The Application of Reactive Silicone Molecules in Coatings

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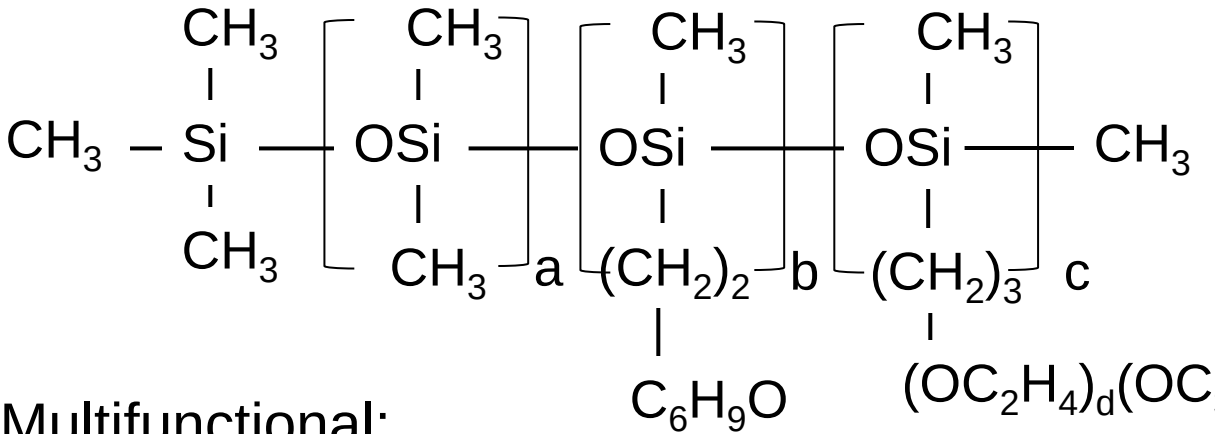
Summary

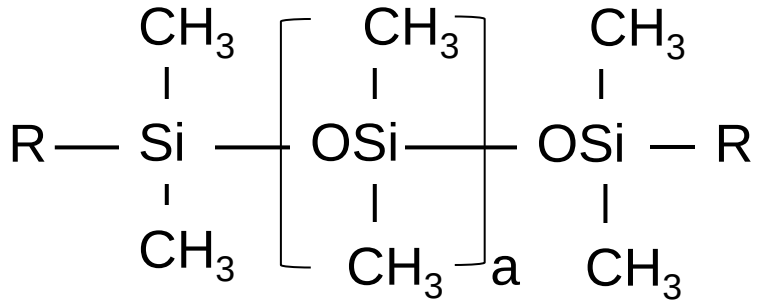
Reactive silicones are available with differing reactive groups.

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`=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=$C_3H_6(OC_2H_4)_d(OC_3H_6)_eO$-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.

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.

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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.

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

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Acrylate Functional

System ACR	Amount
ACR Reactive Silicones	Various
Use level (%)	22.0%
Epoxy Acrylate Resin	CN102Z
Use level (%)	40.0%
Synergist CN386	15.0%
Photoinitiator Esacure TZT	5.0%
Photoinitiator Darocur 1173	1.5%
Silmer ACR D2 (Defoamer)	0.5%
Reactive diluent SR 355 DTPTA	10%
Reactive diluent SR 306 TRPGDA	6%

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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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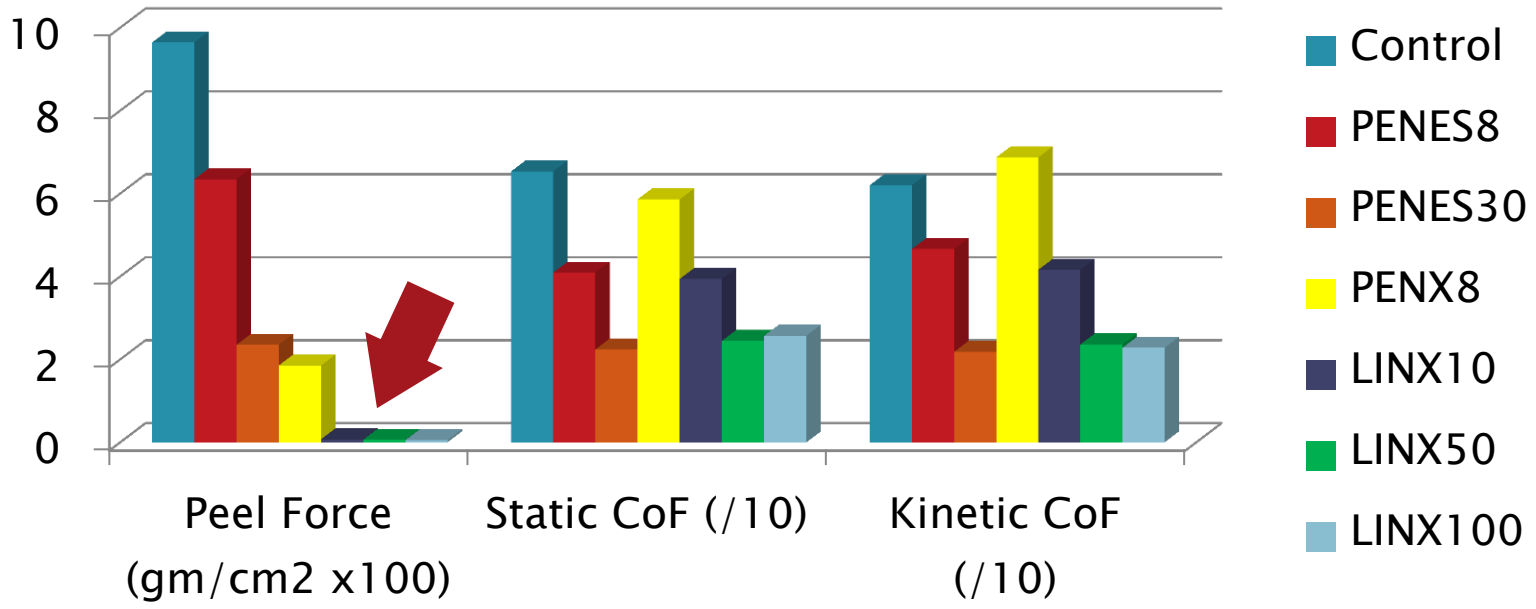
Slip Properties



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

Other Typical Effects

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

SB PU

2K SB PU formulation A	Weight
Desmophen A870 BA	164
Desmophen 670A-80	109.6
Dabco T-12	0.352
n-Butyl acetate	19.3
Glycol ether PM acetate	25.4
Ester EEP	30.9
2K SB PU formulation B	**Weight**
Desmodur N-3390 BA/SN	120.2

- The NCO/Polyol mole ratio is1:1
- 1%-10% of silicone is pre-mixed with Part A

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Results of SB PU

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

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

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WB PU

2K SB PU formulation A	Weight
Bayhydrol A145	145.97
Surfynol 104 DPM	3.48
Borchigel PW25	0.52
Distilled Water	62.16

2K SB PU formulation B	Weight
Bayhydur XP7165	156
Bayhydur XPLS2150/1	55.8
Exxate 600	32

- The NCO/Polyol mole ratio is1.5:1
- 1%-10% of silicone is pre-mixed with Part A

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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

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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

Acrylate Functional Screen

Component	Series A
ACR Reactive Silicones **Use level (%)**	Silmer® ACR D208 0/ 30% /60%
Epoxy Acrylate Resin **Use level (%)**	CN104C75 80%/ 50% /20%
Synergist CN386	13.0%
Photoinitiator Esacure TZT	5.0%
Photoinitiator Darocur 1173	1.5%
Silmer ACR D2 (Defoamer)	0.5%

Results

	Control	A	B
Silmer® ACR D208	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/cm²)	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.

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UV Cured Cycloaliphatic Epoxy

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

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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

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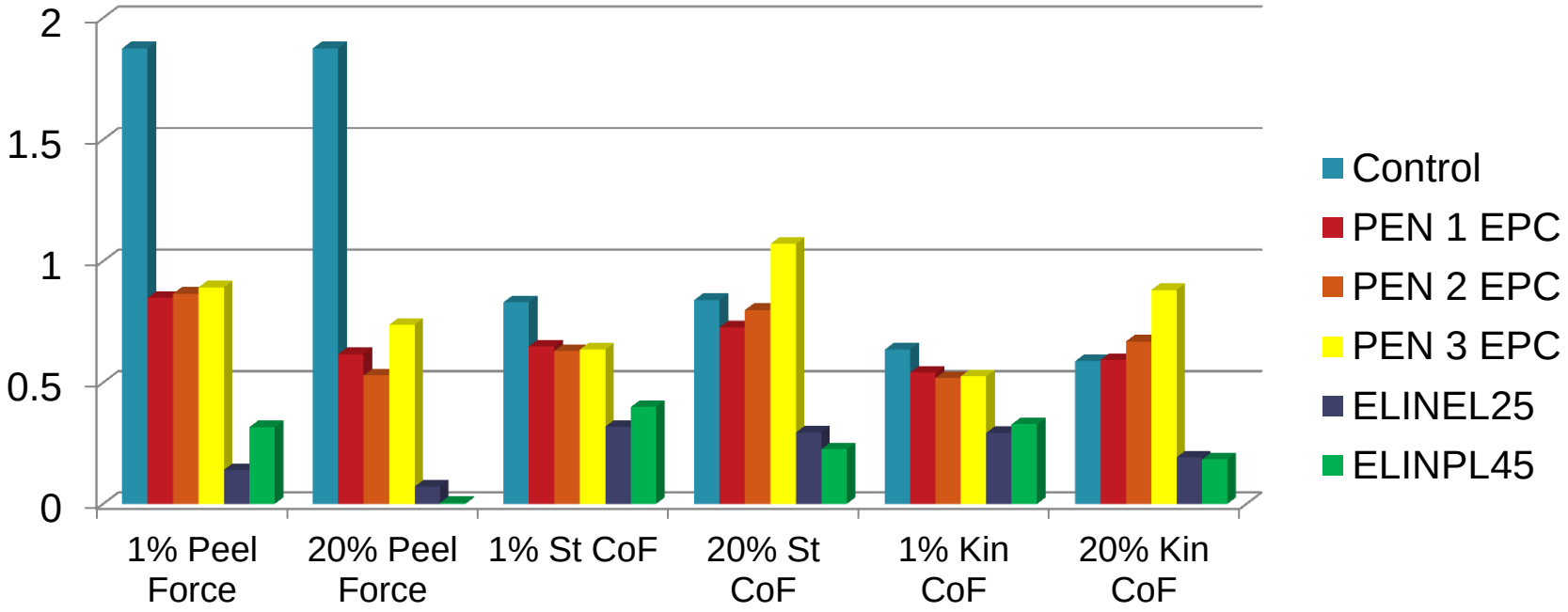
Slip Properties



- The slip and peel release improve with linear materials.
- The improvement is greater in the 20% series.
- Only a small improvement for multifunctional materials.
- Crosslinking increases CoF slightly.

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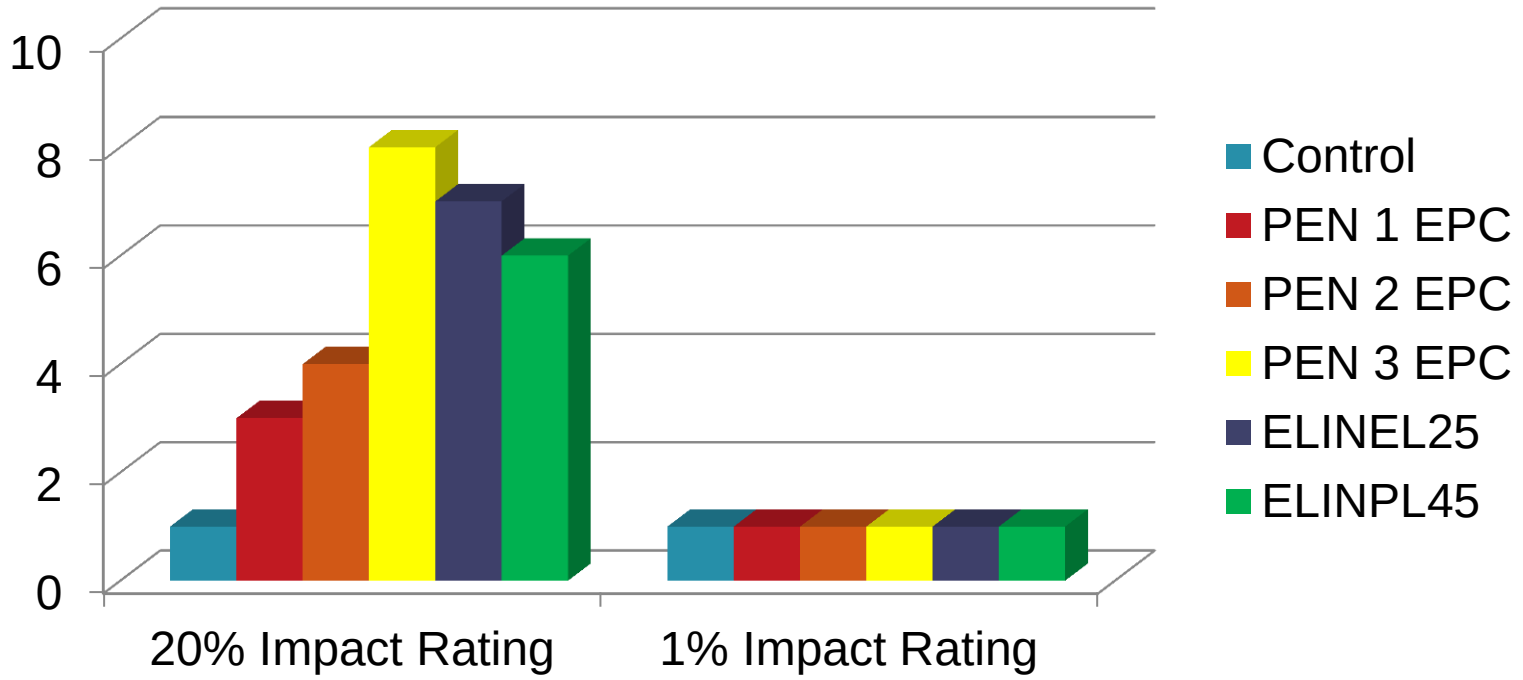
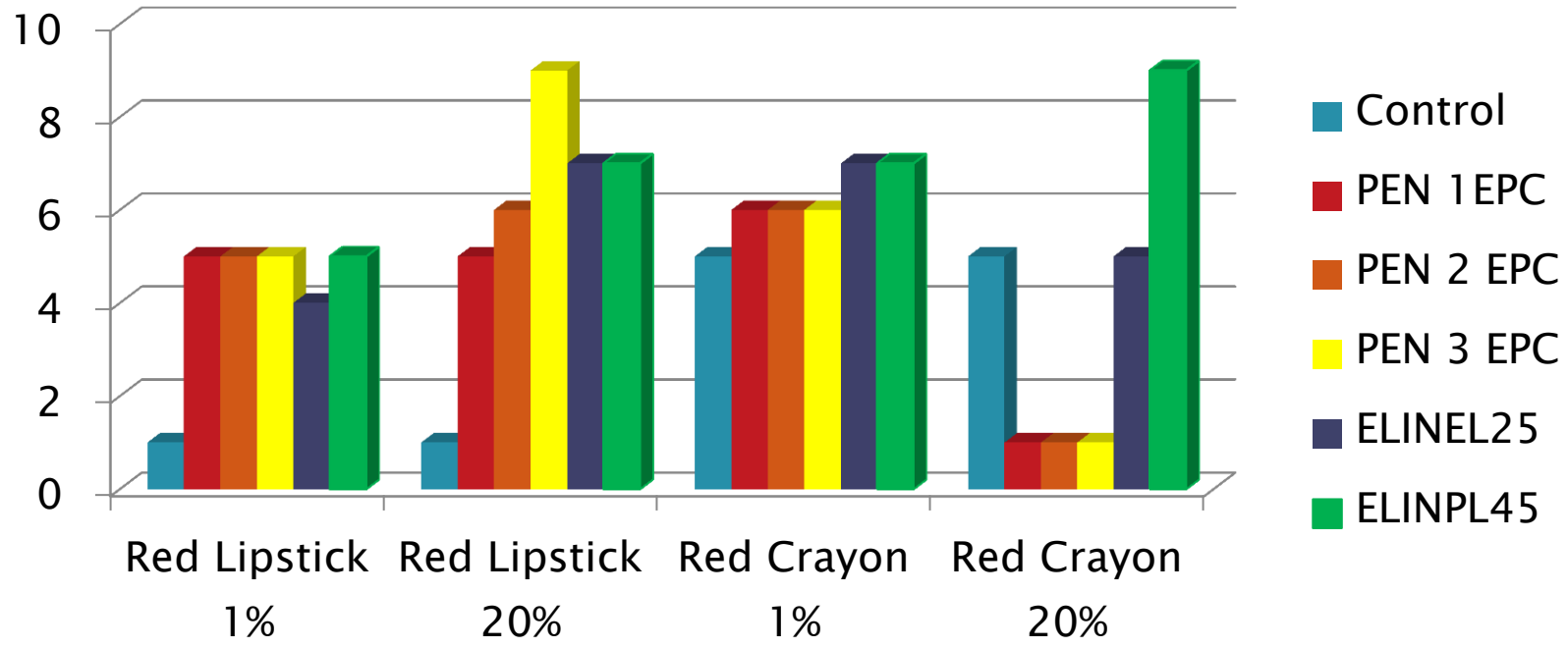
Impact Resistance



- 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 System IIB



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

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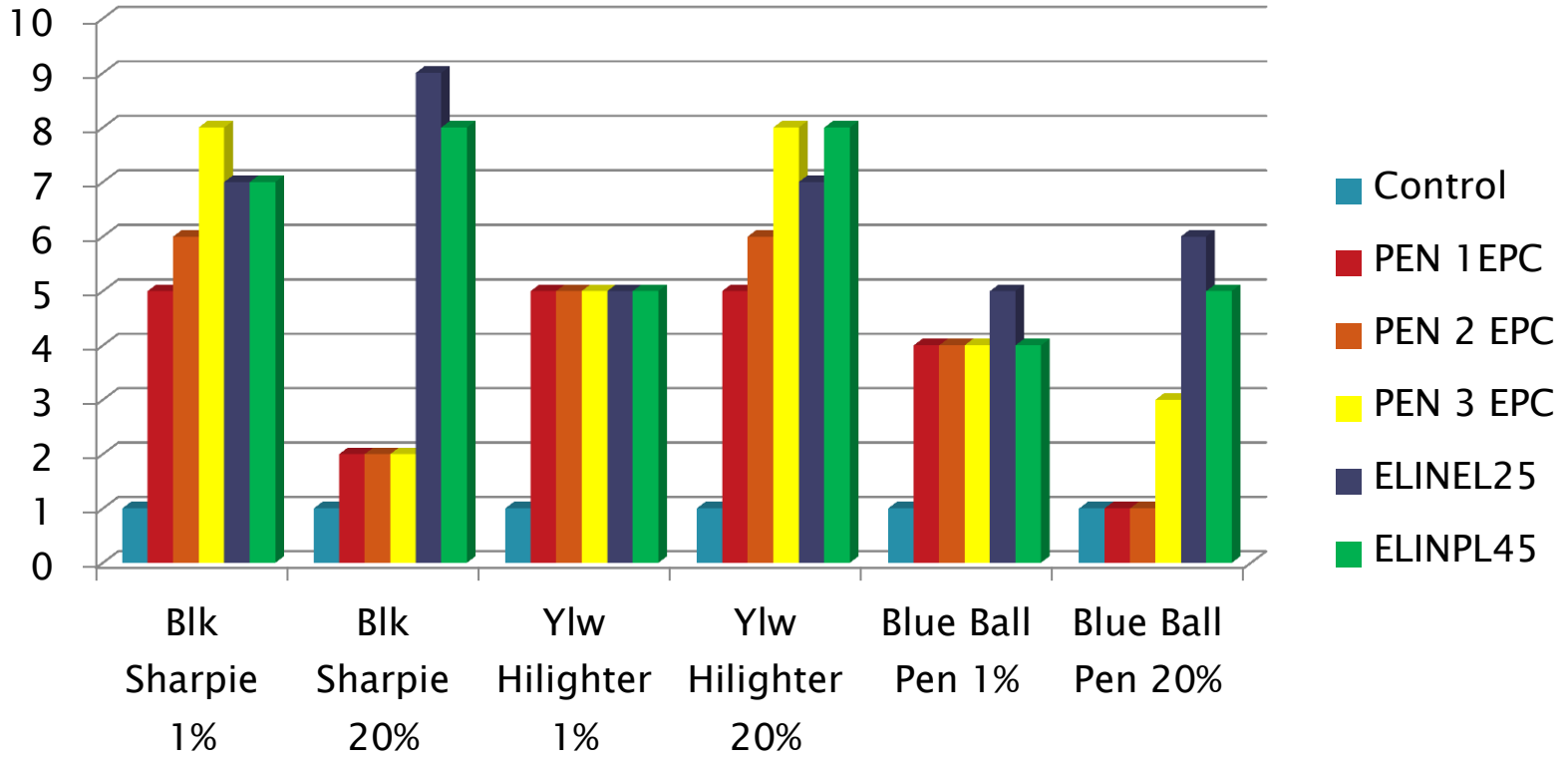
Stain Resistance System IIB



- 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.
- 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.
- Mar resistance is also seen at 1% but is typically not improved at higher levels.
- Impact resistance and moduli show increased flexibility. Higher use levels are needed here with 1% showing little or no effect.

Conclusions

- Stain resistance is seen with most reactive silicones across multiple stains and is often increased at higher use levels such as 20% over 1%.
  - There is no clear structure/ property relationship with stain resistance at this point.
  - High molecular weight and di-functional architecture often give the best stain resistance.
  - Increasing the number of reactive sites often improves this.
- The very high levels of silicone incorporation (60%) tend to make the coating softer and more rubbery.

THANK YOU

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