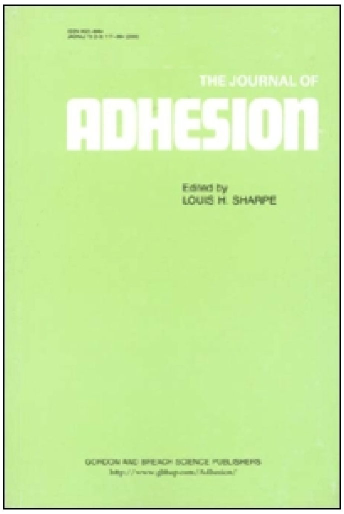

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Bondability of RTV Silicone Rubber†

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A method of improving the bondability of cured RTV silicone is described. The method is based on the use of excited oxygen plasma in a glow discharge chamber. Surface characteristics and bond strength, before and after treatment, are reported. Significance of the results in the light of present adhesion theory is also discussed.

INTRODUCTION

This report describes a method of preparing a bondable surface on a vinyl addition RTV silicone rubber using an activated oxygen plasma generated by a Tracerlab LTA600L low temperature asher.

Ordinarily, cured two-part RTV silicones are not bondable with usual organic adhesives such as epoxies, neoprenes, etc. However, since RTV silicones have ideal properties for applications such as stress relief interlayers between rigid substrates, intermittent attempts have been made in the past to develop bondable surfaces on the cured RTV. These attempts have involved primarily the use of various silicate or silane primers. Success has been marginal, with failures being primarily in adhesion at 100–150 psi using tensile adhesion specimens.

The activated oxygen plasma technique used in this investigation was successful in that cured RTV silicone rubber exposed to this environment was easily bonded with an epoxy adhesive. When tested to failure, the bond area remained intact with failure being restricted to tearing in the RTV silicone. The success of the activated oxygen plasma technique led to a study of the surface characteristics of the RTV silicone both before and after

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activated oxygen treatment. The significance of the surface characteristics in terms of prevailing theory is also discussed.

MATERIALS

Silicone rubber

The silicone rubber used in this study was a vinyl addition type designated General Electric RTV 630. It was degassed at < 5mm Hg for 5 minutes and cast on a machined aluminium form, wiped with reagent grade methyl ethyl ketone to remove conventional contaminants such as machine oil, particulate matter, etc. No release agents were used on the aluminium surface. The form was leveled to give a uniform slab of RTV 630 about 0.120 inch thick, and the RTV was cured in a circulating air oven at 160°F ± 5°F for 5 hours. The slab was easily removed from the form and protected on both sides by a commercially available clean paper to minimize handling and contamination while $1\frac{1}{8}$ inch discs were punched from it. The paper used was checked for silicones by washing with benzene. The benzene extract was dried on the IR absorption crystal and examined by infrared absorption. The extract curves were not significantly different from that of the benzene itself, indicating that no silicone was present.

Adhesive

The adhesive used to bond the treated RTV is a standard Sandia formulation[1] as follows:

Sandia Corporation SRIR
(Semi rigid inspectable resin)

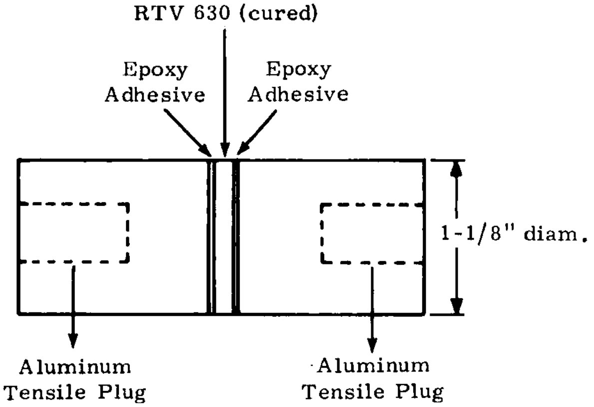
	PBW
Epon 828 (Shell Chemical Company)	100
HHPA (Hexahydrophthalic Anhydride)	76
P 11-80 (Dow Chemical Polyol)	66
BDMA (Benzyl Dimethyl Amine)	2
Neo Novacite (Silica Filler from Malvern Minerals Company, Hot Springs, Arkansas)	488

The silica filler (neo novacite) is used to give a more easily processed paste.
Cure—24 hours at 160°F ± 5°F

The above formulation was selected because it cures at an intermediate temperature (165°F) and since the cure is primarily an anhydride one, there is less likelihood of adverse reaction with the RTV silicone. Previous experience at Sandia indicated that silicones may react with amines.

Test Specimens

Tensile adhesion specimens were formed by bonding the $1\frac{1}{8}$ inch diameter silicone rubber discs to aluminium tensile adhesion plugs with the SRIR epoxy adhesive (Figure 1).



The aluminum surface was sandblasted prior to bonding.

Test Condition - Pulled in tension at 0.05"/min.

FIGURE 1 Bonded Sample.

EXPERIMENTAL PROCEDURE

The RTV discs were evaluated, either before or after exposure to the glow discharge plasma, for contact angle, IR absorption and bondability. No disc was used for more than one evaluation.

RTV glow discharge treatment[2]

The RTV discs were exposed to the plasma in the glow discharge chamber for 10 minutes on each side, at a power level of 250 watts with oxygen pressure regulated at 1 mmHg. The plasma environment is an RF-sustained discharge in oxygen. The capacitance effect between the plasma and the RTV silicone surface has a potential difference of about 100 volts. The RTV discs were stored in glass-covered glass jars before and after treatment until they were bonded or checked for contact angle or for surface extractable resin.

Bonding procedure

The bonded specimens, with both treated and untreated discs, were prepared as shown in Figure 1 with the SRIR adhesive.

Contact angle specimens

Contact angle determinations were made on the discs, before and after glow discharge treatment, using reagent grade glycerin. The specimens for these measurements were prepared at the same time and under the same conditions as the bond test specimens. Contact angles were obtained primarily to serve as an indication of change due to the glow discharge treatment, and were determined about five minutes after the drop of glycerin was placed on the RTV surface when an equilibrium condition seemed to exist with no further change in contact angle occurring.

Infrared analysis specimens

The specimens used for infrared analysis were prepared as above at the same time and under the same conditions as the bond specimens. In order to test for the presence or absence of low molecular weight silicone fractions on the surface of the specimens, both surfaces of the silicone rubber discs were washed with two-second applications of benzene. The solution was concentrated and allowed to dry on the sodium chloride crystals used for infrared absorption analysis. Silicone rubber discs were analyzed in this manner both before and after treatment in the glow discharge chamber. For ATR infrared analysis the silicone rubber discs were pressed against both sides of the ATR crystal.

RESULTS

The results as shown in Table I indicate that the glow discharge treatment was very effective in providing a bondable surface. With no treatment, the bond strength of the epoxy adhesive to the RTV silicone was negligible (< 10 psi). After treatment, the bonded specimens failed at about 500 psi with failures being cohesive in the RTV silicone rubber. The evaluation included aging studies of the bonded specimens over a period of eight weeks. The aging conditions consisted of storage in glass containers at ambient laboratory temperature.

Contact angles on the cured RTV with glycerin were 108–112° before the glow discharge treatment. Contact angle measurements after the treatment ranged from 87° to 94°. The epoxy contact angles, using the SRIR formulation with no filler, decreased from 66° to 52° after exposure to the glow discharge. Both the glycerin and the epoxy contact angles indicated that the RTV surface was being altered by the glow discharge treatment to give a more wettable surface, i.e. a surface with a greater surface tension.

TABLE I

Characteristics of cured RTV 630 treated and untreated in activated oxygen plasma

Tensile adhesion strength (psi)[a,b]

Untreated	Treated and aged after bonding				
	Control	1 week	3	6	8
< 10	529[c] (2.5)[d]	533 (1.7)	517 (2.9)	467 (9.6)	441 (12.8)

Contact angle on cured RTV surface (degrees)

	Untreated		Treated		
Liquid	Initial	1 month	Control	1 week	3 weeks
Glycerin	108–110	112	87–90	94–95	92–94
Epoxy[e]	66	—	52	—	—

[a] All failures 95–100 percent cohesive in RTV 630

[b] Specimens consisted of aluminum tensile plugs bonded to RTV 630 as in Figure 1.

[c] All strength values are average of five test results.

[d] Figures in parentheses are coefficient of variation C_v

$$C_v\% = \text{Coefficient of Variation} = \frac{S}{\bar{X}} \times 100$$

S = Mean deviation

$\bar{X}$ = Average tensile strength (psi)

[e] Epoxy used for contact angle was Sandia SR1R without filler as described in the text.

During the eight weeks, all failures were 95–100 percent cohesive in the RTV 630. The decrease in strength value from 529 psi to 441 psi along with increase in coefficient of variation (C_v) indicates some instability in the RTV 630 rather than a change in bond strength.

The infrared absorption studies of the RTV 630 surfaces are shown in Figure 2. Curve 1 is of the benzene dried on the crystal to insure that the source of the benzene (a polyethylene squeeze bottle) was not contaminated with siloxanes. Curve 2 is of the crystal (NaCl) alone. Curves 3 and 4 are the infrared absorption curves characteristic of extracts obtained by washing the treated glossy side and the two sides of the treated RTV silicone rubber discs, respectively. The glossy side was evaluated separately to see if the characteristic of the free surface differed from the sum of the two surfaces. As is evident in Curve 3, there was no difference in surface characteristics.

Curve 5 is the absorption curve of the untreated RTV silicone rubber disc. These curves indicate that extractable dimethyl siloxane fluid was present at all times on the RTV silicone rubber surface. This material did not interfere with bond formation as might be expected if a "weak boundary layer" were the overriding factor in adhesion failure phenomena. The tests to determine the presence or absence of extractable surface siloxanes were repeated several times in the course of the eight-week study on RTV discs which were aged at the same time as the bonded discs. The extractable siloxane was always present.

As an additional check on the presence of extractable material on the surface of the RTV silicone, an ATR absorption analysis was made by pressing the treated RTV silicone rubber to both sides of the ATR (KRS5) crystal. The characteristic siloxane curves resulted. After the RTV silicone rubber was removed from the two sides of the ATR crystal, another analysis showed that sufficient siloxane fluid from the RTV silicone had transferred to the crystal to again give a characteristic siloxane absorption curve (see Figure 3).

So that some idea of the amount of siloxane material extracted from the RTV silicone surface could be obtained, the benzene washings of both sides of an RTV disc (2 square inches) were dried and weighed on the sodium chloride crystal. The amount of siloxane fluid extracted was of the order of two tenths of a milligram.

DISCUSSION

The presence of fluids, either as low molecular weight fractions or as contaminants, in materials such as polyolefins has long been considered the reason that these materials are difficult to bond. This reasoning resulted in the "Weak Boundary Layer" (WBL) theory first put forth by Bikerman[3] in 1959. This theory states that these weak fluids form continuous layers which isolate the adhesive from the adherend and thereby cause bond failures at the interface. Treatments to improve adhesion, whether chemical in nature as in ASTM D-2093 or in the form of activated gases as in the CASING technique,[4,5] are said to permanently remove this WBL, although evidence verifying that the WBL has in fact been removed seems to be lacking. Henderson[6] estimates that such a WBL, if removed, would reestablish itself by permeation or synerisis within 50 hours. In the work described in this report, extractable fluid was identified as being on the surface within one hour of the treatment.

The significance of the work described in this report as it relates to the WBL theory is that cured RTV silicones are considered unbondable by usual adhesives such as epoxies. At the same time, they do contain low molecular

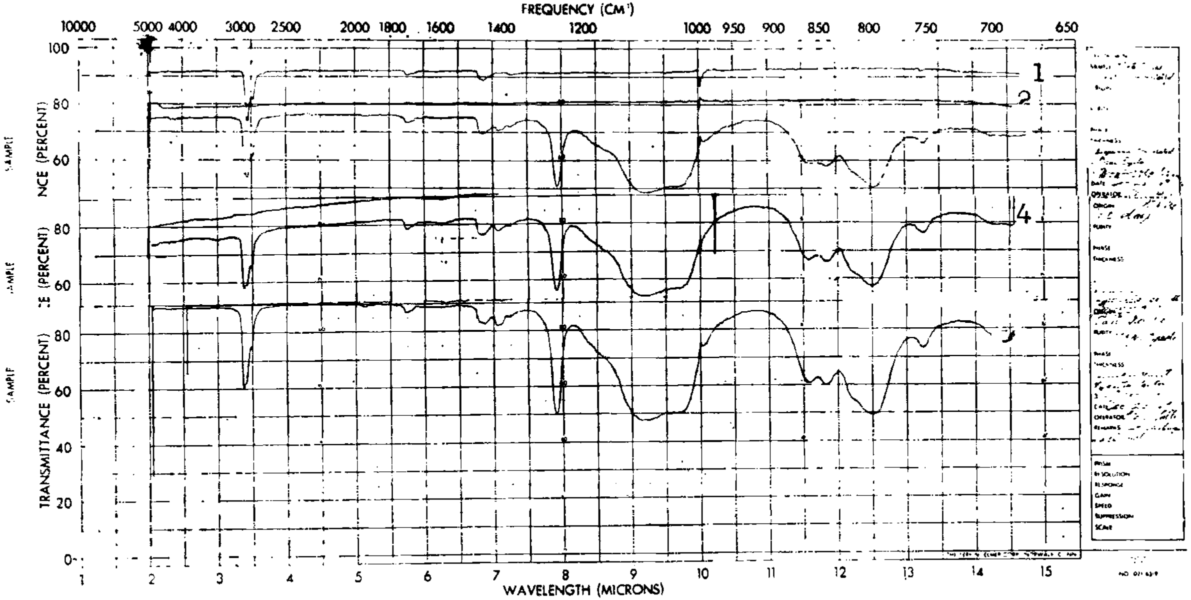


FIGURE 2

1. Benzene used to wash the RTV silicone surface (two seconds squirt per side)
2. Crystal used for absorption specimen
3. Treated RTV silicone glossy side (exposed to air) extract
4. Treated RTV silicone extract (both sides)
5. Untreated RTV silicone extract

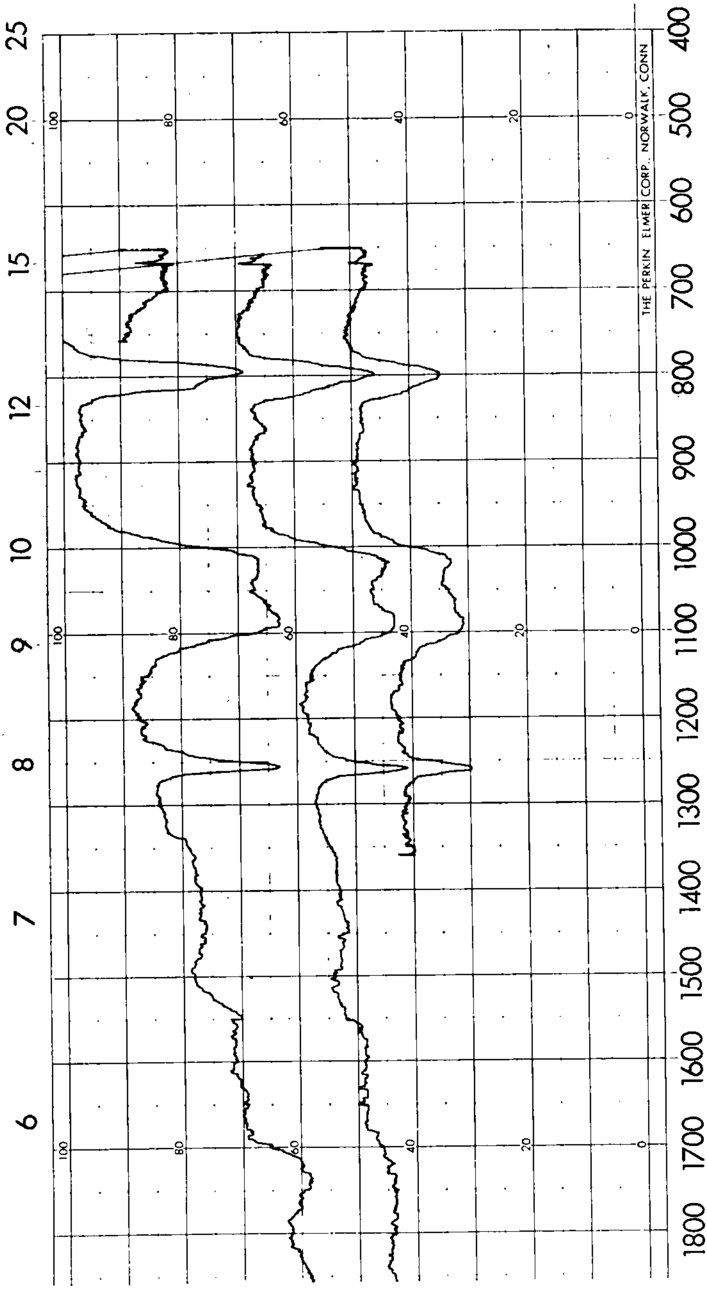


FIGURE 3 ATR curves of treated RTV 630 imprint

weight liquid fractions of linear and cyclic polysiloxanes. Thus, the RTV silicones fit the description of a WBL adherend. By both surface washing and ATR infrared absorption techniques, the low molecular weight polysiloxanes were identified as being present on the cured RTV surface both before and after the oxygen plasma treatment. Since the low molecular weight polysiloxanes and RTV are related species, the former should be uniformly distributed throughout the cured RTV. After plasma treatment, the low molecular weight polysiloxanes might very well be preferentially adsorbed on the activated sites since, according to the energetics theory of adhesion,[7] the solid should have a greater surface tension than the liquid to achieve wettability. On the basis of the decreased contact angles, the treatment has increased the surface tension of the solid.

Thus, in order to bond successfully to the treated RTV, it would be necessary for the epoxy adhesive to desorb the siloxanes from the activated sites in order to be preferentially adsorbed and thereby form a successful bond.

From this, it is logical to conclude that the bonding mechanism for the materials used in this investigation is dependent primarily on the treatment of the substrate. Removal of the WBL, which is necessary to achieve adhesion according to Schonhorn, does not occur. On the contrary, the bond is formed in the presence of what would be called the WBL material, i.e., the low molecular weight polysiloxanes. Therefore, the bonding mechanism probably includes desorption of the polysiloxanes by the more polar epoxy adhesive and preferential adsorption of the adhesive on the activated sites. Displacement or desorption of one liquid by another from a high energy surface has been shown to be quantitative in nature by Hackerman, *et al*,[8] in their work on heats of immersion of alumina first wet with hexane and then immersed in water.

CHEMISTRY

Cure or degree of polymerization of an RTV silicone, as in other polymer resins, is a relative matter depending on time and temperature. A vinyl addition RTV silicone such as is described in this report may show a weight loss varying from 0.01 percent after 24 hours at 165°F to 1.0 percent after 24 hours at 400°F. This weight loss is due to unreacted linear and cyclic dimethyl polysiloxanes[9,10] of varying molecular weights. The linear polysiloxane may or may not have terminal vinyl groups while the cyclic and cyclized polysiloxanes would normally not include terminal reactive groups such as vinyls.

A cure of five hours at 165°F, such as was used for the work reported here, is an intermediate but standard cure for many applications. Since the RTV silicone is not completely cured, it will contain unreacted vinyl groups. In an activated oxygen glow discharge plasma the activated oxygen would have no difficulty in permeating through any unreacted surface layer of linear or cyclic polysiloxanes to add onto the unreacted vinyl groups of the polymer. Silicones are very permeable to most gases including oxygen.[11] The activated oxygen would react preferentially with the vinyl groups rather than the ring structured polysiloxanes. Thus, the low molecular weight unreacted surface layer would remain virtually unchanged to play the role of Weak Boundary Layer.

The effect of oxygen plasma on polymers in general and peroxide cured silicones in particular are discussed in detail in Refs. 12 and 13, respectively.

These studies involved exposures of hours rather than the ten to twenty minutes of this study. The studies were not concerned with the presence or absence of low molecular weight fractions on the material surfaces. Neither were these studies concerned with the effect of these fractions on adhesion.

Probably some oxidation resulted from the ten to twenty minute exposures of this study as evidenced from the change in contact angles and the drastic increase in adhesion. However, this was not sufficient to be detected by infrared analysis. This oxidation does not appreciably affect the presence of extractable siloxane material after the treatment and does not change the conclusions of this report.

CONCLUSIONS

On the basis of the above results, it would seem that, at least for RTV silicone rubber, treatment of the adherend is the basic and dominant factor in improving bondability of the adherend. The presence of extractable material at the adherend surface is a secondary and possibly negligible factor in the bonding process. It need not be removed to achieve adhesion as postulated by Schonhorn. The discharge does not remove any significant amount of surface extractable siloxane resin and this material is present at the time the bond with the epoxy adhesive is formed. Since the extractable material does not interfere with the bond formation, the mechanism of bond formation must include desorption of the siloxane resin from the RTV surface by the epoxy with subsequent adsorption of the epoxy on the adherend. On the basis of the surface energetics theory of adhesion, the ability of a liquid to be adsorbed on a solid surface implies that the critical surface tension (γ_s) of the solid is greater than the surface tension of the liquid (γ_l), i.e.

s = solid adherend

$$\gamma_s > \gamma_l$$

l = liquid adhesive

Thus the improvement in adhesion of the epoxy adhesive coupled with decrease in contact angle of the glycerin and epoxy suggests that the surface tension of the RTV has increased due to the excited oxygen treatment.

It is doubtful that any of the treatments used to improve adhesion to polyolefins and other polymers permanently remove weak boundary layers. Accordingly, it is believed that the presence or absence of "weak boundary layers" or low molecular weight inclusions is a secondary or negligible factor in the bonding process. The treatment of the polymer substrate to make it more bondable is the important factor.

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