

# Durability of Acrylic: Stress and Response Characterization of Materials for Photovoltaics

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**Abstract**— In the development of 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. All PV systems are exposed to multifactor and cyclic environmental stressors including solar irradiance, temperature and humidity which can cause degradation over time. A stress and response framework is being used to link the intensity and accumulation of damaging environmental stressors to changes in materials properties. This allows for determination of appropriate techniques for accelerating environmental stressors, and also allows determination of the effects of stressors at multiple service conditions. Induced absorbance to dose (IAD), a new metric being developed for solar radiation durability studies of solar and environmentally exposed materials, is defined as the rate of photodarkening or photobleaching of a material as a function of total absorbed solar radiation dose. Yellowing rates, the change in ASTM E313 Yellowness Index as a function of absorbed dose, of two grades of acrylic poly(methyl-methacrylate) (PMMA) have been reported. IAD spectra for two formulations of acrylic PMMA are reported.

**Keywords**—Acrylic, Degradation, Photovoltaics, Photodegradation

## I. INTRODUCTION

A recent U. S. Department of Energy workshop on Science for Energy Technologies identified the topic of PV lifetime and degradation science (L&DS) as a critical scientific challenge for robust adoption of PV[1]. 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 degradation and failure modes, so as to enable quantitative lifetime projections.

Colorimetry[2,3], optical density[4,5], UV spectroscopy [2,4,5,6,7,8,9,10,11] and Fourier Transform infrared spectroscopy [2,5,7,8] have been used to optically characterize damage induced in acrylic PMMA. Indoor exposures have been performed under vacuum and in air, with mass loss metrology and gaseous degradation products being identified by mass spectroscopy [7,8]. Others have

performed outdoor exposures with flat plate exposures [3,6,12] and with accelerated tracking exposures [3].

Different formulations of PMMA were exposed to two different single factor accelerated exposures. Changes in optical properties were compared with different formulations of acrylic and different stressors.

## II. STRESS AND RESPONSE FRAMEWORK

A Stress and Response Framework [13] is used to quantify damaging environmental stress and correlate those stresses to material responses. Stressors that impact PV materials and components can be characterized in terms of instantaneous stress level ( $\sigma$ ), 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).

$$S = \int \sigma dt \quad (1)$$

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

A material's response ( $R$ ) to both instantaneous stress level and integrated stress may correspond to 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):

$$R = f(\sigma S) = \int f(\sigma) \sigma dt \quad (3)$$

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

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

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. However, single stress exposures can introduce hazardous assumptions because these stresses have synergistic effects meaning that a correlation function between stress and response in real use environments can depend on all stresses applied to the system. Response is therefore a function of the convolution of multiple stressors at their service-use conditions.

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### III. EXPERIMENTAL

Two formulations of PMMA considered are, multipurpose (MP) acrylic and UV transparent (UVT) acrylic. UVT acrylic contains no UV absorbers and is transparent to 275 nm, while MP acrylic contains UV absorbers giving it an effective UV cutoff of 350nm. These acrylic samples were acquired from Replex Plastics. MP acrylic is used for mirrors and transparent housings and is frequently used in outdoor applications. UVT acrylic is a specialty product that is used in cases where full spectrum light is needed. Baseline abs/cm measurements were performed on the acrylic samples that were never exposed to artificial weathering. The samples have a nominal thickness of 3mm.

Exposures were performed with a Q-Labs QUV Accelerated Weathering Tester (Model QUV/Spray with Solar Eye Irradiance Control) and with a Newport solar simulator. By removing samples at different points in exposure, measurements of optical properties after different increments of exposure dose (or dose steps) were performed. This makes possible determination of the effects of simulated solar irradiance (the stress) in terms of induced degradation rates. Changes in the optical properties of the materials exposed can elucidate the dose dependence of the response.

Parallel exposure of multiple samples on different platforms enables cross correlation and data quality management. This also will allow extraction of robust degradation mechanism and rate information from our L&DS research.

The QUV Accelerated Weathering Tester uses fluorescent lights to expose samples to high doses of UV light. The spectrum of damaging light depends on the bulbs used in the tester. The damaging portion of the solar spectrum was simulated in the QUV by carrying out exposures with UVA-340 bulbs. These bulbs emit radiation between 280 and 400 nm. The UVA-340 emission spectrum is a good match to terrestrial solar AM 1.5 spectra in the most of the UVA (315nm-400nm) and the entire UVB (280nm-315nm) regions when set at a maximum irradiance of 0.32 W/m<sup>2</sup>/nm at 340nm. Because the emission spectra of UVA340 bulbs diverges significantly from the AM 1.5 spectrum at wavelengths longer than 360 nm, and because much of the damaging radiation exists in the solar spectrum at wavelengths shorter than 360nm, the term UVA<sub>340</sub> dose is defined as (Equation 5):

$$UVA_{340} = \iint_{280}^{360} AM1.5 d\lambda dt = \iint_{280}^{360} UVA340 d\lambda dt \quad (5)$$

The QUV was run using ASTM G154 cycle 4 (1.55 W/m<sup>2</sup>/nm at 340 nm at 70°C) without the condensation step for 21 days. By setting the QUV peak intensity to 1.55 W/m<sup>2</sup>/nm at 340 nm a higher level of damage can be induced, making this a high temperature, high UV intensity exposure when compared with outdoor exposures. This 39 day test exposed samples to radiant exposure at wavelengths below 360 nm equivalent to the UVA<sub>340</sub> dose of approximately 2 years tracked solar exposure in Arizona. The first dose was 284 hours long, subsequent steps were 220 hours long each.

The Newport xenon arc solar simulator was used to irradiate material samples with filter matched AM 1.5 radiation. Continuous power monitoring with a Newport power meter was used to monitor the irradiance making it is possible to quantify the irradiance and dose to which a sample was exposed. Using a 13x concentrator with the solar simulator, irradiance levels of 50.4 kW/m<sup>2</sup> were achieved and sample

temperatures approximately 50°C, making this a high irradiance, high temperature accelerated test compared to both UVA-340 and outdoor exposure. This 18 day test exposed samples to doses of UVA<sub>340</sub> radiation equivalent to approximately 6 years of tracked solar exposure in Arizona, or full spectrum dose equivalent to 8 years. Each dose step in the Newport solar simulator was 72 hours of exposure.

Induced absorbance to dose (IAD) is a measurement of the change, at any wavelength, of the optical absorbance per centimeter of a material and is given by (Equation 6)

$$\frac{Abs}{cm} \text{ per } \frac{GJ}{m^2} \text{ Dose} \equiv \frac{Abs_{i+1}(\lambda)/cm - Abs_i(\lambda)/cm}{Dose_{i+1} - Dose_i} \quad (6)$$

IAD values were determined with an Agilent Cary 6000i with a diffuse reflectance accessory and with a Filmetrics PARTS-UV spectrophotometer.

Yellowness index (YI) as defined in the ASTM E313 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 after exposure. Yellowness indices are also useful because they are closely linked to reduced optical performance. YI can be determined by Equation 7:

$$YI = \frac{100(C_x X - C_z Z)}{Y} \quad (7)$$

where X, Y and Z are the CIE tristimulus values. For D65/10°, C<sub>x</sub>=1.3013, C<sub>z</sub>=1.1498 [14]. YI was determined using a HunterLab UltrascanPro colorimeter. Yellowing rates, the rate of change in yellowness as a function of dose, were determined (Equation 8).

$$R_{YI} = \frac{d(YI)}{d(S)} \quad (8)$$

### IV. RESULTS

Baseline absorbance spectra of UVT acrylic with absorbance spectra of successive dose steps are reported for Newport Solar Simulator exposure (Figure 1) and QUV exposure (Figure 2). Selected IAD curves are shown (Figure 3) of the 4<sup>th</sup> Dose QUV exposure and the 1<sup>st</sup> dose Newport Solar Simulator. A graph of the IAD values at selected wavelengths is reported (Figure 4) for all exposures performed on UVT acrylic.

Baseline absorbance spectra of MP acrylic with absorbance spectra of successive dose steps are shown for Newport Solar Simulator exposure (Figure 5) and for QUV exposure (Figure 6). A comparison spectra shows the IAD curves for MP acrylic in the first step of Newport Solar Simulator exposure and for QUV exposure Overlaid with the a baseline absorbance spectra (Figure 7). A graph of IAD values at selected wavelengths is reported for all exposures performed on MP acrylic (Figure 8). A graph of yellowing observed in samples subjected to QUV accelerated testing shows the nearly linear increase in YI (Figure 9).

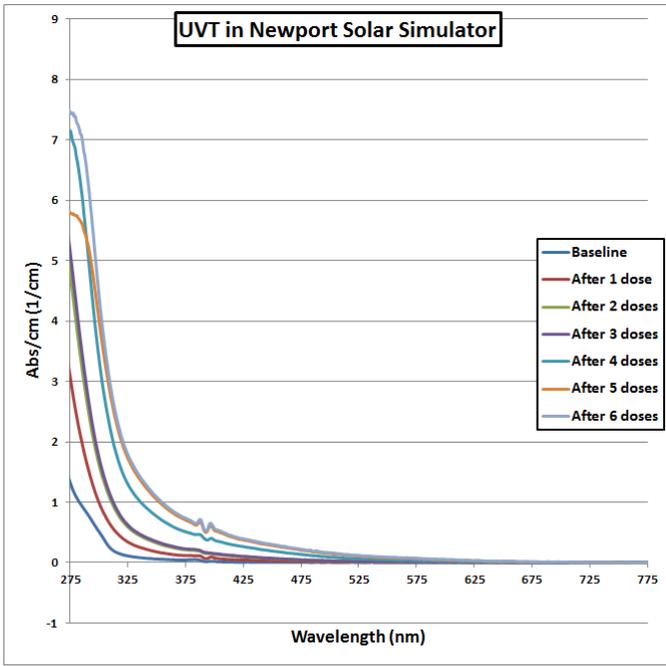


Figure 1: UVT Absorbance Spectra exposed in Newport Solar Simulator

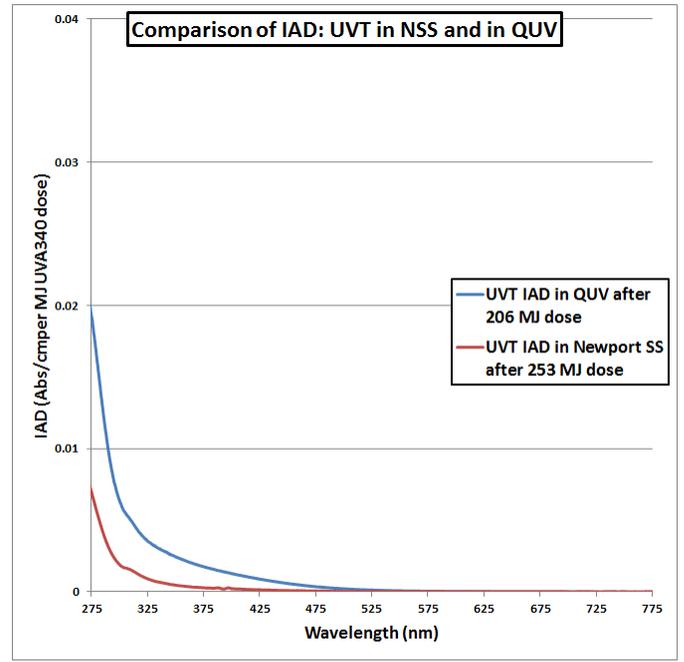


Figure 3: Spectral IAD curves for UVT in QUV and Newport Solar Simulator

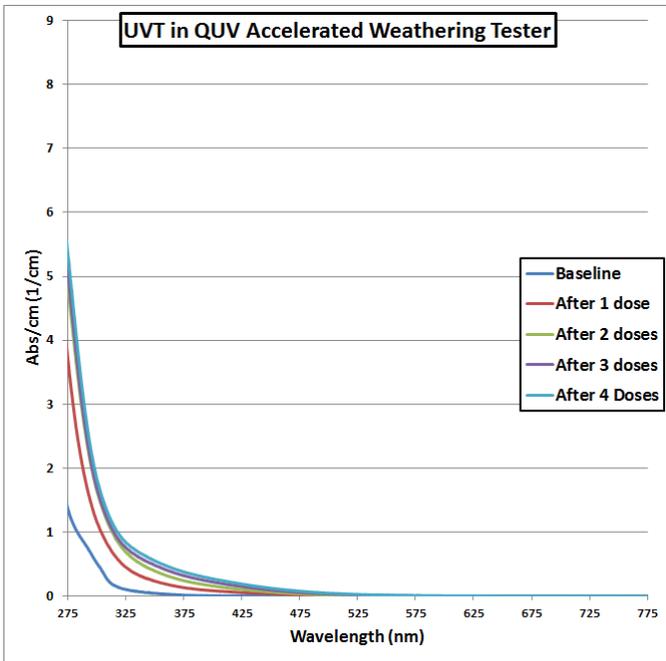


Figure 2: UVT Absorbance Spectra exposed in QUV accelerated weathering tester

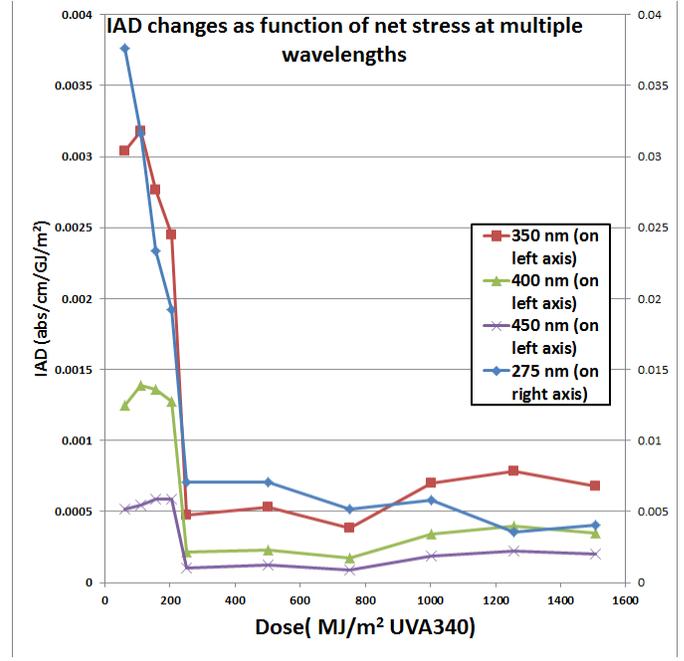


Figure 4: IAD values of UVT at selected wavelengths as a function of total dose

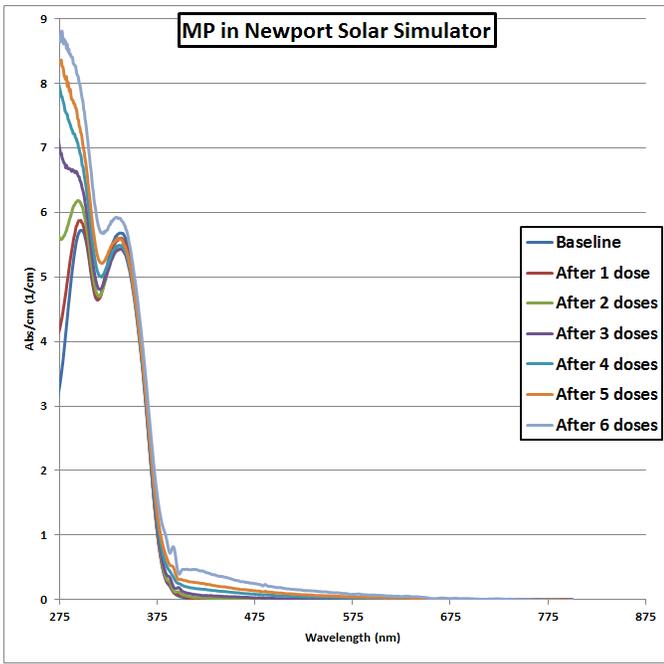


Figure 5: Absorbance Spectra of Multipurpose acrylic in Newport Solar simulator exposure

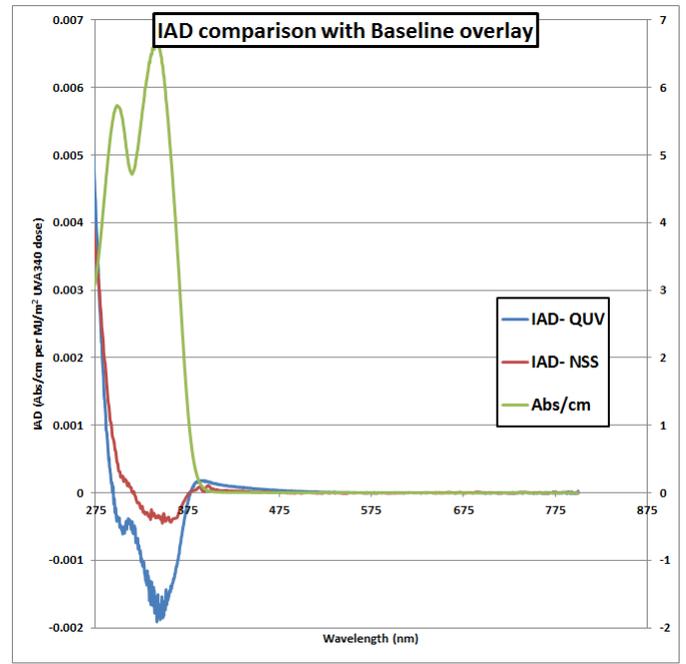


Figure 7: Spectral IAD curves of MP acrylic in two exposures overlaid with baseline Absorbance spectra

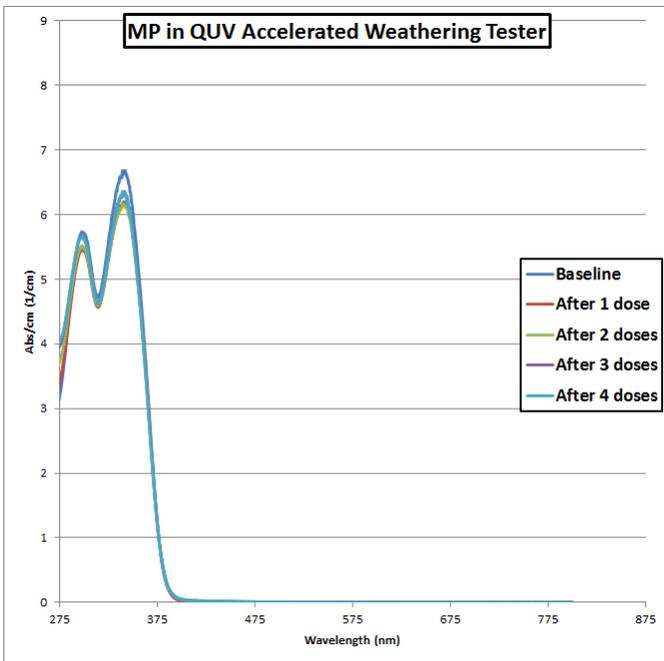


Figure 6: Absorbance Spectra for Multipurpose Acrylic in QUV exposure

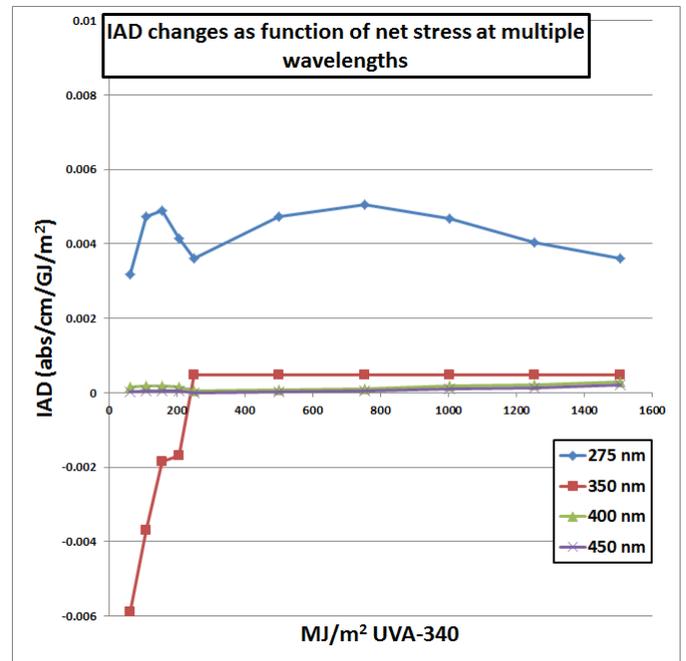


Figure 8: IAD values as a function of total dose at selected wavelengths

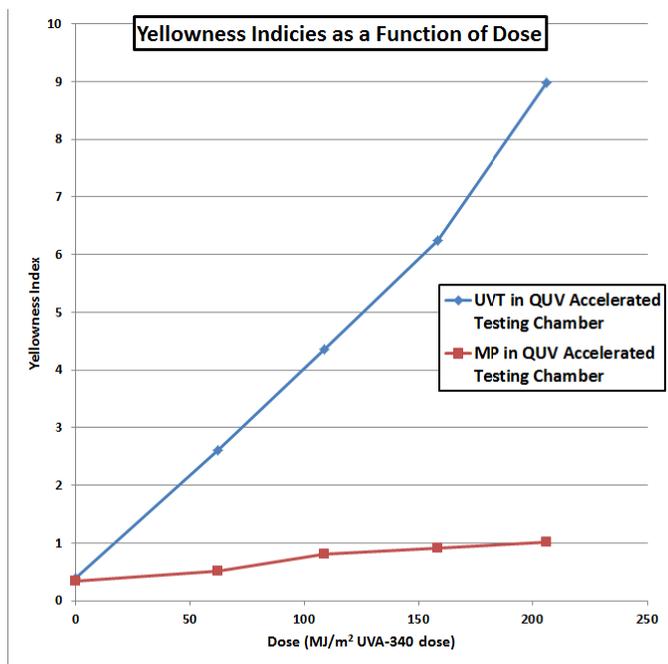


Figure 9: Yellowness Indices as a function of dose

## V. DISCUSSION

Photodarkening is observed when IAD values are positive, photobleaching is observed when IAD values are negative.

UVT shows considerable photodarkening when exposed to either stress profile. However, when normalized to dose, the QUV exposure is 2-6 times more damaging than exposure in the Newport Solar Simulator. This may be attributable to higher temperatures in the QUV tester. The stress may also have been amplified because samples in the QUV are mounted against aluminum plates, meaning that reflection of light back through the sample may increase UV damage. Multipurpose acrylic shows significant photodegradation under either stress profile. MP acrylic shows initial photobleaching of the UV stabilizer package, but this photobleaching is concurrent with photodarkening due to polymer breakdown, similar to degradation seen in UVT acrylic.

Comparison between grades of acrylic shows that UVT acrylic is much more susceptible to degradation than MP acrylic. The rate of yellowing in MP acrylic is decreased by a factor of 12 in QUV exposures. Yellowness indices are not reported for Newport exposures because the aperture area for exposure is too small to measure yellowness, however results suggest that this yellowing continues in the Newport simulator exposures of both materials.

## VI. CONCLUSIONS

Exposures in the Newport solar simulator and the QUV Tester show that both formulations of acrylic are susceptible to photodegradation in these accelerated exposures. Polymer breakdown leading to increased yellowness is observed in all samples, but is greatly reduced by the presence of UV absorbers. UV absorbers appear to be susceptible to photodegradation. This may limit the useful life of these materials for photovoltaic applications. While these highly accelerated tests may not simulate real weathering conditions they provide insights into the long term behavior of these materials.

Continuing work performed will focus on characterizing other material responses, performing longer exposures, linking observed degradation to mechanisms and exploring degradation in other formulations of acrylic. Exposures will include the effects of humidity, and outdoor exposures will be evaluated.

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**Dr. Laura S. Bruckman** is a research associate at CWRU. Dr. Bruckman received her Ph. D. in analytical chemistry from the University of South Carolina in Dr. Michael L. Myrick's research group in August 2011. Her research while at University of South Carolina was on the rapid classification of phytoplankton cells using single-cell fluorescence measurements and multivariate optical computing. Dr. Bruckman's work since joining Dr. Roger French's group at CWRU has been on the degradation mechanisms of acrylic and acrylic back surface mirrors in order to better understand the Lifetime and Degradation Science of these materials.



**Dr. Roger French** (*F. Alex Nason Professor, Department of Materials Science and Engineering*) joined CWRU in August 2010 after 24 years of conducting basic research and product development in DuPont's Central Research. He is the director of the Solar Durability and Lifetime Extension Center at CWRU. Dr. French has a broad experience in developing and commercializing optical materials for many different applications and

in optimizing these materials for improved radiation durability and lifetime. Dr. French is also a nationally recognized expert in Lifetime and Degradation Science (L&DS) for commercial applications, evidenced by his work on attenuating phase shift photomasks, fluoropolymer pellicles for photolithography, immersion lithography imaging fluids, and materials for concentrating photovoltaic systems. He has 22 issued patents and more than 145 publications.

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