Properties of Silicone Modified UV Cured Acrylate and Epoxy Coatings Films

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Abstract

Reactive silicones are reacted with commercially available organic resins which have corresponding reactive groups. The groups explored herein are cycloaliphatic epoxy and acrylate. The effect of using silicone/organic hybrids instead of the pure organic resin is evaluated by measuring properties such as appearance (defects, gloss), slip, flexibility, stain release, mar resistance cure time, and impact resistance.

Introduction

A wide variety of polymers are used as resins in coatings systems. Often defined by their reactive groups, the myriad of resins offer a wide-range of properties. In the coatings industry acrylate, epoxy, urethane and polyester coatings are all quite common and have associated typical properties and expectations. Resin manufacturers have spent countless hours and money fine-tuning and expanding the properties of their core chemistry to vary their utility.[1-6]

One way to alter the fundamental properties of a polymer is to react it with a different polymer generating an AB type co-polymer or hybrid. With low surface energy, ultra low T_g, and strong slip, release and flow properties, polydimethylsiloxane (aka PDMS or silicone) can bring profound property changes to these hybrids.

PDMS itself has no reactive groups although the polymer can be broken under strong base or acid catalysis and reacted with nucleophilic resin systems. Siltech has available a portfolio of modified silicones with each of the reactive groups described above. The reactive sites are made from the same raw materials as the native resin polymers.

The reaction is complicated by the inherent insolubility of silicone in organic resins. The reaction with silicones is often slower and requires stringent mixing methods.

In this paper, we modify a few coatings systems with reactive silicones and examine the effect on their liquid and cured film properties. We have chosen UV cured acrylate and cycloaliphatic epoxy systems as examples, but this concept is valid in heat cured systems as well.

Experimental and Methodology:

The overall design is to use two radiation cured systems, one acrylate and the other cycloaliphatic epoxy cured. The systems were cured in a UV box with a hand lamp, using the following UV lamps and cure conditions, depending on the nature of study:

a. 15Watt Bench UV lamp with 10 mW/cm^2 of UV Full (230nm-410nm); exposure time from 30 min to 1 hour for heat sensitive Leneta panels.
b. Rheometer LED UV Lamp with 132 mW/cm^2 of UV Full; exposure time from 30 sec to 5 min for rheological measurements.
c. PC 100S Spot Lamp with 140 mW/cm^2 of UV Full; exposure time from 30 sec to 5 min for hardness measurements of small button samples.
d. High Pressure Mercury Vapor Lamp with 0.98W/cm^2 of UV Full; exposure time from 1 sec. to 5 sec for metal panels.

A nitrogen blanket is used for curing acrylate coating that contains free radical photoinitiator.

System I: UV cured acrylate (ACR)

Coatings system:

The following UV curable acrylate based coating systems are used for the current study:

System I ACR	**Series A**	**Series B**	**Series C**
ACR Reactive Silicones Use level (%)	Silmer® ACR D208 0/30%/60%	Various 10.0%	Various 22.0%
Epoxy Acrylate Resin Use level (%)	CN104C75 80%/50%/20%	CN104C75 67%	CN102Z 40.0%
Synergist CN386	13.0%	10.0%	15.0%
Photoinitiator Escacure TZT	5.0%	5.0%	5.0%
Photoinitiator Darocur 1173	1.5%	1.5%	1.5%
Silmer ACR D2 (Defoamer)	0.5%	0.5%	0.5%
Reactive diluent SR 355 DTPTA	0%	1%	10%
Reactive diluent SR 306 TRPGDA	0%	5%	6%

In Series A, we use one well studied reactive silicone product, Silmer ACR D208. On average, this is a di-functional silicone acrylate ester with polyethyleneoxide chains for increased solubility. This product is commonly used for screening at Siltech because it has good solubility and good reactivity. Here we examine the silicone at 30% and 60% of the system so that we can see an effect and confirm reactivity.

In Series B, we extend this success with six silicone acrylate esters which vary by linear vs. pendant polymer architecture; presence or absence of a polyalkyleneneoxide chain; and silicone and polyether chain lengths. All of these are run at 10% use level.

Finally in Series C, we run a similar selection of six acrylate ester functional silicones focusing mainly on the linear vs. pendant polymer architecture in a different organic resin system at a 22% use level.

System II: UV cured cycloaliphatic epoxy (EPC)

Coatings system: The following UV Curable EPC blends are used for the current study:

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%

In this different cure system, we evaluate a series (A) of relatively insoluble epoxy silicones which vary by linear vs. pendant polymer architecture, number of reactive sites, and polymer chain length. Each of these is screened at 1% and 20% use levels.

In Series B, we examine polyalkyleneoxide modified epoxy silicones which vary by linear vs. pendant polymer architecture; type and chain length of polyalkyleneoxide; number of reactive sites and silicone and polyether chain lengths. All of these are run at 1 and 20% levels.

Test Panel Preparation

All tested panels are prepared by drawing down approximately 1 ml of the above formulation on a 4"X6.5" white Leneta paper with wire-wound rod #10. The wet film is cured under a UV bench lamp for one hour with nitrogen blanket.

Coefficient of Friction (CoF /Slip)

Slip is measured with ChemInstruments Coefficient of Friction -500. (Test speed: 15 cm/min; travel length: 15 cm; sled weight: 200 grams and sled surface which is covered with ASTM-specified rubber). Static coefficient of friction is directly obtained from the equipment, representing the ratio of the horizontal component of the force (required to overcome the initial friction) to the vertical component of the object weight (200 grams). Kinetic coefficient of friction is also directly obtained from the equipment, representing the ratio of the horizontal component of the force (required to cause the object to slide at a constant velocity) to the vertical component of the object weight (200 grams). The greater the value, the higher the friction is for the substrate. 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. 10 is the best and 0 is the worst.

Gloss:

Gloss is measured with BYK-Gardner 60° micro-glossmeter. The value is directly recorded from the micro-glossmeter. 0 is the lowest and 100 is the highest.

Peel Force Measurements

A 12" long length of 1.89" wide Intertape 6100, clear packing tape is used. Half of length of the tape is applied on the coated panel at a 45° angle with a wooden applicator. Care is taken to ensure good contact between the tape and the substrate. One end of a stainless steel string is attached to the transducer and the other end is fastened onto the remaining half of the tape with a 2" length of standard cellophane tape. Peel force is measured by peeling the tape with ChemInstruments 500 at an angle of 180° and peel rate of 60 cm/min. Record and report an average of ten tests as the peel force in grams/cm^2.

Mar Resistance

Mar resistance is 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. Rubbings are done using a 4 lb test block which is attached with a 2"x 4" nylon scrubbing pad. Gloss is measured immediately after completion of rubbing for each panel. The mar resistance rating is determined by visual inspection of surface defects and by the percentage change in gloss reading before and after the rubbing test. Record percentage loss of gloss and a subjective rating from 0 to 10 where 10 is the best and indicates no visible effect.

Stain Resistance

Stains are applied on the panel using 1-5 drops/mark each on separate locations near the centre portion the panel. The following stains were used: red lipstick, green permanent marker, black permanent marker, brown crayon, purple crayon, pencil, red ball pen, and yellow hi-lighter. All of the stained panels were conditioned at room temperature for 1 hour before testing. All the treated panels were then rinsed with tap water for 1 minute and wiped with an IPA saturated cotton swab. The subjective ratings are obtained by visual comparison of stains remaining on the panels for each series and rating them from 1 to 10 where 10 is best and indicates no remaining stain.

Impact Resistance

The panel to be tested is placed coated side down on the top of a protective paper which sits 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 with a 1.5 cm hole through the middle fitted onto the steel rod drops down freely and vertically along the rod from a distance of 23 cm above the coating surface. The impact resistance is estimated by visual inspection of the size and pattern of the damage. 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.

TEST RESULTS

System 1 Series A: Formulations of UV curable coatings were prepared with epoxy acrylate resin and modified with varying amounts of Silmer® ACR D208 di-functional acrylate ester silicone with a polyethyleneoxide chain for increased solubility

Table IA Film: Properties of UV cured coatings prepared with acrylate resin and modified with varying amounts of Silmer ACR D208

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/cm^2)	179	147	7.2
Impact Resistance	0	8	10
Cured Conditions & Appearance	Cured, slightly yellow, smooth	Cured, slightly yellow, smooth	Cured, slightly yellow, rubbery

Conclusions System I Series A: This screening study shows this low molecular weight polyethyleneoxide, acrylate ester silicone material is highly compatible with this acrylate resin and reacts into the film completely. The film properties of the acrylate UV coating can be modified by incorporation of more than 60% silicone to give very strong release properties. The peel force and impact resistance data show better release and flexibility as more silicone is used as one expects. However the CoF data shows an increase with silicone content. The coating becomes rubbery and very flexible to the hand at these high levels of silicone and we believe this is why the CoF data is skewed.

System I Series B: Formulations of UV curable coatings were prepared with epoxy acrylate resin and modified with varying amounts of silicones, all but one of which are modified by polyalkyleneoxides for solubility, and which differ primarily by silicone and polyether chain lengths. All of these are run at 10% use level.

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

Table IB Liq.: Liquid properties of acrylate resin modified with acrylate ester functional silicones.

System I Series B	LINES15	LINPL45	LINX400	LINEL10	LINPS20	LINEL25	Control
Liquid Coating Properties							
3 hr spread diameter (mm)	1.9	1.5	1.0	2.0	1.9	1.9	0.7
5 min spread diameter (mm)	2.3	2.0	1.9	2.4	2.4	2.4	1.55
Viscosity (cps)	1233	2560	2691	948	986	976	1016
Flow (mm)	9.2	7.2	6.4	9.1	7.6	7.2	8.8
Properties while curing							
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 sl. yellow	Cured sl. yellow	fish eyes, not fully cured, Oily	Cured sl. yellow	Cured sl. yellow	Cured sl. yellow	Cured sl. yellow

Table IB Film: Film properties of acrylate resin modified with acrylate ester functional silicones.

System I Series B	**LINES15**	**LINPL45**	**LINX400**	**LINEL10**	**LINPS20**	**LINEL25**	**Control**
Peel Force (gm/cm^2 x 100)	2.45	2.57	0.08	3.82	0.87	1.18	11.12
Static CoF (/10)	2.54	2.91	0.50	3.66	2.30	2.25	7.52
Kinetic CoF (/10)	3.00	3.40	0.50	4.32	2.18	2.39	7.15
Gloss	96.0	96.4	64.2	97.6	96.3	96.7	99.1
Change in gloss (%)	-4.2	-6.8	-8.2	-5.1	-5.2	-6.6	-2.99
Mar Resistance Rating	2.7	5.1	0.1	5.3	2.3	6.9	8.0
Stain Resist Ratings							
Lipstick	5	6	7	1	2	4	3
Green Permanent Marker	4	5	7	1	2	3	6
Black Permanent Marker	5	6	7	1	2	4	3
Brown Crayon	7	7	7	7	7	7	7
Pencil	6	5	7	1	2	4	3
Purple Crayon	6	5	7	1	2	4	3
Red Ball Pen	5	6	7	1	4	3	2
Yellow Hi-Lighter	7	7	7	7	7	7	7

Conclusions: System I Series B: The LINX400, which has no polyether modification, does not cure completely and leaves unreacted silicone oil on the surface. This means the film property tests may not be measuring an inherent change in the film, but rather the surface oil.

All of the test samples modified with 10% reactive silicones show better spreading than the control. LINEL10 and LINES15 reactive silicones give somewhat better flow than the control. All other samples show poorer flow than the control. The strongest correlation is between flow and viscosity of the coating rather than surface tension reduction due to the reactive silicone. This is perhaps due to the already low surface tension of the control.

The peel force, slip and CoF for each of the test samples prepared with 10% reactive silicone are significantly improved over the control. The best results of the completely cured systems belong to the medium chain length silicones.

There is no dramatic improvement in mar resistance with 10% silicone actives in this series. This may be due to the fact that the coating becomes softer and more rubbery as indicated by storage modulus. Alternatively, since using a small amount of silicone (<1%) as a slip additive in a UV coating typically improves mar resistance significantly, that effect may already be seen in the control film from the 0.5% Silmer ACR D2 used for foam control.

Most of the samples give lower storage and loss modulus than the control. Only LINEL10 gives higher values, a surprising result.

The uncured material using LINX400 gives the best stain resistance perhaps due to uncured silicone. In general, there is some improvement in stain resistance, with the exception of LINEL25 and LINPS20. We have no ready explanation for those exceptions.

<u>System I Series C</u>: In this study, formulations of UV curable acrylate coatings are varied with a selection of acrylate ester functional silicones focusing mainly on absence or presence of a polyalkyleneoxide chain, chain length of silicone and polyether and the linear vs. pendant polymer architecture in a different organic resin systems. All of these are run at 22% use level.

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 of Silicone	3.04	3.61	3.90	3.48	3.71	3.15
Viscosity of silicone (cps)	33	110	144	575	710	158

Table IC liq: Liquid properties of acrylate resin modified with acrylate ester functional silicones.

System I Series C	**LINX10**	**LINX50**	**LINX100**	**PENES8**	**PENES30**	**PENX8**	**Control**
Liquid Coating Properties							
3 hr spread width (mm)	1.1	1.3	1.2	2	1.9	1.4	0.8
5 min spread Diameter (mm)	2.2	2.2	2.1	2.5	2.5	2.3	1.6
Viscosity (cps)	1190	1380	1520	550	1020	1100	5390
Flow (mm)	0.8	0.6	0.6	1.2	0.9	0.6	0.4
Properties while curing							
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	yellow, oily	yellow, oily, defects	yellow, oily	Cured yellow	Cured, yellow	Sl. Tacky, yellow	Cured yellow

Table IC film: Film properties of epoxy acrylate resin modified with acrylate ester functional silicones.

System I Series C	**LINX10**	**LINX50**	**LINX100**	**PENES8**	**PENES30**	**PENX8**	**Control**
Peel Force (gm/cm^2 x100)	0.07	0.06	0.05	6.34	2.35	1.85	9.64
Static CoF (/10)	3.94	2.45	2.57	4.09	2.24	5.86	6.53
Kinetic CoF (/10)	4.16	2.36	2.28	4.66	2.18	6.87	6.2
Gloss	78.83	73.33	74.00	96.80	96.87	84.13	78.83
Change in gloss (%)	-3.1	-1.3	-1.9	-0.4	-0.6	-5.5	-0.7
Mar Resistance Rating	2.3	4.2	3.6	5.0	4.8	0.0	4.7
Stain Resist Ratings							
Lipstick	4	5	7	1	3	6	2
Green Permanent Marker	4	6	7	1	2	5	3
Black Permanent Marker	5	6	7	1	2	4	3
Brown Crayon	7	7	7	7	7	7	7
Pencil	5	6	7	1	3	4	2
Purple Crayon	6	4	7	1	3	5	2
Red Ball Pen	6	5	7	1	3	4	2
Yellow Hi-Lighter	7	7	7	7	7	7	7

Conclusions: System I Series C: The products with no polyether modification do not cure completely and leave unreacted silicone oil on the surface. This means the film property tests may not be measuring an inherent change in the film, but rather the surface oil.

All of the test samples modified with 22% reactive silicones show better spreading than the control. This is perhaps due to the fact that adding a reactive silicone to these systems reduces the viscosity of the resin significantly.

All samples prepared with 22% reactive silicones give much lower peel force and CoF than the control. The peel force for the samples prepared with linear acrylate ester silicones is significantly lower than those prepared with pendant materials. Higher MW also seems to help this effect.

Most of the samples give lower storage and loss modulus than the control. The most cross linked systems, PENES30 and PENX8, give the least reduction in the moduli.

Again a consistent, albeit moderate improvement in stain resistance is seen.

<u>System II Series A</u>: Formulations of UV curable coatings with cycloaliphatic epoxy resin were prepared with 1% and 20% of a series of relatively insoluble epoxy silicones which vary by linear vs. pendant polymer architecture, number of reactive sites, and polymer chain length.

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

Table IIA liq: Liquid properties of cycloaliphatic epoxy resins modified with epoxy functional silicones.

System II Series A (20%)	**ELINX10**	**ELINX50**	**ELINX100**	**ELINX400**	**EPENX45**	**EPENX250**	**EPENX150**	**control**
Properties while curing								
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	Mottled Greasy	Mottled Greasy	Mottled Greasy	Mottled Greasy	Mottled Greasy	Smooth

Table IIA Film: Film properties of cycloaliphatic epoxy resins modified with epoxy functional silicones.

System II Series A (1%/20%)	**ELINX10**	**ELINX50**	**ELINX100**	**ELINX400**	**EPENX45**	**EPENX250**	**EPENX150**	**Control**
1% Peel Release (mg/mm^2)	0.745	0.639	0.767	0.777	0.027	0.183	0.751	1.875
20% Peel Release (mg/mm^2)	0.419	0.475	0.478	0.226	0.013	0.006	0.023	1.875
1% Static CoF	0.433	0.435	0.343	0.32	0.3	0.217	0.319	0.831
1% Kinetic CoF	0.471	0.376	0.285	0.263	0.292	0.176	0.253	0.636

20% Static CoF	0.495	0.262	0.321	0.311	0.24	0.167	0.2	0.84
20% Kinetic CoF	0.512	0.234	0.247	0.194	0.242	0.156	0.153	0.588
1% Impact	1	1	1	1	1	1	1	1
20% Impact	3	3	3	7	8	9	8	1
1% Pencil Hardness	4.5H	4.5H	4.5H	4.5H	4.5H	4.5H	4.5H	4.5H
20% Pencil Hardness	4H	4H	4H	4H	4.5H	4.5H	4.5H	4.5H
1% Gloss	95	95.73	95.23	94.3	93.87	86.2	94.23	93.15
1 % Change in Gloss (%)	-4.7	--4.8	-3.3	-3.5	-3.2	-6.5	-4.7	-39.9
20% Gloss	92.45	89.8	91.55	79.6	89.8	81.2	87.2	93.15
20 % Change in Gloss (%)	-10.5	-3.5	-5.4	-1.8	-5.2	-1.4	-9.6	-39.9
Stain Resist Ratings 1%/20%								
Lipstick	6/9	6/7	6/9	6/5	5/8	9/9	5/7	1
Green Marker	9/9	9/9	9/9	9/9	9/9	9/9	9/9	9
Black Marker	7/5	6/9	7/6	8/8	8/7	9/9	8/7	1
Black Sharpie	8/4	6/8	4/9	8/9	8/5	8/9	7/8	1
Red Crayon	5/7	6/9	6/8	6/8	6/5	9/8	7/9	5
Yellow Hi-lighter	8/9	8/9	8/9	9/9	7/7	9/9	8/9	1
Blue Ball Pen	3/9	7/9	1/9	7/9	5/9	9/9	8/9	1

Conclusions: System II Series A:

As all of these samples show surface defects and a slightly greasy surface, the materials are not completely compatible and may not have completely cured into the film. It is possible that the film properties being measured are due to the surface oil rather than incorporation of silicone into the backbone.

Slip, CoF and Peel force of all of the epoxy silicone modified epoxy coatings is significantly lower than the control. Multifunctional (pendant) epoxy silicones with higher functionality give lower peel force than those with lower functionality. The highest molecular weight linear di-functional epoxy silicone gives lower peel force than the lower molecular weight ones.

Stain and mar resistance improve significantly when the cycloaliphatic epoxy coating is modified with either linear di-functional or multifunctional epoxy silicones. Both stain resistance and mar resistance seem to increase as the molecular weight of either polymer architecture is increased. The mar resistance of the 1% series is slightly better than the 20% series whereas the latter is better than the former with respect to stain resistance.

The impact resistance of epoxy coatings modified with 20% epoxy silicone improves significantly whereas there is no improvement in impact resistance for epoxy coatings modified with the 1% epoxy silicones. Multifunctional epoxy silicones seem to give better impact resistance than the linear di-functional silicones. The highest MW linear di-functional is better than lower ones.

It is surprising to see that the shear modulus increases as the molecular weight of the linear di-functional epoxy silicone increases in the 20% series. The shear modulus of the high MW linear di-functional epoxy silicone is higher than that of the low molecular weight ones. The sample prepared with multifunctional epoxy silicone gives lower shear modulus than those with the linear di-functional ones.

System II Series B: In this series we prepared formulations of UV curable cycloaliphatic epoxy coating resins modified with 1% and 20% of polyalkyleneoxide modified epoxy silicones which vary by linear vs. pendant polymer architecture; type and chain length of polyalkyleneoxide; number of epoxy groups and silicone and polyether chain lengths.

System II Series B	**EPENPL35**	**2EPENPL35**	**3EPENPL35**	**ELINEL25**	**ELINPL45**
Silicone	Pendant, medium	Linear, medium	Linear, large	Pendant, medium	Pendant, large
Polyether	EO/PO large	EO/PO large	EO/PO large	EO large	EO/PO large
# epoxy	1	2	3	2	2
Log MW of Silicone	3.93	3.87	3.80	3.42	3.72
Viscosity of silicone (cps)	798	1000	1010	255	1205

Table IIB liq: Liquid properties of cycloaliphatic epoxy resin modified with epoxy polyether functional silicones.

System II Series B	**EPENPL35**	**2EPENPL35**	**3EPENPL35**	**ELINEL25**	**ELINPL45**	**Control**
Properties while curing						
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	Smooth	Smooth	Fairly Smooth	Fairly Smooth, Greasy	Smooth

Table IIB film: Film properties of cycloaliphatic epoxy resin modified with epoxy polyether functional silicones.

System II Series B	EPENPL35	2EPENPL35	3EPENPL35	ELINEL25	ELINPL45	Control
1% Static CoF	0.649	0.63	0.636	0.318	0.399	0.831
20% Static CoF	0.728	0.799	1.071	0.294	0.225	0.84
1% Kinetic CoF	0.541	0.519	0.526	0.293	0.328	0.636
20% Kinetic CoF	0.593	0.669	0.881	0.192	0.183	0.588
1% Peel Force (mg/mm^2)	0.849	0.866	0.892	0.14	0.316	1.875
20% Peel Force(mg/mm^2)	0.617	0.529	0.738	0.071	0.004	1.875
1% Gloss before rubs	95.8	95.8	95.2	95.5	95.9	93.2
1% Change in Gloss (%)	-9.0	-6.9	-9.8	-6.6	-3.2	-39.9
20% Gloss before rubs	93.1	92.7	92.5	83.7	88.1	93.2
20% Change in Gloss (%)	-12.7	-12.7	-9.7	-14.6	-18.3	-39.9
Appearance	Smooth	Smooth	Smooth	Fairly Smooth	Fairly Smooth, Greasy	Smooth
1% Impact Rating	1	1	1	1	1	1
1% Pencil Hardness	4.5H	4.5H	4.5H	4.5H	4.5H	4.5H
20% Impact Rating	3	4	8	7	6	1
20% Pencil Hardness	3H	3H	3.5H	3H	2.5H	4.5H
Stain Resistance 1%/20%						
Red Lip- Stick	5/5	5/6	5/9	4/7	5/7	1/1
Green Marker	9/9	9/9	9/9	9/5	9/5	9/9
Black Marker	6/2	6/2	6/4	6/8	6/9	1/1
Black Sharpie	5/2	6/2	8/2	7/9	7/8	1/1
Red Crayon	6/1	6/1	6/1	7/5	7/9	5/1
Yellow Hi-lighter	5/5	5/6	5/8	5/7	5/8	1/1
Blue Ball Pen	4/1	4/1	4/3	5/6	4/5	1/1

Conclusions System II Series B: These epoxy silicone polyethers give smooth coating surfaces indicating they are totally compatible with the epoxy resin system used. This is confirmed by gloss reading, where there is no significant change in initial gloss for 1% silicone polyether series. The initial gloss of the 20% series is slightly reduced relative to the control.

The epoxy coating modified with 20% epoxy polyether silicones gives better impact resistance than the control. The impact resistance increases as the number of epoxy groups in the silicones increases but only to the level of the linear, di-functional materials. There is no change in impact resistance and pencil hardness for all 1% epoxy silicone polyether samples.

Stain resistance and mar resistance of silicone polyether modified epoxies is much better than the control for both 1% and 20% series. The 1% epoxy silicone polyether sample gives better mar resistance than the corresponding sample in the 20% series. This may be due to the fact that the latter is softer than the former or that there is enough slip at 1%. The reverse is true for stain resistance.

The slip of epoxy coating improves significantly with linear materials. The improvement is greater in the 20% series. There is only a minor improvement in slip for these multifunctional materials.

The peel release force of epoxy coating is significantly improved, particularly for 20% high MW linear di-functional epoxy silicone polyether materials.

Epoxy coatings modified with 20% epoxy silicone polyether material is more flexible than the control, as indicated by tan delta and impact resistance measurements. The sample with greater number of epoxy groups per silicone polyether molecule results in lower damping factor or lower tan delta. This is attributed to a higher level of cross-linking and is expected.

The curing rate of linear di-functional silicone polyether is faster than multifunctional polyether. The curing rate of silicone polyether samples increases as the number of epoxy groups in the silicone polyether increases. In general, the curing rate, hardness and shear modulus of all silicone polyether modified epoxy coatings is lower than the control.

Overall Conclusions:

- In general, 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 often better than pendant for these properties.
- Mar resistance is also seen at 1% and 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.
- Stain resistance is seen with most reactive silicones across multiple stains and is increased at higher use levels such as 20% over 1%. High molecular weight and di-functional architecture give the best stain resistance. Having some uncured silicone in the film seems to increase stain resistance.
- Impact resistance and moduli indicate the increased flexibility of the systems with silicone reacted into the film. Higher use levels are needed here for significant changes with 1% showing little or no effect.
- In both systems, the incorporation of polyalkyleneoxide into the reactive silicones increases compatibility and degree of curing. More than 60% can be used in one case. This is the recommended path to incorporate silicones into the film. Without exception materials without polyether showed signs of incomplete cure or incomplete incorporation of the silicone into the matrix. Several properties such as stain resistance and CoF were significantly impacted by this free silicone.
- Curing rates are slowed with reactive silicones as compared to the controls.
- The high levels of silicone incorporation tend to make the coating softer and more rubbery.
- Flow and spreading of the coating is improved significantly with reactive silicones, apparently mainly due to reduction in viscosity.

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