

Reactive Silicones as Crosslinkers in UV-Cured Systems

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UV reactive silicones are combined with commercially available organic resins that have the same reactive groups and are cured into films. The effect of using these silicone/organic hybrids instead of the pure organic resin is evaluated by measuring properties such as appearance, gloss, slip, flexibility, stain release, mar resistance, cure time and impact resistance.

This work is a continuation of earlier work¹ in which we screened a variety of acrylate and epoxy-functional silicones in UV and other cured systems, and saw increased impact resistance and stain resistance as a function of crosslinking. This effort looks at UV-cured examples and the consequence of using multifunctional reactive silicones to provide crosslinking in UV-cured systems.

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 substantial money fine-tuning and expanding the properties of their core chemistry to vary their utility.²⁻⁷

One way to alter the fundamental properties of a polymer is to react it with a different polymer, thereby generating an AB-type copolymer or hybrid. With low-surface energy, ultra low T_g , and strong slip, release and flow properties, polydimethylsiloxane (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. Our company offers a portfolio of modified silicones with any of the reactive groups used in coatings. The reactive sites are made from the same raw materials as the native resin polymers.

However, 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 or other techniques to make these materials miscible.

In the previous study,¹ we showed that polyether modification of the silicones is usually necessary for miscibility and complete incorporation of the silicone into the film. In this study, we look only at these soluble species.

This paper details the modification of coatings films *in situ* with reactive silicones and examines 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 other cured systems as well.

Experimental and Methodology

The experimental design used radiation-cured systems. 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:

- 15-watt bench UV lamp with 10 mW/cm² of UV full (230nm-410nm); exposure time from 30 minutes to one hour for heat-sensitive Leneta panels.
- Rheometer LED-UV Lamp with 132 mW/cm² of UV full; exposure time from 30 seconds to five minutes for rheological measurements.
- PC 100S spot lamp with 140 mW/cm² of UV full; exposure time from 30 seconds to five minutes for hardness measurements of small button samples.
- High-pressure mercury vapor lamp with 0.98W/cm² of UV full; exposure time from one second to five seconds for metal panels.

A nitrogen blanket is used for curing acrylate coatings that contain a free-radical photoinitiator.

Test Panel Preparation

All tested panels were prepared by drawing down approximately 1 ml of the above formulation on a 4" x 6.5" (10 x 16.5 cm) white Leneta paper with wire-wound rod #10. The wet film is cured under a UV bench lamp for one hour with a nitrogen blanket.

Coefficient of Friction (CoF/Slip)

Slip was measured with ChemInstruments CoF 500. (Test speed—15 cm/min; travel length—15 cm; sled weight—200 grams and sled surface which was covered

with ASTM-specified rubber). Static CoF was 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 CoF was 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 was for the substrate. The slip rating was 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 was the best and 0 was the worst).

Gloss

Gloss was measured with BYK-Gardner 60° microgloss gloss meter. The value was directly recorded from the microgloss gloss meter (0 was the lowest and 100 was the highest).

Peel Force Measurements

A 5 x 30 cm piece of Intertape 6100 clear packing tape was used. Half of the length of the tape was applied on the coated panel at a 45-degree angle with a wooden applicator. Care was taken to ensure good contact between the tape and the substrate. One end of a stainless steel string was attached to the transducer and the other end was fastened onto the remaining half of the tape with a 5 cm length of standard cellophane tape. Peel force was measured by peeling the tape with ChemInstruments 500 at an angle of 180° and peel rate of 60 cm/min. We recorded and reported an average of 10 tests as the peel force in grams/cm².

Mar Resistance

Mar resistance was measured using a Sutherland 2000 Ink Rub Tester via

a dry rub method with the following settings—500 rubs and 84 rpm stroke speed for all sample sets. Rubbings were done using a 4 lb. test block which was attached with a 2" x 4" (5 x 10 cm) nylon scrubbing pad. Gloss was measured immediately after completion of rubbing for each panel. The mar resistance rating was 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 was the best and indicated no visible effect.

Stain Resistance

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

Impact Resistance

The panel to be tested was placed coated side down on the top of a protective paper which sat on a flat steel plate with a rubber pad on the bottom. A steel rod with a 1 cm diameter round steel ball attached at the end of the rod was placed on the backside of the coating surface. A 700 gram weight with a 1.5 cm hole through the middle fit onto the steel

TABLE 1

Series of basic UV-cured coatings prepared with organic resin and reactive silicone A in various blend ratios

Silicone A	0%	10%	20%	30%	40%	50%	60%	70%	80%
Organic Acrylate Resin	80%	70%	60%	50%	40%	30%	20%	10%	0%
Viscosity (cPs)	8,059	4,361	2,256	1,157	569	284	152	94.9	94.7
Tensile (kPa)	8,335.3	7,300 (calc.)	6,900 (calc.)	6,674.7	3,434.8	1,465.4	978.3	347.2	197.2
Elongation (%)	0.04	0.13	0.14	2.65	5.44	5.61	6.18	5.37	5.01
Total Energy (mJ)	3.26	3.41	5 (calc.)	33.6	27.9	19.9	17.2	9.9	2.8
Shore D Hardness	85	70	66	57	40	20	6	2	1
Thickness	1.28	1.58	1.8	1.44	1.67	2.09	1.37	1.99	1.51
Total Energy/Thickness	2.54	2.16	0.21	23.34	16.71	9.50	12.55	4.96	1.82
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	0.101	0.097	0.044	0.010	0.008
Film Appearance/ Properties	very brittle	very brittle	slightly flexible	more flexible	more flexible	flexible	flexible	no integrity	
Impact Resistance	0	2	4	7	8	5	5	not measured	

rod dropped down freely and vertically along the rod from a distance of 23 cm above the coating surface. The impact resistance was estimated by visual inspection of the size and pattern of the damage. The subjective ratings were obtained by visual comparison of impact damage on the panels for each series from 1 to 10 where 10 was best and indicated no cracking or breaking of the film.

Test Results

A series of basic UV-cured coatings were prepared with a standard organic acrylate resin and reactive Silicone A in various blend ratios. The formulation was 80% total resins, 13% standard amine synergist, 5% benzophenone type photoinitiators, 1.5% α -hydroxy ketone type photoinitiator and 0.5% reactive defoamer (Table 1). The coatings were miscible and cured to completion.

Silicone A is an acrylate functional, reactive silicone which is small with an average of two reactive groups and modified with polyethyleneoxide for solubility.

Modification of this UV-curable acrylate resin with this silicone improves flexibility, impact resistance and toughness of the UV-coating film. The highest use levels of silicone resulted in film that had lost integrity. Increasing the level of silicone in the film decreases tensile strength at break, increases elongation at break, decreases hardness and decreases storage modulus.

Flexibility and elongation properties maximized at 40-60% incorporation of silicone in organic. The tensile strength, storage modulus and hardness have linear relationships with percentage of silicone.

We previously saw¹ similar results in a different acrylate-cured resin system.

In another study, a series of cycloaliphatic epoxy-functional silicones were evaluated at 1% use level with a basic formulation of 89% UV-A cure 1,500 resin, 9% CAPA 1301 multifunctional polyol and 1% UV 9380 photoinitiator. These were repeated at 20% use level with 72% resin, 7% polyol and 1% photoinitiator. The structural information on these silicones is shown in Table 2. Table 3 shows curing and film properties of cycloaliphatic epoxy resin modified with epoxy polyether functional silicones.

The materials in Table 3 all reacted into the film as evidenced by the change in properties while retaining appearance and gloss. There was no significant change in initial gloss for the 1% silicone polyether series. The initial gloss of the 20% series was only slightly reduced relative to the control.

The effect of use level could be clearly seen in this series. That

TABLE 2

Structural information of epoxy silicones

	Silicone B	Silicone C	Silicone D	Silicone E	Silicone F
Silicone (type/chain length)	Pendant medium chain length			Linear, medium	Linear, large
Polyether (type/chain length)	EO/PO large			EO large	EO/PO large
# epoxy sites	1	2	3	2	2
Log MW of Silicone	3.93	3.87	3.80	3.42	3.72
Viscosity of silicone (cps)	798	1,000	1,010	255	1,205

TABLE 3

Curing and film properties of cycloaliphatic epoxy resin modified with epoxy polyether functional silicones

	Silicone B	Silicone C	Silicone D	Silicone E	Silicone F	Control
tan(delta) (20%)	0.66	0.51	0.28	0.34	0.31	0.68
IG*1 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
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
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 Lipstick	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

TABLE 4

Concentration effect of Silicone B

Silicone B	0%	10%	20%	30%	40%	50%
Tensile (kPa)	Too brittle		44,298	31,905	15,628	7,294
Elongation (%)	0.45	0.77	1.78	5.16	19.38	33.52
Total Energy (mJ)	15.09	16.02	97.48	315.33	409.15	426.44
Thickness	1.81	0.68	0.81	1.28	1.03	1.74
Total Energy/Thickness	8.337	23.559	120.346	246.352	397.233	245.081
Viscosity 10/sec	141.41	169.497	197.584	225.671	253.758	281.845
G' (MPa)	5.20	5.20	2.15	0.45	0.05	0.01
G'' (MPa)	1.36	1.06	1.32	0.35	0.05	0.01
tan(delta)	0.26	0.20	0.62	0.78	0.96	0.91
Appearance	hard, brittle	hard, brittle	brittle	hard, less brittle	flexible	more flexible
Shore D Hardness	84	80	78	71	67	44
Impact Resistance	0	2	4	7	8	8

higher use levels affect flexibility was easiest to see in the impact-resistance numbers. In fact, there was little or no change in impact resistance at 1%, but a large influence at 20%. We could see a weak trend of improved stain resistance at the higher use levels.

Slip properties such as COF and mar resistance do not benefit dramatically from higher use levels. Often 1% gives most of the benefit of these properties. What does seem to be very important for slip properties is the type of silicone. The slip improved significantly with the linear silicones with more improvement in the 20% series, but there was only a minor improvement in slip over the control for the pendant multifunctional materials.

The peel-release force was significantly improved at higher use levels. This could be easily seen for 20% high MW linear difunctional epoxy silicone polyether materials Silicone E and Silicone F.

The increase in crosslink density did affect impact resistance, which increased slightly as the number

of epoxy groups in the silicones increased, finally equaling that of the linear, difunctional materials.

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

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

To further demonstrate the relationship between use level and properties, epoxy Silicone B was evaluated at multiple use levels in a

very basic system; 99% a standard cycloaliphatic epoxy resin/Silicone B blend with 1% iodonium salt type photoinitiator. Results are shown in Table 4.

In this very basic system, increasing the reactive silicone improves toughness; increases elongation and impact resistance; and decreases tensile strength, hardness and storage modulus. Toughness as indicated by total energy to break maximizes at 40% silicone.

Conclusions

In general, reactive silicones improved release, slip and CoF at 1% incorporation. In most cases, these properties continued to improve somewhat with more silicone. Linear difunctional materials were often better than pendant for these properties.

Mar resistance was also seen at 1% and was not improved at higher levels.

Stain resistance was seen with most reactive silicones across multiple stains and was increased at higher use levels such as 20% over 1%. High molecular

weight and difunctional architecture gave the best stain resistance.

Impact resistance and moduli indicated the increased flexibility of the systems with silicone reacted into the film. Higher use levels were needed here for significant changes with 1% showing little or no effect. ▶

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