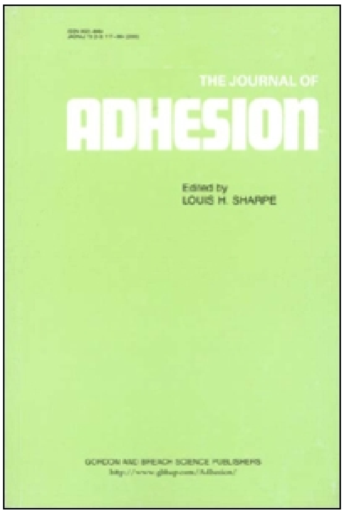

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The Stability of Adhesive Bonding Between Silicone Rubber and Alumina for Neural Prostheses

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Thermodynamic considerations using surface tension data involving model compounds show that the adhesive bond between a silicone rubber and an alumina substrate is not stable in the presence of water if only dispersion forces are effective. The observed stability is due to chemical links which form before the rubber crosslinks thus removing reactivity.

INTRODUCTION

The integrity of certain prosthetic devices depends upon the ability of the encapsulating silicone rubber to form an adhesive bond with the circuit board of the electronic implant used. This substrate is commonly an alumina tile. If there is no bond, or if the bond fails, then water will accumulate at the interface and the electrical circuit fails. The study reported in this paper examines the conditions necessary to produce a bond resistant to water, shows that it is dependent on the nature of the materials employed and indicates methods of achieving satisfactory bonding that will survive *in vivo.*

MATERIALS

Substrate alumina

The alumina substrate (Coors substrate A596F) used in the preparation of the neural prostheses with which we were concerned is manufactured by sintering 95 parts of alumina powder mixed with 5 parts of a powdered calcium magnesium silicate glass at 1700°C. After firing, the alumina powder is found dispersed as particles 2–4 μm in diameter in a glass matrix. From the viewpoint of surface energetics or chemical reactivity, the surface would be one of glass rather than of aluminium oxide.

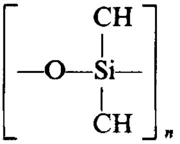
As received, whatever the ultimate nature of the surface, it would have been contaminated both by adsorption from the atmosphere and by handling, however careful.

RTV silicone rubber

The silicone used for non-implanted experimental prostheses by associated colleagues has been an electrical grade Dow Corning 3140, a one part, room temperature vulcanising silicone rubber. This has been used as an encapsulant as it does not release acetic acid to corrode metals, has a convenient viscosity for completing the insulation and separate encapsulation of the minute components of the circuitry, and has apparently good adhesion properties. It cures by moisture activation but in so doing releases an alcohol instead of acetic acid. For implanted prostheses, this electrical grade of silicone rubber is in turn coated with a thin layer of a medical grade of silicone rubber which does not adhere well to the substrate.

Silicone fluids

For certain experiments in which crosslinking of the silicone rubber was undesirable, it was necessary to substitute for the silicone rubber a silicone fluid. This seemed at first sight to be an ideal model for silicone rubber having identical chemical structure made of repeating dimethyl siloxane units but without the reactive end groups responsible for crosslinking. The fluids investigated were Dow Corning 200/20 and 200/1000. As is shown later, these fluids contain small but significant amounts



$$\left[-O-\overset{\displaystyle CH}{\underset{\displaystyle CH}{Si}}- \right]_n$$

of hydroxyl groups which lead to surface reactivity, hence they are less satisfactory as models than had been anticipated and as alternatives trimethylpentane and di-isopropyl ether were tried.

THEORY OF ADHESIVE BONDING OF RUBBER TO SUBSTRATE

Theory of bonding and of displacement by water

If the adsorption of the rubber to the substrate is reversible in the thermodynamic sense that the phases which have been brought together can be separated without undergoing chemical change, then adhesion is said to be physical in nature. Such separation may be accomplished by temperature change, or dissolution of the polymer phase if it is still soluble or by displacement with some other liquid more strongly adsorbed to the substrate. An alternative and desirable mechanism is that the adsorption should be a type that is irreversible by the agencies which can affect physical adsorption. Such alternative mechanisms involve the formation of localized chemical bonds between elements of the substrate surface and functional groups of the superimposed rubber and is frequently referred to as chemisorption.

The situation regarding physical adsorption can be investigated by experiments involving the wetting of surfaces by liquids in order to estimate the surface and interfacial energies involved. The investigation of chemisorption is more problematic and its inference largely depends on the failure of physical adsorption to explain the observed facts.

Conditions for stability of physical adsorption

Considering a system which consists of two phases in intimate contact submerged in a liquid, the free energy will be γ_{12}, the interfacial free energy of the two surfaces. If these two phases are separated to give two new surfaces each now in contact with the liquid, the free energy will be $(\gamma_{1l} + \gamma_{2l})$. The change of free energy will be given by:

$$\Delta W = \gamma_{1l} + \gamma_{2l} - \gamma_{12} \tag{1}$$

The thermodynamic stability of the system will depend upon the sign, whether positive or negative, of ΔW.

If one is considering the adhesion of two materials in the presence of water, then if ΔW is positive the adhesion will be sustained and water will not displace the one material from the other. However, if ΔW is negative then the adhesion will not be stable and water will in time displace the one material from the other and will be preferentially adsorbed. It must, however, always be remembered that these are conditions for thermodynamic stability and do not involve the kinetics or rate at which the process will occur.

To apply these conditions to the particular system under consideration, silicone rubber, alumina substrate and water, Eq. (1) becomes:

$$\Delta W = \gamma_{A-W} + \gamma_{S-W} - \gamma_{A-S} \tag{2}$$

where the subscripts represent

A–W	alumina to water
S–W	silicone rubber to water
A–S	alumina to silicone rubber.

This system might be considered initially with the silicone rubber in its liquid, unvulcanised state in the following way.

Consider the three phase equilibrium in Figure 1 where the contact angle measured in the water is ϕ. Using the same subscripts and substituting surface tensions for surface free energies, following Young, Eq. (3) gives the balance of forces for equilibrium

$$\gamma_{A-S} = \gamma_{A-W} + \gamma_{S-W} \cos\phi \tag{3}$$

and combining these with Eq. (2) gives

$$\Delta W = \gamma_{S-W}(1 - \cos\phi) \tag{4}$$

It must be recognised that as ϕ approaches zero so does ΔW, and the limit where $\Delta W = 0$ represents the limiting condition of stability. If water displaces the silicone a three phase equilibrium does not exist and Eqs (3) and (4) are not applicable. In this case the angle ϕ will

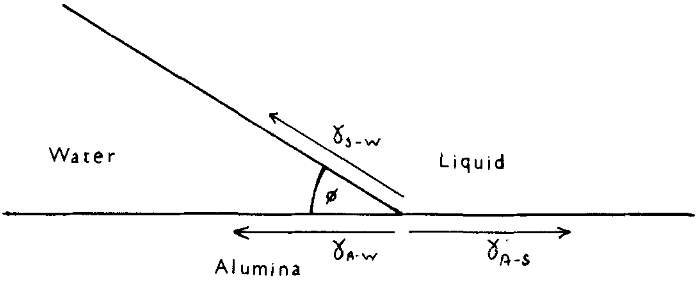


FIGURE 1 Three-phase equilibrium of two liquids and a solid surface.

be zero and no inference can be drawn about the negative magnitude of ΔW

However since the liquid, unvulcanised silicone rubber reacts with water, an unreactive liquid has to be used as a model in experimental measurements. A silicone liquid was used initially although it was found less satisfactory than had been anticipated and alternative organic compounds were also used.

If liquids are used as complete models for the silicone rubber, then the interfacial tension (γ_{S-W}) and the contact angle (ϕ) can be directly measured and thus Eq. (4) is conveniently employed. However, its usefulness depends upon the extent to which the liquids are satisfactory as models.

Alternatively the interfacial tension (γ_{S-W}) between silicone rubber and water, which cannot be measured directly, can be calculated and this may be done by two methods, although these are not entirely independent of each other.

Starting again from a modified form of Young's equation gives:

$$\gamma_S = \gamma_{S-l} + \gamma_l \cos\theta + \pi \tag{5}$$

where γ_S represents the surface free energy of the solid silicone rubber in vacuum, and Π the amount by which this would be lowered by any adsorbed vapour, and l any liquid.

The interfacial free energy between two phases can be expressed in terms of the polar force and the non-polar dispersion force components of the surface free energy following Girifalco and Good[1]

$$\gamma_{1-2} = \gamma_1 + \gamma_2 - 2(\gamma_1^d\,\gamma_2^d)^{\frac{1}{2}} - 2(\gamma_1^p\,\gamma_2^p)^{\frac{1}{2}} \tag{6}$$

where the superscripts refer to the two components of the surface energies.

Combining Eqs (5) and (6) and putting silicone rubber as phase 1 and a liquid as phase 2 gives:

$$\tfrac{1}{2}\gamma_l(1+\cos\theta) = (\gamma_S^d\,\gamma_l^d)^{\frac{1}{2}} + (\gamma_S^p\,\gamma_l^p)^{\frac{1}{2}} - \pi/2 \qquad (7)$$

This can be expressed in the form

$$y = ax_1 + bx_2 + c \qquad (8)$$

By using a range of liquids and fitting Eq. (8) with a least squares technique π, γ_S^d, γ_S^p and hence $\gamma_S = (\gamma_S^d + \gamma_S^p)$ can be evaluated. The value of γ_S can now be used in two ways to give a value of $\gamma_{S\text{-}W}$.

If the polar term can be shown to be zero it may be used in a simplified form of Eq. (6) (i.e. omitting the polar terms) (referred to later as Calculation A).

Alternatively it may be used in Eq. (5) with a measure value of the contact angle of water on silicone rubber and the well known value of the surface free energy of water (referred to later as Calculation B).

It is also possible to calculate the interfacial tension between the model liquids and water using a simplified form of Eq. (6). A comparison of this calculated value with the experimentally observed value enables some estimate to be made of the extent of polar impurities.

SURFACE STUDIES

Alumina substrate

The surface properties of the alumina substrate were investigated by determination of Zisman's Critical Surface Tension γ_c.[2] This Critical Surface Tension is evaluated by extrapolation to unity of a graph of liquid surface tension against the cosine of the contact angle. The contact angle measurements were made using a reflecting type of goniometer[3] and a range of liquids of known surface tension.

A clean alumina surface has a high surface free energy and for such surfaces γ_c is largely meaningless, apart from being impossible to determine because of the absence of any liquids making a finite contact angle. Particularly since a properly cleaned alumina surface is completely wetted by water, it follows that any value of γ_c nominally ascribed to it must be greater than 72.2 mN.m^{-1}, Table I gives the values determined for the substrate material after various cleaning treatments. These show that the material as received, although apparently clean, is contaminated and resistant to cleaning. A solvent extraction followed by detergent mixture followed by water is by far the easiest laboratory method. The most probable contaminent is sebum deposited on the edges in handling and spreading over the surface. Once cleaned, substrates were handled only with cleaned forceps.

TABLE I
Critical Surface Tension of Alumina Substrate

Surface Preparation	γ_c mN.m^{-1}
Degreased in chloroform and then washed with high purity water until conductivity of washing water sinks to 18 Mohm.cm. (As used in experimental prostheses).	24.0
Additionally refluxed with trichloroethane.	41.0
Refluxed with trichloroethane for 1 hr, solvent removed by filter paper before washing by agitation in aqueous solution of 2½% trisodium orthophosphate and ½% Teepol (a sulphonated detergent) for 5 min at 40°C. Then washed in distilled water and dried in air at 70°C.	>72
Heated to 1200°C for 30 min.	>72
Treated in oxygen at 1 torr for 15 min with discharge voltage of 1 kV DC and a current of 130 mA.[4]	>72

Surface of silicone rubber

To obtain good flat sheets of the silicone rubber, the material, as supplied in a collapsible tube, was extruded into dry toluene to make a 30% solution. This solution was allowed to flow over a flat plate covered with Melinex with barriers around the edges. After evaporation of the solvent, sheets were allowed slowly to cure in air, but protected from dust, over a period always in excess of 30 weeks which was considered sufficient for thorough cure and loss of solvent. Contact angles with various liquids were measured on small pieces cut from the sheet. Results are given in Table II. The surface tensions of the wetting liquids were measured on a du Noüy torsion balance immediately before measuring the contact angle and the components γ_L^d and $\gamma_L^p$of the surface tension were proportioned from the published values to allow for the temperature of the laboratory.

Fitting Eq. (8) by least squares to the results from Table II and applying analysis of variance, it was shown that the increment to the variance explained by x_1 through the addition of x_2 was not statistically significant. The coefficient b is therefore zero and hence the polar component of the surface energy of the silicone rubber is similarly zero. With γ_s^p zero, Eq. (8) is replaced by

$$y = ax_1 + c \tag{9}$$

in which y, a and x_1 have the same connotation as before, and $c = \Pi/2$ where Π is the spreading pressure. Fitting Eq. (9) by least squares and analysing the variance shows c also to be zero; *i.e.* as expected, the spreading pressure on this low energy surface is zero.

Finally, the best value for γ_s^d and also for the total surface free energy of the silicone rubber is 28.30 mJ.m^{-2}.

TABLE II

Surface energy determination of silicone rubber

	Surface free energy of liquid[a] mJ.m^{-2}			
Wetting liquid	γ_l	γ_l^d	γ_l^p	cos θ
Hexadecane	29.8	29.8	0	0.90
1-Nitroethane	34.7	29.9	4.5	0.77
1,2-Dichloroethane	35.2	32.8	2.4	0.84
1-Nitromethane	39.6	32.1	7.5	0.54
Benzyl alcohol	42.6	30.5	12.1	0.60
Tritollyl phosphate	43.6	41.8	1.8	0.50
Di-iodimethane	49.0	46.8	2.2	0.34
1-Bromonaphthalene	50.5	50.5	0	0.62
Ethylene glycol	51.5	31.2	20.3	0.00
Formamide	61.4	34.0	27.4	−0.06
Glycerol	65.2	34.7	30.5	−0.09
Water	72.2	22.0	50.2	−0.33

[a] The components γ_l^d and γ_l^p are proportioned from the published results[5] to correct for the experimental temperature.

Three phase contact angle studies

The first liquids chosen as models of the silicone rubber were two polydimethyl silicone fluids manufactured by Dow Corning as 200/20 and 200/1000, and of approximate viscosity 20 cs and 100 cs respectively. At a later stage when it was clear that these were rather imperfect models, organic liquids were sought which would be expected to give an outer region mainly of methyl groups. The two which were found available were di-isopropyl ether and 2,2,4-trimethyl pentane.

The surface tensions of the liquids were determined with a du Noüy balance at room temperature. Interfacial tensions were determined with the same apparatus, immersing the platinum ring in water before the second liquid was added as an upper layer. The ring was then pulled off through the interface. If the ring was lowered onto the interface through an upper layer of non-aqueous liquid, it did not seem possible to measure the interfacial tension satisfactorily, and erratic abnormally low results were obtained. This is in accord with published experience.

Determination of the three phase contact angle proved far more difficult than had been anticipated particularly for the silicone fluids. The method which eventually proved most satisfactory used a piece of alumina substrate 20 × 30 × 0.5 mm which had been cleaned by heating at 1200°C for 30 minutes. This was clamped in a Pyrex cell containing water, so arranged that the alumina was half immersed in the water and able to be rotated carefully about its axis in the surface of the water. The silicone liquid was then poured very carefully onto the water to form an upper layer. The three phase contact angle where the two liquids coincided with the alumina surface was observed and measured with a telescope fitted with a goniometer eyepiece. Replicate observations were made with fresh pieces of alumina, each newly cleaned by heating to 1200°C.

It had been intended to rotate the alumina until the interface was undisturbed and the angle of the piece of substrate was equal to the contact angle, but determination of this position was more difficult and less precise than had been expected.

An alternative technique of placing either a drop of the liquid on the underside of a horizontal piece of alumina completely immersed in water, or of placing a drop of water on the surface of a piece of alumina immersed in the liquid failed with the silicone fluids. In each case the drop failed to displace the liquid already present. These difficulties have relevance to the question of chemisorption and are discussed later.

For di-isopropyl ether, satisfactory results were obtained using a drop of water on top of alumina completely immersed in the less dense liquid, and 2,2,4-trimethyl pentane completely spread over the surface giving a zero contact angle.

The results achieved are all given in Table III but are subject to some reservations which are considered later.

TABLE III

Surface and interfacial tensions and three phase contact angles

Liquid	Surface tension		Interfacial tension with water		Three phase contact angle		
	Mean mN.m^{-1}	No. of expts	Mean mN.m^{-1}	No. of expts	Mean	No. of expts	Range
Dow Corning silicone fluid 200/20	21.3 ± 0.2	6	32.0 ± 0.2	4	34.0 ± 4	12	9.6 ~ 59.5
Dow Corning silicone fluid 200/1000	23.6 ± 0.1	6	25.4 ~ 0.5	7	13.4 ± 0.7	6	12.1 ~ 16.1
Di-isopropyl ether	19.8 ± 0.1	6	14.7 ± 0.06	6	13.4 ± 1.6	6	9.7 ~ 18.0
2,2,4-trimethyl pentane	20.6 ± 0.05	6	43.6 ± 0.1	6	0		

DISCUSSION OF RESULTS OF SURFACE STUDIES

Using Eq. (6) the interfacial tension between two surfaces can be calculated. If the polar component of the interaction can be assumed to be negligible, as has already been shown for the silicone rubber, the calculation becomes particularly simple. These calculations have been made for the model liquids and water and are given in Table 4 together with the experimentally determined values. This table also includes two estimates of the interfacial energy of vulcanised silicone rubber with water.

The differences between the observed and calculated interfacial tensions indicate the existence of polar interaction, which in the case of the silicone fluids will be the results of impurities.

The relevant sections of the infra-red spectra of the two silicone fluids are given in Figure 3, showing the presence of characteristic frequencies for free hydroxyl groups which would account for the observed polarity. This presence could be anticipated from the mode of preparation of these materials. It will be appreciated that, from the Gibbs' adsorption isotherm, the polar-containing siloxanes will concentrate at the interface with another polar material (water or alumina) and hence exert a disproportionate effect on the interfacial tension compared with the effect on the surface tension.

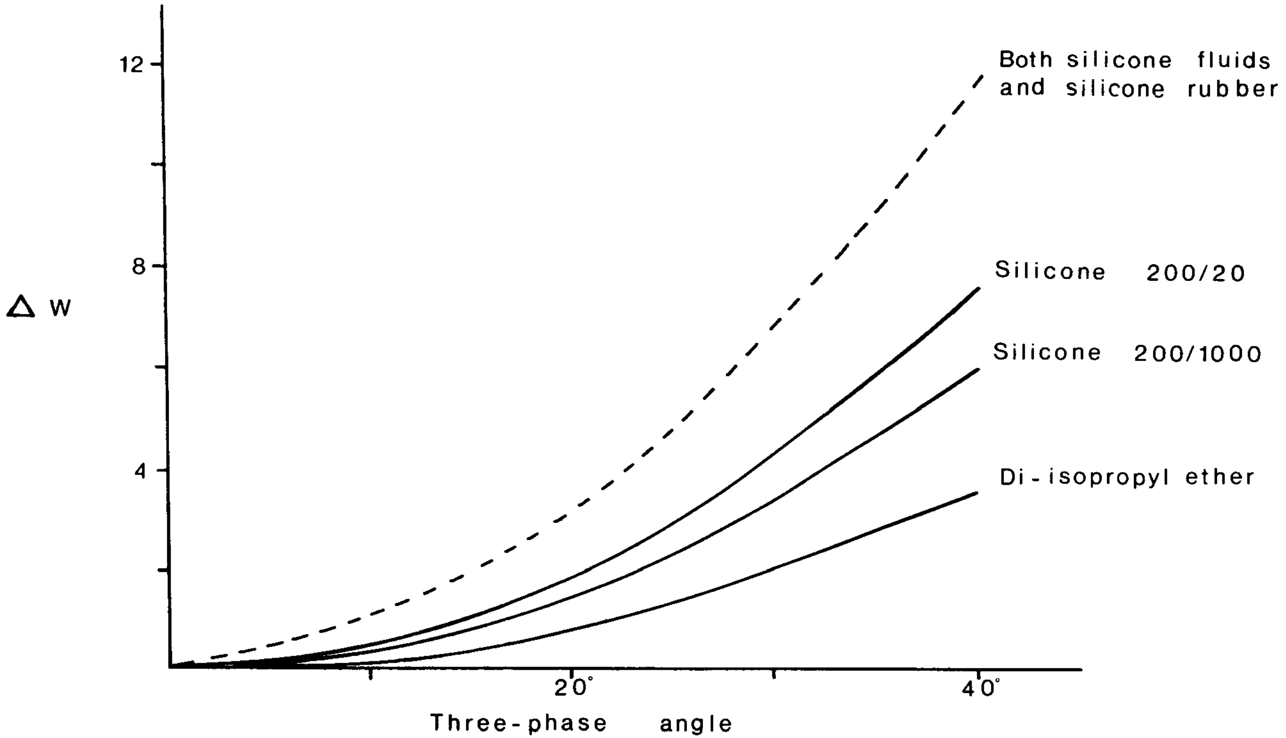


FIGURE 2 Value which ΔW would have *if* the three-phase angle had particular values.
Full lines calculated with observed interfacial tensions and Eq. 4.
Broken line calculated assuming no polar component of the surface free energy and Eq. 6.

The effect of these polar interactions can also be illustrated by considering the relationships between the energetic stability of a physical adhesive bond and the three phase contact angle. This is shown in Figure 2 which shows the value that ΔW would have *if* the angle had particular values. The full lines show the relationship calculated from the observed interfacial tension using Eq. (4) and the broken line shows the relationships calculated for the siloxane fluids on the assumption that they have no polar component in their surface free energy derived using Eq. (6).

TABLE IV

Interfacial tension with water

Substance	Observed	Calculation A	Calculation B
Silicone fluid 200/20	32.0	50.2	
Silicone fluid 200/1000	25.4	50.2	
Di-isopropyl ether	14.7	50.3	
2,2,4-trimethyl pentane	43.6	50.2	
Silicone rubber	—	50.6	52.1

Calculation A Using Eq. (6) without polar terms.
Calculation B Using Eq. (5) and contact angle with water.

It is now possible to calculate the difference in free energy between an adhesive bond and the two surfaces separated in the presence of water and hence the stability of the bond, using the liquids as models for the silicone rubber (*via* Eq. 4). The results of these calculations are given in Table V.

TABLE V

Changes in surface free energy

Model Liquid	ΔW
Silicone fluid 200/20	5.5
Silicone fluid 200/1000	0.7
Di-isopropyl ether	0.4
2,2,4-trimethyl pentane	$\leqslant 0$

Additionally it is possible to calculate from Eq. (7) the magnitude of polar component which would be necessary to account for the difference between the interfacial tension which has been calculated and the observed value for the model liquids (Table 4). For silicone fluid 200/20 it is 1.65 mN.m^{-1} (7.8% of total) and for silicone fluid 200/1000 it is 3.1 mN.m^{-1} (13.0% of total).

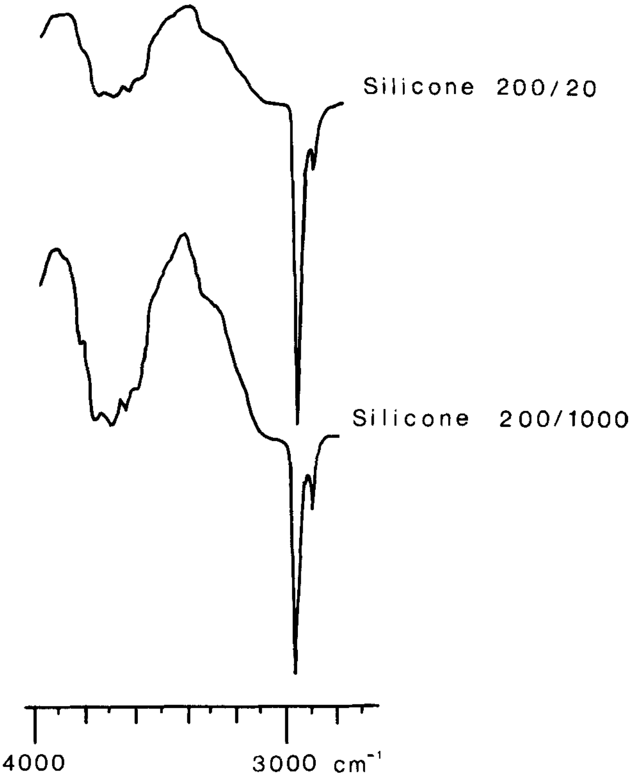


FIGURE 3 Section of infra-red spectra of the two silicones showing characteristic frequencies of hydroxyl groups.

The rather wide spread of the measured replicate three-phase contact angles and the failure to displace one liquid by the other whichever liquid is first applied to the alumina, raises doubts about the validity of the thermodynamic approach adopted. Such approach demands nominal reversibility. If hydroxyl groups on the siloxane chains of the silicone fluids become adsorbed to the *cleaned* alumina surface, then chemisorption is highly probable and will be irreversible. The amount of hydroxyl groups present is small (see Figure 3) but, as has been pointed out, they will be concentrated at the interface with either alumina or water. Since this concentration will vary at the different interfaces, and will be mobile in one case (water) and not the other, the observed angle is likely to be highly dependent on the order and rate of wetting; hence the very variable results.

It is difficult to avoid the conclusion that if the silicone fluids were both completely pure and therefore non-polar, they too, like trimethyl pentane, would have a zero three-phase contact angle with and be displaced by water. The stability of the bond appears to be related to the polarity of the liquid. Similarly silicone rubber in its non-polar, cross-linked state would be displaced were it not that its first contact with the alumina is made before cross-linking has occurred and in this initial state it is highly polar and reactive. The evidence presented in the next section clearly demonstrates the stability of the bond between silicone rubber and the substrate. Since, from the foregoing, physical interaction does not appear to lead to a water-stable bond, the stability must be explained by chemisorption of the uncured rubber when it first makes contact with the substrate. Subsequent curing and cross-linking removes all polarity at least so far as the free surface is concerned.

EVIDENCE OF MECHANICAL DURABILITY

At a very early stage in the experimental work, and before the persistence of the contamination of the substrate was appreciated, a number of lap-shear adhesive bonded joints were prepared and immersed in water for long term studies. The alumina substrate material 0.5 mm thick was cut into strips 10 × 100 mm, degreased with chloroform and conductivity water by the method initially employed in making prostheses (see Table I) and air dried. Lap-shear joints were prepared from these strips with an overlap of 15 mm using silicone rubber 3140. The joints were cured in air for 5 days whilst held by a pressure of 8.1 $kN.m^{-2}$. The thickness of the adhesive was approximately 0.030 mm though some variation was inevitable in the absence of spacers. These joints were immersed in water at 38°C and one or more removed at intervals for strength measurement in a tensile testing machine. The results are given in Table VI.

TABLE VI
Strength of lap-shear joints after immersion in water

Time of immersion	0	7	34	286	405	506	days
Mean lap-shear strength	1455	1400	1430	817[a]	1054	1152	$kN.m^{-2}$
Standard error	107	190	115				
No. of joints	4	3	2	1	1	1	

[a] Cohesive failure in rubber.

There is the suggestion that sometime after 34 days some deterioration may have occurred. The result at 286 days is anomalous because, contrary to all other results, failure was within the rubber. If it is accepted that no change has occurred at 34 days and that the results of the 10 test joints are pooled to give an estimate for the standard deviation of a single result, then the strength recorded at 405 days would be recorded by chance with a probability of 0.07 even if there had been no change in strength. This probability would not normally be accepted as showing significant change.

Comyn[6] has calculated the concentration of water at the centre point of the adhesive in a single lap joint 10 mm × 15 mm using a value of 3.5×10^{-9} $m^2 s^{-1}$ for the diffusion coefficient of water into polydimethyl siloxane. He showed that 50% saturation is achieved in 40 minutes and 95% saturation in 2¼ hours. This rapid penetration is due to the relatively high value of the diffusion coefficient of silicone rubbers (compare 10^{-13} $m^2 s^{-1}$ for epoxides).

Experiments were also made with a configuration which applied a peeling rather than a shear stress to the interface. A length of woven polyester tape was attached to the substrate material with silicone rubber 3140 and the force required to remove the type by peeling at 180° from the substrate was measured. The failure in this type of joint was invariably cohesive within the rubber and, consequently, the results recorded in Table VII reflect the tearing of the rubber as occurring at a lower load than separation from the interface. There is thus no evidence that silicone is displaced from the substrate by water even when a less than perfectly cleaned surface exists on the alumina substrate before bonding.

TABLE VII
Strength of textile reinforced adhesive peeled from substrate

Time of immersion	0	20	75	252	345	days
Prepared as were the lap-shear test joints	726	720	915	787	898	$kN.m^{-1}$
Substrate cleaned by heating to 1200°C	744	761	915	861	800	$kN.m^{-1}$

Clearly water will have reached the interface in all these joints of whatever configuration and if the bond were thermodynamically unstable then there would be a catastrophic fall in strength at an early stage.

CONCLUSIONS

Standard solvent degreasing is not an adequate preparation of an alumina substrate surface for bonding with a room temperature vulcanising silicone rubber, but it is possible by following a solvent degreasing with a detergent/phosphate washing to prepare a surface of high surface free energy. If physical adsorption alone were involved, both thermodynamic theory and measurements with liquids as models for the silicone rubber make it highly unlikely that a bond between a cleaned alumina substrate surface and a completely non-polar silicone rubber would be stable in the presence of water. However, the actual bond immersed in water resists quite strong forces of separation long after the time required for saturation with water at the interface. This is explicable only on the assumption that polar interactions exist across the interface which can no longer be demonstrated on a free surface after curing is complete. In turn this can be explained by chemisorption of the highly polar and reactive rubber when it is first brought into contact with the substrate.

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References

1. L. A. Girifalco and R. J. Good, *J. Phys. Chem.*, **61**, 904 (1957); **64**, 561 (1960).
2. W. A. Zisman, in *Contact Angle, Wettability and Adhesion*, Advances in Chemistry Series **43** (ACS, Washington, DC, 1964), Chap. 1.
3. T. Fort and H. T. Patterson, *J. Colloid Sci.* **18**, 217 (1963).
4. L. C. Jackson, *Adhesive Age*, **21**(9), 34 (1978).
5. P. A. Dynes and D. H. Kaelble, *J. Adhesion*, **6**, 197 (1974).
6. J. Comyn, private communication.