IMPROVING BONDABILITY TO RTV SILICONE
ELASTOMER USING RF-ACTIVATED GAS

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IMPROVING BONDABILITY TO RTV SILICONE ELASTOMER USING RF-ACTIVATED GAS

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Prepared by J. L. Bellah

The effects of an rf-activated gas (plasma) on the bondability to RTV silicone elastomer were studied. Processing guidelines were developed, and a method was sought to satisfactorily bond RTV to the walls of a machined aluminum casting and to provide a surface on the RTV which would best accept bonding to an epoxy encapsulant. Processing parameters, such as gas type and flow rate, reaction chamber pressure, and rf power level, were developed.

AB/tlb

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CONTENTS

Section	Page
SUMMARY.	5
DISCUSSION	6
SCOPE AND PURPOSE.	6
PRIOR WORK	6
ACTIVITY	6
<u>Equipment.</u>	9
<u>Test Method.</u>	9
<u>Theoretical Considerations</u>	16
<u>Recommendations for Production Use</u>	18
ACCOMPLISHMENTS.	20
FUTURE WORK.	20
REFERENCES	21
BIBLIOGRAPHY	22
DISTRIBUTION	23

ILLUSTRATIONS

Figure		Page
1	Voids and Separations Between the Encapsulant and Aluminum Walls in Cured Epoxy Encapsulant Over an RTV Slush Coating (P100434). .	7
2	Gross Separation Between Cured Epoxy Encapsulant and RTV Silicone Elastomer Coating (P100432)	8
3	Plasma Etch System (P100430).	10
4	Plasma Treatment of Surfaces: 100 Percent Argon	12
5	Plasma Treatment of Surfaces: 9 Percent Oxygen, 91 Percent Argon.	13
6	Plasma Treatment of Surfaces: 20 Percent Oxygen, 80 Percent Argon.	14
7	Schematic of Plasma System.	18

TABLE

Number		Page
1	Results of Pull Testing of Plasma-Treated Specimens	15

SUMMARY

An rf-activated gas (plasma) was studied to determine processing techniques to enhance adhesion to a cured RTV silicone elastomer. Using conventional techniques, cured RTV elastomer normally is considered to be unbondable. Plasma treatment of surfaces has been proposed as an alternative to chemical treatment of surfaces. When the RTV surface was treated in an oxygen-argon plasma, tensile adhesion strength between cured RTV elastomer and an epoxy encapsulant was 680 kPa, an increase of 200 percent over non-treated samples.

Contact angle measurements were used to determine the effects of plasma conditions on the relative surface energy of a number of common processing materials. The contact angle measurements indicated that surface treatment time is a function of chamber pressure. At a chamber pressure of 65 Pa, the treatment process essentially is complete after 20 minutes; while at 98 Pa chamber pressure, the process takes 30 minutes to reach completion.

When oxygen gas was added to argon, the bondability of an RTV surface increased. Oxygen is a highly reactive gas which easily forms products that increase surface bondability. Special precautions are required when using oxygen, however, because of the possibility of fire or explosion. Concentration up to 21 percent by volume may be used safely to improve the bondability of an RTV surface.

DISCUSSION

SCOPE AND PURPOSE

An activated gas (plasma) and its effects on the bondability to syntactic RTV to an aluminum component housing and to an epoxy microballoon encapsulant were investigated. Polysulfide conformal coatings have been used to provide an interface barrier between the walls of a housing and an encapsulant, but the coatings began to degrade above 93°C (200°F). As a replacement for polysulfide, syntactic RTV was proposed if suitable processes could be developed to improve its bondability to aluminum and epoxy encapsulant.

Using conventional techniques, cured RTV rubber normally is unbondable. Plasma treatment of hardware seems to be the most promising alternative to chemical treatment. Processing parameters for an activated gas plasma, such as gas type and flow rate, treatment time, and magnitude of applied electromagnetic field, were studied to determine the best conditions for production use. A method was sought to bond RTV to the walls of a machined aluminum casting and to provide a surface on the RTV which would accept encapsulation with epoxy microballoon.

PRIOR WORK

Work at Sandia Laboratories¹ has shown that the bondability to cured silicone RTV 630 can be greatly enhanced by treating the RTV in an activated oxygen plasma. In the Sandia study, RTV wafers were exposed to an oxygen plasma for 10 minutes and then bonded to aluminum test plugs. After being cured, the samples were subjected to a tensile pull at 0.13 cm/minute until fracture. In the untreated sample, fracture occurred at less than 67.2 kPa. Plasma treated samples, however, required approximately 3.36 MPa to fracture the adhesive bonds, indicating that an activated oxygen plasma improves bondability to an RTV.

The contact angle of a drop of reagent grade glycerin has been used to measure the surface energy change of treated RTV silicone and to give a relative indication of surface wetting. Figures 1 and 2 illustrate the problems of poor bonding between epoxy encapsulant and RTV.

ACTIVITY

Plasma, sometimes referred to as the "fourth state of matter," can be generated when an outside energy source electronically

Figure 1. Voids and Separations Between the Encapsulant and Aluminum Walls in Cured Epoxy Encapsulant Over an RTV Slush Coating

Figure 2. Gross Separation Between Cured Epoxy Encapsulant and RTV Silicone Elastomer Coating

excites neutral gas molecules. When an inert gas is excited at the atomic level and partially breaks down to form ions, electrons, and neutral species, it forms a plasma. These ions and radicals can break down chemical bonds on surfaces, resulting in CASING (Crosslinking by Activated Species of INert Gases).

Although the physics of CASING is not clearly understood, the breakdown and crosslinking promote increased wetting of surfaces and increased bondability between two materials. Plasmas can be generated at room temperature in a partial vacuum by applying an electromagnetic field to a gas. Although the plasma is quite active chemically, it normally is considered to be electrically neutral. The combination of low temperatures and neutrality makes the plasma-treatment process especially appealing for use in electronic assemblies which contain heat- and electrostatic-sensitive semiconductor components.²

Equipment

The equipment (Figure 3) used for this investigation is a plasma etch system made up of three main assemblies: a reaction chamber, approximately 660 mm in diameter by 910 mm long, in which treatments take place; an rf generator, which generates a continuously variable power level rf signal, 0 to 500 W output at a frequency of 13.56 MHz; and a controller, which couples the power to the chamber and allows the operator to control gas flow, treatment time, and other conditions. The machine is equipped with a vacuum pump to lower the reaction chamber pressure to 26 Pa (0.2 torr) where the plasma treatment cycle begins. Two gases, oxygen and argon, are controlled and mixed in the controller. The gases are applied to the reaction chamber at flow rates of approximately 250 cc/minute (oxygen) and 1000 cc/minute (argon).

Test Method

A drop test using deionized water provided data on plasma effectiveness. A number of common processing materials used in production, such as polyethylene, Teflon (TFE), nylon, and sheet rubber, were used in the drop test (Teflon is a trade name of Du Pont Corporation). Bonding to these materials is generally considered to be difficult, if not impossible. The mechanism of effectiveness of a plasma in preparing a surface for bonding is determined by the plasma's ability to break down surface bonds and form CASING products. One theory of bondability is that an adhesive must thoroughly wet a surface to bond to it. Relative surface wetting was determined indirectly by measuring the diameter of a constant volume drop of deionized water. In this way, a relative indication of plasma treatment effectiveness could be determined quickly and easily for a number of different applied conditions.

Figure 3. Plasma Etch System

The data from the water drop tests are graphically represented in Figures 4 through 6. Larger drop diameters indicate lower contact angles and greater surface wetting. The data taken in the drop tests indicate a significant relationship between surface wetting, treatment time and chamber pressure. Using a chamber pressure of 65 Pa and a power of 500 W, the plasma treatment process appears to be essentially complete after the surfaces have been treated for 20 minutes (Figure 4). That is, any further treatment will have little beneficial effect on increasing wettability. When the chamber pressure is increased to 85 Pa, the process time increases to 25 minutes (Figure 5); and at 98 Pa chamber pressure, the process takes approximately 30 minutes to reach its asymptote. There was no evidence to suggest that treatment times could be decreased by using different power levels; although surface wetting may be highest when materials are treated at maximum rf power. As can be seen from the figures, Teflon was not wettable at any of the times or pressures tested.

A butt pull test was performed to apply the bondability data collected from the water drop test in a simulated unit environment. Tensile adhesion specimens were formed by bonding 29 mm diameter aluminum plugs with RTV silicone rubber. After cleaning and sanding, the test samples were exposed to an argon plasma for 20 minutes at a power of 500 W and a pressure of 65 Pa. Silicone RTV metal primer was applied before plasma treatment, after it, or both, depending on the sample being tested. After the rubber was cured, the samples were pulled at 0.13 cm/minute until they fractured (Table 1).

In the samples that were plasma treated after priming, fracture was in the RTV itself; while in the samples that were not plasma treated, fracture occurred at the bond line between the aluminum and the RTV.

As a final test of the plasma process, three dummy assemblies were plasma treated, encapsulated, and subjected to required environmental extremes of temperature and humidity. A summary of the plasma treatments of the units follows.

Unit 1

- Prime bare aluminum walls of housing with primer.
- Plasma treat housing in pure argon at 91 Pa and 500 W for 20 minutes.
- Slushcoat with RTV.
- Plasma treat as above.
- Encapsulate with epoxy microballoon.

Figure 4. Plasma Treatment of Surfaces: 100 Percent Argon

Figure 5. Plasma Treatment of Surfaces: 9 Percent Oxygen, 91 Percent Argon

Figure 6. Plasma Treatment of Surfaces: 20 Percent Oxygen, 80 Percent Argon

Table 1. Results of Pull Testing of Plasma-Treated Specimens

Sample		Fracture Load (kg)	Normalized Load (kg)*
1	Prime RTV	65.4	71.3
2	Prime, plasma treat, RTV	107.1	112.6
3	Plasma treat, prime, plasma treat, RTV	130.8	130.8
4	Plasma treat, prime, RTV	68.1	70.8

*Normalized load = (surface area) (fracture load) /
(surface area - surface void areas)

Unit 2

- Prime aluminum.
- Slushcoat with RTV.
- Plasma treat in pure argon at 91 Pa and 500 W for 10 minutes.
- Encapsulate with epoxy microballoon.

Unit 3

- Prime aluminum.
- Plasma treat in 80 percent argon, 20 percent oxygen at 91 Pa and 500 W for 30 minutes.
- Slushcoat with RTV.
- Plasma treat in 80 percent argon, 20 percent oxygen as above.
- Encapsulate with epoxy.

After environmental testing, the units were X-rayed from three mutually perpendicular axes to see if voids in the materials or separations between encapsulant and RTV had been formed during the encapsulation process. The units then were cross-sectioned and examined.

In all three cases, the bond between the aluminum and the RTV was satisfactory. The RTV could be separated from the walls of the housing only by vigorous scraping, which caused the RTV to lacerate. Several small voids, probably attributable to trapped air and the encapsulation process itself, appeared in the cured epoxy encapsulant in each of the three units. No separations between the aluminum walls and the RTV or between the RTV and the epoxy could be found.

Core samples approximately 19 mm diameter were drilled from each of the three test units. The samples were examined with a 25-power microscope for cracks and separations at the aluminum-RTV and the RTV-epoxy interfaces. Attempts were made to fracture the materials at their interfaces using mechanical prying.

Samples were removed intact from Unit 1. Probing with a dental pick caused the epoxy to separate easily from the RTV. The separation between the RTV and the epoxy was clean, implying that the RTV-epoxy bond was weaker than the strength of either the RTV or the epoxy.

Samples were removed intact from Unit 2 and examined in a similar manner. When forced with moderate finger pressure, the epoxy separated from the RTV. As in the first unit, the RTV in Unit 2 was securely bonded to the walls of the housing.

Three test plugs were drilled from Unit 3. Two of the three plugs were removed intact and were forced with the fingers to see if the epoxy could be separated from the RTV. The epoxy was securely bonded to the RTV and could not be separated with finger pressure. The test plugs were halved on a band saw, but the epoxy still remained bonded to the RTV. Finally, the epoxy was struck with a hammer and a chisel and broke away cleanly from the RTV.

Theoretical Considerations

The data taken in the water drop test indicate a significant relationship between wettability (drop size) and chamber pressure and treatment time. For a given input power, it has been shown that "completion" of the plasma process--maximum wettability--is a function of treatment time.

This phenomenon is explained in terms of average kinetic energy, $\langle \epsilon \rangle$. A gas breaks down electronically in an electromagnetic

field when the rate of ionization overcomes the loss of electrons created by thermal effects, molecular collisions, and other processes. The average kinetic energy $\langle \epsilon \rangle$ created by the applied electromagnetic field $\bar{E}$ causes these electrons to collide with neutral gas molecules, forming new species, such as free radicals and ions. These species are highly reactive and unstable, and the plasma quickly degenerates back into the gaseous state when $\bar{E}$ is removed.

Several researchers have quantitized $\langle \epsilon \rangle$ by solving the Boltzmann equation, which defines the net rate of electron transfer from an incremental volume in phase space. Most importantly, it can be shown that $\langle \epsilon \rangle$ is a function solely of E/p , where E is the magnitude of the applied electromagnetic field vector $\bar{E}$, and p is the chamber pressure. When $\langle \epsilon \rangle$ is plotted versus the extent of ionization of a gas (due to collisions, thermal and other effects), a series of distinct energy levels appear, dependent only on E/p . These energy strata, which are nearly independent of the degree of ionization, are lowest at lower values of E/p and increase as the ratio of the magnitude of $\bar{E}$ to pressure increases.

Since $\langle \epsilon \rangle$ is a function of average electron velocity, at high values of E and low values of p , the velocity of the free electrons will be high, and collisions with neutral molecules will be numerous and vigorous.

The magnitude of $\bar{E}$ is dependent on the geometry of the chamber and the amplitude of the applied electromagnetic source (Figure 7).

$$V_o = \sqrt{PZ_L}$$

$$|\bar{E}| = \left[V_o / \ln(b/a) \right] (1/r) \text{ for } a < r < b$$

$$= 0 \text{ elsewhere}$$

$$|\bar{E}|_{\text{rms}} = E_e = \left[V_o / \ln(b/a) \right] (1/r)_{\text{rms}}$$

$$\approx V_o \text{ for } b \approx a$$

The actual value of E_e will vary with frequency (ω is fixed constant at 8.52×10^7 radians/second in this machine), but when $\omega^2 \ll \nu_m^2$ (the natural collision frequency of the gas molecules in the chamber), E_e is approximately equal to $V_o/\sqrt{2}$.

It was observed, for example, that at a chamber pressure of 65 Pa, using pure argon, a power level of 70 W was required

Figure 7.. Schematic of Plasma System

to ignite a self-sustaining plasma. Using the above equations, it is possible to calculate E_e in the chamber.

The load impedance Z_L of the reaction chamber varies with type of gas, pressure, and other conditions, but a typical value is $Z_L = 12 - j62 \Omega$ ($63.2 \angle -79^\circ$). If there is a 3dB power loss across the coupler, E_e can be calculated as

$$\begin{aligned}
 E_e &= V_o / \sqrt{2} \\
 &= \sqrt{\frac{70}{2} (63.2)} \\
 &= 33.2 \text{ V/cm}
 \end{aligned}$$

At a pressure of 65 Pa, $E_e/p = 0.51\text{V/cm-Pa}$. This value compares favorably with $E_e/p = 0.66\text{V/cm-Pa}$ predicted by theoretical data.^{3, 4}

Recommendations for Production Use

Oxygen gas, added to the argon medium, increased bondability noticeably over argon alone. Oxygen is a highly reactive gas and easily forms radicals and other products which promote increased bondability on the surfaces of the materials tested. However, at

low pressures, oxygen presents a potential safety hazard, because of the possibility of fire and explosion. Oxygen may be used safely, however, if its concentration is limited to no more than 21 percent by volume.

After the plasma treatment process is complete, the surfaces are ready for bonding. The reaction products on the surface of the process materials are only a few microns deep. These reaction products are relatively stable over time, but parts which have been plasma treated must be handled carefully to prevent the reaction products from being wiped off with the fingers.

Based on test data and information collected, the following guidelines are recommended for plasma treating syntactic RTV for production.

- All pouring and slushcoating should be started no later than 30 minutes after the plasma treatment is complete. Although there is evidence that plasma treated surfaces degrade only slightly over several days, airborne contaminants can affect the quality of bonds adversely.
- Plasma treated surfaces should not be touched after treatment. The cross-linking products on the surfaces are very thin and easily can be removed by touching with the fingers or by other slight rubbing.
- The cured RTV surfaces should be treated in a 20 percent by volume oxygen/80 percent by volume argon plasma at a pressure of 91 Pa for 30 minutes at a power of 500 W.
- Units should be placed open side up in the reaction chamber.

An additional plasma treatment immediately before the RTV slushcoat will enhance the bond between a primed aluminum surface and the RTV. In all tests, when primed aluminum surfaces were not plasma treated, the aluminum RTV bond was satisfactory; however, the addition of a plasma treatment may be used to enhance the bond where extra assurance against RTV separation is required.

Plasma treatment data should be collected on a continuing basis. Production process samples can be treated along with production parts. Current data can then be compared with existing data and refinements made in the process. Collection of production test samples also would enable Engineering to sample the quality of surface treatment without resorting to destructive testing.

ACCOMPLISHMENTS

A production process to treat a slush-coated part in an rf plasma was developed and evaluated. The resulting process provides satisfactory bonds between syntactic RTV and an epoxy encapsulant, allowing the part to operate within its specified environmental extremes. The process is safe for personnel to use in production environments and is time efficient.

FUTURE WORK

No additional plasma treatment work is planned on this process. Process repeatability, treatment verification, and measurement of plasma uniformity covering a range of general product applications are being studied. Effort on that project will be directed at evaluating flat cable adhesives and at selecting an encapsulant resin for use on cable assemblies.

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