

# Degradation of Poly(ethylene-terephthalate) Under Accelerated Weathering Exposures

Abdulkerim Gok, Cara L. Fagerholm, Devin A. Gordon, Laura S. Bruckman, Roger H. French

Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, OH, 44106, USA

**Abstract**—Poly(ethylene-terephthalate) is one of the most critical materials in photovoltaic module backsheets due to its dielectric breakdown strength. Unfortunately, PET is susceptible to environmental stressors and subject to degradation over time. Stabilizers are added to increase its service lifetime; however, even these degrade over time and leave the material vulnerable. To study degradation of polyester films, various accelerated weathering exposures are applied to PET grades with different stabilizers. A lab-based experiment was performed utilizing a randomized longitudinal design where samples were assigned to four exposure types and followed over time with repeated measurements in order to determine the effect of common stresses like UV light and humidity on the main polymer and stabilizer additives. It was found that material yellowing is dominant with UV light exposures while moisture mostly causes hazing of the samples. Effects were more severe when light was coupled with moisture. UV-Vis absorbance, infrared, and fluorescence spectroscopy provided valuable insights into the chemical degradation mechanisms such as formation of degradation byproduct, chain scissions, and change in crystallinity under different exposure conditions.

**Index Terms**—accelerated weathering exposures, hazing, hydrolysis, photolysis, poly(ethylene-terephthalate), yellowing, degradation.

## I. INTRODUCTION

Photovoltaic (PV) module backsheets are gaining great importance as reliability issues have arisen with outdoor deployed PV modules[1], [2]. Environmental stressors such as light, heat, and humidity seen in real-world conditions play a critical role in degradation of polymeric components of solar modules, causing performance loss. In previous studies [3], [4], it was shown that degradation of PET-based backsheets caused moisture ingress that led to moisture-driven hydrolysis of the encapsulant material (EVA(ethylene-vinyl acetate)). The formation of acetic acid due to the EVA degradation then resulted in corrosion of solar cell metallization and therefore power loss of the PV modules.

PET is widely used in PV backsheets as an electrical barrier, but it is highly susceptible to moisture and ultraviolet (UV) light [5]. PET degradation mainly occurs via photolytic and hydrolytic cleavage of an ester bond and results in discoloration and/or hazing, decreased molecular weight, and changed morphology. Photodegradation and/or photo-oxidation mainly occurs via Norrish type I or Norrish type II reactions[6], [7], [8]. When chemical reaction rate controlled processes, i.e., autocatalysis due to active carboxylic acid end groups, are taken into account, hydrolysis mechanisms become more complex to interpret. Various kinetic models of these reactions have been discussed in the literature [9],

[10], [11], [12]. Failures including cracking and delamination in backsheet films caused by aging [13], [14] may result not just in performance loss of the module but also in dielectric withstand breakdown of the PV systems and lead to electrical safety hazards. The polymer is protected from degrading to some extent because polymer additives for UV and hydrolysis stabilization are used to increase service lifetime during harsh outdoor conditions, but even these stabilizers can be degraded over time and leave the material vulnerable [15], [16]. Therefore, it is critical to understand degradation mechanisms of PET polymer with or without stabilizer additives upon exposure to environmental stressors.

## II. EXPERIMENTAL

The three PET grades used in this study are unstabilized (Dupont-Teijin Melinex 454), UV stabilized (Dupont-Teijin Tetoron HB3), and hydrolytically stabilized (Mitsubishi 8LH1). These are clear films with thicknesses of 3 mil, 2 mil, and 5 mil, respectively.

To study degradation of these polyester films, a lab-based, completely randomized, longitudinal study design was used where PET samples were randomly assigned to four exposure types and followed over time with repeated measurements. The study consists of exposure and measurement step sizes of one week (168 hours) with a total of 7 steps (1176 hours). In addition, one sample was withdrawn from further exposure at each time step to create a retained sample library for future investigation. The four laboratory-based accelerated conditions are 1) cyclic exposure of UVA-340 light at  $1.55 \text{ W/m}^2/\text{nm}$  at  $70^\circ\text{C}$  for 8 hours and condensing humidity at  $50^\circ\text{C}$  in the dark for 4 hours in accordance with ASTM G154-cycle 4 [17], 2) continuous UVA-340 light at  $1.55 \text{ W/m}^2/\text{nm}$  at  $70^\circ\text{C}$ , 3) damp heat exposure ( $85^\circ\text{C}/85\%$  relative humidity), and 4) modified humidity freeze exposure (cyclic  $70^\circ\text{C}/85\%$  relative humidity and  $-40^\circ\text{C}$ ) per IEC 61215 standard[18]. Note that these exposures in the text are referred as CyclicQUV, HotQUV, DampHeat, and FreezeThaw, respectively.

Yellowness index (YI) and haze (%) measurements were conducted using a HunterLab UltrascanPro colorimeter. YI is the measure of yellowing of a sample and calculated using transmission spectrum in the UV-Vis region as defined by ASTM E313 standard [19]. Haze (%) is the measure of cloudiness of a sample caused by scattering of light due to particles or impurities in the material. It is the ratio of diffuse transmittance to total transmittance in the visible region as defined by ASTM D1003-13 standard [20]. Changes in YI and

haze (%) are seen as early indicators of chemical changes in polymers due to chromophores or crystallites that are formed during degradation.

Optical absorbance (Abs/cm) changes in degraded samples were evaluated using Agilent Cary 6000i UV-Vis-NIR spectroscopy with a DRA-1800 Diffuse Reflectance Accessory. The center mount absorbance spectra were taken from 250 to 900 nm every 0.50 nm with a scan rate of 112.5 nm/min and a spectral bandwidth of 4.00 nm in the measurement region. This measurement monitors the changes in optical absorbance characteristic such as change in the fundamental absorption edge and degradation of UV stabilizer in the material during exposure.

An Agilent 630 FTIR spectrometer with a diamond attenuated total reflectance accessory (ATR) was used for infrared spectra of the degraded films. The spectra were taken between 650 and 4000  $\text{cm}^{-1}$  every 2  $\text{cm}^{-1}$  resolution with 8 scans for both background and samples. Due to the problems that arise from the sample contact with the diamond crystal, all spectra were first baseline corrected using polynomial fitting and then normalized to the band intensity at 1410  $\text{cm}^{-1}$  [21], [22], [23]. Although each IR band might indicate specific chemical information about the degradation mechanisms, only the band at 1711  $\text{cm}^{-1}$  due to carbonyl ( $C = O$ ) stretching (as a signature of chain scissions) and the ratio of the *trans* and *gauche* ( $\text{CH}_2$ ) wagging bands at 1340  $\text{cm}^{-1}$  and 1370  $\text{cm}^{-1}$  (as an indicator of crystallinity) will be presented in this work.

A Cary Eclipse Fluorescence Spectrophotometer was used for fluorescence spectra measurements. Photoluminescence (PLE) excitation-emission maps were generated on the unexposed baseline sample and the very last exposed sample from each grade and each exposure type in order to observe the changes in fluorescence characteristics. The method used for 3D mapping is as follows: the emission spectra was collected between 300 nm and 800 nm every 1 nm with a scan rate of 600 nm/min with excitations from 280 nm to 780 nm with 5 nm increments.

Finally, single data points from spectral information were extracted and plotted as a function of exposure time. For UV-Vis measurement, features that are associated with the fundamental absorption edge of the polymer at 312 nm and the increased absorbance due to the formation of degradation byproducts at 340 nm were selected. For IR measurement, as mentioned earlier, peak height of the carbonyl band and peak height ratio of the two conformers of  $\text{CH}_2$  wagging band in the ethylene glycol unit were chosen. From fluorescence maps, single excitation wavelengths were also determined for future investigation.

### III. RESULTS AND DISCUSSION

#### A. Yellowness Index and Haze (%)

Yellowness index is one of the performance level responses of the degraded films and understanding its temporal evaluation is critical. Figure 1 shows a crossed panels figure of the change in YI in all grades and exposure types versus time. Note that grades are plotted as rows and exposures as columns.

Since one sample was retained after each step of exposure, the number of data points, starting from 0 hours, decreases by one and only one data point remains at the last step (1176 hours). There is a significant increase in YI with HotQUV and CyclicQUV exposures and negligible changes with DampHeat and FreezeThaw exposures. The reason for this is that, given the exposure time, UV light induces more yellowing and thus greater degradation when compared to exposures without UV light. Damage accumulation in DampHeat and FreezeThaw exposures may result in more severe degradation than what is observed here once it reaches a critical level. The second point is the effect of UV stabilizer during HotQUV and CyclicQUV exposures. There is a change point after the first step of exposure before which YI doesn't show any change, but after that, somewhat linear increase is observed.

Figure 2 shows temporal evolution of haze development in all grades and exposures. Moisture induced hazing is seen in all PET grades with high humidity exposures. The role of hydrolytic stabilization seems to be unclear on all exposures except for CyclicQUV exposure under which the unstabilized grade led to higher haze (%) than the hydrolytically stabilized grade. Sample to sample variance is large compared to YI measurement, which suggests the sensitivity of haze measurement specifically at high haze (%) values. The unstabilized grade under CyclicQUV seems to have the highest haze (%) values among other grades and exposures, with greater sample variance, where the data scattered the most in between samples. Note that sample retainment after each exposure step leads to smaller sample-measurement number and variance becomes less apparent. Only the UV stabilized grade under DampHeat exposure seems to follow a linear trend.

The most important observation is that there was severe change with CyclicQUV in all grades, but small to negligible change with all other exposures. This can be attributed to high humidity content of CyclicQUV. It is also shown that HotQUV did not induce significant hazing despite the high level of UV dose and light induced yellowing, as discussed earlier. Therefore, it can be said that hazing is more likely to be a hydrolytic phenomena rather than photolytic. Since no significant changes in YI and haze (%) were seen with DampHeat and FreezeThaw exposures, the rest of the discussion will only include HotQUV and CyclicQUV exposures.

#### B. UV-Vis Optical Absorbance

The UV-Vis changes at 312 nm and 340 nm are depicted in Figure 3. Under HotQUV exposure, unstabilized (B1, B2) and hydrolytically (A1, A2) stabilized grades show an increase at both 312 nm and 340 nm, probably due to vast number of chain scissions, but UV stabilized grade (C1, C2) doesn't exhibit significant changes. Under CyclicQUV exposure, optical density at 312 nm does not seem to be affected markedly in unstabilized (B1) and hydrolytically stabilized (A1) grade; however, there is a significant decrease in UV stabilized (C1) grade. At 340 nm, both unstabilized (B2) and hydrolytically stabilized (A2) grades increase, but the degree of increase is less than that in HotQUV, probably because of the lesser

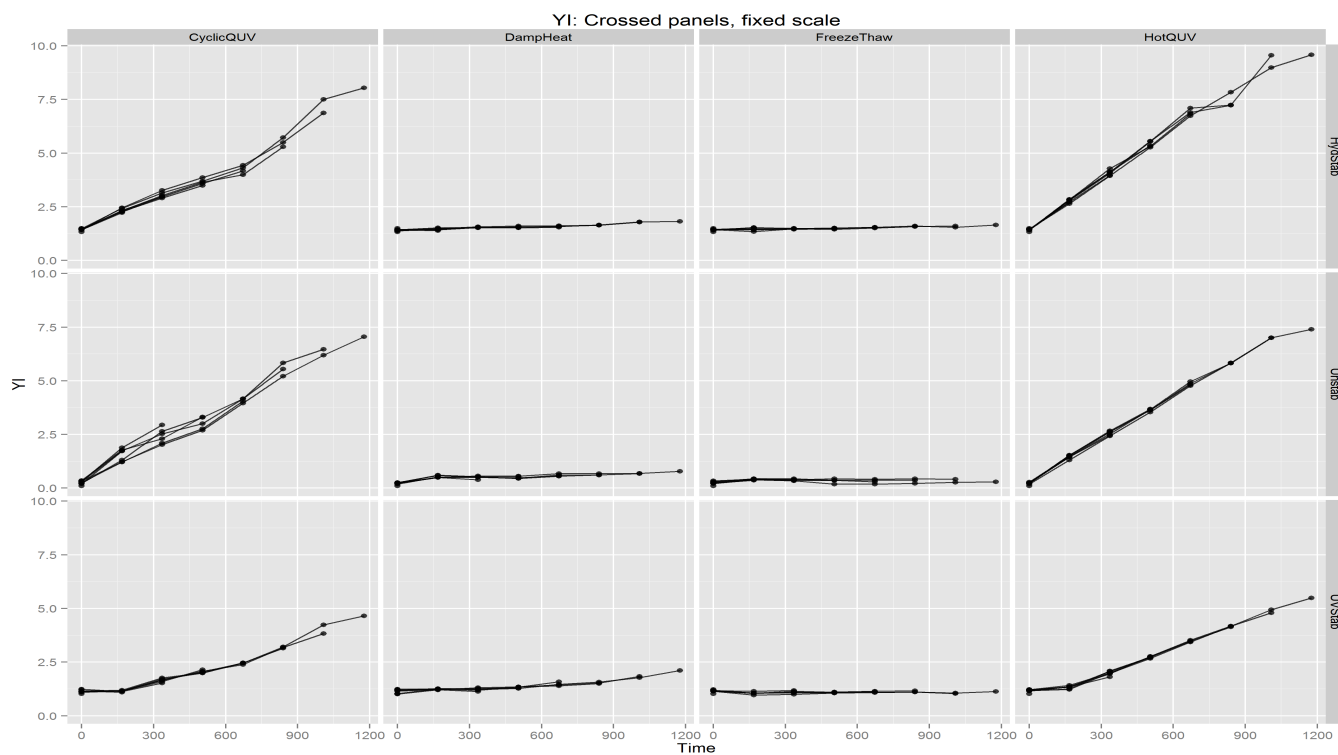


Fig. 1: Cross panel figure showing change in YI with exposure time for each of the three grades of PET

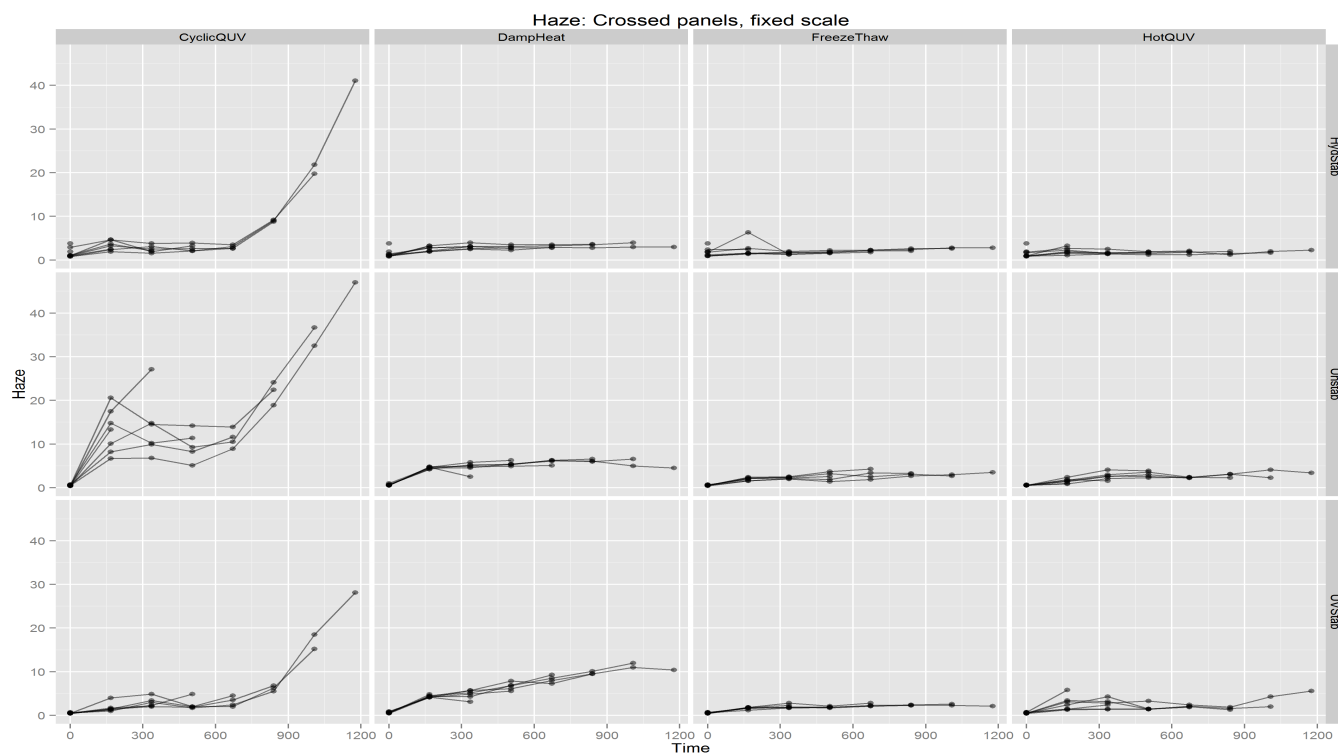


Fig. 2: Cross panel figure showing change in haze (%) with exposure time for each of the three grades of PET

amount of photodose. In the UV stabilized grade (C2), the trend is quite similar to that at 312 nm, decreasing over time. Note that in this particular grade, there is a strong cut-off at 400 nm due to the presence of UV stabilizer and this 340 nm absorption mostly represents the evolution of the UV stabilizer, which is being depleted with successive exposure.

### C. FTIR-ATR

Figure 4 shows the temporal evolution of the two specific infrared features. The bands that are attributed to *trans* and *gauche* conformations of the ( $CH_2$ ) wagging at  $1340\text{ cm}^{-1}$  and  $1370\text{ cm}^{-1}$  are known to change intensity during degradation as *trans* form is favored by crystalline phase due to its close packing nature[21], [22], [23], [24] so the ratio of these two bands indicates a change in crystallinity. There is a strong decrease in this ratio under HotQUV exposure in all grades, suggesting that UV light (with the effect of temperature) is leading to amorphitization; however, CyclicQUV causes a slight increase, indicating a hydrolysis driven crystallization. Note that CyclicQUV also consists of UV light, which is 2/3 of that in HotQUV, so the two degradation modes, photodegradation and hydrolysis, seem to be acting as competitive mechanisms. The band at  $1711\text{ cm}^{-1}$  depicts an overall decrease in all grades and exposures, implying a large number of scissions in the polymer chain. Only UV stabilized

grade under CyclicQUV exposure does not exhibit a significant change, which needs further investigation.

### D. Photoluminescence (PLE) Maps

For the unstabilized grade at time zero, only one distinct region of fluorescence emission is seen in Figure 5-B1: a broad emission with 320 nm to 370 nm excitation (with the highest intensity located at 340 nm) with a peak emission at 390 nm that corresponds to a ground state dimer [25], [26]. There are, in fact, other features in this region, but they are only visible in the spectra with single 340 nm excitation. When exposed, this broad region disappears and two new features are created under both exposures. In HotQUV (B2), the emissions, both centered around 460 nm, are largely separated into two regions: one with 340 nm excitation and the other with 380 nm excitation. In CyclicQUV (B3), the same emission behavior is seen with greater fluorescence intensities that overlap in the middle region. In hydrolytically stabilized grade (A1-A3), the overall result is quite similar to what is observed in unstabilized grade, but features are more pronounced in this case. No additional feature in the spectra is seen due to the presence of stabilizer.

The emission characteristics of the UV stabilized grade is different from the unstabilized grade. The baseline emission (C1) is now between 380 nm and 460 nm with 320 nm to 390 nm excitation and there seems to be three different

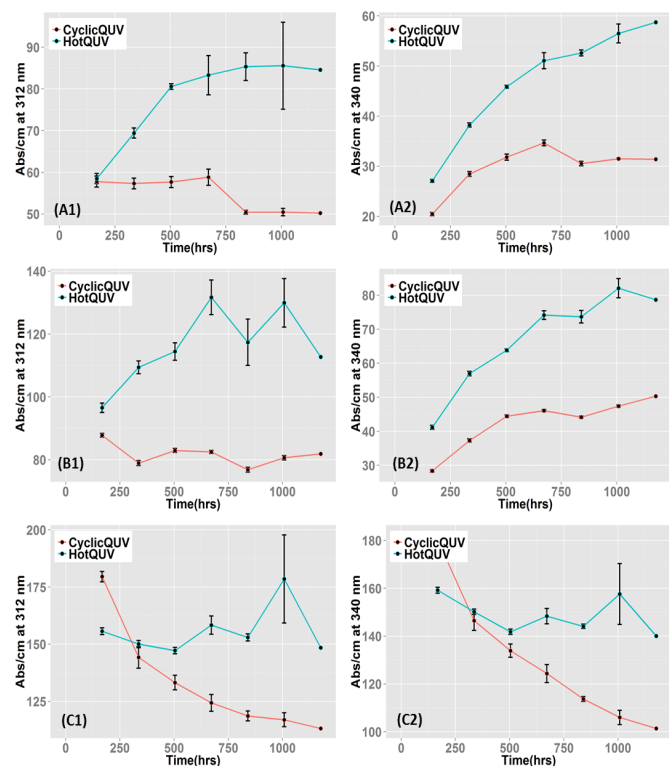


Fig. 3: UV-Vis optical absorbance at 312 nm (1) and 340 nm (2) with exposure time (A: Hyd.stabilized, B: Unstabilized, C: UVStabilized)

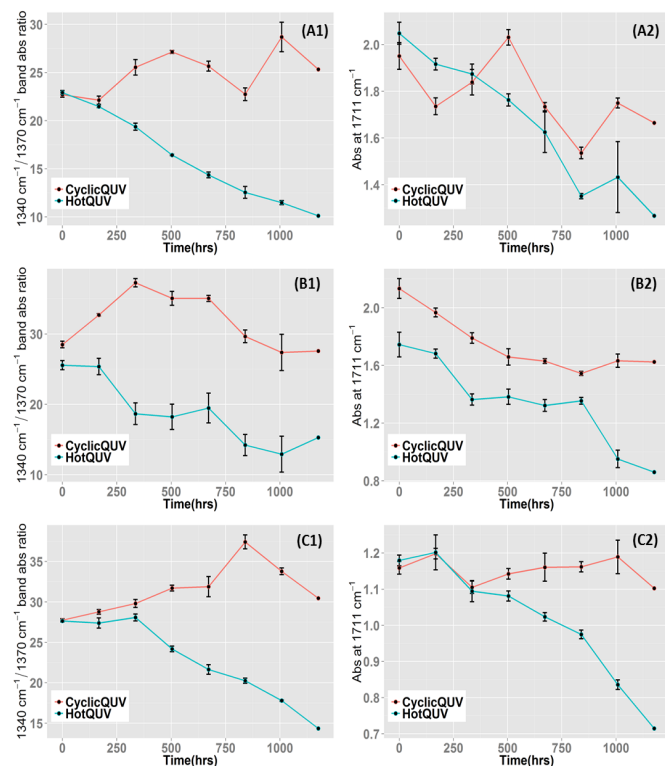


Fig. 4: IR absorbance at  $1340\text{ cm}^{-1}/1370\text{ cm}^{-1}$  (1) and  $1711\text{ cm}^{-1}$  (2) with exposure time (A: Hyd.stabilized, B: Unstabilized, C: UVStabilized)

peaks present. The maximum emission intensity is obtained by the excitation at 380 nm. Since no characteristic features of the bare polymer are seen in this particular grade, this change in emission behavior can be attributed to the presence of the UV stabilizer. Despite the high level of yellowing in HotQUV exposure (C2), negligible change in the fluorescence characteristics is seen. There is little increase in the emission intensity and little broadening into higher wavelengths, but the overall shape is preserved with its distinct peaks. In CyclicQUV exposure (C3), these peaks disappear and the emission region has grown in both intensity and area. Similar to the unstabilized grade, this region, centered around 460 nm emission, is separated into two parts. Despite the lower level of photodose than that in HotQUV, CyclicQUV has caused significant changes in the fluorescence spectra even though their YI measurements are close to each other. So, this change is strongly correlated with the presence of moisture and moisture driven hydrolysis. Hazing can also contribute to this behavior in two ways: one is increased effective path-length of the light within the material and the other is formation of fluorescing species with hydrolysis.

The strong emission at 460 nm is mainly attributed to hydroxylated species that are formed during degradation. Under oxidative conditions, it is suggested that hydroxylated species oxidize to form quinonoid structures which lead to yellowing and reduction in fluorescence intensity. Yellowing effect of quinones is attributed to its high extinction coefficient that is associated with the absorption of visible light [25], [26]. So, this can explain the reduction of fluorescence under HotQUV with extended exposure time; however, in the case of CyclicQUV, additional formation of hydroxylated species as a result of hydrolysis is found to be causing more fluorescence.

#### E. Future Work

Statistical and domain analytics are now required to determine relationships between these mechanisms and stress conditions as degradation mostly occurs via initial stress, stress accumulation, mediating factors, main degradation mechanism, and failure of system level response. It is very important that contributing factors to observed and measured variables are assessed and models that tie these stressors and responses are determined. It is highly essential that very well designed laboratory-based studies are conducted in order to minimize errors due to sampling and measurements. Physical and statistical models can then be developed that help determine the temporal evolution of the degradation [27]. Modeling that links the exposure stressors and measured responses through domain-guided statistical degradation pathways is in progress.

#### IV. CONCLUSION

PET with its high dielectric breakdown strength and low price is widely used in multilayer backsheets as a core layer but it is vulnerable to ultraviolet light and humidity and degrades during outdoor service. It is therefore very critical to understand PET's degradation behavior. Stabilizer added to the main polymer withstands these stresses to some

extent but even these stabilizers are subject to degradation. With this purpose, the photolytic and hydrolytic degradation of PET was studied under accelerated weathering exposures using a lab-based experiment with a completely randomized longitudinal design. Yellowing was mostly caused by UV light exposures and hazing was predominant in humidity exposures. Effects were more severe when light and moisture were coupled. UV stabilizing protected the polymer during the first course of exposures; however, a linear increase in YI was observed afterwards. The effect of hydrolysis stabilization was uncertain and further study is suggested to elucidate its mechanism. DampHeat and FreezeThaw exposures did not result in a significant degradation for a given exposure. FTIR analysis showed that chain scission is the common mechanism under both HotQUV and CyclicQUV exposures, yet light and humidity were found to have an adverse effect on crystallinity. Photoluminescence mapping was shown to be a useful method to determine all possible fluorescence processes during degradation. Even though similar yellowing values were reported for both HotQUV and CyclicQUV exposures, the reduced intensity in HotQUV was attributed to oxidation of fluorescing species; however, increased intensity in CyclicQUV was due to the presence of moisture and hence hydrolysis.

#### ACKNOWLEDGMENT

This research was performed at the SDLE Center (funded through Ohio Third Frontier, Wright Project Program Award Tech 12-004) at Case Western Reserve University. The authors would like to acknowledge the support from DOE-BAPVC (Award No. DE-EE0004946) and 3M, and thank Tekra Corporation and Mitsubishi Polyester Films for providing samples.

#### REFERENCES

- [1] Marc Kontges, Sarah Kurtz, Corrine Packard, Ulrike Jahn, Karl Berger, Kazuhiko Kato, Thomas Friesen, Haitao Liu, and Mike Van Iseghem. IEA-PVPS {Task 13}: Review of failures of PV modules. Technical report, May 2104.
- [2] Ronald G. Ross. PV reliability development lessons from JPL&#x0027;s flat plate solar array project. *IEEE Journal of Photovoltaics*, 4(1):291–298, January 2014. 00000.
- [3] Laura S. Bruckman, Nicholas R. Wheeler, Junheng Ma, Ethan Wang, Carl K. Wang, Ivan Chou, Jiayang Sun, and Roger H. French. Statistical and domain analytics applied to PV module lifetime and degradation science. *IEEE Access*, 1:384–403, 2013.
- [4] N.R. Wheeler, L.S. Bruckman, Junheng Ma, E. Wang, C.K. Wang, I. Chou, Jiayang Sun, and R.H. French. Statistical and domain analytics for informed study protocols. In *2013 IEEE Energytech*, pages 1–7, 2013.
- [5] Thomas C. Felder, William J. Gambogi, James G. Kopchick, R. Scott Peacock, Katherine M. Stika, T. John Trout, Alexander Z. Bradley, Babak Hamzavtehrany, Abdulkarim Gok, Roger H. French, Oakland Fu, and Hongjie Hu. Optical properties of PV backsheets: key indicators of module performance and durability. page 91790P, October 2014.
- [6] M. Day and D. M. Wiles. Photochemical decomposition mechanism of poly(ethylene terephthalate). *Journal of Polymer Science Part B: Polymer Letters*, 9(9):665–669, 1971.
- [7] M. Day and D. M. Wiles. Photochemical degradation of poly(ethylene terephthalate). i. irradiation experiments with the xenon and carbon arc. *Journal of Applied Polymer Science*, 16(1):175–189, 1972.
- [8] M. Day and D. M. Wiles. Photochemical degradation of poly(ethylene terephthalate). II. effect of wavelength and environment on the decomposition process. *Journal of Applied Polymer Science*, 16(1):191–202, 1972.

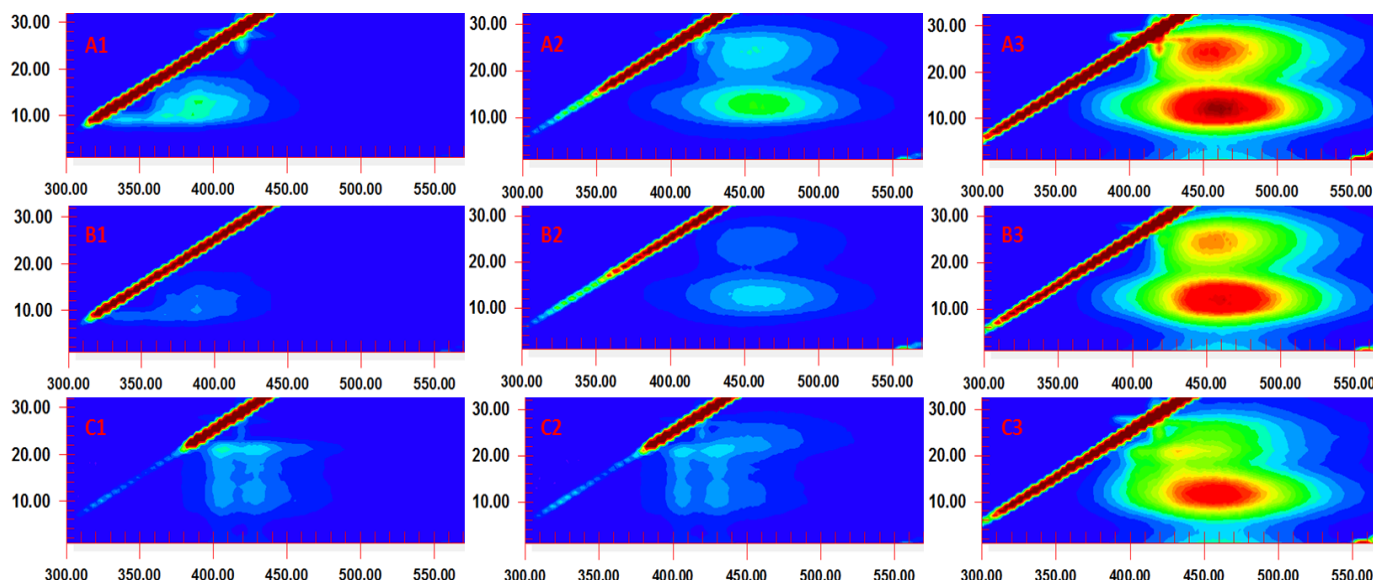


Fig. 5: Photoluminescence (PLE) maps. Note that emission wavelength is on the x-axis, excitation wavelength on the y-axis is obtained by  $280 \text{ nm} + 5 \text{ nm} \times \text{x-axis value}$ , and intensity is pointing outward. The red line along the diagonal is the back reflection of the incident light. (A: Hyd.stabilized, B: Unstabilized, C: UVStabilized, 1: Unexposed, 2: HotQUV, 3: CyclicQUV)

- [9] William McMahon, H. A. Birdsall, G. R. Johnson, and C. T. Camilli. Degradation studies of poly(ethylene terephthalate). *Journal of Chemical & Engineering Data*, 4(1):57–79, January 1959.
- [10] A. Launay, F. Thominet, and J. Verdu. Hydrolysis of poly(ethylene terephthalate): a kinetic study. *Polymer Degradation and Stability*, 46(3):319–324, 1994.
- [11] L. Turnbull, J. J. Liggit, and W. A. MacDonald. Ageing of poly(ethylene terephthalate) and poly(ethylene naphthalate) under moderately accelerated conditions. *Journal of Applied Polymer Science*, pages n/a–n/a, 2011.
- [12] James E. Pickett and Dennis J. Coyle. Hydrolysis kinetics of condensation polymers under humidity aging conditions. *Polymer Degradation and Stability*, 98(7):1311–1320, July 2013.
- [13] G. Oreski and G.M. Wallner. Aging mechanisms of polymeric films for PV encapsulation. *Solar Energy*, 79(6):612–617, December 2005.
- [14] Fernando D. Novoa, David C. Miller, and Reinhold H. Dauskardt. Environmental mechanisms of debonding in photovoltaic backsheets. *Solar Energy Materials and Solar Cells*, 120, Part A:87–93, January 2014.
- [15] James E Pickett and James E Moore. Photodegradation of UV screeners. *Polymer Degradation and Stability*, 42(3):231–244, 1993.
- [16] Laura S. Bruckman, Nicholas R. Wheeler, Ian V. Kidd, Jiayang Sun, and Roger H. French. Photovoltaic lifetime & degradation science statistical pathway development: Acrylic degradation. In *Reliability of Photovoltaic Cells, Modules, Components, and Systems VI*, volume 8825, Bellingham, 2013. Spie-Int Soc Optical Engineering. WOS:000325973200011.
- [17] G03 Committee. Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials. Technical Report G154-06, ASTM International, 2006.
- [18] IEC. IEC61215 ed2.0 - crystalline silicon terrestrial photovoltaic (PV) modules - design qualification and type approval | IEC webstore | publication abstract, preview, scope, 2005.
- [19] E12 Committee. Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color Coordinates. Technical report, ASTM International, 2015.
- [20] D20 Committee. Test method for haze and luminous transmittance of transparent plastics. Technical report, ASTM International, 2013.
- [21] Jean-Michel Andanson and Sergei G. Kazarian. In situ ATR-FTIR spectroscopy of poly(ethylene terephthalate) subjected to high-temperature methanol. *Macromolecular Symposia*, 265:195–204, 2008. WOS:000256716900022.
- [22] Kenneth C. Cole, Abdellah Ajji, and Eric Pellerin. New Insights into the Development of Ordered Structure in Poly(ethylene terephthalate). 1. Results from External Reflection Infrared Spectroscopy. *Macromolecules*, 35(3):770–784, January 2002.
- [23] Chris Sammon, Jack Yarwood, and Neil Everall. An FTIR study of the effect of hydrolytic degradation on the structure of thin PET films. *Polymer Degradation and Stability*, 67(1):149–158, January 2000.
- [24] B. J. Holland and J. N. Hay. The thermal degradation of PET and analogous polyesters measured by thermal analysis Fourier transform infrared spectroscopy. *Polymer*, 43(6):1835–1847, March 2002.
- [25] M. Edge, N. S. Allen, R. Wiles, W. McDonald, and S. V. Mortlock. Identification of luminescent species contributing to the yellowing of poly(ethylene terephthalate) on degradation. *Polymer*, 36(2):227–234, 1995.
- [26] G.J.M. Fecine, M.S. Rabello, R.M. Souto Maior, and L.H. Catalani. Surface characterization of photodegraded poly(ethylene terephthalate). the effect of ultraviolet absorbers. *Polymer*, 45(7):2303–2308, March 2004.
- [27] Roger H. French, Rudolf Podgornik, Timothy J. Peshek, Laura S. Bruckman, Yifan Xu, Nicholas R. Wheeler, Abdulkarim Gok, Yang Hu, Mohammad A. Hossain, Devin A. Gordon, Pei Zhao, Jiayang Sun, and Guo-Qiang Zhang. Degradation science: Mesoscopic evolution and temporal analytics of photovoltaic energy materials. *Current Opinion in Solid State and Materials Science*, January 2015.