

Novel Cured Silicone and Silicone/Organic Hybrids

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Abstract

The effect of modifying some organic epoxy resins with various epoxy, hydroxyl or amine functional silicones is shown as a function of silicone structure and ratio of epoxy silicone to organic epoxy. In some cases, hardness of the hybrid resins was kept within 10% of that of the pure organic resin while impact resistance, release and coefficients of friction increased dramatically. In the final example, impact resistance and hardness are both increased significantly.

Introduction

Reactive silicones can be synthesized to have the same reactive moieties as those used in standard resin polymers. These will react during the curing step. Solubility, steric and electronic affects alter the kinetics of the reaction, but they can be made to react into the matrix.¹

In this paper we focus on the effects of silicones reacted with epoxy resins, an important class of reactive polymer in many composites. The reaction of these strained rings is normally initiated by opening the epoxide with an amine generating a primary hydroxyl to propagate the chain with other epoxy groups. Most commonly these amines are multifunctional which, coupled with their greater nucleophilic strength, causes them to crosslink or harden the resin.²

In many applications, epoxy resin users would like to improve impact resistance or toughness (fracture) without compromising hardness (durometer).³

Silicones are relatively flexible polymers with low surface energy, low glass transition temperatures (T_g), stability to free radical reactions (including thermal degradation), and transparency in the ultraviolet region of the EM spectrum. The incorporation of reactive silicones into resins generally results in a hybrid matrix with reduced Coefficient of Friction (CoF), increased mar, abrasion and stain resistance and increased flexibility without compromising thermal or UV stability. The hardness of the hybrid material is often less than the pure organic polymer, but some silicone structures can offset that.¹

In this work we have used glycidyl epoxy, cycloaliphatic epoxy, primary amine, and primary hydroxyl functional silicones to react with organic epoxy resins. While most of the products used are commercially available, generic descriptors are used to preserve academic integrity.

Table 1. Silicone Structures Used

Silicone	Function	Amine, epoxy or hydroxyl value*	# reactive sites	Equivalent Weight
EPOXY A	Glycidyl and OH (polyether)	1.8% epoxy 70 OH value	one epoxy three hydroxyl	2400 on epoxy 800 on OH
EPOXY B	Cycloaliphatic and OH (polyether)	0.5% epoxy 34 OH value	one epoxy five hydroxyl	8200 on epoxy 1640 on OH
AMINE A	NH ₂	180	four	300
AMINE B	NH ₂ and OH	22 amine value	one amine	2550 on NH ₂

	(polyether)	65 OH value	three hydroxyl	850 on OH
AMINE C	NH ₂	125	two	450
HYDROXY A	OH	15	three	3800
HYDROXY B	OH	28	two	1980
HYDROXY C	OH	155	four	360

*For this table the amine, epoxy or hydroxyl values are estimated from the target structure

Experimental And Results

Silicone Organic Epoxy Hybrids

Heat Cured Epoxy

In the first experiment, a typical commercially available epichlorohydrin/ bisphenol A type epoxy resin was reacted with varying amounts (0-50%) of a multifunctional glycidyl type epoxy functional silicone with polyethyleneoxide groups to improve miscibility. This is designated as EPOXY A. Methylhexahydrophthalic anhydride (MHHPA), a reactive defoamer and a catalyst were used as well.

The rheological data and mechanical properties are obtained directly from Brookfield DV-III Rheometer AR-G2 and Instron Model #1122 curing at 110°C for 4 hours.

The data are reported in Figures 1-3. As one replaces more and more organic resin with silicone resin the hardness, tensile strength, and storage and loss moduli are all reduced while elongation at break increases to a maximum of 120% at 45% EPOXY A.

The curvature is not steep at the onset of the hardness curve indicating that small amounts of silicone reduces the hardness more slowly than one might expect considering the very low Tg of silicone. However, as large amounts of silicone are incorporated, the inherent hardness of the organic epoxy resin is lost.

The storage and loss moduli also show shallow curvature followed by a steeper drop off as more silicone is used.

The total energy required to reach the break point and the elongation at that break point, both show a maximum value. The data point marked as 25% EPOXY A has a nice balance of properties with hardness reduced only from 88 to 72 Shore D and elongation increased to 60%.

Figure 1: Shore D And Tensile Strength Of Epoxy Modified With Silicone EPOXY A.

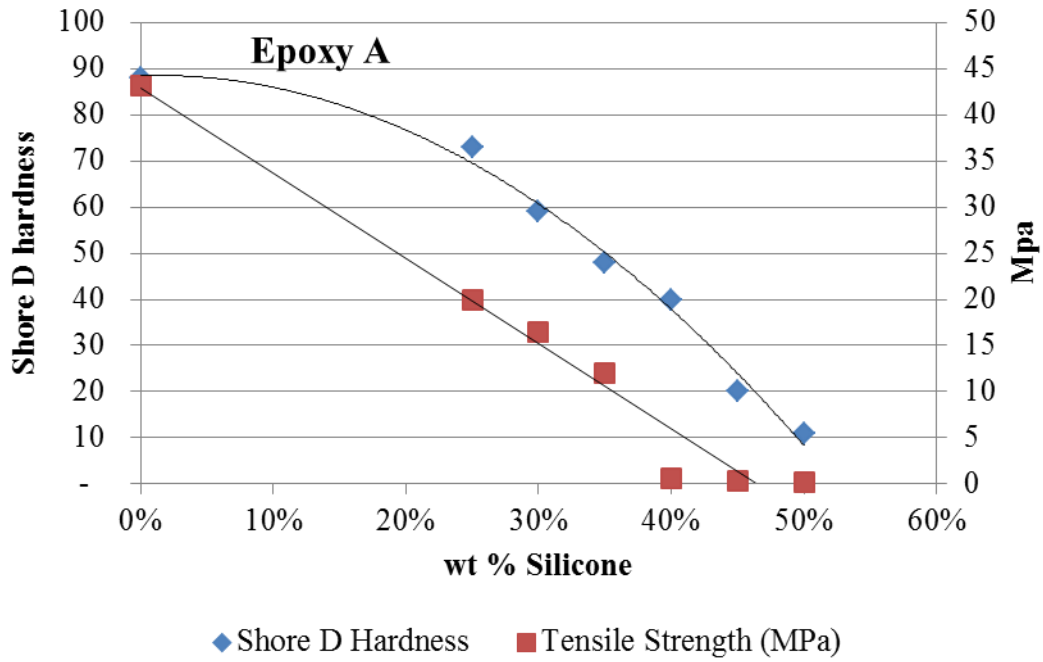


Figure 2: Storage and Loss Moduli of Epoxy Modified With EPOXY A

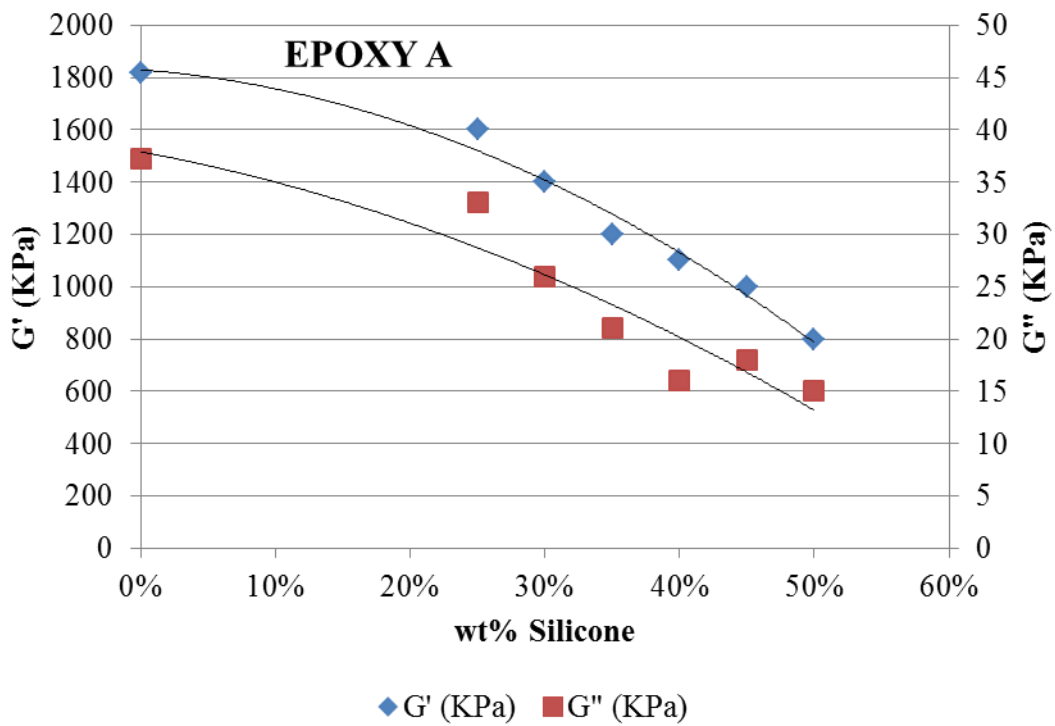


Figure 3: Total Energy to and Elongation at Break of Epoxy Modified With EPOXY A

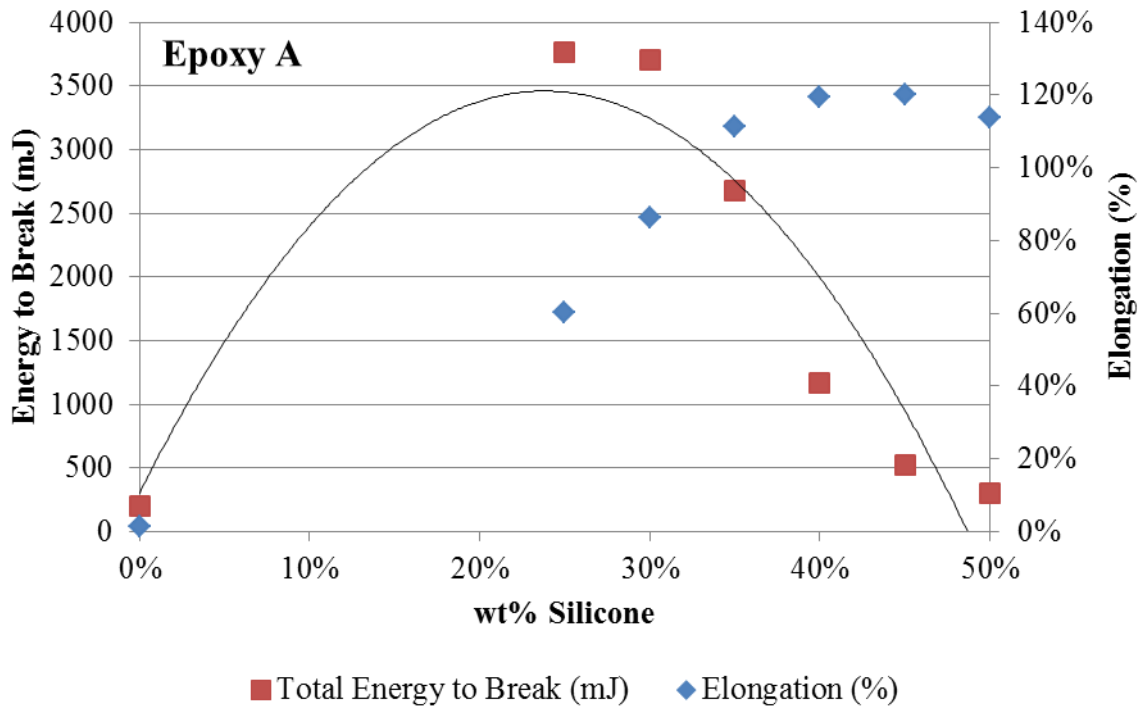
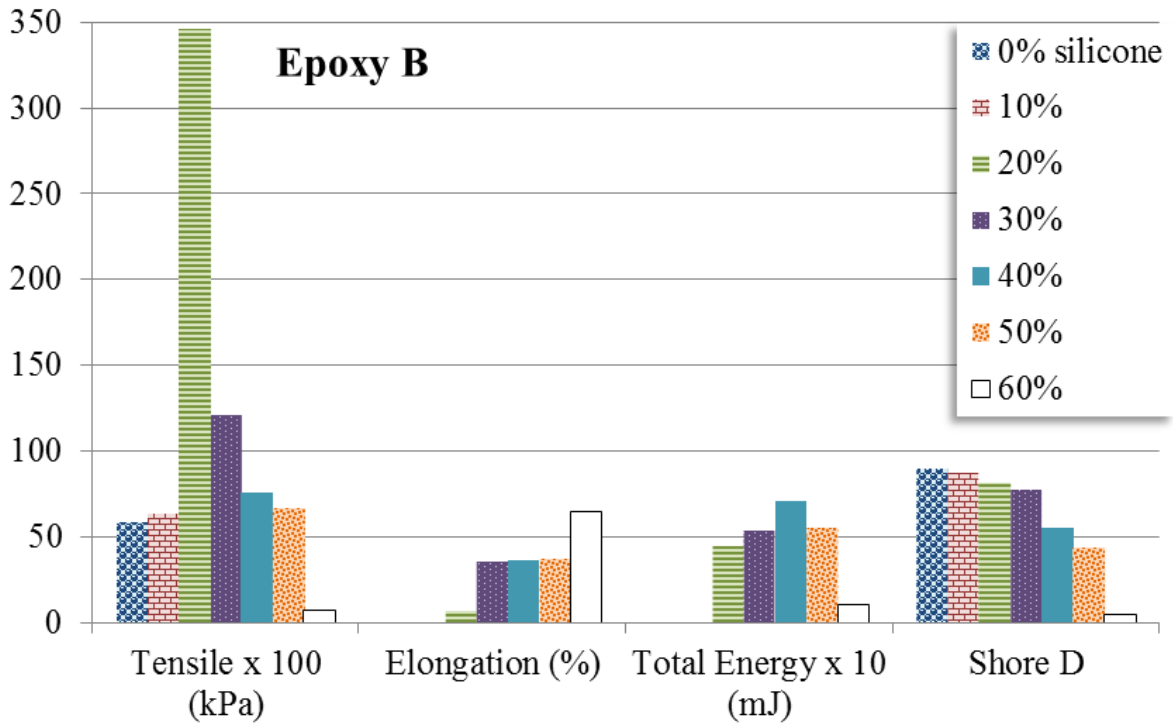


Figure 4: Properties of Epoxy Modified With EPOXY B



UV Cured Epoxy

In the second example, a UV cured cycloaliphatic epoxy resin is reacted with a multifunctional cycloaliphatic epoxy silicone with polyether for miscibility designated EPOXY B. These are cured under UV initiated acid cure conditions. To simplify, we have plotted these properties in one figure. See Figure 4.

Again there is a shallow curvature for low amounts of silicone plotted against hardness. Elongation increases as the amount of silicone is increased with no maximum shown through 60% EPOXY B. Tensile strength maximizes at 20% EPOXY B and total energy at break point maximizes at 40% EPOXY B. The hybrid material with 25-30% EPOXY B has Shore D hardness decreased only about 10% but elongation, tensile strength and total energy at break point are all dramatically increased.

In both of these examples, the hardness of the original organic epoxy is diluted by the silicone. The elongation and energy at break point were improved implying a more flexible material.

It is tempting to think that the higher number of cross link sites on EPOXY B allowed it to better retain the virgin organic epoxy's hardness with more silicone. But we cannot be sure as the molecular weight, base resin and even epoxy type are all changed as well.

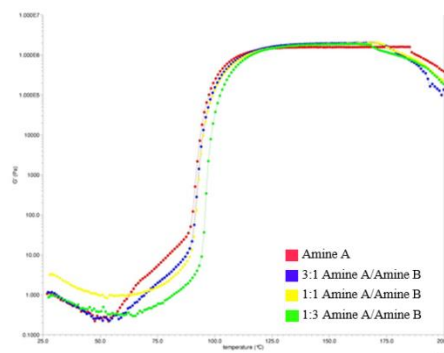
Silicone Amine Hardener

Identifying the System

In the third example, an ambient cured amine hardened epoxy is reacted. Part of the organic amine hardener is replaced with Silicone AMINE A or the much more compatible polyether containing Silicone AMINE B. The base formula is 1:1 D.E.R. 331⁴ and Ancamine 1618⁵ with 0.5% Imcurecure AMI-1 catalyst⁵. AMINE A resulted in a tacky, incomplete cure, while AMINE B resulted in a fully cured system after 12 hours at ambient temperatures.

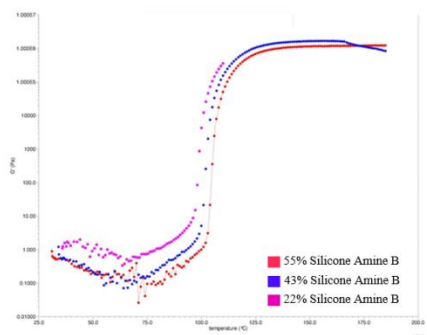
The G' versus cure time plots of the system with increasingly higher ratios of AMINE B to AMINE A is shown in Figure 5. The more AMINE B that is used, the cleaner the cure plot becomes. The final resin also goes from cloudy to clear as one uses more of the soluble AMINE B instead of the immiscible AMINE A. It is critical for the silicone to be miscible in the system an effect that is expected with reactive silicones.¹

Figure 5: Cure Profile of Epoxy Hardened with AMINE A, AMINE B and Blends



Next the optimum level of Silicone AMINE B was determined by varying the organic hardener and Silicone AMINE B ratio, keeping the epoxy/amine content at 1:1 in each experiment. Figure 6 shows the cure profile for these three runs. Relative to the organic hardener, the silicone cures slightly slower and provides a slightly softer material.

Figure 6: Cure Profile of Epoxy Hardened AMINE B and Ancamine 1618 Blends



Effect of Silicone Amines as Hardener

The remaining experiments were done with the optimized system of 41% Silicone AMINE B/ 59% Ancamine 1618, keeping the epoxy/amine ratio at 1:1. This system was cured with AMINE B, EPOXY A, and a 1:1 blend of AMINE B and EPOXY A. EPOXY A is the same siloxane backbone as AMINE B with glycidyl epoxy groups instead of alkyl amines. The only differences should be due to the reactive group. Physical properties of these were measured and shown in Table 2 and Table 3.

Table 2. Tensile Properties of Epoxy Resin Hardened with Amine B, Epoxy B and blends

	AMINE B	1:1 Blend	EPOXY A	Control
Tensile x 100 (kPa)	216	246	278	578
Shore D Hardness	71	73	75	81
Elongation x 0.1 (%)	89	106	47	33
Total Energy (mJ)	527	764	406	383
Thickness	1.7	1.97	1.88	1.52
Total Energy/Thickness (mJ)	310	388	216	252

Table 3. Flexure Properties of Epoxy Resin Hardened with Amine B, Epoxy B and blends

	AMINE B	1:1 Blend	EPOXY A	Control
Max Flexure Stress (MPa) x10	2.0028	2.1594	2.84	6.5375
Flexure Strain at Max Flexure Stress (%)	5.19	4.94	4.56	3.71
Energy at Max Flexure Stress x 0.01 (J)	9	10	10	8
Flexure Stress at Break (MPa)	17.1	19.2	25.7	63.9
Flexure Stress at Break (%)	8.3	7.4	6.5	4.3
Total Energy x 0.01(J)	17	17	16	10
Thickness	2.38	2.42	2.15	1.59
Total Energy /Thickness x 0.01 (J/mm)	7.1	7.0	7.4	6.3
Modulus (GPa)	0.70538	0.71458	1.01238	2.74138

All of these are softer than the control and elongation and flexibility are improved. Comparing EPOXY A and AMINE B, it seems that the amine is more effective at incorporating the silicone properties into the final resin. The blend of both techniques gives a very interesting resin.

Rubber Particle Epoxy Composite

In the final example, a composite of rubber particles filled into a two part, amine hardened, epichlorohydrin/ bisphenol A type epoxy is reacted with two different ratios of several multi-functional silicones with primary hydroxyl or amine reactivity or both. The ratios are 5% and 10%, designed to remain on the shallow part of the hardness curve.

Sample Preparation

Mix Part's A and B until homogeneous, add 5-10% reactive silicone to Part B and mix again to homogeneity. Combine Part A and Part B mixtures in a 1 to 1.3 molar ratio (epoxy to amine) and mix until homogeneous. Add rubber crumbs into the A/B mixture in a 1:2 by volume ratio and mix until homogeneous. Weigh 50 grams and spread evenly on 6"X6" Teflon mold. Remove from mold after 24 hours and continue to cure at ambient for 7 days in total.

Testing Procedure Low Temperature Impact Resistance (-15°C)

Measure the thickness of the test sample. Place cured sample in -15°C freezer for 3-4 hours. Drop a 16.3 g steel ball from 30 cm height on the cured sample in the frozen compartment. Repeat if necessary until fracturing occurs. Based on severity of cracks and number of drops, record rating vs. control (10 is the best). The ratio of the impact strength rating to average sheet thickness was calculated to compensate for the fact that the samples had differing thickness.⁶

Testing Procedure Low Temperature Impact Resistance (-30°C)

Measure the thickness of the test sample. Place cured sample in an ice box filled with dry ice (-30°C) for 1-2 hours. Monitor temperature with a handheld infrared thermometer. Collect data as in 2.3.2

Results

The results are shown in Table 4. AMINE A shows a dramatic improvement in hardness and toughness as seen by the low temperature fracturing at both use levels as well as tensile strength. With four reactive amines, this silicone is likely increasing the cross link density relative to the organic resin, causing this improvement.

AMINE B, which has hydroxyl groups as well as amines, shows no exciting improvements perhaps because the less nucleophilic hydroxyl groups are not reacting into the matrix in the same way.

AMINE C shows improved performance but only at the higher 10% use level. Relative to AMINE A it has less reactive sites, also this is a di-functional linear modified silicone (reactive groups are only at the ends of the polymer) so it should not be changing the cross link density.

HYDROXY C gave a strong fracture result at -30°C but not at -15°C. Besides this one positive data point the hydroxyl functional materials were not very effective at retaining or increasing the shore hardness. They gave minor improvement in elongation but reduced hardness and tensile strengths.

Although the data are not shown here, blends of the silicones above did not show synergy but behaved as if the better product were simply used at a lower percentage.

Table 4. Properties of Composite Made with Silicone Epoxy and Rubber Particles

Additive	%	Hardness (Shore A)	Tear Strength (N/mm)	Tensile Stress at Absolute Peak (kPa)	Elongation at Absolute Peak (%)	- 15°C Fracture Rating	- 30° Fracture Rating
Control	0	37	3.19	500.14	170.9	5	6*
AMINE A	5%	45	3.64	635.45	113.79	8	7*
AMINE A	10%	49	3.96	943.37	68.14	9.5	9*

AMINE B	5%	27	2.05	298.72	190.59	5	5.5
AMINE B	10%	25	1.8	260.52	164.31	4.5	2.5
AMINE C	5%	31	2.69	353.9	175.9	4.5	3
AMINE C	10%	43	3.71	542.69	97.66	9.5	8*
HYDROXY A	10%	35	2.61	352.8	176.43	6	5
HYDROXY B	10%	30	2.59	429.84	201.6	3	4
HYDROXY C	10%	32	2.19	290.63	161.93	4	8.5*

* Indicates two impacts were needed to cause fracturing.

Conclusion

Epoxy, hydroxyl and amino silicones can be reacted into organic epoxy resin systems. The properties are dependent on the structure and amount of silicone used. In general, these materials can make hybrid systems which are softer but one can increase the hardness with highly cross linking silicones. These hybrids have higher impact resistance and behave quite differently from either pure polymer. Some of the products can be used to increase elongation or others to increase hardness and toughness.

The amine functional silicones were very effective at increasing hardness and low temperature fracturing in the somewhat unique composite system used.

References

1. There are many examples in the literature, but for example Cheung, Tom; Ruckle, Robert; "Properties of Silicone Modified Films." *Proceedings of the Waterborne Symposium*, **2013**.
2. Frederick H. Walker; *Introduction to Polymers and Resins 2nd ed.* Federation of Societies on Coatings Technology, **1999**.
3. Verbal reports to us from multiple customers.
4. Available from Dow Chemical
5. Available from Air Products
6. This calculation is not reported herein for simplicity but made no differences to the relative results.