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Degradation of Silicone Encapsulants in CPV Optics

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ABSTRACT — Concentrator photovoltaic (CPV) modules operate in extreme conditions, which poses a unique materials challenge for guaranteeing operational lifetimes of at least 25 years. The encapsulants used in the optical elements are critically susceptible to environmental degradation during operation. We studied the effects of weatherings on adhesion using an outdoor concentrator operating in excess of 1100 times the AM1.5 direct irradiance and in environmental chambers with broadband ultraviolet (UV) irradiation combined with controlled temperature and humidity. We observed a sharp initial increase in adhesion energy followed by a gradual decrease in adhesion as a result of both outdoor concentrator exposure and indoor UV weathering. We characterized changes in mechanical properties and chemical structures using XPS, FTIR, and DMA to understand the fundamental connection between mechanical strength and the degradation of the silicone encapsulant.

Index Terms — adhesion, CPV, reliability, silicone, UV degradation

I. INTRODUCTION

The reliability of optical elements in CPV modules poses a unique materials challenge due to increased ultraviolet (UV) irradiance, elevated operating temperature and frequent thermal cycling. We conducted a survey of the CPV industry to determine the critical interfaces and materials for study. The most critical interface for CPV reliability was determined to be the junction between the secondary optical element (SOE) and the anti-reflective (AR) coating on the CPV cell. The silicone adhesive used at the joint can be subject to greater than 1000 times the terrestrial solar flux, which can cause degradation and adhesive failure. Optical attenuation, including reflection loss at delamination at interfaces or cracks within the encapsulant, as well as loss of thermal management, even resulting in combustion of the encapsulant, have been observed in field studies [1].

Accordingly, the present study investigated the effects of photo-degradation on the silicone encapsulant and its adjacent interfaces. Specimens were aged in an outdoor concentrator to simulate operating conditions or in an environmental chamber with UV radiation to isolate environmental variables. Mechanical tests were carried out to determine the adhesion energy of the sample interface. Fourier transform infrared spectroscopy (FTIR) studies were conducted to examine the change in chemistry of bulk silicone as a result of weathering. We observed a significant change in adhesion energy along with change in failure mode as result of UV and outdoor weathering.

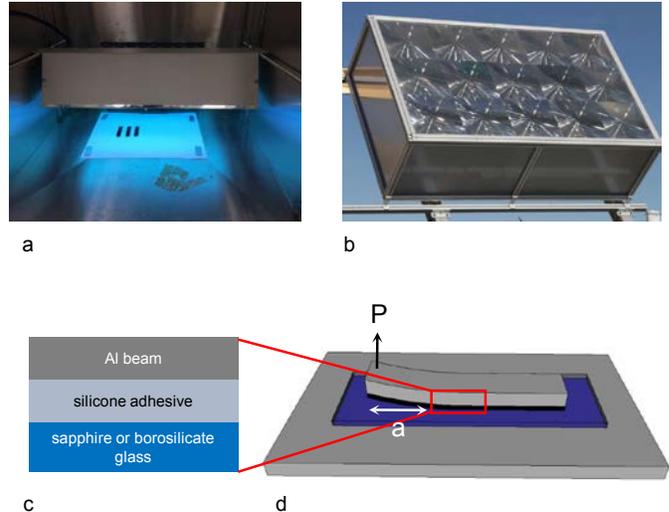


Fig. 1. Weathering of silicone specimens was conducted (a) in an environmental chamber under a UV lamp, (b) and in an outdoor concentrator. The samples are exposed through the transparent sapphire or glass superstrate (c), which was adhered to an aluminum plate (d) for mechanical testing of adhesion energy.

II. EXPERIMENTAL

Specimens were fabricated to model the adhesion of the silicone to the AR coatings of the multijunction CPV cells. Common AR materials, such as Al_2O_3 and silicon oxide, were modeled with sapphire wafers or B270 borosilicate glass, respectively, to allow for UV weathering and outdoor concentrator solar exposure. Two thermally cured silicone elastomers (Dow-Corning Sylgard 184 and NuSil Technology LS2-6140) were examined. To examine the effects of an adhesion promoting primer, a Ti-based primer (Dow-Corning 92-023) was applied to both the aluminum beam substrate and the sapphire or borosilicate glass superstrate before application of the Sylgard silicone (Fig. 1c). The primer was not applied to specimens with the LS2-6140 silicone as its formulation contained an adhesion promoting additive. The silicone were cured following the curing procedure recommended by the manufacturers.

Silicone specimens were aged in an indoor environmental chamber under UV illumination for accelerated aging (Fig. 1a). Outdoor exposure studies were conducted on Sylgard 184 specimens using a solar concentrator (Fig. 1b). The concentrator optics allowed for 1100 times solar concentration onto a 1 cm^2 area on the specimen, representing operating conditions in a contemporary CPV module design

Similar to the examination of EVA in flat-panel PV [2-4], mechanical tests were carried out using a DTS 8.2 mechanical load frame (Fig 1d). The adhesion energy, G_c , was calculated using the equation:

$$G_c = \frac{6P^2a^2}{B^2E'h^3} \quad (1)$$

where P is the load at the start of crack propagation, a is the length of the crack, B is the width of the sample, E' is the plain strain modulus, and h is the thickness of the aluminum beam [5]. G_c is the energy required to delaminate a unit surface area of silicone from the superstrate. The critical adhesion energy, G_c , characterizes the adhesive strength of the system, which can be used to quantify the degree of degradation.

III. RESULTS

The Sylgard 184 specimens aged in the outdoor concentrator (Fig. 2a) underwent an initial increase in adhesion energy up to ~ 250 J/m² at ~ 700 hours of exposure followed by a subsequent decrease in adhesion energy to ~ 5 J/m² at ~ 7000 hours of outdoor concentrator exposure. The failure mode for the field aged specimens changed from adhesive failure to cohesive failure with increased radiant exposure.

UV weathering at 110 °C caused a significant change on the adhesion energy of the Sylgard 184 and LS2-6140 silicone adhesives (Fig. 2b). All specimens exhibited an increase in adhesion energy from 6.3 J/m² to ~ 100 J/m² after cumulative UV dosage, H , ~ 30 MJ/m². With further UV exposure, the adhesion energy decreased to ~ 20 J/m² at $H \sim 200$ MJ/m². The failure mode changed from adhesive failure at the interface of the silicone and the sapphire superstrate to cohesive failure within the silicone encapsulant with prolonged weathering. The presence of the primer or adhesion promoter did not appear to affect the degradation of the silicone.

To determine the effect of temperature during UV exposure, the mechanical characterization was conducted for Sylgard 184 with applied primer specimens aged at 50 °C, 80 °C, and 110 °C (Fig. 4a and 4b). In the 80 °C series, the adhesion increased to a maximum of ~ 175 J/m² at a cumulative UV exposure of ~ 50 MJ/m². In the 50 °C series, the adhesion increased to a maximum of ~ 150 J/m² at a cumulative UV exposure of ~ 150 MJ/m². Specimens aged at 80 °C and 50 °C both exhibited change from adhesive to cohesive failure with increased cumulative radiant UV exposure.

Transmission FT-IR was conducted to determine the bulk chemistry of the silicone as a function of UV exposure (Fig. 3a and 3b). The silicone specimen exhibited an increase in the Si-O peak at 1088 cm⁻¹ as a result of UV exposure. The silicone exhibited a 6% increase in Si-O bonds after ~ 200 MJ/m² UV exposure (Fig. 3c). The measured percentage increase in Si-O bonds is normalized to the Si-O bonds in the silicone backbone.

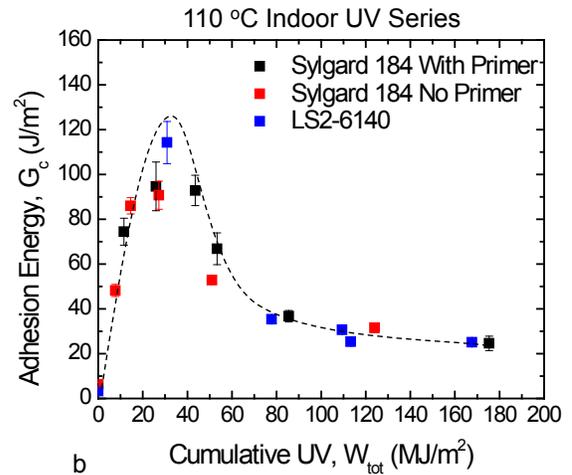
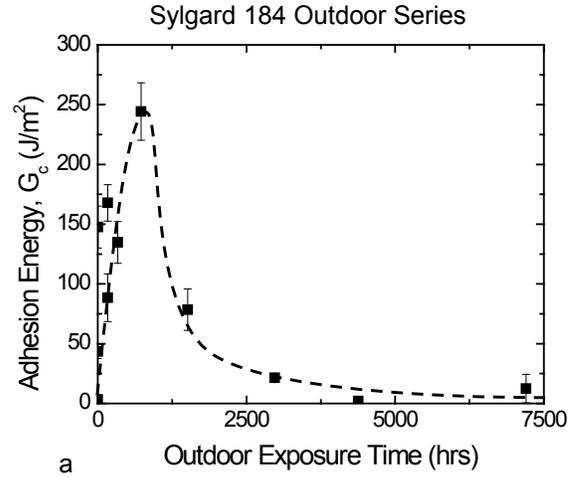


Fig. 2. Specimens aged in outdoor concentrator exhibit increase followed by decrease in adhesion energy (a). Specimens with different silicone formulation and surface treatments (b) exhibited similar trends during UV aging at 110°C.

IV. DISCUSSION

FTIR studies showed that the silicone was oxidized during exposure to UV at 110 °C (Fig. 3a and 3b). Literature identifies that UV-C radiation coupled with ozone treatment of silicone can cause oxidation of the silicone [6-7] but the effects of UV-A and UV-B radiation have not been widely studied. Traditionally, thermally cured silicone such as Sylgard 184 was thought to be unreactive to UV in the 300 nm to 400 nm range [8]. One possible mechanism for the oxidation of the silicone under these conditions is the cleavage of the Si-C bonds on the methyl side groups to form Si-OH groups [9], which can then react to form Si-O-Si bonds through a condensation reaction [6] (Fig. 3d).

Based on the calculated increase in Si-O bonds from FT-IR measurements (3c), the relationship between the increase in crosslink density, ΔN and H can be modeled by:

$$\Delta N = k_{UV} e^{-\frac{E_a}{k_b T}} H \quad (2)$$

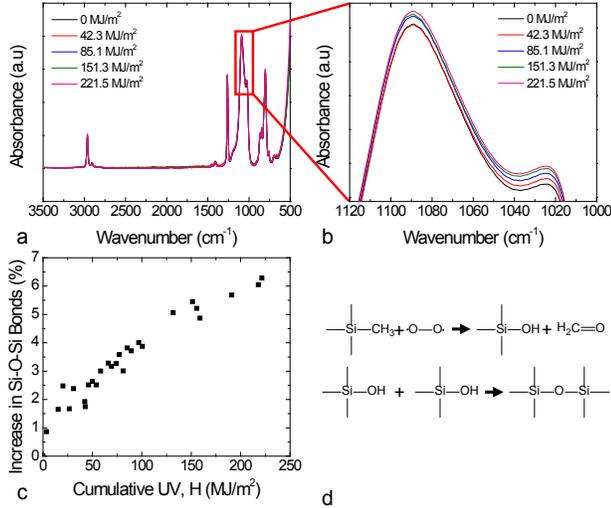


Fig 3. Transmission FTIR characterization of silicone after UV exposure (a) & (b) showed an increase in intensity for the Si-O stretching mode peak with increased cumulative radiant UV exposure, H . The percentage increase in Si-O bonds (c) can be calculated using the relative peak intensity at each H . A possible reaction scheme (d) for the oxidation of the silicone involves the formation of crosslinks following from UV mediated scission methyl side groups.

where k_{uv} is a proportionality constant, similar to a frequency factor. The temperature effects are accounted for with an Arrhenius term where E_a is the activation energy, k_b is the Boltzmann constant, and T is the temperature at which the specimens were aged.

The initial increase in G_c can be attributed to the increase in the number of bonds between the silicone and the underlying substrate and can be modeled as linearly proportional to the crosslink density between the silicone and the superstrate [10]:

$$G_c = k_s * \Delta N + G_0 \quad (3)$$

where k_s is a proportionality constant and G_0 is the initial adhesion energy with no UV exposure. Using Eq. (2) and Eq. (3), we obtain:

$$G_c = k_1 H e^{-\frac{E_a}{k_b T}} + G_0 \quad (4)$$

where k_1 is the consolidated constant taking into account both k_s and k_{UV} .

Data in the initial UV aging regime at 50 °C, 80 °C, and 110 °C were used to determine the activation energy. The activation energy was calculated to be 32 kJ/mol, which is in the range of 20 kJ/mol to 40 kJ/mol reported for oxidation of silicone under UV-ozone treatments [11]. The activation energy for the degradation seen here is significantly less than the 90 kJ/mol to 125 kJ/mol activation energy reported for thermal oxidation of silicone [12]. The measured adhesion energy with no UV exposure, G_0 , was 6.3 J/m². Using the values for G_0 and E_a , k_1 was fitted to obtain $2.3 \cdot 10^5$ 1/s.

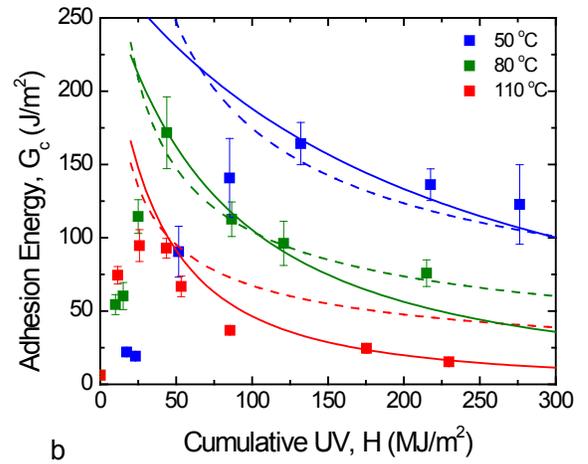
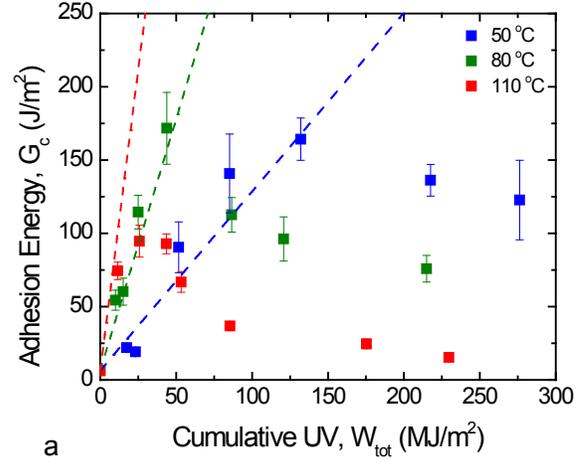


Fig. 4. The linear fit (a) from Eq. 4 characterizes the initial increase in adhesion. The power function (b) from Eq. 6 characterizes the decrease in cohesion with the dotted line representing the ideal $M_c^{1/2}$ scaling for a planar crack and the solid line representing the fitted $M_c^{1.66}$ scaling for a meandering crack.

The dependence on temperature and cumulative radiant UV exposure in the model fit the observed trends in G_c (Fig. 6a) with the calculated value of E_a and the fitted value of k_1 .

With prolonged UV aging, the most stable crack path instead propagates through the bulk silicone [13]. The decrease in G_c can be attributed to embrittlement as a result of increased crosslinking in the bulk silicone material. Literature reports that the cohesion energy, G_c , in elastomeric polymers scales as

$$G_c \sim n * M_c^{\frac{3}{2}} \quad (5)$$

where n is the number of chains that bridge a crack front and M_c is the average molecular weight between crosslinks [14]. The term $M_c^{3/2}$ describes the average energy required to rupture one chain. n is directly proportional to the crosslink density, ΔN , as each additional crosslink creates two

additional chains and as M_c scales inversely with ΔN , n would scale as M_c^{-1} . Therefore G_c scales as $\Delta N^{1/2}$ accounting for the competing effects of increasing volume density of chains and decreasing energy required to rupture the chains [15].

Using Eq. (2), the relationship between G_c and H can be written as

$$G_c = \frac{k_2}{\left(k_3 + He^{-\frac{E_a}{k_b T}}\right)^{\frac{1}{2}}} \quad (6)$$

where k_2 is a proportionality constant that relates crosslink density to cohesion energy and k_3 is a constant that reflects the initial degree of crosslinking. The constants k_2 and k_3 were fitted and the predicted behavior is plotted against the experimental values (Fig. 6b). The model, which scales as $M_c^{1/2}$, is indicated with a dashed line for all three aging temperatures.

The model predictions deviate from the experimentally measured G_c values at higher temperature and cumulative radiant UV exposure because it assumes a planar crack path. In materials with higher network connectivity, the crack will meander through the material and follow a path of lower resistance compared to a planar crack [16].

A meandering crack path would affect the scaling of G_c with ΔN since the crack would seek paths with shorter chains and corresponding lower rupture energy. In effect, the shortest chains determine the fracture energy of the bulk material in this regime. The fracture energy is accordingly more sensitive to changes in crosslink density and therefore would scale as $\Delta N^{-1/2}$. A fitting of experimental data to determine the scaling reveal that G_c scales as $\Delta N^{1.66}$, plotted as a solid line (Fig. 4b). The greater scaling exponent gives a better fit for the dependence of G_c on H . Experimental data in the literature shows similar trends of higher scaling power for materials with higher crosslink density. [24]

V. CONCLUSION

We studied the effects of terrestrial UV on silicone adhesives for CPV applications. Specimens aged in the outdoor concentrator exhibited an increase in adhesion energy to $\sim 200 \text{ J/m}^2$ with initial exposure and subsequent decrease in adhesion to $\sim 2 \text{ J/m}^2$ with prolonged exposure. Similar behavior was observed for UV weathering. The initial increase in adhesion was attributed to an increase in the population of bonds between the silicone and the underlying superstrate. The subsequent decrease in adhesion was attributed to the embrittlement of the silicone as a result of UV-photochemical crosslinking. A fracture mechanics model was developed to model the adhesion energy and can be used to predict the behavior of encapsulant materials with accelerated aging testing. We find that UV crosslinking could limit the life of silicone encapsulation used in CPV modules through reduced adhesion or embrittlement and subsequent cracking of the bulk

material. The durability of materials under high UV flux must be considered to ensure the reliability of CPV modules.

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