Durability of Materials in a Stress-Response Framework:
Acrylic Materials for Photovoltaic Systems

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ABSTRACT

In the development of novel materials for enhanced photovoltaic (PV) performance, it is critical to have quantitative knowledge of the initial performance, as well as the performance of these materials over the required 25-year lifetime of the PV system. Lifetime and degradation science (L&DS) allows for the development of new metrology and metrics, coupled to degradation mechanisms and rates. Induced absorbance to dose (IAD), a new metric being developed for solar radiation durability studies of solar and environmentally exposed photovoltaic materials, is defined as the rate of photodarkening or photobleaching of a material as a function of total absorbed solar radiation dose. In a reliability engineering framework, these quantitative degradation rates can be determined at various solar irradiances making possible real time and accelerated testing. The potential to predict power losses in a photovoltaic system over time caused by the accumulation of this kind of degradation can be calculated for real time applications or extrapolated for accelerated exposure conditions. Three formulations of poly (methyl methacrylate) (PMMA) used for mirror augmented PV systems were analyzed for the changes in IAD after accelerated testing.

INTRODUCTION

A recent U. S. Department of Energy workshop on Science for Energy Technologies [1] identified the topic of PV lifetime and degradation science (L&DS) [2-5] as a critical scientific challenge for robust adoption of PV. The 25-year lifetime performance of PV requires a better understanding of the degradation mechanisms in PV materials and systems. By developing metrics, metrology and tools to compare and quantify the response of PV systems, components and materials to a variety of stressors such as ultra-violet (UV) radiation, humidity, and temperature variation for both accelerated and outdoor testing, we can link stresses to observed responses in materials in a stress-response framework and quantitative rates of degradation can be determined. L&DS requires the development of quantitative degradation mechanisms and rates for failure modes, so as to enable quantitative lifetime projections.

Stressors that impact PV materials and components can be characterized in terms of instantaneous stress level (σ), and net stress or integrated stress (S), which is the instantaneous stress level integrated over the length of time the stress was applied (Equation 1). Changing the instantaneous stress level may change the material's response characteristics; therefore, stressors must be quantified in terms of both instantaneous stress level and integrated stress (Equation 2)

$$S = \int \sigma \, dt \qquad\qquad (1)$$

$$\sum S = \int (\sigma_i \otimes \sigma_j \dots \otimes \sigma_n) dt \qquad\qquad (2)$$

where σ_i and σ_j are different stress types and levels. Since environmental stressors can be synergistic, the net stress a system sees is a convolution of these stressors.

A material's response (R) to both instantaneous stress level and integrated stress may be a change in the optical properties of a material, a loss of mechanical strength, or any measurable change in properties arising due to stressors applied over time. The general relationship between stress and response is a function of that stress (Equation 3):

$$R = f(^{\sigma}S) = \int f(\sigma)\sigma dt \qquad (3)$$

An expansion of this methodology to multiple stresses gives (Equation 4):

$$R(S_i, S_j, \dots S_n) = f(\sigma_i, \sigma_j, \dots \sigma_n) \int (\sigma_i \otimes \sigma_j \dots \otimes \sigma_n) dt \qquad (4)$$

where $S_i, S_j, \dots S_n$ are different stresses that cause responses. The benefit of such a framework is that stresses can be separated and accounted for in this methodology. The convolution of these stresses implies that they can have synergistic effects, and the correlation function, while unknown, depends on all stresses applied to the system.

EXPERIMENTAL

Exposure of multiple samples on different platforms will enable cross correlation and data quality management and allow extraction of robust degradation mechanism and rate information from our L&DS research. The results of two different types of exposures on three formulation types of acrylic poly (methyl methacrylate) (PMMA) are reported. The three different formulation types of PMMA are ultraviolet transmitting (UVT), multipurpose (MP), and ultraviolet absorbing (UVA). Exposures were performed with a Q-Labs QUV accelerated weathering tester [6] and with a Newport solar simulator. By repeat evaluations following exposures of material samples, it is possible to determine the correlation between optical properties and photo-induced degradation.

QUV accelerated weathering tester uses fluorescent lights to expose samples to high doses of UV light simulating different types of damaging environmental stress conditions. The exposures were performed with UVA-340 lamps, which emit radiation between 280 and 400 nm. The UVA-340 emission spectrum is a good match to the AM 1.5 spectra in the UVA and B regions when set at a maximum irradiance of 0.32 W/m^2/nm at 340nm. Therefore the UVA-340 exposure matches closely to the AM 1.5 spectra at wavelengths shorter than 360 nm, where much of the damaging radiation exists in the solar spectrum. The QUV was run using ASTM G154 cycle 4 (1.55 W/m^2/nm at 340 nm at 70ºC) [7] without the condensation step for 21 days. By setting the QUV peak intensity to 1.55 W/m^2/nm at 340 nm a higher level of damage can be induced, making this a single-factor accelerated test compared to outdoor weathering. This 21 day test exposed samples to radiant exposure at wavelengths below 360 nm equivalent to approximately 1 year tracked solar exposure in Arizona.

The Newport xenon arc solar simulator was used to irradiate material samples with filter matched AM 1.5 radiation. Using continuous power monitoring of the irradiance, it is possible to quantify the irradiance and radiant exposure to which a sample was exposed. Using a Newport 13x high flux concentrator accessory with the solar simulator, irradiance levels of 48.4 kW/m^2 of AM 1.5 were achieved, making this a single-factor accelerated test compared to both UVA-340

and outdoor exposure. This 18.3 day test exposed samples to radiant exposure at wavelengths below 360 nm equivalent to approximately 6 years of tracked solar exposure in Arizona, or full spectrum dose equivalent to 8 years.

QUANTITATIVE METRICS

Induced absorbance to dose (IAD) is a measurement of the change, at a particular wavelength, of the absorbance per centimeter of a material and is given by (Equation 5):

$$Incremental\ \frac{Abs}{cm}\ per\ \frac{GJ}{m^2}\ Dose \equiv \frac{\frac{Abs_{i+1}(\lambda)}{cm} - \frac{Abs_i(\lambda)}{cm}}{Dose_{i+1} - Dose_i}$$

(5)

IAD values were determined with an Agilent Cary 5000 with a diffuse reflectance accessory (solar simulator spectra), a Filmetrics PARTS-UV spectrophotometer (QUV spectra).

Yellowness index (YI) as defined in the ASTM E313 [8] is a colorimetric measure of yellowing. Because YI is measured over a broad wavelength range it is more sensitive than typical spectral measurements. Increased yellowness was seen in all samples post exposure. Yellowness indices are also useful because they are closely linked to reduced optical performance [9]. YI can be determined by Equation 6:

$$YI = \frac{100(C_X X - C_Z Z)}{Y}$$

(6)

where X, Y and Z are the CIE tristimulus values. For D65/10º Cx=1.3013, Cz=1.1498. YI was determined using a HunterLab UltrascanPro colorimeter. Yellowing rates, the rate of change in yellowness as a function of dose, were determined (Equation 7).

$$R_{YI} = \frac{d(YI)}{d(S)}$$

(7)

RESULTS AND DISCUSSION

In this experiment, three regions of interest in the UV/Vis regions are under investigation. Region 1 is the fundamental absorption edge of acrylic, regions 2 and 2' are peaks from the UV absorber package, and region 3 is the yellowing region.

IAD results:

The UVT acrylic exposure with UVA-340 shows the UV degradation of unprotected PMMA acrylic because this material does not contain a significant UV absorber package (Figure 1). On the left, optical absorbance per centimeter is shown for each step, on the right IAD is reported. Photodarkening can be seen at all wavelengths, indicated by a positive IAD value. UVA-340 dose proves highly effective at degrading this polymer. A large amount of photodarkening can be seen in region 1 associated with polymer breakdown, and region 3 where visible yellowing occurs.

The MP acrylic exposure results are shown for UVA-340 (Figure 2) and xenon arc (Figure 3) exposures. The absorbance per centimeter spectrum (Figure 3 left) shows the two peaks of the UV absorber package at 2 and 2'. In the first dose step photobleaching is indicated by a negative IAD value (figure 3 Right). This photobleaching is likely due to degradation of the UV stabilizer package with absorbance peaks at 2 and 2'. However, after the second step of
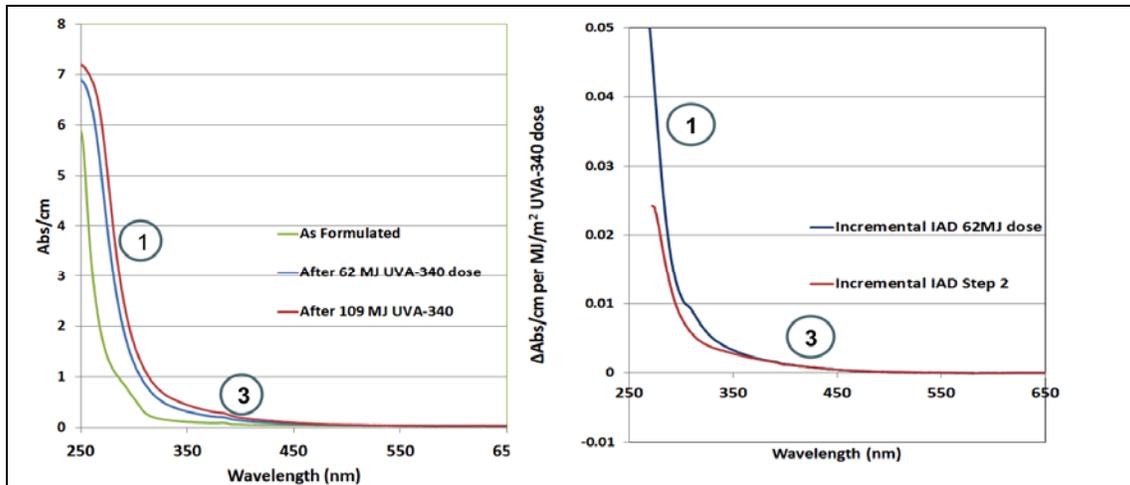
Figure 1:*Left* Absorbance per centimeter (Abs/cm) and *right* Induced absorbance to dose (IAD) for UVT with UVA-340 exposure in the QUV accelerated weathering tester

exposure, degradation reaction products have already started to accumulate leading to photodarkening in region 2. Photobleaching in regions 2 and 2' has occurred in both steps slows the degradation of the base polymer.
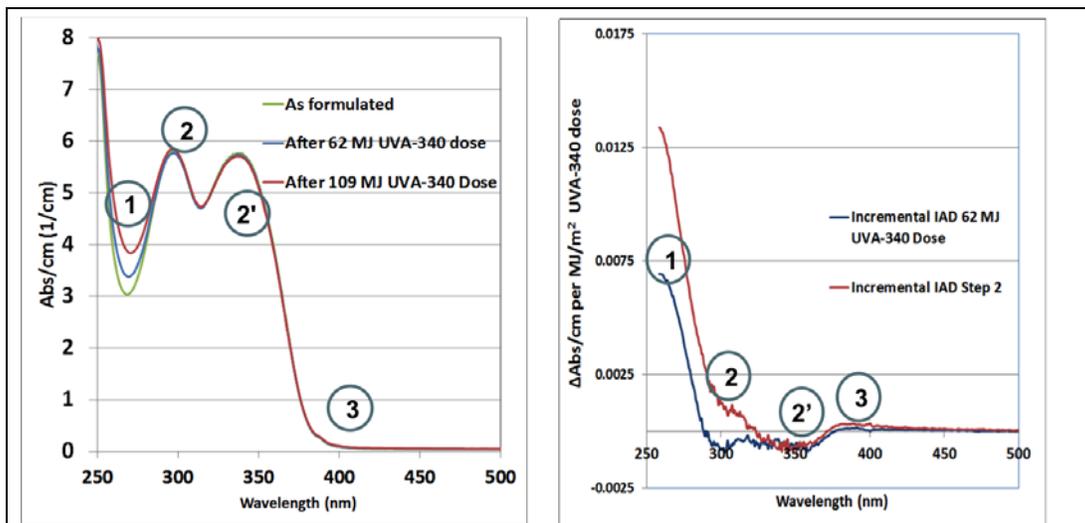

Figure 2: *Left* Absorbance per centimeter (Abs/cm) and *right* Induced absorbance to dose (IAD) for MP acrylic with UVA-340 exposure in a QUV accelerated weathering tester

When exposed to xenon arc radiation a similar phenomenon is observed, where overall polymer degradation is observed, but photobleaching of the UV stabilizer package is apparent in the IAD in regions 2 and 2', slowing polymer breakdown. The 18 day exposure leads to a significant loss of optical performance in all regions of interest and across the ultra-violet, visible and infrared spectra (Figure 3).

The initial spectrum of UVA acrylic, which is heavily UV stabilized, is shown in Figure 4 on the left. Because it is so strongly absorbing, determination of IAD in UVA acrylic has not been accomplished to date.

Figure 4 right shows a comparison between grades of acrylic and exposure conditions. Similar behavior can be seen in the average induced absorbance for UVT and MP at the fundamental absorption edge in region 1. The UV absorber package in MP acrylic offers protection that slows this degradation by a factor of 6 compared to the degradation seen in UVT acrylic. It also appears that after photobleaching of the light stabilizer package in regions 2 and 2' there may be an increase in yellowing in MP acrylic. UVA acrylic showed no observable IAD with our current methods so its curves were omitted.
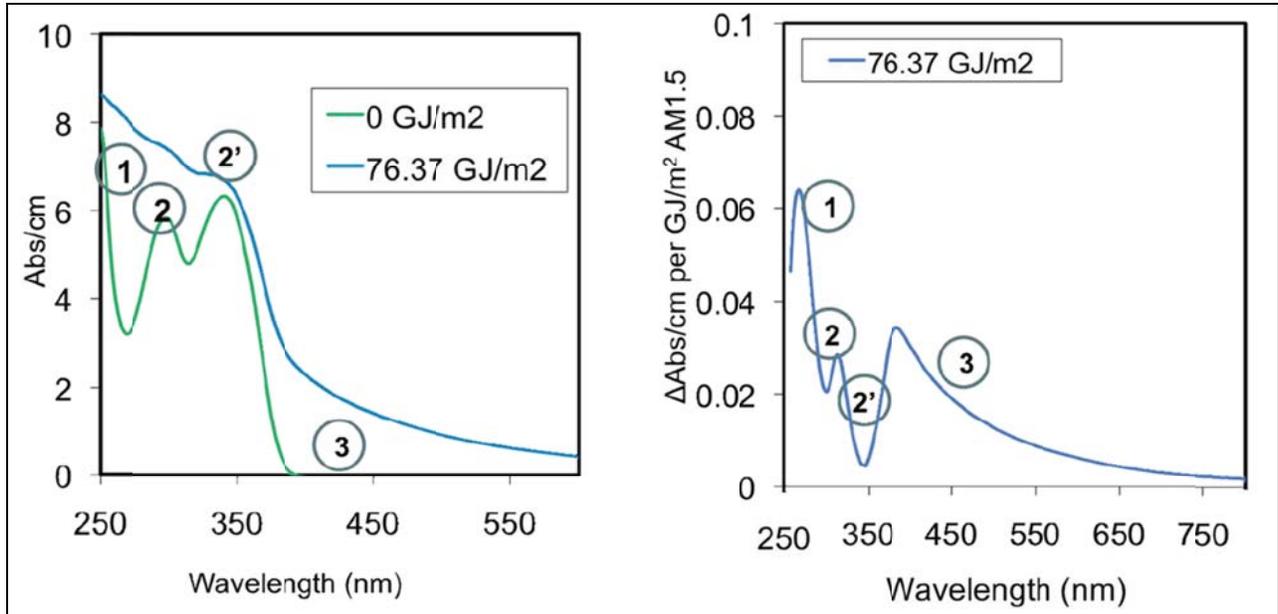

Figure 3: Left Absorbance per centimeter (Abs/cm) and *right* Induced absorbance to dose for MP acrylic with AM 1.5 solar simulator exposure at 48.4 kW/m^2
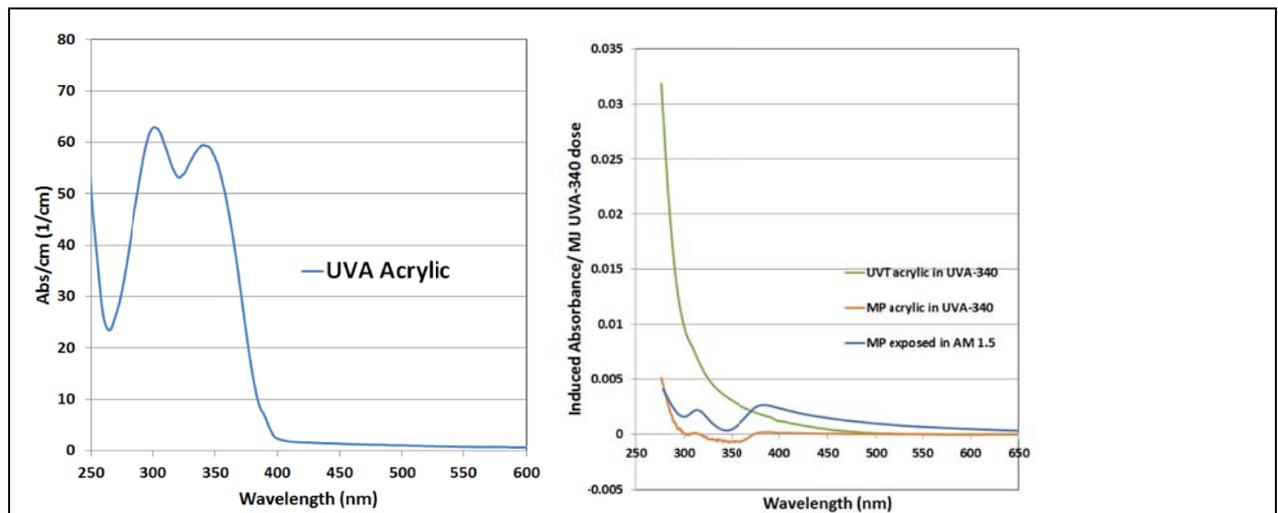

Figure 4: Abs/cm of UVA acrylic (right) and comparison of IAD across experiments (left)

Yellowness Indices:

Yellowness indices show that yellowness increases nearly linearly in all samples exposed to UVA-340 radiation (Figure 5). Yellowing rates are reported, and it can be seen that the yellowing rate of UVT acrylic (0.0365) was 8x higher than that of MP acrylic (0.0043); the YI for UVA acrylic (0.0018) performed over 2x better than the MP acrylic. Yellowness change is not reported for AM 1.5 exposures because the exposed area of the sample was too small to analyze with current instrumentation.

CONCLUSIONS

Three formulations of acrylic PMMA were exposed to two different stresses in order to better understand the stress-response framework by analyzing the quantitative metrics of IAD and YI. MP PMMA acrylic showed similarities in its degradation with two different exposures. It appears that materials additivity may hold true across the samples of PMMA containing UV stabilizers (MP) and not (UVT). The high dose exposure of MP grade acrylic appears to degrade the UV stabilizers, making it behave similar to UVT. This may be transferrable across multiple material systems exposed to different instantaneous stress levels and different integrated stresses. Further study into degradation mechanisms of acrylic will elucidate the exact phenomena that contribute to the material response to stress.
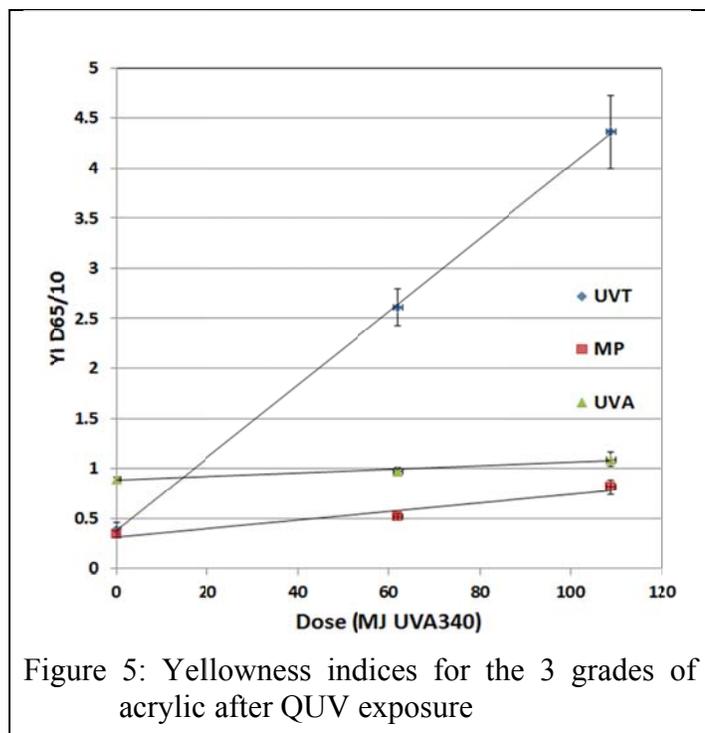

Figure 5: Yellowness indices for the 3 grades of acrylic after QUV exposure

Continuing work will require identification and quantification of stressors and identification of ways to meaningfully accelerate stresses and reproduce naturally occurring degradation mechanisms. The application of this framework to other stressors such as temperature, humidity, mechanical load corrosive environments, and applied loads will be investigated. An understanding of the stress-response framework in the photovoltaic lifetime and degradation science will allow for the same framework be applied to real world environmental conditions to enable indoor testing to be correlated to outdoor lifetimes.

ACKNOWLEDGMENTS

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