Degradation in PV Encapsulation Transmittance: An Interlaboratory Study Toward a Climate-Specific Test

David C. Miller¹, Eleonora Annigoni², Amal Ballion³, Jayesh G. Bokria⁴, Laura S. Bruckman⁵, David M. Burns⁶, Xinxin Chen⁷, Lamont Elliott⁸, Jiangtao Feng⁷, Roger H. French⁵, Sean Fowler⁹, Xiaohong Gu¹⁰, Peter L. Hacke¹¹, Christian C. Honeker¹¹, Michael D. Kempe¹, Hussam Khonkar¹², Michael Köhl³, Laure-Emmanuelle Perret-Aebi¹³, Nancy H. Phillips⁶, Kurt P. Scott⁸, Fanny Sculati-Meillaud², Tsuyoshi Shioda¹⁴, Shigeo Suga¹⁵, Shin Watanabe¹⁵, and John H. Wohlgemuth¹

¹National Renewable Energy Laboratory (NREL), 15013 Denver West Parkway, Golden, CO 80401, USA
²École Polytechnique Fédérale de Lausanne (EPFL), Rue de la Maladière 71B, Ch-2002 Neuchâtel, Switzerland
³Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstrasse 2, 79110 Freiburg, Germany
⁴Specialized Technology Resources, Inc. (STR), 10 Water Street, Enfield, CT, USA 06082
⁵Case Western Reserve University (CWRU), White 538, 10900 Euclid Avenue, Cleveland, OH 44106, USA
⁶The 3M Company, 3M Center, Building 235-67-15, St. Paul, MN, 55144, USA
⁷China National Electric Apparatus Research Institute Co., Ltd. (CEI), Guangzhou, 510663, P. R. China
⁸Atlas Material Testing Technology LLC, 1500 Bishop Court, Mount Prospect, IL 60056, USA
⁹Q-Lab Corporation, 800 Canterbury Road, Cleveland, OH 44145 USA
¹⁰National Institute of Standards and Technology (NIST), 100 Bureau Dr., Gaithersburg, MD 20899-8615, USA
¹¹Fraunhofer Center for Sustainable Energy Systems (CSE), 5 Channel Center, Boston, MA 02210, USA
¹²King Abdulaziz City for Science and Technology (KACST), 17 King Abdullah Road, Riyadh, 11442, Saudi Arabia
¹³Centre Suisse d’Electronique et Microtechnique SA. (CSEM), Rue Jaquet-Droz 1, Ch-2002 Neuchâtel, Switzerland
¹⁴Mitsui Chemicals, Inc., 580-32 Nagaura-cho, Sodegaura-shi, Chiba, 299-0265, Japan
¹⁵Suga Test Instruments Co., Ltd., 5-4-14 Shinjuku, Shinjuku-ku, 160-0022, Tokyo Japan

*Presenter & TG5 US: David.Miller@nrel.gov; TG5 China: fengjt@cei1958.com (Leo Feng); TG5 Europe: michael.koehl@ise.fraunhofer.de; TG5 Japan: Tsuyoshi.Shioda@mitsui-chem.co.jp

IEEE Photovoltaics Specialists Conference 2015 ("IEEE PVSC 42")

Area 11: Module materials and Component Reliability

#972; 11:00-11:15 Fri, 2015/6/19, Hyatt Regency - New Orleans, Strand 10 (Level 2)

NREL/PR-5J00-64628

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.
Goal and Activities for PVQAT TG5 (UV, T, RH)

- PV safety, qualification tests (61215, 61646, 61730-2) presently prescribe up to 137 days equivalent IEC 60904-3 AM 1.5G UV-B radiation dose. This is $<<$ 25 years!

- **TG5 Goal**: develop UV- and temperature-facilitated test protocol(s) that may be used to compare PV materials, components, and modules relative to field service.

Applications:

- IEC 62892 (climate- and configuration-specific weathering).
  1. General UV weathering test.
  2. Start of “Leg 2” test series to query delamination. (UV→DML→HF10→DH500)

- IEC 62788-7 (PV materials and components weathering). Accelerated aging test(s) for encapsulation, backsheet, adhesives...
Motivation for the $k_d$ Interlaboratory Experiment (PVQAT TG5 US)

- Knowing $E_a$ is critical to prescribing & interpreting a UV- and T-mediated test.
- Unfortunately, $E_a$ is not known for the UV degradation of common PV materials.

$$k_d = A \left[ \frac{T}{T_0} \right]^n e^{-\frac{-E_a}{RT}}$$

**Arrhenius representation for rate of $\Delta$ characteristic**

Goals for the interlaboratory experiment:

1. Quantify $E_a$.
   Provide a sense of the range of $E_a$ by examining “known bad,” “known good,” and “intermediate” material formulations.

2. Determine if there is significant coupling between relevant aging parameters, *i.e.*, UV, temperature, and humidity.
   What weathering parameters must be considered in a standardized test?

3. Investigate the spectral requirements for UV light sources, *i.e.*, by comparing specimens aged by Xe-arc, UVA-340, metal-halide.
   Is visible light required (*e.g.*, enabling photobleaching)?
The Materials Used in the $k_d$ Experiment

- Discoloration of encapsulation somewhat studied in the literature:
  - We have a sense of the general rate of degradation.
  - Use historical (literature) and contemporary formulations.

- 6 Materials examined in interlaboratory study:
  - Compare peroxide used for cross-linking (module manufacture).
  - Compare type or use of UV absorber.
  - TPU formulation: not for PV, but chosen as a reference material.

### INGREDIENT | DESCRIPTION | MAKER | MASS {g}
--- | --- | --- | ---
Elvax PV1400 | EVA resin, 33 wt% Vac | E. I. du Pont | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | N/A
Z6030 | silane primer, gamma-methacryloxy propyl trimethoxysilane | Dow-Corning Corp. | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | N/A
TBEC | curing agent, OO-Tertbutyl-O-(2-ethyl-hexyl)-peroxycarbonate | Arkema Inc. | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | N/A
Lupersol 101 | curing agent, 2,5-Bis(tert-butyleroxy)-2,5-dimethylhexane | Arkema Inc. | 1.5 | N/A | N/A | N/A | N/A | N/A
Tinuvin 329 | UV absorber, benzotriazole type | BASF Corp. | N/A | N/A | N/A | 0.3 | N/A | N/A
Cyasorb UV-531 | UV absorber, benzophenone type | Cytec Industries Inc. | 0.3 | 0.3 | 0.3 | N/A | N/A | N/A
Tinuvin 770 | hindered amine light stabilizer (HALS) | BASF Corp. | 0.1 | 0.1 | 0.1 | N/A | N/A | N/A
Tinuvin 123 | non-basic amineether-hindered amine light stabilizer (NOR-HALS) | BASF Corp. | N/A | N/A | N/A | 0.1 | 0.1 | N/A
Naugard P | anti-oxidant (AO), phosphite containing | Chemtura Corp. | 0.2 | 0.2 | N/A | N/A | N/A | N/A

| Designation (Note) | EVA-A (known bad, "slow cure") | EVA-B (improved, "fast cure") | EVA-C (known good) | EVA-D (modern) | EVA-E (no UV absorber) | TPU (known bad) |
--- | --- | --- | --- | --- | --- | ---

Encapsulation materials being compared in the transmittance (discoloration) experiment.
Interlaboratory Effort Enables a Wider Range of Study

- Indoor aging is expensive. No institution has all the resources or bandwidth to apply the complete set of parameters TG5 wanted to examine.
- Discoloration studied at (14) volunteer institutions.
- Example: compare similar instrument models (e.g., Ci5000 & QSUN XE3).

- Standard condition (60°C chamber ambient) to compare a broad variety of light sources.
- Baseline irradiance of 1.0 W·m⁻²·nm⁻¹ at 340 nm for UV sources.

- Rate of indoor degradation will ultimately be compared against field data to determine site-specific acceleration factors.
- Outdoor data will verify the validity of indoor weathering.
Details of the $k_d$ Methods and Experiment: Encapsulation Transmittance Test

- Silica/polymer/silica coupon specimens measured using a spectrophotometer (with integrating sphere).
- Measure at specimen center (anaerobic, minimal $O_2$) and periphery (aerobic).
- Analyze: solar-weighted transmittance, yellowness index, and UV cut-off $\lambda$.

User summary:
- Geometry: silica/polymer/silica (3.2 mm/0.5 mm/3.2 mm).
- Size: 2” x 2”.
- Quantity: 3 replicates of 6 materials (pre-conditioned), and 1 reference (not pre-conditioned).
- Aging: 0, 15, 30, 45, 60, 75, 90, 120, 150, 180 cumulative days (indoors).
  or 0, 1, 2, 3, 4, 5 years (outdoors).
- Measurements (non-destructive): repeatedly age and measure at each laboratory/test site.
UVA-340 vs. Xe: A Comparison of $\tau_{rs\text{w}}$ With Age

- Representative solar weighted transmittance ($\tau_{rs\text{w}}$) evaluated for $300 \leq \lambda \leq 1250$ nm.
- TPU affected more in Xe ($\Delta \tau_{rs\text{w}}$ -5.1%) than UVA-340 ($\Delta \tau_{rs\text{w}}$ -3.4%).
- EVA-A affected continuously for Xe, delayed for UVA-340. Same $\Delta \tau_{rs\text{w}}$ -2.3%.
- EVA-C improved ($\Delta \tau_{rs\text{w}}$ 1.0% for UVA-340)!

Change in $\tau_{rs\text{w}}$ with H for the NREL aged transmittance coupons (center measurements).

The data points have been connected to guide the eye.

This presentation: H shown for $295 \leq \lambda \leq 360$ nm.
UVA-340 vs. Xe: Insights From $YI$

- Yellowness index ($YI$) calculated from measured $\tau_h$.
- Repeatability: $YI$ (0.27) < $\tau_{rsw}$ (0.63).
  
$YI$ is overt indicator of degradation trends.

- Many instances of ~linear change with time.
- Inflection ($\Delta$slope) in some profiles: EVA-A (UVA-340); EVA-C (UVA-340); TPU (Xe).
- Initial yellowing to stable-state for EVA-D (UVA-340 & Xe).

$\Rightarrow$ Effects of aging are dominated by interactions between additives, not base material!

---

**UVA-340 fluorescent UV source**

**Xe UV source**

Change in $\tau_{rsw}$ with $H$ for the NREL aged $\tau$ coupons (center measurements).
The data points have been connected to guide the eye.

**This presentation: data shown for average of 3 replicates, with error bars for 1 S.D.**
UV spectral transmittance for the NREL aged τ coupons (center measurements).

- u (solid lines) indicates unaged specimens; - a (dashed lines) indicates specimens aged for 6 months.

- EVA-A, EVA-D, and TPU show a significant rounding of the UV cut-off (shifted ↓, right) and increased YI corresponding to Δvisual appearance.
- Likely explained by chromophore formation (from peroxide, AO, and UV absorber).

For EVA-B, EVA-C, EVA-E, the UV cut-off wavelength is instead decreased (shifted left) and there is an increase in τ. τ_{rs} is increased for EVA-C about ~350 nm.
- Likely explained by the loss of additive(s) with age.

- EVA-A: is UV absorber lost for UVA-340 source? VIS required (photobleaching for Xe)?
Methods of Analysis for the $k_d$ Data

- Verify what data may be analyzed. *e.g.*, delayed loss of formulation additive.
- Here: consider inflections in $\Delta \tau_{rs}$ or $YI$ data.

- Degradation rate (linear) or shift factor (logarithmic) comparison may be used to examine different test conditions, *e.g.*, UV sources.
- Example: what $k_H$ is required map the UVA-340 data parallel to the Xe data?

Arrhenius analysis used for different applied temperatures. ($E_a \propto m \cdot R$).
- EVA undergoes a melt transition at $\sim 60^\circ$C.

Degradation rate comparison, applied to compare UVA-340 and Xe sources. Data shown for the NREL aged $\tau$ coupons (center measurements).
UVA-340 vs. Xe: Insights From $k_H$ Analysis

- $295 \leq \lambda \leq 360$ nm may be best criteria between Xe and UVA-340, because UVA-340 provides limited emission $360 \leq \lambda \leq 400$ nm.

- $k_H = 0.6$ for TPU (same order of magnitude).
- $T_{UVA-340} \sim 55^\circ C$; $T_{Xe} \sim 63^\circ C$.
- $\Delta T \sim 10^\circ C \Rightarrow 1.4^{-1} \Rightarrow 0.7$.
- $k_H = 0.08$ for EVA-A.
- EVA-A not affected early for UVA-340.
- Different aging mechanisms initially dominate for UVA-340 or Xe.
- $k_H = 3.4, 1.1$ for EVA-C, EVA-D.

Data shown for NREL aged EVA-A and TPU coupons (center measurements).
Effect of Temperature Stands Out in Early Comparison

• Effect of $T$ examined directly at 3M: same irradiance, $RH$ applied using three similar chambers (Ci5000, Xe lamp with Right Light filter).

• Strong effect of aging as $T$ is increased.

• Exception: EVA-E (no UV absorber). $\Delta \tau \sim 0$.

• $T$ coupling anticipated from field observation, e.g., increased discoloration at local module hot spots.

• $E_a$ on order of $\sim 60 \text{ kJ} \cdot \text{mol}^{-1}$ (0.6 eV) estimated for EVA-A from interim experiment.
Summary

• ”$k_d$” interlaboratory experiment presently being conducted to provide a quantitative basis for UV weathering tests.

Interim results:

• Material specific aging behavior $\Rightarrow$ discoloration follows foremost from the formulation additives (Lupersol 101, Naugard P, Tinuvin 770 or Tinuvin 123), rather than the base resin.

Regarding Xe and UVA-340 sources:

• Substantial $\Delta \lambda_{cUV}$, greater $\Delta \gamma I$ for EVA-A aged with UVA-340. $k_H$ of 0.08. $k_H$ of 0.6 (0.7 ideal), 3.4, and 1.1 observed for TPU, EVA-C, and EVA-D.

• $\Delta$ slope (apparent degradation rate) observed for specific combinations of UV source and test materials.

$\Rightarrow$ Xe and UVA-340 sources may not always be applied equally for accelerated aging of encapsulation.

• $E_a$ on the order of $\sim 60 \text{kJ} \cdot \text{mol}^{-1}$ (0.6 eV) is estimated for EVA-A.

• Test $T$, e.g. 70, 80, or 90 °C, presently being evaluated for UV tests.
Acknowledgements

There has been fantastic participation in TG5.

*Thank you to the many participants for your ongoing support!!!*

- If interested in TG5 activities or the experiments, please contact the corresponding regional leader. (See title slide)
- Stay tuned for examination of encapsulant attachment strength. (PVQAT TG5 $k_d$ “part II”).

👋 Your questions and feedback are much appreciated! Please help me to cover the important details & perspectives.

This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08-GO28308 with the National Renewable Energy Laboratory.
Use of REDCap Database for Transmittance Data

- A LARGE QUANTITY- of transmittance data will be generated for experiment.
- Case Western Reserve University volunteered the REDcap database to TG5.
- REDCap comes from the medical research industry.

**Benefits:** Ensures designed experiments, high data capacity, simultaneous user access, automated data quality verification.
- REDCap allows users to view and analyze results in real-time.

Transmittance results will be uploaded to REDCap using an Excel template file.

Home screen for https://dcru.case.edu/redcap
Most Materials More Affected at Center in $k_d$ Experiment

- Loss in $\tau_{rs}\text{w}$ less significant at the specimen periphery.
  - Example: EVA-A. Significant heterogeneity.
  - Exceptions: EVA-C, TPU. Affected relatively uniformly throughout specimen.

- In EVA, a photobleaching effect typically occurs at periphery, but is limited by rate of $O_2$ diffusion to interior.

Change in transmittance for the NREL UV Suitcase aged specimens.
Data points connected to guide the eye.
Comparing UVA-340 and Xe sources

UV spectral transmittance of the encapsulation materials examined. The subscript \(-u\) (solid lines) indicates the data for unaged specimens, while the subscript \(-a\) (dashed lines) indicates the data for specimens aged for 6 months in the NREL UV Suitcase (60°C/≈7%RH). Results for specimen-periphery (top) and -center (bottom).
Comparing UVA-340 and Xe sources

Major changes: (most overt to least affecting differences between weathered samples)

• The spectral bandwidth was greatly increased ($\Delta \lambda_{cUV}=-64$ nm) for EVA-A for the UVA-340 light source but not for Xe ($\Delta \lambda_{cUV}=-6$ nm). This implies the UV absorber was uniquely degraded or depleted for the fluorescent light source. The result is consistent with the UV-VIS fluorescence spectra observed for EVA-A, which could be distinguished between the different weathering chambers.

• A more severe rounding of the cut-on profile was observed for EVA-A aged using UVA-340 ($\Delta YI=13.7$) then for Xe ($\Delta YI=7.9$). A more severe rounding of the cut-on profile was observed for TPU aged using Xe ($\Delta YI=17.2$) then for UVA-340 ($\Delta YI=15.6$). Increased yellowness implies the formation of optically absorbing chromophore species. These results suggest the action spectrum for TPU includes the full range of UV wavelengths (*i.e.*, $300 \leq \lambda \leq 400$ nm as supplied by a Xe source). The difference for EVA-A may result from a photobleaching process, enabled by the longer wavelengths of UV light present in Xe.

• EVA-C was more affected by UVA-340 ($\Delta \lambda_{cUV}=-11$ nm for UV Suitcase ) than Xe ($\Delta \lambda_{cUV}=-5$ nm for Ci5000) spectrum. Transmittance reduction from discoloration ($\Delta YI=2.1$ and $\Delta YI=1.1$) was outweighed by the increased spectral bandwidth, increasing transmittance ($\tau_{rsw} 0.6\%$ and $\tau_{rsw} 0.4\%$) for EVA-C in UVA-340 and Xe, respectively.

Lesser changes:

• The spectral bandwidth was slightly more increased for EVA-D at its periphery ($\Delta \lambda_{cUV}=-3$ nm) than at its center ($\Delta \lambda_{cUV}=-1$ nm). EVA-D, however, was more discolored at its center ($\Delta YI=2.7$ and $\Delta YI=2.9$) than at its periphery ($\Delta YI=0.8$ and $\Delta YI=0.8$), for UVA-340 and Xe, respectively.
Summary of the results for samples weathered in the NREL UV Suitcase (UVA-340) and NREL Ci5000 (Xe) chambers.
$k_d$ Experiment Examines Relevant Source Spectra

- Will compare Xe, UVA-340, M-H, and terrestrial light sources for all formulations examined.
- Depending on specimen’s action spectrum (damage susceptibility), the UV source (e.g., 360-400) could render different results.
- Other base materials or components (backsheets) may have even stronger spectral dependence than encapsulation.
- NIST SPHERE experiment (passband filters) will provide additional insight.
- Also method: ASTM G178.

Overlay of representative common artificial UV sources, relative to the AM1.5 global spectrum.
Fluorescence Spectroscopy: Additional Insights

- Anaerobic center and aerobic periphery are readily distinguished with a black light.
- Different extent of regions observed on EVA’s. TPU is homogenous.
- Minimal UV-VIS fluorescence observed at periphery relative to specimen interior.

Examples of the test configurations for the UV-VIS fluorescence spectrophotometer. The examination region can be confirmed from the spot, which appears different (based on its fluorescence) at the center or periphery of the specimen. The size and shape of the discolored anaerobic region can be confirmed when the excitation beam is placed at the edge of the silica superstrate.
Effects of Additives in EVA and Polymers

- Representative (normalized) results shown for ~0.01% wt. concentration additive in hexane.
- UV absorbers often feature double absorptance peaks; Anti-Oxidants often characterized by absorptance at even shorter wavelengths.
- UV absorbers often characterized by single thermalization emission peak at ~400 nm, *e.g.*, I168.
- AOs may characterized by more specific excitation & emission peaks, although a few common peak sets were observed here.
- Fluorescence signature may be very different when multiples additives are present (and interacting).

Optical absorptance spectra for UV absorbers and AOs used in the TGS EVA formulations, including: Cyabsorb UV-531, Tinuvin 123, Tinuvin 328, Tinuvin 329, Tinuvin 770; butylated hydroxytoluene (BHT), and Naugard P.

Representative fluorescence spectra (excitation on left; emission on right) for AOs often used in contemporary polymers, including butylated hydroxytoluene (BHT), Irgafos 168, Irganox 245, Irganox 1010, Irganox 1076, and Naugard P. Some additives have multiple fluorescence peaks.
Transmittance: Comparison to Historic & Outdoor Data

- Historically, yellowness index has been used to compare between indoor- and field-aged encapsulation.
- We examine 2 of the classic formulations, using a modern version of the same glass.
- $\Delta YI$, EVA-A: $\sim 8$ (Xe, 60°C) vs. $\sim 55$ (Xe, 70°C).
- Same & similar formulations in $k_d$ experiment deployed at APS in 1996.
- Conclusion: discoloration resulted from additive interactions (as in $k_d$ experiment).
- Location specific results (center vs. periphery) as in $k_d$ experiment.
- TG5 will determine location specific acceleration factor for Cleveland, Golden, Miami, Phoenix, & Riyadh.

Assessing degradation from change in YI.

Localized discoloration of EVA
(known formulation in module) at the APS site.