

Polymer Modification with Reactive Silicones

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Overview

Resins used in coatings, composites and other specialty thermoset systems can generically be thought of as a base polymer and reactive groups. Although we commonly name the resin by the type of reactive group, for example an epoxy resin, many of the final properties come from the base polymer itself. Sticking with the epoxy resin example; aliphatic epoxy, aromatic epoxy, urethane epoxy, and acrylic epoxy resins are all commonly available. While the epoxy reactive group gives much of the strength, adhesion and toughness; the backbone is responsible for UV degradation and gloss in the aromatic epoxies, oil solubility and UV stability in the aliphatic epoxies, flexibility in the urethane epoxies, and water solubility in the acrylic epoxies.

The same point can be made of other reactive group named resins such as amine, isocyanate, hydroxyl, acrylate ester, carboxylate, etc. Some properties result from the connectivity and some from the base polymer or backbone.

At Siltech, our forte is silicone so the resins which we develop use silicone as the base polymer. The reactive groups are appended on the ends of the silicone polymer, giving an extender; on the middle segments of the polymer, giving a cross linker; or both. We have attached each of the commonly used reactive groups onto the silicone and have conducted laboratory work to show how the silicone backbone affects the final properties of a cured system. There is a great deal of commonality to the properties when reactive silicones are used.

As homopolymers, silicones are generally soft, flexible, tough, water resistant, non-conductive to both heat and electrical potentials and offer extraordinary elongation values. Elongation is routinely up to 300% for cross-linked, all silicone systems. Hybrid systems with co-reacted silicone and organic backbone resins are usually 50-100% elongation.

Hybrid systems, where organic backbones and silicone backbones with the same or complementary reactive groups cure, usually show a compromise of the properties brought by the two based polymers. In this manner, aliphatic epoxy resins which can be brittle and non-flexible, can be made to withstand low temperature impacts and other shear forces by co-polymerizing with a reactive silicone.

These hybrid systems are the primary topic of this white paper.

Reactive Groups

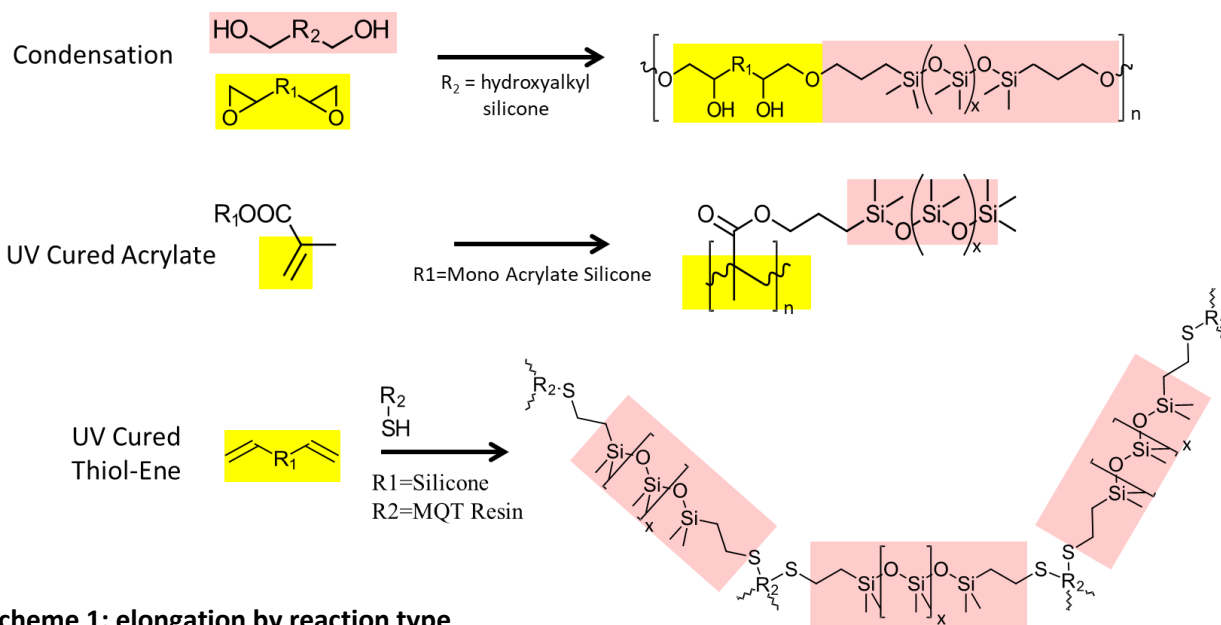
Reactive moieties available for epoxy reactions are glycidyl and cycloaliphatic epoxy groups. Also, in the case of epoxy resins, hydroxyls will readily react into this system and amino functional siloxanes can even be substituted for the amine functional epoxy hardeners. Siltech has Silmer[®] NH materials which are primary amine functional and which work well for this use. More commonly available are aminoethylaminopropyl substituted silicones which have both a secondary and primary amine on the side chain. It is difficult to cleanly react one in the presence of the other so the Silmer NH approach

gives a much cleaner reaction. Having said that, the aminoethylaminopropyl silicones do give interesting results in many cases.

For polyurethane systems, the viable reactive species available are Silmer OH primary hydroxyl, Silsurf® hydroxyl functional polyether silicones, and Silmer NCO isocyanate functional silicones. The NCO polymer is important because isocyanate functional prepolymers which are available on the market are often made with an excess of the hydroxyl component to leave the more stable OH groups on the ends of the prepolymer. If one wants to further react this, an isocyanate group is needed.

For polyesters, hydroxyl functional and carboxylic acid modified silicones are used. Polyimides can be modified with the aforementioned Silmer NH products.

For acrylate ester (often called vinyl ester) reactive groups, a large variety of acrylate functional silicones are available. The commercial use of these in UV cured overprint varnishes and paper release products has fostered the development of many variations. Siltech offers Silmer ACR products and Silmer OH ACR products. Both have the acrylate ester group for UV initiated free-radical polymerization, but the latter type also offers an hydroxyl group for secondary cure. Both of these product types can easily be co-reacted with organic backbone based acrylate resins for modified properties.



Scheme 1: elongation by reaction type

This UV cured acrylate system is the exception to the ultra-high elongation expected with silicone polymers. In these systems, typical elongations are under 25%. We believe this is because the main polymer is built incorporating the silicone chains as side-chains instead of in the main polymer chain. See Scheme 1.

We have recently demonstrated the use of Silmer SH thiol functional silicones with multiple reactive sites in a UV initiated thiol-ene reaction which provides elongation up to 200%. The thiol-ene reaction adds across the double bond instead of initiating a polymerization cross-linking is provided by the highly functionalized silicone base polymer. We have also used very highly functionalized Silmer SH Q type silicon resins in this reaction.

Free-radical formed polymers like acrylic and polyolefin resins are formed and laid down on a surface by coalescence, and so do not react with the silicone at the end use. The properties of these non-reactive systems can be altered during the resin manufacture with acrylate or vinyl functional silicones.

Alternatively, our Silmer TMS trialkoxysilane modified silicone can react with the reactive sites on the base polymer during coalescence altering some properties of the final matrix.

This group of silicone polymers with trialkoxy silane groups appended to the silicones behave like silane cross linkers. As monomers, alkoxy silanes are well known and often used to provide improved macro-adhesion, cross-link density and adhesion to molecular surfaces. We see all of those properties with this trialkoxy silane functional silicones in addition to improved flexibility and hydrophobicity.

Besides the Silmer TMS chemistry, we have some other atypical resin cross linkers. Another group has multiple hydroxyl groups on the same side chains. These Silmer OHT resins are surprisingly effective at imparting stain resistance, macro-surface adhesion properties to hybrid systems often out performing our fluorosilicone products.

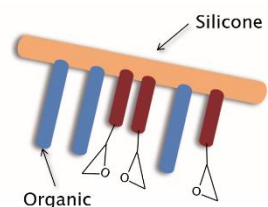
With all-silicone systems, a unique reaction can be used. Silicon-hydride functional silicones are reacted with vinyl silicones using a trace of Platinum catalyst to cause addition of the silicon groups across the double bond. This hydrosilation is the basis for many LSR or silicone adhesives. While the reaction of the SiH functional silicones with organic double bonds does work, there has not been much work with curing hybrid resin systems in that manner.

Solubility Modifiers are Very Desirable

Early in the work we've done with reactive silicones we experimented with simple reactive silicones. Due to the lack of miscibility of the silicone backbone with organic backbones, it can be difficult to react these materials. Either very high shear conditions must be used or silicone/ organic emulsifiers can be used to compatibilize the two disparate polymers.

Another approach is to modify the silicone backbone with reactive groups AND organic groups to provide reactivity as well as solubility in the resin.

The cartoon in scheme 2 shows this concept in the example of epoxy silicones. The organic chains (blue) provide miscibility with the organic backbone resins while the epoxy groups (maroon) are available for the polymerization reaction.



Scheme 2: compatibilized reactive silicone

The problem and solution are indicated by the following examples in which we reacted silicones modified with acrylate moieties. See Figure 1. Some of the Silmer ACR products are also reacted with polyether chains for solubility and others are not. This UV cured system and the Silmer ACR structural variations tested are shown below as well. The silicone is either linear di-functional or pendant multifunctional. These is an organic modifier on two and not on the others.

<i>Ingredient</i>	<i>Wt %</i>	<i>Silmer</i>	<i>Silicone</i>	<i>Organic Modification</i>
<i>Various Silmer ACR Reactive Silicones</i>	22	<i>ACR Di-10</i>	Linear, small	None
<i>Epoxy Acrylate Resin CN104C75</i>	40	<i>ACR Di-50</i>	Linear, medium	None
<i>Synergist CN386</i>	15	<i>ACR Di-100</i>	Linear, large	None
<i>Photoinitiator Escacure TZT</i>	5	<i>ACR D208</i>	Pendant, small	EO small
<i>Photoinitiator Darocur 1173</i>	1.5	<i>ACR E608</i>	Pendant, medium	EO Small
<i>Silmer ACR D2 (Defoamer)</i>	0.5	<i>ACR D2</i>	Pendant, small	None
<i>Reactive diluent SR 355 DTPTA</i>	10	Above: Silmer ACR Structures		
<i>Reactive diluent SR 306 TRPGDA</i>	6			

The results are shown below.

	<i>Control</i>	<i>Di-10</i>	<i>Di-50</i>	<i>Di-100</i>	<i>D208</i>	<i>E608</i>	<i>ACR D2</i>
<i>G' (MPa)</i>	20.1	8.3	18.5	11.91	9.71	11.64	20.06
<i>G'' (MPa/10)</i>	1.56	0.71	3.19	1.88	0.82	0.91	1.42
<i>tan(delta)/(/100)</i>	7.93	8.71	17.3	15.82	8.58	7.86	7.25
<i>Cure & Appearance</i>	Cured	Oily	Oily, Defects	Oily	Cured	Cured	Tacky

Figure 1: non-compatible results.

The four materials without organic modification all show oily uncured silicone, defects, tackiness and high tan(delta) values which indicate incomplete cure. The acrylate groups on the immiscible silicone are not available to react with the groups on the organic resins. This phenomenon is also expressed in very low COF values and excellent release properties of the samples when this uncured silicone blooms to the surface. The Silmer ACR D208 and Silmer ACR E608, with organic groups, show complete reaction and incorporation into the matrix.

Typical Properties Expected.

In this example of a hybrid organic/silicone epoxy resins system, we reacted an organic cycloaliphatic epoxy with a cycloaliphatic epoxy modified silicone. The silicone used is Silmer EPC F418-F, which is also modified with a EO/PO polyether chains for miscibility. A silicone concentration ladder study of this reaction is conducted from 0-50% in units of 10%. The materials are cured at 110°C for 4 hours and, in the last column, another set of similar formulations is UV cured at 365 nm. See Figure 2.

<i>Ingredient</i>	<i>Name</i>	<i>Wt% (heat)</i>	<i>Wt% (UV)</i>
<i>Organic Cycloaliphatic Epoxy Resin</i>	UVACURE 1500 Epoxy Resin	42-16	99-49
<i>Anhydride Curative</i>	MHHPA	58-24	na
<i>Cycloaliphatic Epoxy Polyether Silicone</i>	Silmer EPC F418-F	0-60	0-50
<i>Catalyst</i>	AMI-1	0.06-0.1	na
<i>Photoinitiator</i>	UV9380C	na	1

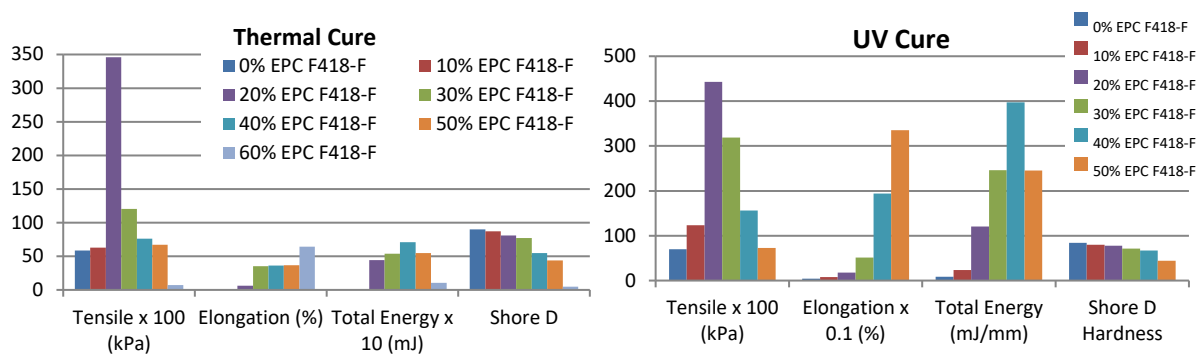


Figure 2: epoxy/silicone hybrids by thermal and UV cure.

Mechanical properties show a reduction in Shore D hardness which exhibits a dose response that slopes slowly at lower concentrations. Elongation increases directly with higher concentrations of silicone. Interestingly, tensile strength and total energy to break show a maximum peak. This peak is very strong in tensile strength. We believe this is the result of two opposing trends, flexibility and softness. At lower concentrations the material is still hard but more flexible resulting in strength and toughness. At higher concentrations the material becomes too soft. The same two materials were also reacted, with different promoters, under UV excitation. A similar trend was seen in properties. Shown on the right in the figure above.

In the next experiment, a different standard aryl epoxy was reacted with Silmer EP D208, a different epoxy functional silicone, at 110°C for 4 hours using the formula and showing the results in Figure 3.

The mechanical properties are reported in the graphs below. As more of the silicone is used in the formulation, hardness is reduced. The slope of the curve of the reduction in hardness is nearly flat until about 20% incorporation, where about 10% of the hardness is lost, and then drops off quickly with more silicone.

Similarly, viscosity of the formulation is reduced in a nearly linear relationship. Tensile strength is reduced but elongation increases to about 100% at 40% incorporation of the silicone resin. We do not see the peak in tensile strength which we have seen in so many systems, this is perhaps because we did not do concentrations between 0 and 20% silicone.

<i>Ingredient</i>	<i>Name</i>	<i>Wt%</i>
Organic Epoxy Resin	D.E.R. 671-X75	53%-32%
Anhydride Curative	MHHPA	23%-17%
Glycidyl Epoxy Polyether Silicone	Silmer EP D208	25%-50%
Cycloaliphatic Epoxy Silicone (defoamer)	Silmer EPC D2	0.15%-0.2%
Catalyst	AMI-1	0.06%-0.1%

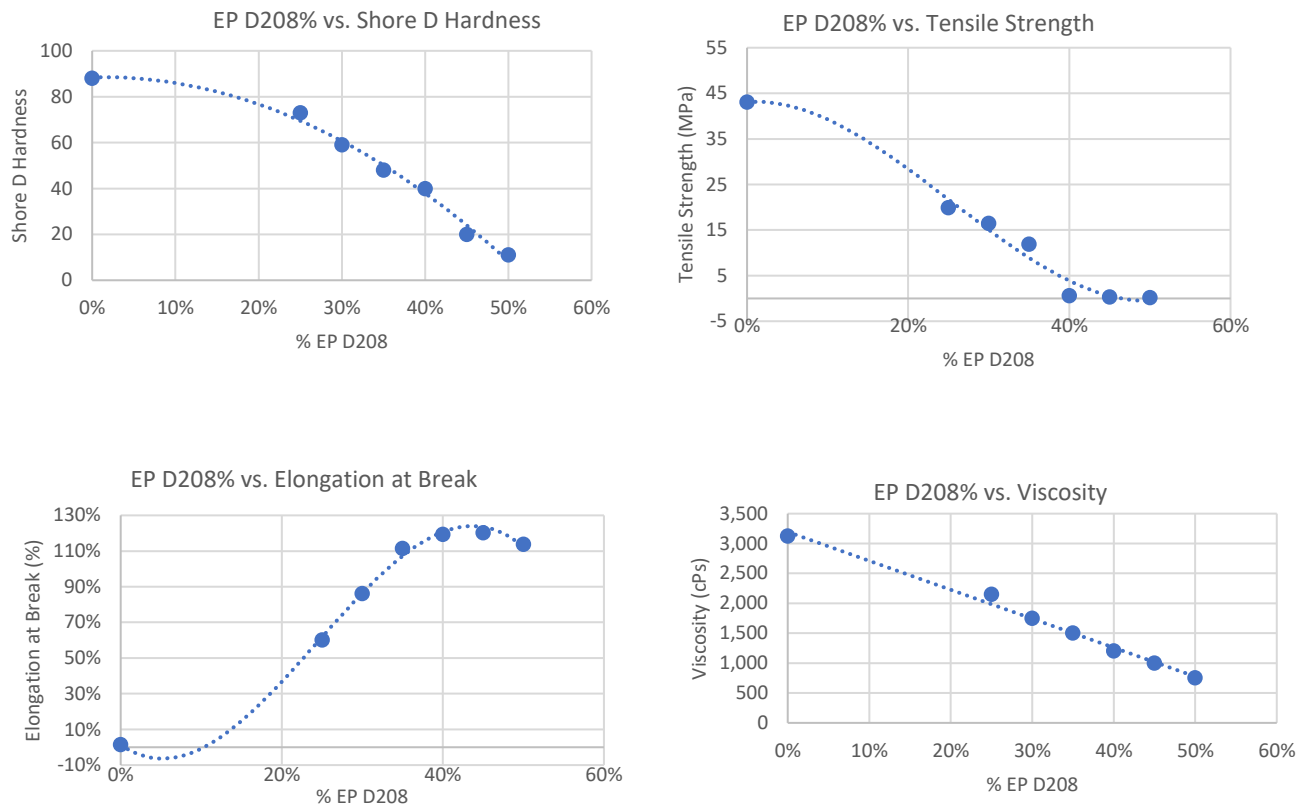


Figure 3: Silmer D208 with D.E.R. 671-X75

A different aryl epoxy resin, D.E.R. 331, which is harder and faster curing than the first example is also reacted with the same epoxy silicone, Silmer EP D208.

<i>Ingredient</i>	<i>Name</i>	<i>Wt%</i>
Organic Epoxy Resin	D.E.R. 331	37%-25%
Anhydride Curative	MHHPA	37%-25%
Glycidyl Epoxy Polyether Silicone	Silmer EP D208	25%-50%
Cycloaliphatic Epoxy Silicone (defoamer)	Silmer EPC D2	0.15%-0.2%
Catalyst	AMI-1	0.06%-0.1%

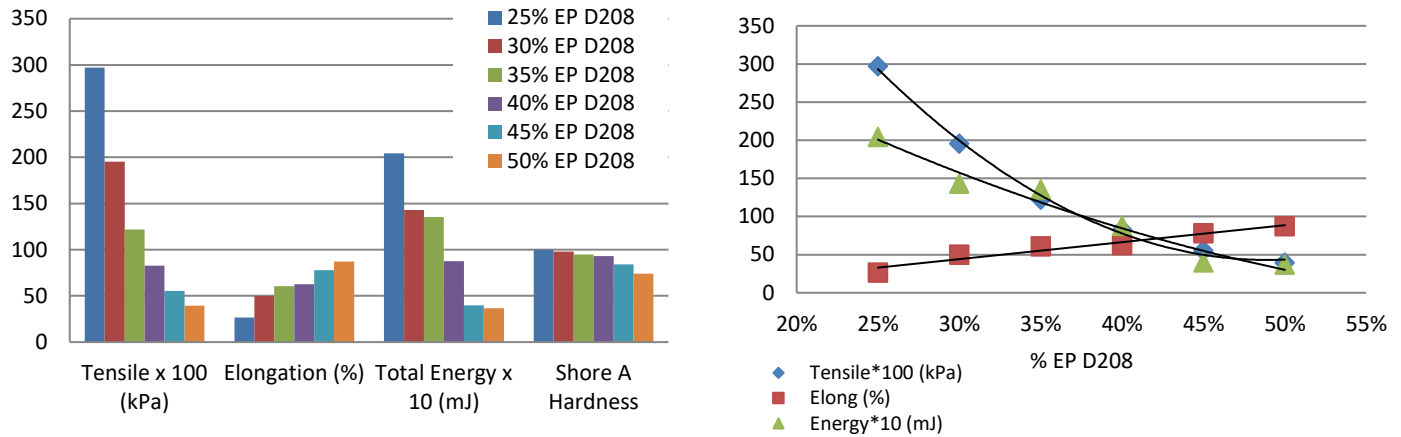


Figure 4: Tensile Properties of D.E.R. 331 epoxy anhydride system with varying Silmer EP D208 levels.

Interestingly, due to the complex mechanism of epoxy/ anhydride cured systems, we are able to react a silicone with only hydroxyls instead of epoxy reactive groups. The Silsurf D208 is similar to the Silmer EP D208 but without epoxy groups. Again, this was cured at 100°C for 4 hours. See Figure 5.

Ingredient	Name	Wt %
Organic Epoxy Resin	D.E.R. 331	37%-25%
Anhydride Curative	MHHPA	37.5%-25%
-OH Polyether Silicone	Silsurf D208	25%-50%
Catalyst	AMI-1	0.06%-0.1%

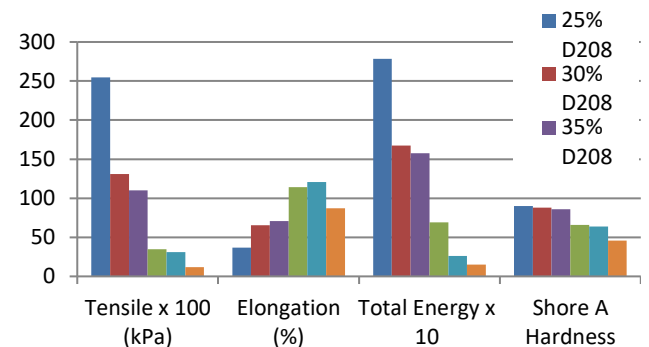


Figure 5: hydroxyl only functional silicone with epoxy resin

We have been able to substitute silicone amines in place of amine hardeners in epoxy systems with success. In this customer proprietary formulation, we replace 20% of his amine hardener in a tough epoxy garage floor coating with these flexible hardeners. In separate experiments, we also replaced some of the resin with OH functional silicones. The amine approach was as effective, if not more effective at improving low temperature impact resistance.

Measured after 1 week of ambient cure, a steel ball bearing was dropped from a set height on pre-cooled molded resin. Most fractured on 1 drop but some needed a second drop to fracture. The severity of the fracture pattern was rated 0-10 where 10 is no fracture. Figures 6-9.

Additive	Wt %	Shore A	Tear (N/mm)	Tensile (kPa)	Elongation (%)	- 15° C 0-10(best)	- 30° C 0-10(best)
Control	0	37	3.2	500	171	5	6*
Silamine D2 EDA	5%	45	3.6	636	114	8	7*
Silamine D2 EDA	10%	49	4.0	943	68	9.5	9*
Silamine D208 EDA	5%	27	2.1	299	191	5	5.5
Silamine D208 EDA	10%	25	1.8	261	164	4.5	2.5
Silmer NH Di-8	5%	31	2.7	354	176	4.5	3

Silmer NH Di-8	10%	43	3.7	543	98	9.5	8*
Silmer OH C50	10%	35	2.6	353	176	6	5
Silmer OH Di 50	10%	30	2.6	430	202	3	4
Silmer OH D2	10%	32	2.2	291	162	4	8.5*
*Indicates two drops were needed to fracture							

Figure 6. comparison of amine and hydroxyl silicones in epoxy system

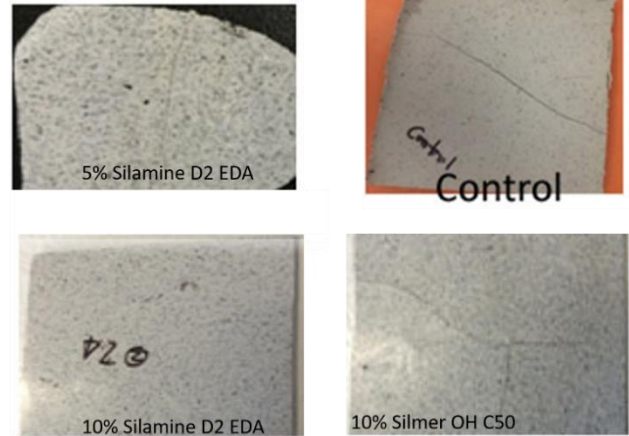
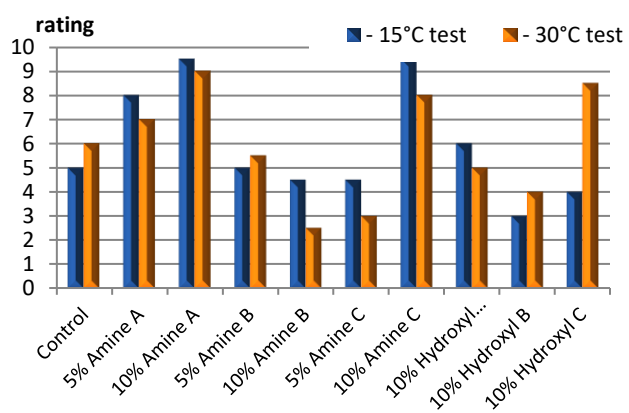
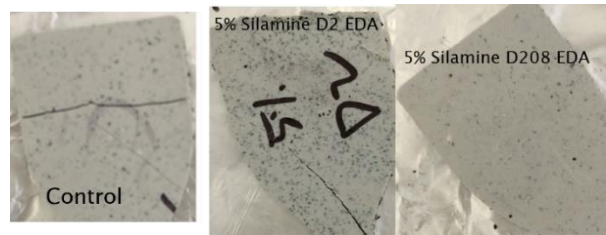


Figure 7 above: impact resistance data

Figure 8 above: -15°C fracture pattern examples

Figure 9 right: -30°C fracture pattern examples



Homopolymers of Silicones

One can of course, cure the silicone resins without organic hybrids. The resultant resins are typically soft and often tacky with large elongation values. In the below cycloaliphatic epoxy system, we cured the linear di-functional epoxy silicone Silmer EPC-Di-10 with multifunctional Silmer EPC G36 in varying ratios. The system was catalyzed with 0.9 moles of MHPA and 0.1% AMI-1 and cured at 110°C for 8-16 hours.

In Figure 10 we see the mechanical properties as a function of Silmer EPC Di-10 (chain extender) content. Tensile strength, and hardness are increased with more of the extender molecule while elongation and storage modulus are diminished.

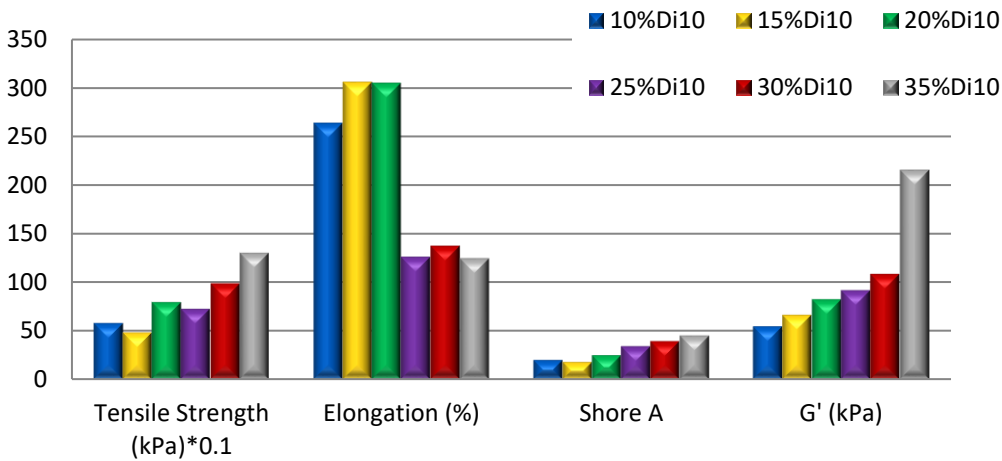


Figure 10: homopolymer of epoxy silicone.

Beyond Epoxy Resins

Epoxy resins are ubiquitous so much of our work over the years has been done with them. But we have done similar work on other resin systems. For example, another system we have done a lot of experimentation with is UV cured acrylated silicones. An aliphatic epoxy based acrylate functional resin is cured at 365 nm with an acrylate functional polyether silicone, Silmer ACR D208. See Figure 11.

Ingredient	Name	Wt%
Acrylated organic resin	CN 104C75	0% to 80%
Organic miscible acrylated silicone	Silmer ACR D208	80% to 0%
Catalyst	Esacure TZT	5%
Coinitiator	Sartomer CN 386	13%
Catalyst	Irgacure 184	1.5%
Acrylated silicone	Silmer ACR D2	0.5%

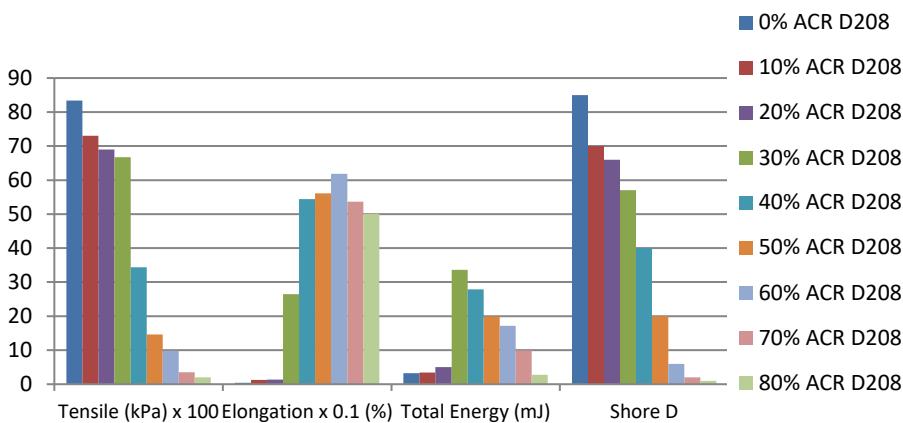


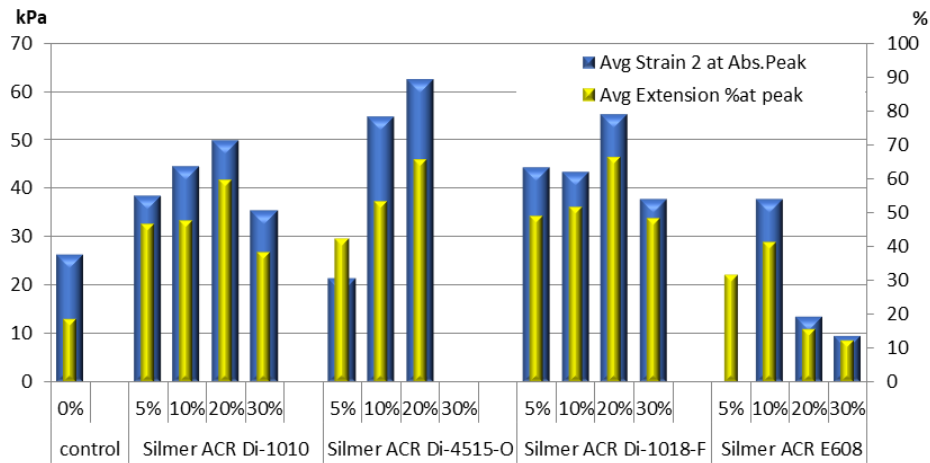
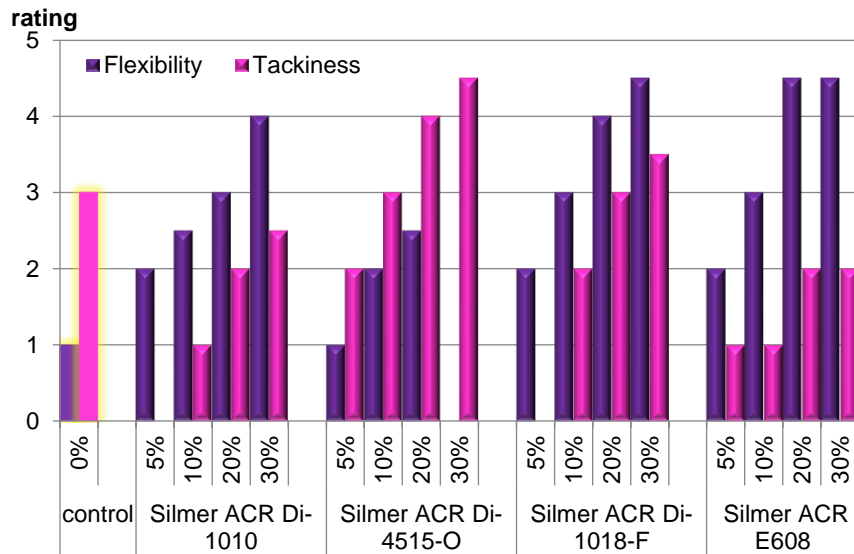
Figure 11: UV cured acrylate hybrid resin

The mechanical properties show a similar trend to what we have seen. In this case, where we have put in very high levels of silicone (up to 80%) we see a spike for elongation and total energy to break but no spike in tensile strength. We believe the material is so soft that is dominating the test results.

The hybrid UV cured acrylate formulation was also an early development effort for us for 3D printing. Various Silmer ACR structures are evaluated in a ladder study of 5%, 10%, 20%, and 30% in a formulation of three organic based acrylate resins. These were cured at 365 nM in an SLA printer. See Figure 12.

<i>Ingredient</i>	5%	10%	20%	30%	<i>Silmer ACR</i>	<i>Type</i>	<i>Eq. Wt.</i>
Sartomer CN 991	8.4%	8%	7.1%	6.6%	Di-1010	Di-functional	650
Laromer UA-9072	47.1%	44.6%	39.6%	34.6%	Di-1018-F	Di-functional	1000
Laromer LR-8887	34.4%	32.6%	28.9%	25.3%	Di-4515-O	Di-functional	2500
Sartomer SR833S	3.9%	3.7%	3.3%	2.9%	E608	Multi-Functional	600
Silicone ACR xxx	5.0%	10.0%	20.1%	30.1%			
TPO	1.0%	1.0%	0.9%	0.8%			
Silmer ACR Di-10*	0.17%	0.17%	0.15%	0.13%			

*reactive defoamer



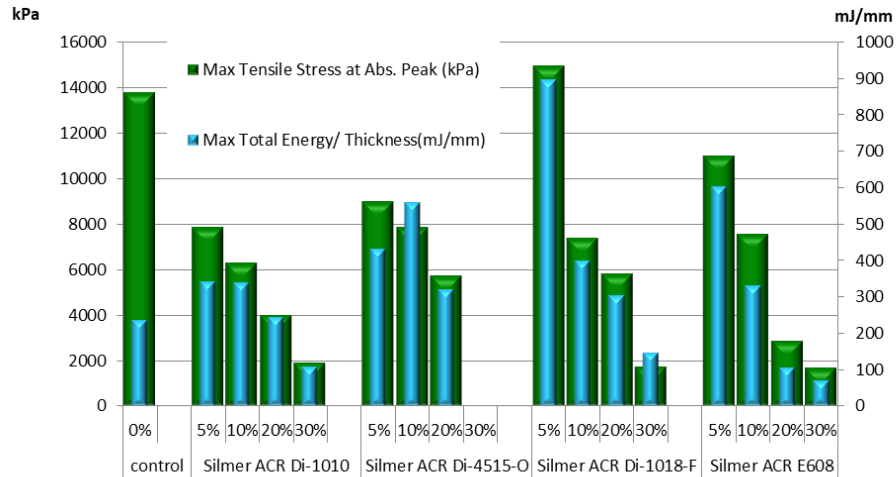


Figure 12:

Some properties of the hybrid resins are shown. Flexibility and extension are increased and show a dose response, although at 30% incorporation of silicone that starts to drop off. Toughness follows a similar pattern as indicated by strain. Total energy to break and maximum stress measurements show an increase at 5% and then a drop off.

Urethanes

Silicone modification of urethane resins can be accomplished with either OH functional reactive silicones such as Silmer OH or the multifunctional Silmer OHT product families or with isocyanate functional Silmer NCO species.

Below is a basic example wherein linear di-hydroxyl silicones are reacted with a Desmodur W, dicyclohexylmethane diisocyanate, to form a urethane with alternating silicone and cyclohexyl blocks. The series of urethanes made with Silmer OH Di-50 to Silmer OH Di-400 represent increasing silicone chain length. White cotton and red bolt fabrics are treated with a 1% solution and evaluated with several criteria for water resistance. The criteria are used to assign a rating from 0-10 (best). These are compared to the untreated control and an all silicone urethane made from Silmer OH C50 and Silmer NCO Di-50. The organic hybrid materials are much better than the control and nearly as effective as the all silicone urethane. See figure 13.

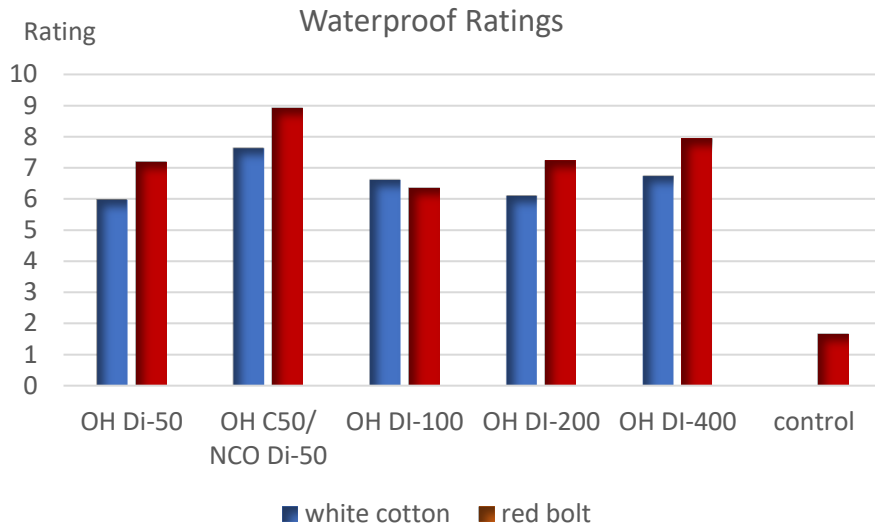


Figure 13: simple hybrid urethane waterproofing results.

Low use levels

In a more fully formulated urethane system, a series of hydroxyl functional silicones were reacted with a 2 part WB/PU system and evaluated for stain resistance. As we were looking to change the surface properties rather than the mechanical properties, a small use level of 2% silicone was evaluated. We did not run tests to confirm that reaction occurred, but assume that it has. The results across a wide variety of different staining materials was used to generate a rating 1-10 (best). These ratings are shown in Figure 14 compared to no additive, a commercial competitive additive and our own fluorosilicone polymers.

In general, the more highly functionalized Silmer OHT products show better stain resistance and many of the hydroxyl silicone materials outperformed the fluorine containing Fluorosil products.

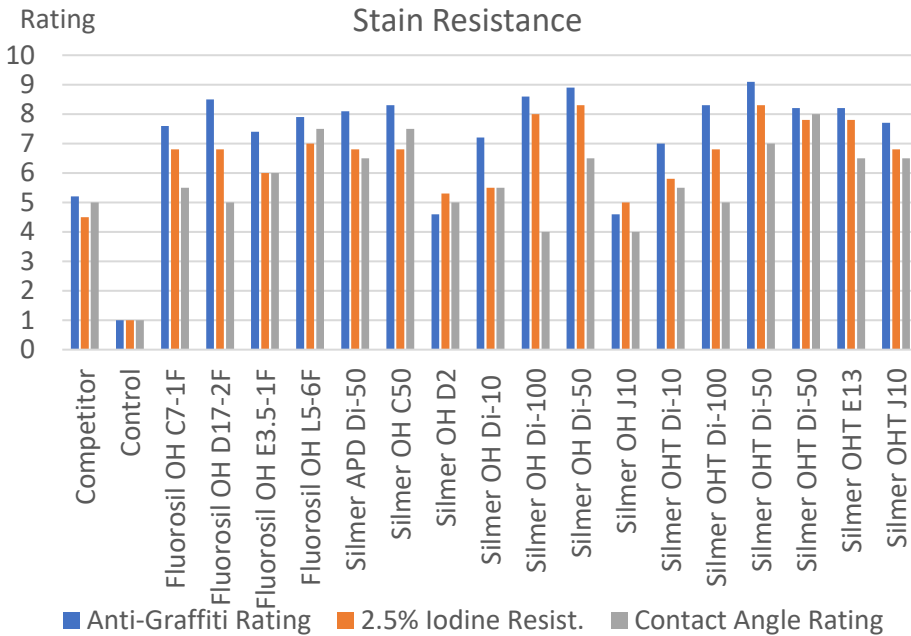


Figure 14: surface effects with low incorporation in a urethane system

Silane and Isocyanate Silicones

We have done work in a UV cured system in which we demonstrated a secondary condensation cure after the UV initiated free radical reaction. For this we use Silmer TMS Di-10 or Silmer TMS Di-50 trialkoxy silane modified silicones or Silmer NCO Di-10 or Silmer NCO Di-50 isocyanate functional silicones. The formulations were UV cured and then left on a benchtop at ambient for 7 days to ensure complete condensation cure. The improvement in pencil hardness storage moduli show increased cross-linking has occurred. See Figure 15.

Ingredient	Amount (when x=50)	Purpose
<i>Silmer OH ACR Di-50</i>	47.50%	Energy Cure
<i>TMS or NCO type</i>	47.50%	Secondary Cure
<i>DBTDL</i>	0.25%	Condensation Catalyst
<i>Darocur 1173</i>	4.75%	Photoinitiator

Property	<i>Silmer TMS Di-10</i>	<i>Silmer TMS Di-50</i>	<i>Silmer NCO Di-10</i>	<i>Silmer NCO Di-50</i>
<i>G' (Pa) first cure</i>	6.51*10 ⁵	9.08*10 ⁴	6.33*10 ⁵	2.58*10 ⁵
<i>G' (Pa) seven days</i>	1.34*10 ⁶	2.42*10 ⁷	2.79*10 ⁶	1.08*10 ⁷
<i>G' change (%)</i>	106%	26,561%	341%	4086%
<i>G'' (Pa) first cure</i>	2.73*10 ³	3.19*10 ²	9.19*10 ³	3.62*10 ³
<i>G'' (Pa) seven days</i>	8.32*10 ³	1.52*10 ⁶	5.43*10 ⁵	4.23*10 ⁵
<i>G'' change (%)</i>	205%	476,389%	5,809%	11,585%
<i>Tan delta first cure</i>	0.0048	0.004	0.015	0.014
<i>Tan delta seven day</i>	0.0063	0.063	0.195	0.0392
<i>Tan delta change (%)</i>	31%	1,660%	1,238%	180%
<i>Pencil Hardness first cure</i>	2B	<6B	2B	<6B
<i>Pencil Hardness seven day</i>	7H	HB	>9H	<6B

Figure 15: secondary condensation cure with unique silicones

Sulfur Functional Silicones

In our latest Silmer family, we have developed a series of thiol silicones and MQT silicon resins. They react with vinyl functional silicones and vinyl functional silicon Q resins. The cure mechanism is the well known thiol-ene reaction. The cured materials are strong, tough and flexible and opaque white. The elongation is up to 200%, something that cannot be done with acrylate functional UV curing.

Component	Silmer SH Q20	Silmer SH Q20	Silmer SH J0
Proprietary MQT(SH) or SH Silicone	21.5%	15.6%	15.1%
Silmer VIN 65K	42.3%	51.7%	45.8%
Silmer VQT83-30	35.6%	0	38.6%
Silmer VQ92	0	32.0%	0
TPO-L	0.6%	0.7%	0.6%
SH/vinyl	3.63	4.88	3.63
Properties			
Tensile Strength (kPa)	3,495.98	4027.13	2,303.68
Elongation (%)	99.07	202.96	55.87
Total Energy (J/m)	262.95	762.75	104.34
Tear Strength (N/mm)	6.81	8.19	5.33
Shore A Hardness	55.00	46	53.00
G' (Pa)	6.41E+05	4.73E+05	1.20E+06
G'' (Pa)	1.14E+05	5.26E+04	5.23E+04
tan delta	0.18	0.1112	0.04
Cure rate (Pa/s)	8.65E+04	7.62E+04	2.87E+05

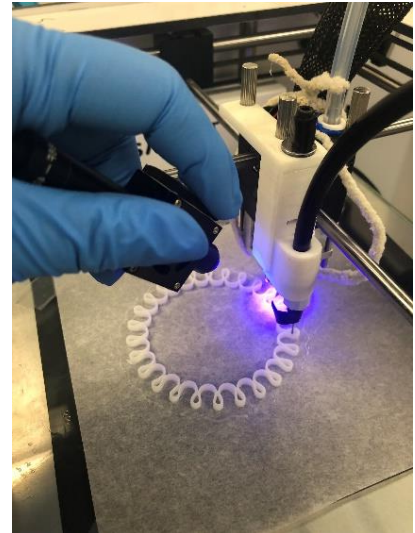


Figure 16: Silmer SH cured properties and an example being 3D printed.

Conclusion

Incorporation of reactive silicone into organic based polymers, is readily accomplished. The resultant hybrid polymers or polymerized matrix and usually somewhat softer, with dramatically improved flexibility, impact resistance and elongation. In these properties more silicone provides more of the effect up to a point where the system becomes too soft.

Other mechanical properties such as tensile strength and total energy to break are often improved likely from the increased flexibility. In these properties there is an optimum degree of incorporation, generally around 20% silicone, which needs to be discovered in each system with a ladder study.

All of the source papers with more detail are available on www.siltech.com