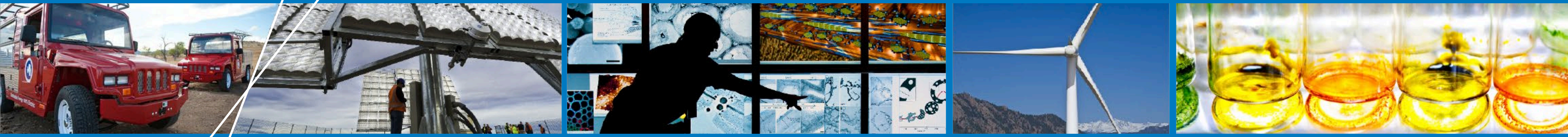
Durability of Polymeric Encapsulation Materials for a PMMA/glass Concentrator Photovoltaic System



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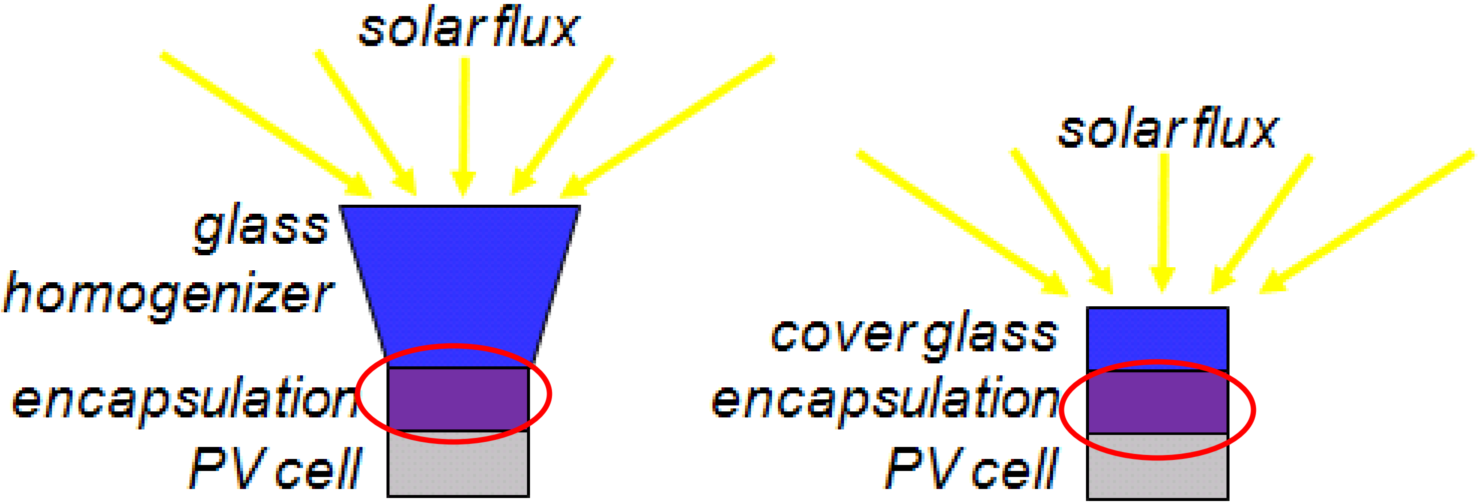
***Updated from*: 10th International Conference on Concentrator Photovoltaic Systems (April 7-9, 2014, Albuquerque, NM)**

Hyatt Regency, Grand Pavilion, 2014/04/08 (Tues) 09:30 – 09:45 am

PR-5J00-66332

Motivation for the NREL Field Study



Cross-sectional schematic of the components near the cell in CPV systems (not to scale).

corrosion prevention, optical coupling : CPV systems typically use encapsulation to adhere optical component(s) or cover glass to the cell

encapsulation durability (25 year field deployment) is unknown:

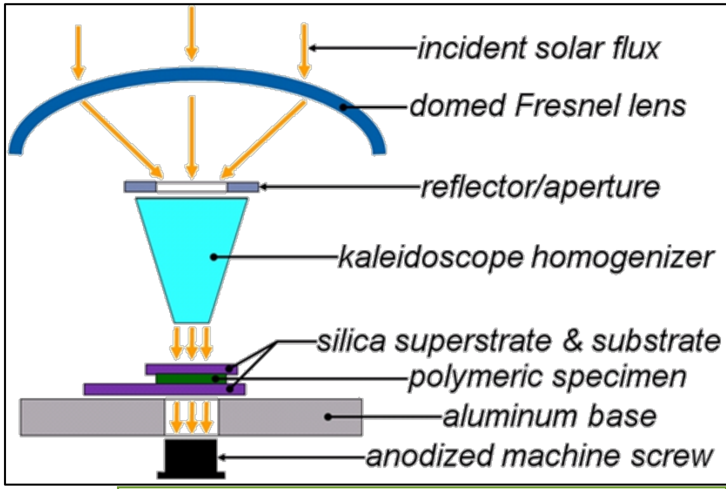
- identify field failure modes
- gain insight related to failure mechanisms
- identify method(s) for assessing aging
- distinguish between types of encapsulation
- identify materials for future study (qualification & comparative tests)
- aid a technical basis for future qualification/reliability standards

Details of the Experiment (Material, Specimens, Apparatus)

hydrocarbons
(representative types)

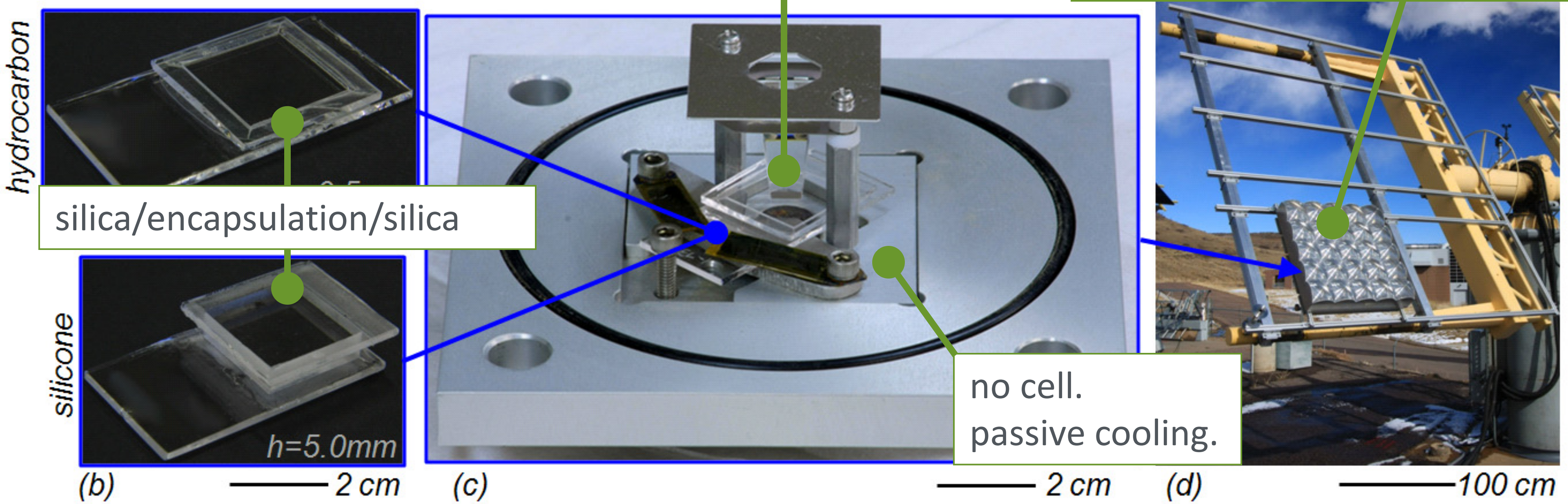
silicones
(representative grades)

MATERIAL	ON-TEST	IN QUEUE	FAILED TEST
EVA	6	2	
ionomer	1	0	
polyolefin	2	1	
PVB	1	0	1
TPU	1	2	
PDMS	12	9	2
PPMS or PDPDMS-CH=CH$_2$	2	1	1
TOTAL	**25**	**15**	**4**



glass secondary optic (homogenizer)

domed PMMA Fresnel lens @ C_g 500x



silica/encapsulation/silica

no cell.
passive cooling.

Test coupons are mounted in a modified CPV module product on a 2-axis tracker in Golden, CO.

Details of the Experiment (Measurands & Schedule)

"Continuous" measurements:

ambient conditions (irradiance, temperature, wind…)
CPV fixture temperature (via thermocouple)

Periodic measurements:

→ transmittance ($T[\lambda]$, hemispherical & direct)
⇒from $T[\lambda]$, calculate: yellowness index (D65 source,1964 10° observer), haze, $\lambda_{\text{UV cut-off}}$ …
mass
appearance (photography and photoelasticity)

→ fluorescence spectroscopy

Raman spectroscopy

Final measurements (possible):

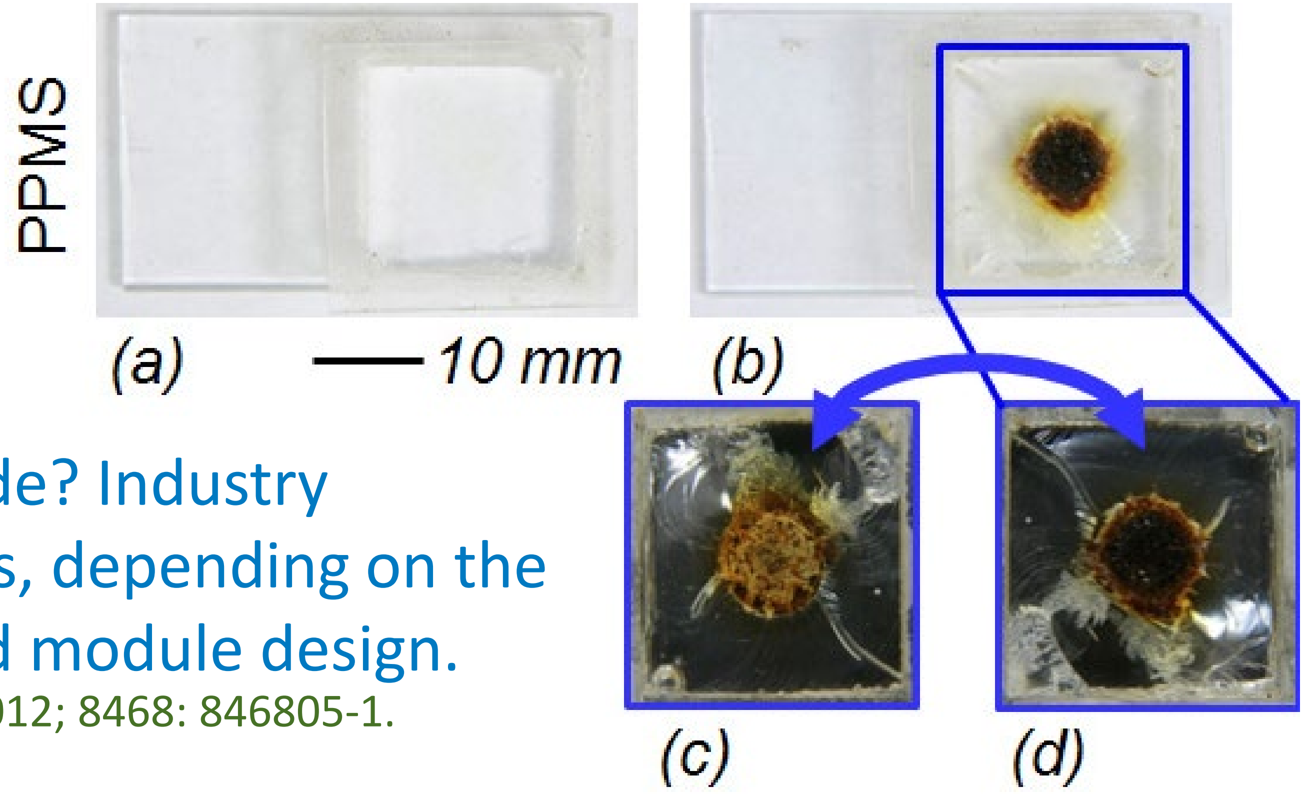
ATR-FTIR, NMR
DSC, TGA (polymer physics)

Test schedule:

0, 1, 2, 4, 6, 12, 18, 24, 30, 36, 48, 60, 72 … months

One Silicone Specimen Failed the Formal Study by Decomposition

- Failure occurred soon after 24 months cumulative deployment.
- No overt indication of pending failure.
- Silicone contains phenyl-methyl chemistry.



- Relevant failure mode? Industry feedback suggests yes, depending on the materials present and module design.

Winter *et. al*., Proc. SPIE. 2012; 8468: 846805-1.

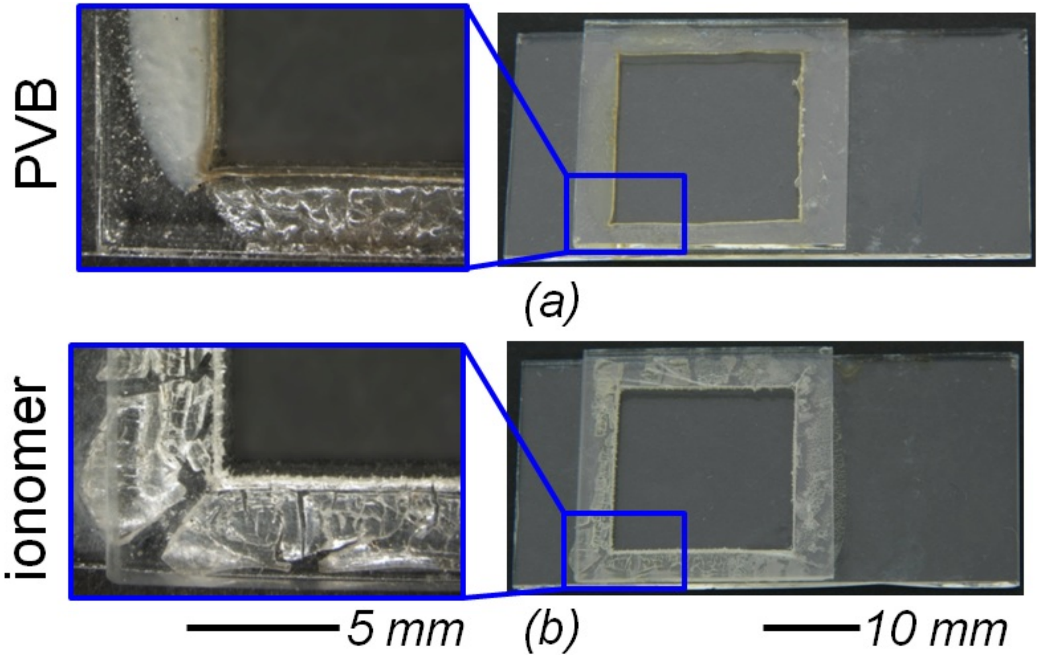
Optical photos of the failed PPMS-$CH=CH_2$ specimen, including (a) appearance at 24 months, and (b) appearance of failed specimen at >24 months. The (c) back and (d) front of the failed specimen were photographed on a black background to render the fracture of the silica substrate and superstrate obvious (and to also reveal any delamination occurring within the specimen).

Peripheral Evidence of Environmental Damage

- PVB 2 specimen discolored (6 months) and combusted (10 months).
  See: *Miller et. al., SOLMAT, **111**, 2013, 165.*

- At 24, 18 months, the periphery of the PVB 1 and ionomer specimens showed damage, *both haze and fracture, with mass loss.*
- *PVB 1 is discolored (yellow) at its periphery.*
- Both specimen interiors appear intact and remain transmitting.
- The damage here may be oxygen dependent.

- No new failures here. Long term performance continues to be quantified.



Photographs showing cracks at the periphery of the PVB 1 and ionomer specimens at 36 months. A yellow discoloration occurs at the outside of PVB 1. The images were obtained on a black background to improve contrast.

Results of the Formal Experiment

(Silicone Specimens)

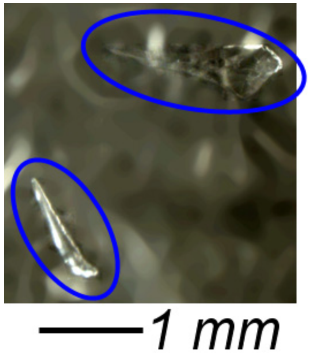
- Observations of silicone specimens include: (a) optical “densification”, (b) haze formation, and (c) cracking

No mass loss with time for the
(7) optically affected specimens.

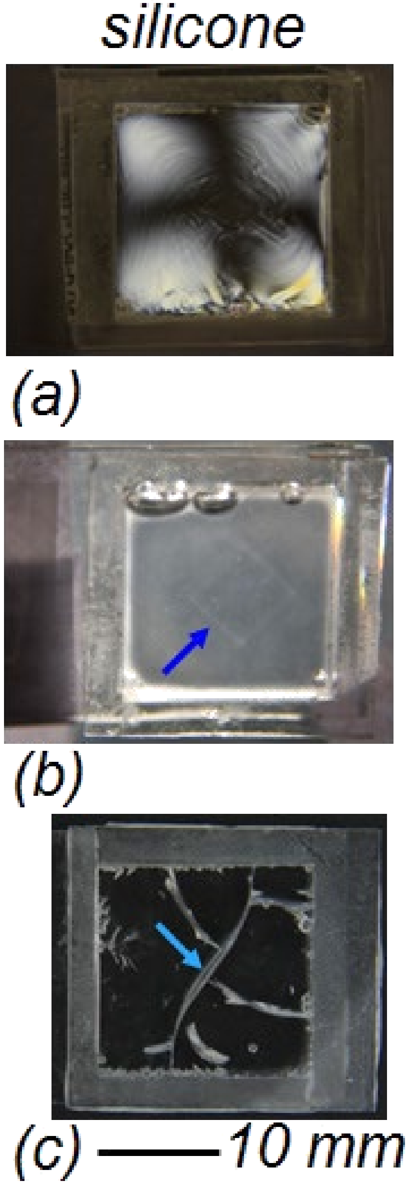
Haze formation is attributed to PDMS 9’s unique formulation.

Crack advancement occurred for PDMS 6 during cold weather periods only ⇒ likely motivated by CTE misfit.

Lesser individual cracks were recently observed in (3) additional specimens.

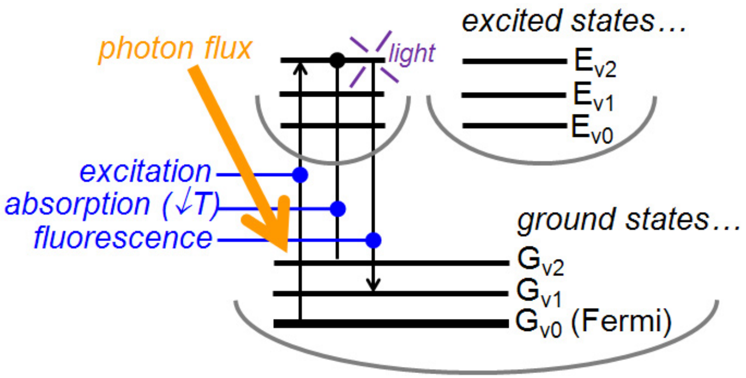


Photograph of an internally cracked PDMS specimen at 36 months. Images obtained on black background to improve contrast.



Optical images of silicone specimens, including those obtained using (a) cross-polarization, (b) back-lighting, or (c) black background.

The "Mechanics" of Fluorescence



- In polymers, illumination can generate optical absorption and ***fluorescence*** where:

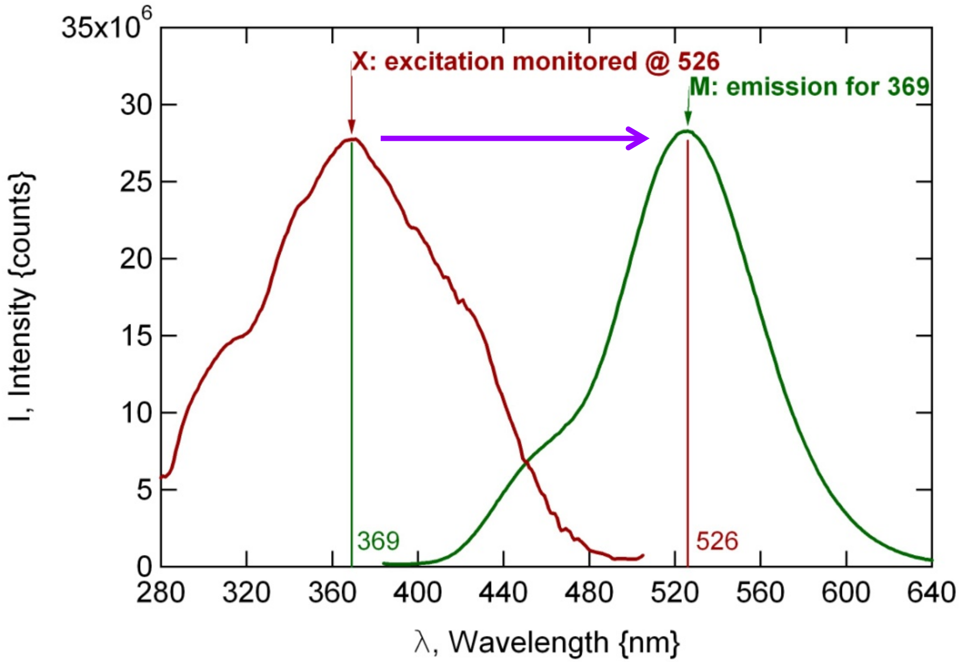
  intensity $\propto$ lumophore concentration

  wavelength $\propto$ lumophore composition

lumophore sites: UVA, impurities, chromophores

1. Excite at 369 nm, measure emission from 384-723 nm

- Avoid harmonics ($\lambda_h=2\lambda_x$) e.g., 768 nm
- There is a peak @ 526 nm!



X and M fluorescence spectra for "Night Glow" tape.

2. Measure at 526, excite from 280-511

- There is a peak @ 369 nm!

3. Iterate for any other observed excitation & emission peaks

- Peak pair: there is a peak at 369 motivating emission @ 526 nm

Fluorescence Indicates EVA's Are Affected with Age (2)

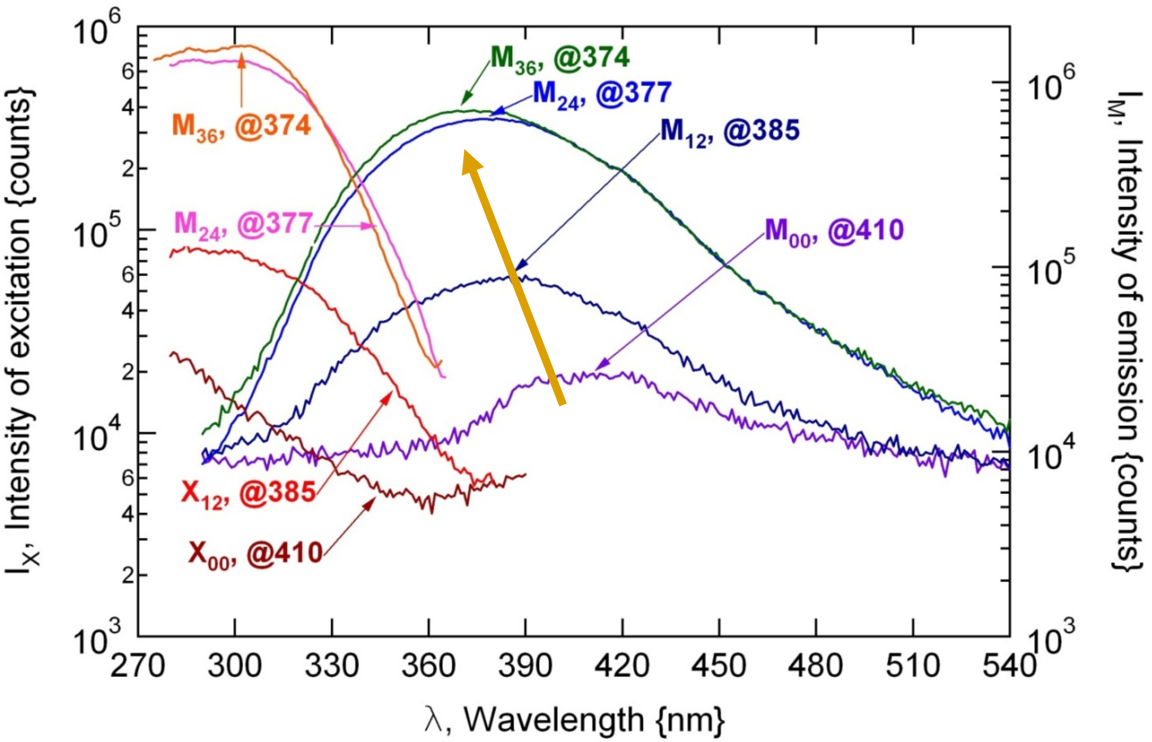
EVA 4 and EVA 5 show a similar pronounced effect with age:

- Intensity of fluorescence is greatly increased (logarithmic scale).
- λ_m is seen to shift, from 410 to 374 nm in example.

- Little field emission: excitation is mostly < 375 nm, the λ_{cUV} for the test fixture.

- Unclear if any EVA's are "more durable" (no field failures yet).

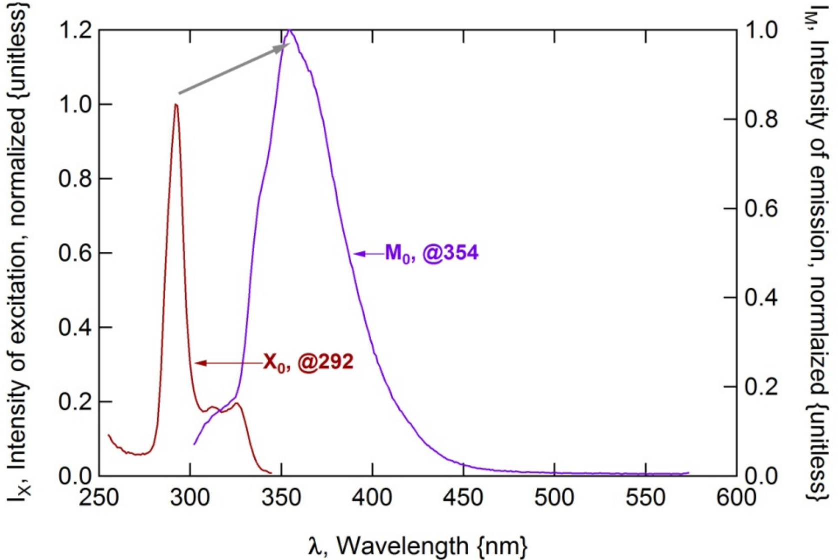
- Ionomer, PO, PVB 1, and TPU also demonstrate measurable change in fluorescent signature.



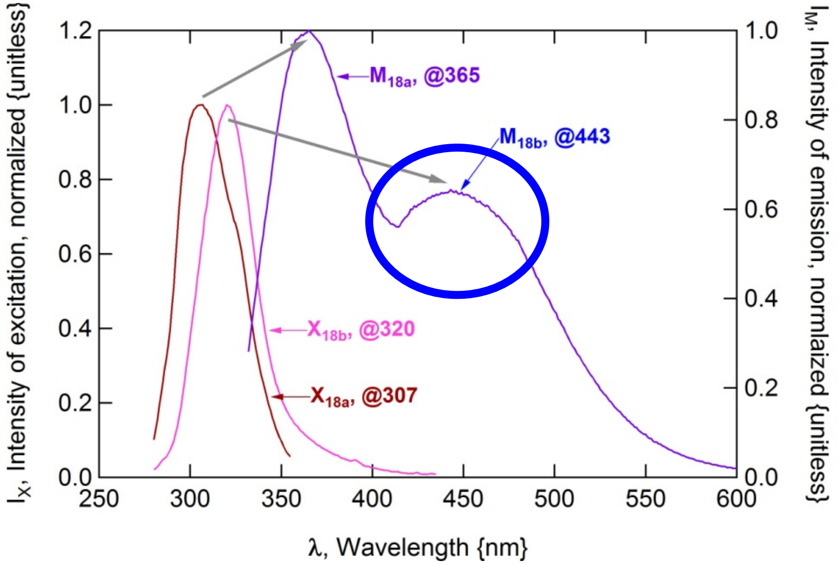
Excitation spectra (X, left) and corresponding emission spectra (M, right) for a representative formulation (EVA 4). The nomenclature in the figure identifies the age (month) at examination and the wavelength of maximum emission (for M) or wavelength monitored during excitation (X).

Fluorescence Identifies the Silicones Are Affected

- A fluorescence signature was identified for all silicone specimens.
- Strong signature was not expected, *e.g.*, no C=C bonds in PDMS.
- Possible origin(s): Pt catalyst, primer, inhibitor, crosslinker, filler, specific formulation additive, or residual in precursors.
- Upon aging, the fluorescent intensity may be increased.
- Upon aging, the peak locations (λ) may shift.
- Upon aging, a second emission (and excitation) peak is sometimes observed.



Excitation spectra (X, left) and corresponding emission spectra (M, right) for a representative fluorescence spectrum for the silicone PPMS-CH=CH_2 at 0 months. Corresponding excitation and emission peaks share the same subscript number.

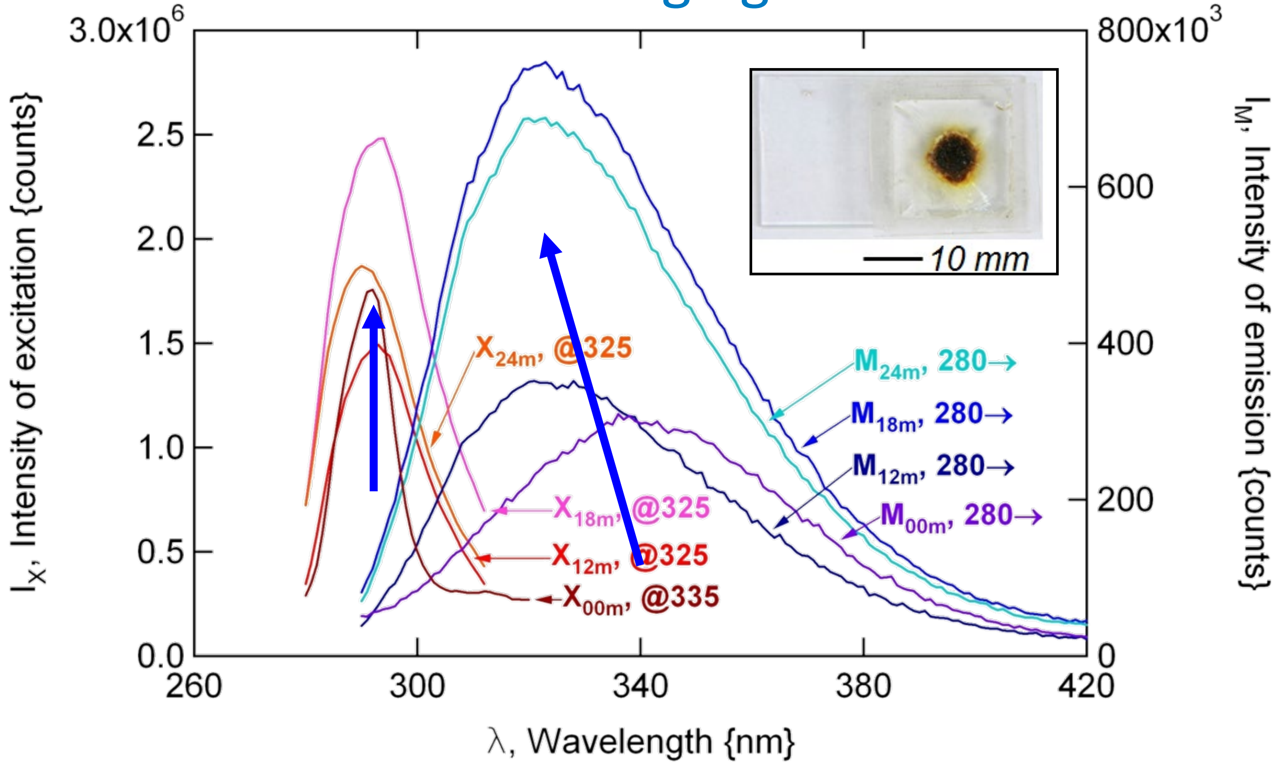


Excitation spectra (X, left) and corresponding emission spectra (M, right) for a representative fluorescence spectrum for the silicone PPMS-CH=CH_2 at 18 months. Corresponding excitation and emission peaks share the same subscript.

Fluorescence Suggests Aging Within Failed Silicone Specimen

- The intensity of fluorescence of failed PPMS-CH=CH_2 specimen was among the strongest of the silicones.
- Intensity generally increased with time.
- A shift in the peak location was observed with aging.

- Fundamentally, fluorescence implies a specimen-photon interaction.
- Unclear if fluorescence is directly related to failure.
- What mechanism(s) might be involved in fluorescence?

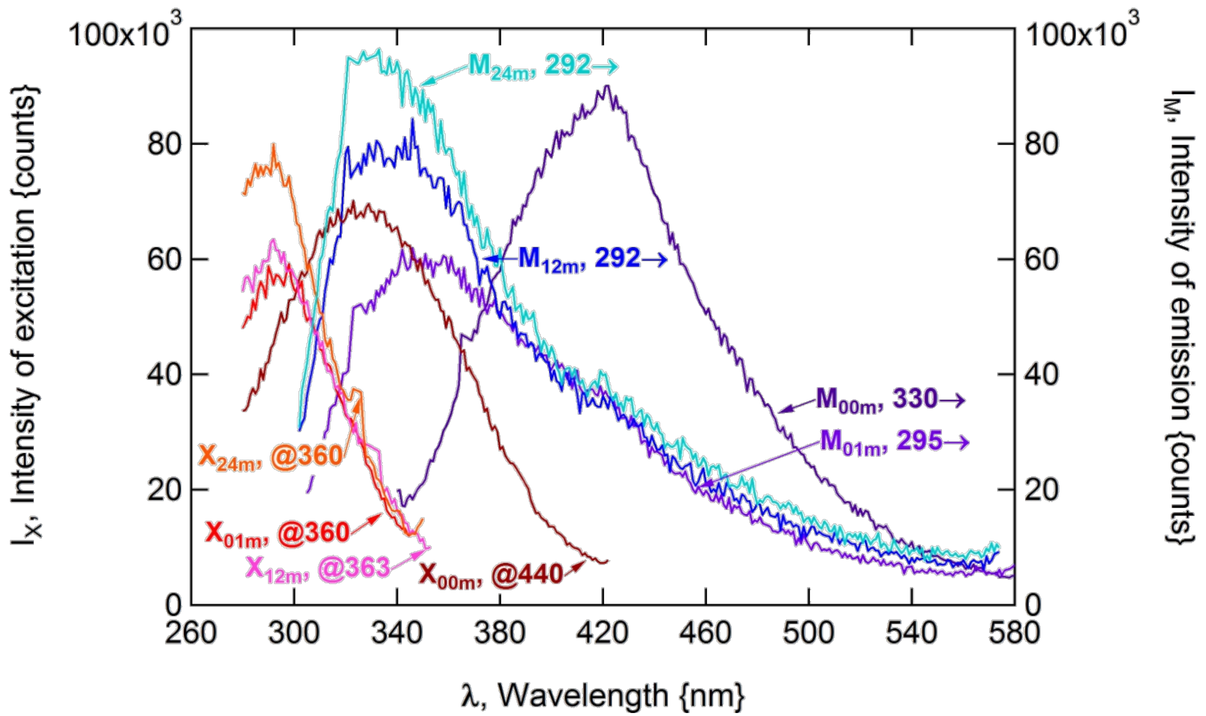


Evolution of fluorescence, "standard" emission peaks (M, right) and corresponding excitation peaks (X, left) for the failed PPMS-CH=CH_2 specimen (inset). The nomenclature in the figure identifies the age (month) at examination and the wavelength of maximum emission during excitation (X). All emission scans were obtained from 280 nm to 550 nm, as indicated "280→".

Fluorescence Is Still Observed for Peroxide Cured Silicone

- Peroxide was used instead of Pt to facilitate cross-linking.
- Luperox TBEC peroxide was chosen, based on the PV literature.
- The initial fluorescence signature is distinct from Pt cured silicone.
- Fluorescence is evolving over time to resemble Pt cured silicone.

- Results being verified against Luperox 231 (peroxide) cured silicone.
- Fluorescence may still come from presence and/or interaction of crosslinker, inhibitor, or a residual.



Fluorescence spectra for peroxide (TBEC) cured PDMS. Excitation (X, left) and the corresponding emission (M, right) spectra are provided. The nomenclature in the figure identifies the age (month) at examination and the wavelength of maximum emission during excitation (X). The initial (shortest) wavelength for the emission scans is indicated, e.g., "330→".

Summary & Conclusions

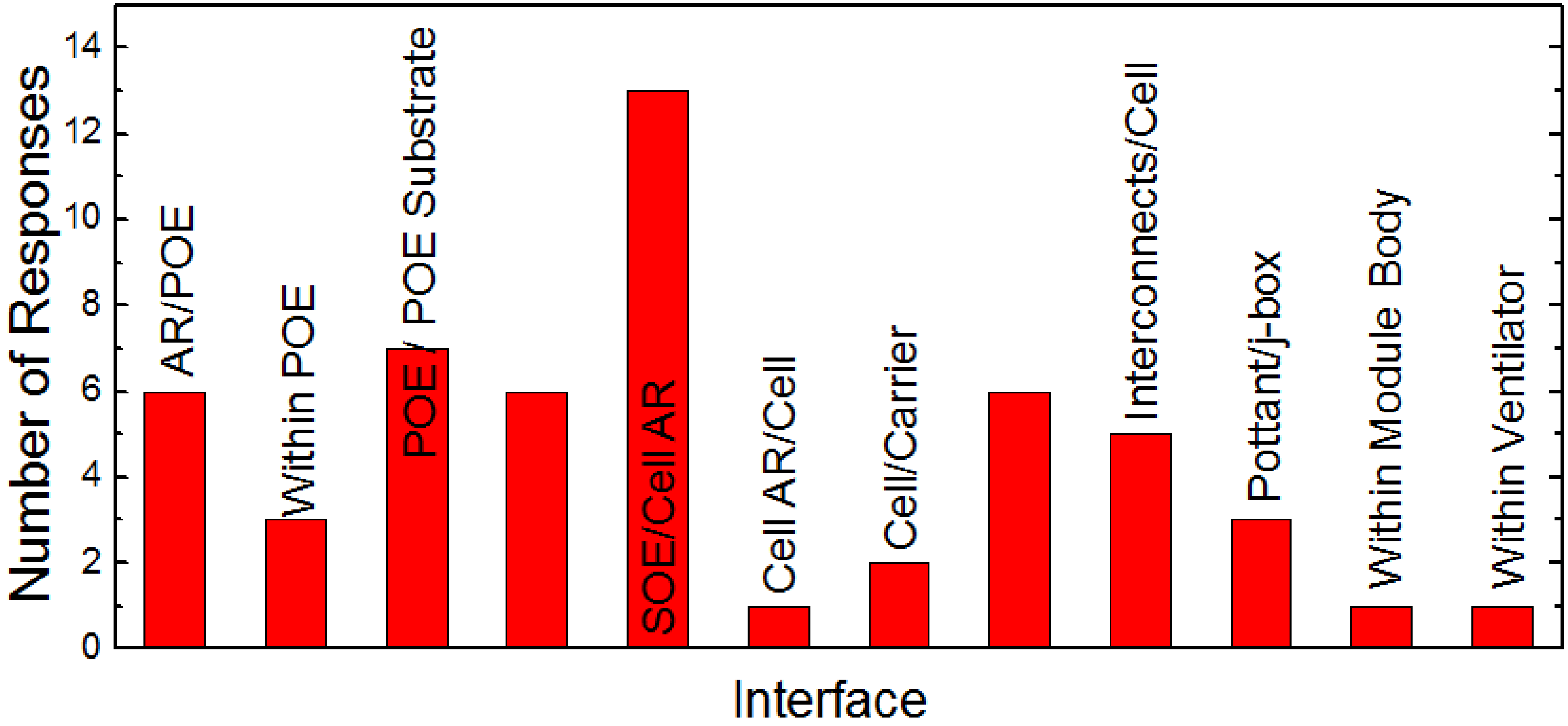
Field study of the durability of polymeric encapsulation materials for CPV

- Most specimens show minimal evidence of aging, and only 4 of 29 specimens have "failed" to date.
- Failure modes including combustion, thermal decomposition, fracture, and haze formation have been observed.
- Effects of aging are suggested by peripheral appearance, photoelasticity (see paper), and fluorescence spectroscopy.
- Thermal degradation unlikely to contribute to immediate or long-term degradation of siloxanes unless aided by another mechanism, *e.g.*, discoloration.
- In siloxanes, fluorescent spectra do not require catalyst, primer, crosslinker, or inhibitor.
- Limited UV transmittance of PMMA lens reduces the activation spectrum, mitigating affects of aging.

See: *Miller et. al., Opt. Eng., 50, 2011, 013003.*

DOE “PREDICTS” FOA DE-FOA-0000861

- Stanford, NREL, and Spectrolab won one of the “PREDICTS” grants.
- Our 3 year goal: characterize the durability of adhesion at key CPV interfaces.
- Task: Identify the most important interfaces within a CPV module to be studied by surveying the industry.
- Additional survey participants are invited, to maximize the usefulness of the study.



Pareto results to date. Q: Do these results represent your CPV system?

Results of survey (11 participating entities) identifying the critical interfaces within different CPV module makes.

Acknowledgements

- NREL: Dr. Afshin M. Andreas, Dr. Nick S. Bosco, Dr. Keith Emery, Dr. Cheryl Kennedy, Dr. Erica Gjersing, Dr. Aron Habte, Dr. Daryl Myers, Dr. John Pern, Dr. Ibrahim Reda, Dr. Robert Reedy, Cameron Barnhart, Kathleen Baughman, Matt Beach, Scott Deibert, Lynn Gedvilas, Christa Loux, Tom Moricone, Marc Oddo, Joel Pankow, Bryan Price, Ian Tappan, Kent Terwilliger, and Robert Tirawat.

- Also look for "Durability of Polymeric Encapsulation Materials in a PMMA/glass Concentrator Photovoltaic System" (*in preparation*).

NREL STM campus, Dennis Schroeder

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

Additional Slides for Reference

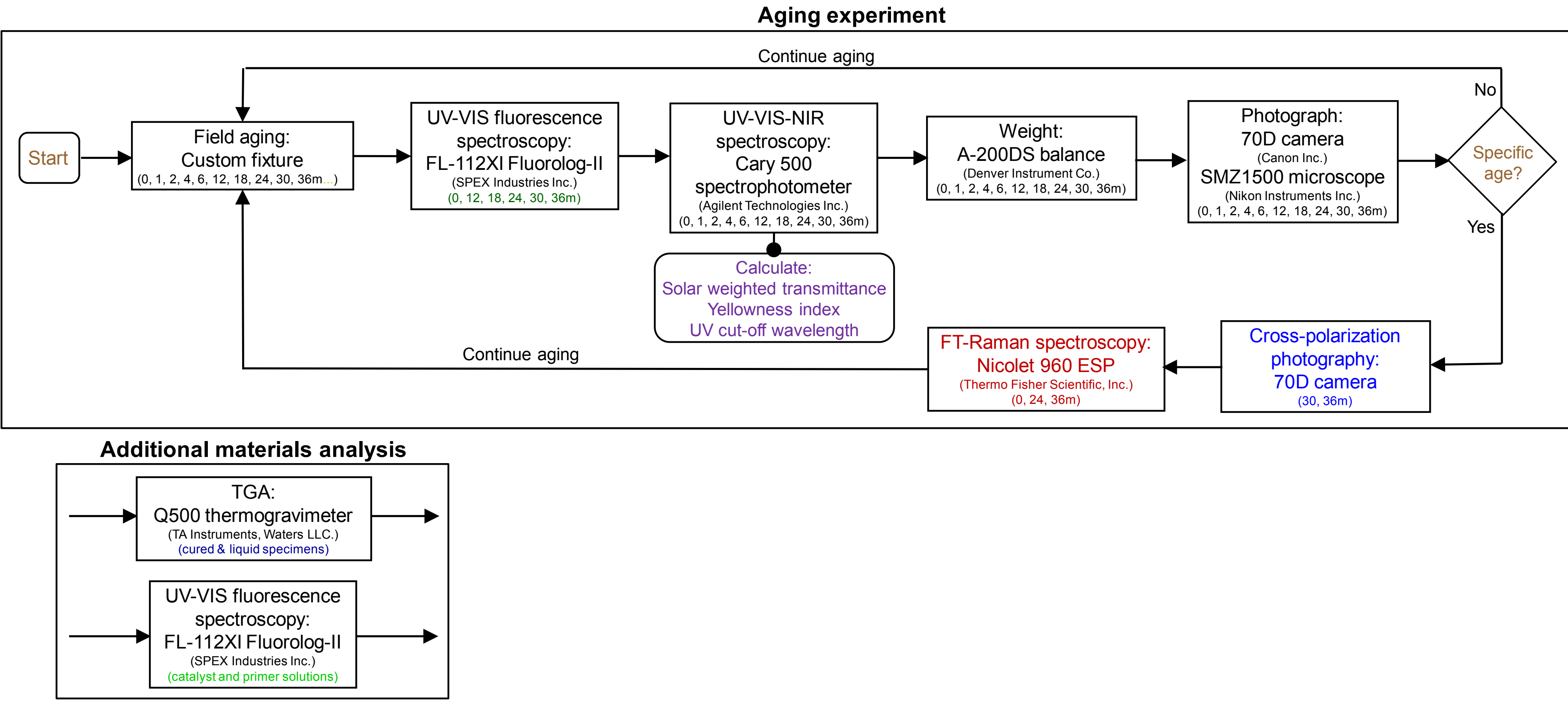
- These slides contain additional information that is referenced in the companion journal paper.

Test Matrix

MATERIAL		EXPERIMENT							
SPECIMEN	DESCRIPTION	FIELD AGING	FLUORESCENCE SPECTROSCOPY	UV-VIS-NIR SPECTROSCOPY	WEIGHT	PHOTOGRAPHIC IMAGING	CROSS-POLARIZATION PHOTOGRAPHY	FT-RAMAN	TGA
EVA 1	FP-PV grade	>36m	X	X	X	X	X	X	N/A
EVA 2	FP-PV grade	>36m	X	X	X	X	X	N/A	N/A
EVA 3	FP-PV grade	>36m	X	X	X	X	X	N/A	N/A
EVA 4	FP-PV grade	>36m	X	X	X	X	X	X	N/A
EVA 5	FP-PV grade	>36m	X	X	X	X	X	N/A	N/A
EVA 6	FP-PV grade	>36m	X	X	X	X	X	N/A	N/A
PVB 1	FP-PV grade	>36m	X	X	X	X	X	X	N/A
PVB 2	FP-PV grade	322d<thermal decomposition<329d	X	X	X	X	N/A	N/A	N/A
ionomer	FP-PV grade	>36m	X	X	X	X	X	X	N/A
polyolefin 1	FP-PV grade	>36m	X	X	X	X	X	X	N/A
polyolefin 2	FP-PV grade	>36m	X	X	X	X	X	N/A	N/A
TPU	FP-PV grade	>36m	X	X	X	X	X	N/A	N/A
PDMS 1	aerospace grade	>36m	X	X	X	X	X	N/A	X
PDMS 2	military grade	>36m	X	X	X	X	X	X	X
PDMS 3	LED grade	>36m	X	X	X	X	X	N/A	N/A
PDMS 4	LED grade	>36m	X	X	X	X	X	X	N/A
PDMS 5	industrial grade	substituted >36m	X	X	X	X	X	N/A	N/A
PDMS 6	LED grade	38d<fractured<45d	X	X	X	X	N/A	N/A	N/A
PDMS 7	electronics grade	>36m	X	X	X	X	X	N/A	N/A
PDMS 8	electronics grade	18m<substituted<24m	X	X	X	X	X	N/A	N/A
PDMS 9	optical grade	1m<haze formation<2m	X	X	X	X	N/A	N/A	N/A
PDMS 10	LED grade	>36m	X	X	X	X	X	N/A	N/A
PDMS 11	aerospace grade	>36m	X	X	X	X	X	X	N/A
PDMS 12	fast cure	>36m	X	X	X	X	X	X	N/A
PDMS 13	peroxide cure	>36m	X	X	X	X	X	N/A	X
PDMS 14	peroxide cure	>30m	X	X	X	X	X	N/A	X
PDMS 15	oil	>6m	X	X	X	X	X	N/A	X
DPDMS-CH=CH$_2$ 1	LED grade	>36m	X	X	X	X	X	X	X
DPDMS-CH=CH$_2$ 2	optical grade	>36m	X	X	X	X	X	X	X
PPMS-CH=CH$_2$	LED grade	748d<thermal decomposition<754d	X	X	X	X	N/A	X	X
PPMS	additional FS	>36m	X	X	X	X	X	X	N/A
PDMS 16	LED grade	N/A	N/A	N/A	N/A	N/A	N/A	N/A	X
catalyst 1	Karstedt's	N/A	X	X	N/A	N/A	N/A	N/A	N/A
catalyst 2	Karstedt's	N/A	X	X	N/A	N/A	N/A	N/A	N/A
catalyst	Ashby's	N/A	X	X	N/A	N/A	N/A	N/A	N/A
primer	Ti-based	N/A	X	X	N/A	N/A	N/A	N/A	N/A

Summary of the material characteristics, status, and the characterization methods applied for all specimens examined. An "X" is used in the table to identify where a characterization was performed, while "N/A" indicates where characterization was not applied. Specific methods and results are described in the sections identified at the bottom of the table, in addition to the references cited.

Order of Operations for Experiment



Aging experiment

Continue aging

Start

Field aging:
Custom fixture
(0, 1, 2, 4, 6, 12, 18, 24, 30, 36m...)

UV-VIS fluorescence spectroscopy:
FL-112XI Fluorolog-II
(SPEX Industries Inc.)
(0, 12, 18, 24, 30, 36m)

UV-VIS-NIR spectroscopy:
Cary 500 spectrophotometer
(Agilent Technologies Inc.)
(0, 1, 2, 4, 6, 12, 18, 24, 30, 36m)

Calculate:
Solar weighted transmittance
Yellowness index
UV cut-off wavelength

Weight:
A-200DS balance
(Denver Instrument Co.)
(0, 1, 2, 4, 6, 12, 18, 24, 30, 36m)

Photograph:
70D camera
(Canon Inc.)
SMZ1500 microscope
(Nikon Instruments Inc.)
(0, 1, 2, 4, 6, 12, 18, 24, 30, 36m)

Specific age?

No

Yes

Cross-polarization photography:
70D camera
(30, 36m)

FT-Raman spectroscopy:
Nicolet 960 ESP
(Thermo Fisher Scientific, Inc.)
(0, 24, 36m)

Continue aging

Additional materials analysis

TGA:
Q500 thermogravimeter
(TA Instruments, Waters LLC.)
(cured & liquid specimens)

UV-VIS fluorescence spectroscopy:
FL-112XI Fluorolog-II
(SPEX Industries Inc.)
(catalyst and primer solutions)

Flowchart identifying the order of operations for the experiment. The sequence for the field aging experiment is shown in addition to materials analysis that was performed based on its results.

The Field Conditions (Irradiance & Ambient Temperature)

Golden, CO: Steppe climate, elevation 1.79 km, 39.740°N latitude

***H*:** Seasonal effects (winter cloudiness and latitude-related) observed during first 68 days

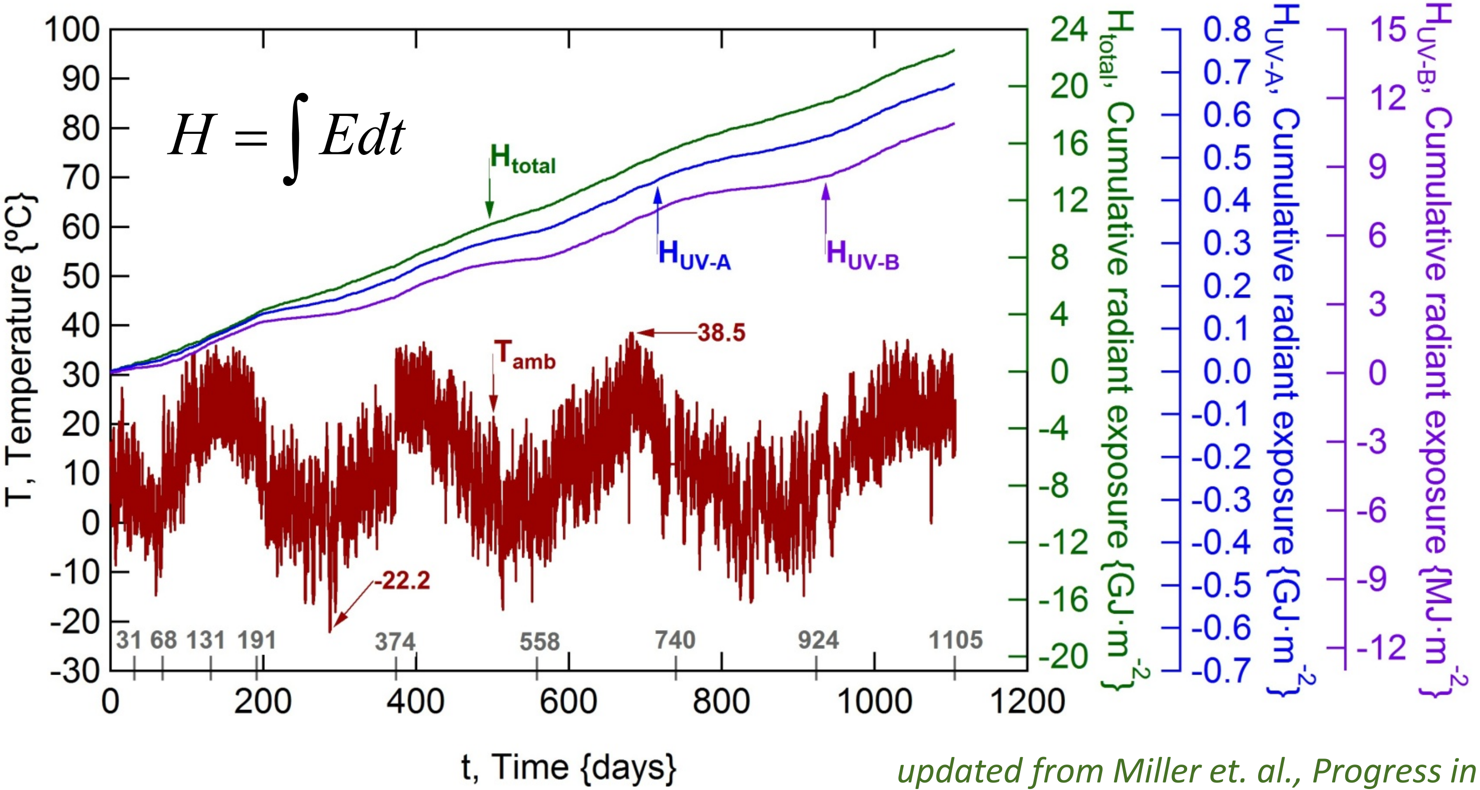
$$\boxed{\frac{H_{UV-A,\,summer}}{H_{UV-A,\,winter}} = 2.3} \qquad \frac{H_{UV-B,\,summer}}{H_{UV-B,\,winter}} = 4.3$$

***H*:** Consider seasonal, optical design, and material's action spectrum

*D.C. Miller, M.D. Kempe, C.E. Kennedy, S.R. Kurtz, Optical Engineering, **50** (1), 2010, 013003.*

***T*:** Ambient shown. Module's back and inside monitored too.

- In Golden, hottest & coldest days often lag solstice by ≤1 month. UV accumulates fastest in autumn.
- In Golden (steppe climate), sudden cold weather may occur in autumn, winter, and spring.



Raw field data for irradiance and module (back) temperature. The beginning/end days for the deployment intervals are indicated at the bottom of the figure (31, 68, 131, 191, 374, 558, 740, 924, and 1105 days), which are different than the nominal examination intervals of 30, 60, 120, 180, 360, 540, 720, 900, and 1020 days because they include non-tracking periods (e.g., system down-time for upgrades).

*updated from Miller et. al., Progress in PV, **21** (4), 2013, 631-651.*

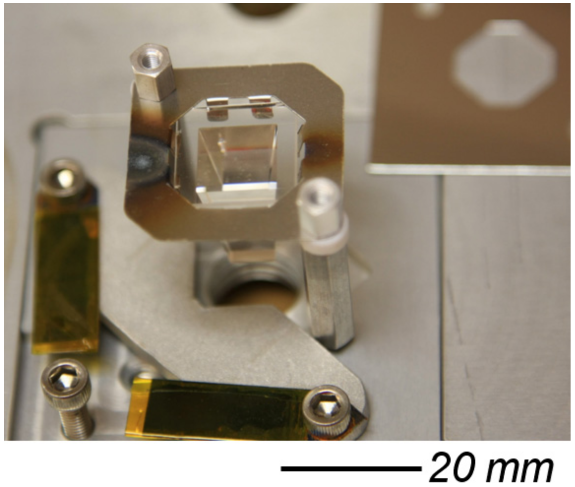
The Field Conditions (Irradiance & Ambient Temperature)

- *H* does not include diffuse radiation, which may enter CPV modules.
- *H* does not account for radiation spectra, *e.g.*, more damaging with altitude.
- *RH* in a sealed module is typically less than RH_{ambient}.
- *RH:* Air exchange is achieved through wire mesh ports in this experiment.

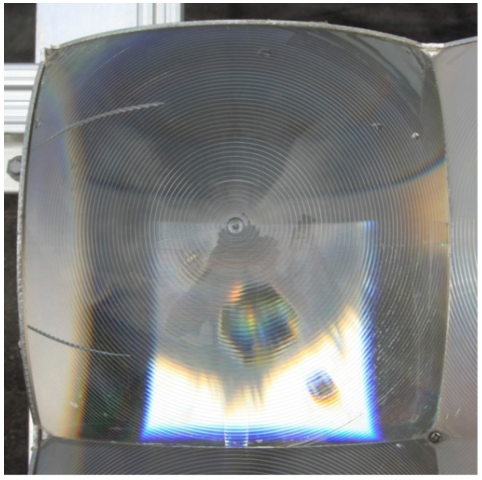
YEAR	H_{total}, direct, {GJ·m^{-2}}	$H_{\text{UV-A}}$, direct, {GJ·m^{-2}}	$H_{\text{UV-B}}$, direct, {MJ·m^{-2}}	T_{avg} day & night {°C}	T_{max} day & night {°C}	T_{min} day & night {°C}	RH_{avg} day only {%}	w_{avg} day only {m·s^{-1}}	w_{max} day only {m·s^{-1}}
2015	6.567	0.202	0.0	11.9	36.6	-17.5	39	2.1	12.9
2014	6.811	0.207	0.0	10.7	35.7	-24.8	38	2.2	14.9
2013	7.202	0.214	3.5	10.5	35.9	-21.9	39	2.1	12.9
2012	7.347	0.217	3.5	12.6	37.9	-15.4	31	2.2	18.7
2011	7.605	0.217	3.5	10.9	34.9	-27.2	36	2.2	19.0
2010	7.450	0.219	3.4	11.0	36.5	-18.0	38	2.2	15.4
2009	7.105	0.202	3.4	10.2	34.5	-22.3	41	2.3	16.0
2008	7.597	0.217	3.7	10.6	36.6	-24.4	35	2.8	18.6
2007	7.362	0.220	3.4	11.2	35.3	-22.3	39	2.6	20.6
2006	7.401	N/A	3.0	11.5	36.3	-25.0	36	2.8	21.2
2005	7.320	N/A	2.9	11.3	37.7	-22.0	38	2.6	22.8
2004	7.095	0.189	2.8	10.8	35.9	-20.5	41	2.4	25.5
2003	7.075	0.198	2.7	11.4	35.9	-20.2	39	2.6	19.8
2002	7.418	0.202	2.7	10.9	37.5	-18.2	35	2.7	18.7
2001	6.972	0.176	3.2	11.3	35.0	-19.4	40	2.4	16.8
AVG	**7.222**	**0.206**	**2.8**	**11.1**	**36.2**	**-21.3**	**38**	**2.4**	**18.2**
ST DEV	**0.289**	**0.013**	**1.2**	**0.6**	**1.0**	**3.3**	**3**	**0.3**	**3.5**
CoV {%}	**4.0**	**6.4**	**42.1**	**5.2**	**2.9**	**-15.3**	**6.7**	**10.8**	**19.4**
MAX	**7.605**	**0.220**	**3.7**	**12.6**	**37.9**	**-15.4**	**41**	**2.8**	**25.5**
MIN	**6.567**	**0.176**	**0.0**	**10.2**	**34.5**	**-27.2**	**31**	**2.1**	**12.9**
DIFF	**1.038**	**0.044**	**3.7**	**2.3**	**3.5**	**11.8**	**10**	**0.8**	**12.6**

Summary of the field conditions at the test site, for 2001-2015. The annual cumulative irradiance, ambient temperature, relative humidity, and wind speed are examined. Key statistics, including the average, standard deviation, coefficient of variation, maximum, minimum, and difference are provided. The cumulative annual radiant exposure is provided, in addition to data obtained during daylight (“day only,” for ϕ_{total} > 50 W·m^{-2}) or entire day (“day & night”).

Fixture Difficulties, Early in the Experiment

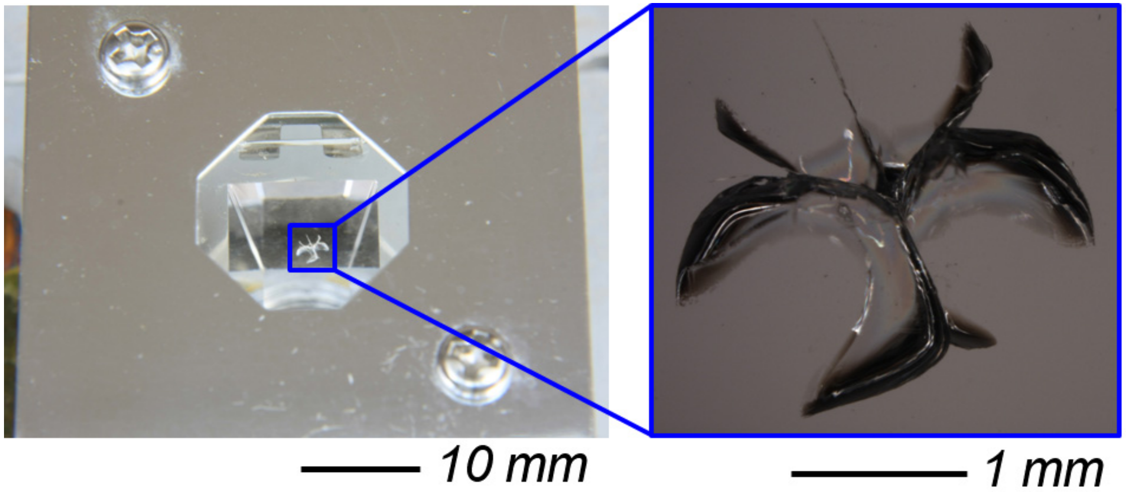


Scorched component(s) when sunshield removed during alignment for initial exposure.



1 of 5 lens sites damaged (cracked) in a hail storm on 2010/6/11.

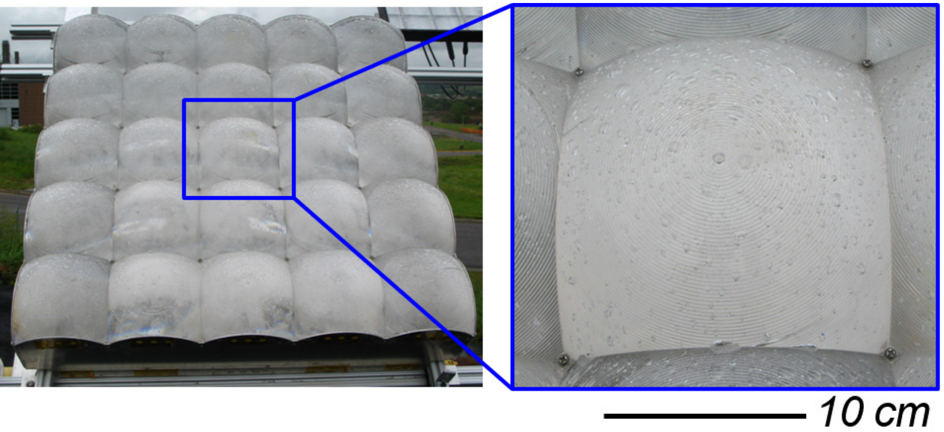
See also: Muller et. al., Proc Int. Conf. CPV, 2012.



Crack in the first surface of one of the secondary optics at a point defect, observed after 2 months cumulative exposure. The fractography, where separate crack fronts radiate from a central location, suggests that crack propagation occurred about a single initial defect. For example, a surface defect may have resulted from the manufacture or subsequent handling of the SOE. The SOE glass (subject to concentrated flux) is optically absorbing and therefore subject to diurnal and weather-motivated thermal cycling, e.g., cloud transients.

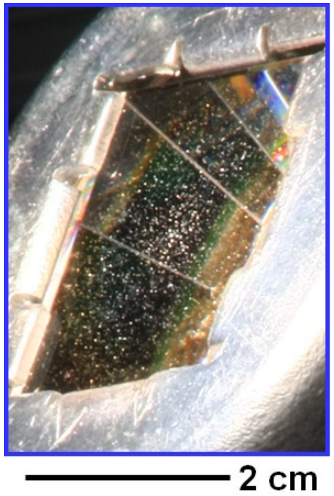
Additional Fixture Difficulties

Internal soiling was common at corners or crevices at the bottom of the fixture. Natural soiling was greatest at corners and crevices within the module, including the lens facets. Some seals were removed from the module through the experiment to allow fixture maintenance. The module interior (back of lens and housing) were subsequently cleaned every 6 months.



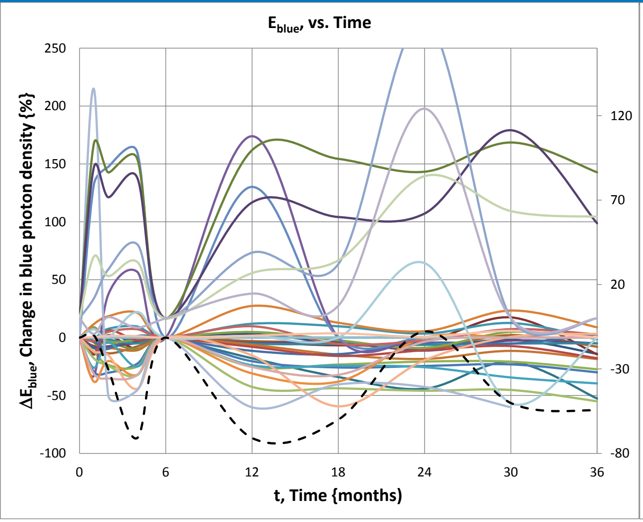
Internal condensation was typical in the morning, following wet weather.

Snow could become trapped by the topography present on the front of the fixture.

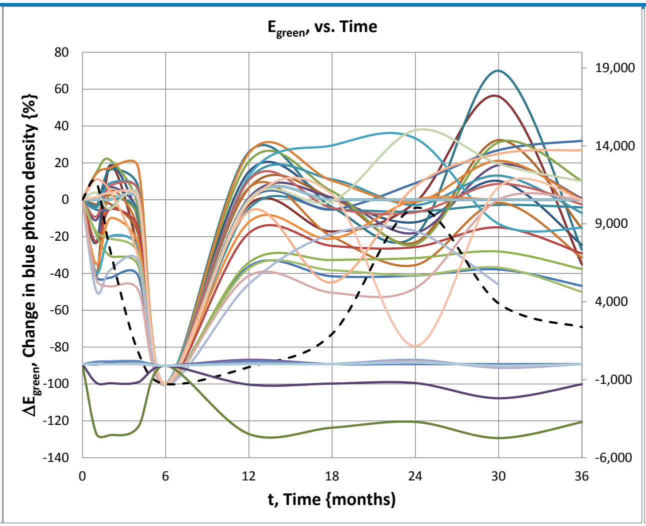


Adhesion of thermally decomposed airborne particulate matter onto the first surface of an early prototype fixture (no module sides present - open to the environment).

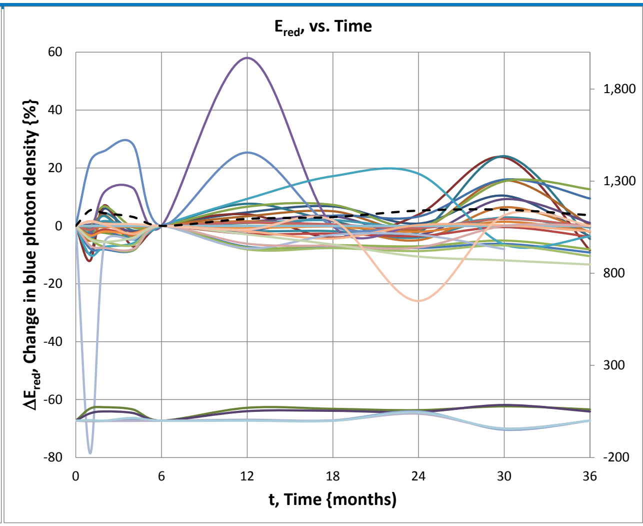
Trends for Specimen Transmittance with Time



Specimens (hydrocarbons and siloxanes). Outliers (above) are plotted on the right axis.



Specimens (hydrocarbons and siloxanes). Outliers (below) are plotted on the right axis.



Specimens (hydrocarbons and siloxanes). Outliers (below) are plotted on the right axis.

- Measured τ is compensated to 0.5 mm thickness (by analysis, particularly for the siloxanes).
- Generally, there is a trend for transmittance to be decreased with time.
- Transmittance affected least in the IR wavelengths.
- True change in transmittance is minimal with time, exaggerated here from the direct τ.
- Spurious data was obtained at 6 months, from an instrument error.
- (6) "densified" materials likely increase the variation for siloxane
- Outliers…

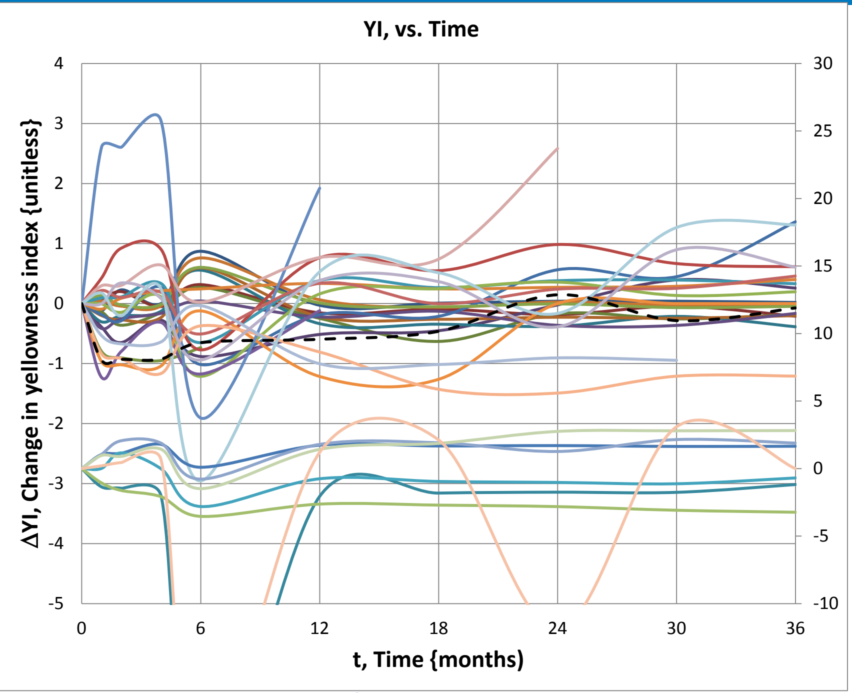
$300 \leq \lambda \leq 650$nm: EVA 3, EVA 4, PO 1, PDMS 12, PDPDMS-CH=CH_2 1&2, PPMS

$650 \leq \lambda \leq 890$nm : EVA 3, EVA 4, PDMS 6, PDMS 12, PDPDMS-CH=CH_2 1&2, PPMS

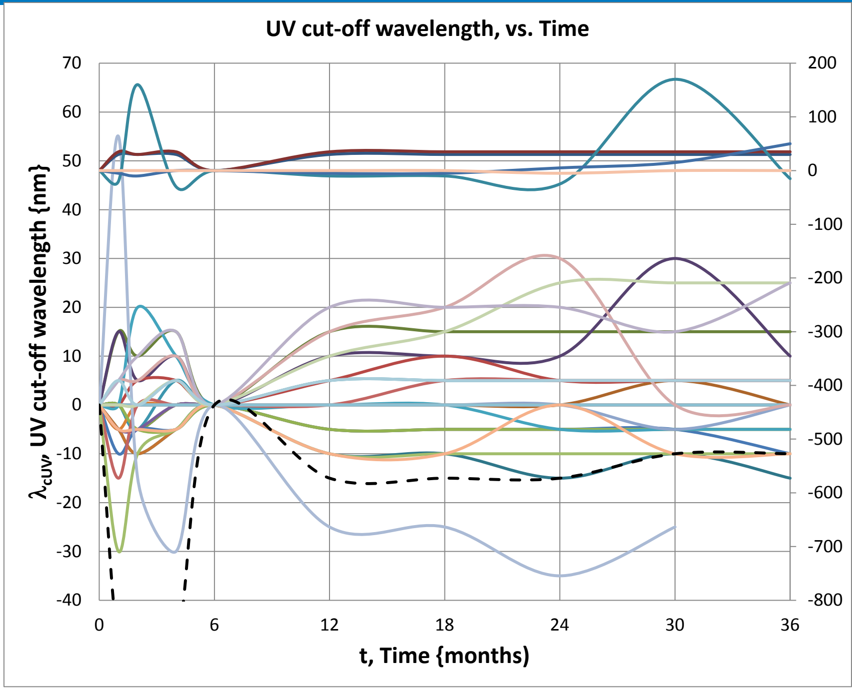
$890 \leq \lambda \leq 1800$nm : EVA 3, EVA 4, PDMS 12, PDPDMS-CH=CH_2 1&2, PPMS

- The outliers here reflect specific formulations of the material types.

Trends for Specimen YI and λ_{cUV} with Time



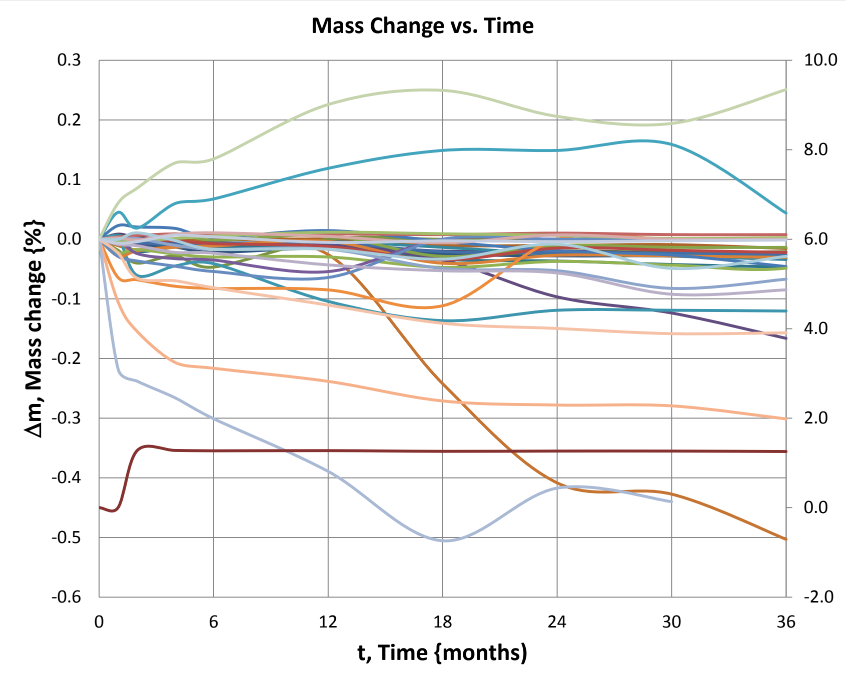
Trend in *YI* over time for all specimens (hydrocarbons and siloxanes). Outliers (below) are plotted on the right axis.



Trend in λ_{cUV} over time for all specimens (hydrocarbons and siloxanes). Outliers (above) are plotted on the right axis.

- The average *YI* for all specimens is increased slightly with time.
- Average *YI* is increased for both hydrocarbon & siloxane specimens.
- Spurious data (excluded here) was obtained at 6 months, from an instrument error.
- *YI* outliers: include PO, PDMS, DPDMS.
- The average λ_{cUV} for all specimens is increased with time.
- Average λ_{cUV} is increased for both hydrocarbon & siloxane specimens.
- λ_{cUV} outliers: include PO 1, PDMS 7, PDMS 11, PDMS 12, and PDPDMS-CH=CH_2 1
- The outliers for *YI* and λ_{cUV} reflect specific formulations of material.

Trends for Specimen Mass with Time



Trend in mass over time for all specimens (hydrocarbons and siloxanes). Outliers (below) are plotted on the right axis.

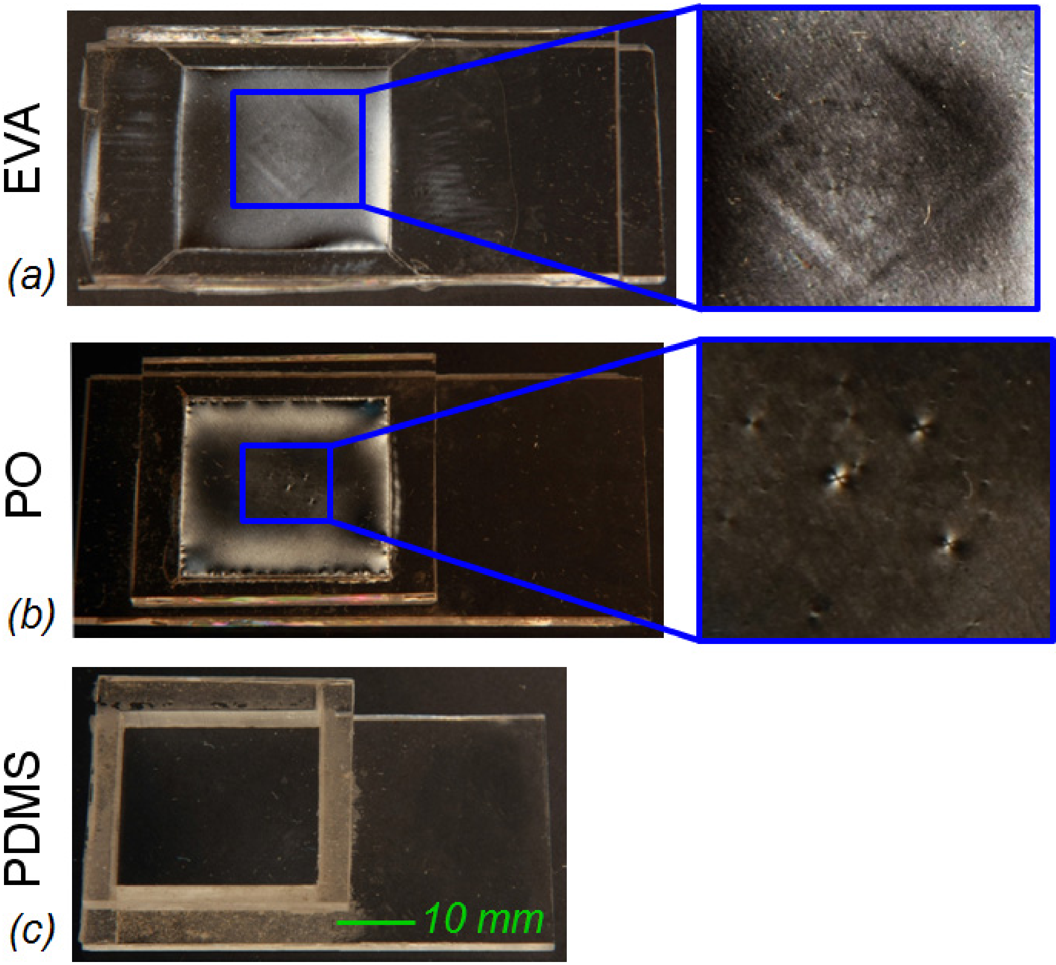
- Mass loss observed for: edge affected PVB 1, ionomer, PDMS 13, PDMS 14.
- Mass increase observed for: siloxane gels (soiling at sticky unpacked edges).
- Mass decrease for peroxide cured siloxanes (presumably excess peroxide and/or oligomers).
- One outlier: EVA 1, glass substrate chipped in handling during test at 2 months.

Effects of Aging Appear as Photoelastic Features

- EVA and PO are birefringent.
  →Residual stress is evident from pattern of secondary optic visible in many samples.
  →Confirms repeatable sample placement in the fixture during study.

- Localized stress sites evident in (1) EVA 4 & (1) PO 2 specimens.
  →Contamination or localized damage: yielding, tearing, or cavitation (from residual σ).

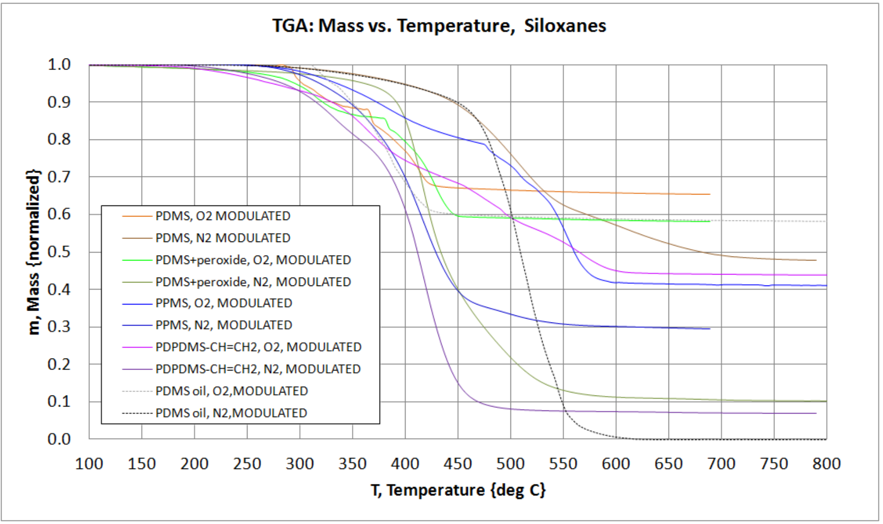
- PDMS, PVB, TPU did not demonstrate photoelastic features @ 36 months.



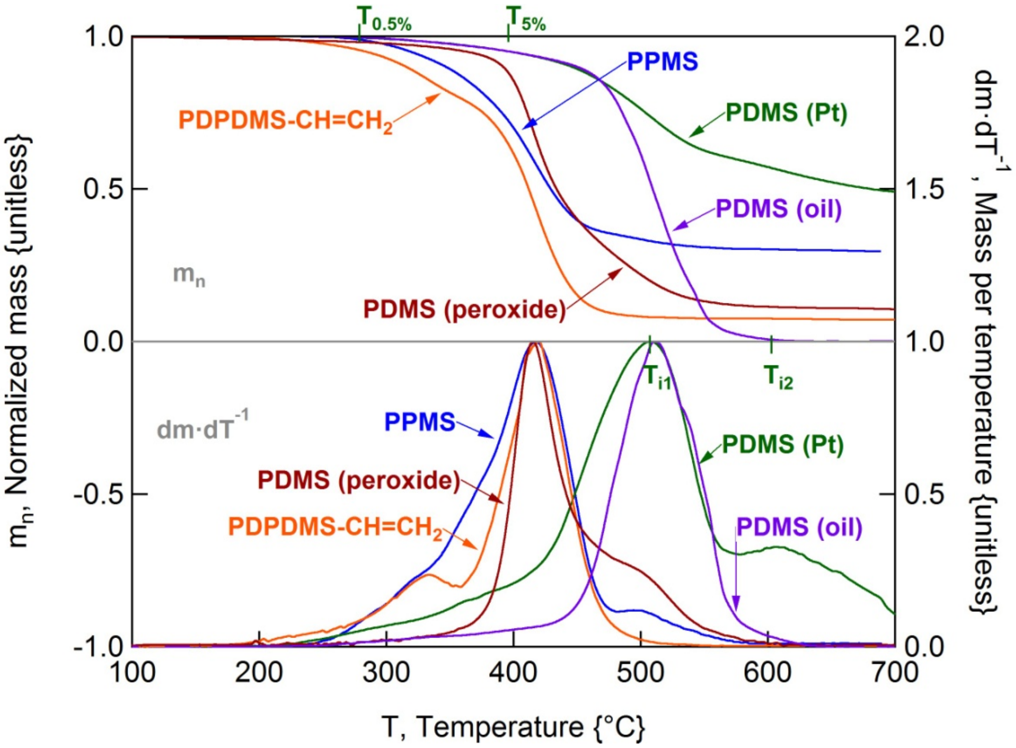
Images of: (a) representative EVA, (b) polyolefin 2, and (c) representative PDMS obtained using cross-polarization photography.

Modulated TGA Compares Stability of Siloxanes

- Thermal stability (ranked by $T_{0.5\%}$): PDPDMS-CH=CH$_2$, PPMS, PDMS (peroxide), PDMS (Pt), PDMS (oil).
- Mass loss for PDMS (peroxide) becomes surpassed with T by PPMS.
- For PDPDMS-CH=CH$_2$, the main decomposition peak is uniquely preceded by a secondary peak.
- A tail (but no 2nd peak), uniquely seen for PDMS (peroxide) in addition to main decomposition peak.
- Char (rank, by m, in N$_2$): PDPDMS-CH=CH$_2$, PDMS (peroxide), PPMS, PDMS (Pt), and PDMS (oil).



Comparison of the same test specimens in a pure N$_2$ ambient vs. reconstituted air (containing O$_2$).



TGA results for representative siloxane specimens examined in an N$_2$ atmosphere, including Pt catalyzed and peroxide cured PDMS, uncross-linked PDMS oil, vinyl terminated PDPDMS, and PPMS. The normalized mass and its derivative are shown in the top left and bottom right of the figure, respectively. The temperatures at 0.5% and 5% mass loss, as well as the temperatures at the inflection points for dm·dT^{-1} , are identified for the PDMS sample as an example.

Comparing the Stability of Siloxanes in N_2 and O_2

- Characterization with O_2 present less repeatable. Sudden (sometimes complete) drops in mass with temperature.
- Thermal stability: with $O_2 < N_2$ only ambient for PDMS; with $O_2 > N_2$ for PPMS, PDPMS.

- O_2 containing atmosphere increased thermal stability here (opposite the literature).
- Black & white char always observed with N_2 or O_2, respectively, consistent with literature.
- Greater residual *m* with O_2 present.

- Sudden mass loss events & corresponding spurious $dm \cdot dT^{-1}$ peaks in O_2 not found in literature.
- Diffusion limiting silica shell likely formed around specimen in O_2 containing atmosphere.
- Thinner layer of silica observed to coat the sample pans in O_2 (this study) than at fast test rate (previous study).
- Outer silica layer formed during decomposition acts as a barrier to reactant and product species, enabling the formation of pockets of gaseous product species, or regions of unreacted material.
- Events including the release of trapped volatile products and/or the fracture of the outer layer (and subsequent rapid decomposition of freshly exposed material) are then able to misbalance the specimen.
- Grind siloxane to powder for examination in O_2, if possible (gels may adhere to grinder).

Representative photo of residual char from specimens tested in an O_2-containing or N_2-only atmosphere.

Modeling the Time to 1% Mass Loss for Siloxanes

Model of activation energy weighted annual equivalent specimen temperature, T_{eqv} {°C}.

M.D. Kempe M.D., Proc PVSC 2014,614.

$$T_{eqv} = \frac{-E_a}{k_B \ln\left[\frac{\sum e^{\left(\frac{-E_a}{RT_s}\right)}}{n}\right]}$$

- Parameters: activation energy, E_a { kJ·mol-1}, use measured E_{a1} for each material; Boltzmann constant, k_B {1.381·10−23 J·°C $^{-1}$}; ideal gas constant, R {8.314 J·°C $^{-1}$·mol^{-1}}; specimen temperature, T_s {°C}; number of discrete temperature datapoints {*n*, unitless}.
- Assume a 38.5°C temperature increase above the ambient for the instantaneous specimen temperature, based on previous thermography of specimens in test fixture, in direct proportion to the measured global solar irradiance.
- Annual specimen equivalent temperature of 38.5°C (similar to instantaneous specimen temperature rise, by coincidence) for PDMS (Pt cured) is greater than the T_{avg} of 11.1°C in Golden.
- Annual specimen equivalent temperature of 55°-125°C, corresponding to an operating temperature rise of 60°-150°C above ambient in Golden follows for the operating limit from the Arrhenius analysis for PDMS (Pt cured).
- Because of the substantial variation for c_{p1} & $E_{a,p1}$ here, verification of material durability (*e.g.*, using isothermal characterization at elevated temperatures) is advised.
- Generic thermal index (upper limit of annual specimen equivalent temperature, for long-term use) for silicone of 105°C is recommended for design in the absence of material specific results.

Additional Observations & Conclusions From Modulated TGA

MATERIAL	CURE SCHEME	$T_{0.5\%}$ mass loss {°C}	$T_{5\%}$ mass loss {°C}	$T_{i1,}$ max[dm/dT] {°C}	$T_{i2,}$ max[dm/dT] {°C}	FREQUENCY FACTOR: $c_{p1,\ avg}$ $\{s^{-1}\}$	$E_{a,p1,}$ avg±s.d. $\{kJ \cdot mol^{-1}\}$	FREQUENCY FACTOR: $c_{p2,\ avg}$ $\{s^{-1}\}$	$E_{a,p2,}$ avg±s.d. $\{kJ \cdot mol^{-1}\}$	*m*, NORMLAIZED MASS CHAR {unitless}	$t_{1\%}$ mass loss, $E_{a,p1}$ {years}
PDMS	Pt catalyst	279	396	507	603	$6.0 \cdot 10^1$	88±8	$2.5 \cdot 10^6$	186±60	0.477	65-145
PDMS	peroxide cure	141	362	415	N/A	$4.8 \cdot 10^4$	109±10	N/A	N/A	0.103	230-297
PDMS	oil	284	396	518	N/A	$1.2 \cdot 10^9$	188±24	N/A	N/A	0.001	$8.0 \cdot 10^7$-$2.6 \cdot 10^{15}$
PPMS	Pt catalyst	264	318	418	494	$7.6 \cdot 10^3$	101±4	$9.3 \cdot 10^{12}$	254±17	0.296	10-550
PDPDMS-CH=CH_2	Pt catalyst	201	283	334	420	$1.2 \cdot 10^2$	74±9	$8.1 \cdot 10^4$	110±11	0.070	0.3-2621

Summary of the representative siloxane specimens, including: temperature at a specified mass loss (0.5, or 5%); inflection-point temperature(s), *i.e.*, where $d^2m/dT^2 = 0$; frequency factor and activation energy [at the inflection point(s), if applicable]; normalized mass of the residual char; and the duration to 1% mass loss at the fixture equivalent temperature (weighted by the activation energy, with bounds from the c_{p1} and $E_{a,p1}$ average±1S.D.)

- Immediate thermal decomposition unlikely, T_{max} typically 60°-110°C in CPV is < $T_{0.5\%}$ here.
  Suspect then: UV degradation ⇒ discoloration ⇒ thermal runaway.
- Large volume of dark material could have formed via (oxygen limited) thermal decomposition after UV mediated thermal runaway.
- PDMS (Pt and peroxide cured) expected to be durable, but $t_{1\%}$ approaches module lifetime of 25 years for T_{eff} = 55-125°C. $T_{eff,Golden}$= 37-40°C.

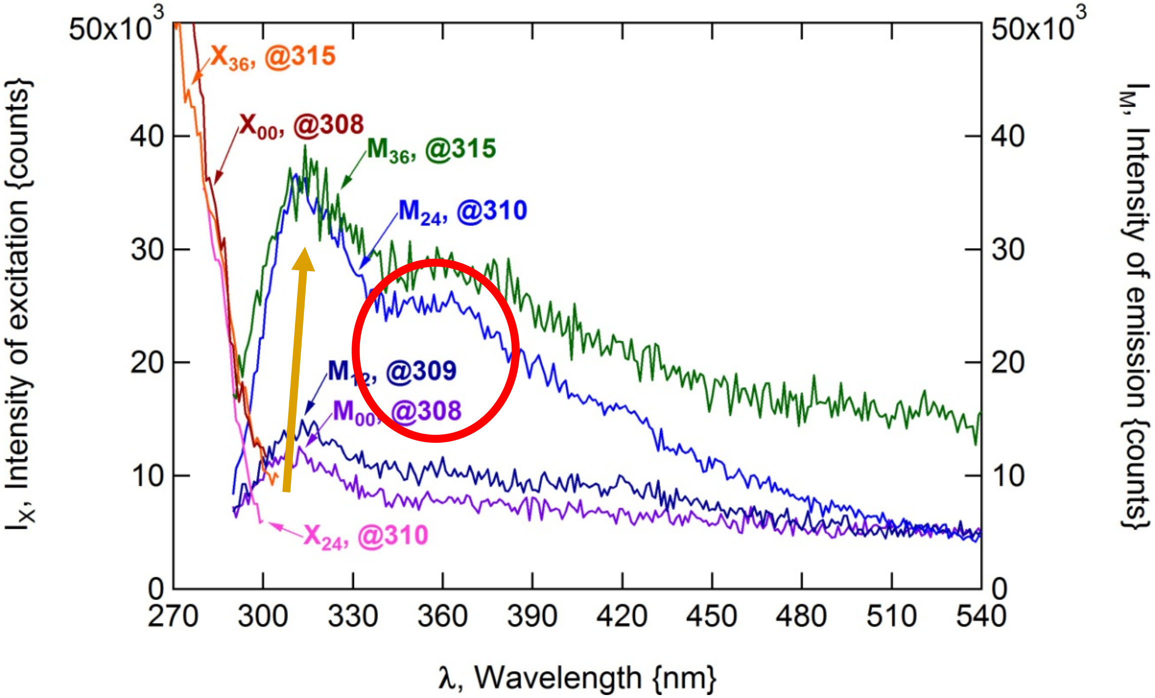
- PDMS most thermally stable here (opposite PPMS as in the literature).
- Thermal stability, however, does not necessarily correlate with ignitability or flammability.
- T_i for decomposition consistent with literature. Onset of mass loss ($T_{0.5\%}$) sometimes lower here than in literature.
- E_a for decomposition lower here than in much of the literature, but still within bounds of the literature.
- Slower test rate for TGA here should favor corresponding lesser $T_{0.5\%}$, T_i , and E_a values than in literature.
- Commercial formulations (including additives) examined here; many of the literature materials were highly pure specimens prepared for academic study.
- Lower $T_{0.5\%}$ here could follow from loss of residual inhibitor or decomposition of cross-linker
- Two decomposition peaks observed here in here in N_2 (single peak observed in literature).
- Lower temperature peak could correspond to loss of vinyl terminaton in DPDMS-CH=CH_2.
- Single peak for PDMS (oil), similar to that of PDMS (Pt), resembles the literature, suggesting that additional peaks in other siloxanes may result from formulation additives or fillers. Low c_{p1}, $E_{a,cp1}$ for oil may motivate further study (also no additives, reduced contamination, no possible fracture).
- Greater maximum mass of the residual char observed here than in literature.
- Minimal residual char for PDMS (oil) results for material free of mechanical reinforcement, *e.g.*, fumed silica.

Fluorescence Indicates EVA's Are Affected with Age (1)

EVA 1, -2, -3, and -6 show a similar modest effect with age:

- Intensity of fluorescence is increased.
- The λ_m is seen to shift, from 308 to 315 nm in example.
- Often, a second (convoluted) peak emerges at ~365nm.

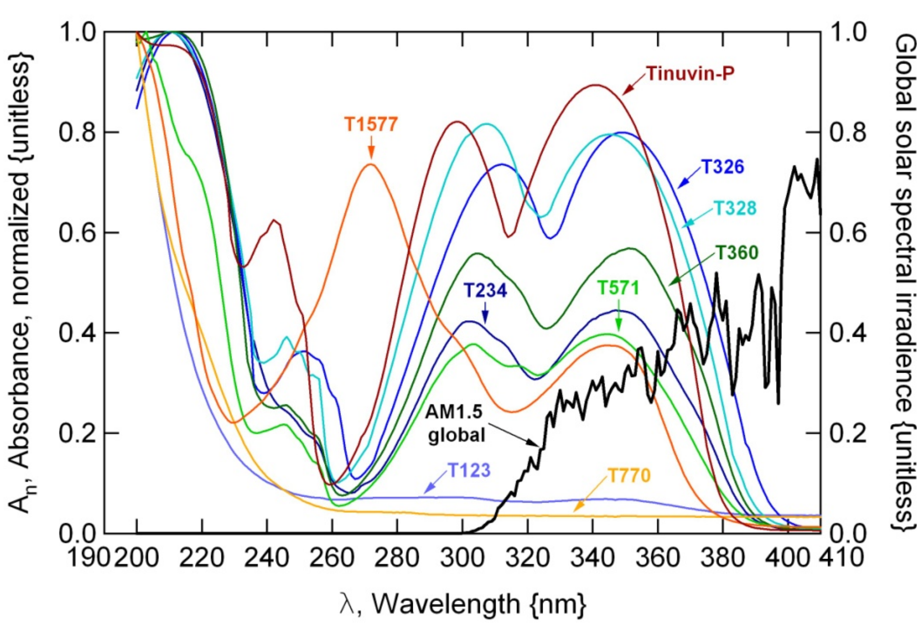
- The similar aging characteristics for the 4 EVA's suggests similar chemistry (formulation additives).



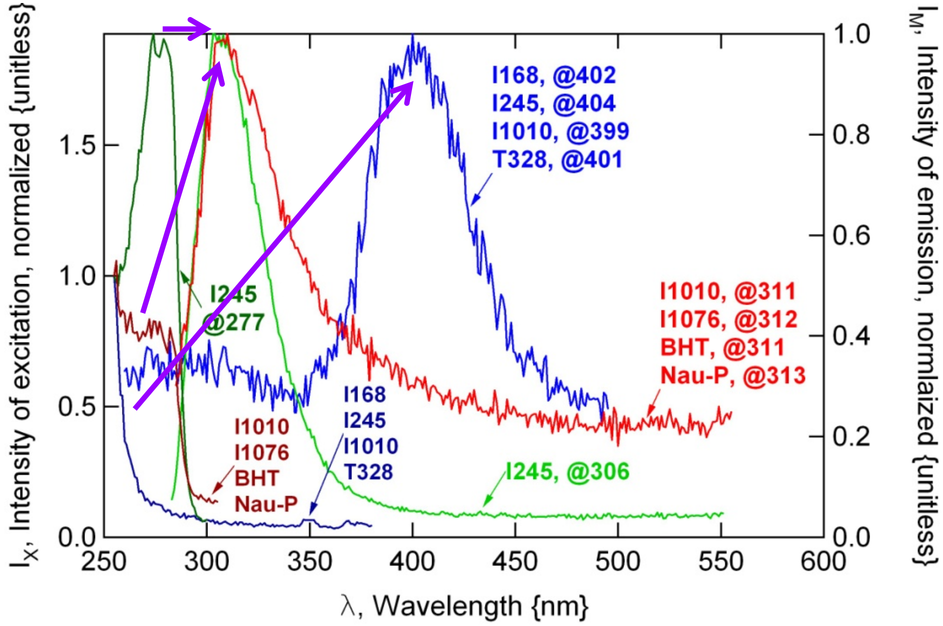
Excitation spectra (X, left) and corresponding emission spectra (M, right) for a representative less-affected formulation (EVA 1). The nomenclature in the figure identifies the age (month) at examination and the wavelength of maximum emission (for M) or wavelength monitored during excitation (X).

The Initial Transmittance and Fluorescence Follows From the Formulation Additives

- UVAs: Optical absorbance doublet peak
  UV thermalization peak near 400nm.
- AOs & HALs: Minimal optical absorbance > 250nm
  Sometimes unique fluorescence peak(s) and/or thermalization.
- Fluorescence signature may be very different when multiples additives are present (and interacting).



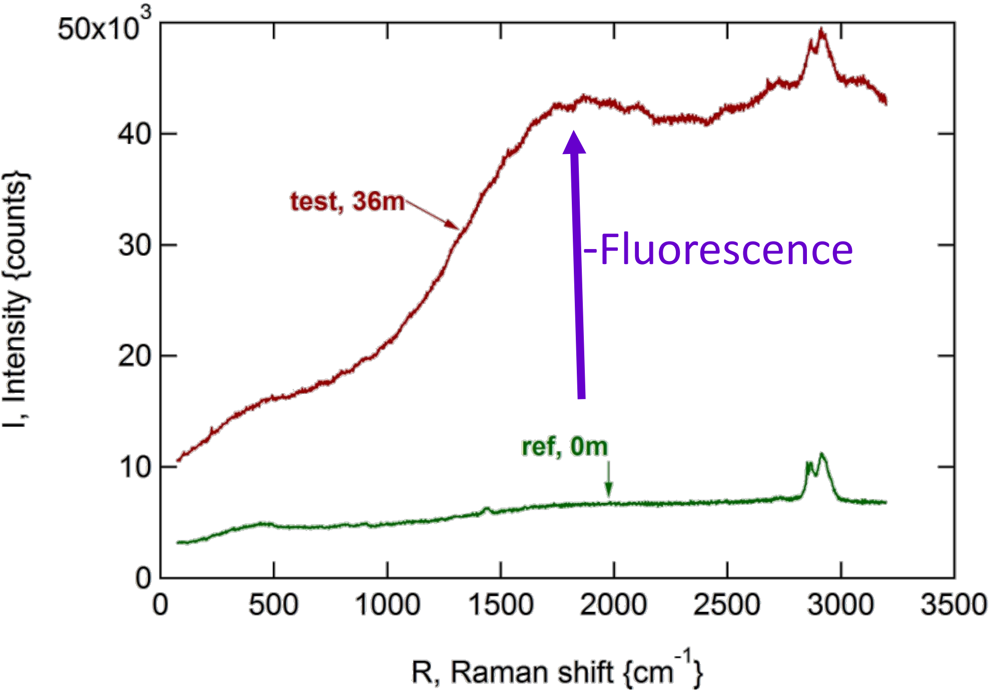
Optical absorbance (approximate) for UVAs including Tinuvin 234, Tinuvin 326, Tinuvin 328, Tinvin 360, Tinuvin 571, Tinuvin-P, and Tinuvin 1577 and HALS Tinuvin 123, Tinuvin 770.



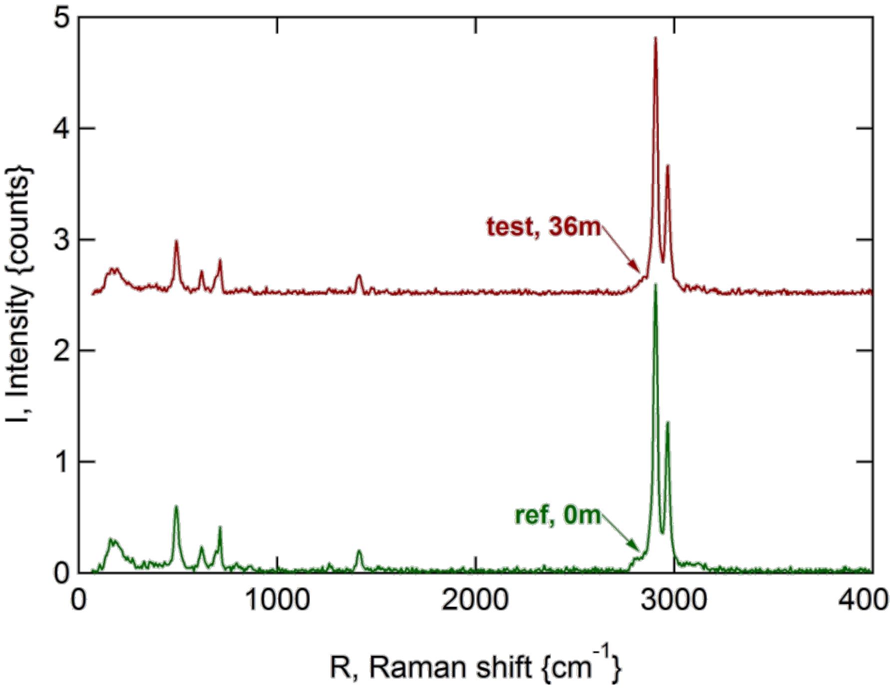
Fluorescence spectra for UVAs including Tinuvin 328 (typical) and AOs butylated hydroxytoluene (BHT), Irgafos 168, Irganox 245, Irganox 1010, and Irganox 1076.

Raman Spectra Suggest Aging Has Sometimes Occurred

- Raman can be used to examine polymer specimens laminated between glass.
- The most strongly UV-VIS fluorescent specimens were examined via Raman.
- Some materials (EVA, ionomer, PVB) evidenced fluorescence spectra, which was greatly reduced for 1064 nm excitation.
- Some materials (EVA, ionomer) evidenced minor changes in peak shape (note, 1% of EVA molecules are cross-linked, Hirschl *et. al.*, Proc. Euro. PVSC, 2013.)
- The siloxanes did not evidence fluorescence for Raman using 532 & 1064 nm excitation.
- Raman does not seem to provide a distinct signal for aged specimens, beyond fluorescence, *i.e.*, at short excitation wavelengths.



Overlay of Raman spectra for PVB 1 specimen at 36 (aged) and 0 (unaged) months. Excitation performed at 532 nm.



Overlay of Raman spectra for PDMS specimens at 36 (aged) and 0 (unaged) months. Excitation performed at 1064 nm.

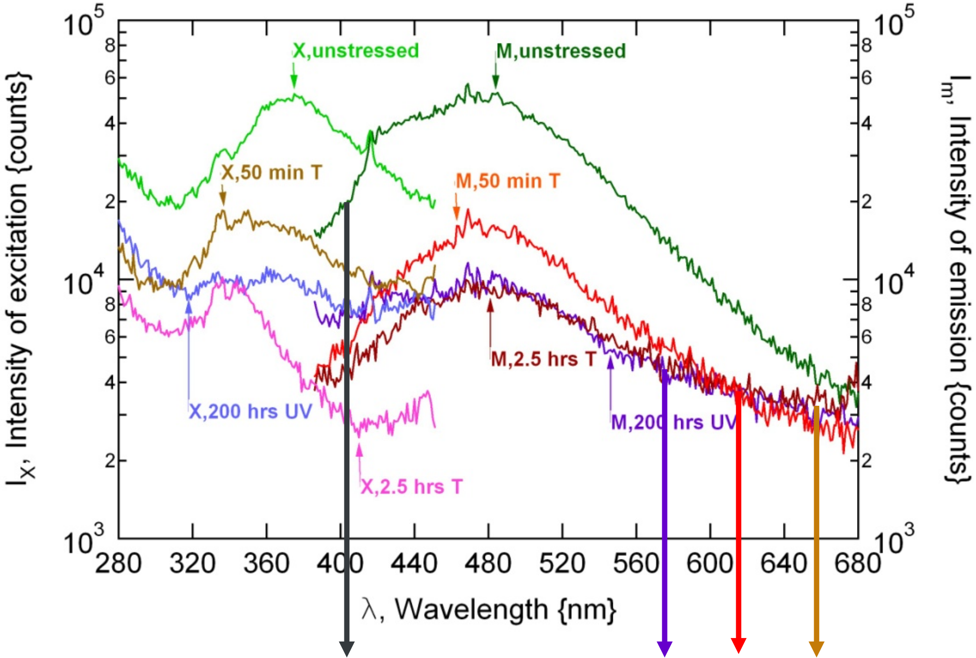
UV and/or Temperature Can Degrade Pt Catalyst

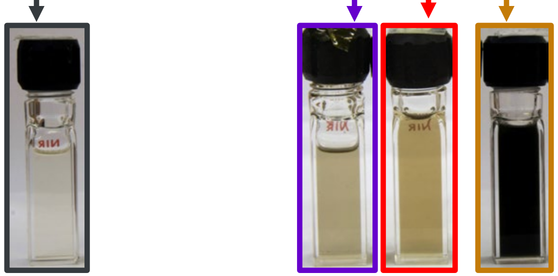
- Karstedt's catalyst, Pt(0), examined in tetramethyldivinyldisiloxane.
- Intensity of fluorescence lost with UV or T aging.
- Organometallic literature: mononuclear Pt with ligands ages to colloidal Pt, 3-5 nm ∅.

- Discoloration (optical absorptance) here could motivate thermal runaway.

- Fluorescence λ's for catalyst solution do not correspond identically to that in x-linked PDMS, nor does they shift in λ with age.

Excitation (X, left) and emission (M, right) spectra for a Pt catalyst solution.




unstressed *200 h UV* *50 m @ 100℃* *2.5 h @ 100℃*

color-corrected specimen photographs

- If catalyst problematic, alternate CPV solutions:
different catalyst type (ligands), peroxide cured silicone, or silicone oil (no catalyst).

UV Can Affect Silicone Primers

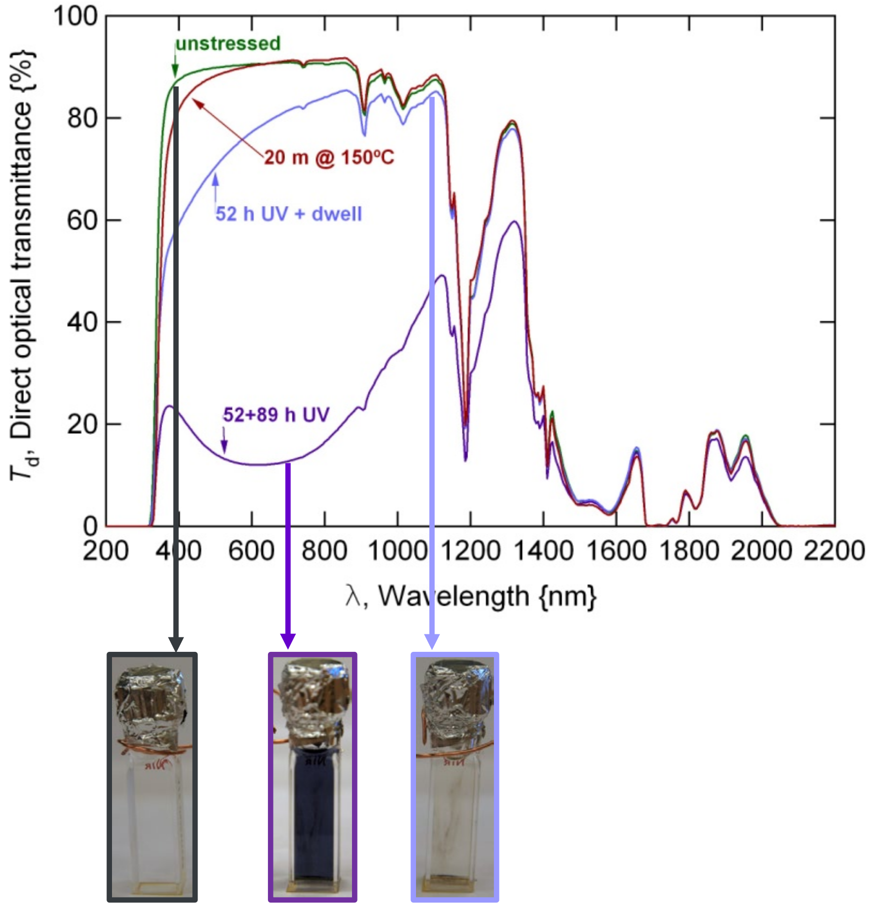
- Dow-Corning 92-023 used in all NREL silicone specimens.
- Ti based primer reduces UV transmittance for λ< 300 nm. (*n* TiO_2 = 2.5).

silica slides: λ_{cUV}<200→245nm.
cuvettes: λ_{cUV}245→330nm.

- Experiments identify primer is quite photoactive: significant discoloration.
- Transparency recovered with time (O_2 facilitated?)

- ”Typical” fluorescence spectra observed for silicone prepared *without* primer.
- Discoloration could contribute to absorptance and thermal runaway.

Transmittance for primer solutions (in isopropyl alcohol). Test specimens were subject to UV irradiation or thermal aging at 150℃.



unstressed *52+89h UV* *52 h UV + dwell*

- Anatase TiO_2 is used in self cleaning coatings.

(UV driven consumption of organic contamination). Affect on PDMS is unclear.

- Alternate CPV solution: tin- or silica-catalyzed primers (*n* SnO = 2.1).