



# Accelerated Stress Testing of Hydrocarbon-Based Encapsulants for Medium-Concentration CPV Applications

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# ACCELERATED STRESS TESTING OF HYDROCARBON-BASED ENCAPSULANTS FOR MEDIUM-CONCENTRATION CPV APPLICATIONS

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## ABSTRACT

Concentrating photovoltaic (CPV) systems have great potential to reduce photovoltaic (PV) electricity costs because of the relatively low cost of optical components compared to PV cells. A transparent polymeric material is used to optically couple the PV cell to optical components and is thus exposed to the concentrated light source at elevated temperatures. In this work polymeric encapsulant materials are positioned close to a Xenon arc lamp to expose them to ultraviolet radiation (UV) that is about 42 times as intense as sunlight. Furthermore, different glass types are used as filters to modify the spectral distribution of light in the UV range. A strong sensitivity of non-silicone-based encapsulants to light below ~350 nm is demonstrated. Of all the materials examined in this study, the polydimethyl silicone samples performed the best. The next best material was an ionomer which maintained optical transmission but became photo-oxidized when exposed to the atmosphere.

## INTRODUCTION

Concentrating photovoltaic (CPV) systems have great potential to reduce systems cost and the cost of electricity produced by photovoltaic (PV) cells. The relatively small amount of area covered by the cells allows high performance cells to be used with concentration factors as high as 500X to 1000X. At low to medium concentration, (less than 50X) monocrystalline silicon-based cells typically balance the considerations of cell cost and performance. However at high concentration (250X to 1000X) high performance III/V multijunction cells are used exclusively because the high cost of the cells is compensated by their high performance.

For CPV systems, a transparent polymeric material is commonly used to optically couple the PV cell to optical components and to provide electrical insulation against condensed moisture that may create a grounding hazard and/or increase corrosion rates. The light intensity and wavelength distribution are important considerations for choosing an encapsulant. At low concentration, <5X, typical hydrocarbon-based encapsulants, such as ethylene vinyl-acetate (EVA), should be capable of performing well for the desired 20-year service lifetime if they are formulated correctly. At higher concentrations, >50X, siloxane-based encapsulants [e.g. polydimethyl silicone (PDMS)] are used exclusively as they are extremely resistant to thermal and light-induced degradation. Furthermore, the greater price of silicone encapsulants is justified at higher concentration. For medium concentration systems, 5X to 50X, the higher relative area to be encapsulated and the ease of handling a film [e.g. (EVA)], as opposed to a typical silicone fluid with a

catalytic curing agent, make EVA and other hydrocarbon-based films more desirable for some applications.

We have developed methods to expose transparent encapsulant materials to high optical fluxes (40 to 45 suns) of UV radiation under different ultraviolet (UV) wavelength distributions in order to evaluate the action spectrum [1] of a variety of hydrocarbon and silicone-based materials. The parameters of interest include the yellowness index (YI) and the quantum efficiency/solar spectrum weighted transmission. By using glass that transmits more UV light than a typical CPV optical configuration, greater accelerated aging is obtained [2]. Additional acceleration is obtained because our test apparatus runs 24 h/day giving an additional ~ 3X acceleration relative to outdoor exposure. With all these considerations, it is possible to evaluate materials for 20 yr exposure in medium concentration CPV applications.

## EXPERIMENTAL PROCEDURE

Ultraviolet exposure was obtained using an Atlas Ci4000 Weather-Ometer® with a light intensity of 114 W/m<sup>2</sup> between 300 nm and 400 nm. The light was filtered using a type “S” borosilicate inner and outer filter. This light intensity (about 2.5 AM 1.5 global UV Suns) is experienced by samples placed at a radius of  $r=32.4$  cm from the lamp. To increase the UV dose, test samples were placed at a radius of  $r=7$  cm from the lamp. The UV dose at this radius was estimated by approximating the lamp as a 12.5 cm long line source with the light intensity decreasing as  $1/r^2$  from each point along the length.

$$I = I_o \int_{\frac{Z_{sample}-\frac{l}{2}}{2}}^{\frac{Z_{sample}+\frac{l}{2}}{2}} \frac{1}{z^2 + r^2} dz \quad (1)$$

Here  $z$  is the vertical distance from the center point of the lamp,  $r$  is the horizontal radial distance from the lamp,  $l$  is the total length of the lamp, and  $I_o$  is a factor for the lamp intensity (See Fig. 1). Integration of Eq. 1 yields,

$$I = I_o \frac{1}{r} \left[ \tan^{-1} \left( \frac{Z_{sample} + \frac{l}{2}}{r} \right) - \tan^{-1} \left( \frac{Z_{sample} - \frac{l}{2}}{r} \right) \right] \quad (2),$$

where  $I_o$  can be solved from the known condition that the UV intensity at  $r=32.4$  cm and  $Z=0$  cm is 2.5 suns.

Using Eq. 2, the intensity at a radius of  $r=7$  cm as a function of height was estimated as shown in Fig. 2. To avoid using regions where the light intensity changes rapidly, only the vertically central  $Z=\pm 3.8$  cm region was used. In this region, the calculated irradiance varies between 39.3 UV suns and 44.0 UV suns with an average of  $42.3 \pm 1.5$  UV suns. Whenever a sample was removed for measurement, the positions of all the samples were randomized to help eliminate any location specific

variations in light intensity. The Ci4000 Weather-Ometer® was set at 30°C and 30% RH with baffles placed to enhance air flow to the specimens, keeping them cooler. The black panel temperature was set at 29°C to force the recirculation blower to continually operate at maximum speed to provide the maximum convective cooling possible.

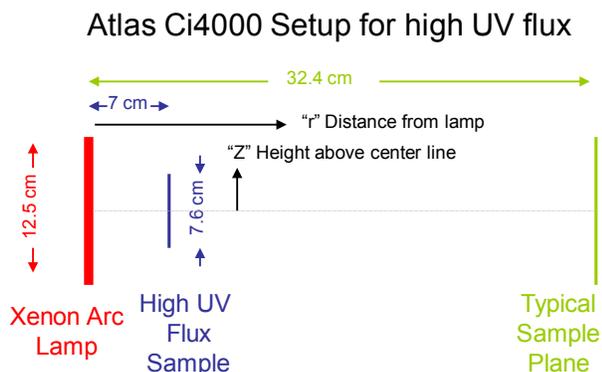


Figure 1. Schematic of Atlas Ci4000 Weather-Ometer® setup with samples placed close to the lamp.

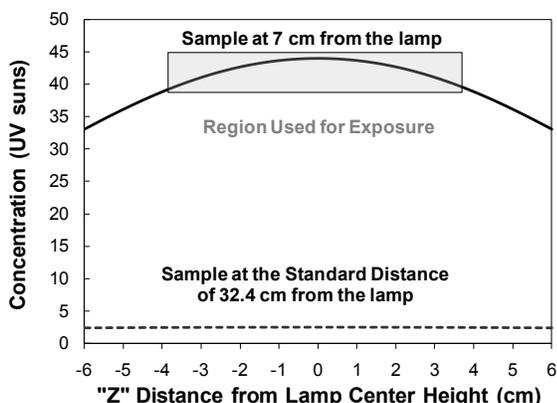


Figure 2. Plot of the calculated light flux on a sample at a fixed radius,  $r$ , from the lamp as a function of height  $Z$ .

To check the validity of Eq. 2, measurements of the light intensity as a function of radial distance  $r$  were performed by Atlas weathering services in an Atlas Ci5000 Weather-Ometer® using an integrating sphere attached to a fiber optic cable and a spectroradiometer, Fig 3. The dashed lines a slope of  $1/r^2$ , which is what one would expect at large distances from the light source, and  $1/r$ , which is what one would expect for an infinitely long linear light source. For most of the range of distances measured, the calculated line (Eq. 2) closely matches the measurements. However, at large distances (and low light intensities) the measured values are high which could be explained as reflected light within the chamber. At small distances ( $<7$  cm) there is a negative deviation. While the deviation may be attributable to the limitations of the optical measurement, this analysis demonstrates that Eq. 2 is a reasonable representation of the light intensity within a Xe arc lamp chamber.

At a radius of 7 cm in the Ci4000 Weather-Ometer®, an uncertainty in radius  $r$  of  $\pm 1$  mm corresponds to about 1 sun uncertainty in irradiance. When one considers that the ability to position the samples should be accurate to  $\pm 3$  mm, then the greatest sources of uncertainty in the irradiance level are due to the vertical position as well as the radial distance.

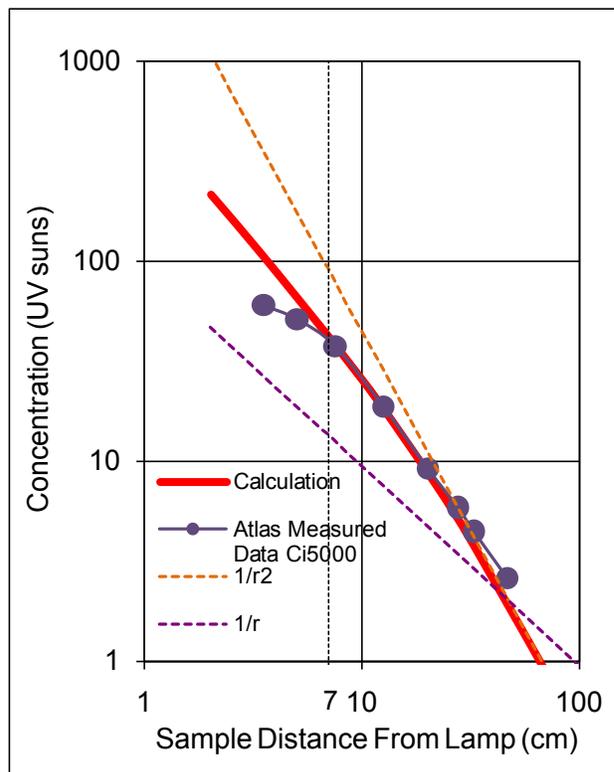


Figure 3. Plot of the calculated light flux on a sample at a fixed height,  $z=0$ , as a function of radial distance,  $r$ . The calculated line was for an Atlas Ci5000 Weather-Ometer® using Eq. 2, with 2 UV suns at  $r=47$  cm with a 25 cm long bulb.

The samples used in this experiment were made using a  $\sim 0.5$ mm thick polymer laminated between two 2.5 cm square, 3.18 mm or 2.95 mm thick glass sheets. Because the samples are transparent, they remained at temperatures between 78°C and 95°C depending on the age, and hence relative amount of IR radiation, of the Xe arc lamp. It was also observed that as samples begin to turn yellow and become more optically absorbing, the steady-state temperature increases. Black samples were found to reach temperatures of around 150°C to 170°C. Samples with significant changes in YI were found to reach temperatures of 110°C to 120°C.

After exposure to UV light, the transmission of the samples was measured using a Varian Cary 6000i UV-VIS-NIR spectrophotometer equipped with an integrating sphere. From this the yellowness index (YI) was calculated according to ASTM E313 using D65 as the illuminant (solar equivalent spectrum) and the 1931 procedure [3]. Because medium-concentration CPV systems typically use monocrystalline silicon cells, the light

transmission was weighted against the AM 1.5 direct solar spectrum [4] and the quantum efficiency of a typical monocrystalline silicon PV cell.

Some samples began to degrade at their perimeter as a photo-oxidation process dominated the degradation. Others (all EVA samples tested), turned yellow in the center first as the photo-oxidative process serves to remove chromophores. In both cases these perimeter oxidative effects were limited to the outer few mm of the samples. Because a cell used in a medium CPV application (or a non-concentrating system) typically uses a glass front sheet located in front of a relatively large cell, it was thought that the anaerobic center of our samples would be more representative of the majority of the encapsulant used in a PV application. Therefore, all transmission measurements were made in the center of the samples. This assumption is more applicable for CPV systems than non-concentrating systems because of the relative high acceleration of UV irradiation relative to modest increases in oxygen diffusion rates.

## RESULTS

Different materials used in CPV applications absorb different portions of the UV spectrum. Even though this represents only a small amount of the total solar energy, the photons in this region (especially below 350 nm) are extremely effective at degrading polymeric materials [1, 5, 6]. In Fig 4., the transmission of low-Fe glasses, with and without Ce, are shown to illustrate how the addition of trace amounts of Ce affects the absorption in the UV band [7]. The addition of Ce also reduces transmission of infrared light, yielding a loss in transmission that develops upon exposure to UV light as shown in Fig. 5. This solarization effect produces a 1% loss in transmission for low-Fe, Ce-containing glass along with a 0.2 change in YI [8]. This small loss in transmission influenced the PV industry in its recent move to discontinue using glass with Ce. While this may be appropriate for flat-panel PV systems, medium-X CPV systems may require Ce-doped glass to enable the use of EVA as opposed to silicone-based encapsulant materials.

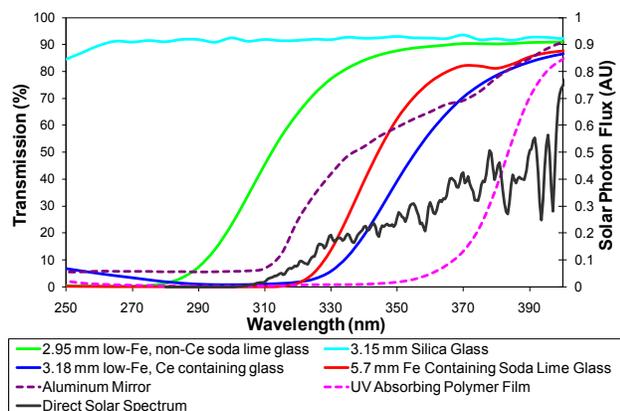


Figure 4. UV transmission or reflection of representative materials used in CPV applications after solarization.

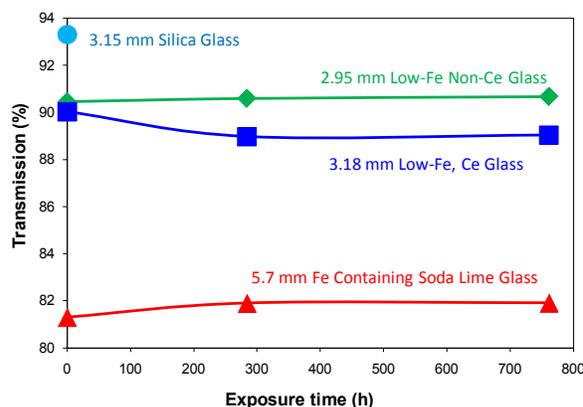


Figure 5. Transmission as a function of exposure to 42 UV suns.

Four different EVA formulations were obtained from different manufacturers and tested for changes in YI and transmission as a function of exposure (Fig. 6). The type of glass used, was changed to demonstrate how blocking UV radiation below  $\sim 350$  nm can have a dramatic effect on changes in YI and optical transmission. Changes in YI correlate well with optical transmission changes in EVA and with all the polymeric materials tested in this study. The YI values generally display significant changes sooner than the weighted transmission, making them good predictors of material performance. However, the Ce-glass itself produces an initial drop in transmission over the first  $\sim 200$  hr that is attributable to the solarization of the glass that does not correlate with a change in yellowness index. In Fig. 6, one can see significant differences between the different EVA formulations illustrating the importance of using a well formulated EVA.

Because the loss of transmission causes significant heating via optical absorption, the exact shape of the different curves might not be useful for comparison between different samples. Initially, all samples should be at nearly the same temperature, but as they become more absorbing, thermally induced degradation may begin to further differentiate the degraded samples. However, the onset of degradation should correlate well with UV dose as thermal runaway doesn't occur until after significant degradation has accumulated.

After 1056 h all the non-Ce EVA samples are starting to show some changes in YI, whereas none of the Ce-containing samples show statistically significant increases in YI until after 2000 h. Transmission for EVA #2 behind Ce-containing glass, appears to be dropping at 2000 h but lack of data between 2000 h and 4000 h indicates it could be longer than 4000 h before significant degradation occurs. For EVA #1 behind Ce-containing glass, somewhere between 2000h and 4000 h the sample began to delaminate making accurate measurements of YI and transmission not possible. This sample will be repeated to determine if this delamination is an inherent problem for this formulation.

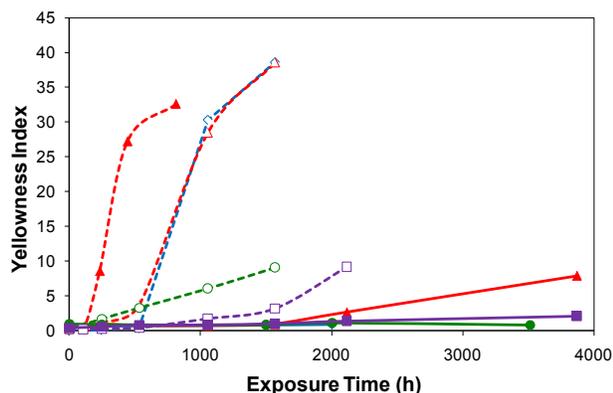
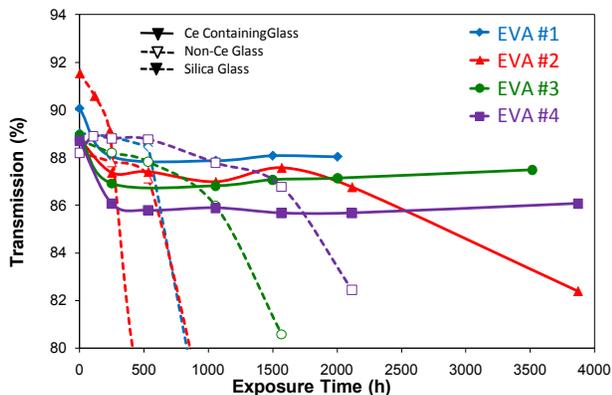


Figure 6. Transmission and yellowness index of different EVA materials as a function of exposure to 42 UV suns of radiation behind different glass materials.

The yellowness index gave similar results to the transmission measurements. For EVA sample #2, onset of significant increases in YI occur at ~2000 h, 500 h, and 100 h for Ce, non-Ce, and silica glass respectively. In Fig. 7 one can see an example of a typical EVA sample. The ingress of oxygen from the perimeter bleaches the chromophores making the samples more transparent around the edges [5, 9]. This trend continued, and at 1568 h (Fig. 8) the UV blocking Ce glass sample is still relatively transparent as compared to the non-Ce sample. However, after 4000 h of exposure behind Ce-containing glass, EVA # 1, #2 and #4 (and #3 to a much lesser extent) are showing yellowing around the oxygen-exposed perimeter as opposed to the more anaerobic center (Fig. 9). This demonstrates that there are at least two different processes causing yellowing.

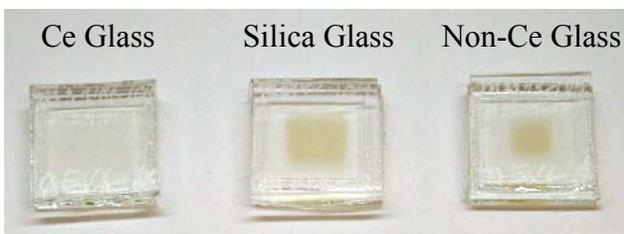


Figure 7. EVA #5 after 400h of 42 UV suns.

For EVA #2, it can be seen that the removal of Ce causes the onset of transmission loss to occur about 4 to 6 times sooner. For EVA #2 a sample was made using silica glass for which the onset of transmission loss was almost immediate. This indicates the high potential of UV-B ( $\lambda=285$  nm to 320 nm) to cause degradation. This estimate of a 4 to 6 times reduction in the time required for the onset of degradation is probably a low estimate for these conditions. The observation that most of the EVAs tested behind Ce-glass maintained good transmission for long exposure times, indicates that the blocking of UV-B light may generally reduce discoloration by more than 6 times. On the time-scale of these experiments, it is apparent that oxygen has not fully diffused throughout the samples; therefore, this result may not be applicable to non-concentrating systems where there may be sufficient time for oxygen ingress for photo-oxidative bleaching.

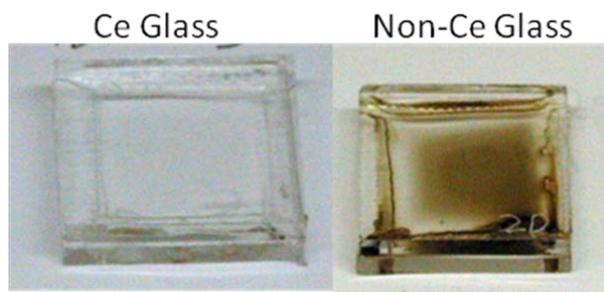


Figure 8. EVA #2 after 1568 h of 42 UV suns.

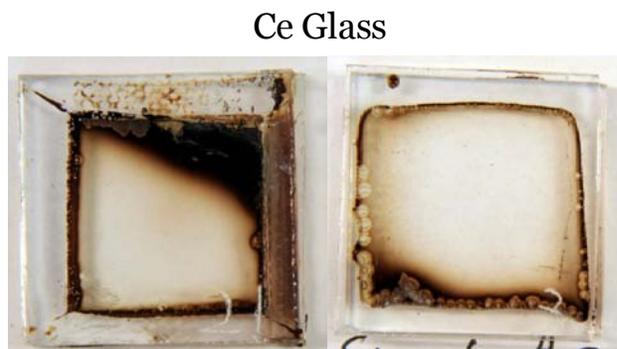


Figure 9. EVA #2 (left) EVA #4 (Right) after 4125 h of 42 UV suns.

Other hydrocarbon-based polymers were examined (Fig 10). Only the ionomer showed better performance relative to EVA. The thermoplastic polyurethane (TPU) was comparable to EVA in its YI and transmission changes. It also showed photo-oxidative bleaching around the perimeter in the non-Ce glass sample but not the Ce-glass sample after 4000 h. However, the non-Ce glass TPU sample delaminated after 2000 h of exposure.

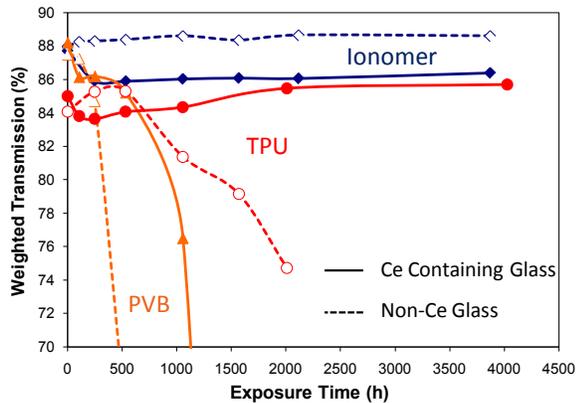


Figure 10. QE- and solar-weighted transmission for a thermoplastic polyurethane (TPU), an ionomer, and polyvinyl butyral (PVB) as a function of exposure to 42 UV suns. The changes in YI for the ionomer, PVB and TPU correlate well with changes in optical transmission.

The polyvinyl butyral (PVB) samples in particular showed problems very early on, even with the UV-blocking Ce-glass. The PVB tested turned yellow in all areas exposed to UV radiation; there were no perimeter yellowing or oxidative bleaching effects. For the PVB sample, it can be seen that the use of non-Ce glass causes degradation to begin about 2 to 5 times faster relative to Ce-containing glass.

While the transmission data for the ionomer showed no degradation after nearly 4000 h, visual inspection of the sample clearly shows some photo-oxidative degradation that is more significant for the non-Ce glass (Fig. 11). In the figure, optical degradation is located on the perimeter indicating that it is an oxygen-induced degradation. Furthermore, the non-Ce glass sample shows more degradation suggesting that the process is accelerated by UV radiation (especially the UV-B portion of the spectrum).

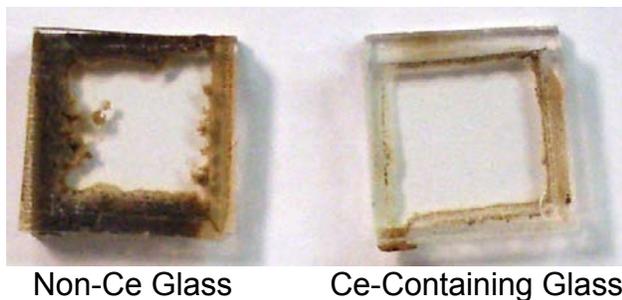


Figure 11. Photograph of the ionomer samples after 3900 h of exposure to 42 UV suns.

The PDMS samples tested performed exceptionally well (Fig. 12). With a  $\pm 1\%$  uncertainty in transmission measurements, the only statistically significant changes in the silicone samples pertain to solarization in the Ce-containing glass, not to silicone degradation. These silicone-based encapsulant samples clearly show superior performance as compared to all the hydrocarbon-based

materials. There were no visual signs of degradation, even on the perimeters, of any of these samples.

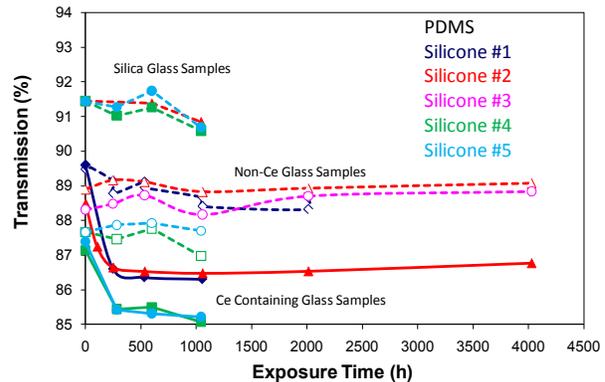


Figure 12. Measured optical transmission for PDMS specimens. No changes in YI were observed.

## DISCUSSION

At 42 UV suns running 24 hr/day, our modified test instrument provides a UV dose that is about  $42 \times 3 = 126$  times as damaging as typical outdoor field exposure on a tracking system. Therefore, 1000 h of exposure roughly corresponds to about 14 years at 1 sun, provided a linear relationship exists between exposure intensity and degradation. This assumption is tenuous at the extreme exposure conditions utilized here, but when making comparisons to CPV systems at 10X to 50X, this assumption is more robust because the instantaneous dose is at most about 4.2 times as intense. Typically, the relationship between UV dose at high concentrations is sublinear (i.e. 10 suns equals less than 10X acceleration) [10, 11, 12]. Furthermore, an Atlas Weather-Ometer® configured with a borosilicate inner and outer filter on the xenon arc lamp, is designed to emulate the global spectrum not the direct solar spectrum utilized in CPV applications. The direct spectrum has  $30.5 \text{ W/m}^2$  and the global spectrum has  $46.1 \text{ W/m}^2$  between 300 nm and 400 nm; therefore, there is another 1.5X acceleration factor for concentrating systems. This results in an irradiance of  $42 \times 3 \times 1.5 = 190$  times the direct UV solar spectrum.

If these are the only factors being considered, it would take about 9,300 h or 1.1 years for 20 years equivalent exposure in a system operating at 10X concentration and 46,000 h or 5.3 years for a 20 year equivalent exposure for a system operating at 50X concentration.

The equivalent test time can be further reduced if one considers that the mirrors and polymeric Fresnel lenses used in CPV applications act to reduce the amount of UV light transmitted as concentrated light, Fig. 4. Medium concentration CPV methods typically use linear concentration in the form of Fresnel mirrors or lenses or trough reflectors.

Fresnel lenses are most often constructed using an acrylate polymer (e.g. polymethyl acrylate) that is stabilized using UV absorbers that will yield a transmission profile similar to the UV absorbing film shown in Fig. 4.

Because this spectral distribution blocks much more UV light than the region tested here, extrapolation to this condition would be very tenuous. It is possible with so little UV light that other processes, such as thermal degradation, may instead dominate.

For the case of a mirror used to concentrate the light prior to transmission through a low-Fe non-Ce glass, inspection of Fig. 4 indicates that the spectral distribution would roughly be represented by the transmission through a low-Fe, Ce-containing glass. In this work, exposure to high UV flux has indicated that the replacement of Ce-glass with non-Ce glass causes degradation to occur between 2 and 6 times faster with 4X being typical. If one considers the performance of samples behind non-Ce glass for comparison to a mirror/non-Ce glass concentrating system, then an additional 4X acceleration factor can be assumed as a first-order approximation bringing the total acceleration factor to  $190 \times 4 = 760$ . With these assumptions, samples behind low-Fe, non-Ce glass will have to withstand 2,300 h or 12,000 h for use in a 10X and 50X CPV system respectively for 20 yr. Because the effects of oxygen ingress are not adequately controlled in this experiment, and because the extra UV-B radiation with non-Ce glass has the potential to accelerate non-representative failure modes, this extra 4X acceleration factor should be used with caution.

All the silicone materials have so far demonstrated this criteria (>2000 h exposure) for the 10X CPV conditions. It is very likely that they will continue to perform well for the 50X CPV equivalent exposure. For the hydrocarbon-based materials, only the ionomer (see Figs. 6 and 8) is demonstrating UV stability for 10X CPV applications. Continued study will soon evaluate the 50X CPV exposure condition. Even if it does continue to perform well, the perimeter degradation shown in Figure 9 is an important concern. Significant material degradation around the perimeter could create an electrical insulation hazard before the degradation reached the active PV material to reduce performance. However, extra UV protection around the oxygen-exposed parts may be sufficient to alleviate this concern. Further study is necessary to confirm this.

Another aspect to consider for materials selection is the total light transmission. In prior work, it was estimated that PDMS silicones transmit about 0.7% more light (for normal incidence) than some of the best hydrocarbon-based materials (e.g. EVA and PVB) [2]. With continued exposure, there may be some additional light transmission losses relative to the silicone-based materials. The 0.7% difference in performance should be considered the lowest possible differential because properly formulated PDMS materials are less likely to experience transmission losses after exposure. If the price difference between using a silicone and a hydrocarbon-based material is less than 0.7% of the overall price, then a silicone is likely to be more cost effective solution. As the concentration ratio gets higher, the relative amount of area (and materials) required to encapsulate a polymer will decrease making the case for a silicone-based encapsulant stronger.

Lastly, this analysis has only considered the effects of degradation on light transmission. An encapsulant material must also maintain good adhesion. If delamination occurs there will not only be a loss of light transmission and enhanced corrosion, but there is also the potential for a safety hazard to occur, making the system inoperable, which would be a greater concern.

## CONCLUSION

A method was developed for exposing transparent encapsulant materials to about 42 UV suns of radiation. Test samples were constructed using Ce- and non-Ce-containing glasses to control the spectral distribution of the UV light in order to evaluate the spectrum-specific response of the degradation modes. It was found that samples with non-Ce glass transmit more UV light and cause loss of transmission somewhere between 2 and 6 times faster than Ce-containing glass.

As a first-order approximation, it was estimated that under these conditions a UV dose equivalent to 20 years for a system using mirrors and non-Ce glass can be obtained in 2,300 h and 12,000 h for 10X and 50X CPV systems respectively. However, exposing samples to a UV-B rich environment has the potential to introduce non-representative degradation; therefore, if the spectrum is matched, 9,300 h and 46,000 h would be required for a 10X and 50X CPV system respectively. This allows for evaluation of candidate materials in a more reasonable amount of time.

For the PDMS materials, no signs of degradation were seen after as long as 4000 h of exposure to 42 UV suns. The best hydrocarbon-based polymer tested was an ionomer. After 4000 h of exposure no transmission loss or YI index change was observed for the central portion of the ionomer samples; however, the edges that were exposed to air experienced severe UV-induced degradation. If adequate protection of these exposed surfaces were provided, it might be possible to use this material in a medium-concentration CPV application.

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