

A STRUCTURE PROPERTY STUDY OF EPOXY RESINS REACTED WITH EPOXY SILICONES

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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.

We find that there is typically an ideal window of charge ratio of epoxy silicones reacted into organic epoxy resins which gives only a small reduction in hardness with a large increase in flexibility and total energy to break.

In the case of the multifunctional amine reactive silicone used as a hardener with epoxy resin, hardness is increased but surprisingly the low temperature impact resistance was also dramatically improved, indicating a harder, more impact resistant epoxy resin.

1. 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.

2. EXPERIMENTAL

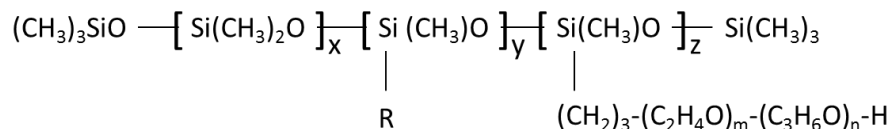


Figure 1: General Pendant Structure.

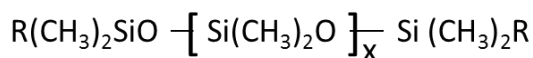


Figure 2: General Linear Structure.

The silicones used herein are functionalized with glycidyl type epoxy, cycloaliphatic epoxy, amine and/or hydroxyl groups for reactivity. Most of the structures used are modified in the middle of the silicone polymer as in Figure 1, but AMINE C and HYDROXY B are linear silicones with the reactive groups on the ends of the polymer (Figure 2). Finally some of the structures include polyalkyleneoxide groups for compatibility and others do not. Table 1 shows the specific structural variations as well as the equivalent weights.

Table 1. Silicone Structures Used

Silicone	Type	x	y	z	m	n	Reactive Function (-R)	# Reactive Sites	Equivalent Weight
EPOXY A	Fig 1	8	1	3	8	0	Glycidyl and OH (polyether)	one epoxy three hydroxyl	2400 on epoxy 800 on OH
EPOXY B	Fig 1	24	1	5	18	6	Cycloaliphatic and OH (polyether)	one epoxy five hydroxyl	8200 on epoxy 1640 on OH
AMINE A	Fig 1	8	4	0	0	0	NH ₂	Four	300
AMINE B	Fig 1	8	1	3	8	0	NH ₂ and OH (polyether)	one amine three hydroxyl	2550 on NH ₂ 850 on OH
AMINE C	Fig 2	8					NH ₂	Two	450
HYDROXY A	Fig 1	150	3	0	0	0	OH	Three	3800
HYDROXY B	Fig 2	50					OH	Two	1980
HYDROXY C	Fig 1	8	4	0	0	0	OH	Four	360

2.1 Silicone Organic Epoxy Hybrids

2.1.1 Heat Cured Epoxy

In the first experiment, a typical commercially available epichlorohydrin/ bisphenol A type epoxy resin, D.E.R. 671-X75 [4], was reacted with varying amounts (0-50%) of a multifunctional glycidyl type epoxy functional silicone with polyethyleneoxide groups to improve miscibility. This silicone is designated as EPOXY A (Table 1).

The formulation also included Methylhexahydrophthalic anhydride curative (MHHPA), a reactive defoamer and a catalyst (Imicure AMI-1) [5]. The control is the base formula without reactive silicones. Charges are shown in Table 2.

Table 2. Charges for Heat Cured Epoxy Experiments

Component	Control	25%	30%	35%	40%	45%	50%
D.E.R. 671-X75	76.54%	51.54%	47.72%	43.90%	40.08%	36.26%	32.44%
EPOXY A	0.00%	25.00%	30.00%	35.00%	40.00%	45.00%	50.00%
Silmer EPC D2	0.15%	0.15%	0.15%	0.15%	0.15%	0.15%	0.15%
MHHPA	23.25%	23.25%	22.07%	20.89%	19.71%	18.53%	17.35%
AMI-1	0.06%	0.06%	0.06%	0.06%	0.06%	0.06%	0.06%

The rheological data are obtained directly from Brookfield DV-III Rheometer AR-G2 five minutes after mixing. A portion of the mixed material was also poured into a Teflon mold, and cured in an oven for 110°C for four hours. A dog bone was cut according to ASTM 412 and the mechanical properties were measured on Instron Model #1122. Hardness was measured on a durometer.

2.1.2 Cycloaliphatic Epoxy

In the second example, a cycloaliphatic epoxy resin, UVACURE 1500 [6], was reacted with a multifunctional cycloaliphatic epoxy silicone with polyether for miscibility designated EPOXY B. These are cured with the anhydride and accelerator as in 2.1.1. No reactive defoamers was used in this example. The charges are shown in Table 3.

Table 3. Charges for Cycloaliphatic Epoxy Experiments

Component	Control	10%	20%	30%	40%	50%	60%
UVACure-1500	41.74%	37.48%	33.24%	28.98%	24.72%	20.48%	16.22%
Epoxy B	0%	10%	20%	30%	40%	50%	60%
MHHPA	58.20%	52.46%	46.70%	40.96%	35.22%	29.46%	23.72%
AMI-1	0.060%	0.060%	0.060%	0.060%	0.060%	0.060%	0.060%

2.2 Silicone Amine Hardener

2.2.1 Identifying the System

In the third example, a proprietary ambient cured, amine hardened Ancamine 1618 [5] 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 to improve impact resistance. All the formulas used in this experiment are based on the epoxy/total amine molar ratio of 1:1 with 0.5% Imicure AMI-1 catalyst [5].

The rheological data are obtained directly from Brookfield DV-III Rheometer AR-G2 five minutes after mixing. A portion of the mixed material was also poured into a Teflon mold, and cured in an oven for 110°C for four hours. A dog bone was cut according to ASTM 412 and the mechanical properties were measured on Instron Model #1122. Hardness was measured on a durometer.

2.3 Rubber Particle Epoxy Composite

In the final example, a composite of rubber particles filled into a two part, amine hardened, proprietary epoxy was reacted with two different ratios of 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. The control is the base formula without reactive silicones.

2.3.1 Sample Preparation

Part's A and B were mixed until homogeneous, the 5-10% reactive silicone was added to Part B and mixed again to homogeneity. Part A and Part B mixtures were combined in a 1 to 1.3 molar ratio (epoxy to amine) and mixed until homogeneous. Rubber crumbs were added into the A/B mixture in a 1:2 by volume ratio and mixed until homogeneous. For impact testing, 50 grams was spread evenly on 6"X6" Teflon mold, removed from the mold after 24 hours and continued to cure at ambient for 7 days in total. For mechanical properties, a portion of the mixed material was also poured into a Teflon mold, and cured as above. A dog bone was cut according to ASTM 412 and the mechanical properties were measured on Instron Model #1122. Hardness was measured on a durometer.

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

The thickness of the test sample was measured, then the sample was placed in a -15°C freezer for 3-4 hours. A 16.3 g steel ball was dropped from 30 cm height on the cured sample in the frozen compartment. This was repeated, if necessary, until fracturing occurs. Based on severity of cracks and number of drops, a rating (1-10, 10 is the best) was recorded vs. control. The ratio of the impact strength rating to average sheet thickness was calculated to compensate for the fact that the samples had differing thickness.[7]

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

Procedure 2.3.2 was repeated with the samples placed in an ice box filled with dry ice (-30°C) for 1-2 hours instead of the -15°C freezer. The temperature was monitored with a handheld infrared thermometer.

3. RESULTS AND DISCUSSION

3.1 Silicone Organic Epoxy Hybrids

3.1.1 Heat Cured Epoxy

The data are reported in Table 4 and graphically in Figures 3-5. As one replaces more and more of the organic resin with the much softer and more flexible silicone resin, the hardness, tensile strength, and storage and loss moduli are all reduced. But, the elongation at break increases to a maximum of 120% at 45% EPOXY A and total energy at break increases to 3500 mJ (from 200 mJ) at about 25% incorporation of EPOXY A.

Table 4: Properties for EPOXY A Reacted with D.E.R 671-X75

%EPOXY A	0% (control)	25%	30%	35%	40%	45%	50%
Shore A Hardness	>100	>100	98	95	92	65	51
Shore D Hardness	88	73	59	48	40	20	11
Tensile Stress at Absolute Peak (MPa)	43.14	19.91	16.50	11.95	0.65	0.33	0.20
Tensile Stain at Absolute Peak (%)	1.53	60.25	86.23	111.4	119.3	120.3	113.9
G' (KPa)	1818	1600	1400	1200	1100	1000	800
G'' (KPa)	37.2	33	26	21	16	18	15
Tan Delta	0.021	0.021	0.020	0.019	0.016	0.020	0.021
Tack	No	No	No	No	No	Yes	Yes
Appearance	Clear	Clear	Clear	Clear	Clear	Clear	Clear
Colour	Almost colorless	Almost colorless	Almost colorless	Almost colorless	Almost colorless	Almost colorless	Almost colorless
Viscosity (cPs @ 25°C) DV-III, CP-51, 5 rpm	3122	2150	1750	1500	1200	1000	750

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 T_g of silicone. However, as large amounts of silicone are incorporated, the inherent hardness of the organic epoxy resin is lost. Figure 3. The storage and loss moduli also show shallow curvature followed by a steeper drop off as more silicone is used. Figure 4.

Considering Figure 5, both the total energy required to reach the break point and the elongation at that break point 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%. It is interesting to us that one can bring a lot of flexibility and break strength into the resin without too much compromise in the hardness.

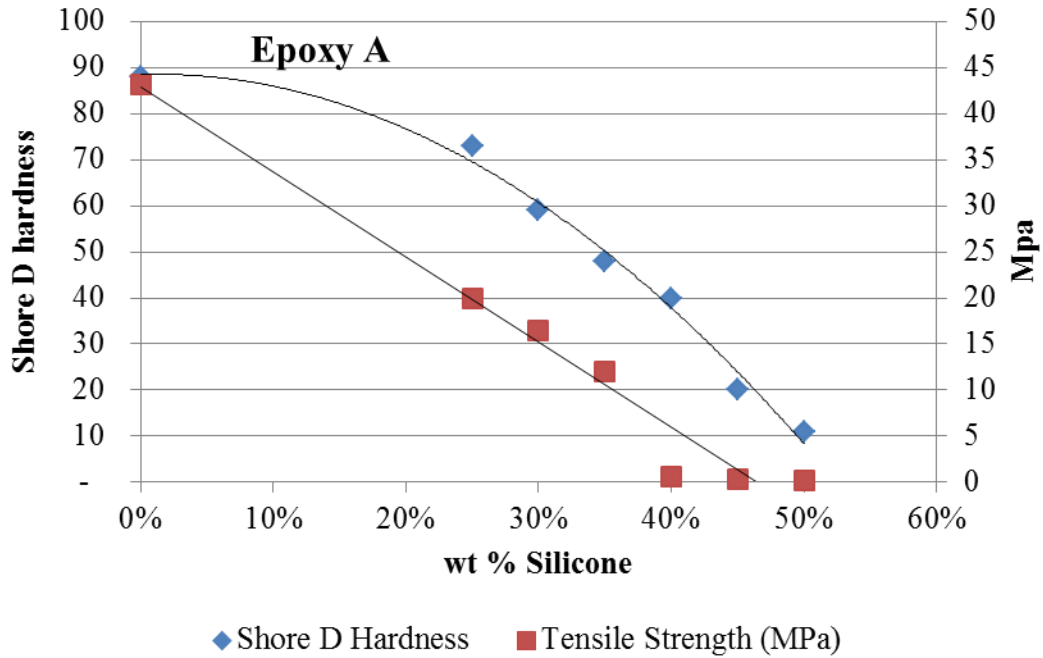


Figure 3: Shore D And Tensile Strength Of Epoxy Modified With Silicone EPOXY A.

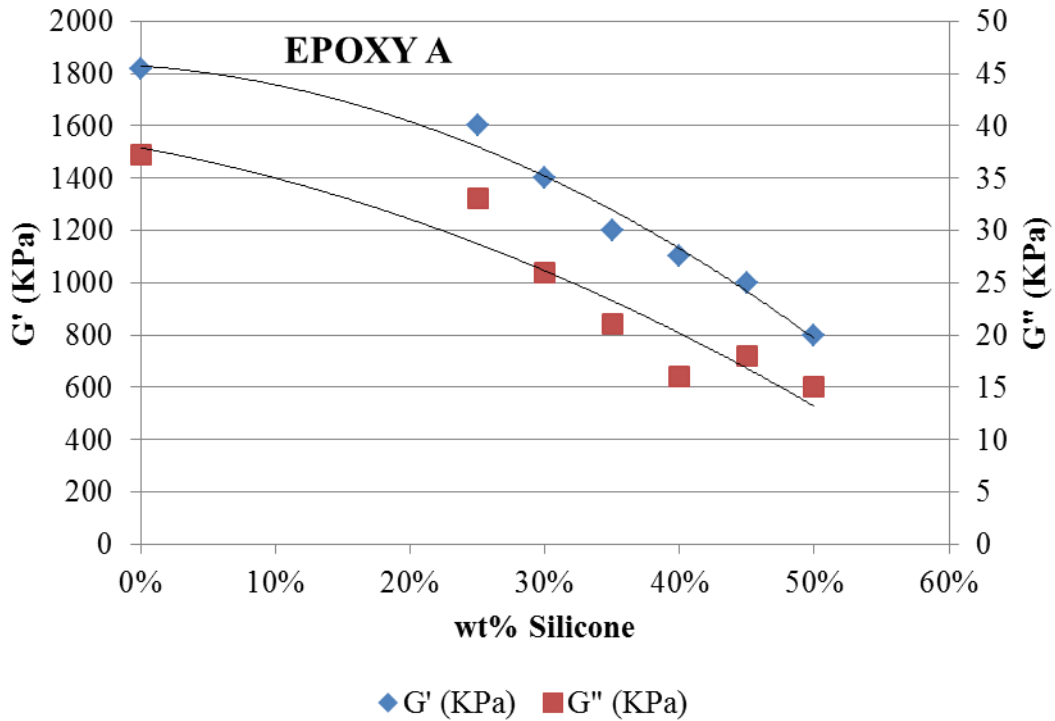


Figure 4: Storage and Loss Moduli of Epoxy Modified With EPOXY A

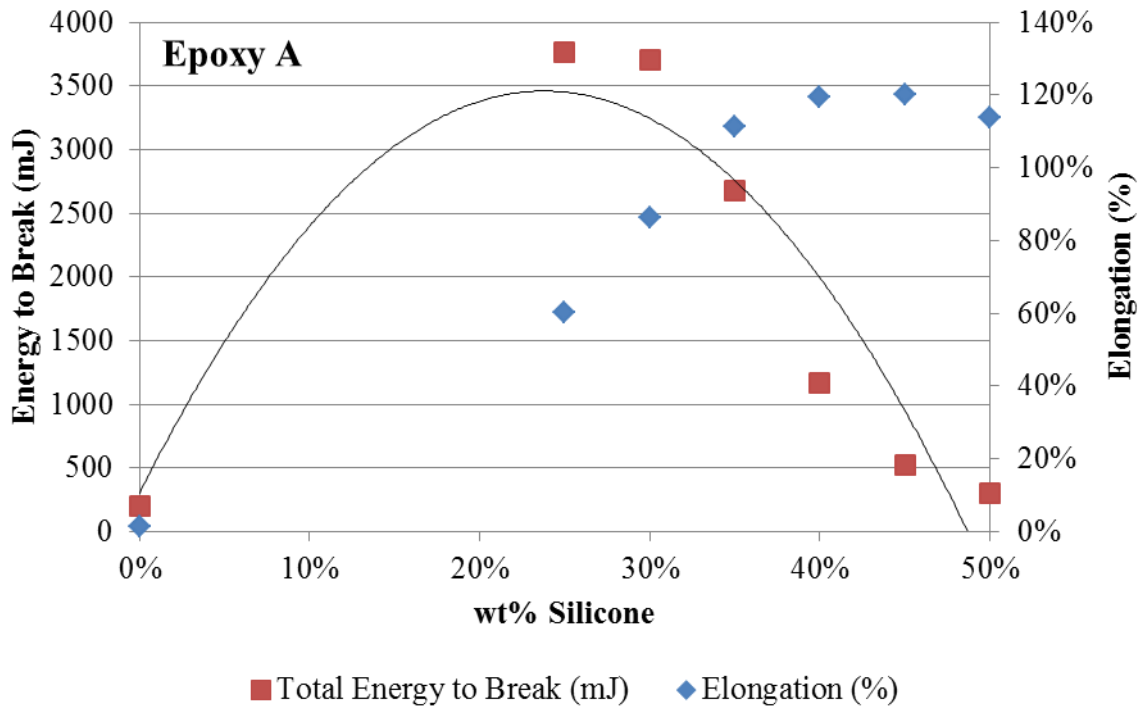


Figure 5: Total Energy to and Elongation at Break of Epoxy Modified With EPOXY A

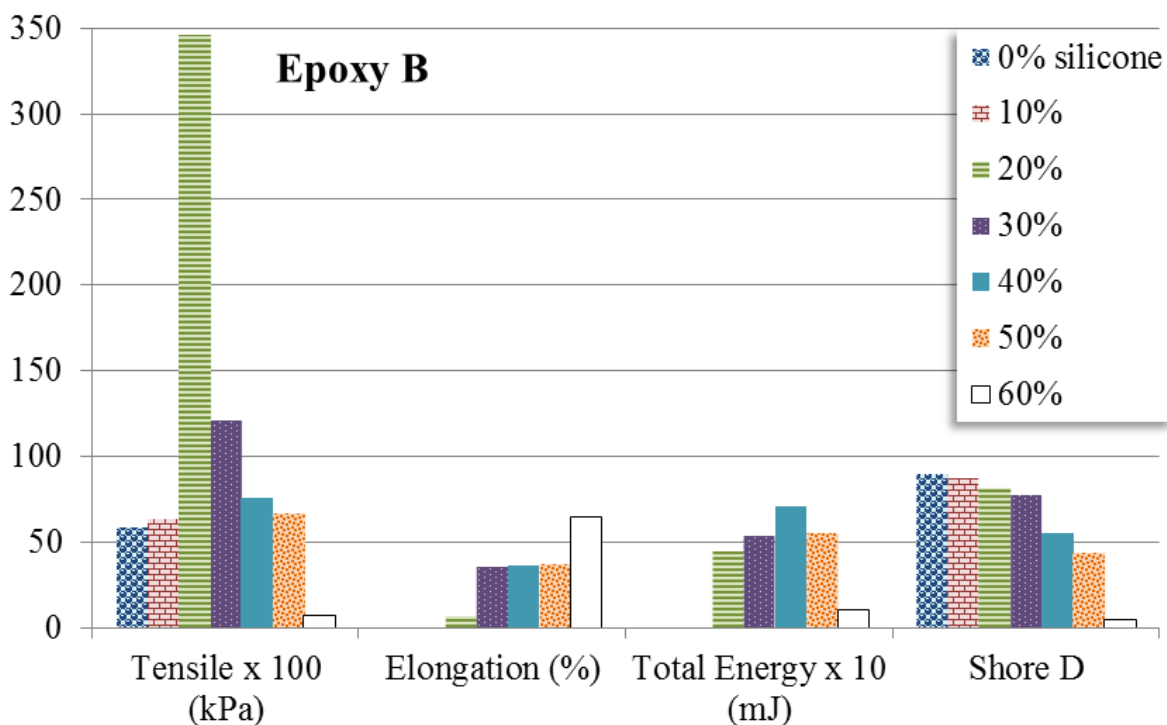


Figure 6: Properties of Epoxy Modified With EPOXY B

3.1.2 Cycloaliphatic Epoxy

In the second example, a heat cured cycloaliphatic epoxy resin is reacted with a multifunctional cycloaliphatic epoxy silicone with polyether for miscibility designated EPOXY B. These properties results are shown in Table 5 and, to simplify, in one chart (Figure 6).

Table 5: Properties for Epoxy B Reacted with UVACURE 1500

	Control	10%	20%	30%	40%	50%	60%
G' (Mpa)	6.600	4.500	2.700	1.600	0.280	0.110	0.058
G'' (Mpa)	0.450	0.800	0.700	0.360	0.032	0.005	0.0002
Tan(delta)	0.068	0.178	0.261	0.228	0.113	0.043	0.037
Tensile (kPa)	5841*	6293*	34613	12047	7608	6695	721
Elongation (%)	0.1*	0.49*	6.24	35.2	36.27	36.83	64.51
Total Energy (mJ)	0.01*	9*	443	538	710	550	105
Shore D Hardness	90	87	81	77	55	44	5
Shore A Hardness	>100	>100	>100	>100	>100	>95	45
Thickness	1.8	2.54	1.39	1.705	1.95	1.9	2.68
Total Energy/Thickness	0.01	3	318	315	364	289	39

* Too brittle to be measured accurately

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.

3.2 Silicone Amine Hardener

3.2.1 Identifying the System

In the third example, Silicone amine was used to replace some organic amine in the epoxy system to improve the low temperature flexibility, the organic amine hardener was replaced with Silicone AMINE A or the much more compatible polyether containing Silicone AMINE B. 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 7. 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. All of these results indicate that it is critical for the silicone to be miscible in the system which is expected with reactive silicones. [1]

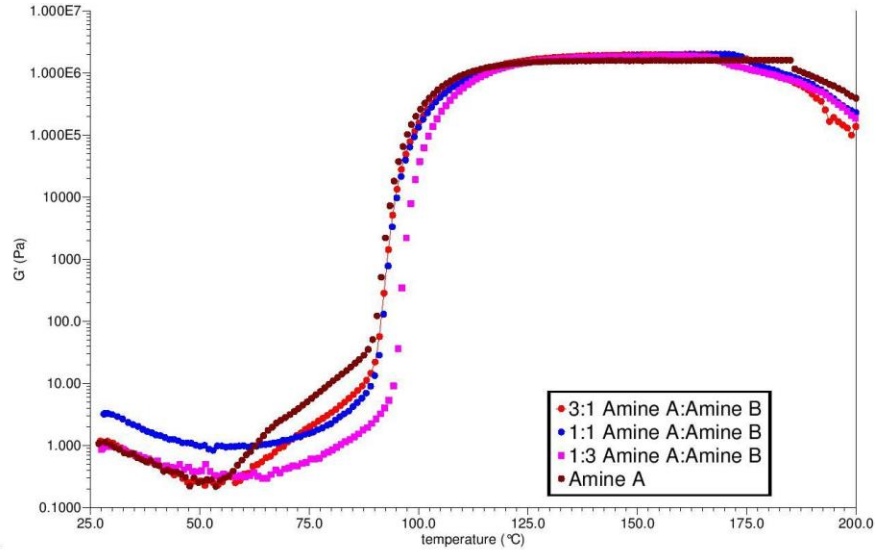


Figure 7: Cure Profile of Epoxy Hardened with AMINE A, AMINE B and Blends

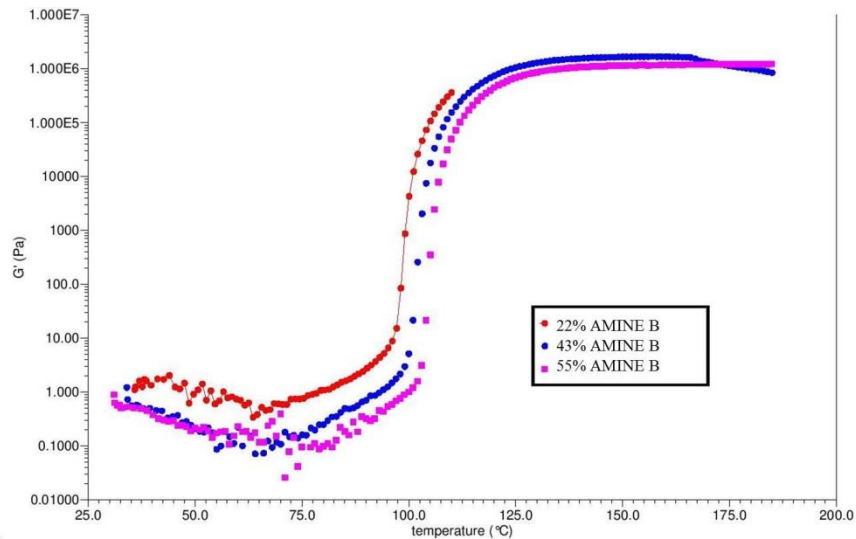


Figure 8: Cure Profile of Epoxy Hardened with AMINE B / Ancamine 1618 Blends

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 8 shows the cure profile for these three runs. Relative to the organic hardener, the silicone cures slightly slower and provides a slightly softer material.

3.2.2 Effect of Silicone Amines as Hardener

Using the results from 3.2.1, the remaining experiments in this section were done with the optimized hardener of 41% Silicone / 59% Ancamine 1618. Three experiments were done

varying the silicone blended with Ancamine 1618 keeping the total 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 6 and Table 7.

Table 6. 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 7. Flexure Properties of Epoxy Resin Hardened with AMINE B, EPOXY B and blend

	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 organic resin 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 in our opinion.

3.2.3 Rubber Filled Composites with Epoxy Resins

The results are shown in Table 8. AMINE A shows a dramatic improvement in hardness and toughness as seen by the low temperature fracturing at both use levels. There is also an increase in 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 8. 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°C 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.

4. 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.

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3. Verbal reports to us from multiple customers.
4. Available from Dow Chemical
5. Available from Air Products
6. Available from Allnex
7. This calculation is not reported herein for simplicity but made no differences to the relative results.