Degradation of Thermally-Cured Silicone Encapsulant under Terrestrial UV

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ABSTRACT

Concentrator photovoltaic (CPV) modules operate in extreme conditions, including enhanced solar flux, elevated operating temperature, and frequent thermal cycling. Coupled with active environmental species such as oxygen and moisture, the operating conditions pose a unique materials challenge for guaranteeing operational lifetimes of greater than 25 years. Specifically, the coatings and encapsulants used in the optical elements are susceptible to environmental degradation during operation. For example, the interfaces must remain in contact to prevent optical attenuation and thermal runaway. We developed fracture mechanics based metrologies to characterize the adhesion of the silicone encapsulant and its adjacent surfaces, as well as the cohesion of the encapsulant. Further, we studied the effects of weathering on adhesion using an outdoor concentrator operating in excess of 1100 times the AM1.5 direct irradiance and in indoor 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. We developed physics based models to explain the change in adhesion and to predict operational lifetimes of the materials and their interfaces.

Keywords: silicone, UV degradation, adhesion, reliability

INTRODUCTION

High efficiency multijunction solar cells in terrestrial concentrator photovoltaic (CPV) modules are becoming an increasingly cost effective and viable option in utility scale power generation. As with other utility scale photovoltaics, CPV modules target to maintain operational lifetimes of greater than 25 years. 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 associated with the concentrated solar flux. The polymeric and thin film materials used in the optical elements are susceptible to UV damage, thermal-mediated stress cycling and active chemical species, such as oxygen and water, from the environment. Understanding the underlying mechanisms of materials degradation under elevated stress conditions is critical for commercialization of CPV technology and can offer unique insights into degradation modes in similar materials used in other photovoltaic modules.

To determine the critical interfaces and materials for study, a survey of the CPV industry was conducted. A total of 13 CPV module and optics manufacturers were surveyed. Each was asked to identify the 3 to 5 most critical interfaces for study and the results were tabulated (Figure 1). 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 SOE, typically a glass homogenizer, is adhered to the surface of the AR coating, typically Al_2O_3 or TiO_2 , with a silicone adhesive. During operation, the silicone adhesive can be subject to greater than 1000 times the terrestrial solar flux and elevated temperatures in excess of 100 °C. Under these conditions, degradation of the silicone encapsulant can cause adhesive or cohesive failure, terminating the operational lifetime of the CPV module. 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 with Al_2O_3 and silicon oxide. The goal of the study was to develop a model that might be used to predict the lifetime of those interfaces with the encapsulant. Specimens were aged in an outdoor concentrator to simulate operating conditions or in an environmental chamber under UV illumination to isolate environmental variables. Mechanical tests were carried out to determine the adhesion energy of the sample

interface. X-ray photoelectron spectroscopy (XPS) studies were conducted to examine the chemistry of delaminated surfaces after mechanical tests and Fourier transform infrared spectroscopy (FTIR) studies were conducted to examine the change in chemistry of bulk silicone as a result of weathering. The adhesion energy between the silicone to the adjacent interfaces increased by ~ 2 orders of magnitude, from 6.3 J/m^2 to $\sim 200 \text{ J/m}^2$ during initial UV weathering. Subsequent exposure decrease the adhesion energy to $\sim 20 \text{ J/m}^2$. The rate of change in adhesion energy as a result of UV exposure varied significantly with temperature. Specimens aged in the outdoor concentrator exhibited a similar 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. The failure mode changed from adhesive to cohesive in both UV weathering and outdoor exposure. The change in adhesion in the silicone can be attributed to an increase in crosslink density and a model was developed to quantify the change.

METHODS AND MATERIALS

Specimens were fabricated to model the adhesion of the silicone to the AR coatings of the multijunction CPV cells. Common materials at the interface, such as Al_2O_3 and silicon oxide, were modeled with double side polished sapphire wafers or B270 borosilicate glass (SCHOTT Corp.), respectively, to allow for UV weathering and outdoor concentrator solar exposure. Two polydimethylsiloxane silicone elastomers (Dow-Corning Sylgard 184 and NuSil Technology LS2-6140) were examined. Both elastomers were thermally cured and crosslinked through vinyl-hydride chemistry. The silicone adhesives were applied to a sapphire and borosilicate glass superstrate and sandwiched with an aluminum beam substrate on top (Figure 2c). Excess silicone was trimmed and the edges of the silicone were left exposed to the environment. Note also that the PDMS cured to manufacturer's specifications typically contains diffused oxygen and moisture. A $250 \text{ }\mu\text{m}$ thick PTFE-coated fiberglass release liner was use to maintain the thickness of the silicone adhesive layer. The B270 glass was buffed with pumice powder to remove coarse contaminants as well as residual adipic acid powder and cleaned with a detergent (Billco, Billco Manufacturing Inc.), deionized water, and then isopropyl alcohol prior to assembly. The sapphire and the borosilicate glass had a surface roughness of $R_a < 2 \text{ nm}$, and $R_a < 2.5 \text{ nm}$, respectively. 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. The primer was not applied to specimens with the LS2-6140 silicone as its formulation contained an adhesion promoting additive. The Sylgard 184 silicone was cured at 100 °C for 1 hour and the LS2-6140 silicone was cured at 150 °C for 1 hour following the recommended curing schedule from the manufacturers.

To study the effects of photo-degradation, silicone specimens were aged in an indoor environmental chamber (AES BHD-508) under UV illumination for accelerated aging (Figure 2a). The light source, 15 W mercury based UV bulbs (UVP XX-15MR), was peaked at 302 nm with an irradiance of 45 W/m² at the specimen surface (Figure 2b). The silicone was exposed to UV through the sapphire and borosilicate glass superstrate at 50 °C with 10% relative humidity (RH), 80 °C with 10% RH, and 110 °C with uncontrolled humidity.

Similar to the examination of EVA in flat-panel PV, mechanical tests were carried out using a DTS 8.2 mechanical load frame for single cantilever beam specimens to characterize the adhesion of the silicone material after various aging treatments [2-4] (Figure 2d). Samples were loaded from one end of the aluminum beam and a crack was propagated through the silicone. After testing, the adhesion energy, G_c , was calculated using the equation:

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

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 , the critical adhesion energy, is the energy required to delaminate a unit surface area of silicone from the superstrate. G_c characterizes the strength of the adhesive bond, which can be used to quantify the degree of degradation.

Outdoor exposure studies were conducted on Sylgard 184 specimens using a solar concentrator (Figure 3a). The concentrator optics allowed for solar concentration, with a nominal 1100x geometric concentration ratio, onto a 1 cm² area on the specimen (Figure 3b), representing operating conditions in contemporary CPV module design. No noticeable non-uniformities were apparent in the solar flux and no apparent indications of such non-uniformities were observed on the exposed specimens. The illumination at the specimen was based on the ideal nominal terrestrial direct solar flux, with no local concentration from the optical design or any imperfections in the optics. Because Al has good reflectance at UV wavelengths [6], the UV radiant exposure for the silicone within the samples is nearly doubled. The spectral irradiance at

the specimen was determined from the optical transfer function using the measured spectral transmittance of each optical component at 1100 times the AM1.5D spectrum (Figure 3c). At solar noon on sunny days, the specimens experienced daily operating temperatures from 30 °C to 80 °C depending on the season and local weather. Thermal paste was used to ensure thermal contact between each specimen and its underlying aluminum heat sink. A magnetic clamp was used to secure the specimen to the irradiated area under the SOE. Adhesion measurements were conducted after outdoor exposure to characterize the change in adhesion of the silicone.

RESULTS

Indoor UV exposure at 110 °C caused a significant change on the adhesion energy of the Sylgard 184 and LS2-6140 silicone adhesives (Figure 4a). To determine the effect of the Ti-based primer, one set of Sylgard 184 specimens was treated with the primer before the application of the silicone. All specimens exhibited an increase in adhesion energy from 6.3 J/m² to ~100 J/m² after ~30 MJ/m² of UV exposure. During the initial weathering, the failure mode was predominantly adhesive with the sapphire superstrate. With further UV exposure, the adhesion energy decreased to ~20 J/m² at ~200 MJ/m² of cumulative UV exposure. Typically, 5 to 10 measurements of adhesion are included in each data point. The standard deviation is reported as the error bars which for some cases was smaller than the size of the data symbol. The failure mode changed from adhesive failure at the interface of the silicone and the sapphire superstrate to cohesive failure within the silicone encapsulant. Channel cracks were also observed in the delaminated silicone specimens.

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 (Figure 4b). Samples in all series of experiments exhibited similar behavior with an initial increase in adhesion followed by a decrease in cohesion with increased cumulative UV exposure. 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.

The adhesion energy of silicone specimens aged in outdoor concentrator (Figure 5a) exhibited similar trends to those aged under UV in environmental chambers. The Sylgard 184 specimens aged in the outdoor concentrator underwent an initial increase in adhesion energy up to $\sim 250 \text{ J/m}^2$ at ~ 700 hours of exposure followed by a subsequent decrease in adhesion energy to $\sim 10 \text{ J/m}^2$ at ~ 7000 hours of exposure. The results were reported as a function of hours of exposure in the concentrator instead of cumulative radiant UV exposure because the specific UV wavelengths most important for the degradation process was unknown. Similar to UV aged specimens, the failure mode for the field aged specimens changed from adhesive failure to cohesive failure with increased radiant exposure. In addition, a number of samples developed a network of cracks in the silicone encapsulant that was weathered in the outdoor concentrator. Optical images (Figure 5b) showed the defect evolution in the silicone encapsulant over the first 4400 hours of a specimen weathered in the outdoor concentrator. The optical images showed separate instances of edge and interior initiated cracks. The initiation process was not the subject of the present study. Adhesion data were determined from samples that did not exhibit excessive cracking in the silicone layer.

XPS characterization was conducted on the opposing delaminated surfaces at all temperatures after mechanical testing to verify the failure pathway. Surface characterization showed that with no UV exposure, the samples delaminated at the interface of the silicone adhesive and the sapphire superstrate (Figure 6a). The sapphire side showed Si peaks from residual silicone and Al peaks characteristic of the sapphire surface. With increased UV radiant exposure, the failure mode transitioned to cohesive failure within the silicone encapsulant (Figure 6b). XPS characterization of the delaminated sapphire superstrate showed no aluminum peak, indicating a layer of silicone film on the surface. With further UV exposure, the residual layer of silicone after delamination became macroscopic and could be observed visually.

Transmission FT-IR was conducted to determine the bulk chemistry of the silicone as a function of UV exposure (Figure 7a,b). A thin layer of Sylgard 184 silicone was cured between two NaCl windows and aged under UV at 50°C . The silicone specimen exhibited an increase in the Si-O peak at 1088 cm^{-1} as a result of UV exposure. The fractional increase in Si-O bonds were calculated with the ratio of the peak height for a given cumulative radiant UV exposure to the peak height with no exposure. The silicone exhibited a 6% increase in Si-O bonds after ~ 200

MJ/m² UV exposure (Figure 7c). The measured percentage increase in Si-O bonds is normalized to the Si-O bonds in the silicone backbone.

DISCUSSION

The temperature at which the UV exposure was conducted affected the degradation of the Sylgard 184 silicone (Figure 4b). While all specimens exhibited the characteristic local maximum in adhesion, specimens aged at a higher temperature exhibited a higher rate of the increase in adhesion and the subsequent decrease in cohesion with increasing cumulative radiant UV exposure. The presence of the Ti-based primer used with the Sylgard silicone and the adhesion promoter in the LS2-6140 silicone formulation did not appear to affect the adhesion energy of the indoor UV aged specimens (Figure 4a). The specific role of environmental oxygen or humidity concentration on the crosslinking reaction were not examined but should be considered in future studies.

FTIR studies of bulk silicone specimens under UV irradiation showed that the silicone was oxidized during exposure to UV at 110 °C (Figure 7a,b). The literature identifies that UV-C radiation coupled with ozone treatment of silicone can cause oxidation of the silicone [7-11] 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 and insensitive to UV in the 300 nm to 400 nm range [12]. One possible mechanism for the oxidation of the silicone under these conditions is that UV irradiation at these wavelengths induces a reaction that cleaves the Si-C bonds on the methyl sidegroups to form Si-OH groups [13], which can then react to form Si-O-Si bonds through a condensation reaction [7] (Figure 7d). The mechanism of UV facilitated crosslinking noted in the literature [7-9] is different than the mechanisms of thermal decomposition of silicone to silicon oxide observed in high temperature studies [1]. The cleaving of carbon side chains to form Si-O-Si bonds would increase the crosslink density in the silicone, leading to the decrease in adhesion energy as a result of UV exposure.

Based on the calculated increase in Si-O bonds from FT-IR measurements (Figure 7c), the relationship between the increase in crosslink density, ΔN and the cumulative radiant UV exposure, H , can be modeled by:

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

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. A linear relationship between ΔN and H can be explained as a 0th order reaction for crosslinking because the number of possible reaction sites for crosslinking is much greater than the number of crosslinks that forms during UV exposure.

During initial aging (0 to ~50 MJ/m²), the increase in G_c can be attributed to the increase in the number of bonds between the silicone and the underlying substrate. Similar to bulk silicone, silicone atoms at the interface can be oxidized to form Si-O bonds, which attaches to the oxygen atoms on the surface of the sapphire or B270 superstrate. The adhesion energy between the silicone and the superstrate can be modeled as linearly proportional to the crosslink density between the silicone and the superstrate [14-16]:

$$G_c = k_s * \Delta N + G_0 \quad \text{Eq. (3)}$$

where k_s is a proportionality constant that accounts for the increase in adhesion per unit increase in the bond population at the interface between the silicone and the superstrate and G_0 is the initial adhesion energy with no UV exposure. Using Eq. (2) and Eq. (3), we obtain:

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

where k_l is the consolidated constant taking into account both k_s and k_{UV} . Here, we assume that the photo-chemical crosslinking reaction at the interface is similar that observed in the bulk silicone.

Data in the initial UV aging regime at 50 °C, 80 °C, and 110 °C were used to determine the activation energy. The natural log of the slope is plotted against the inverse of temperature for Arrhenius analysis (Figure 8). 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 [17]. 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 [18, 19] identifying that UV contributes to the degradation here. 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_l was fitted to obtain 2.3×10^5 . The dependence on temperature and cumulative radiant UV exposure in the model fit the observed trends in G_c (Figure 9a) with the calculated value of E_a and the fitted value of k_l .

With prolonged UV aging, the delamination pathway was observed to move into the bulk silicone, away from the interface, as seen in XPS characterization of the delaminated surface (Fig. 5). The crack path changed due to the increased adhesion between the silicone and the interface. The most stable crack path instead propagates through the bulk silicone [20]. 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

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

where n is the number of chains that bridge a crack front and M_c is the average molecular weight between crosslinks [21]. Equation (5) represents the elastic energy required to rupture polymer chains ahead of the crack front. Higher chain density would result in higher fracture energy as more chains would need to be ruptured to propagate the crack. The term $M_c^{3/2}$ describes the average energy required to rupture one chain. It accounts for the statistical distribution in chain lengths in the elastomer and the end-to-end length in each 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 [21-24].

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

$$G_c = \frac{k_2}{\left(k_3 + H e^{-\frac{E_a}{k_b T}}\right)^{\frac{1}{2}}} \quad \text{Eq. (6)}$$

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 and determines G_c of the bulk silicone with no UV exposure. The constants k_2 and k_3 were fitted and the predicted behavior is plotted against the experimental values (Figure 9b). The model, which scales as $M_c^{1/2}$, is plotted with dashed line for all three aging temperatures with good overlap to the data for the silicone after prolonged aging.

The model predicts greater deviation from the experimentally measured G_c values at higher temperature and cumulative radiant UV exposure. The model, however, assumes a planar

crack propagation path through the silicone encapsulant. In a material with higher network connectivity, the crack often does not follow a planar path. Instead, the crack will meander through the material and follow a path of lower resistance compared to a planar crack [25].

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 and avoid paths with longer chains and higher rupture energy. Therefore the crack path will no longer sample the statistical average of chain length in the silicone. 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 (Figure 9b). 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]

CONCLUSION

We studied the effects of terrestrial UV on silicone adhesives for CPV applications. Representative coupon specimens systems were used to simulate critical interfaces (silicone/glass or silicone/ Al_2O_3) and allow for weathering in an outdoor concentrator and under UV in an environmental chamber. The adhesion energy between the silicone to the adjacent interfaces increased by ~ 2 orders of magnitude, from 6.3 J/m^2 to $\sim 200 \text{ J/m}^2$ with initial UV weathering. The initial increase in adhesion was attributed an increase in the population of bonds between the silicone and the underlying superstrate. Subsequent exposure decrease the adhesion energy to $\sim 20 \text{ J/m}^2$, which, is caused by the embrittlement of the bulk silicone as a result of UV-photochemical crosslinking. The rate of change in adhesion energy as a result of UV exposure varied significantly with temperature. Specimens aged in the outdoor concentrator exhibited a similar 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. The crack path changed from the interface of the silicone and the superstrate for short exposure times to within the silicone for long exposure times. A fracture mechanics model was developed to model the adhesion energy as a function of cumulative radiant UV exposure and temperature and can be used to predict the behavior of encapsulant materials with accelerated aging test. 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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References

- [1] Miller DC, Muller MT, Kempe MD, Araki K, Kennedy CE, Kurtz SR. Durability of polymeric encapsulation materials for concentrating photovoltaic systems. *Progress in Photovoltaics: Research and Applications* 2013;21:631-51.
- [2] Dauskardt RH, Lane M, Ma Q, Krishna N. Adhesion and debonding of multi-layer thin film structures. *Engineering Fracture Mechanics* 1998;61:141-62.
- [3] Kook S-Y, Dauskardt RH. Moisture-assisted subcritical debonding of a polymer/metal interface. *Journal of Applied Physics* 2002;91:1293-303.
- [4] Novoa FD, Miller DC, Dauskardt RH. Adhesion and debonding kinetics of photovoltaic encapsulation in moist environments. *Progress in Photovoltaics: Research and Applications* 2016;24:183-94.
- [5] Birringer RP, Shaviv R, Besser PR, Dauskardt RH. Environmentally assisted debonding of copper/barrier interfaces. *Acta Materialia* 2012;60:2219-28.
- [6] Miller DC, Kempe MD, Kennedy CE, Kurtz SR. Analysis of transmitted optical spectrum enabling accelerated testing of multijunction concentrating photovoltaic designs. *Optical Engineering* 2011;50:013003--17.
- [7] Israeli Y, Philippart JL, Cavezzan J, Lacoste J, Lemaire J. Photo-oxidation of polydimethylsiloxane oils: Part I—Effect of silicon hydride groups. *Polymer Degradation and Stability* 1992;36:179-85.
- [8] Israël Y, Cavezzan J, Lacoste J. Photo-oxidation of polydimethylsiloxane oils: II—Effect of vinyl groups. *Polymer Degradation and Stability* 1992;37:201-8.
- [9] Israël Y, Lacoste J, Cavezzan J, Lemaire J. Photo-oxidation of polydimethylsiloxane oils Part III—effect of dimethylene groups. *Polymer Degradation and Stability* 1993;42:267-79.
- [10] Efimenko K, Wallace WE, Genzer J. Surface Modification of Sylgard-184 Poly(dimethyl siloxane) Networks by Ultraviolet and Ultraviolet/Ozone Treatment. *Journal of Colloid and Interface Science* 2002;254:306-15.
- [11] Oláh A, Hillborg H, Vancso GJ. Hydrophobic recovery of UV/ozone treated poly(dimethylsiloxane): adhesion studies by contact mechanics and mechanism of surface modification. *Applied Surface Science* 2005;239:410-23.
- [12] Tsougeni K, Tserepi A, Gogolides E. Photosensitive poly(dimethylsiloxane) materials for microfluidic applications. *Microelectronic Engineering* 2007;84:1104-8.
- [13] Delman AD, Landy M, Simms BB. Photodecomposition of polymethylsiloxane. *Journal of Polymer Science Part A-1: Polymer Chemistry* 1969;7:3375-86.
- [14] Brown HR. Effects of chain pull-out on adhesion of elastomers. *Macromolecules* 1993;26:1666-70.
- [15] Deruelle M, Leger L, Tirrell M. Adhesion at the Solid-Elastomer Interface: Influence of the Interfacial Chains. *Macromolecules* 1995;28:7419-28.
- [16] Chang RJ, Gent AN. Effect of interfacial bonding on the strength of adhesion of elastomers. I. Self-adhesion. *Journal of Polymer Science: Polymer Physics Edition* 1981;19:1619-33.
- [17] Klumpp A, Sigmund H. Photoinduced transformation of polysiloxane layers to SiO₂. *Applied Surface Science* 1989;43:301-3.
- [18] Thomas TH, Kendrick TC. Thermal analysis of polydimethylsiloxanes. I. Thermal degradation in controlled atmospheres. *Journal of Polymer Science Part A-2: Polymer Physics* 1969;7:537-49.

- [19] Camino G, Lomakin SM, Lazzari M. Polydimethylsiloxane thermal degradation Part 1. Kinetic aspects. *Polymer* 2001;42:2395-402.
- [20] Fleck NA, Hutchinson JW, Zhigang S. Crack path selection in a brittle adhesive layer. *International Journal of Solids and Structures* 1991;27:1683-703.
- [21] Lake GJ, Thomas AG. The Strength of Highly Elastic Materials. *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* 1967;300:108-19.
- [22] Ahagon A, Gent AN. Threshold fracture energies for elastomers. *Journal of Polymer Science: Polymer Physics Edition* 1975;13:1903-11.
- [23] Tsunoda K, Busfield JJC, Davies CKL, Thomas AG. Effect of materials variables on the tear behaviour of a non-crystallising elastomer. *Journal of Materials Science* 2000;35:5187-98.
- [24] Gent AN, Tobias R. Threshold tear strength of elastomers. *Journal of Polymer Science: Polymer Physics Edition* 1982;20:2051-8.
- [25] Oliver MS, Dubois G, Sherwood M, Gage DM, Dauskardt RH. Molecular Origins of the Mechanical Behavior of Hybrid Glasses. *Advanced Functional Materials* 2010;20:2884-92.

FIGURES

Figure 1. Pareto of critical adhesive interfaces for study in CPV modules. 13 CPV module or optics manufacturers were surveyed to identify the most critical interfaces. The attachment of the secondary optical element to the anti-reflective coating of the multi-junction cell was determined to be the most critical for CPV reliability.

Figure 2. UV exposure of silicone specimens was conducted in (a) an indoor environmental chamber at 50 °C, 80 °C or 110 °C at 10% relative humidity under a UV lamp, (b) with a peak intensity at 302 nm and total UV irradiance from 280 nm to 400 nm of 4.5 mW/cm² at the specimen. 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.

Figure 3. The outdoor concentrator optics (a) allowed for exposure with 1100 times solar concentration onto a 1 cm² target (b). The spectral irradiance at the sample surface (c) was determined from the optical transfer function using the spectral transmittance of all the optical elements for the source of AM1.5D spectrum.

Figure 4. Specimens with different silicone formulation and surface treatments (a) exhibited similar trends during UV aging at 110 °C. Temperature during UV aging (b) was found to have a significant effect on the rate of degradation of the silicone.

Figure 5. Specimens aged in outdoor concentrator exhibit increase followed by decrease in adhesion energy (a), similar to specimens aged under UV. Optical images (b) show formation and growth of cracks through 4400 hours of aging under outdoor concentrator.

Figure 6. XPS characterization of the sapphire superstrate aged at 110 °C after delamination. The delaminated surface on the sapphire side with no UV exposure (a) shows strong Al peaks, while (b) the delaminated surface on the sapphire side with minimal UV exposure (b) shows no Al peak.

Figure 7. Transmission FT-IR 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. The percentage increase in Si-O bonds (c) can be calculated using the relative peak intensity at different cumulative radiant UV exposure. A possible reaction scheme (d) for the oxidation of the silicone involves the formation of crosslinks following from UV mediated scission methyl sidegroups.

Figure 8. Arrhenius analysis of the change in adhesion energy during the initial UV exposure. The activation energy of 32 kJ/mol follows from the analysis.

Figure 9. Overlay of the experimental and modeled behavior for UV aged silicone encapsulant. 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.

Graphical Abstract