



Properties of Silicone Modified Coatings Films

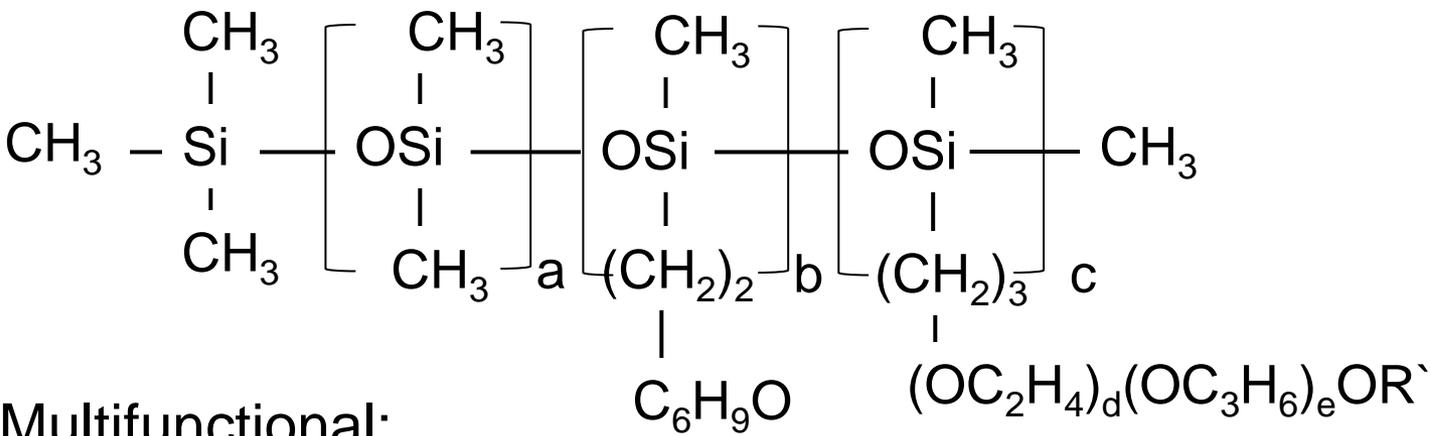
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Summary

Reactive silicones are available with differing reactive groups.

Using various resins and cure systems and multiple testing procedures as examples, this work summarizes what to expect when you incorporate these silicones into your films.

Silicone Variations



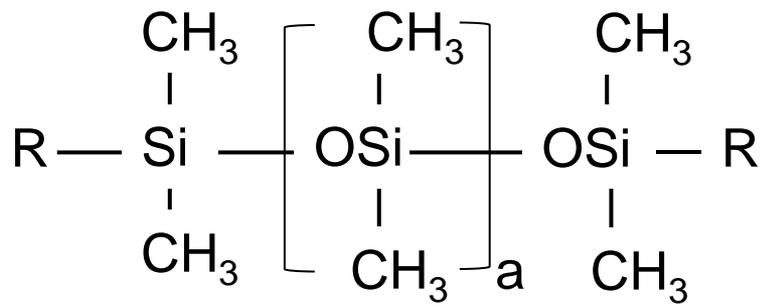
Multifunctional:

ACR series: $b=0$ and $R' = \text{Acrylate ester}$

EPC series: $b \neq 0$ and $R' = \text{H}$

Polyether series: $c \neq 0$

Non-polyether series: $d, e = 0$



Linear di-functional:

ACR series: $R = \text{Acrylate ester}$

or $R = \text{C}_3\text{H}_6(\text{OC}_2\text{H}_4)_d(\text{OC}_3\text{H}_6)_e\text{O-Acrylate ester}$

EPC series: $R = \text{C}_8\text{H}_{13}\text{O}$



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/cm².

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)

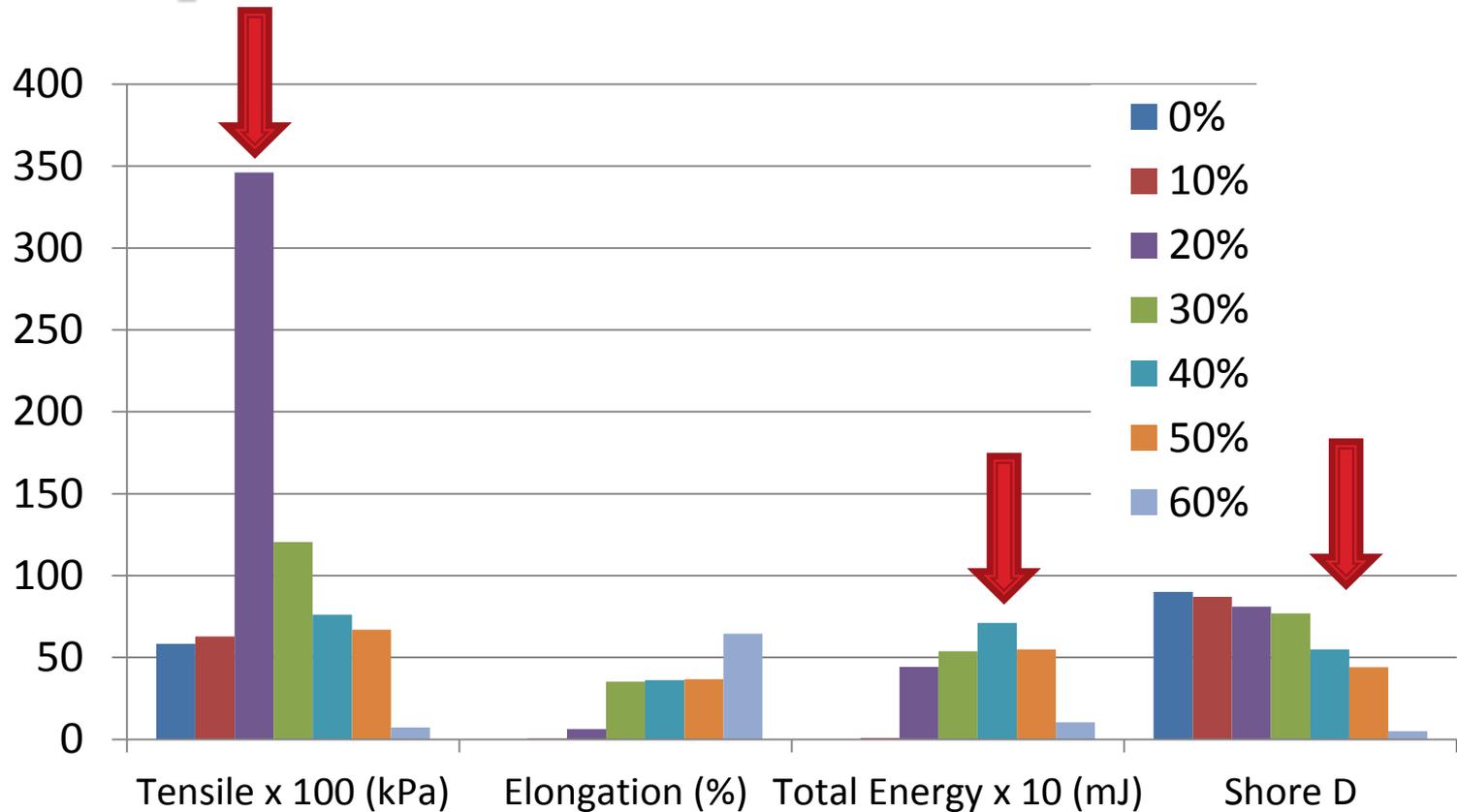
Impact Resistance The panel to be tested is placed coated side down on the top of a protective paper on a flat steel plate with rubber pad on the bottom. A steel rod with a 1 cm diameter round steel ball attached at the end of the rod is placed on the back side of the coating surface. A 700 gram weight 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: Gel

Component	Name	Level
Organic Resin	Epoxy Resin	42–16%
Anhydride Curative	MHHPA	58–24%
Cycloaliphatic Epoxy Polyether Silicone	EPENPL35	0–60%
Catalyst		0.06–0.1%

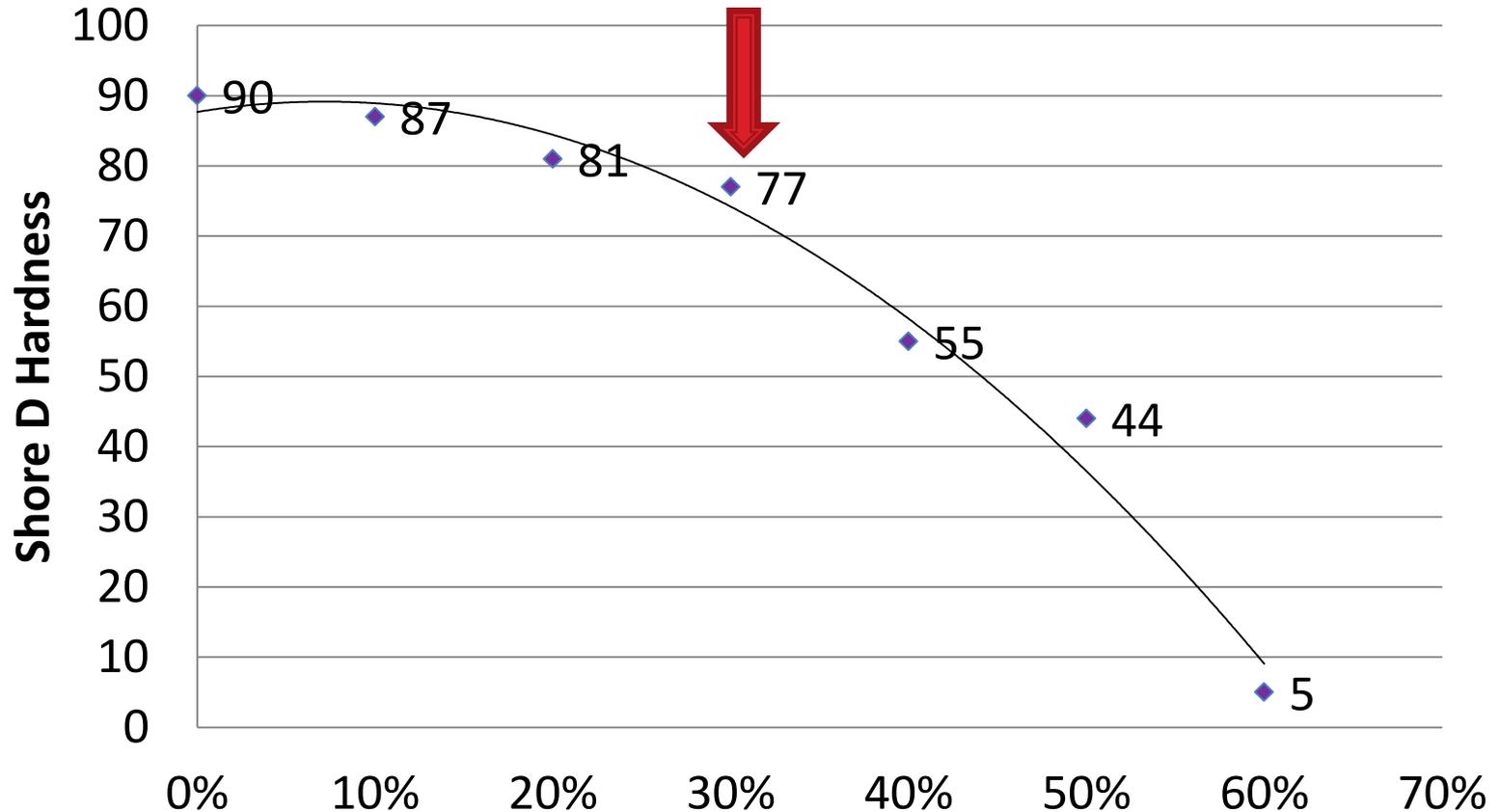
- EPENPL35 has polyethyleneoxide and polypropyleneoxide groups for compatibility as well as cycloaliphatic type epoxies for reactivity.
- The rheological data and mechanical properties are obtained directly from Brookfield DV-III Rheometer AR-G2 and Instron Model #1122 using the following cure conditions: 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

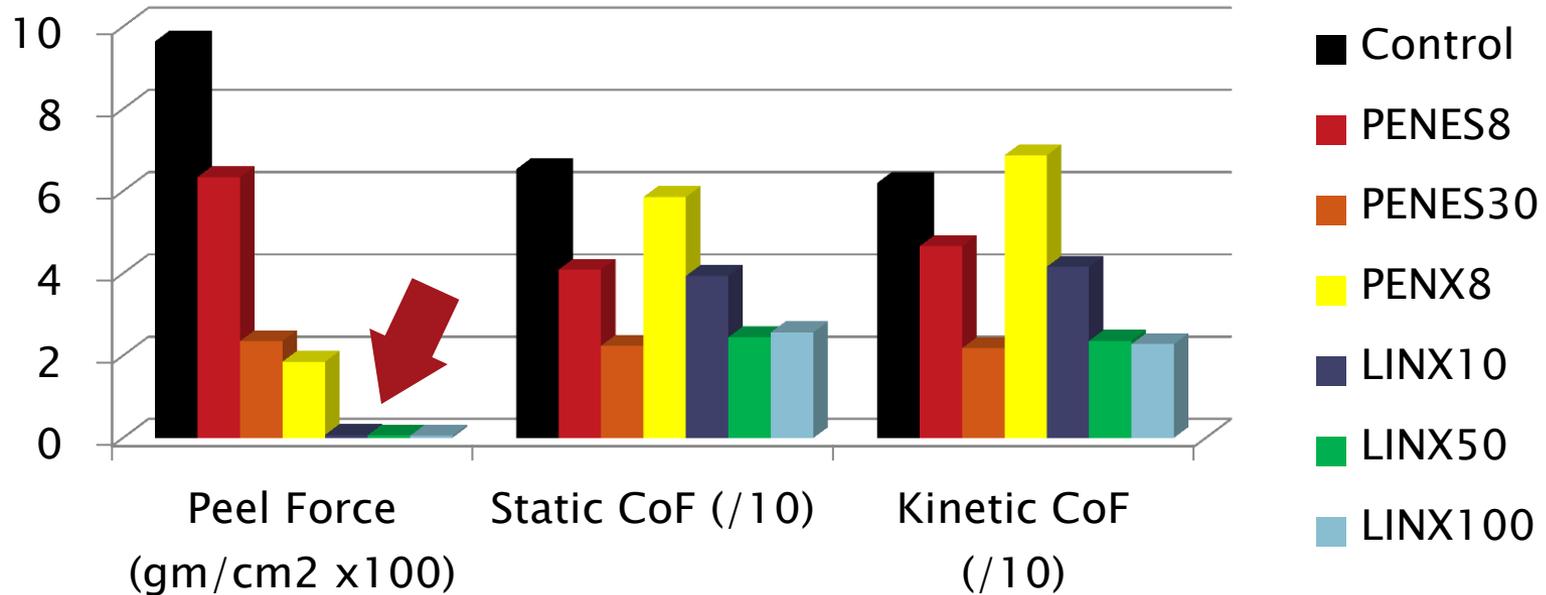
System ACR	Amount
ACR Reactive Silicones Use level (%)	Various 22.0%
Epoxy Acrylate Resin Use level (%)	Resin 40.0%
Amine Synergist	15.0%
Photoinitiator "E"	5.0%
Photoinitiator "D"	1.5%
Reactive Defoamer	0.5%
Reactive Diluent DTPTA	10%
Reactive Diluent TRPGDA	6%

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

Slip Properties

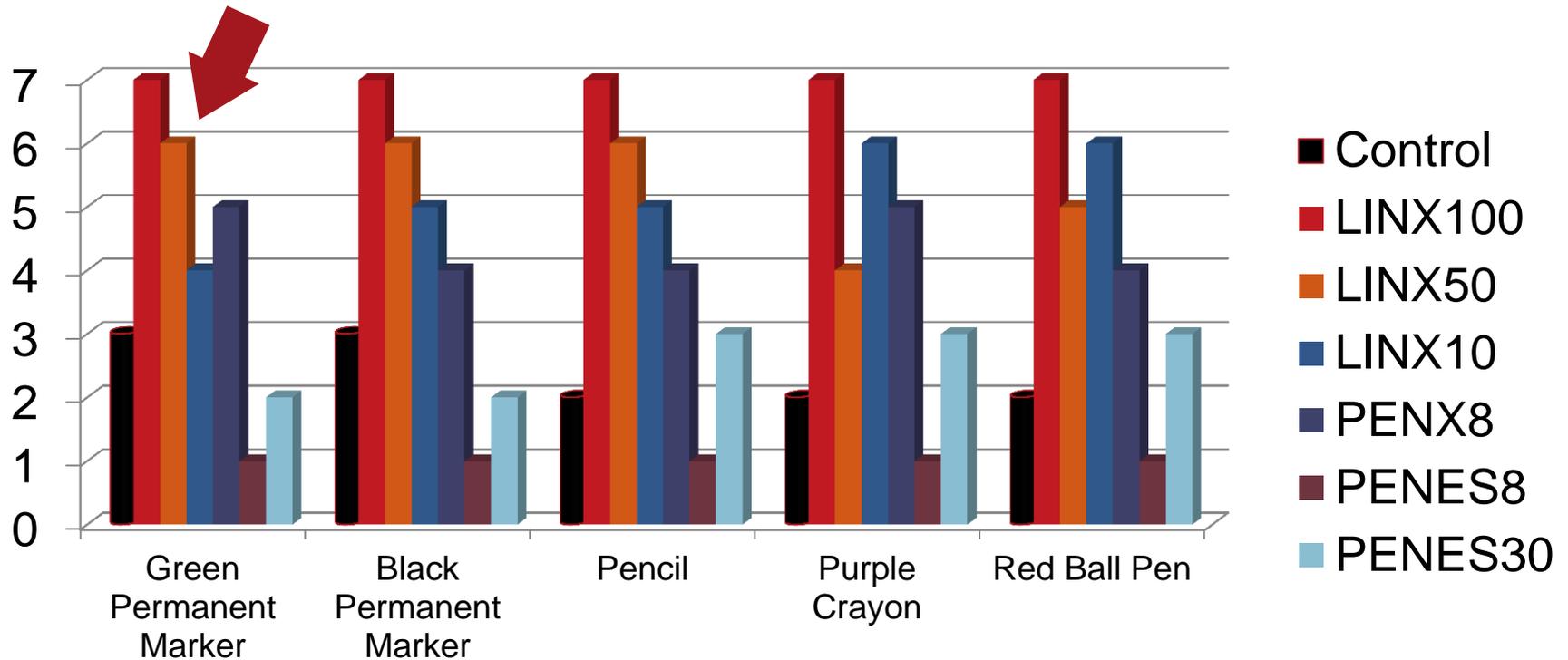


- Peel force and CoF are lowered.
- Extremely low when incompletely reacted

Other Typical Effects

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

Stain Resistance



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

SB PU

2K SB PU formulation A	Weight
Part A1	164
Part A2	109.6
Dabco	0.352
n-Butyl acetate	19.3
Glycol ether PM acetate	25.4
Ester EEP	30.9
2K SB PU formulation B	Weight
Part B	120.2

- The NCO/Polyol mole ratio is 1:1
- 1%–10% of silicone is pre-mixed with Part A

Results of SB PU

10% of 1° OH Silicone	Gloss	Static CoF	Kinetic CoF	Stain Resist	Mar Resist	Impact Resist
Linear 10	85.3	1.089	1.065	10.0	3.3	Improved
Linear 25	85.1	0.966	0.953	7.8	5.6	Improved
Linear 50	87.5	0.729	0.730	6.7	7.8	Improved
Linear 100	76.6	0.626	0.543	4.4	8.9	Improved
Pendant 10 xl	76.0	1.607	2.117	5.6	4.4	Improved
Pendant 3 xl	74.8	0.558	0.485	8.9	7.8	Improved
Control	94.0	2.154	2.489	0.0	0.0	Poor

- Gloss drop shows these are incompatible
- Impact resist increase shows incorporation
- CoF decreases
- Mar resist increases
- Stain resist increases

WB PU

2K WB PU formulation A	Weight
Part A1	145.97
Wetting agent	3.48
Thickener	0.52
Distilled Water	62.16

2K WB PU formulation B	Weight
Part B1	156
Part B2	55.8
Solvent	32

- The NCO/Polyol mole ratio is 1.5:1
- 1%–10% of silicone is pre-mixed with Part A

WB PU

1% in WB/PU	Gloss	Static COF	Kinetic COF	Stain Resist	Mar Resist	Appearance	Impact Resist
Linear 10 w/EO	89.4	1.998	1.846	7	7.8	Smooth	Low
Linear 50 w/ EOPO	89.3	1.937	1.684	7	7.4	Smooth	Low
Control	89.5	2.446	2.497	0	0	pinholes	Low

- Gloss shows compatible
- No effect on impact resistance (1% too low)
- CoF decreases
- Mar resist increases
- Stain resist increases

Use Level Effect

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

Use Level Study

Component	Amount
ACR Reactive Silicones	PEN ES8
Use level (%)	0% - 80%
Epoxy Acrylate Resin	Resin
Use level (%)	80% - 0%
Amine Synergist	13.0%
Photoinitiator "E"	5.0%
Photoinitiator "D"	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

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

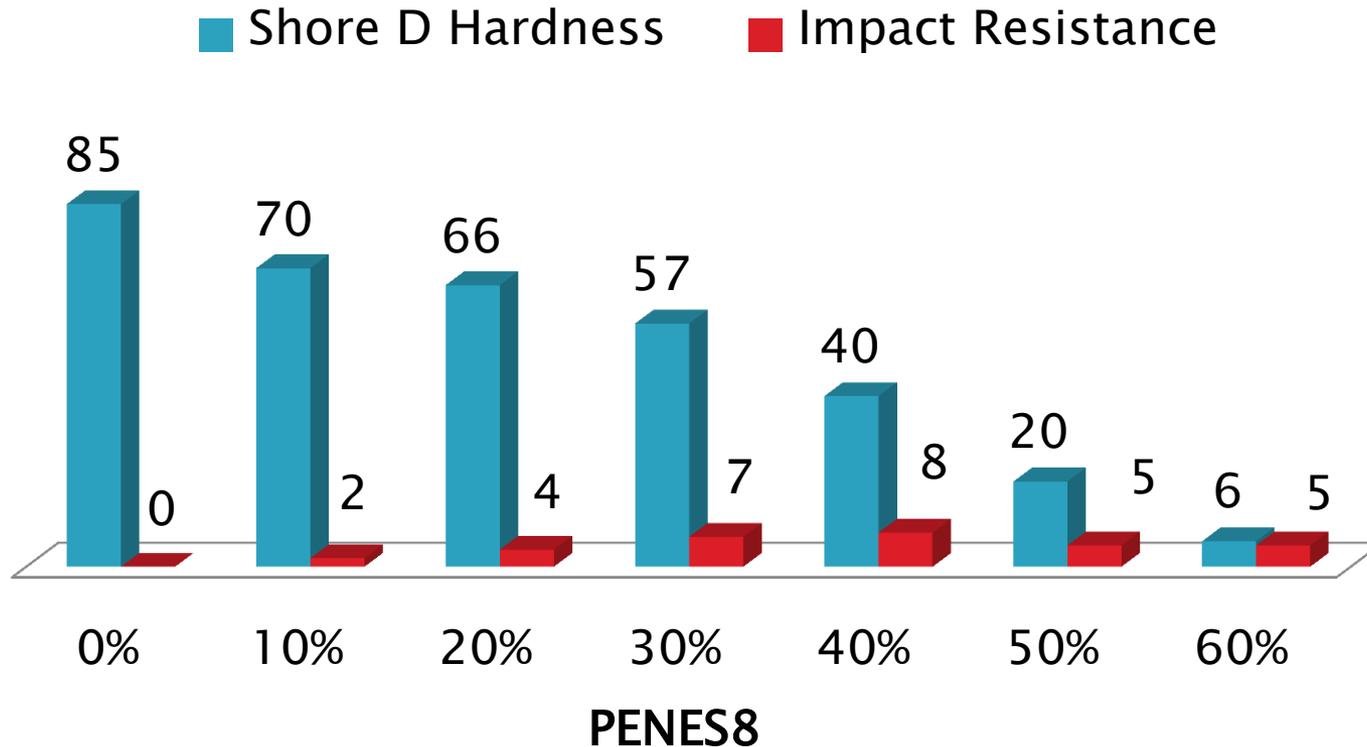
- Highly compatible: completely reacts
- Release and flexibility as more silicone is used.
- 60% silicone gives very strong release properties.
- In this example, CoF increases with silicone content.

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	

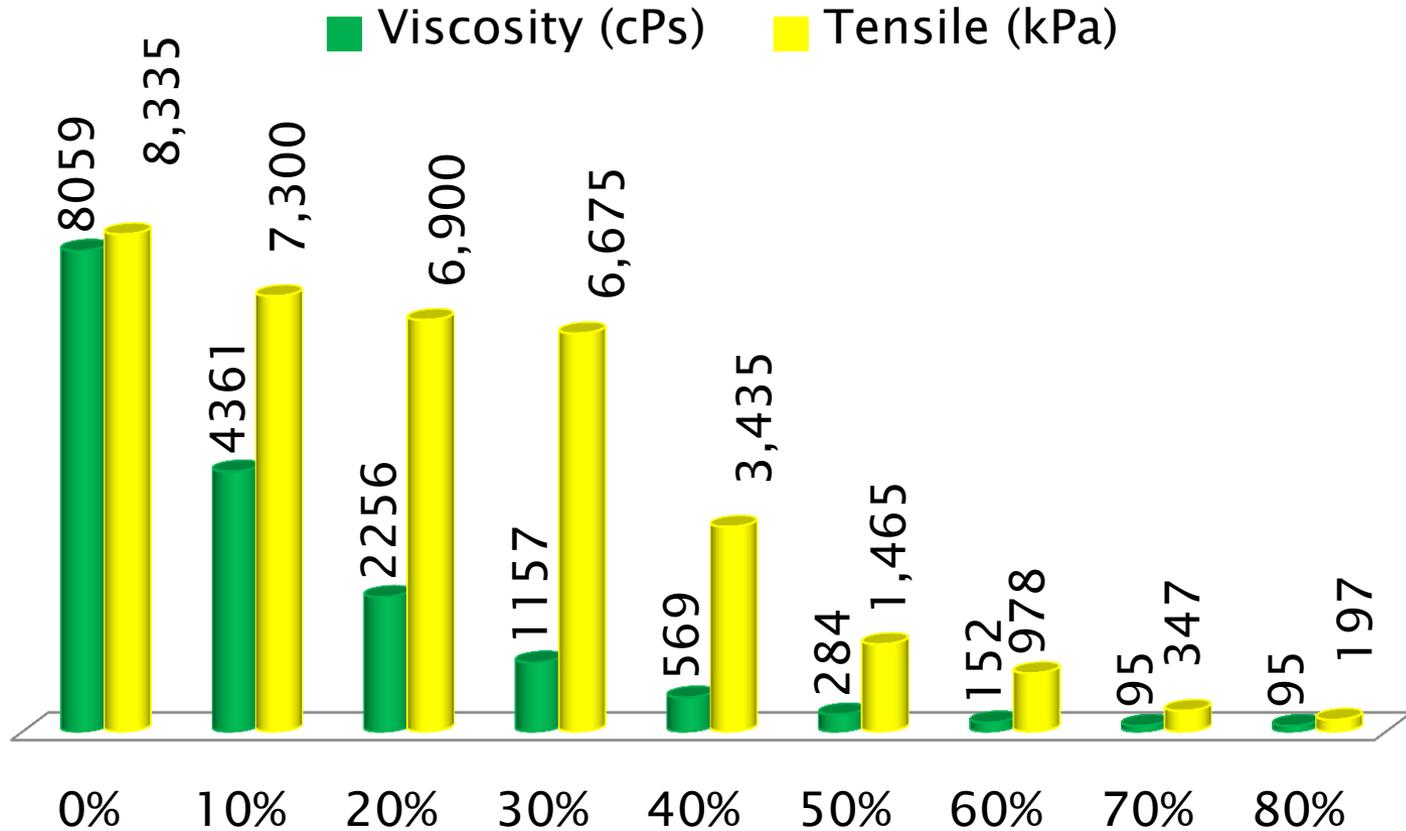
- Flexibility and elongation properties maximize at 40–60% incorporation of silicone in organic.
- The tensile strength, storage modulus are approximately linear with percentage of silicone.

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 change slip properties

UV Cured Cycloaliphatic Epoxy

Component	Level
Types of epoxy silicones	Polyether modified
Use level of epoxy silicones (wt %)	1% / 20%
UV Epoxy cured resin	89 / 72%
Multifunctional Polyol	9% / 7%
UV 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

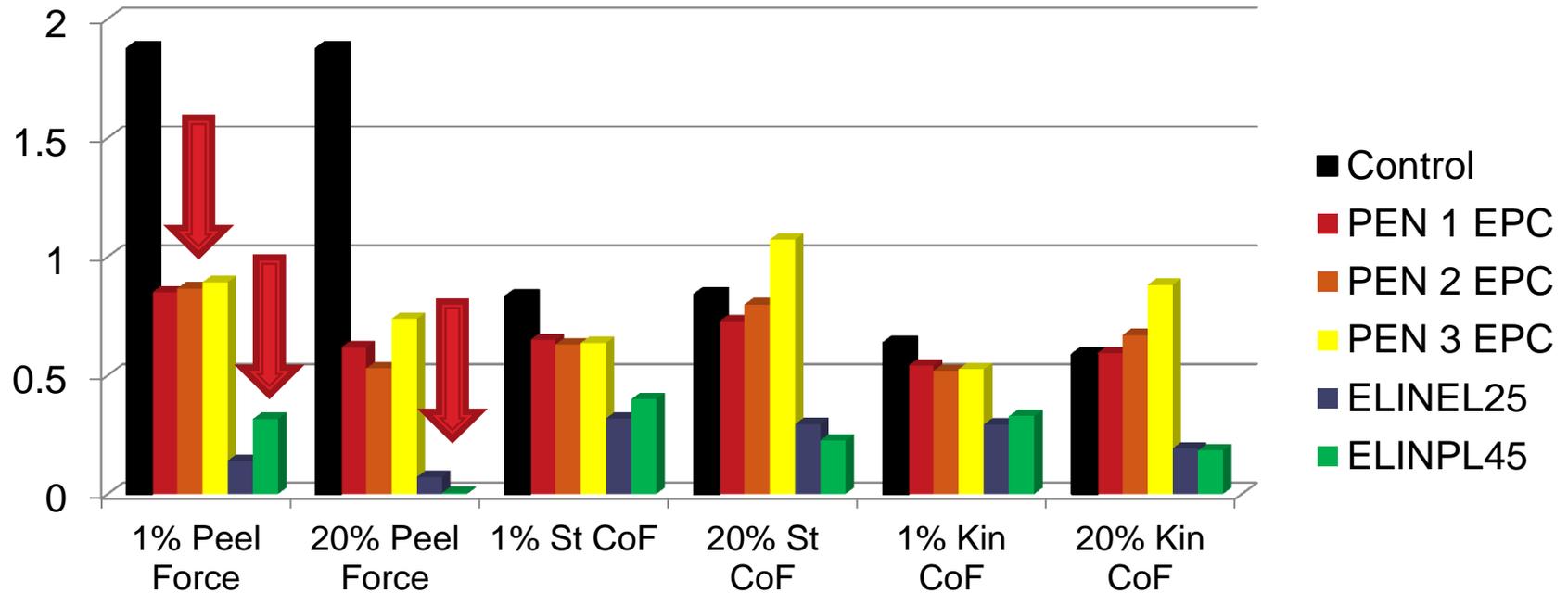


Results

	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

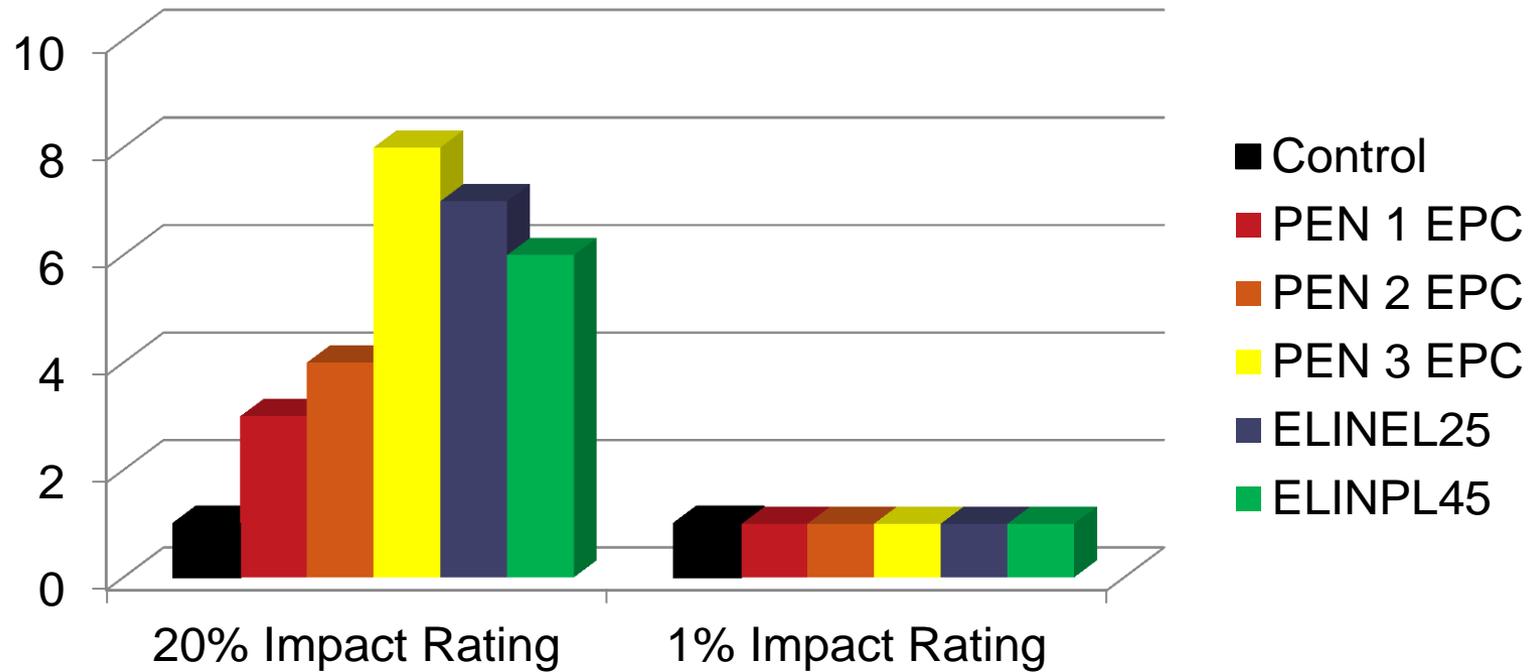
- These polyether functional epoxy silicones react into the coating
- ELINPL45 is borderline

Slip Properties



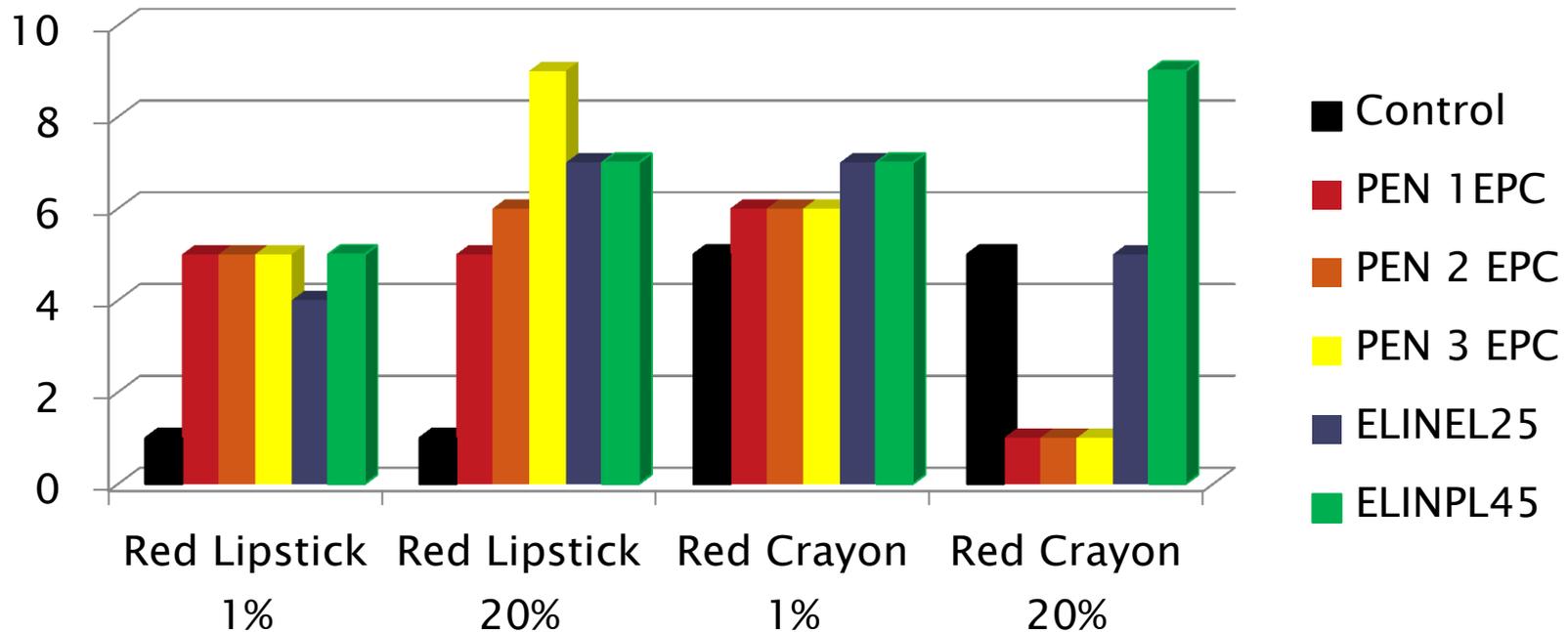
- The slip and peel release improve most with linear.
- The improvement is not much greater in the 20% series.
- Only a small improvement for multifunctional materials.
- Crosslinking increases CoF slightly.

Impact Resistance



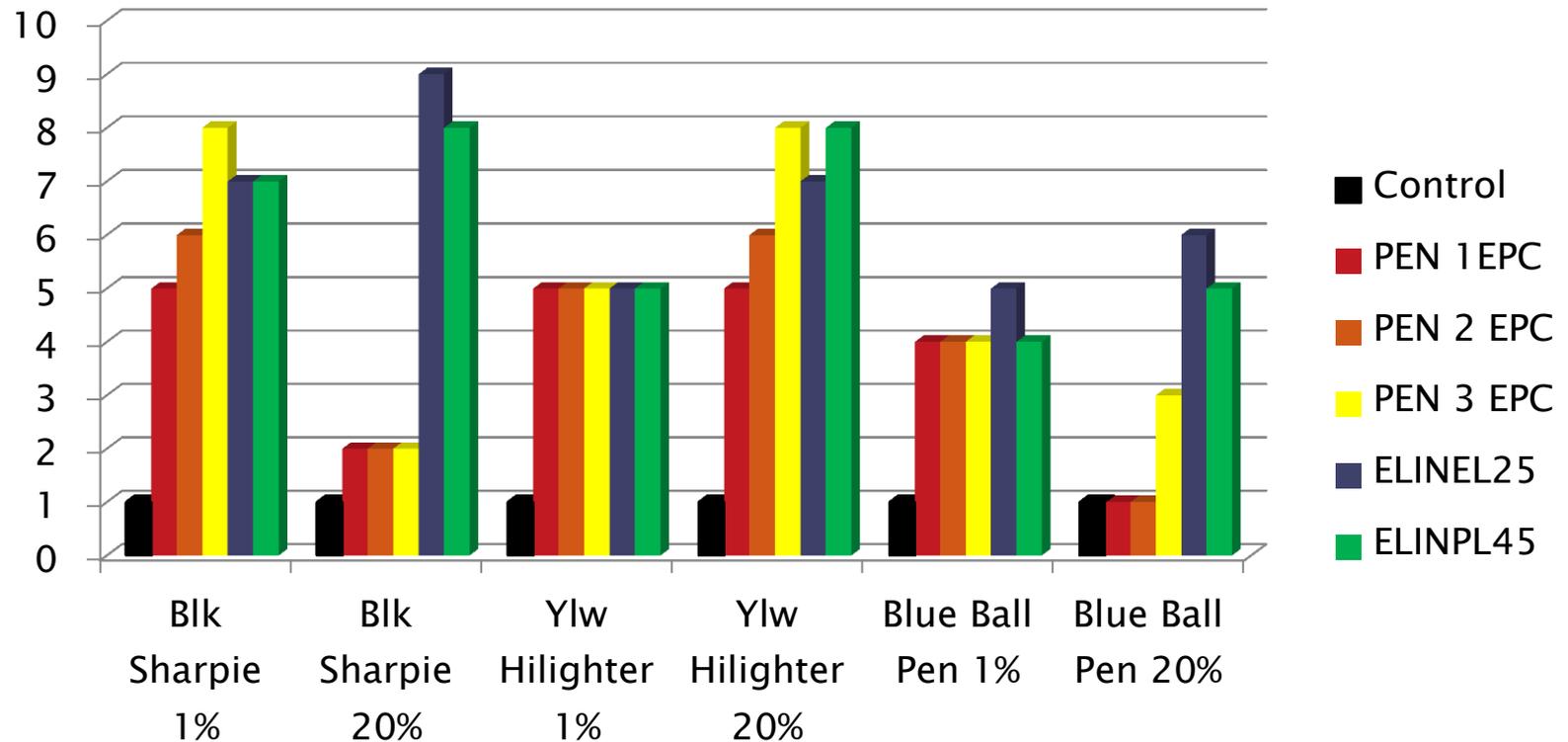
- There is no change in impact resistance at 1% loading.
- The 20% loading shows a strong effect.
- Increases as the number of epoxy groups increases

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 changes this slightly

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

