Accelerating Cure of Silicone Adhesives

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ABSTRACT

This paper will demonstrate the availability of dramatically accelerating the cure of certain silicone adhesives and their advantage to the manufacturing process.

A 'fast cure' adhesive is defined as full cure in less than ten minutes—or partial cure for handling under five minutes and full cure at room temperature in 8 hours or one shift.
Using a specific cure system and materials that have been developed to obtain fast-cure with heat acceleration, an experiment was performed to determine how fast, and at what temperatures these adhesives will cure.

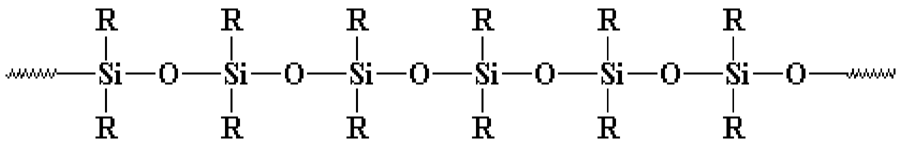
In conclusion, to obtain fast-cure at low temperature, 65ºC, R31-2186 can be fully cured in one minute. When adhering to temperature sensitive substrates, this provides a fast-cure choice. Although needing a higher temperature to obtain 'fast-cure', R32-2186 fully cures in 2 minutes at 100ºC. This can be useful because of R32-2186's extended worktime. LSR-9820-20 proves the best choice for high temperature cure, 185ºC. In just 30 seconds it has a 300psi lap shear. Although this figure reaches optimum over time, for many applications this is a great partial cure.

KEY WORDS: Adhesives, Silicones

1. INTRODUCTION

" A new beauty has been added to the splendor of the world - the beauty of speed", Tommaso Marinetti, Italian playwright in the early 1900s. Speed, or doing something faster is looked upon very favorable in our society today. It provokes the thought that this is a more efficient use of time. This mantra holds for adhesives, as well.
For the purposes of this paper, an accelerated or 'fast-cure' is defined as full cure in less than ten minutes—or partial cure for handling under five minutes and full cure at room temperature in 8 hours or one shift.

Silicone adhesives have been around for over sixty years(1). Silicones is actually a misnomer; while not actually containing a double bonded oxygen in the backbone, early founders thought it did, hence following chemical nomenclature of adding 'one' to the suffix. Polysiloxane is the correct name for silicones, which are an inorganic polymer, no carbon atoms on the backbone



[1]

R=CH3, phenyl, Fl3CCH2CH2

Polysiloxanes offer excellent elastomeric properties, wide temperature range, (phenyl substituted—115-260°C), fuel resistance (Trifluoropropyl substituted), optical clarity (refractive index as high as 1.54), low shrinkage (2-%), low shear stress(2) and are found in a wide array of applications.

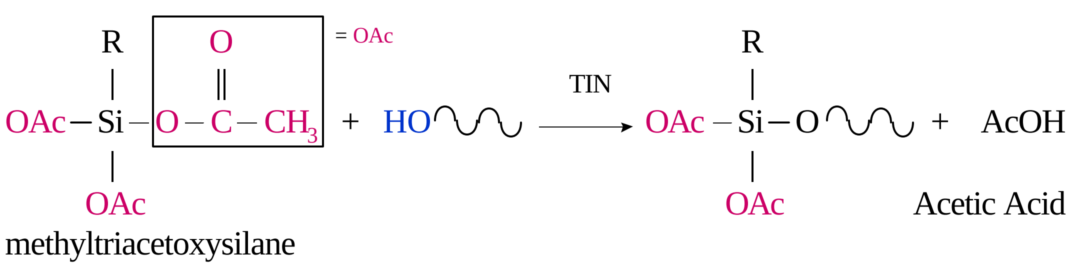
With these multiple applications have come the desire to increase cure time for a variety of reasons:

Manufacturing Advantages to Accelerating Cure of Silicone Adhesives

Speed up bottle necks in production process
Space savings
Faster production rates
Lower labor costs
Eliminate scheduling headaches
Faster customer response time
Improved Quality Control
Eliminate odors
Lower capital costs
Ability to Optimize cure

2. DISCUSSION

One-part adhesives are the most common silicone adhesive, used in such diverse applications as bathtub caulk to adhering pace maker leads. These one-part adhesives are based on acetoxy (alkyltriacetoxysilane) or alcohol (alkoxy) crosslinked cure systems. The following demonstrates the reaction which requires water to cure.

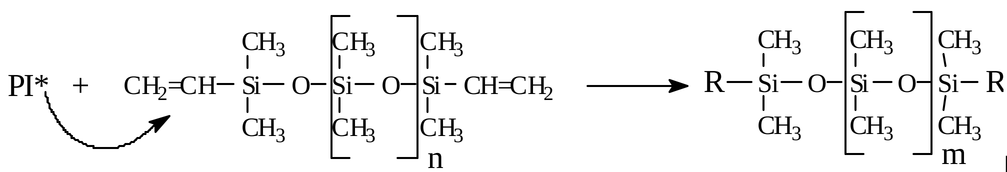


[2]

These materials are very effective when cured in thin section and provide excellent adhesion to most substrates. On exposure to ambient humidity these one component systems, composed of a hydroxyl terminated silicone polymer, alkyltriacetoxysilane or tetraalkoxysilane crosslinker and tin catalyst will vulcanize. Acetic acid or an alcohol is liberated during cure. Therefore, these adhesives require a controlled humidity environment and exposure to the air, often difficult in many applications. Full cure will occur in 3-7 days depending on thickness. Heat will not accelerate this cure. In our ‘faster’ work environment, 3-7 days is prohibitive.

UV cure was thought to be the ‘holy grail’, and silicone UV cure the solution. UV is not the only way to very fast cure, nor it is it problem free. UV-cured adhesives are solvent-free adhesives that are cured when exposed to radiant energy. These adhesives use photoinitiators to activate the cure. Light energy in the ultraviolet range of the spectrum (200-500 nanometers) is absorbed by the photoinitiators, causing a photochemically driven cure that is completed in seconds, throughout the bond(3).

$$\text{Photoinitiator (PI)} \xrightarrow[\text{365 nm}]{\text{(UV Light)}} \text{Photoinitiator Radical (PI*)}$$



[3]

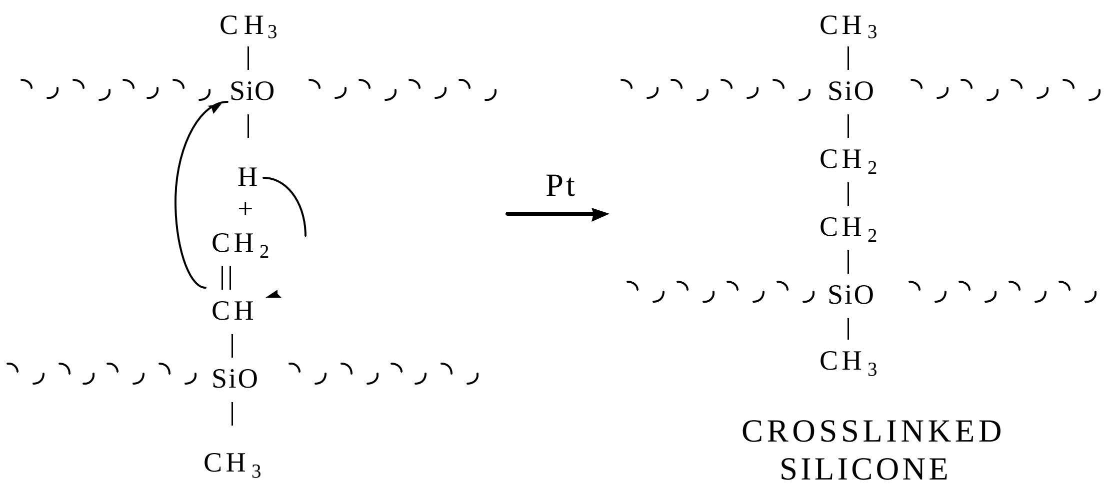
Components of a UV light curing system include a light source that is usually a quartz lamp, power supply, reflectors to focus or diffuse the light, cooling systems to remove heat, and a conveyor to move coated substrate to and from the light source.

The available UV silicone adhesives in the market are not always fast-cure. The alcohol-cure systems can be partially cured in 20 seconds, but take 72 hours for full cure(4)! Other systems can take as long as twenty minutes for full cure because they have to go through the light tunnel repeatedly. Other problems include line of sight curing or not curing in shadowed areas. Costly capital expenditures, qualification and maintenance can also minimize the potential benefits.

‘Fast-cure’ adhesives, based on a two-part platinum catalyst system or commonly called addition cure, do not require moisture or open air. The two parts generally both contain vinyl functional silicone polymer with the platinum catalyst added to the Part A and hydride functional crosslinker and inhibitor added to the Part B.   Also often included in both parts are reinforcing fillers, pigments and special additives such as barium sulfate for radio-opacity or boron nitride for thermal conductivity.

The cure, involves the direct addition of the hydride functional crosslinker to the vinyl functional polymer forming an ethylene bridge crosslink.

CROSSLINKER



POLYMER

CROSSLINKED SILICONE NETWORK

[4]

Because this mechanism involves no leaving group, un-like the one-parts, these systems can cure in closed environments.

Most platinum systems can fully cure at room temperature in twenty-four hours or can be accelerated with heat. They can be partially cured, tack-free, with heat and packaged. Curing will continue in the sealed package with no adverse effects. Special care to eliminate the presence of contaminants that might have a negative impact on the catalyst may be necessary.

3. EXPERIMENTAL

Several fast-cure adhesives from NuSil Technology were accelerated cured and evaluated against time to determine at what temperatures cure and handling could be achieved. These adhesives were specifically formulated to allow quick crosslink curing with various worktime ranges for optimal application choices.

R31-2186 is a silica filled, addition-cure general adhesive.   It's versatility makes it useful in electronics, automotive, or aviation. It has a 15-30 minute work time and will fully cure at room temperature in 4-6 hours. Typical physical properties:

Viscosity, cP, 25C	80,000
Work Time, minutes, 25C	15
CURED-24 hours at 25°C	Mix Ratio 1:1
Specific Gravity	1.10
Durometer, Type A	15

Tensile, psi	900
Elongation, %	850
Tear, ppi	70

R32-2186 is very similar to R31 except it has an extended work time of 6 hours and must be cured with heat. Typical physical properties:

Viscosity, cP, 25C	80,000
Work Time, hours, 25C	6 hours
CURED-15minutes@150°C Mix Ratio 1:1	
Specific Gravity	1.10
Durometer, Type A	15
Tensile, psi	900
Elongation, %	850
Tear, ppi	70

LSR-9820-20 is a high durometer, tough adhesive , designed for the aviation industry. It has a work time of 15-30 minutes and will cure in 8-10 hours at room temperature.

Extrusion Rate, g/minute (1/8" tip, 90psi, 5 seconds)	200
Work Time, minutes, 25C	15
CURED-2 hours@65°C Mix Ratio 1:1	
Specific Gravity	1.19
Durometer, Type A	50
Tensile, psi	1000
Elongation, %	400
Tear, ppi	100
Stress@200% Strain, psi	450
Lap Shear Strength, psi, unprimed	300
primed with CF1-135	700
180º Peel Strength, ppi, unprimed	20
primed with CF1-135	50

CF1-135 is an addition-cure primer, used with all the adhesives to obtain a standard level of adhesion.

Each adhesive was used to make several lap-shears with primed (CF1-135) aluminum laps. A bond target thickness of 5ml (0.005 in) was used. Each adhesive lap shear was tested at five different times; 30 seconds, 1minute, 2 minutes, 5 minutes and 10 minutes, and three different temperatures; 65°C, 100°C and a heat-gun(obtained consistent temperature of 185°C before placing it 3 inches from substrate). Three lap-shear panels were tested at each combination to adjust for variances. Lap-shear tested per ASTM D1002. Because curing would continue after heated at room temperature, lap shear testing was performed within two hours of removing from heat.

4. RESULTS

Table 1 shows the results for 65°C numerically, Figure 1 graphically. Table 2 and Figure 2 show the results for 100°C. The heat-gun is represented by Table 3 and Figure 3. Table 4 and Figure 4 illustrate the temperature 3 inches away from the substrate, 185°C, after the heat gun was brought to a steady temperature as illustrated in Table 5.

5. CONCLUSION

To obtain fast-cure at low temperature, 65°C, R31-2186 can be fully cured in one minute. When adhering to temperature sensitive substrates, this provides a fast-cure choice. From the data it could be surmised that a partial cure could be obtained in 15-30seconds with full cure in a few hours at room temperature. This route would be effective in packaging an assembled part after the quick partial cure. As we learned earlier, two-part, addition-cure systems can be cured in enclosed environments.

Although needing a higher temperature to obtain 'fast-cure', R32-2186 fully cures in 2 minutes at 100°C. This can be useful because of R32-2186's extended worktime. In electronic assembly, R32-2186 could use the same mix tip through-out an entire shift.

LSR-9820-20 proves the best choice for high temperature cure, 185°C. In just 30 seconds it has a 300psi lap shear. Although this figure reaches optimum over time, for many applications this is a great partial cure. For aviation repair work, the adhesive could be applied, heated with a hot heat gun for 30 seconds, then fully cured at room temperature over time. Table 6 data can be useful in deciding if or how long to pre-heat the heat gun.

The data also points out the detrimental effect of over-curing. Like reduced physicals with post-cure, over-curing will reduce the optimal bond strength of an adhesive.

NuSil Technology has the ability to formulate many different materials into fast-cure systems; high temperature, fluorosilicone, optically clear, USP Class VI, and low outgassed E-595.

6. REFERENCES

(1) W. Noll, Chemistry and Technology of Silicones, Academic Press, New York, 1968.

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(3) C.Bachmann, " UV Structural Adhesives and Sealants", *Adhesives Age*, April 1999, Pg. 24.

(4) C. Salerni, " Selecting Engineering Adhesives for Medical Device Assembly", *Medical Device & Diagnostic Industry*, June 2000, Pg. 90.

TABLE 1 **65°C**

	time(min.)	*0.5*	*1*	*2*	*5*	*10*
R31-2186	*low*	170	226	247	187	203
	middle	215	277	265	231	227
	high	291	343	310	267	247
	mean	225	282	274	228	226
	median	215	277	265	231	227
	st.dev. (s)	61	59	32	40	22
	c.o.v.	27.14	20.80	11.84	17.55	9.76
R32-2186	*low*	138	174	147	286	233
	middle	173	190	147	317	303
	high	186	348	208	380	328
	mean	166	237	167	328	288
	median	173	190	147	317	303
	st.dev. (s)	25	96	35	48	49
	c.o.v.	14.99	40.52	21.05	14.62	17.10
LSR-9820-20	*low*	n/a	n/a	11	71	412
	middle	n/a	n/a	13	77	428
	high	n/a	n/a	16	80	486
	mean	7	11	13	76	442
	median	7	11	13	77	428
	st.dev. (s)	n/a	n/a	3	5	39
	c.o.v.	n/a	n/a	18.87	6.03	8.81

Mean lap shear results:

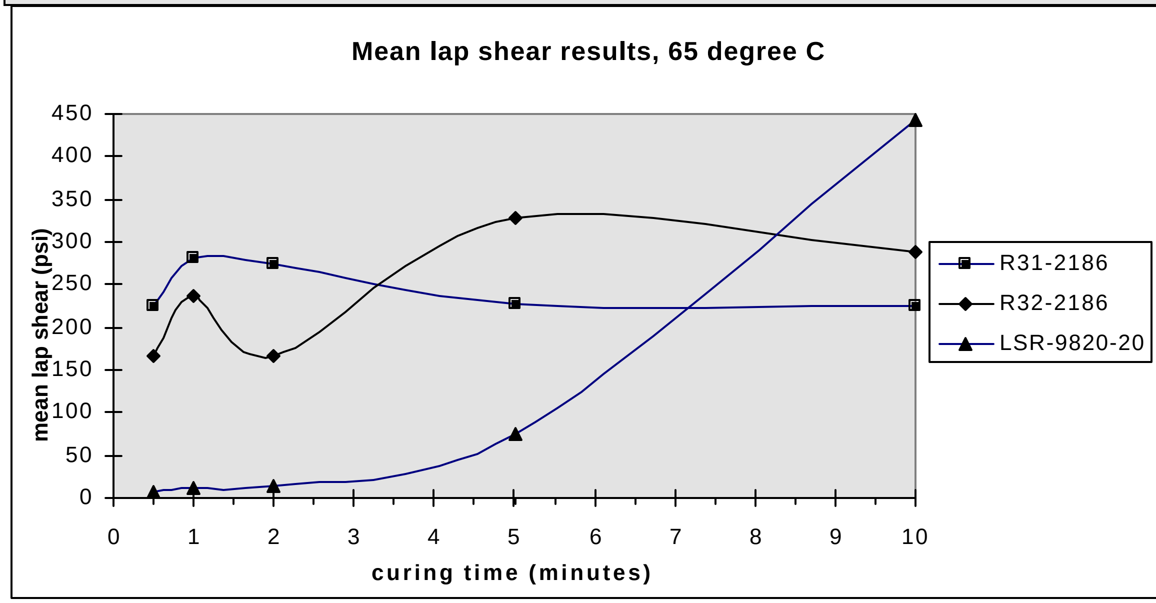
time	*R31-2186*	*R32-2186*	*LSR-9820-20*	
0.5	225	166	7	

1	282	237	11
2	274	167	13
5	228	328	76
10	226	288	442

Median lap shear results:

time	*R31-2186*	*R32-2186*	*LSR-9820-20*
0.5	215	173	7
1	277	190	11
2	265	147	13
5	231	317	77
10	227	303	428

FIGURE 1



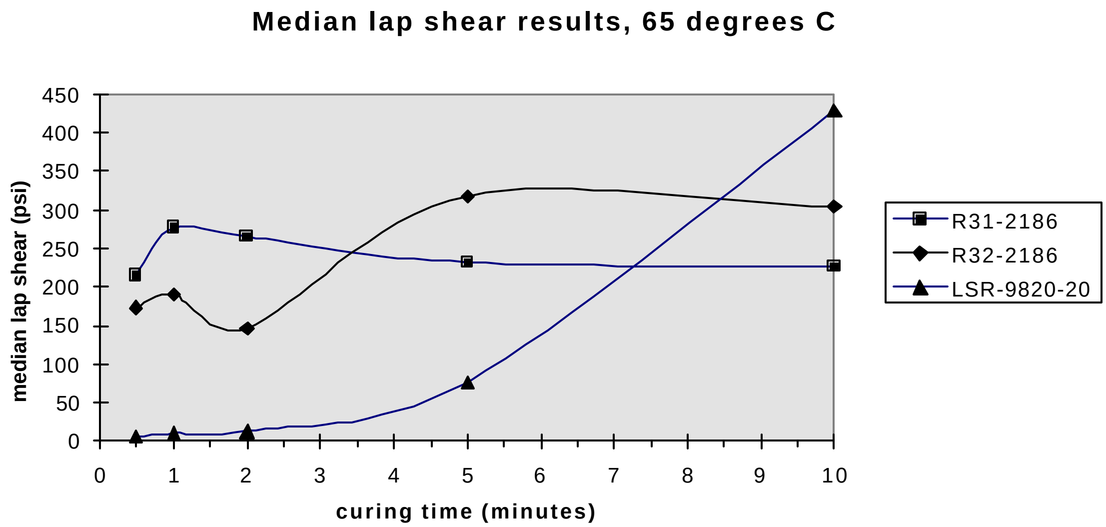


TABLE 2	100°C

R31-2186

time	0.5	1	2	5	10
low	130	206	198	237	127
middle	175	242	205	291	145
high	246	244	248	301	188

mean	184	231	217	276	153
median	175	242	205	291	145
st.dev. (s)	58	21	27	34	31
c.o.v.	31.84	9.27	12.48	12.46	20.44

R32-2186

low	132	115	255	268	194
middle	168	116	318	274	244
high	216	170	329	304	359

mean	172	134	301	282	266
median	168	116	318	274	244
st.dev. (s)	42	31	40	19	85
c.o.v.	24.50	23.54	13.28	6.84	31.85

LSR-9820-20

low	436	370	466	524	407
middle	444	458	475	539	426
high	484	490	552	552	450

mean	455	439	498	538	428
median	444	458	475	539	426
st.dev. (s)	26	62	47	14	22
c.o.v.	5.66	14.14	9.50	2.60	5.04

Mean lap shear results:

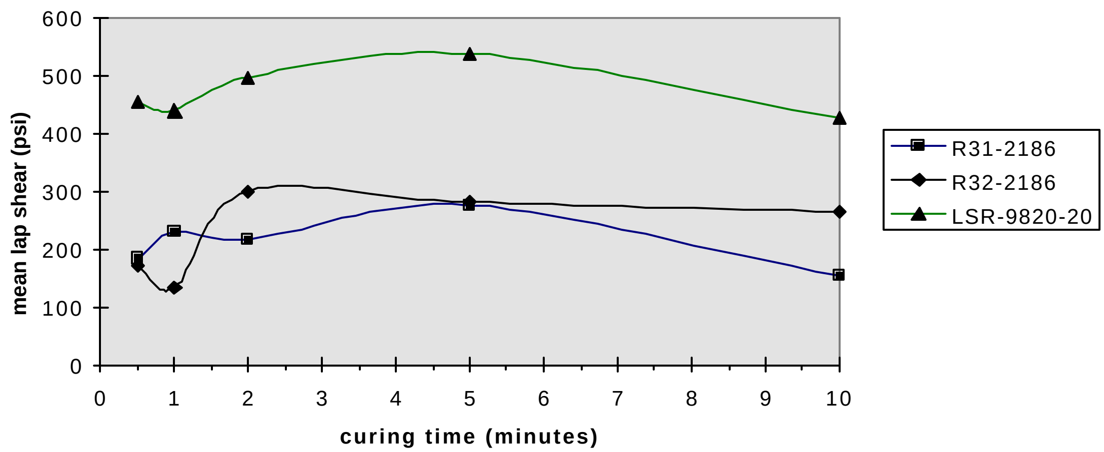
time	*R31-2186*	*R32-2186*	*LSR-9820-20*
0.5	184	172	455
1	231	134	439
2	217	301	498
5	276	282	538
10	153	266	428

Median lap shear results:

time	*R31-2186*	*R32-2186*	*LSR-9820-20*
0.5	175	168	444
1	242	116	458
2	205	318	475
5	291	274	539
10	145	244	426

FIGURE 2

Mean lap shear results, 100 degrees C



Median lap shear results, 100 degrees C

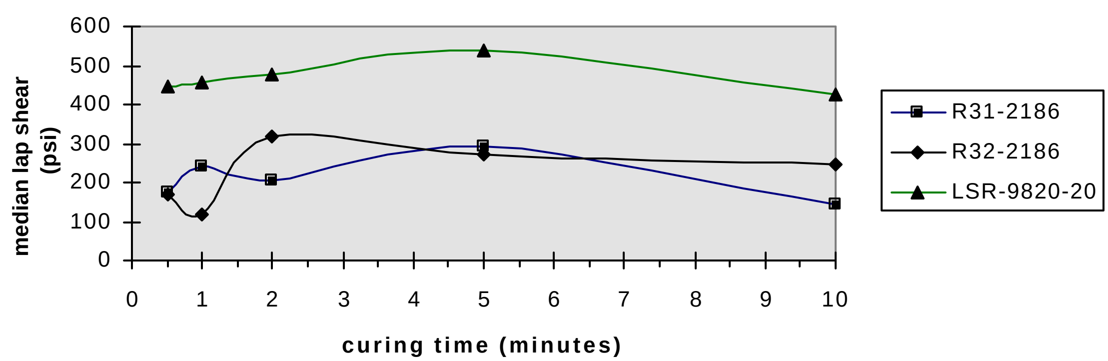


TABLE 3 **heat-gun 188°C**

R31-2186

time	*0.5*	*1*	*2*	*5*	*10*
low	95	180	148	263	234
middle	100	188	221	271	278
high	106	242	225	289	330

mean	100	203	198	274	281
median	100	188	221	271	278
st.dev. (s)	6	34	43	13	48
c.o.v.	5.49	16.59	21.89	4.85	17.12

R32-2186

low	199	202	216	218	369
middle	222	252	260	301	371
high	274	285	298	327	433

mean	232	246	258	282	391
median	222	252	260	301	371
st.dev. (s)	38	42	41	57	36
c.o.v.	16.59	16.96	15.91	20.19	9.31

LSR-9820-20

low	201	324	379	473	662
middle	319	481	413	604	663
high	375	542	512	628	668

mean	298	449	435	568	664
median	319	481	413	604	663
st.dev. (s)	89	112	69	83	3
c.o.v.	29.77	25.05	15.90	14.68	0.48

Notes:

Surface temperature under heat gun was 188.5 +/- 0.5 degrees C

Distance from sample to heat gun was ~ 3.25 +/- 0.25"

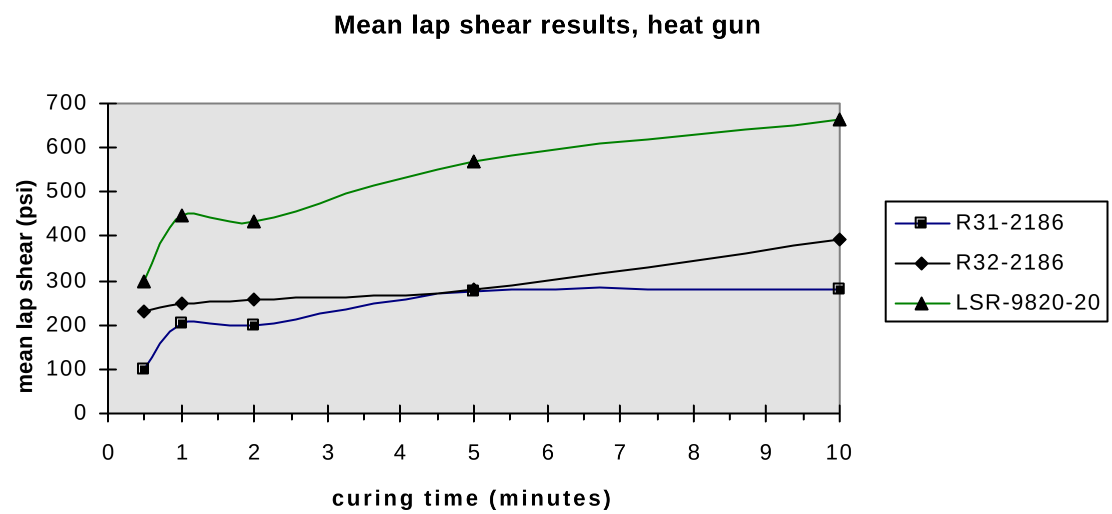
Mean lap shear results:

time	*R31-2186*	*R32-2186*	*LSR-9820-20*
0.5	100	232	298.3333333
1	203	246	449
2	198	258	435
5	274	282	568
10	281	391	664

Median lap shear results:

time	*R31-2186*	*R32-2186*	*LSR-9820-20*
0.5	100	222	319
1	188	252	481
2	221	260	413
5	271	301	604
10	278	371	663

FIGURE 3



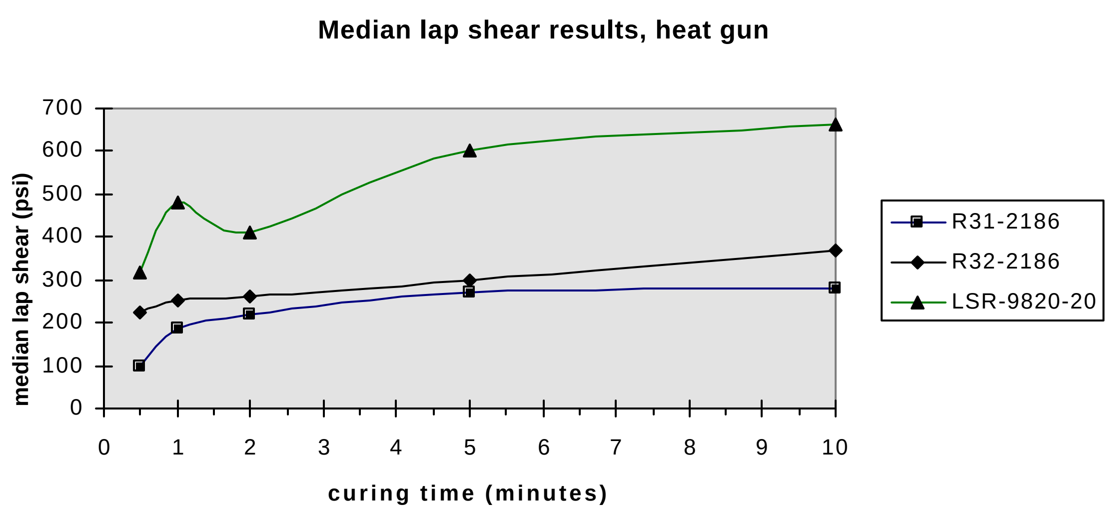


TABLE 4 HEAT GUN TEMPERATURE

3" from temperature probe

time minutes	temperature degrees C	delta T 1 (X1+n)-(X0+n)
0	177.8	0.0
1	179.4	1.6

2	180.5	1.1
3	181.5	1.0
4	183.9	2.4
5	183.8	-0.1
6	186.4	2.6
7	186.5	0.1
8	188.0	1.5
9	188.2	0.2
10	188.2	0.0

FIGURE 4

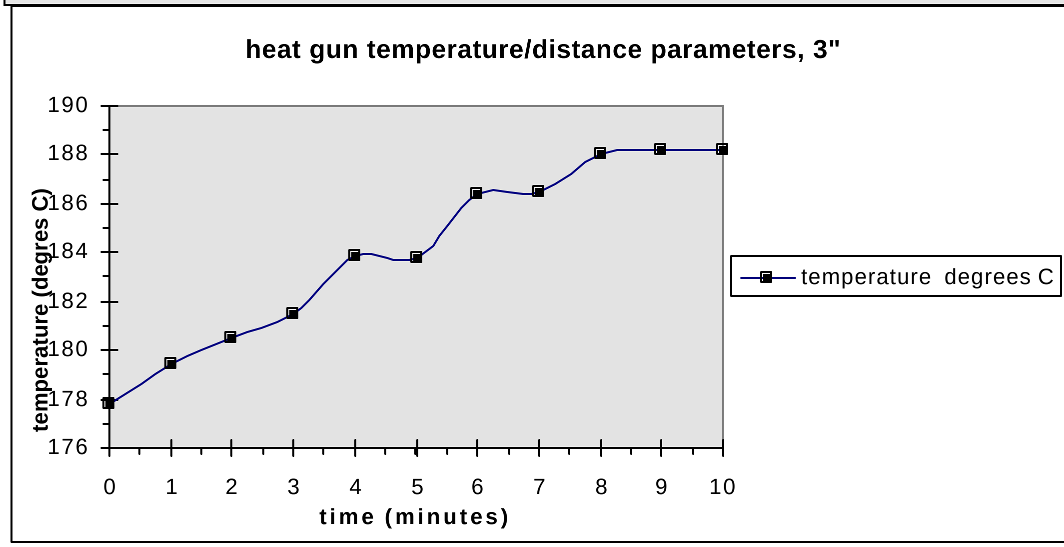


TABLE 5 HEAT GUN TEMPERATURE

6" from temperature probe 3" from temperature probe

time	temperature	delta T 1	temperature	delta T 1
minutes	degrees C	(X1+n)-(X0+n)	degrees C	(X1+n)-(X0+n)
0	21.0	0.0	21.9	0.0

0.5	28.4	7.4	33.4	11.5
1	41.3	12.9	50.9	17.5
2	62.2	20.9	82.5	31.6
3	80.9	18.7	108.9	26.4
4	95.0	14.1	129.9	21.0
5	106.4	11.4	146.7	16.8
6	115.0	8.6	159.0	12.3
7	122.3	7.3	169.1	10.1
8	127.1	4.8	177.2	8.1
9	131.8	4.7	183.8	6.6
10	135.1	3.3	189.0	5.2
11	137.4	2.3	193.4	4.4
12	139.8	2.4	197.3	3.9
13	141.6	1.8	200.0	2.7
14	142.8	1.2	203.0	3.0
15	143.7	0.9	206.0	3.0
16	144.3	0.6	208.0	2.0
17	145.6	1.3	209.0	1.0
18	145.4	-0.2	210.0	1.0
19	145.0	-0.4	210.0	0.0
20	145.0	0.0	211.0	1.0

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Bill has a B.S. in Chemistry from the University of California at Santa Barbara and a Masters in Business from Pepperdine University.

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