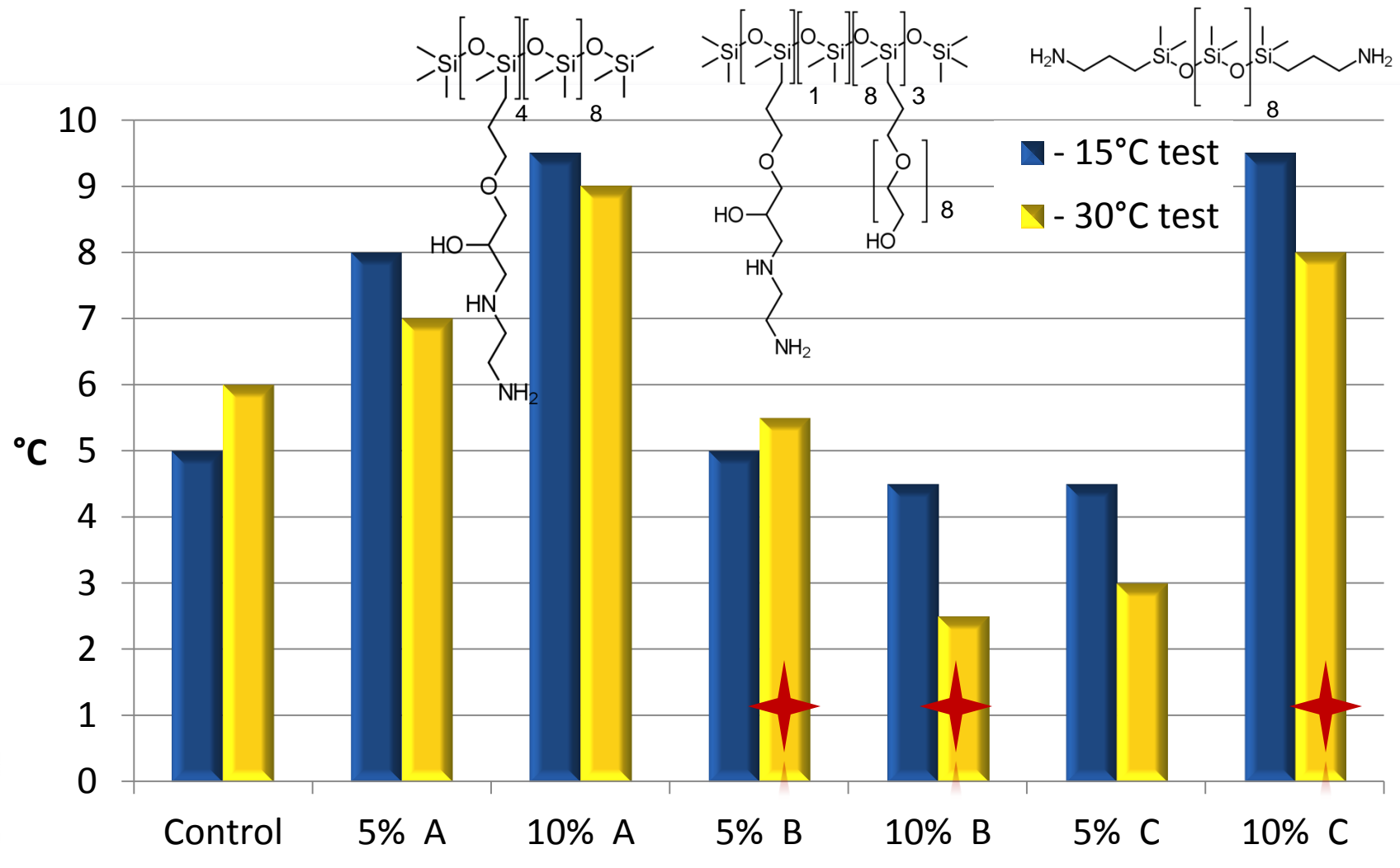
10% Amine A



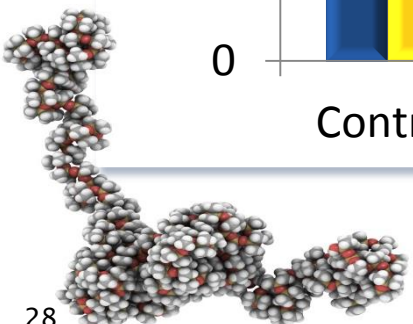
10% Amine B



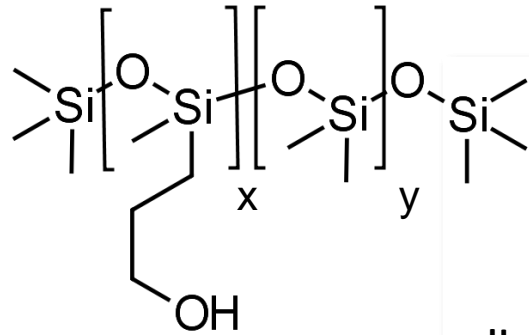
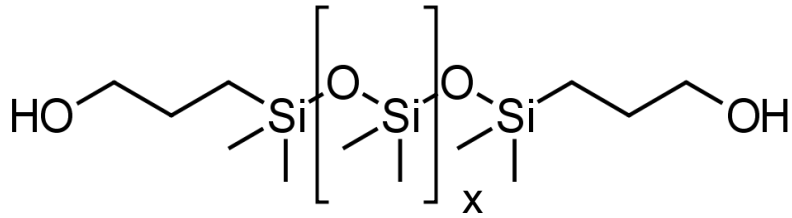
Low Temperature Impact



 Fractured on second of two impacts

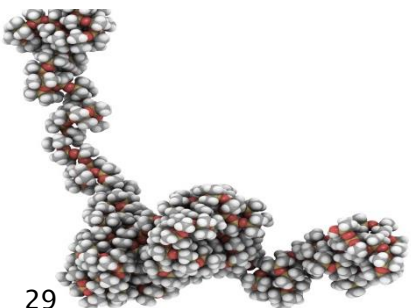
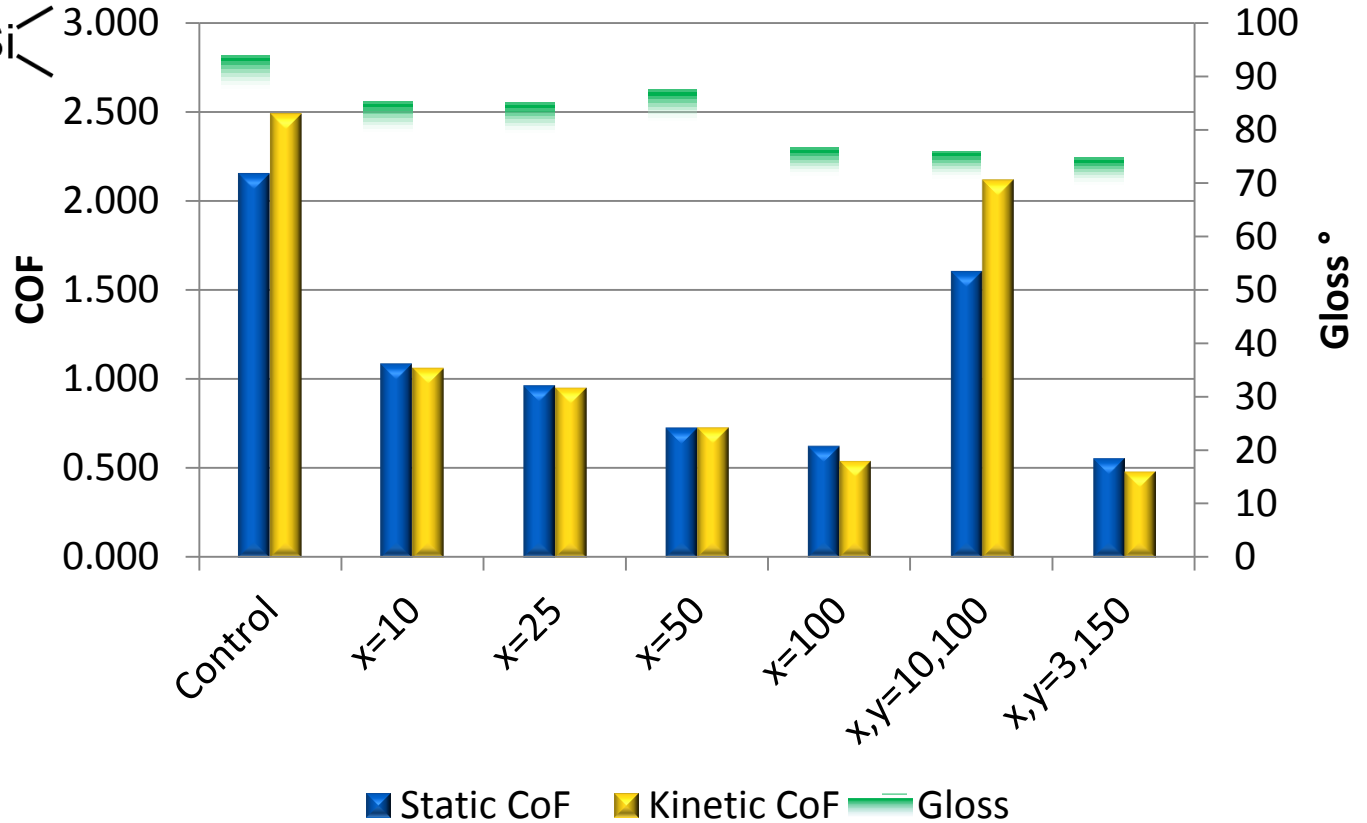


OH Silicone/ SB Polyurethane

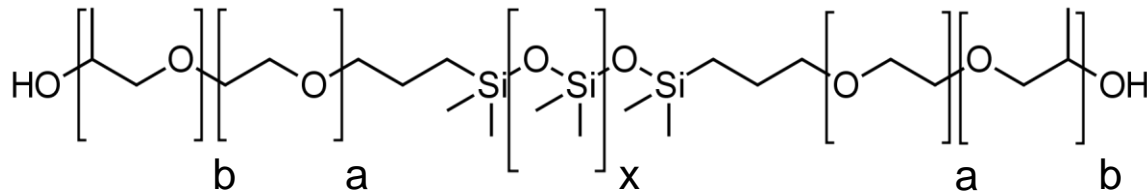


10% in part A

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

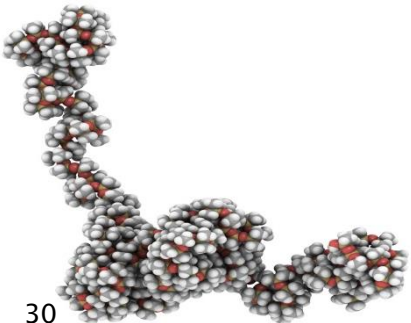
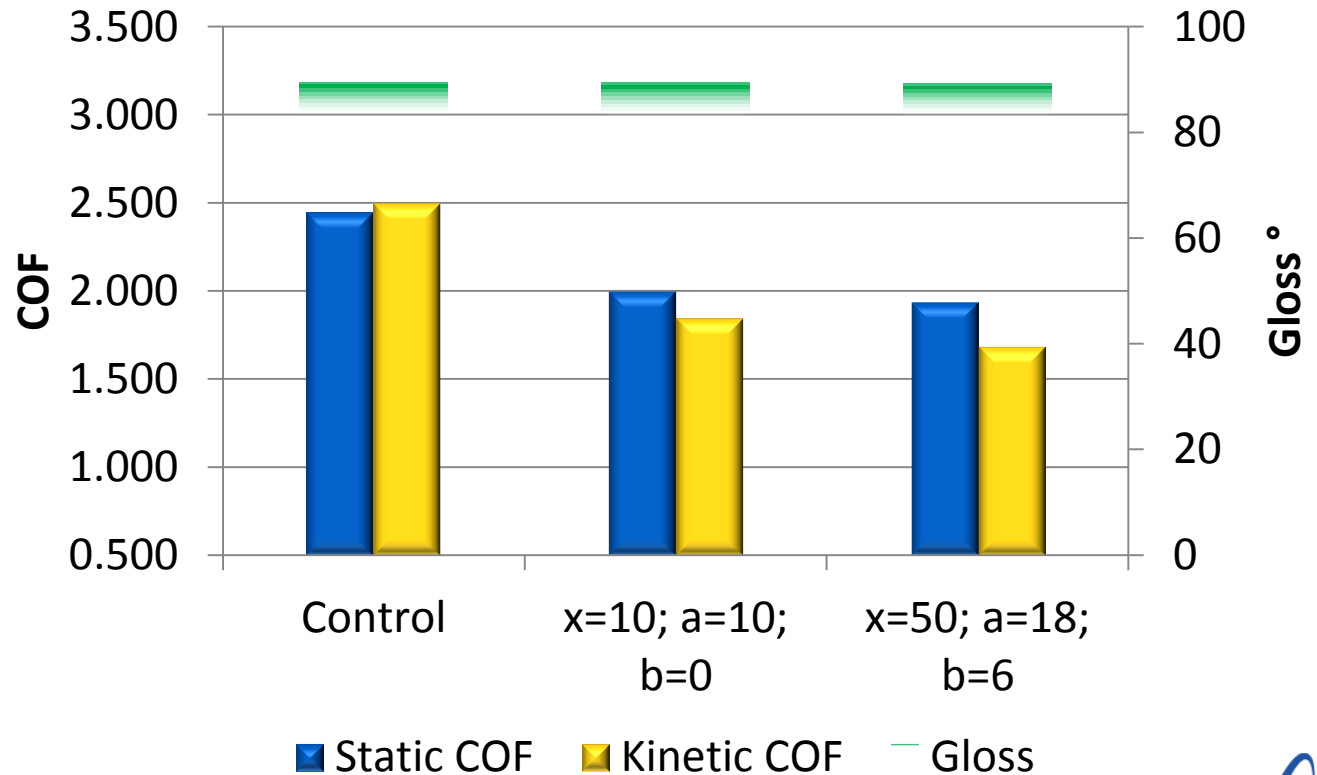


OH Silicone/ WB Polyurethane



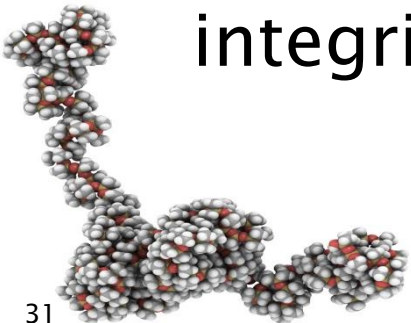
1 %
→

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



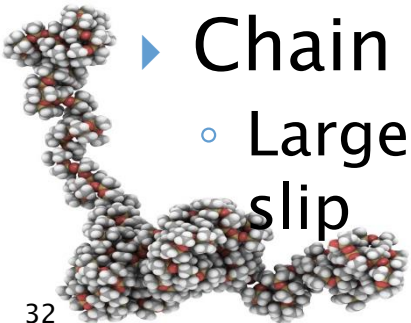
Conclusions

- ▶ 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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