Properties of Silicone Modified Films

Tom Cheung, Bob Ruckle
Siltech Corp, Toronto, ON

Abstract

The effect of using epoxy or acrylate reactive silicones in organic resin systems is evaluated by measuring properties such as appearance (defects, gloss), slip, flexibility, stain release, mar resistance, cure time, and impact resistance.

Experimental and Methodology:

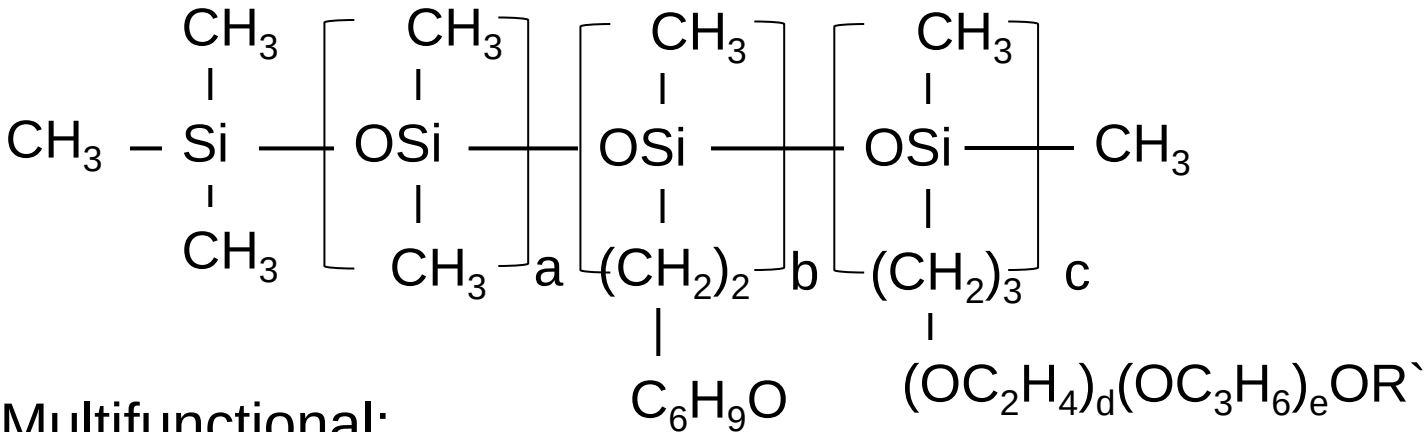
The overall design is to use two radiation cured systems, one acrylate and the other cycloaliphatic epoxy cured.

Various silicones are used.

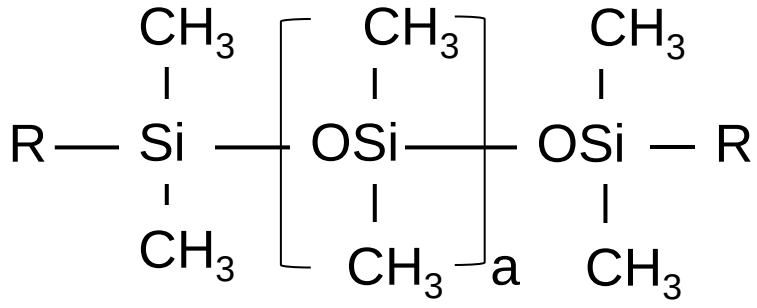
The systems were cured in a UV box with a hand lamp, using various UV lamps and cure conditions, depending on the nature of study.

A nitrogen blanket is used for free radical cured systems.

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.

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.

System IA Acrylate Functional

System I ACR	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 Escacure TZT	5.0%
Photoinitiator Darocur 1173	1.5%
Silmer ACR D2 (Defoamer)	0.5%

Results System IA

System I Series A	Control		
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 and reacts into the film completely.
- One sees release and flexibility as more silicone is used.
- The film properties can be modified by incorporation of 60% silicone to give very strong release properties.
- Paradoxically, CoF increases with silicone content.

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System IB Acrylate Functional

System I ACR	Series B
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%
Silmer ACR D2 (Defoamer)	0.5%
Reactive diluent SR 355 DTPTA	1%
Reactive diluent SR 306 TRPGDA	5%

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System IB Linear Silicones

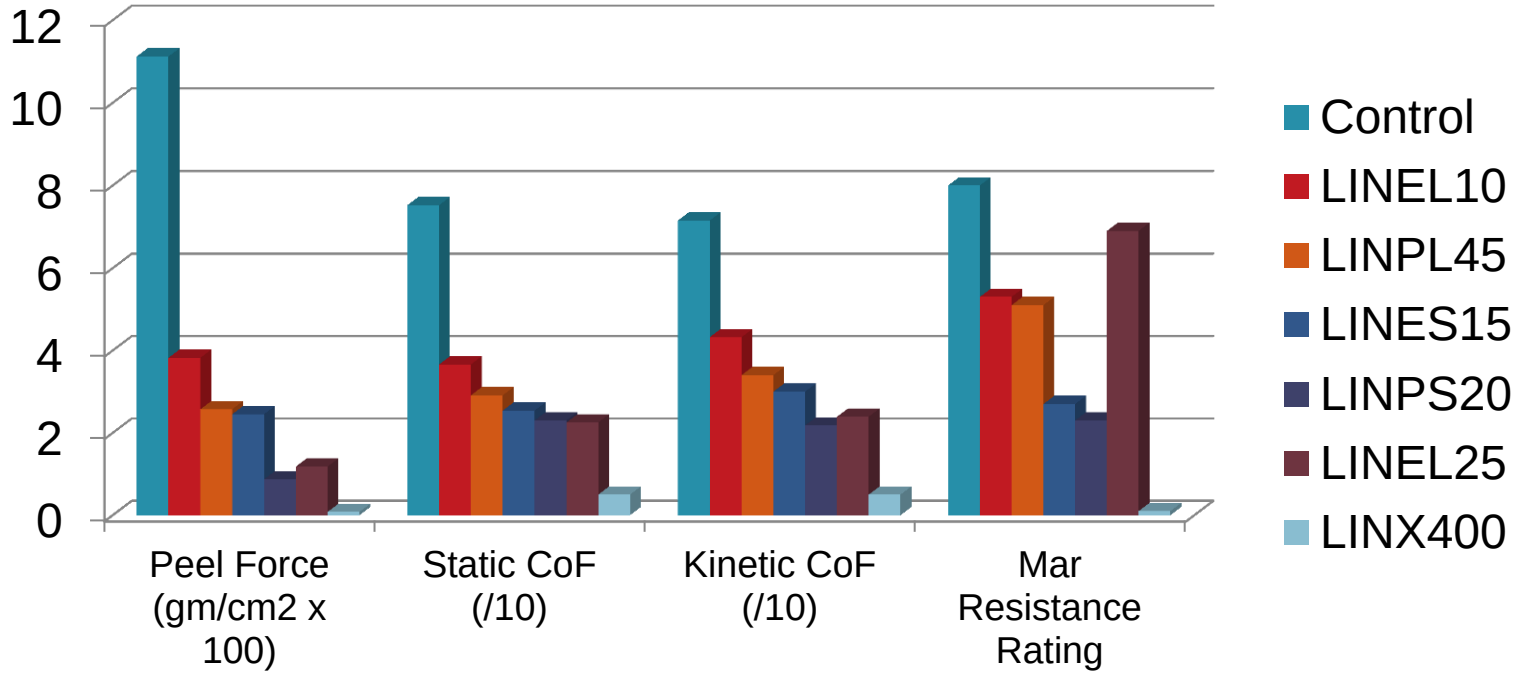
Variation	LINES15	LINPL45	LINX400	LINEL10	LINPS20	LINEL25
Silicone	Linear, small	Linear, large	Linear, v. lg.	Linear, small	Linear, medium	Linear, medium
Polyether	EO Small	EO/PO Large	None	EO Large	EO/PO Small	EO Large
Log MW	3.34	3.83	4.48	3.3	3.54	3.49
Viscosity (cps)	160	2400	2400	160	210	330

Results System 1B

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			

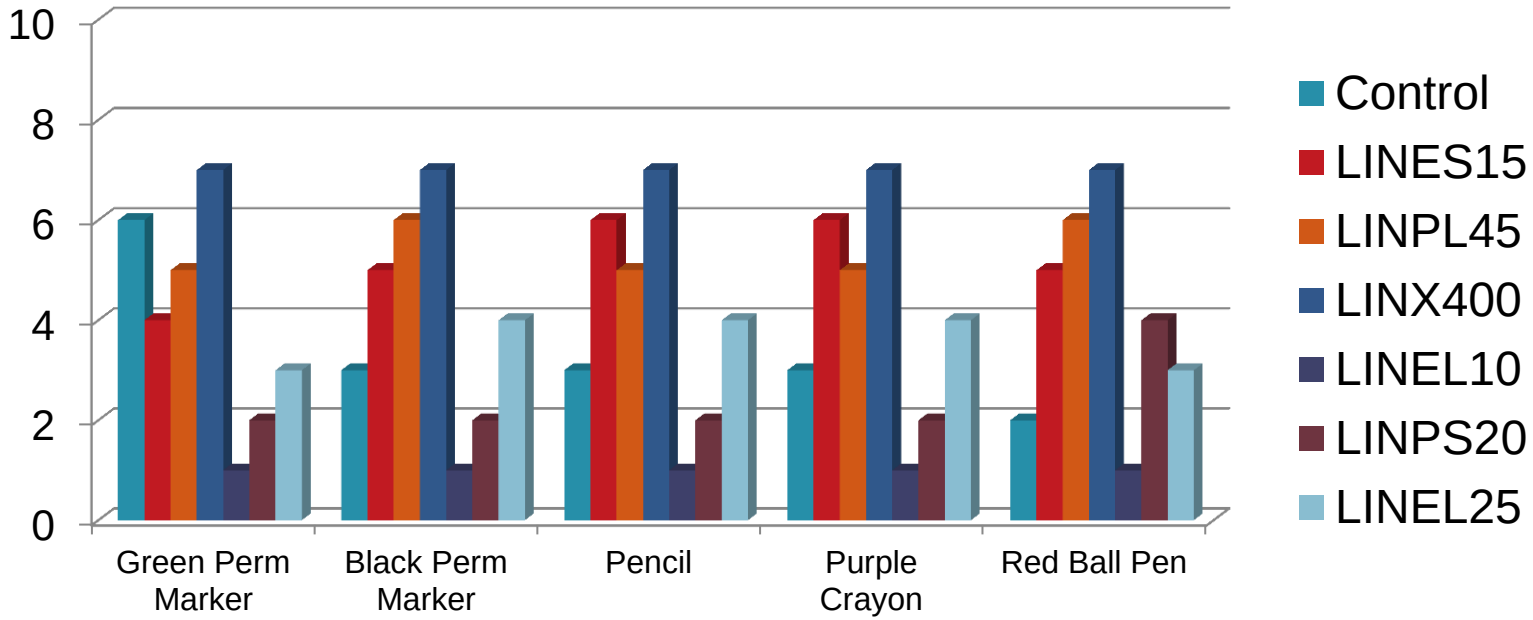
- All give lower moduli except LINEL10
- All cure except non-polyether LINX400

Slip Properties System 1B



- The peel force, slip and CoF are improved.
- LINX 400 best – b/c uncured?
- The best results of the completely cured systems belong to the medium chain length silicones.
- There is no dramatic improvement in mar resistance.

Stain Resistance System 1B



- There is improvement in stain resistance.
- LINEL10 and LINPS20 are worse
- The LINX400 gives the best stain resistance perhaps due to some uncured silicone.

System IC Acrylate Functional

System I ACR	Series C
ACR Reactive Silicones	Various
Use level (%)	22.0%
Epoxy Acrylate Resin	CN102Z
Use level (%)	40.0%
Synergist CN386	15.0%
Photoinitiator Escacure 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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System IC

System I Series C	LINX10	LINX50	LINX100	PENES8	PENES30	PENX8
Silicone	Linear, small	Linear, medium	Linear, large	Pendant, small	Pendant, medium	Pendant, small
Polyether	None	None	None	EO small	EO Small	None
Log MW	3.04	3.61	3.90	3.48	3.71	3.15
Viscosity)	33	110	144	575	710	158

Results System IC

System I Series C	LINX10	LINX50	LINX100	PENES8	PENES30	PENX8	Control
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
tan(delta)(/100)	8.71	17.3	15.82	8.58	7.86	7.25	7.93
Cure Condition & Appearance	oily	oily, defects	oily	Cured	Cured	Sl. Tacky	Cured

- most lower moduli
- Again non-polyether materials do not completely cure

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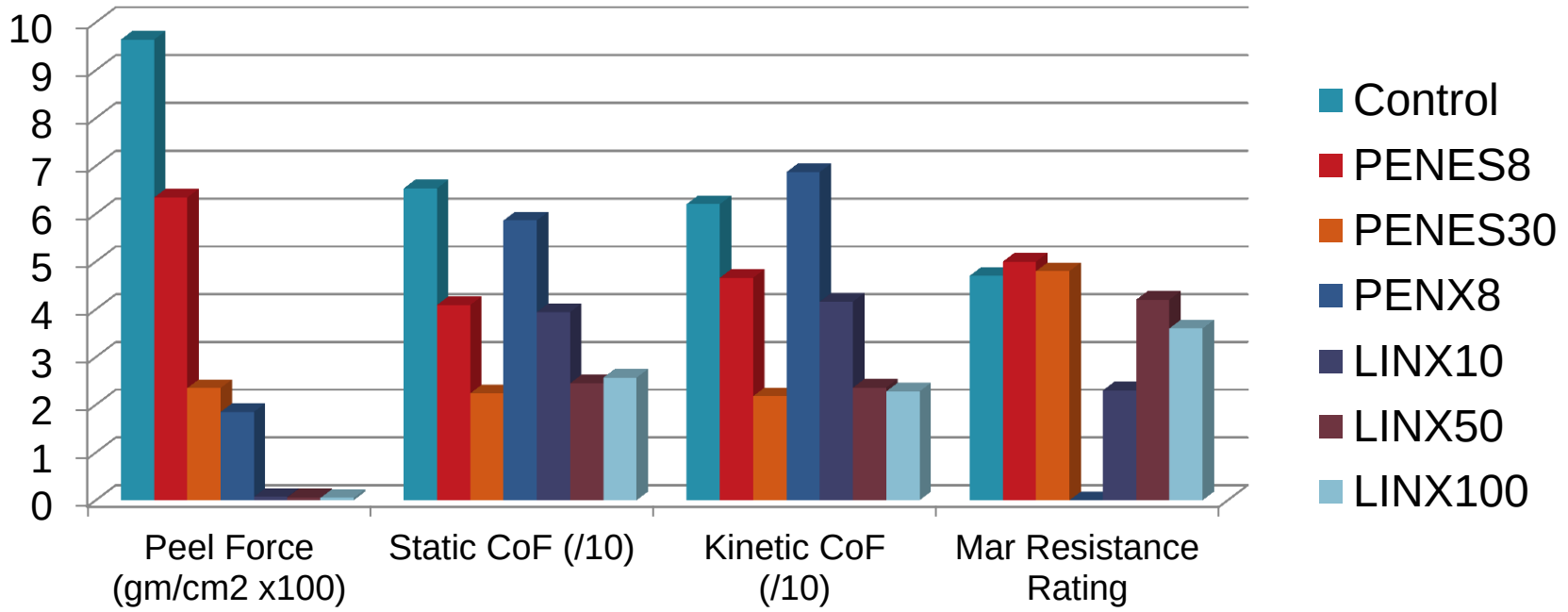
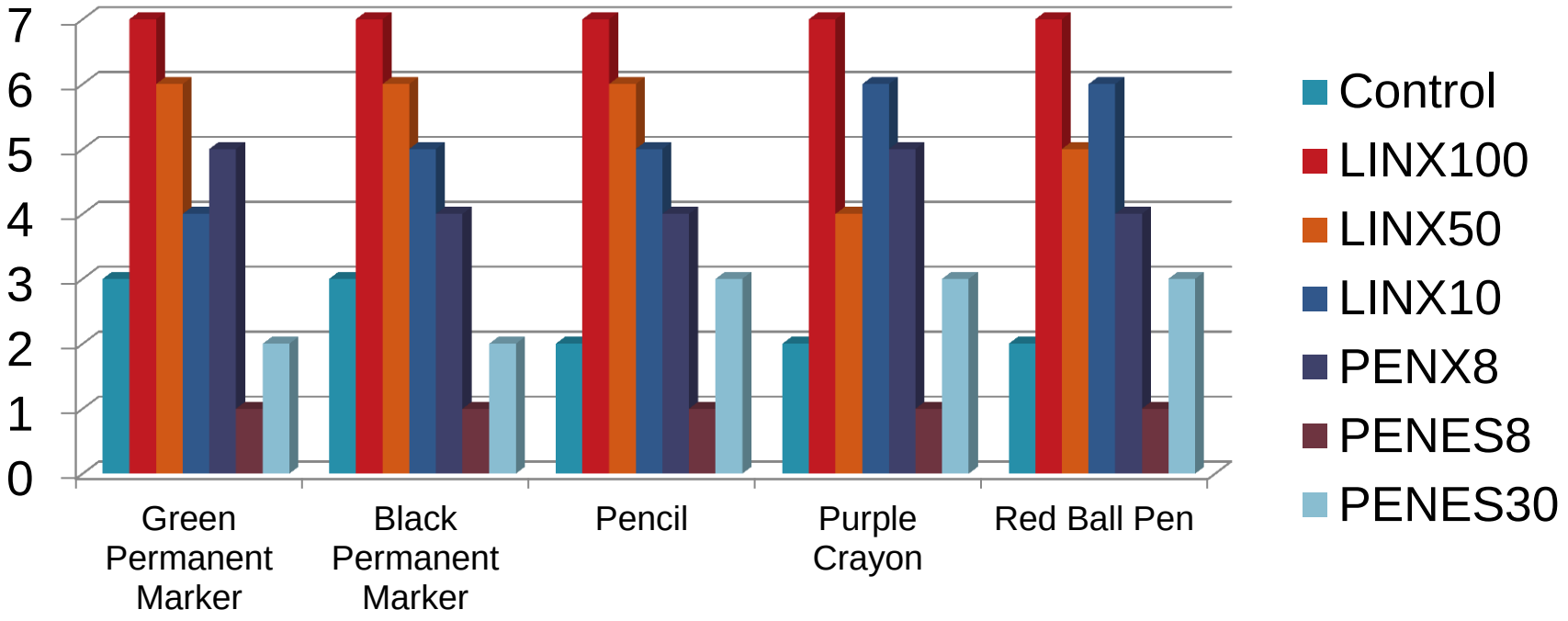
Slip Properties System IC



- Peel force and CoF are lowered.
- The peel force with linear silicones is lower.
- Higher MW also seems to help this effect.
- Mar resistance mostly has little impact.

Stain Resistance System 1C



- Many of these are improved over control
- The incompletely cured materials again give improved stain resistance.

System II Cycloaliphatic Epoxy

System II EPC	Series A	Series 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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System II A Silicone Variations

System II Series A	ELINX10	ELINX50	ELINX100	ELINX400	EPENX45	EPENX250	EPENX150
Silicone	Linear, small	Linear, med.	Linear, lg.	Linear, v. lg.	Pendant, med.	Pendant, very lg.	Pendant, lg.
Polyether	None	None	None	None	None	None	None
Log MW	3.07	3.82	3.95	4.23	3.60	4.31	4.07
Viscosity (cps)	27	74	200	1050	138	1390	495

Results System II A EPC

System II Series A (20%)	ELINX10	ELINX50	ELINX100	ELINX400	EPENX45	EPENX250	EPENX150	control
tan(delta)	0.48	0.36	0.35	0.46	0.46	0.33	0.36	0.68
Shear Modulus |G*| (Pa E+7)	2.07	2.29	2.26	2.96	2.86	1.79	1.95	3.84
Cure Condition & Appearance	Smooth Greasy	Mottled Greasy						Smooth

- Mottled and Greasy indicate these non-polyether epoxy silicones did not cure in completely
- Flexibility is improved in all by moduli

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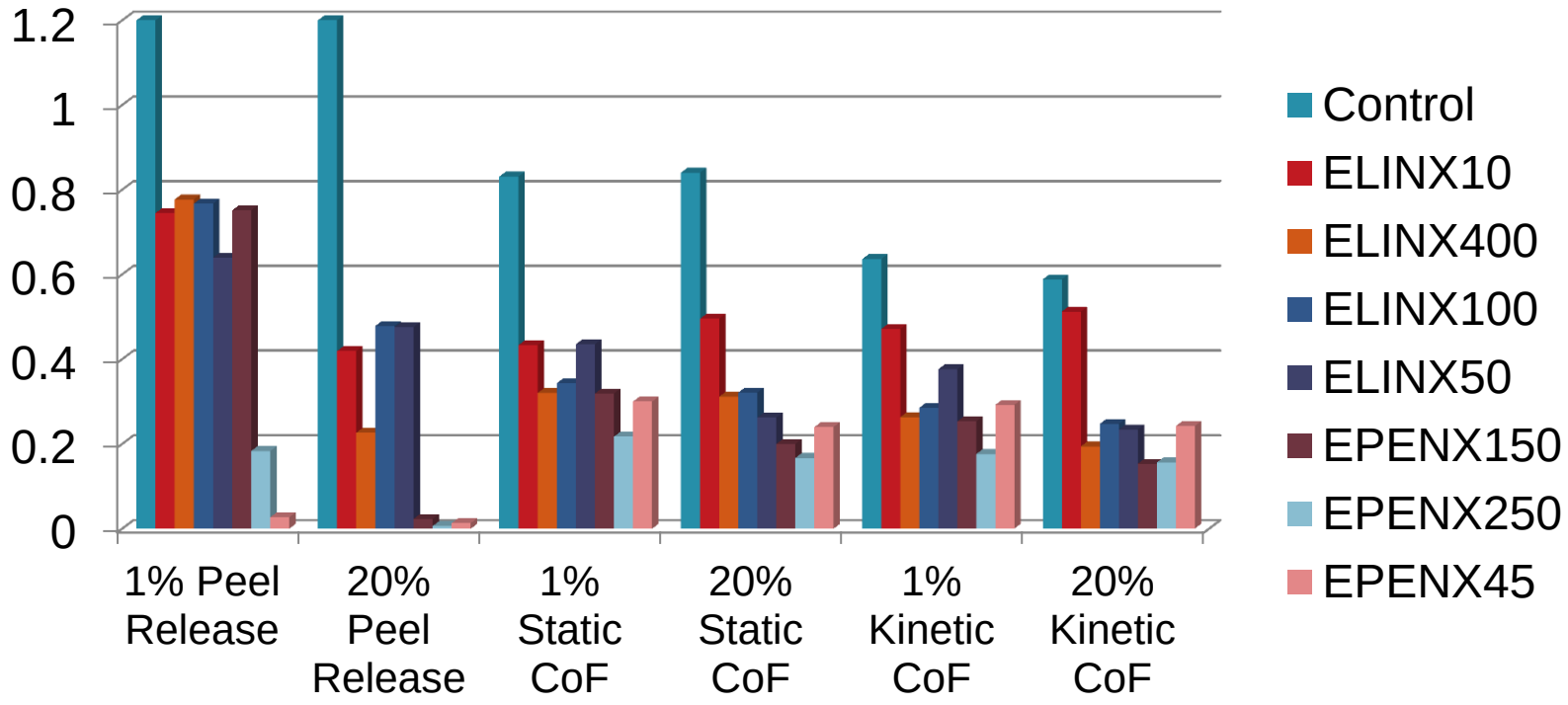
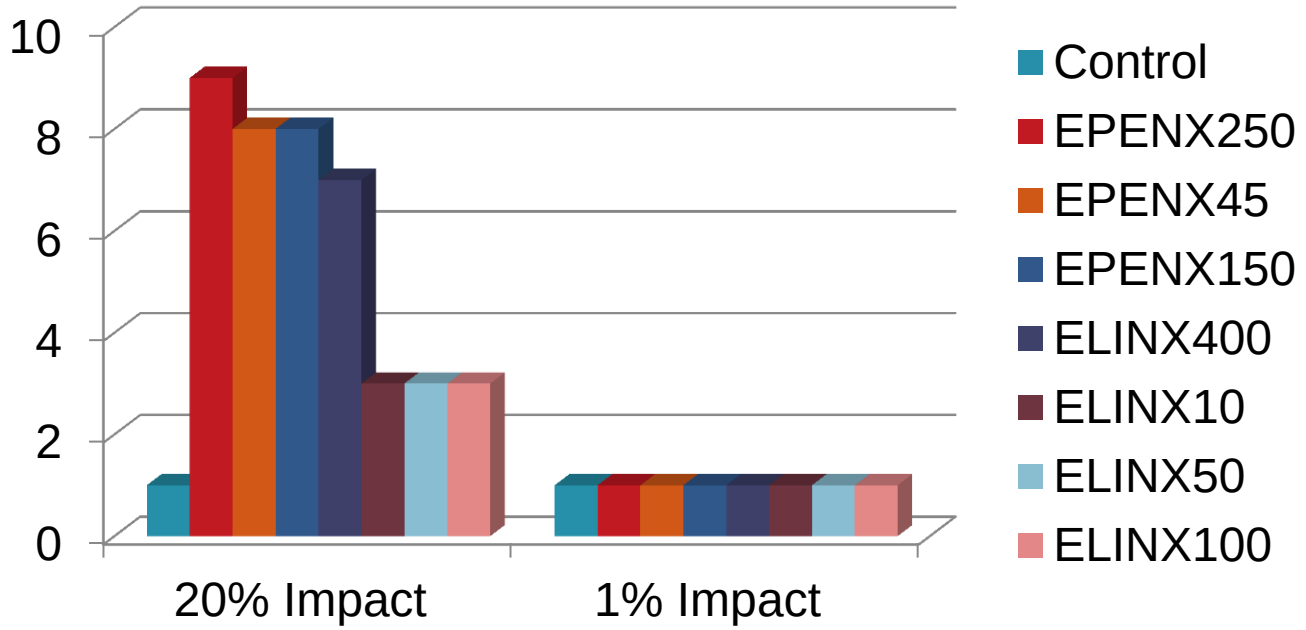
Slip Properties System II A



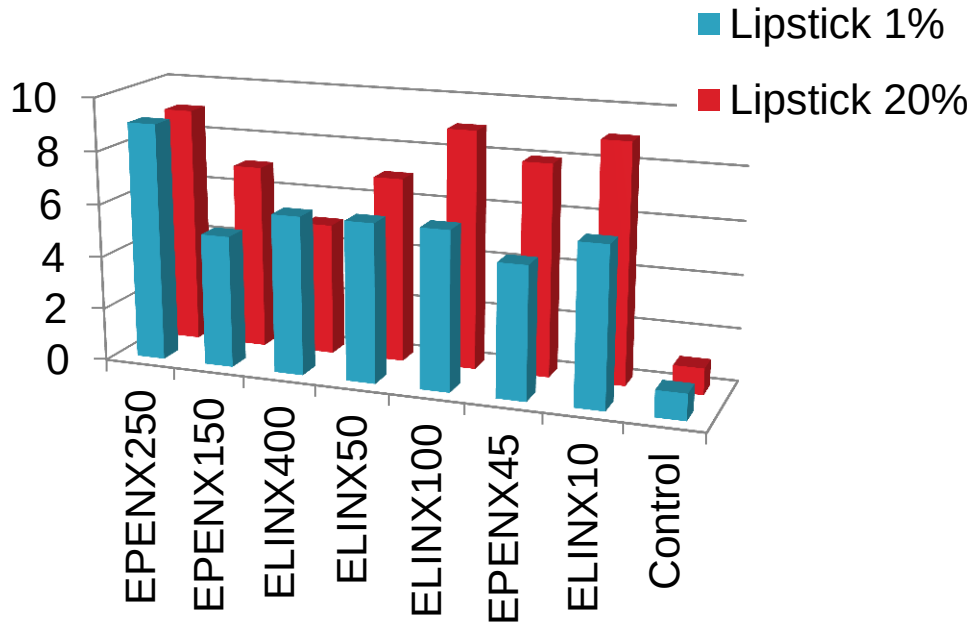
- Slip, CoF and peel force are significantly lower than the control.
- 20% is more effective especially for tape release.
- The highest MW silicones do the best in this system.

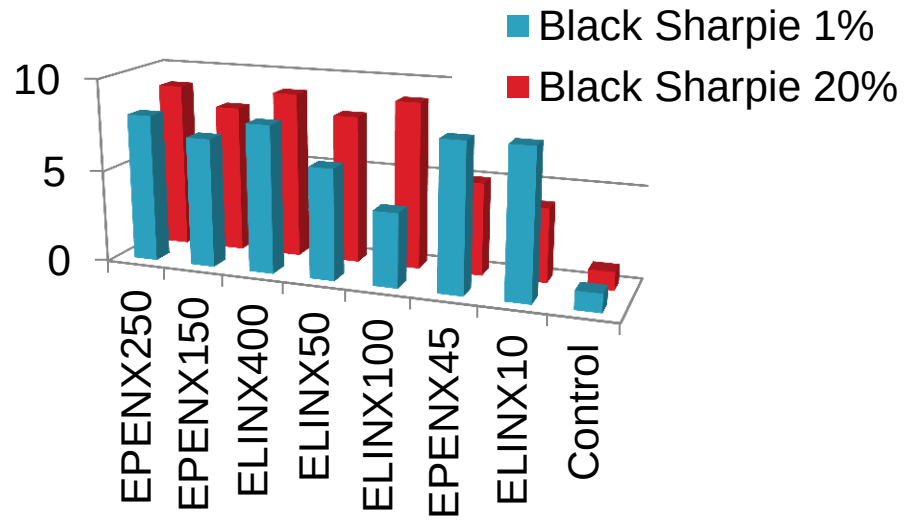
Impact Resistance System IIA



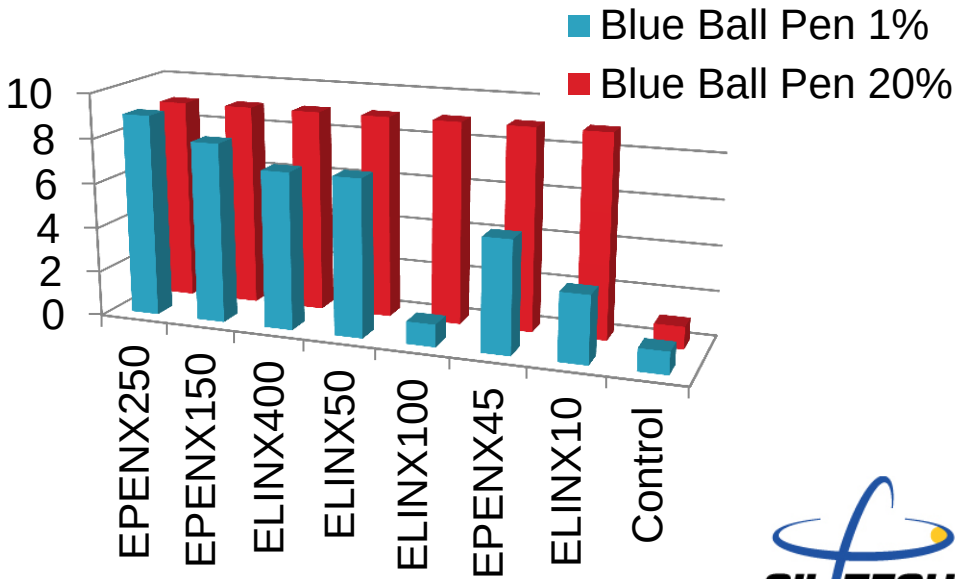
- At 1% there is no improvement.
- At 20% impact resistance improves significantly
- Multifunctional silicones give better impact resistance.
- The highest MW linear di-functional works well also.

Stain Resistance System IIA





- Stain and mar resistance improve
- Increases as MW increases.
- Stain resistance is better at 20%.



System II B Silicone Variations

System II Series B	EPENPL35	2EPENPL35	3EPENPL35	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 System IIB EPC

System II Series B	EPENPL35	2EPENPL35	3EPENPL35	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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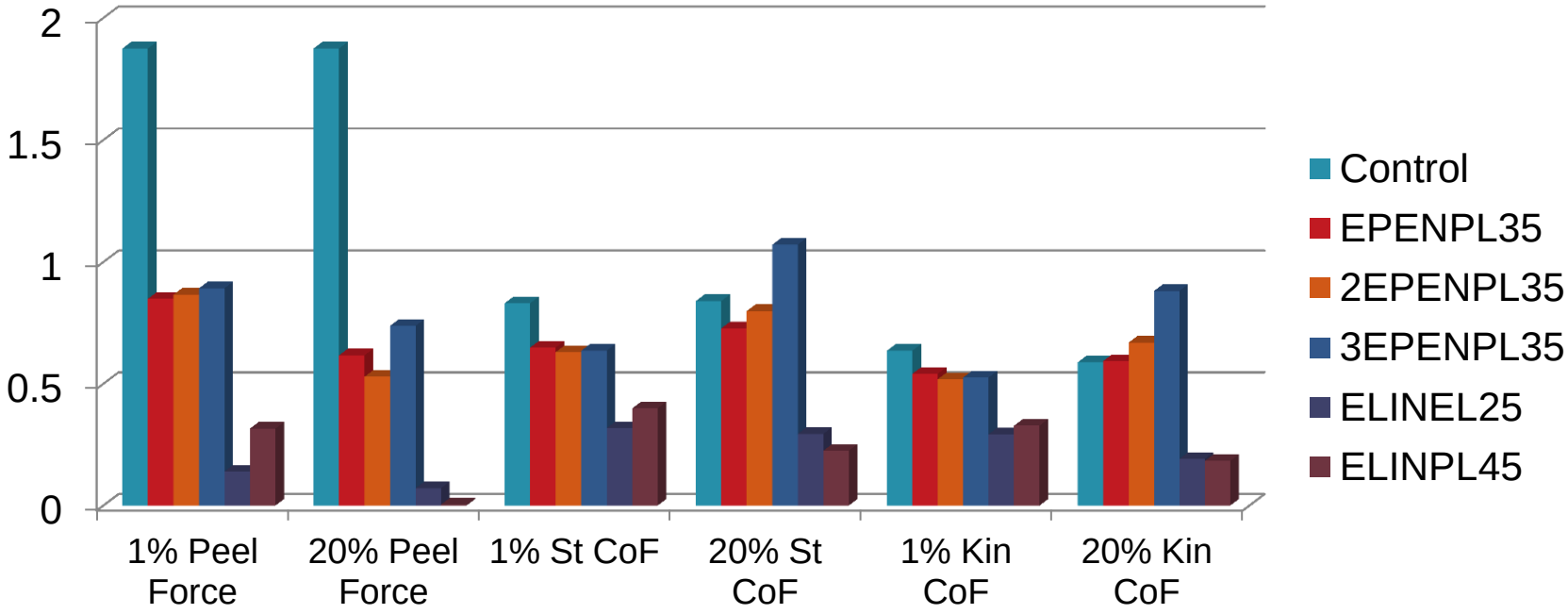
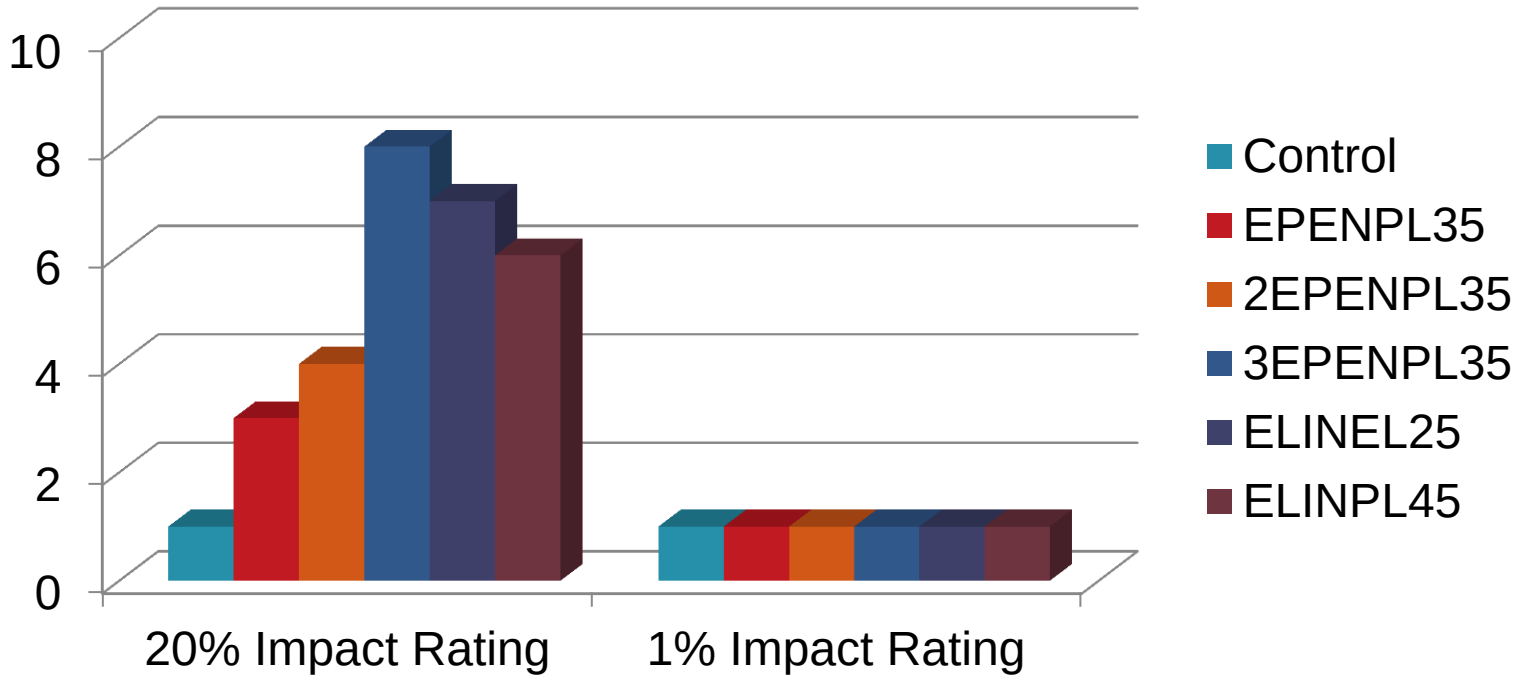
Slip Properties System IIB



- 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 slip.

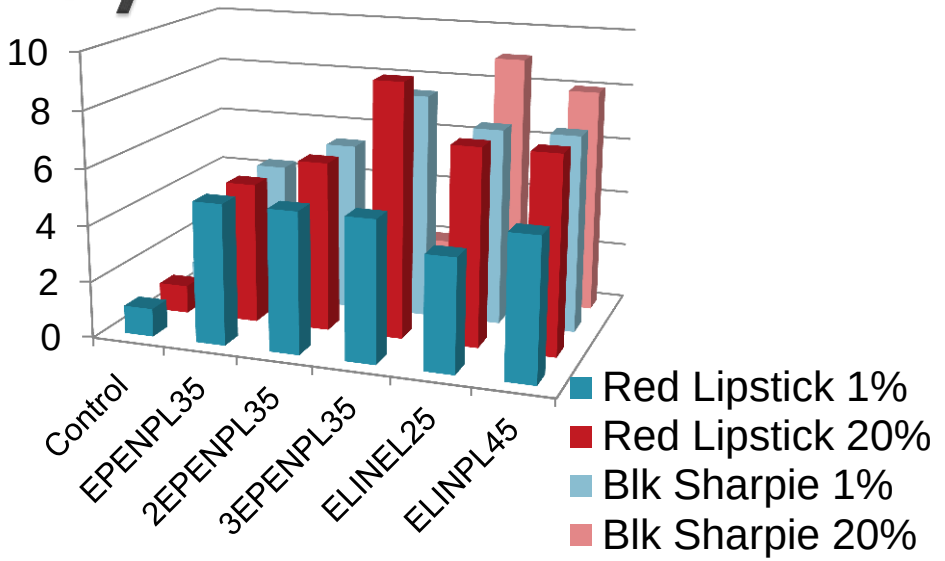
Impact Resistance System IIB

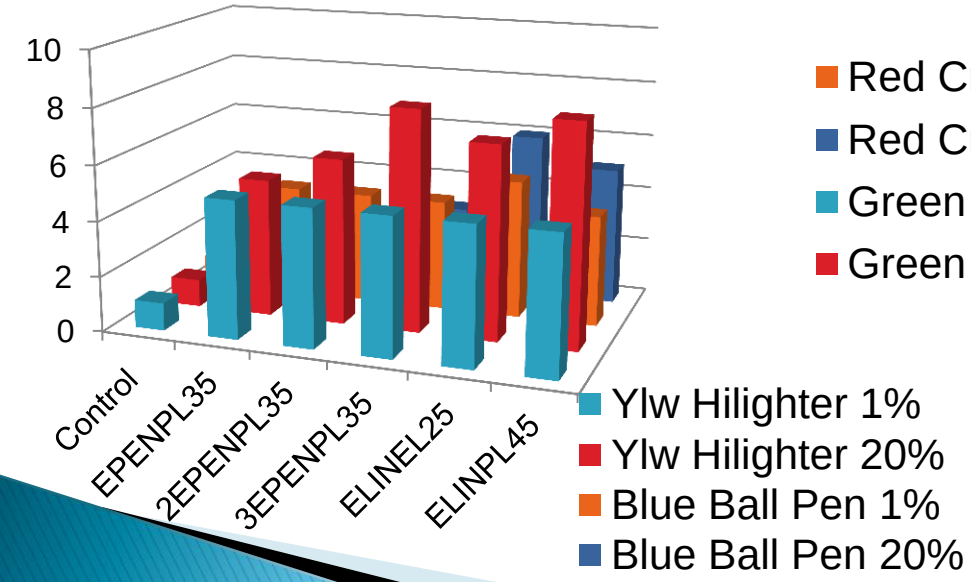


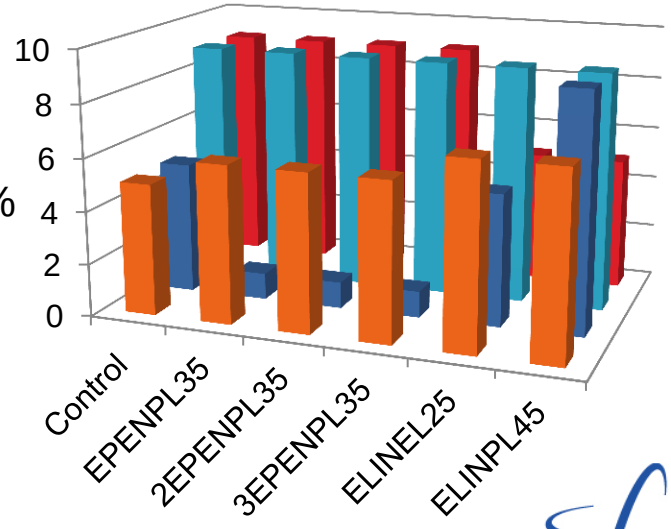
- There is no change in impact resistance at 1% loading.
- The 20% loading shows a strong effect.
- Increases as the number of epoxy groups increases

Stain Resistance System IIB

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







Conclusions

- Solubilized reactive silicones become part of the film. Without solubilizing pieces 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 better than pendant.
- Mar resistance is also seen at 1% but is not improved at higher levels. In fact, the mar resistance properties are often lost at higher loadings which is believed to be an artifact of the softer films.
- Impact resistance and moduli show increased flexibility. Higher use levels are needed here with 1% showing little or no effect.

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Conclusions

- Stain resistance is seen with most reactive silicones across multiple stains and is sometimes increased at higher use levels such as 20% over 1%.
  - High molecular weight and di-functional architecture give the best stain resistance.
  - Increasing the number of reactive sites improves this.
  - Having some uncured silicone in the film seems to increase stain resistance.
- The high levels of silicone incorporation tend to make the coating softer and more rubbery.

THANK YOU

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