

Hydrolytic Stability of Single-Package Silicone Sealant

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Synopsis

Stability of a commercially available single-package silicone sealant has been investigated under different water immersion temperatures. The study involved water sorption, weight loss, thermal stability, and strength reduction. It is believed that the deterioration of silicone sealant was due to the combined effects of leaching, water swelling, and hydrolysis. Water uptake of about 2% was crucial for its hydrolytic degradation, especially at higher temperatures.

INTRODUCTION

Polymeric sealants are widely used in the building industry^{1,2} for external sealing of gaps and joints, and are also used in roofings. These bonded composites suffer severe deterioration when exposed to a tropical environment. High ambient temperature, humidity, and ultraviolet radiation³ are responsible for the deleterious effect.

Water or moisture could be the main culprit for deteriorating most of the adhesively bonded composites.⁴⁻⁷ Water may penetrate the bonded composites through bulk polymer and/or substrate-polymer interface and/or substrate oxide layer. Its diffusion into bulk polymer of the bonded structure may considerably reduce the cohesive strength of the polymeric material. Main chain scission, transformation of side and end groups could be the result of hydrolysis of the bulk polymer. Such a chemical degradation of transformation would undoubtedly weaken the composite.

A commercial silicone sealant may consist mainly of liquid silicone polymer, inorganic filler(s), and a cross-linking agent.⁸ The deterioration of its bonded composites during the short-term outdoor exposure might be largely due to the action of water. This paper focuses on the hydrolytic durability of a cured silicone sealant at different temperatures. It is a continuation of the investigation on durability of silicone/aluminium lap joint immersed in water.^{6,7}

EXPERIMENTAL

Silicone Sealant

A single-package transparent silicone sealant of acetoxy type (Perennator V23-2), commercially available, was used. The sealant was cured at room temperature for 28 days in the form of thin sheet cast on a polythene film.

WATER IMMERSION TEST

Test specimens of the cured silicone sealant of approximately $15 \times 15 \times 1$ mm each were cut out from the sheet. Each specimen was identified by cutting notches in code on the edges. They were then immersed in distilled water in the sealed glass containers at room temperature, 50, 70, and 90°C for different lengths of time.

Two test pieces were removed at a certain time interval for weighing immediately after their surfaces had been blotted with filter paper. The weight of sorbed water was deduced from the weight differences before and after water immersion. They were then vacuum dried at 60°C for a day, and the weight lost due to leaching of water-soluble materials (W_1) was calculated. In addition, the same test pieces were further subjected to isopropyl alcohol (IPA) extraction in a soxhlet for 8 hours in order to remove polymeric materials of low molecular weights (W_2). With the above sequence of treatments on each set of specimens, the amount of sorped water, water-extractable materials (W_1), and IPA-extractable materials (W_2) were monitored.

THERMOGRAVIMETRY (TG)

The effect of hydrolytic deterioration on the silicone sealant was assessed by TG. TG curves ranging from 300 to 535°C were recorded using a Perkin Elmer TGS-1 thermal balance with a UU-1 temperature programmer at 10°C/min in static air.

STRENGTH OF THE CURED SILICONE SEALANT

The test pieces of the cured silicone sealant of 1×5 mm (thickness \times width) were cut out from a sheet by a dumb-bell-shape cutter. Tensile property of the cured silicone sealant was measured by an Instron 1026 machine at a strain rate of 7 mm/min.

RESULTS AND DISCUSSION

The sealant used was a commercially available single-package acetoxy type of silicone which depends on moisture for cross-linking reactions. Potential crosslinkers and catalyst are incorporated in the methyl diacetoxy-silane terminated polydimethylsiloxane (PDMS). It also contains about 40% inorganic filler. Upon contact with moisture present in the air, a potential crosslinker of methyltriacetoxysilane⁹ is hydrolyzed and condensed to a series of real crosslinking agents of $\text{H—OSiOHCH}_3\text{—OH}$ oligomers and acetic acid. These silanol crosslinkers then react with PDMS to form a three-dimensional polymeric network. In this study, the sealant was cured in a form of thin sheet at room temperature for 28 days which were more than enough for its optimum cure time.

WATER SORPTION

The plots of water uptake by the cured silicone in Figure 1 show the attainment of equilibrium sorptions at different temperatures, except for

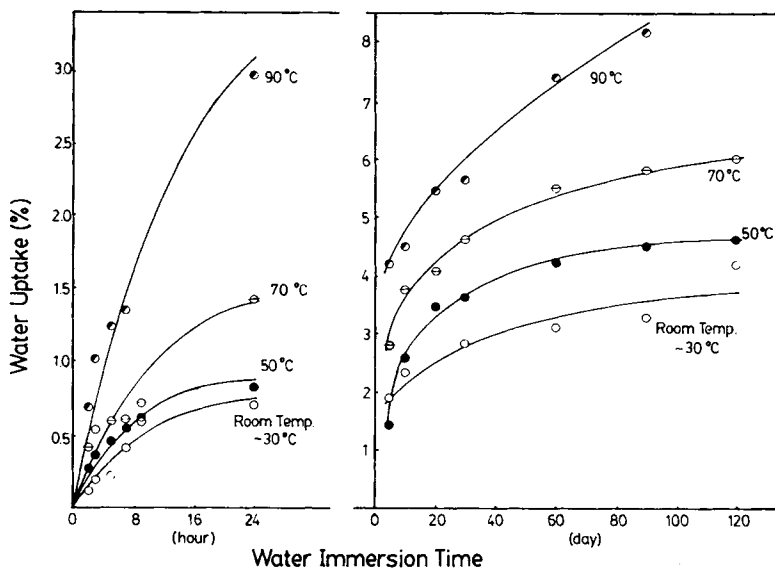


Fig. 1. Water uptake by the cured silicone sealant.

90°C. The maximum water sorption was about 4% at room temperature, and 6% at 70°C after one year of immersion. However, no equilibrium water uptake was observed at 90°C. At higher temperatures, a substantial hydrolytic degradation of polymeric matrix might occur. This would in turn affect the dynamic equilibrium between leaching and water sorption.

The sorption of water is also expressed by the extent of water uptake (M_t/M_∞), where M_t is the weight of water gained in any time of immersion and M_∞ is the maximum weight gained. When the data (M_t/M_∞) are plotted versus the square root of time ($t^{1/2}$), an initial rectilinear behavior is evident from Figure 2. The rate of water uptake in the rectilinear region increased with increasing temperature. The initial part of the sorption curve (rectilinear region) is controlled by the Fickian diffusion and it is correlated by the following equation¹⁰

$$M_t/M_\infty = 4/h(Dt/\pi)^{1/2}$$

where h is the thickness of the specimen and D is the diffusion coefficient. Using this equation, the water diffusion coefficients of silicone sealant at different temperatures were calculated from the gradients of the linear portions of the plots in Figure 2. The values of D are reported in Table I and they increased with temperature as expected. The Arrhenius plot of the logarithm of the diffusion coefficients (D) against the reciprocal of the absolute temperature is linear over this temperature range. The activation energy for the diffusion of water in this silicone (E_d) is calculated to be 19.2 kJ/mol. This value is slightly higher than 12.6 kJ/mol obtained for polydimethylsiloxane.¹¹ However, silicone sealant contains a rather large quantity of inorganic fillers, such as silica, which can increase E_d .

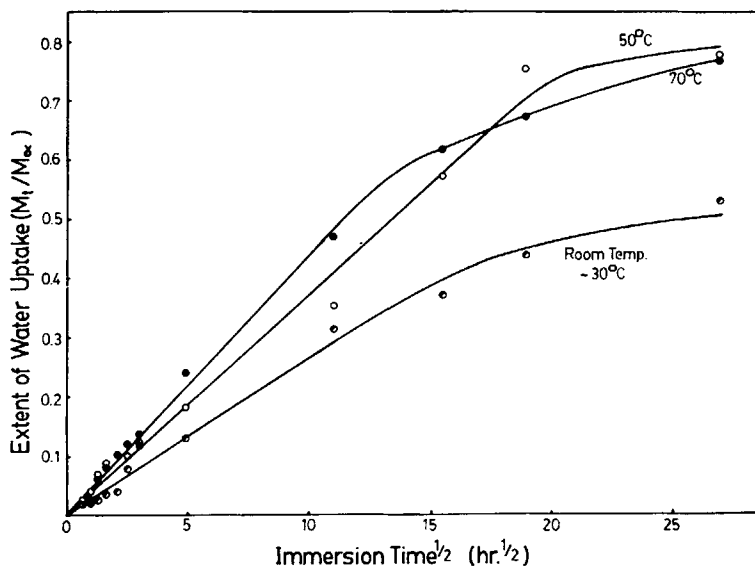


Fig. 2. The extent of water uptake versus the square root of immersion time.

WEIGHT LOSS IN WATER IMMERSION

The specimens after immersion in water for different time intervals were determined for their weight losses in water (water-extractable materials) and in isopropyl alcohol (IPA-extractable polymers). The results are presented in Figure 3. The amount of the water-extractable materials (W_1) was negligible at room temperature for the first 2 months of water immersion. It increased slowly to about 0.8% in one year. At higher temperatures, the water extraction was substantial even in the early state. The weight loss doubled to 1.6% for those immersed at 50 and 70°C for one year.

The water-extracted composites further lost their weights (W_2) in IPA extraction. The plots in Figure 3(b) include the amount of 22.3% extractable by IPA before water immersion. The leached materials show numerous peaks in a chromatogram, as expected from a commercial silicone sealant. No attempt has been made to characterize them as to which could be derived from plasticizer, crosslinker, and the low-molecular weights of silicone. The IPA-extracted sealant suffered additional weight loss of about 8% after water immersion for one year at 70°C or 2 months at 90°C. They seem to have a

TABLE I
Water Diffusion for a Single-Package Acetoxy Type Silicone Sealant

Temperature of water immersion (°C)	$D \times 10^{10}$ (m ² /s)	E_d (kJ/mol)
30	1.396	
50	2.803	19.2
70	3.726	

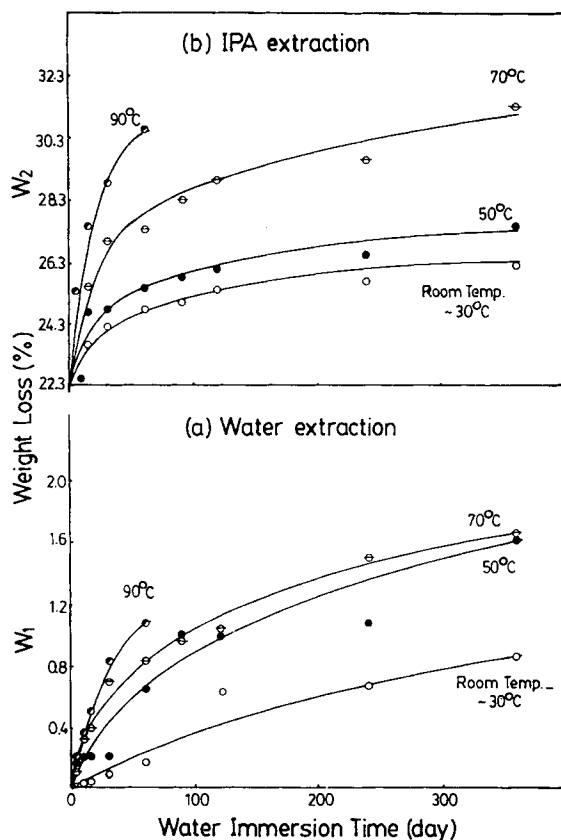
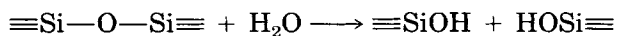


Fig. 3. Water and isopropyl alcohol extractions.

linear relationship between water uptake and IPA-extractable materials as shown by the least-squares fit plot of Figure 4. From the extrapolation, it implies that a critical water concentration of about 1.8% in silicone sealant may cause some materials to be extracted by IPA. The pronounced increase in the IPA-extractable materials after prolonged water immersion might be due to hydrolytic degradation of the silicone composite. The hydrolytic reactions would break down some of the polysiloxane chains to lower molecular weight fragments.

Direct evidence for the hydrolysis of polysiloxane network detected by FT-IR has been reported.¹² The band appearing at 890 cm^{-1} after hydrothermal treatment is attributed to the hydrolytic product of silanol group (Si—OH). Water could cleave the siloxane linkage to give two silanol groups, for example,



Hydrolysis is greatly facilitated by a catalyst and the activation energy¹³ is about 25 kJ/mol. Acid-forming peroxides from the polymeric system could act as catalysts. In the present case, the infrared (IR) spectrum for the IPA-

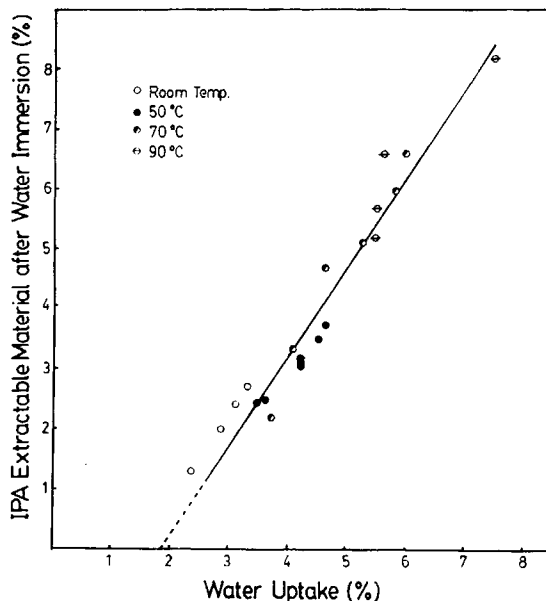


Fig. 4. Effect of water uptake on IPA extractions.

extracted silicone sealant before water immersion showed a strong and broad absorption band around 900 cm^{-1} . This was due to abundance of the silanol-terminated PDMS and the cross-linking agents of $\text{H}-\text{OSi}(\text{OH})\text{CH}_3-\text{OH}$ oligomers presented in the composite material. On prolonged water immersion, this strong and broad absorption band became narrower indicating some of the materials might have been leached out. Additional work is needed to establish it.

THERMAL STABILITY

The dynamic TG curves in Figure 5 show a marked decrease in the overall thermal stability for the three sealants which had either been immersed in water or exposed to outdoor for 300 days as compared to the one aged at room temperature only. A further comparison of stability can be made based on the temperature at which 50% weight loss has occurred ($T_{50\%}$). Data summarized in Table II indicate very clearly that the silicone sealant immersed in water at 90°C had the lowest $T_{50\%}$ and hence was the least stable. The crossing over of the curves at higher temperatures is indicative of the complex thermo-oxidative mechanisms arising from competing cyclization, random chain scission, and unzipping reactions.¹⁴ The presence of other components in the sealant complicates the analysis.

While the thermal degradation of pure silicone polymer has been extensively studied,¹⁴⁻¹⁶ there is little in the literature concerning the hydrolysis of silicone sealant composite. The present TG results suggest that hydrolytic reactions at both elevated and room temperatures could have disrupted the polymer matrix. This might provide some initial sites for thermal degradation to accelerate the weight loss as recorded by TG. However, the small

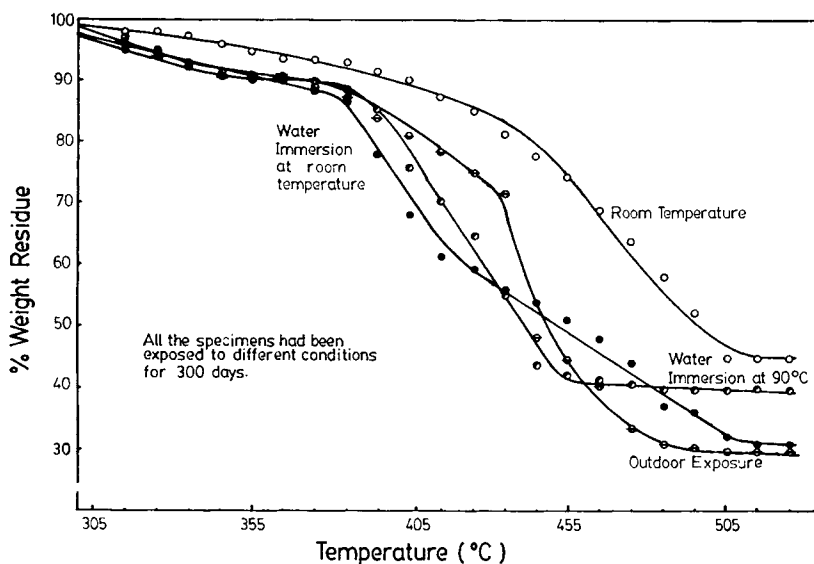


Fig. 5. Thermal stability of the cured silicone sealant.

differences in thermal stability in the range of 305–385°C between the sealants seem to imply that there was only slight main chain scission due to hydrolysis. The weight loss was expected to be much steeper in that temperature range if considerable hydrolytic degradation had occurred.

STRENGTH DETERIORATION UNDER WATER IMMERSION

The change of tensile strength (f/f_0) of the cured silicone sealant immersed in water at different times and temperatures is shown in Figure 6. A marked reduction in tensile strength was observed. After one month of water immersion, the strength reduction was about 20, 30, and 45% at 30, 50, and 90°C, respectively. The strength deterioration could be due to the combined effects of leaching, water swelling, and hydrolytic degradation.

The swelling effect of solvents on strength of an elastomer has been related to a theoretical equation,¹⁷ $f = f_0 V_r^{2/3}$, where V_r , f , and f_0 are the volume fraction of rubber, strength in the swollen and dry states, respectively. The effect of water on the strength reduction for the silicone sealant was simi-

TABLE II
Thermal Stability Indices (T50%) for Silicone Sealant After 300 Days of Treatments

Silicone specimen	Treatment	T50% (°C)
1	Aged at room temperature	500
2	Immersed in water at room temperature	460
3	Outdoor weathering	451
4	Immersed in water at 90°C	435

T50%, temperature at which 50% weight loss has occurred under dynamic TG.

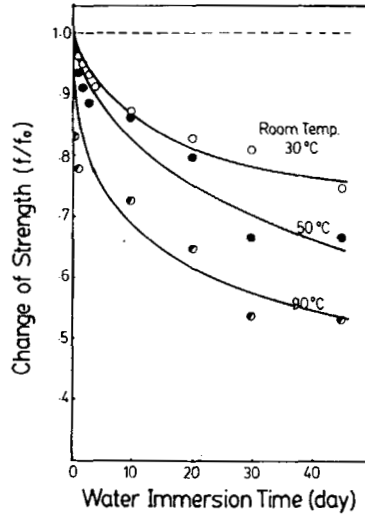


Fig. 6. Change of tensile strength of the cured silicone sealant immersed in water.

larly analyzed with respect to the volume fraction of silicone sealant in the swollen state (V_2). The water uptake was inversely proportional to V_2 . By plotting (f/f_0) versus $(V_2^{2/3})$ as shown in Figure 7, a linear relationship was obtained up to $V_2^{2/3} = 0.998$. It deviated from the linear behavior when $V_2^{2/3} < 0.998$. In terms of percentage, $V_2^{2/3}$ at 0.998 was equivalent to about 2% water uptake. This is approximated to a critical water concentration of about 1.8% obtained from the extrapolation of the IPA extraction (Fig. 4). The deviation from the linear plot of Figure 7 at higher water sorptions/higher immersion temperatures was thus caused by hydrolytic degradation.

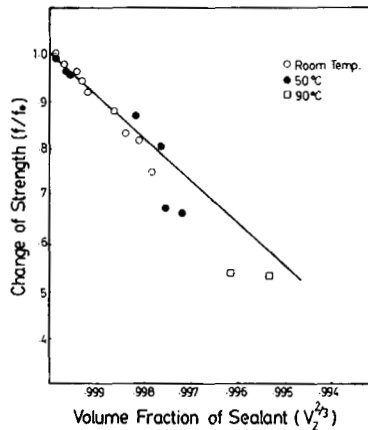


Fig. 7. Effect of water sorption on strength of the cured silicone sealant.

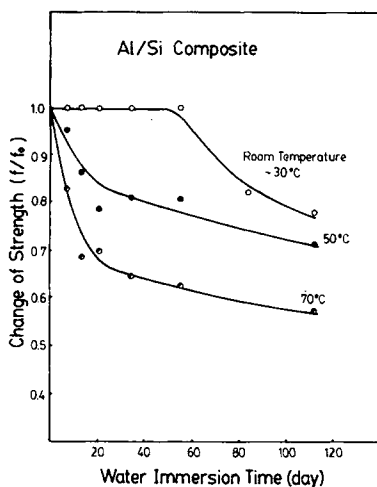


Fig. 8. Effect of water immersion on strength of aluminium/silicone composite.

The present results are consistent with the previous findings for the bond durability of silicone/aluminum lap joint immersed in water.⁶ The progressive reduction in joint strength with immersion time (Fig. 8) and the changing mode of joint failure from cohesive to adhesive pattern was attributed to interfacial debonding by slow hydrolysis through water penetration. The deterioration observed for the silicone joint composites in the short time exposure to equatorial environment might be mainly due to the humidity effects of swelling and hydrolysis rather than the photo-oxidative degradation.

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