Properties of Silicone Modified Coatings Films

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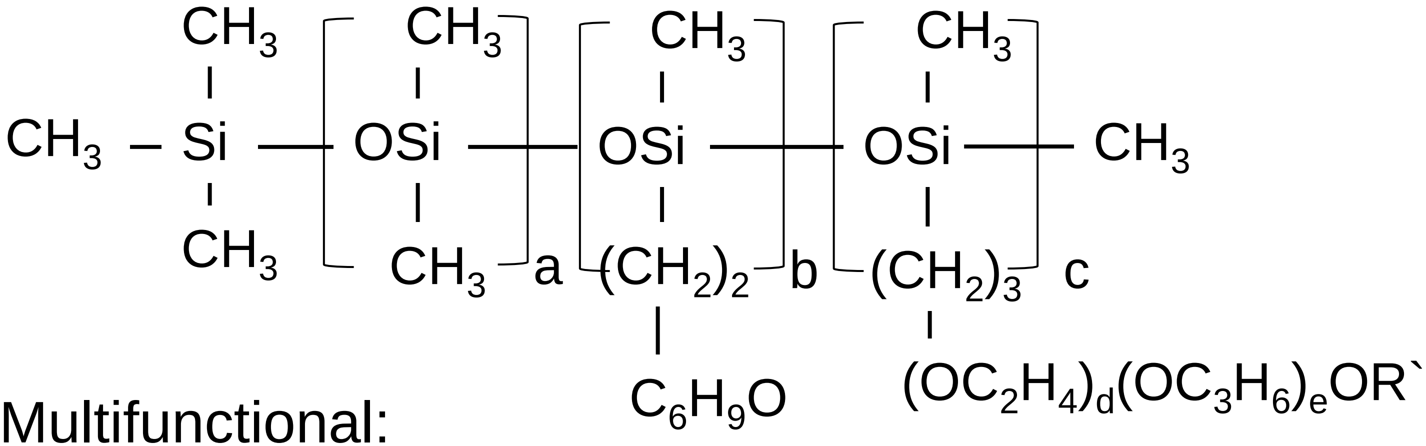
Summary

- Reactive silicones are available with differing reactive groups including acrylate and cycloaliphatic epoxy.
- Using UV cured resins and multiple testing procedures as examples, this work summarizes what to expect when you incorporate these silicones into your films.

Silicone Variations



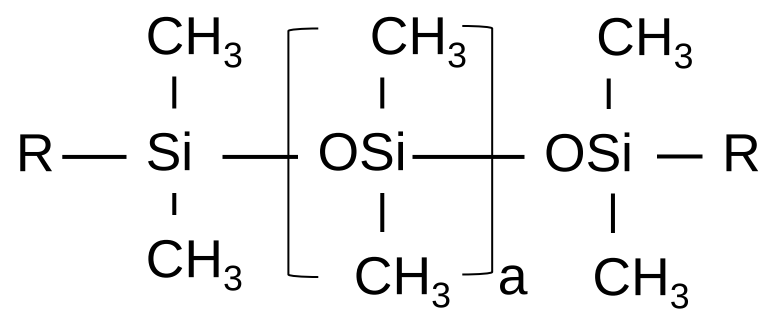
Multifunctional:

ACR series: b=0 and R`=Acrylate ester

EPC series: b≠0 and R`=H

Polyether series: c≠0

Non-polyether series: d,e=0



Linear di-functional:

ACR series: R=Acrylate ester

or R=$C_3H_6(OC_2H_4)_d(OC_3H_6)_e$O-Acrylate ester

EPC series: R=$C_8H_{13}O$

Testing

Test Panel Preparation: 1 ml is drawn down on a white Leneta paper with wire-wound rod #10.

Coefficient of Friction (CoF /Slip): A ChemInstruments Coefficient of Friction -500 measures static and kinetic coefficients of friction directly. The slip rating is determined by averaging % change of CoF with weighting factors against the control in the same series and normalizing to 10 with all the test samples.

Gloss: Measured with BYK-Gardner 60° micro-glossmeter.

Peel Force Measurements: measured by peeling 6``of Intertape 6100 with ChemInstruments 500 at an angle of 180° and peel rate of 60 cm/min. Report an avg of ten in gm/cm^2.

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Testing (cont)

Mar Resistance: measured using a Sutherland 2000 Ink Rub Tester - Dry Rub method with the following settings: 500 rubs, 84 rpm stroke speed for all sample sets using a 4 lb test block and a 2"x 4" nylon scrubbing pad. Gloss is measured immediately after rubbing for each panel. Record the loss of gloss(%) before and after rubs and a subjective rating from 0 to 10 where 10 is the best and indicates no visible effect.

Stain Resistance: Stains are applied using 1-5 drops/mark near the centre portion the panel, conditioned at room temperature for 1 hour then rinsed with tap water for 1 minute and wiped with an IPA saturated cotton swab. The subjective ratings are obtained from the stains remaining on the panels from 1 to 10 where 10 is best and indicates no remaining stain.

Testing (cont)

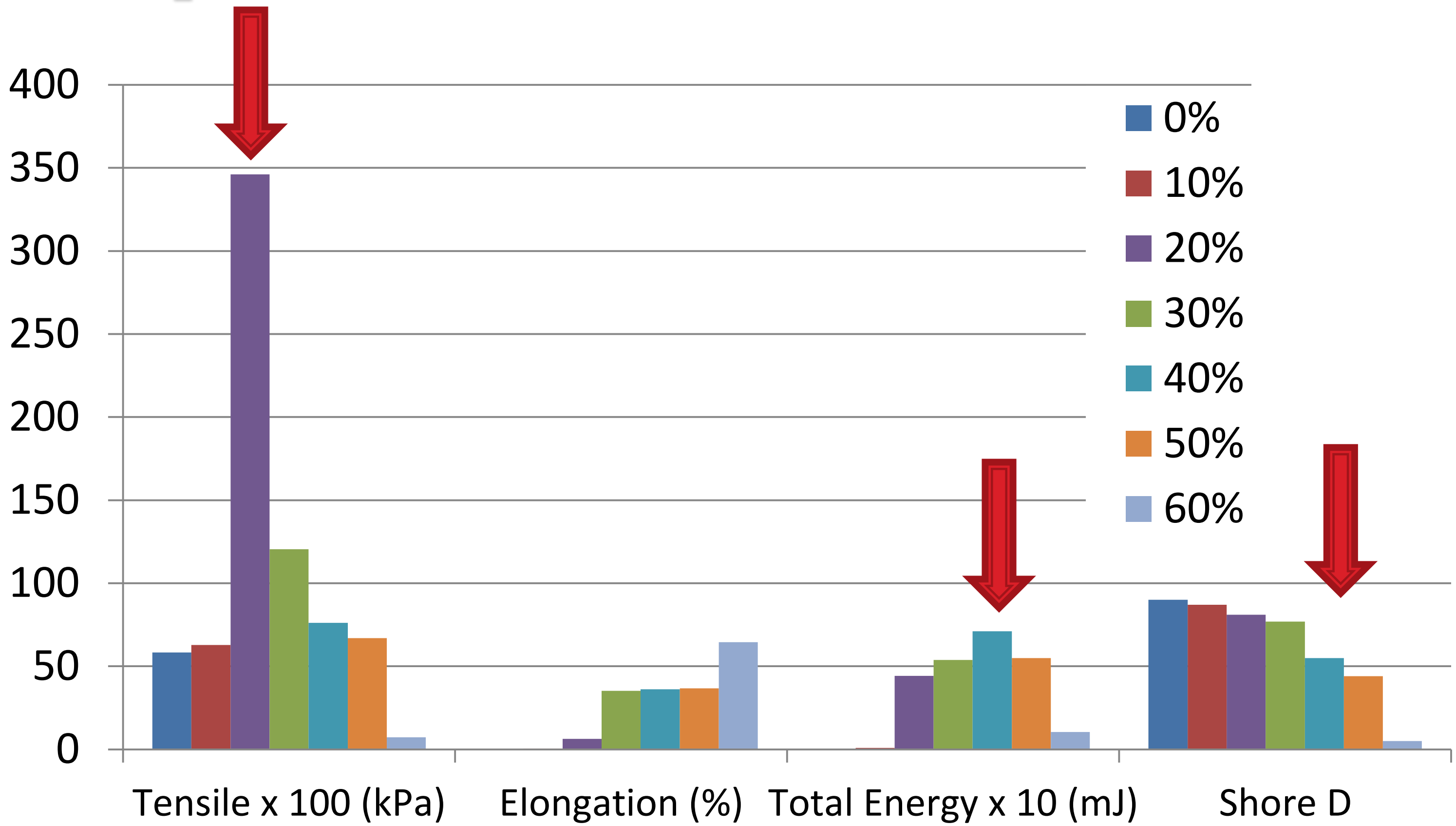
Impact Resistance The panel to be tested is placed coated side down on the top of a protective paper on a flat steel plate with rubber pad on the bottom. A steel rod with a 1 cm diameter round steel ball attached at the end of the rod is placed on the back side of the coating surface. A 700 gram weight drops vertically along the rod from a distance of 23 cm above the coating surface. The subjective ratings are obtained by visual comparison of impact damage on the panels for each series from 1 to 10 where 10 is best and indicates no cracking or breaking of the film.

Proof of Concept: Cured Gel

Component	Name	Level
Organic Resin	UVACURE Epoxy Resin	42-16%
Anhydride Curative	MHHPA	58-24%
Cycloaliphatic Epoxy Silicone	EPENPL35	0-60%
Catalyst	AM-1	0.06-0.1%

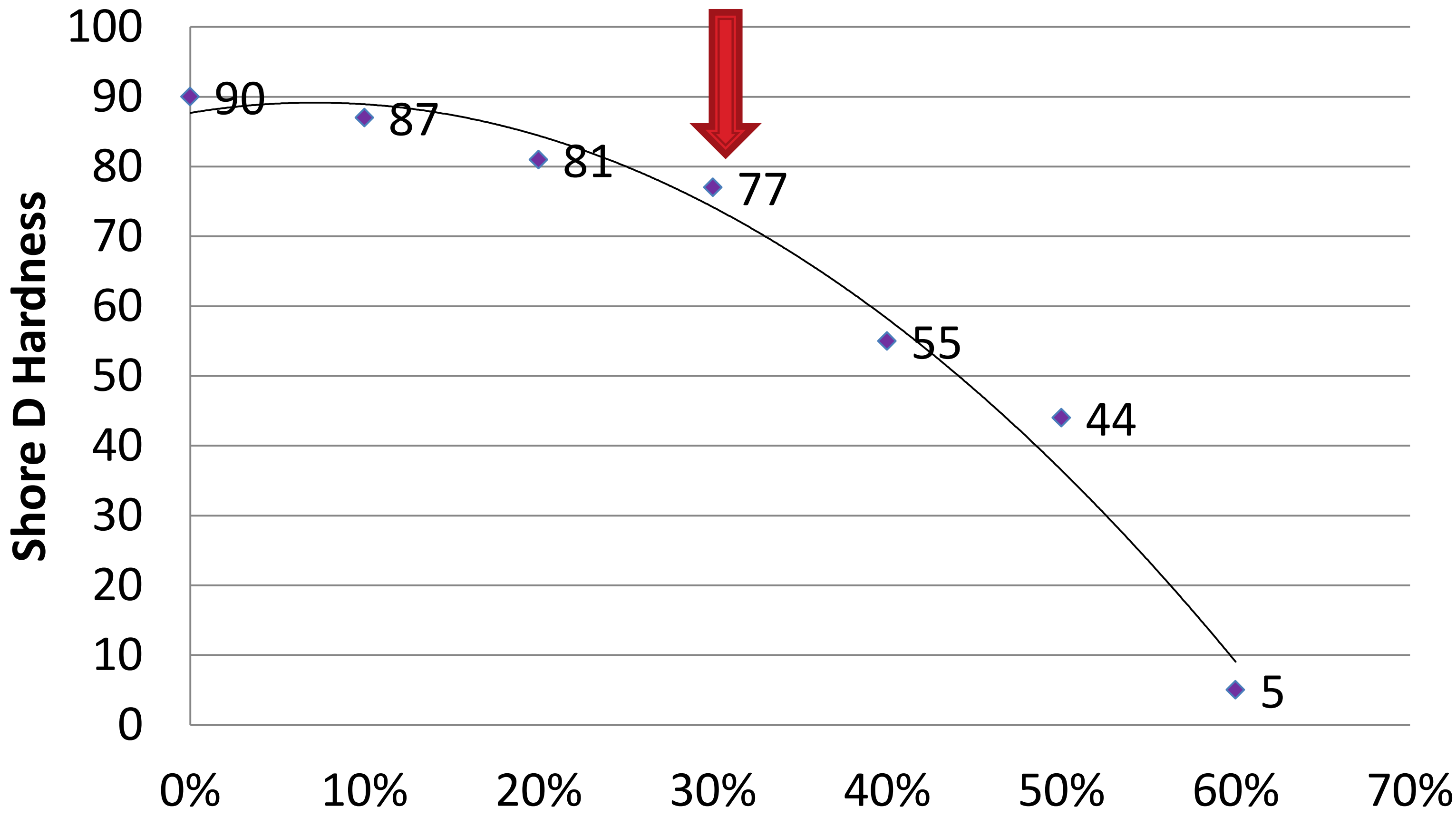
- EPENPL35 has polyalkyleneoxide groups for compatibility as well as cycloaliphatic epoxy groups for reactivity.
- The rheological data and mechanical properties are obtained directly from Brookfield DV-III Rheometer AR-G2 and Instron Model #1122 using the following cure conditions: 110°C and Cure Time: 4 Hours.

Properties



- Increasing silicone decreases hardness slightly.
- Toughness maximizes at 40%.
- Tensile strength spikes at 20%

Hardness



- Up to 30% silicone reduces hardness by only 15%

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
- With inclusion of silicone, films become:
  - more flexible
  - more slippery

Acrylate Functional

Component	Level
ACR Reactive Silicones Use level (%)	Various 22.0%
Epoxy Acrylate Resin Use level (%)	CN102Z 40.0%
Synergist CN386	15.0%
Photoinitiator Esacure TZT	5.0%
Photoinitiator Darocur 1173	1.5%
Reactive Defoamer	0.5%
Reactive Diluent SR 355 DTPTA	10%
Reactive Diluent SR 306 TRPGDA	6%

Results

	LINX10	LINX50	LINX100	PENES8	PENES30	PENX8	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
Cure Condition & Appearance	oily	oily, defects	oily	Cured	Cured	Sl. Tacky	Cured

- Most show lower moduli indicating reaction
- Only the solubilized materials completely cure

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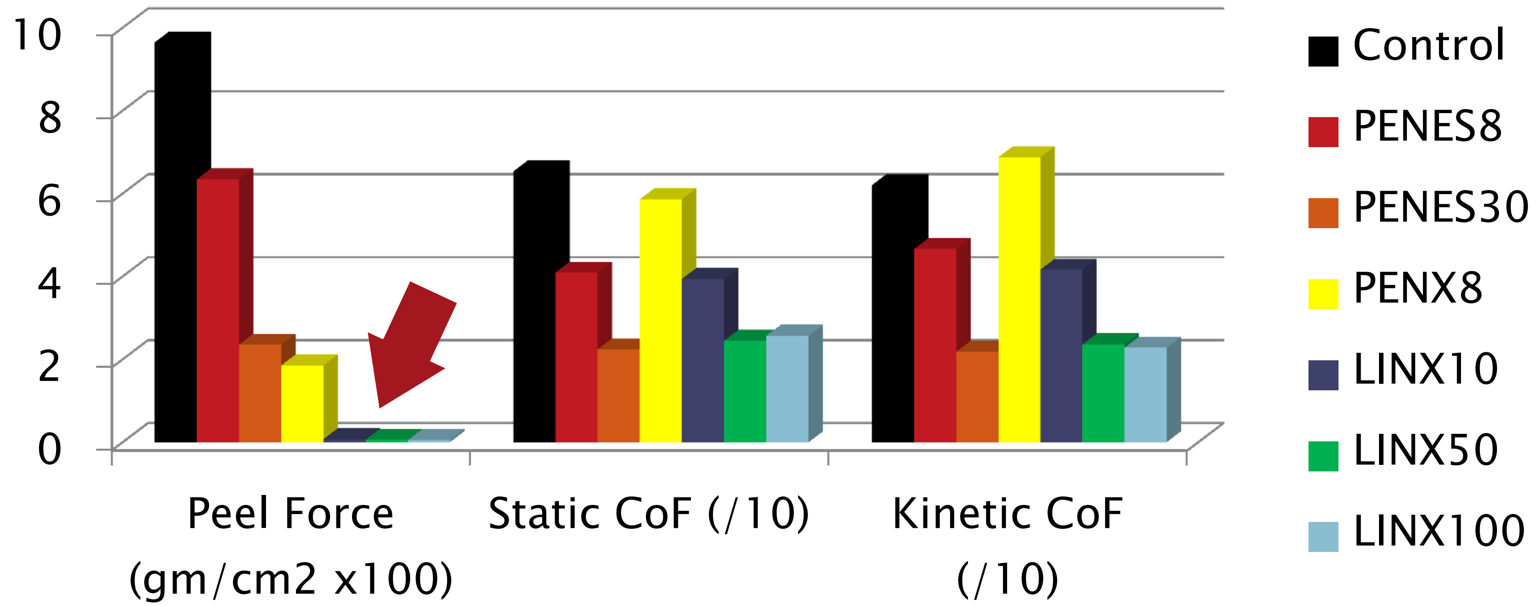
Slip Properties

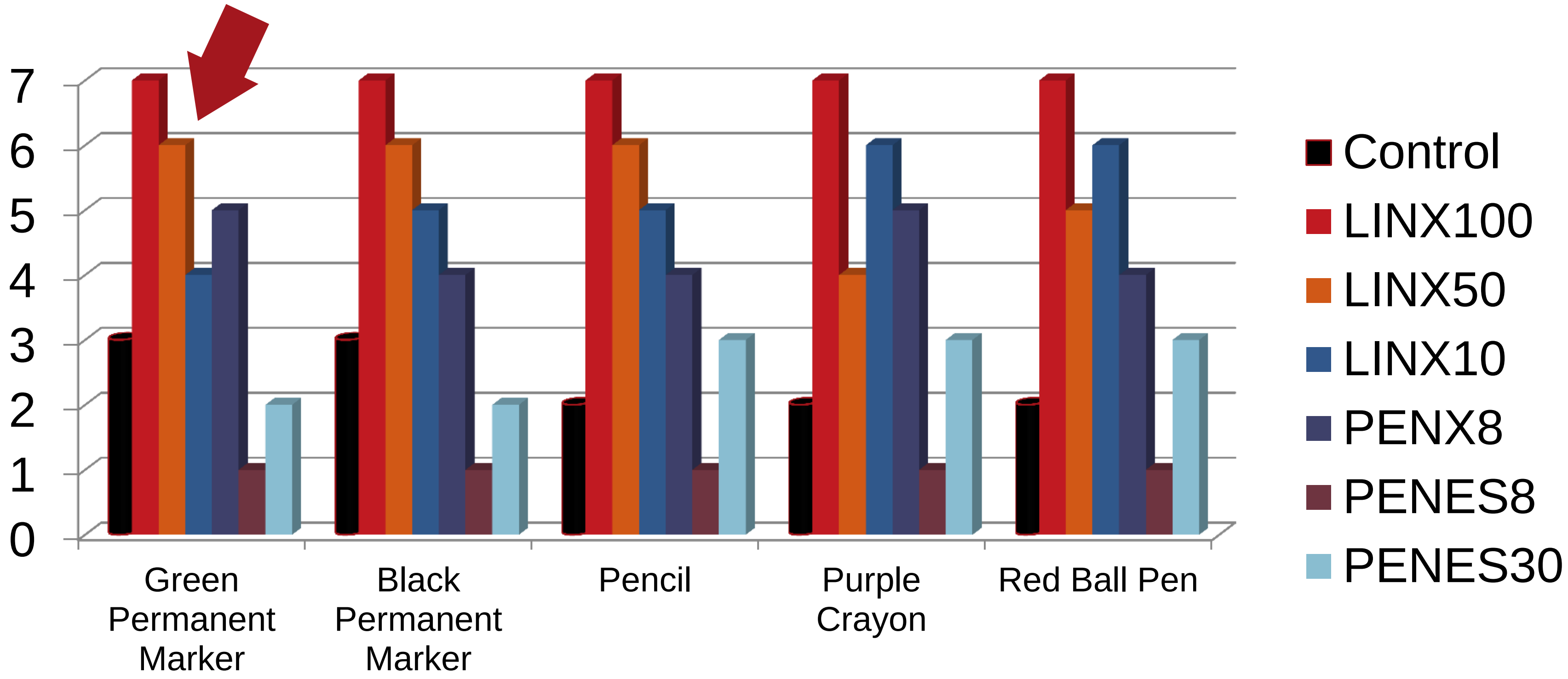


- Peel force and CoF are lowered.
- Extremely low when <u>incompletely</u> reacted

Other Typical Effects

- Flexibility increases
- CoF decreases
- Stain resistance increases
- Mar resistance increases

Stain Resistance



- Many of these are improved over control
- The incompletely cured materials give the most improvement.

Acrylate Functional

Component	Lever
ACR Reactive Silicones Use level (%)	Various 10.0%
Epoxy Acrylate Resin Use level (%)	CN104C75 67%
Synergist CN386	10.0%
Photoinitiator Escacure TZT	5.0%
Photoinitiator Darocur 1173	1.5%
Reactive Defoamer	0.5%
Reactive diluent SR 355 DTPTA	1%
Reactive diluent SR 306 TRPGDA	5%

Silicones Used

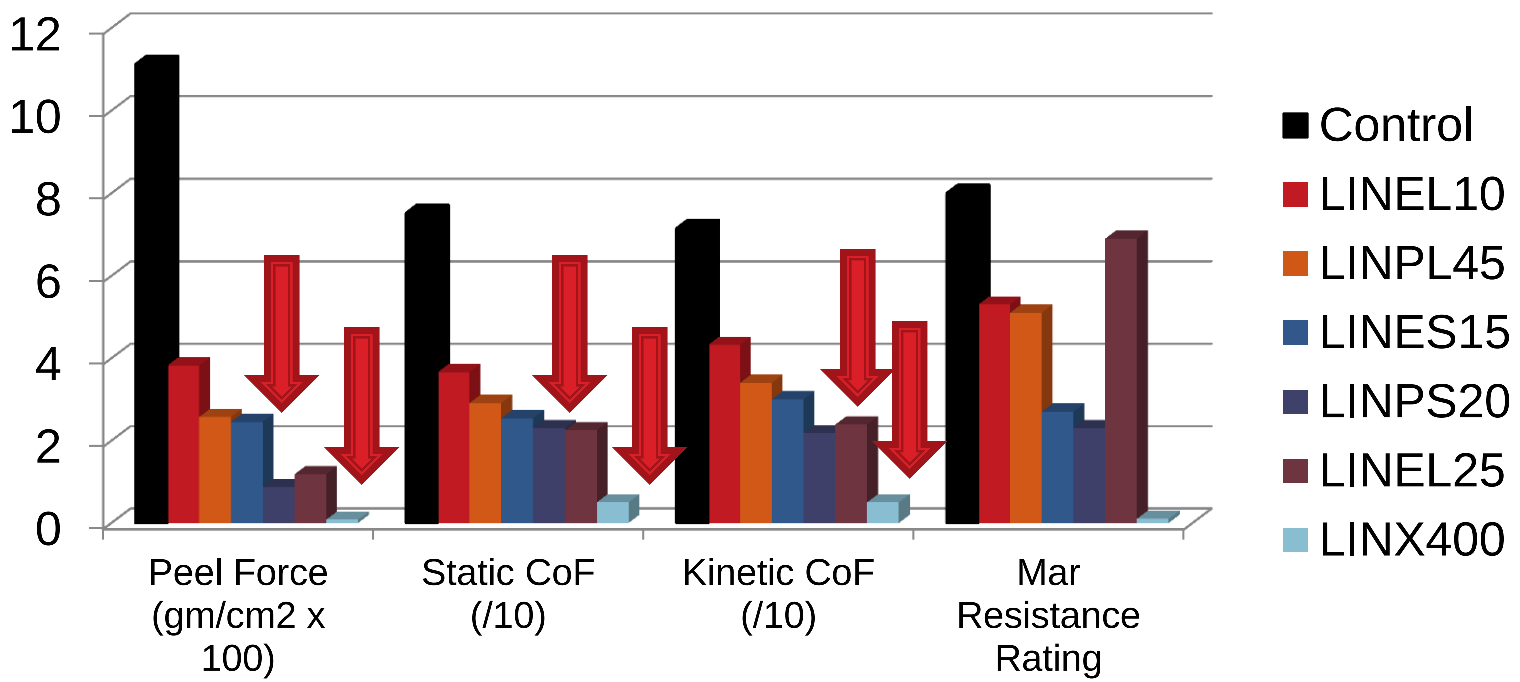
Variation	LINES15	LINPL45	LINX400	LINEL10	LINPS20	LINEL25
Silicone	Linear, small	Linear, large	Linear, v. lg.	Linear, small	Linear, medium	Linear, medium
Polyether	EO Small	EO/PO Large	None	EO Large	EO/PO Small	EO Large
Log MW	3.34	3.83	4.48	3.3	3.54	3.49
Viscosity (cps)	160	2400	2400	160	210	330

Results

System I Series B	LINES15	LINPL45	LINX400	LINEL10	LINPS20	LINEL25	Control
Storage Modulus G' (MPa)	16.5	11.6	14	17	17	16.3	17
Loss Modulus 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
Cure Condition & Appearance	Cured		Un-cured	Cured			

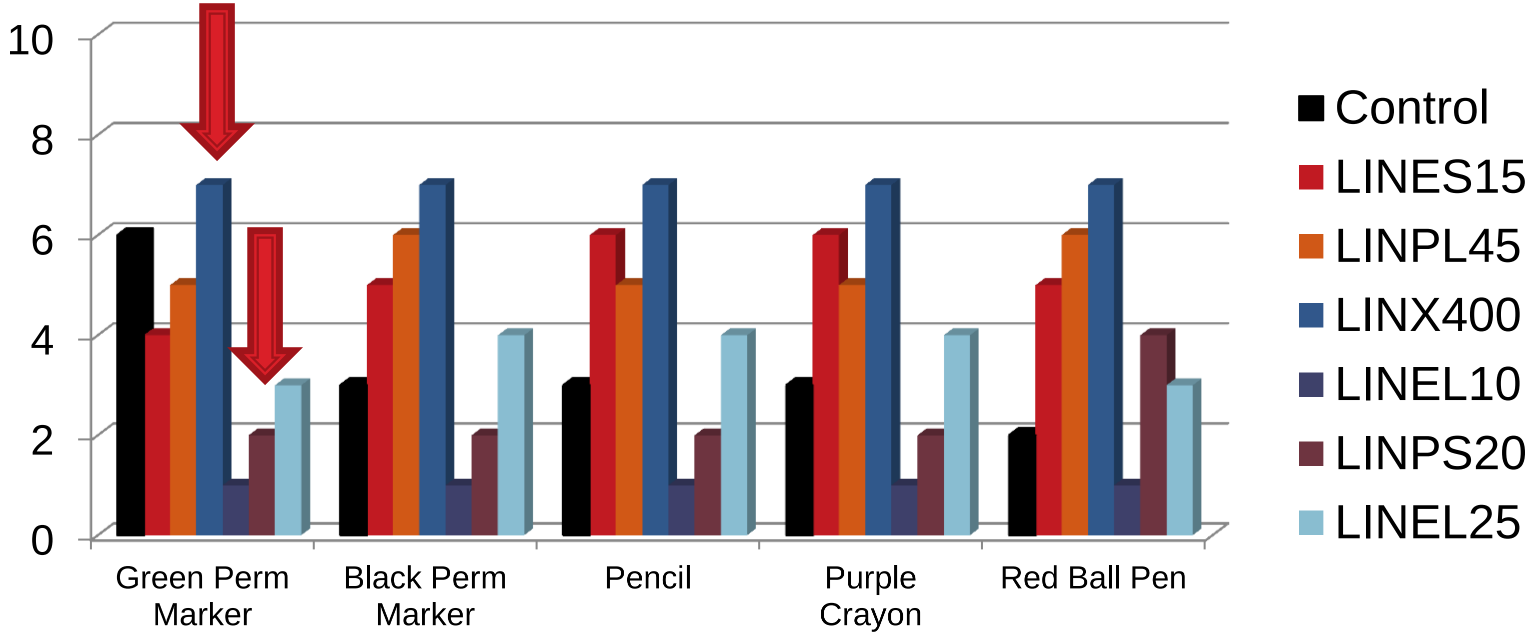
- All give lower moduli except LINEL10
- All cure except non-polyether LINX400

Slip Properties



- The peel force, slip and CoF are improved.
- LINX 400 best – incompatible
- The best results of the completely cured systems belong to the medium chain length silicones.
- There is improvement in mar resistance.

Stain Resistance



- There is general improvement in stain resistance.
- LINEL10 and LINPS20 are consistently worst
- The LINX400 gives the best stain resistance perhaps due to incompletely cured silicone.

Use Level Effect

- One can go very high, but film integrity can be lost
- For some properties 1% is adequate.
  - Slip
  - Release
  - Mar Resistance
- Other properties require more silicone
  - Impact Resistance
  - Stain Resistance

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Use Level Study

Component	Amount
ACR Reactive Silicone **Use level (%)**	PENES8 0% - 80%
Epoxy Acrylate Resin **Use level (%)**	CN104C75 80% - 0%
Synergist CN386	13.0%
Photoinitiator Escacure TZT	5.0%
Photoinitiator Darocur 1173	1.5%
Reactive Defoamer	0.5%

- “PEN ES8” is a small acrylate functional, silicone with an average of two reactive groups and modified with polyethyleneoxide for solubility
- Reactive defoamer is an insoluble acrylated silicone

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Results: Broad View

	Control	A	B
Silicone PEN ES8	0.0%	30.0%	60.0%
Gloss	99.0	93.4	83.7
Static CoF	0.615	0.665	2.111
Kinetic CoF	0.551	0.531	2.367
Peel Release (gm/cm^2)	179	147	7.2
Impact Resistance	0	8	10
Cured Conditions & Appearance	Cured, smooth		Cured, rubbery

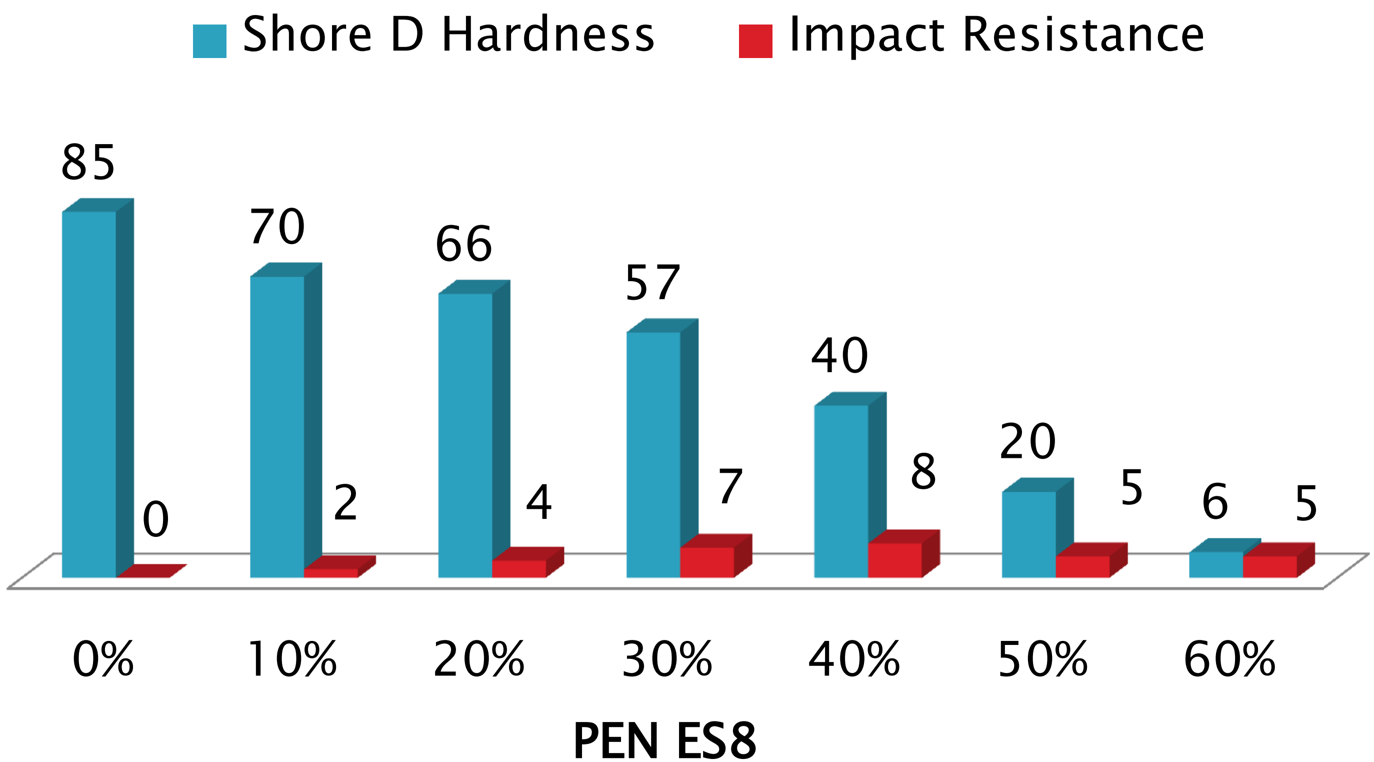
- Highly compatible: completely reacts
- Release and flexibility as more silicone is used.
- 60% silicone gives very strong release properties.
- In this example, CoF increases with silicone content.

Results: Closer Look

PENES8	0%	10%	20%	30%	40%	50%	60%	70%	80%
Viscosity (cPs)	8059	4361	2256	1157	569	284	152	95	95
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. flexible	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	

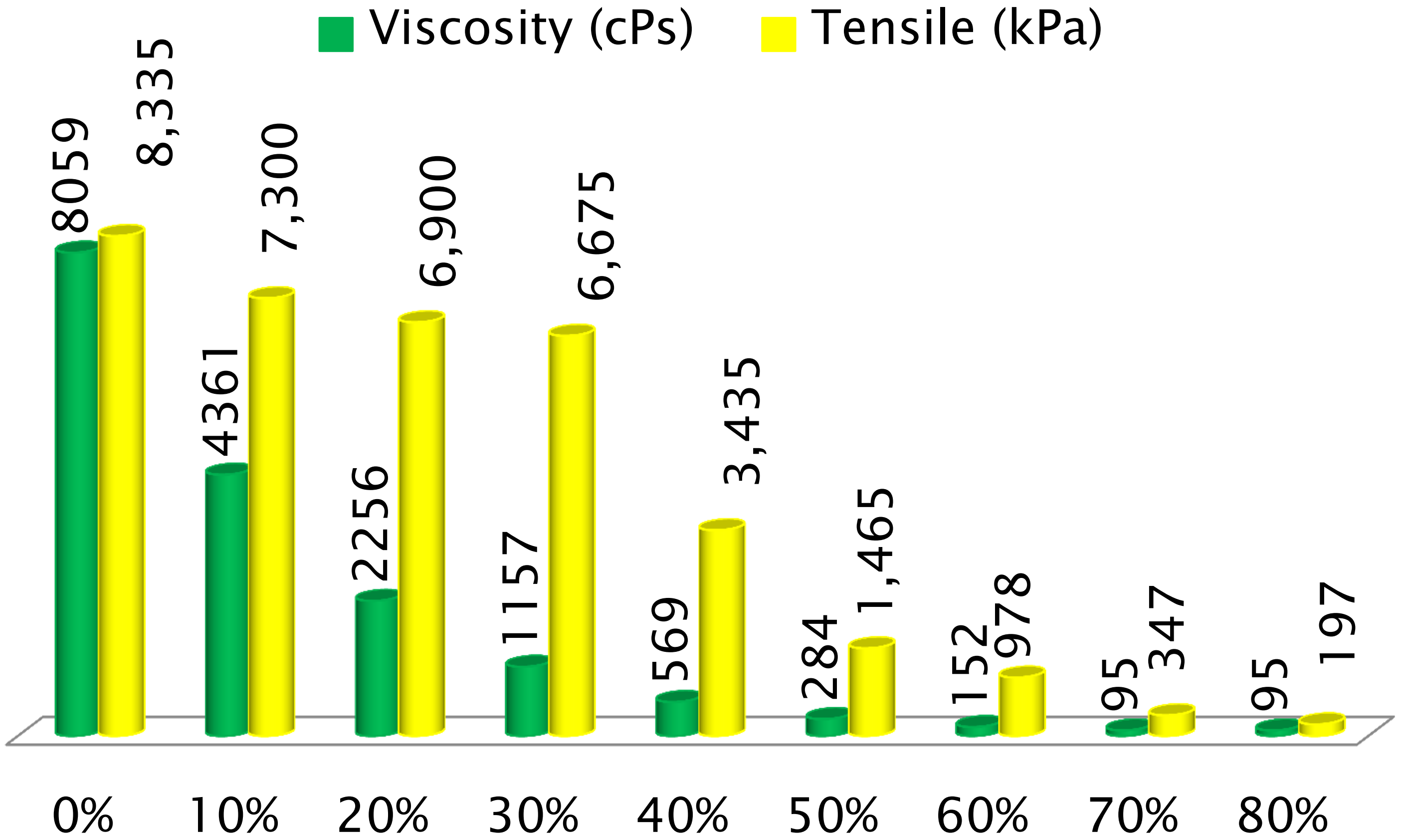
- Flexibility and elongation properties maximize at 40–60% incorporation of silicone in organic.
- The tensile strength, storage modulus are approximately linear with percentage of silicone.

Flexibility



- Flexibility and elongation properties maximize at 40–60% incorporation of silicone in organic.

Viscosity and Tensile



- The tensile strength, storage modulus and hardness have linear relationships with percentage of silicone.

Cross Link Density

- More reactive groups on the silicone seems to increase stain resistance and slip properties

UV Cured Cycloaliphatic Epoxy

Component	Level
Types of epoxy silicones	Polyether modified
Use level of epoxy silicones (wt %)	1% / 20%
UVA Cure 1500 resin	89 / 72%
CAPA 3041 Multifunctional Polyol	9% / 7%
UV 9380C Photoinitiator	1%

Silicone Variations

	PEN 1 EPC	PEN 2 EPC	PEN 3 EPC	ELINEL25	ELINPL45
Silicone	Pendant, med.	Pendant, med.	Pendant, med.	Linear, med.	Linear, lg.
Polyether	EO/PO large	EO/PO large	EO/PO large	EO large	EO/PO large
# epoxy	1	2	3	2	2
Log MW	3.93	3.87	3.80	3.42	3.72
Viscosity (cps)	798	1000	1010	255	1205

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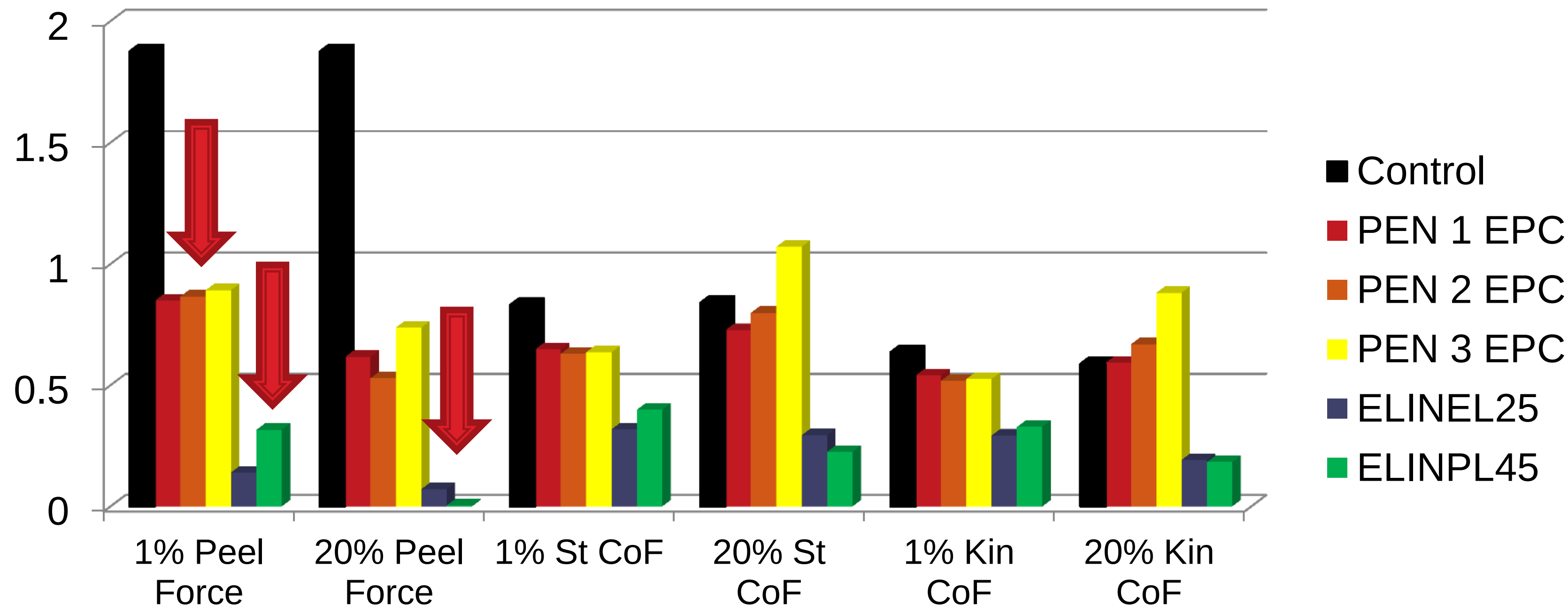
Results

	PEN 1 EPC	PEN 2 EPC	PEN 3 EPC	ELINEL25	ELINPL45	Control
tan(delta) (20%)	0.66	0.51	0.28	0.34	0.31	0.68
|G*| Pa E+7 (20%)	0.51	0.74	1.09	1.31	0.87	3.84
Cure Condition & Appearance	Smooth			Fairly Smooth	Fairly Smooth, Greasy	Smooth

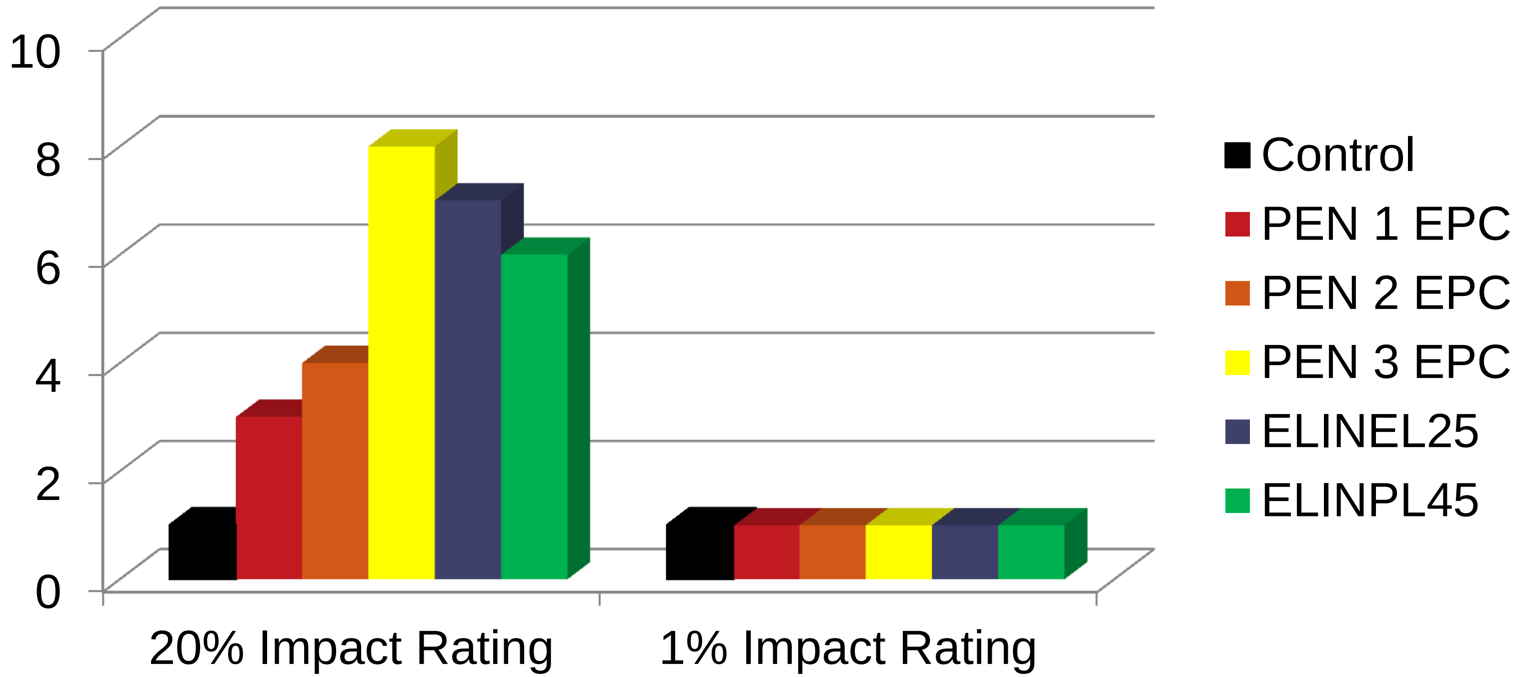
- These polyether functional epoxy silicones react into the coating
- ELINPL45 is borderline

Slip Properties



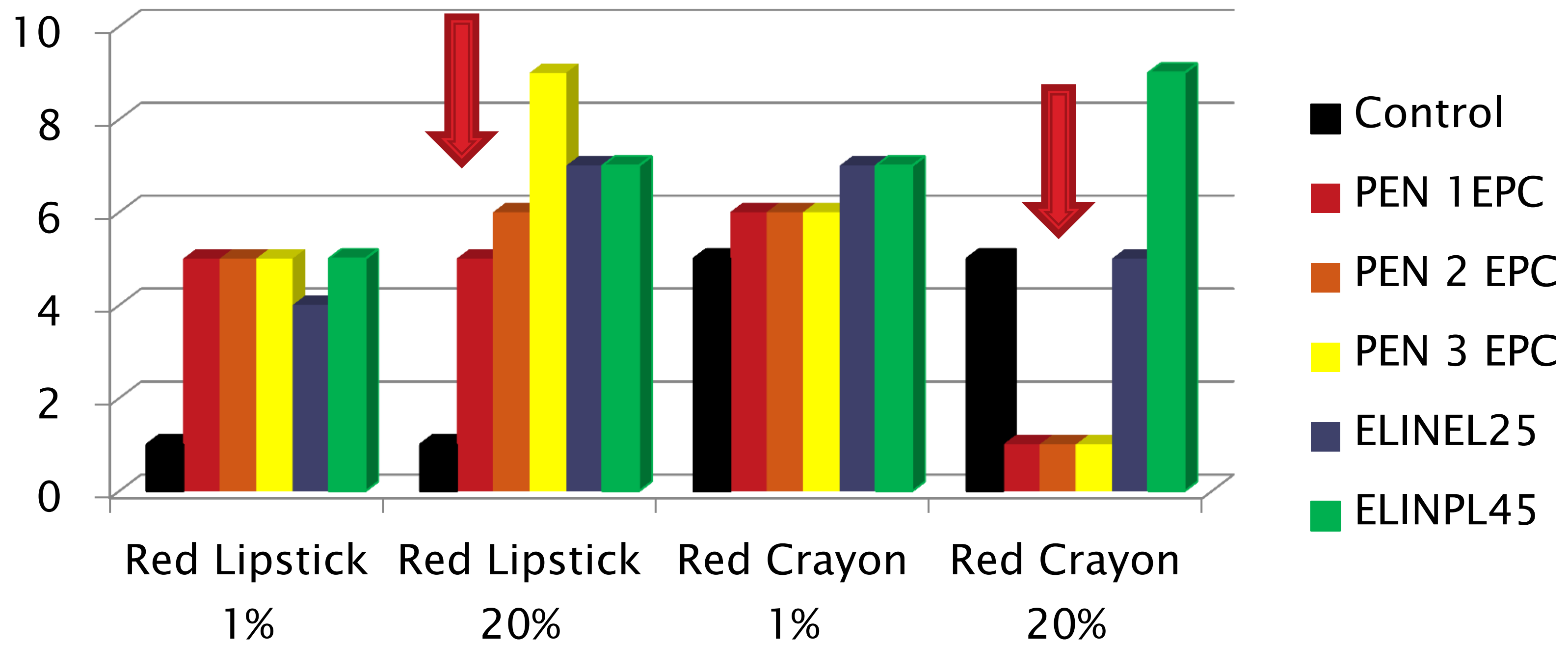
- The slip and peel release improve most with linear.
- The improvement is not much greater in the 20% series.
- Only a small improvement for multifunctional materials.
- Crosslinking increases CoF slightly.

Impact Resistance



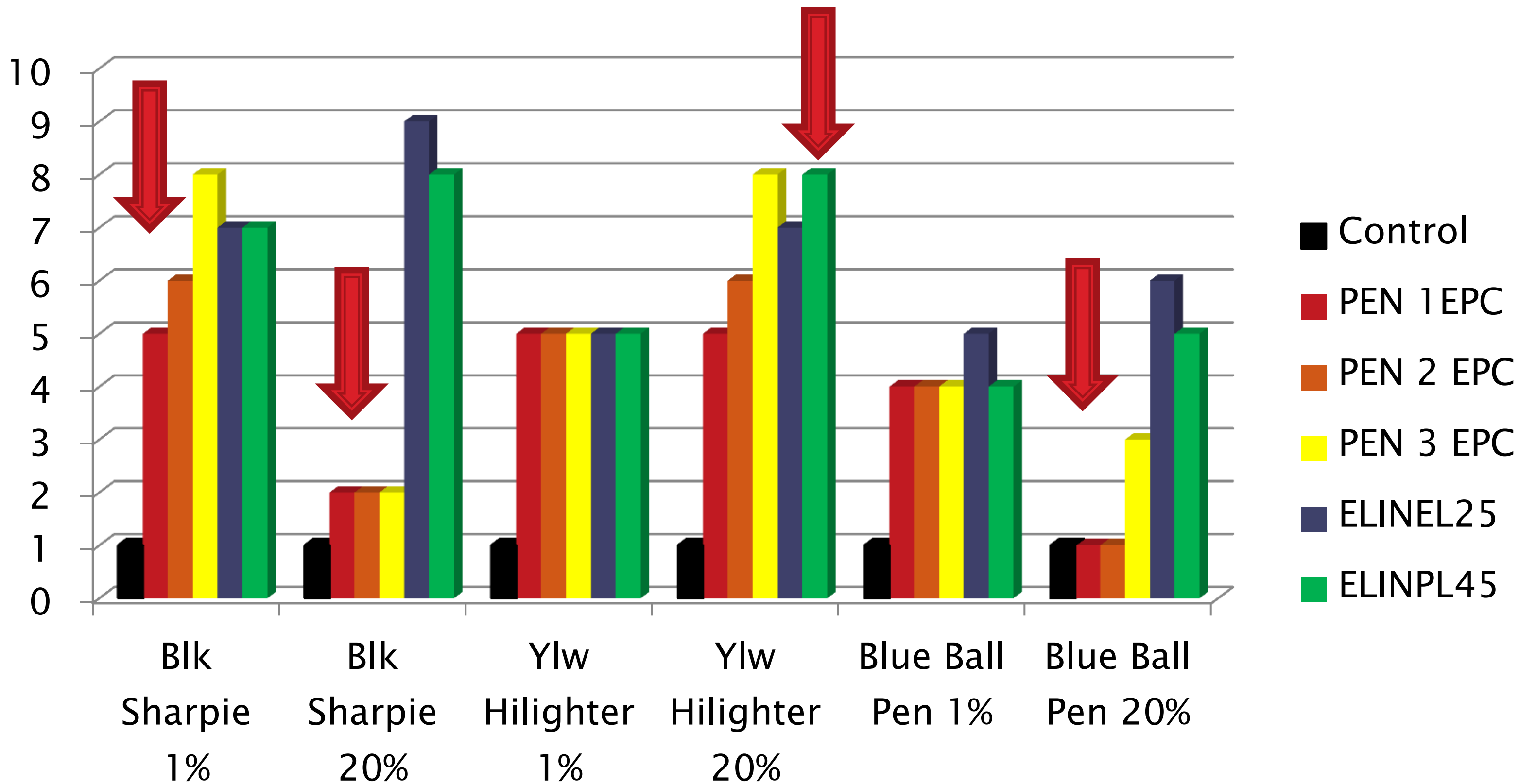
- There is no change in impact resistance at 1% loading.
- The 20% loading shows a strong effect.
- Increases as the number of epoxy groups increases

Stain Resistance



- Stain resistance is improved over control
- Improved with crosslinking
- 20% level sometimes is not as good in this system

Stain Resistance



- Stain resistance is improved over control
- Often improved with crosslinking
- 20% level sometimes is not as good in this system

Conclusions

- Reactive silicones become part of the film. Without solubilizing groups they do not fully react.
  - Outcomes of incompatibility can be unstable formulas, slow reaction, oily films, defects and very low CoF
- Reactive silicones improve release, slip and CoF at 1% incorporation.
  - In most cases these properties continue to improve with more silicone.
  - Linear di-functional materials are usually better than pendant.
  - Increased cross-linked density improves this slightly

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Conclusions

- Mar resistance is seen at 1% but may not be improved at higher levels.
- Impact resistance and moduli show increased flexibility.
  - Higher use levels are needed here with 1% showing little or no effect
- Stain resistance is seen with most reactive silicones across multiple stains and is sometimes increased at higher use levels.
  - High molecular weight and di-functional architecture often give the best stain resistance.
  - Increasing the number of reactive sites improves this.

THANK YOU