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Effect of Photodegradation on Chemical Structure and Surface Characteristics of Silicone Pottants Used in Solar Cell Modules

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4. Absorption Spectrum of RTV-615 ------------------------ 5
5. Decrease in Absorbance at 3400 cm\(^{-1}\) with Time -------- 9
6. Increase in Absorbance at 1720 cm\(^{-1}\) with Time -------- 10
7. Increase in Absorbance at 2130 cm\(^{-1}\) with Time -------- 11

Tables
1. Materials Used in Test Coupons ----------------------------- 3
2. Acceleration Factors Determined Actinometrically --------- 6
3. Water Immersion and Irradiation Sequence ------------------- 7
4. Surface Energy Analysis of Irradiated Silicones ----------- 12
5. Irradiation of RTV-615 Deposited on Substrates ----------- 13
SECTION I
INTRODUCTION

A. PROBLEM

Solar cell modules of Block I and Block II purchase delaminated in the field after passing JPL acceptance tests. Attempts to simulate field failure using conventional thermal and humidity cycling tests were unsuccessful. It was surmised that delamination might be caused by degradation of the adhesive bond caused by solar ultraviolet.

B. SOLUTION

A failure analysis was carried out in terms of generic physiochemical mechanisms which included a careful assessment of time acceleration of ultraviolet radiation. The proposed model included rate of change of silicone material properties, including properties of the surface as a function of aging under well characterized ultraviolet irradiation and rate of change in bond strength. Failure observed in the field was then simulated in test specimens, and the failure rate was compared to that observed in the field.

C. APPROACH

The inherent variability of the silicone surface from point to point often exceeds changes in properties caused by aging, and it is therefore difficult to obtain unambiguous results from the failure analysis described above. This ambiguity may be resolved by monitoring more than one surface property whose degradation correlates with the failure mechanism under study. For delamination of silicones (RTV-615 and Sylgard-184) from certain hydrophobic substrates we have identified material properties of the polymer which correlate with bonding properties of its surface and therefore predict environmental aging conditions under which debonding would occur from a specific substrate. This type of analysis of the failure mechanism probes into the molecular basis of the failure and is of use in designing accelerated tests which would allow predicting lifetimes under given (or known) environments. Figure 1 summarizes this mechanistic approach to failure analysis and lifetime prediction.

It has been demonstrated analytically and experimentally that if one can determine the photochemical mechanism of degradation which will control the failure, it is possible to accelerate the failure mechanism using well characterized ultraviolet sources rather than sources which simulate the solar spectrum. In the absence of detailed understanding of the degradation mechanism one is constrained to simulate the solar spectrum in order to study failure mechanisms.
Figure 1. Mechanistic Approach to Failure Analysis in Silicones
SECTION II
TEST DESIGN

Polydimethyl siloxane films (RTV-615 and Sylgard-184) were initially irradiated with ultraviolet light and their degradation monitored by recording weight change, IR and UV-visible spectra, and by surface energy analysis (SEA). A mechanism of photodegradation was proposed on the basis of experimental data on freestanding films 1 to 2 mil thick. This mechanism was then utilized along with SEA to predict change in bond strength of the silicone to various substrates and to predict conditions under which photodegradation would induce debonding to occur. These predictions were tested using coupons two inches square of RTV-615 attached to various substrates. The materials used in these coupons are listed in Table 1. The design of the coupons is shown in Figure 2. These coupons were irradiated, subjected to temperature cycling, and subsequently to a water soak. Parallel experiments were carried out with coupons receiving no ultraviolet radiation but experiencing otherwise identical stresses.

Table 1. Materials Used in Test Coupons

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Adhesive</th>
<th>Pottant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>RTV-108</td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td>Q36-060</td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>SS-4120</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. Design of Test Coupons
A. RADIATION SOURCES AND THEIR CALIBRATION

Two types of radiation sources were used in this study: a high pressure xenon arc and a medium pressure mercury arc. Their spectra are shown in Figure 3. Light intensity was monitored radiometrically and actinometrically. A benzophenone- trans 1,3-pentadiene actinometer was used to monitor the 3130Å band intensity of the mercury arc which was isolated by the K2Cr2O7 - NaHCO3 solution filter. Both the lamps were monitored during test exposure by o-nitrobenzaldehyde actinometry, with the actinometer in the form of thin polymer films placed in the same position as the samples of silicone being tested. In this manner an attempt was made to take into account light being incident on the sample over a certain range of viewing angles.

The absorption spectrum of RTV-615 (1 mil) is shown in Figure 4. This spectrum may be superimposed on the irradiance maps of the lamps (Figure 3); the area under the intersection of the two curves is proportional to the amount of light being absorbed by the sample. This approach was used to calculate the approximate acceleration factor for the mercury lamp relative to the xenon lamp (both unfiltered and filtered through Pyrex) as well as to the AM-1 solar spectrum (Figure 4). The acceleration factors are approximate since measurement of light intensity was carried out radiometrically and therefore does not take into account the surface geometry of the samples. Another series of acceleration factors were calculated by using the ONBA actinometer on both lamps; these factors do take into account the sample geometry, since the film actinometer occupies the same position as the sample. There was fair agreement between these calculations. These calculations assume that the quantum efficiency of degradation is independent of wavelength in the region of 230 to 320 nm in RTV-615, an assumption
which was tested by calculating acceleration factors for the unfiltered xenon lamp relative to the filtered xenon lamp and then measuring degradation rates under these conditions. The calculated acceleration factor is $33 \pm 8$ and the observed ratio of rates of increase in absorbance at $3400 \text{ cm}^{-1}$ is $29.0$. Other experiments (vide infra) also indicate that the mechanism of photodegradation is wavelength-independent in this region. Table 2 is a summary of the acceleration factors estimated in this study.

B. SPECTRAL ANALYSES OF RTV-615 FILM

Transmission and ATR IR spectra were recorded on a Perkin Elmer model 220 grating spectrophotometer; UV visible spectra were run on a Cary-14 spectrophotometer. Wettability measurements and surface energy analysis were carried out at the Science Center, Rockwell International. The solid vapor surface energies were calculated as dispersion (London) $\gamma_s^d = \alpha^2$ and polar (Keesom) $\gamma_s^p = \beta^2$ components of the solid surface tension $\gamma_s$ so that $\gamma_s = \gamma_s^d + \gamma_s^p = \alpha^2 + \beta^2$. 

Figure 4. Absorption Spectrum of RTV-615
Table 2. Acceleration Factors Determined Actinometrically

<table>
<thead>
<tr>
<th>Radiation Source</th>
<th>Filter</th>
<th>Acceleration Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM-1 Sunlight</td>
<td>-</td>
<td>1.0(^a)</td>
</tr>
<tr>
<td>HP Xenon Photochemical Reactor</td>
<td>-</td>
<td>40 ± 8(^b)</td>
</tr>
<tr>
<td>Mercury Lamp, Medium Pressure</td>
<td></td>
<td>750 ± 150(^b,c)</td>
</tr>
</tbody>
</table>

a. Normalized.

b. Measured actinometrically, sample distance = 12 inches.

c. Sample distance ≈ 0.5 inches.

C. IRRADIATION OF 2-INCH SQUARE COMPOSITE COUPONS

Three different substrates and three different adhesives were employed in the test samples. Figure 2 shows the geometry and design of the test specimens. Each sample was alternately irradiated with light from the mercury lamp and immersed in water for the length of time and in the sequence shown in Table 3.*

* Unpublished data by the Failure Analysis Group.
Table 3. Water Immersion and Irradiation Sequence

<table>
<thead>
<tr>
<th>Water Immersion (hours)</th>
<th>UV (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.0</td>
<td>6&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>16.0</td>
<td>6</td>
</tr>
<tr>
<td>17.0</td>
<td>6</td>
</tr>
<tr>
<td>16.0</td>
<td>6</td>
</tr>
<tr>
<td>64.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6</td>
</tr>
<tr>
<td>16.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td>5.5</td>
</tr>
<tr>
<td>16.0</td>
<td>6</td>
</tr>
<tr>
<td>16.0</td>
<td>23.5&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>65.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td>---</td>
</tr>
<tr>
<td>25.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td>---</td>
</tr>
</tbody>
</table>

a. Radiation level was one sun; level for remaining samples was 50 suns of UV.

b. Delamination of the epoxy/fiberglass with RTV-108 was visible.

c. Vacuum of 20 inches Hg was applied.
SECTION III
TEST RESULTS

A. WEIGHT CHANGE

Measurements indicate that there is no significant change in weight during irradiation. Slight weight gains were observed but the accuracy of the measurement was not sufficient to obtain rate plots for weight change.

B. UV-VISIBLE SPECTRA

UV-visible spectra showed no change except on prolonged irradiation, when a small increase in absorbance at 300 nm was observed. The magnitude of the increase was not sufficient to construct a rate plot.

C. IR SPECTRA

IR spectra were obtained as a function of the irradiation period. Figures 5, 6, and 7 show the rate of increase of absorbance at 3400 cm\(^{-1}\), 1720 cm\(^{-1}\), and 2130 cm\(^{-1}\), respectively, as a function of the irradiation period. These irradiations were carried out using the mercury lamp. The absorbance at 3400 cm\(^{-1}\) is due to hydroxyl groups. The broad peak which develops on irradiation is due to hydrogen bonded aliphatic hydroxyl groups and hydroperoxy groups. The absorbance at 1720 cm\(^{-1}\) is due to formation of carboxyl groups. The 2130 cm\(^{-1}\) peak has been assigned to Si-H groups in the polymer. Portions of delaminated encapsulants from modules exposed outdoors in Cleveland were studied by ATR IR spectroscopy. A small but definite increase in absorbance at 3400 cm\(^{-1}\) was observed in many cases. This was attributed to an increase in aliphatic hydroxyl groups in the system. By comparing peak ratios at 3400 cm\(^{-1}\) and at 1720 cm\(^{-1}\) we could determine the relative abundance of OH groups, for which a negligible decrease in concentration is assumed to occur, to -CH\(_3\) groups. This procedure allowed us to calculate the molar concentration of OH groups. Since reliable insolation data at Cleveland do not exist, we used standard AM-1 insolation data in order to form an impression of the rate of decrease in concentration. This approach is not expected to yield accuracy greater than 50%; it was actually undertaken not to calculate rate of hydroxyl formation outdoors, a calculation which would require more accurate insolation data, but to determine if the acceleration factors calculated for the lamps would agree with an estimate of this order of magnitude of actual acceleration achieved by the lamps. The outdoor rate is determined to be 800 ± 400 times slower than the rate obtained with the mercury lamp. By extrapolation, the calculated acceleration factors (Table 2) suggest that the observed OH concentration in the encapsulants from the modules in Cleveland would accumulate in 320 ± 160 days.
Figure 5. Decrease in Absorbance at 3400 cm$^{-1}$ with Time
Figure 6. Increase in Absorbance at 1720 cm$^{-1}$ with Time
Figure 7. Increase in Absorbance at 2130 cm$^{-1}$ with Time
D. WETTABILITY MEASUREMENTS AND SURFACE ENERGY ANALYSIS

Samples were prepared at JPL and at the Science Center. The JPL samples were prepared by superimposing one film of RTV-615 on top of another and irradiating the sandwich maintained freestanding. Surface energy measurements were carried out on the freshly peeled surfaces (α and β) by pulling apart the sandwich. Care was taken to maintain the temperature at 25°C. Details of the Science Center measurements may be found in their annual report. Table 4 gives the data obtained.

Table 4. Surface Energy Analysis of Irradiated Silicones

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Surface Energy $\alpha$ (dynes$^{1/2}$ cm$^{-1/2}$)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.82</td>
<td>JPL control, RTV-615</td>
</tr>
<tr>
<td>2</td>
<td>4.76</td>
<td>Science Center control, RTV-615</td>
</tr>
<tr>
<td>3</td>
<td>5.05</td>
<td>Science Center control, Sylgard-184</td>
</tr>
<tr>
<td>4</td>
<td>4.68</td>
<td>JPL sample, RTV-615, 1-hour equivalent radiation in Hg lamp</td>
</tr>
<tr>
<td>5</td>
<td>4.57</td>
<td>JPL sample, RTV-615, 4-hour equivalent radiation in Hg lamp</td>
</tr>
<tr>
<td>6</td>
<td>4.45</td>
<td>Science Center sample, RTV-615, 156-hour radiation in HP xenon lamp</td>
</tr>
<tr>
<td>7</td>
<td>4.60</td>
<td>Science Center sample, Sylgard-184, 30.7-hour radiation in HP xenon lamp</td>
</tr>
</tbody>
</table>
E. DELAMINATION TEST

Test samples (Figure 2) attached to various substrates with different adhesives were subjected to a delamination test. Table 5 gives the composition of the samples and the results.

Table 5. Irradiation of RTV-615 Deposited on Substrates

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Substrate</th>
<th>Adhesive</th>
<th>Delamination in equivalent hours of AM-1 sunlight(^a) UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Epoxy</td>
<td>RTV-108</td>
<td>600 hrs</td>
</tr>
<tr>
<td>2</td>
<td>Epoxy</td>
<td>Q 36-060</td>
<td>1200 hrs</td>
</tr>
<tr>
<td>3</td>
<td>Epoxy</td>
<td>SS-4120</td>
<td>No delamination</td>
</tr>
<tr>
<td>4</td>
<td>Glass</td>
<td>RTV-108</td>
<td>No delamination</td>
</tr>
<tr>
<td>5</td>
<td>Glass</td>
<td>Q 36-060</td>
<td>No delamination</td>
</tr>
<tr>
<td>6</td>
<td>Glass</td>
<td>SS-4120</td>
<td>No delamination</td>
</tr>
<tr>
<td>7</td>
<td>Aluminum</td>
<td>RTV-108</td>
<td>No delamination</td>
</tr>
<tr>
<td>8</td>
<td>Aluminum</td>
<td>Q 36-060</td>
<td>900 hrs</td>
</tr>
<tr>
<td>9</td>
<td>Aluminum</td>
<td>SS-4120</td>
<td>No delamination</td>
</tr>
</tbody>
</table>

\(^a\) obtained by accelerating at 50 sun (UV) level.
SECTION IV
ANALYSIS AND INTERPRETATION

A. MECHANISM OF PHOTOOXIDATION

The following mechanism of photooxidation (References 1, 2) has been proposed for polydimethylsiloxanes:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_2\text{OH} & \quad \text{CH}_3 \\
\text{Si} \quad \text{O} \quad \text{Si} & \quad \text{h}^+ \quad \text{O}_2 & \quad \text{Si} \quad \text{O} \quad \text{Si} & \quad \text{Si} \quad \text{O} \quad \text{Si} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

The absorption spectrum of our samples of RTV-615 show a weak bond at 300 nm which might be due to impurities in the polymer or the curing catalyst. It is possible that the photooxidation is impurity- or catalyst-mediated, so that the initial step is a complex formation between the chromophore and oxygen. The 3400 cm\(^{-1}\) band is attributed to aliphatic hydroxyl groups (the curing catalyst has phenols which have sharp absorption peaks in this region which remain unchanged) presumed to be photooxidation products. Formation of hydroxyl groups would tend to make the polymer and its surface more hydrophilic, a hypothesis confirmed by surface energy analysis. This change in surface characteristics would reduce adhesion to hydrophobic substrates such as epoxy, but not to glass. Hence debonding is expected to occur if a bond between the silicone and the hydrophobic substrate, weakened through photooxidation of the silicone, is immersed in water, but no debonding would occur between the silicone and glass. These predictions were qualitatively verified by the tests carried out with the coupons.
B. CONCLUSION

We have identified a mechanism of degradation which controls a failure mode in modules containing certain silicone pottants. We have linked the bond strength to change in chemical structure of the silicone. We have also demonstrated an experimental capability for accelerating the failure mode by use of a well characterized radiation source and actinometry. This is a preliminary study in the sense that more precise measurement of rate of degradation during outdoor exposure, and more accurate accelerated test data are needed. In addition the effect of primers on the debonding phenomenon must be evaluated, and the effect of UV radiation on polymeric substrates such as epoxy may also be important. Preliminary tests indicate that although the epoxies discolor on long term outdoor exposure, there is no significant change in ATR IR spectra. However, improved surface monitoring techniques may allow us to determine whether any photo reaction is taking place.
REFERENCES

