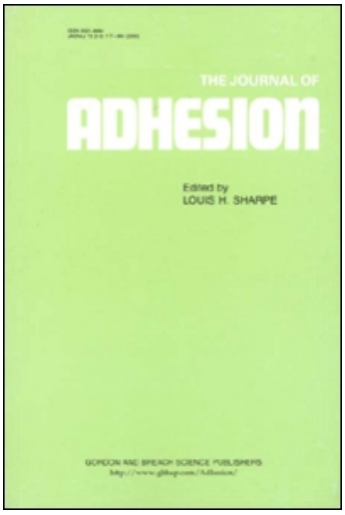

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Kinetics of Moisture Cure of Silicone Sealants*

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The depth of moisture cure (z) has been measured for lap joints in aluminium with a conventional sealant based on polydimethylsiloxane and one based on polytrifluoropropylmethylsiloxane. The cured sealant acts as a barrier to the permeation of water; any water which passes through this barrier causes further cure which thickens the barrier. The depth of cure is given by $z = (2PVpt)^{1/2}$, where P is the permeability coefficient of water in cured sealant, V is the volume of sealant which reacts with 1 mole of water, p is the vapour pressure of water and t is time.

Keywords: Silicone sealant; fluorosilicone sealant; permeability to water vapour; amount of water needed for cure; kinetics of moisture cure; mechanism of moisture cure

INTRODUCTION

Most silicone sealants that cure at room temperature (so-called RTV materials) rely on chemical reactions with water from the atmosphere to effect their cure. The reactive groups may be acetates, ethers or ketoximes, and in each case the initial hydrolysis reaction forms silanols, and these subsequently condense in a bimolecular reaction. Here the kinetics and mechanism of cure of two silicone sealants have

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been explored; the materials used were a silicone with ketoxime groups and a fluorosilicone with acetate groups.

The method employed was to make single lap joints in aluminium, to store them at constant humidity at 25°C and then to break them and measure the depth of penetration of cure.

EXPERIMENTAL

The fluorosilicone was Dow Corning 730 which contains trimethylated silica, vinyltriacetoxysilane, titanium dioxide, and hydroxy-terminated polytrifluoropropylmethylsiloxane; it was used with Dow Corning 1200 primer. Ambersil 1050N is a polydimethylsiloxane which cures by elimination of butanone ketoxime; it was supplied by Ambersil Ltd, Bridgwater, Somerset, UK.

The adherend was aluminium sheet 2 mm thick, type 1050A of 99.5% purity. Adherends measuring 20 × 55 mm were used to make single lap joints with 10 mm overlap. Initially, joints were cured in ambient conditions and mechanically tested. They were made with Dow Corning 730, and the adherends were immersed in 1200 primer for about 1/2 minute and then allowing them to drain and dry with the bond region uppermost. They were allowed to dry for between 60 and 70 minutes at room temperature, and two lengths of nylon fishing line, 0.185 mm diameter, were taped around one of the adherends to act as a spacer. Clips held the joints together during cure. After overnight cure the fillets were cut off. Joints were tested using a Hounsfield W-type tensometer at a crosshead speed of 8 mm min^{-1}.

Later joints which were aged at constant relative humidity (r.h.) were made without the primer and using 5a fuse wire (RS tinned annealed copper of diameter 0.195 mm) as a spacer in place of fishing line; fuse wire was easier to use. The primer was not used as it was considered unnecessary in experiments in which joint strengths were not measured, and where the process of cure being studied involves water diffusion through the bulk of the sealant. Liquid sealant fillet was removed with a sharp screwdriver tip. After exposure these joints were broken by hand. Duplicate joints were used. Measurements on the surfaces of broken joints were made to the nearest 0.05 mm using a Peak Scale Lupe 7 × microscope.

Exposure to constant relative humidity at 25°C was over water or saturated salt solutions, contained in polyethylene containers measuring approximately 250 × 150 × 90 mm and contained in an air-thermostat. Lap joints were placed on a shelf of acrylic plastic drilled with 15 holes 16 mm in diameter, supported on two rings of polyester about 35 mm high. The depth of the solutions was about 10 mm. All items were rinsed with deionised water before use, and the solutions were made with deionised water. The salt solutions and their relative humidities at 25°C, interpolated from the data of Wink and Sears [1], are NaCl, 75.4%; $Mg(NO_3)_2 . 6H_2O$, 53.0%; and $MgCl_2 . 6H_2O$ 32.7%.

Films of the sealants were required for measurements of water permeability and were made by spreading on polyethylene sheet supported on glass, and leaving to cure in air for at least 5 days. Spreading was by a metal scraper supported at the ends on brass spacer wires. Weight changes on curing were measured on samples of about 10 g spread on polyethylene. Densities of cured sealants were measured by weighing films in air and then in water, and were 1.43 g cm^{-3} for Dow Corning 730 and 1.42 g cm^{-3} for Ambersil 1050N. The amount of acetic acid liberated when Dow Corning 730 cures was measured by immersion in deionised water for 3 days, and then titrating with N/10 sodium hydroxide solution using phenolphthalein as indicator.

Water permeabilities of cured films of the sealants were measured in the following manner. Thicknesses of Ambersil 1050N films were measured at 5 points (centre and towards each corner) with a micrometer but, as Dow Corning 730 is soft and readily adheres to itself and to metals, making it difficult to handle in a screw-action micrometer, a caliper gauge was used for those films. The films were bonded to the rims of 60 or 100 cm^3 glass jars using minimal quantities of the same sealant, and left to cure for 1 day. Previous to this, small knitted nylon bags containing about 10 g of freshly-dried silica gel granules had been placed in the jars. The diameter of the mouths of the jars were 29.0 mm. The jars were stored at constant humidities at 25°C and periodically weighed. The first weighings were made after 1-day exposure, in order to allow permeation to attain the steady state, and to avoid errors due to the time lag [2]. Experiments were mostly performed in duplicate.

RESULTS

Joints Cured in Air

Strengths of joints with Dow Corning 730 after curing in ambient conditions for various times are plotted in Figure 1. The failure pattern of these joints was that the outer regions failed interfacially, but inside the sealant had not cured and remained a liquid. This is illustrated for two joints in Plates 1 and 2, which were actually cured at constant humidity. The depth of cure (z) was measured with the Lupe microscope, and values are shown in Figure 1. It is clear that joint strength increases in parallel with the depth of cure, and reaches a maximum when the joints are fully cured ($z = 5$ mm). This is in contrast to the case of joints with rigid adhesives such as epoxides, where strength is independent of bonded area [3], due to the concentration of mode I and mode II stresses at the edges. The difference in behaviour must be due to the high compliance of the fluorosilicone.

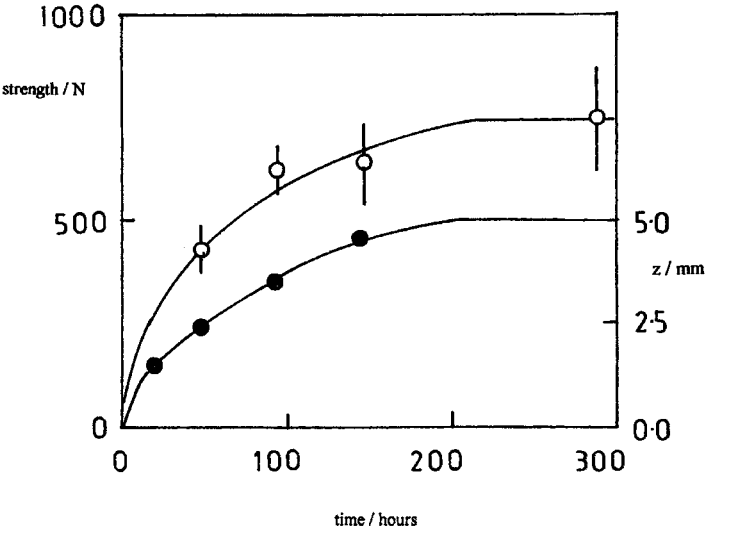

FIGURE 1 Strengths of lap joints with fluorosilicone sealant on curing in air ○, and the depth of cure ●.

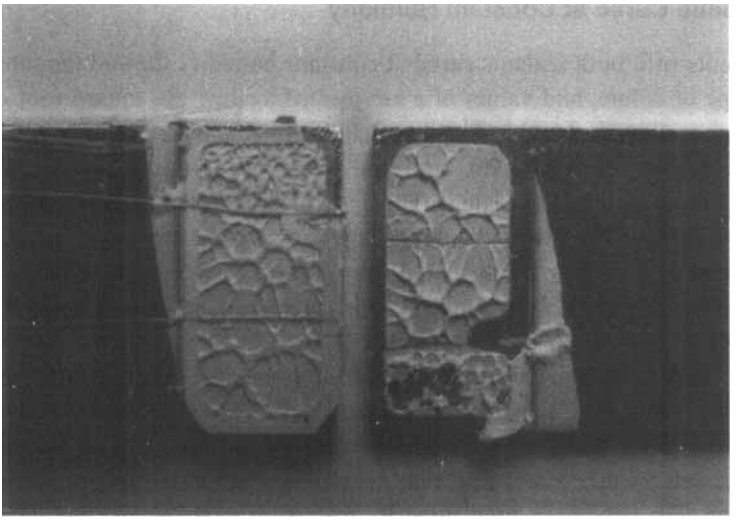

PLATE 1 Failure surfaces of joints with fluorosilicone sealant after curing at 53.0% r.h. for 8.3 h.

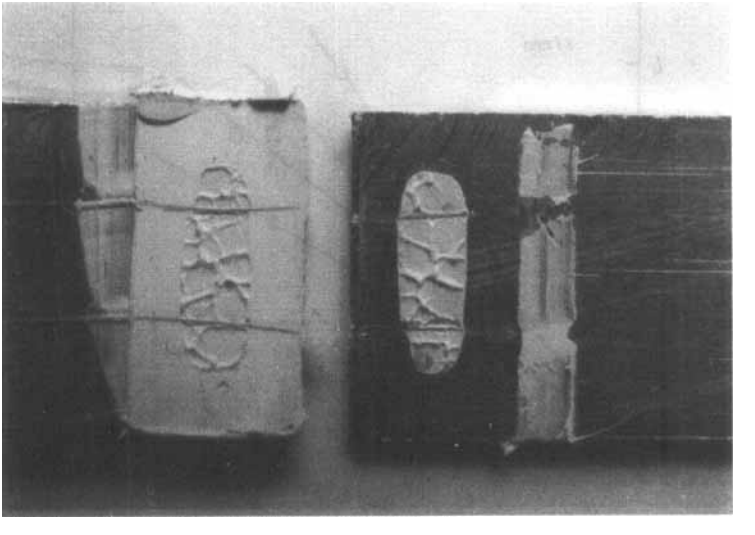

PLATE 2 Failure surfaces of joints with silicone sealant after curing at 53.0% r.h. for 71.3 h.

Joints Cured at Constant Humidity

Joints with both sealants cured at constant humidity showed the same type of failure, and values of z are plotted against the square root of time in Figures 2 and 3. There were four possible places where z could be measured on each joint, but some of these were obscured by smearing or rupture of the sealant. These are clearly seen in Plates 1 and 2 as the zones between the long edges of overlap and the uncured sealant which has a reticulated appearance. Measurement of z was more difficult with the Ambersil silicone sealant because of its black colour; Dow Corning 730 is white.

There were, thus, up to 8 single measurements contributing to the points in Figures 2 and 3, and standard deviations were mostly 4–6%. Apart from small uncertainties concerning whether the lines pass through the origin, it is clear that z is proportional to the square root of time. The lines have been fitted by regression analysis, and the intercepts on the abscissae represent time delays of no more than about 20 minutes, which is about the time needed to prepare a set of joints and place them in the thermostat. Also, after opening the constant humidity

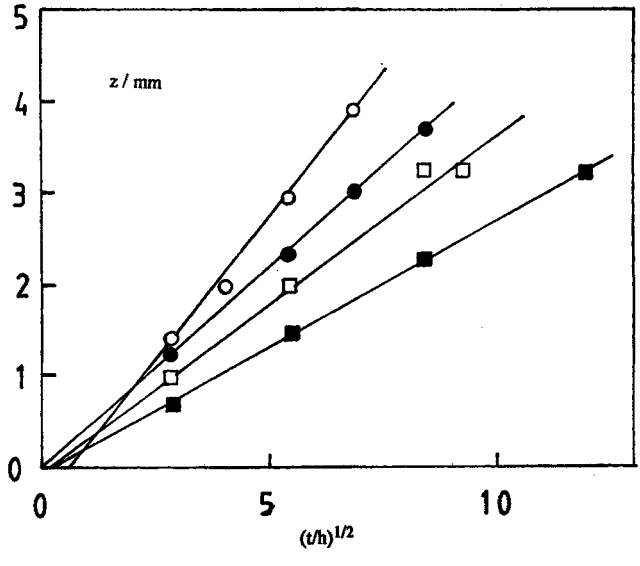

FIGURE 2 Width of zone with interfacial failure on curing joints with fluorosilicone sealant at the following relative humidities ○ 100%, ● 75.4%, □ 53.0% and ■ 32.7%.

vessels, some time will be needed to regain equilibrium. The slopes of the lines in Figures 1 and 2 are given as values of $zt^{-1/2}$ in Tables I and II.

Amount of Water Needed to Cure the Sealants

The sequence of reactions involved in the moisture-cure of Dow Corning 730 sealant is hydrolysis of acetate units followed by condensation

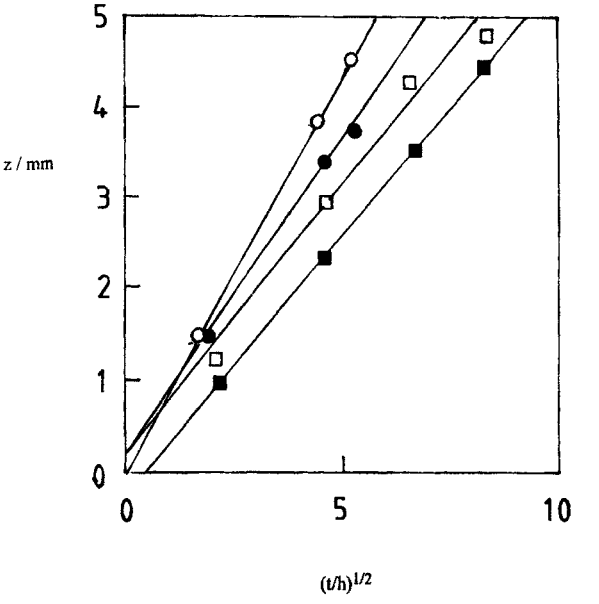

FIGURE 3 Width of zone with interfacial failure on curing joints with silicone sealant at the following relative humidities ○ 100%, ● 75.4%, □ 53.0% and ■ 32.7%.

TABLE I Terms in $z = (2VPpt)^{1/2}$ for joints with fluorosilicone sealant

r.h./%	$zt^{-1/2}/10^{-6} ms^{-1/2}$	$(2VPp)^{1/2}/10^{-6} ms^{-1/2}$
100	10.4 ± 0.7	6.14 ± 0.05
75.4	7.3 ± 0.2	4.32 ± 0.01
53.0	6.2 ± 0.5	4.55 ± 0.04
32.7	4.7 ± 0.1	3.28 ± 0.01

TABLE II Terms in $z = (2VPpt)^{1/2}$ for joints with silicone sealant

r.h./%	$zt^{-1/2}/10^{-6} ms^{-1/2}$	$(2VPp)^{1/2}/10^{-6}\ ms^{-1/2}$
100	14.4 ± 0.2	13.4 ± 0.2
75.4	11.3 ± 0.9	11.0 ± 0.3
53.0	9.7 ± 0.9	9.6 ± 0.5
32.7	9.5 ± 0.2	8.0 ± 0.9

of silanols, *i.e.*,

$$\text{—SiOCOCH}_3 + \text{H}_2\text{O} = \text{—SiOH} + \text{CH}_3\text{COOH}\uparrow$$

$$\text{—SiOH} = 1/2\text{—Si—O—Si—} + 1/2\text{H}_2\text{O}$$

The overall reaction is

$$\text{—SiOCOCH}_3 + 1/2\text{H}_2\text{O} = -1/2\text{—Si—O—Si—} + \text{CH}_3\text{COOH}\uparrow$$

Hence, by these reactions the absorption of 1 mole water causes the liberation of 2 moles acetic acid. Weight losses on duplicate films about 0.8 mm thick after curing in air for 12 days were 5.32 and 5.37%. Thus, the amount of sealant which reacts with 1 mole of water is 1.91 kg or $V = 1330\ \text{cm}^3$.

The first reaction in the cure of Ambersil 1050N is by hydrolysis of ketoxime end groups, with the liberation of butanone ketoxime.

$$\text{—Si—O—N=C(CH}_3\text{)(C}_2\text{H}_5\text{)} + \text{H}_2\text{O} = \text{—SiOH}$$

$$+ \text{HO—N=C(CH}_3\text{)(C}_2\text{H}_5\text{)}\uparrow$$

Here the overall reaction is

$$\text{—Si—O—N=C(CH}_3\text{)(C}_2\text{H}_5\text{)} + 1/2\text{H}_2\text{O} = 1/2\text{—Si—O—Si—}$$

$$+ \text{HO—N=C(CH}_3\text{)(C}_2\text{H}_5\text{)}\uparrow$$

Films of Ambersil 1050N spread on low density polyethylene took 5 days to reach constant weight. After drying for a further day over silica-gel because the cured sealant absorbs a small amount of water,

overall weight losses were 2.80%, 2.78% and 2.83%; the mean is 2.80%. Hence, the amount of sealant which reacts with 1 mole of water is 5.57 kg or $V = 3920\,cm^3$.

Water Permeability of Cured Sealants

Q is the amount of water permeating a film of area A and thickness l in time t, in the steady state. It is related to the permeability coefficient, P, saturated vapour pressure of water, p_o, and relative humidity by Equation (1). At 25°C the saturated vapour pressure of water is 3167 Pa.

$$Q = PAtp_o \text{ (r.h./100)}/l \quad (1)$$

Permeation cells were weighed daily for 4–6 days, and linear regression analysis was used to obtain the term Q/t. Values of P are given in Tables III and IV. Water may enter the permeation cells by passing through the film, or through the annulus of the same material which acts as an adhesive. It is estimated that the rate of permeation through the film is about 400 times that through the annulus; thus, permeation through the annulus can be neglected.

Plots of P against r.h. (which are not shown) show moderate scatter but no clear trend. The soundest interpretation is that P does not vary with r.h.

MECHANISM OF CURE

Cure takes place in joints with these sealants by water diffusing to meet and react with immobile sites. Hence, the concentration of water

TABLE III Water permeabilities of fluorosilicone sealant

r.h./%	film thickness/mm	$P/10^{-12}\,mol\,s^{-1}\,m^{-1}\,Pa^{-1}$
100	0.220	4.84 ± 0.08
	0.220	4.77 ± 0.08
75.4	0.240	5.06 ± 0.04
	0.240	5.05 ± 0.03
53.0	0.260	4.57 ± 0.08
	0.200	4.70 ± 0.15
32.7	0.300	4.95 ± 0.01
	0.250	3.90 ± 0.26

TABLE IV Water permeabilities of silicone sealant

r.h./%	*film thickness/mm*	$P/10^{-12}\,mol\,s^{-1}m^{-1}\,Pa^{-1}$
100	0.507 ± 0.007	7.42 ± 0.26
	0.515 ± 0.008	7.51 ± 0.25
75.4	0.337 ± 0.010	6.58 ± 0.34
	0.423 ± 0.035	6.56 ± 0.64
	0.497 ± 0.046	6.41 ± 0.83
53.0	0.497 ± 0.046	7.20 ± 1.26
	0.337 ± 0.010	7.95 ± 0.86
32.7	0.423 ± 0.035	8.14 ± 1.86

(*c*) at any point will be given by Equation (2), where k is a second order rate constant and s is the concentration of sites. The Dd^2c/dz^2 term is for water diffusion into the adhesive and D is the diffusion coefficient.

$$dc/dt = Dd^2c/dz^2 - kcs \tag{2}$$

We have not been able to find a solution for Equation (2). However, the following simpler approach gives an equation which fits the experimental facts of z being proportional to the square root of time. It is assumed that the chemical reaction is much faster than the rate of diffusion, and this is supported by the observations that both sealants quickly form skins in air, and the fluorosilicone material instantly smells of acetic acid.

At time t the thickness of the cured adhesive is z, and this acts as a barrier for the permeation of water to the uncured sealant. Any water which passes through this barrier quickly reacts with uncured sealant and, thus, the barrier is thickened.

The amount of water permeating unit cross section of the cured layer is

$$dn/dt = Pp/z \tag{3}$$

Here n is the number of moles of water and p the vapour pressure of water in the surroundings. The volume equivalent of the sealant is V and this is the volume of sealant which reacts with 1 mole of water. The volume of sealant which is cured is

$$dv = Vdn \tag{4}$$

Because we are dealing with unit cross sectional area $dz = dv$, thus

$$dn = dz/V \tag{5}$$

$$dz/dt.V = Pp/z \tag{6}$$

$$zdz = VPpdt \tag{7}$$

Integrating Equation (7), with the condition that $z = 0$ when $t = 0$ gives

$$z = (2VPpt)^{1/2} \tag{8}$$

COMPARISON OF THEORY AND EXPERIMENT

The gradients of the lines in Figures 2 and 3 are equal to $zt^{-1/2}$, and by Equation (8) this should equal $(2VPp)^{1/2}$. Values of these terms for the sealants are compared in Tables I and II, where it can be seen that those for the silicone sealant are in good or excellent agreement, confirming the proposed mechanism of cure in this case.

With the fluorosilicone, however, values of $zt^{-1/2}$ are greater than $(2VPp)^{1/2}$, due to V being greater than the expected from weight changes during cure. The reason for this is that the uncured sealant contains some silanol groups, which will participate in the following pair of reactions.

$$\text{—SiOCOCH}_3 + \text{H}_2\text{O} = \text{—SiOH} + \text{CH}_3\text{COOH}\uparrow$$

$$\text{—SiOH} + \text{—SiOH} = \text{—Si—O—Si—} + \text{H}_2\text{O}$$

The overall reaction, which does not consume water but liberates acetic acid is

$$\text{—SiOCOCH}_3 + \text{—SiOH} = \text{—Si—O—Si—} + \text{CH}_3\text{COOH}\uparrow$$

The amount of acetic acid liberated on curing under water was equivalent to $8.97 \pm 0.01\,cm^3\,g^{-1}$ of N/10 alkali, giving a new and higher value of $V = 1560\,cm^3$. This would have the effect of increasing the values of $(2VPp)^{1/2}$ in Table I by a factor of 1.08, which is not enough to make them equal $zt^{-1/2}$.

The cause of V being still larger is that water is not consumed in the last reaction.

Errors of Observation

The errors in $zt^{-1/2}$ were obtained by linear regression analysis on the points in Figures 2 and 3, and those in the values of P for the fluorosilicone were obtained by linear regression analysis on Q-t data. Errors in P for the silicone sealant were calculated from the latter and standard deviations of film thickness using the calculus method described by Topping [4]. Errors in $(2VPp)^{1/2}$ are based on the values of P with least error.

CONCLUSIONS

1. Partially cured joints with the silicone sealants show an outer zone of cured adhesive of depth z; inside this the sealant is a liquid.
2. The depth of moisture cure for the silicone sealant is given by the equation $z = (2VPpt)^{1/2}$.
3. With the fluorosilicone sealant $z > (2VPpt)^{1/2}$, because the term V is greater than indicated by weight changes or the amount of acetic acid liberated on cure.
4. The rate of cure is controlled by the rate of water permeation in the cured adhesive.

Acknowledgement

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