Accelerated Laboratory Testing towards SLP of PV Polymers:
Reciprocity Study and Spectral UV Wavelength Effect on PV Components Degradation

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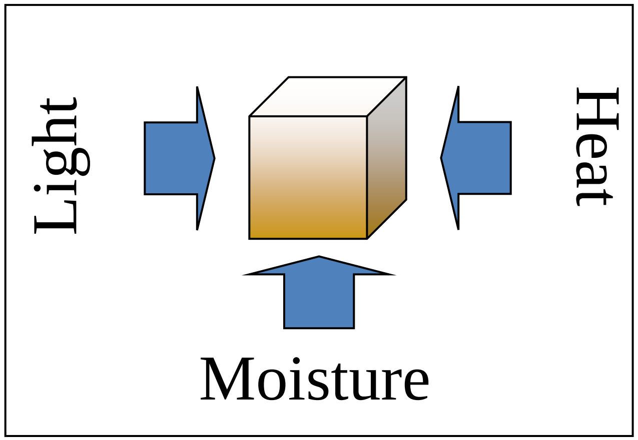
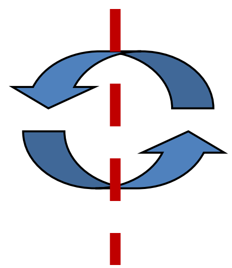
NIST

Conventional Methodology

Laboratory Exposure



Linkage



Outdoor Exposure

Designed to simulate the outdoors

Standard of Performance

A **comparison** methodology: product A > product B > product C

- There is general agreement that field results are neither repeatable nor reproducible.
- Experiments only performed on end-products; contribution from individual component unknown.
- **Difficult to quantitatively link field and laboratory exposure results.**

New Methodology: Reliability-Based SLP Methodology

Reliability-based Methodology

Degradatio mode

Laboratory Exposure

Effects of key environmental factors on polymer degradation (UV (I, λ), T, RH, σ/ε, …)

Outdoor Exposure

(UV Spectral irradiance, T, RH recording)

linkage

Cumulative Damage
Model

- **Multi-property measurements**
- **Degradation mechanism study**
- **Database; Predictive models**

lidated by outdoor
osure results

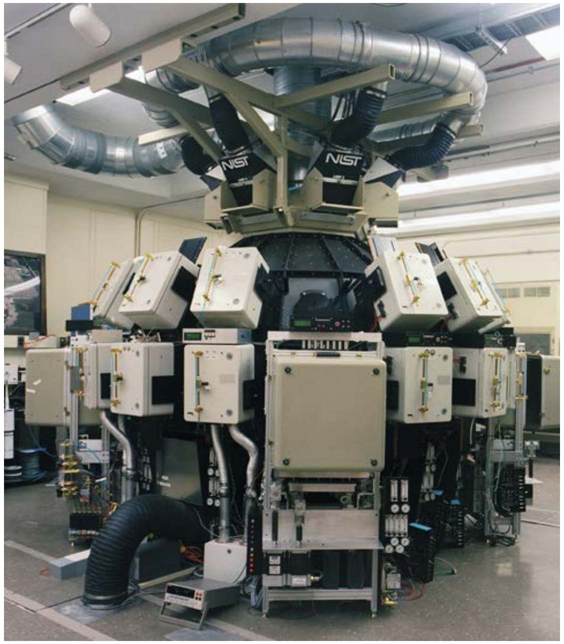
- **The parameters of predictive models are estimated solely from laboratory experiments; outdoor exposure results are used to verify the models using field exposure conditions as input (*Prediction models suitable to different climates*).**

➢ To predict the service life of a polymeric material

Linking Laboratory and Field Exposures for SLP

Outdoor Weathering

Indoor Accelerated Weathering



- Light Intensity Effect (Reciprocity Law?)
- Wavelength Effect (different light source)
- Temperature Effect
- Moisture/RH Effect
- Mechanical Stress Effect

Multi-property Measurement and Degradation Mechanism Study

Total Effective Dosage Model

- To allow for the environmental effects, consider

$$S(t) = \int_0^t f[\mathrm{Temp}(\tau)]g[\mathrm{RH}(\tau)] \int_{\lambda_{\min}}^{\lambda_{\max}} E(\tau,\lambda)\left[1-e^{-A(\lambda)}\right]\phi(\lambda)d\lambda d\tau$$

Accumulative Damage Model

The cumulative Damage is $D(t) = D(t-1) + \Delta D(t)$

The instantaneous damage is $\Delta D(t) = \sum_\lambda \Delta D(t,\lambda)$

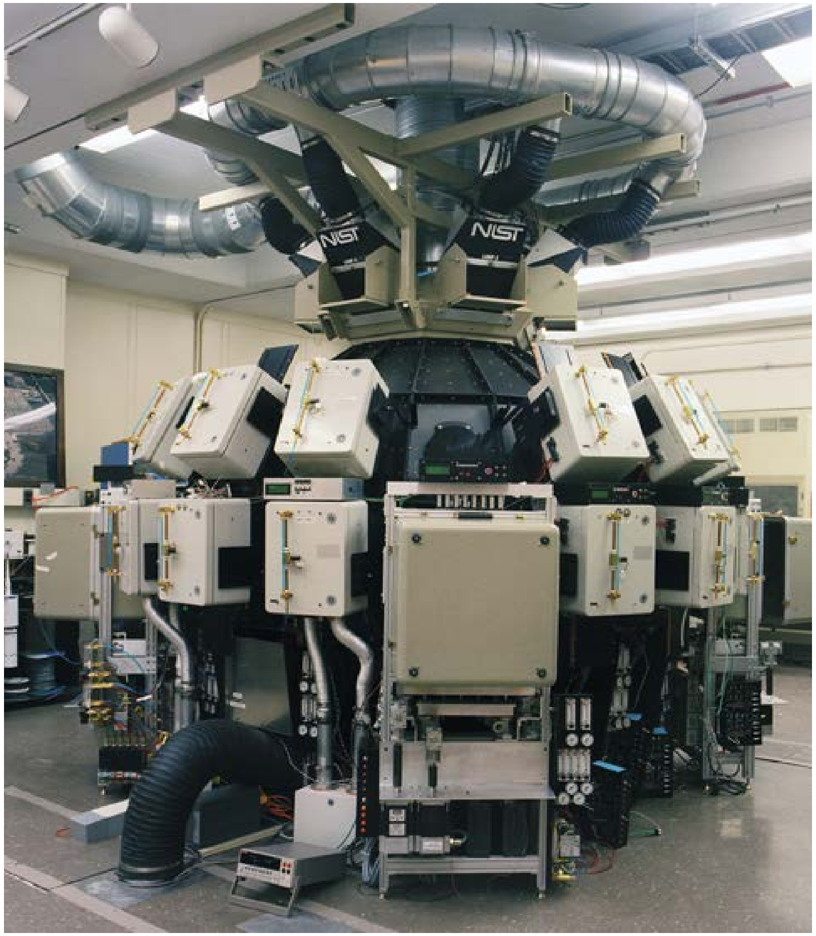
The damage at time t by wavelength λ is
$\Delta D(t,\lambda) = g'(t,\lambda) \times \Delta d(t,\lambda)$

The rate of damage is $g'(t,\lambda) = \frac{1}{d(t)\sigma_\lambda} \times \frac{\alpha_0 \exp(z)}{(1+\exp(z))^2}$

Here $z = \frac{\log[d(t)]+\eta_0-\frac{\frac{E_a}{R}}{TempK}+\beta_{\mathrm{RH}}(\mathrm{RH}-\mathrm{rh}_0)^2}{\sigma_0+\exp(\sigma_1+\sigma_2\times\lambda)}$

- Gu, X., Dickens, B., Stanley, D., Byrd, W., Nguyen, T., Vaca-Trigo, I., Meeker, W. Q., Chin, J., and Martin, J. (2009). Linking accelerating laboratory test with outdoor performance results for a model epoxy coating system. In: Service Life Prediction of Polymeric Materials.
- Vaca-Trigo, I. and Meeker, W. Q. (2009). A statistical model for linking field and laboratory exposure results for a model coating. In: Service Life Prediction of Polymeric Materials.
- Hong, Y., Duan, Y., Meeker, W. Q., Stanley, D. L., and Gu, X. (2015), Statistical methods for degradation data with dynamic covariates information and an application to outdoor weathering data, Technometrics, 57 (2), 180-193.
- Duan, Y., Hong, Y., Meeker, W. Q., Stanley, D. L., and Gu, X. (2015), Service life prediction of field-exposed units based on laboratory accelerated degradation test data, submitted.

Exposure: NIST SPHERE with Simultaneous UV/T/RH



NIST SPHERE

- **Simulated Photodegradation via High Energy Radiant Exposure (SPHERE)**
- **2 m integrating sphere-based UV chamber**
- **High Power Mercury Lamp**

  8400 W UV
- **95% exposure uniformity**
- **Low wavelength <290 nm removed**
- **Most visible and infrared radiation removed**
- **Exposure conditions of 32 chambers can be individually controlled (UV, RH,T)**
- **Capability for mechanical loading**

- *Martin and Chin, U.S. Patent 6626053*
- *Chin et al. Review of Scientific Instruments, 75(11), 4951-4959, 2004.*

NIST Project on *Developing Measurement Science for Service Life Prediction of PV Polymeric Materials*

Materials

- EVA
- Ionomer
- Fluoropolymers
- Polyolefin
- Polyesters

Components

- Frontsheet
- Encapsulant
- Backsheet

Modules/System

- Multi-component Laminated Coupons
- Single Cell PV Module
- Mini-module
- Full Scale Module

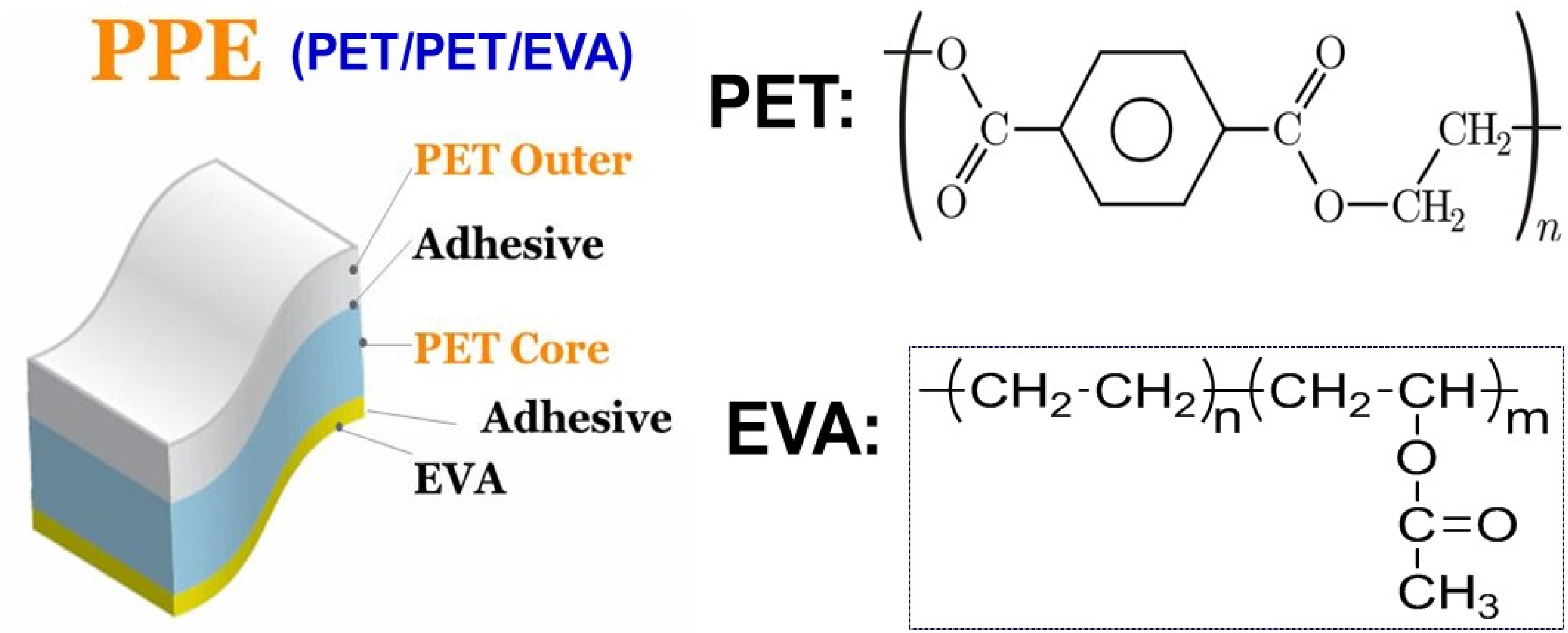
Chemical, Optical, Mechanical, Electrical, Adhesion Properties
During Accelerated Laboratory and Outdoor Exposures

Degradation Mechanism Study
Service Lifetime Prediction Model
Linking Indoor to Outdoor

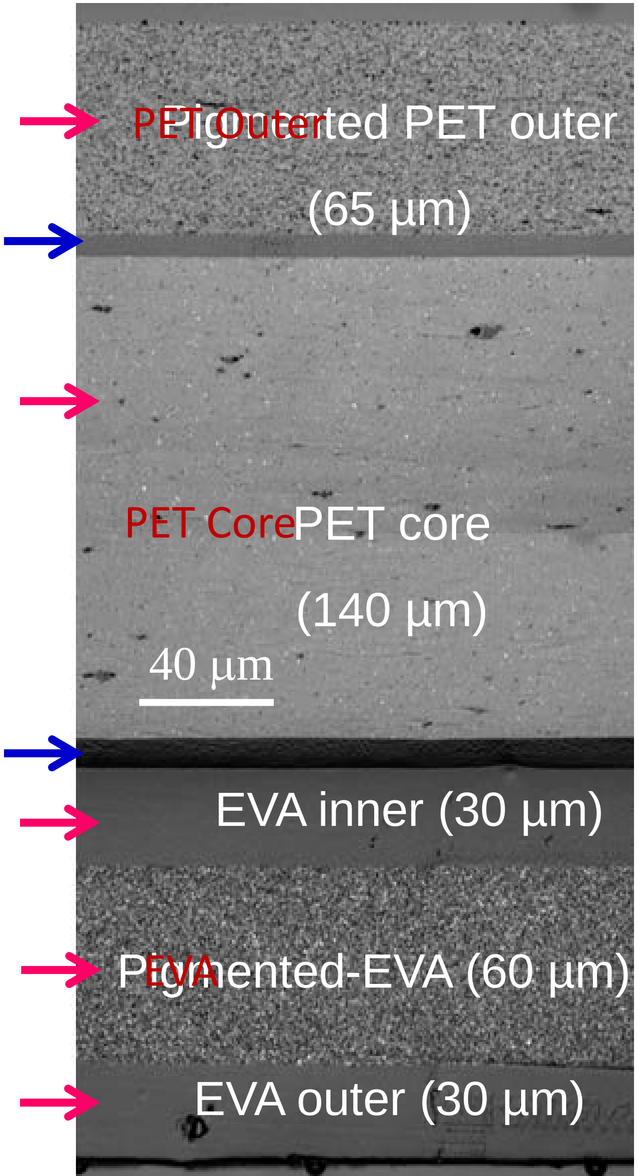
Scientific background

Develop Standards and Tools for Accelerated Testing and SLP of PV Materials and Modules

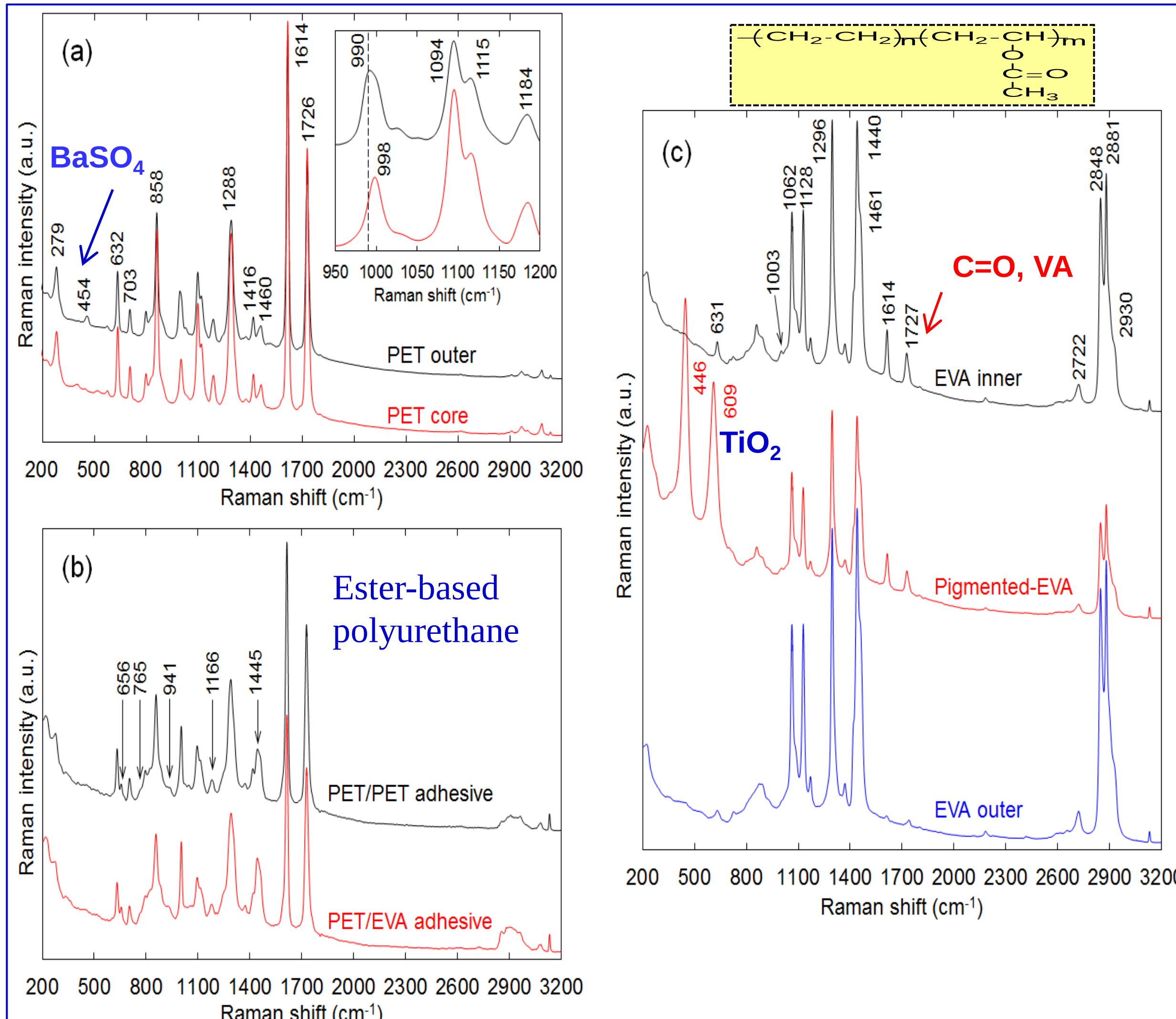
Backsheet Materials: PPE (PET/PET/EVA)



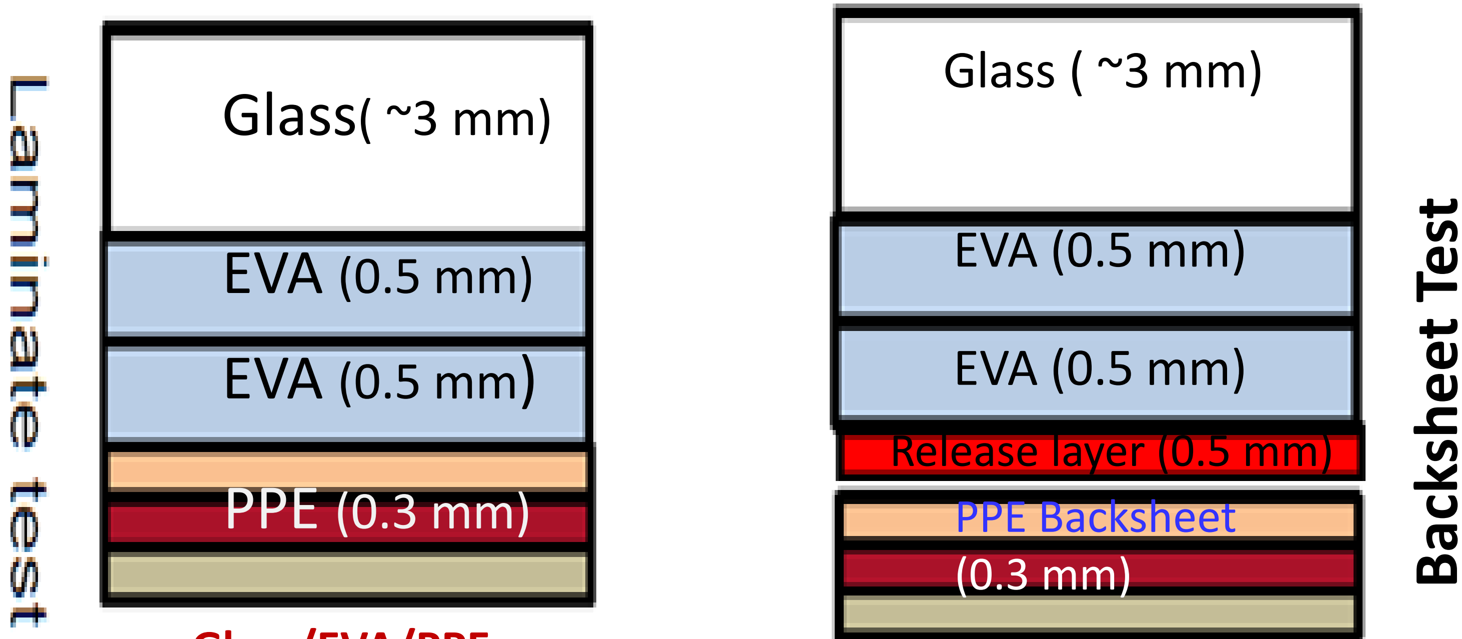
Confocal Imaging and Raman Microscopic Analysis of Cross-sectional PPE Backsheet Sample



Raman Spectra of PPE Multilayers



Sample Preparation-Materials and Construction



Glass/EVA/PPE

Without Release Layer

Glass/EVA/RL/PPE

With Release Layer

Glass: Two side-polished fused silica (quartz), 3 mm thick

EVA: UF-EVA (Photocap 15420P/UF)

Release Layer: FEP film, 500 µm,

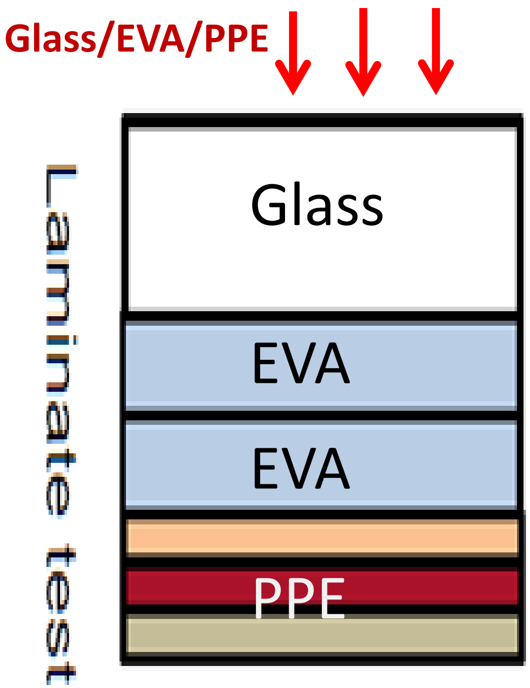
PPE Backsheet: Provided by NIST PV Consortium member

- Total thickness of laminated sample (~4.5 mm)
- Samples were made in DuPont PV Solution, Wilmington, Delaware.

Exposure Direction and Critical Measurements

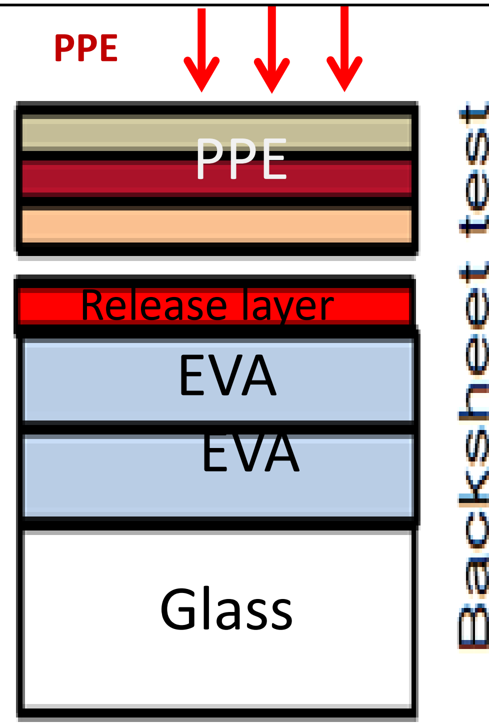
Three Exposure Configurations:

UV Through glass/encapsulant



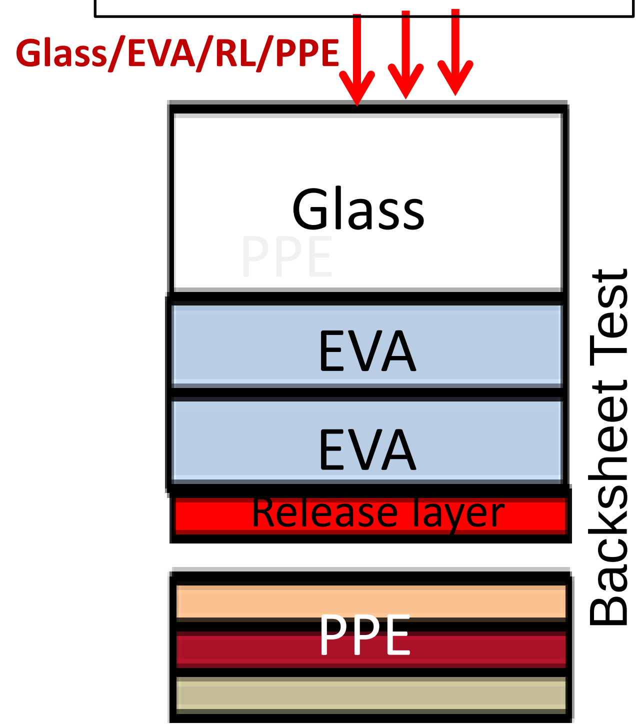
- Top EVA-Optical property through glass (UV-vis); Raman
- Bottom PPE-no light (UV-vis; ATR; microscopy)
- Possible adhesion test

Direct UV radiation on PPE backsheet



- Top PPE- UV-vis; ATR; microscopy; mechanical (tensile, nanoindentation)
- Bottom EVA- No light (PPE non-transparent), UV-vis, Raman

UV Through glass/encapsulant

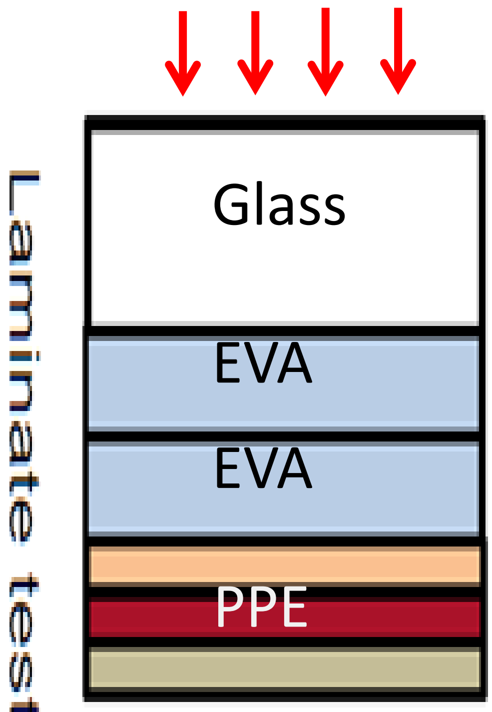


- Top EVA-Optical property through glass (UV-vis); Raman
- Bottom PPE-no light on PET side, only on E side (UV-vis; ATR; microscopy on PET, tensile)

I. Effect of Light Intensity and Wavelength on Degradation of Laminated Glass/EVA/PPE Specimens

Effect of Light Intensity and Wavelength on Degradation of Laminated Glass/EVA/PPE

UV Through glass/encapsulant



Glass/EVA/PPE Samples

No release layer between encapsulant and backsheet

85 °C/0% R.H on SPHERE

- Effect of Light Intensity on (Reciprocity Study)

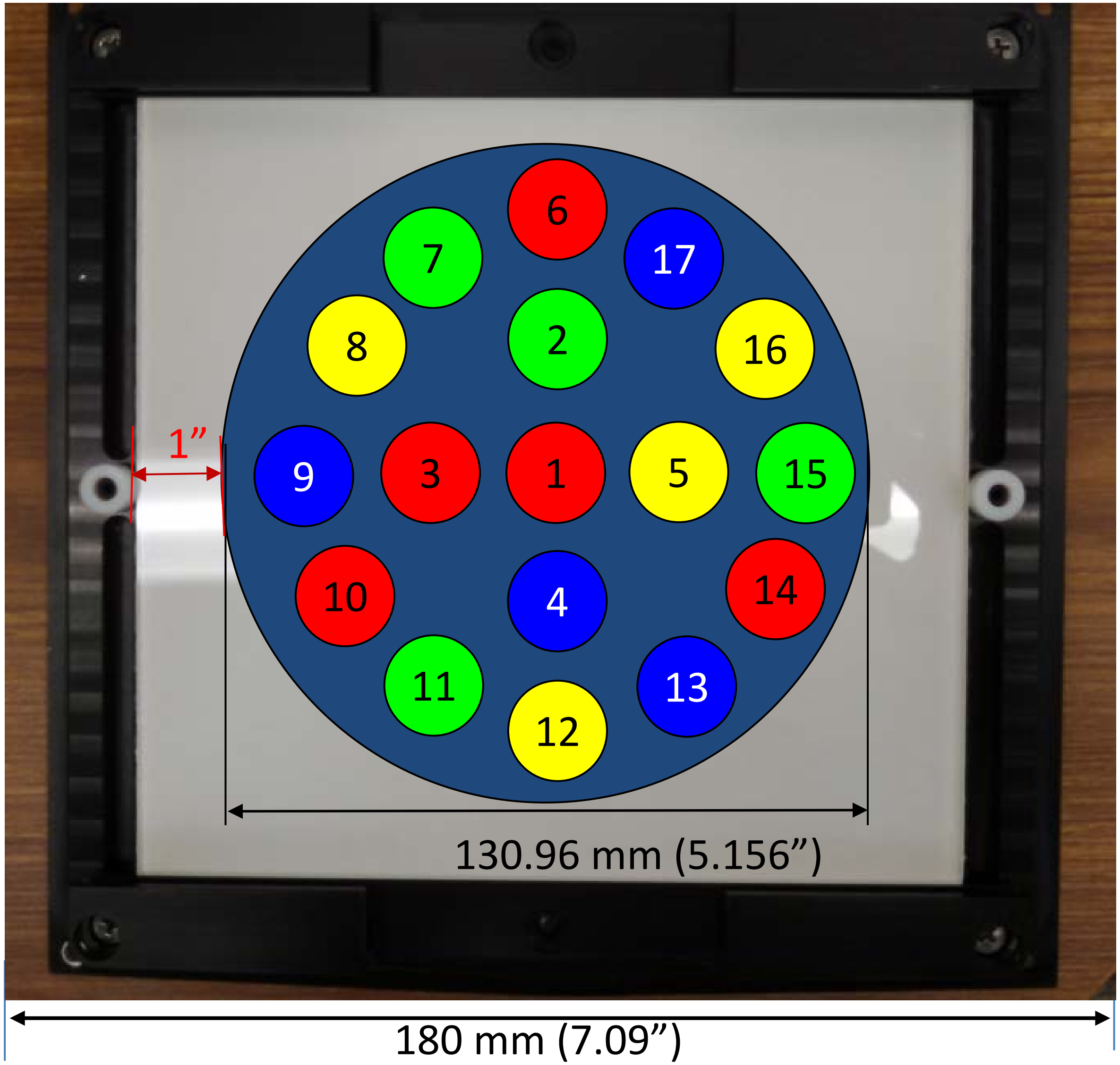
- Effect of Wavelength (Action Spectrum)

- Top EVA-Optical property through glass (UV-vis); Raman
- Bottom PPE-no light (UV-vis; ATR; microscopy)
- Possible adhesion test

Large samples (180 mmx180 mm) to avoid the edge effect on yellowing data

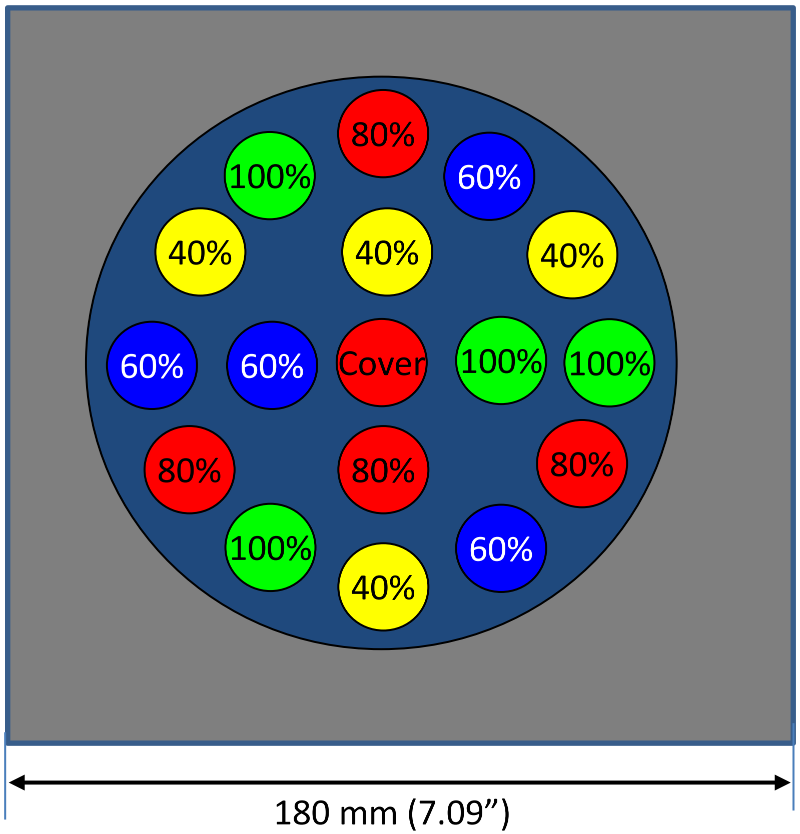
Exposure of Glass/EVA/PPE Laminated Specimen With Filters

Filters placed in front of glass/EVA/PPE large samples during exposure on SPHERE



Exposure of Glass/EVA/PPE Laminated Samples

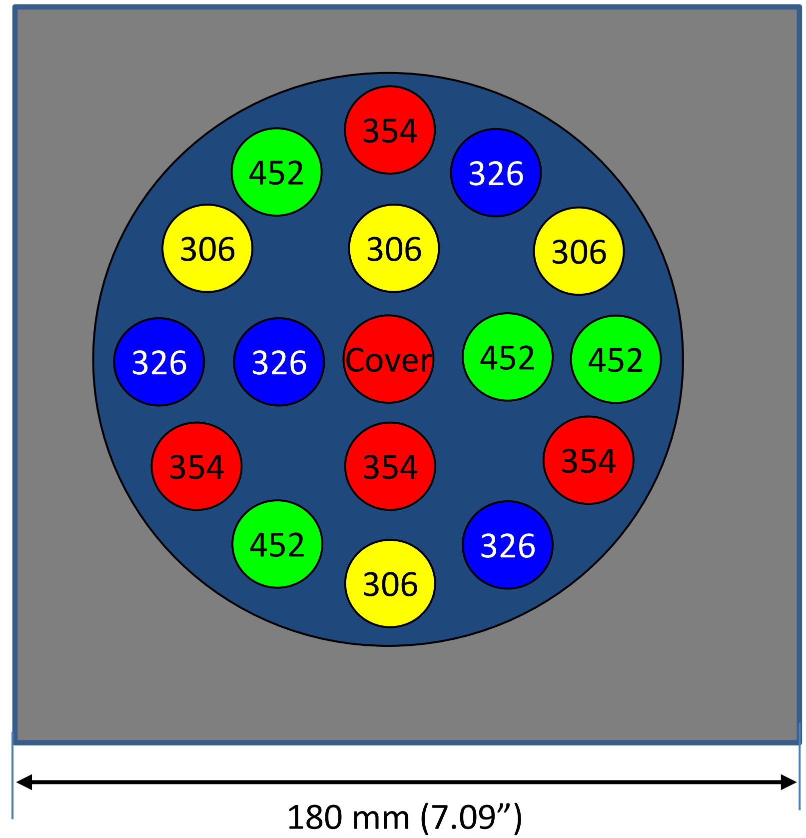
1) Reciprocity Study: Neutral Density filters



Varying light intensity with 40, 60, 80, and 100 % of ND filters

Integral UV irradiance: 170 W/m^2 (300-400 nm) → 68, 102, 136, 170 W/m^2, specifically through filters on specimens

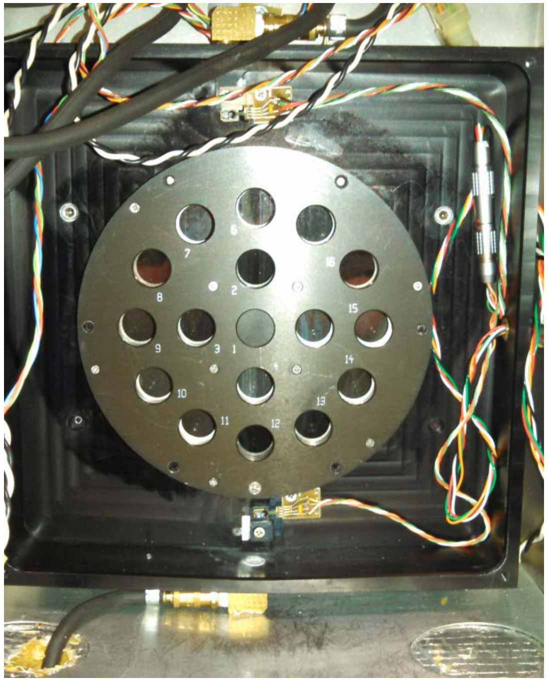
2) Wavelength Study: Band pass filters



Varying wavelength range with narrow band pass filters, (306 ± 3) nm, (326 ± 6) nm, (354 ± 12) nm and (452 ± 24) nm.

Exposure of Samples in SPHERE Chamber

- **Filter holder placed in front of sample inside chamber**



Neutral density filters (Reciprocity Study)

Narrow band pass filters (Wavelength Study)

- **Glass/EVA/PPE sample in holder**

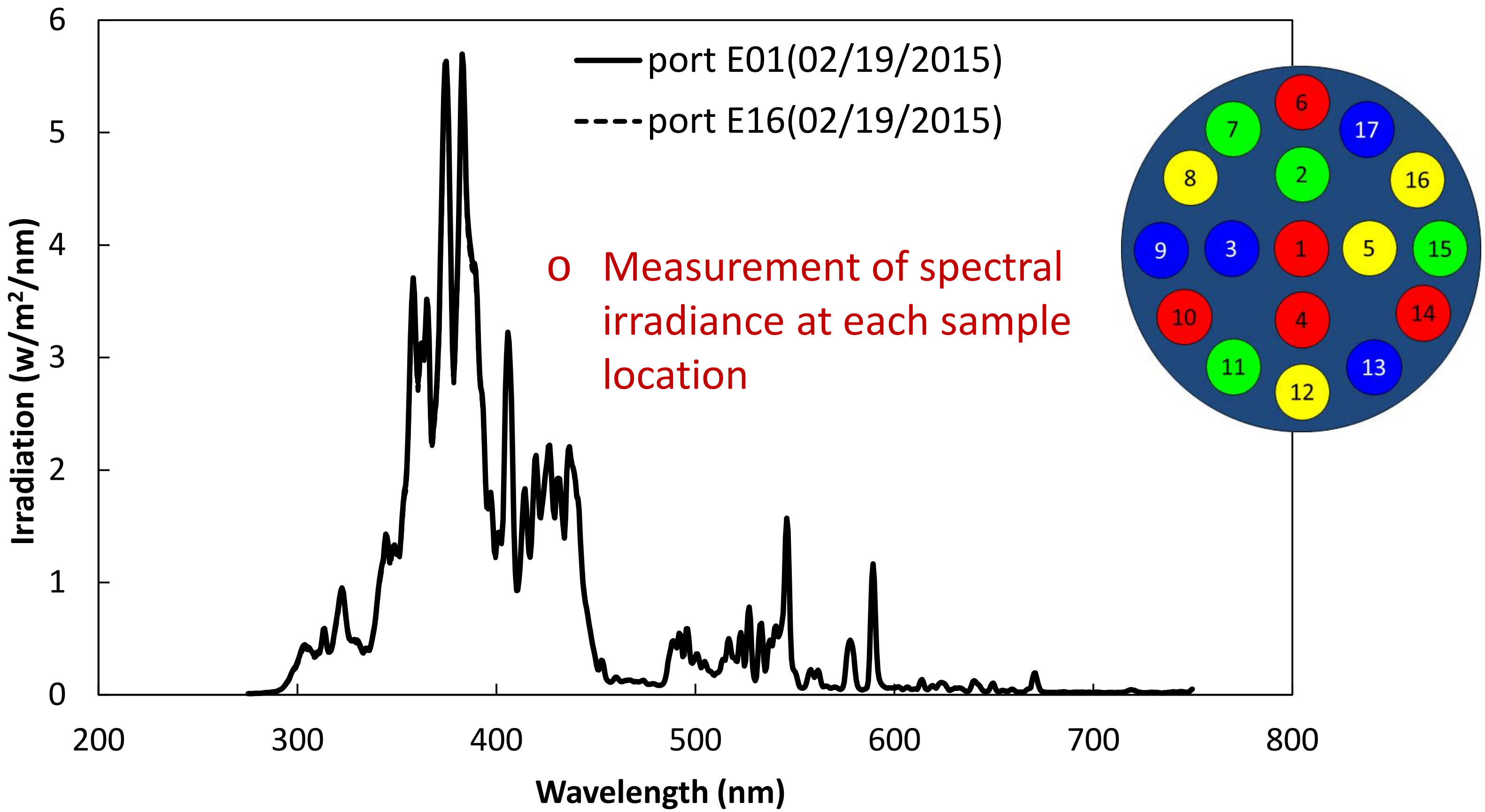
Exposure of Samples in SPHERE Environmental Chambers

- Closed chamber

- Chamber door open

Sample cover with heating pad. The sample is held inside.

A Typical Spectral Irradiance Distribution of the Light at the Sample Position in SPHERE Environmental Chambers

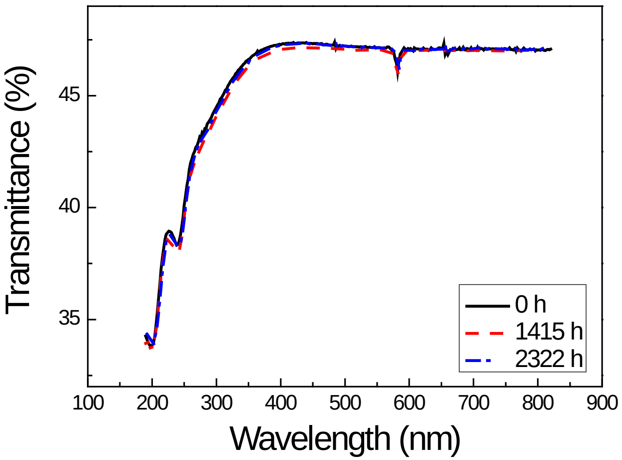


- Measurement of spectral irradiance at each sample location

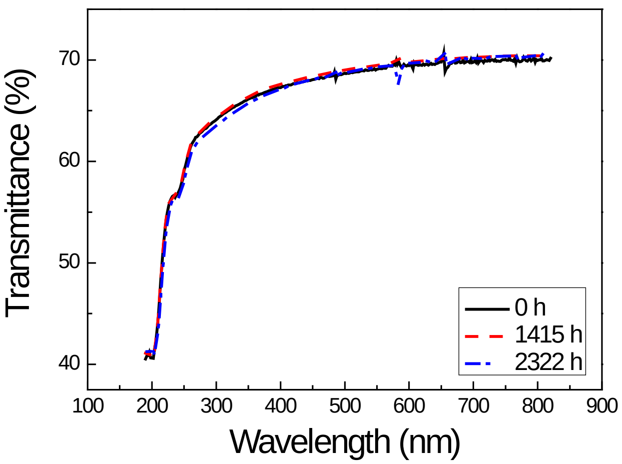
➢ For quantitative study such as reciprocity and action spectrum, the accurate measurement of the spectral irradiance that sample received/absorbed is crucial to the quality of the results.

Stability of Neutral Density Filters during UV Exposure at 85 °C/0 % RH

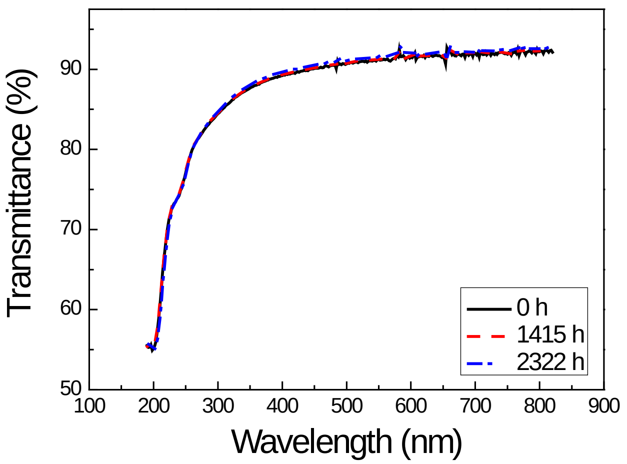
UV-vis Transmittance, 40% ND



UV-Vis Transmittance, 60% ND



UV-Vis Transmittance, 80% ND



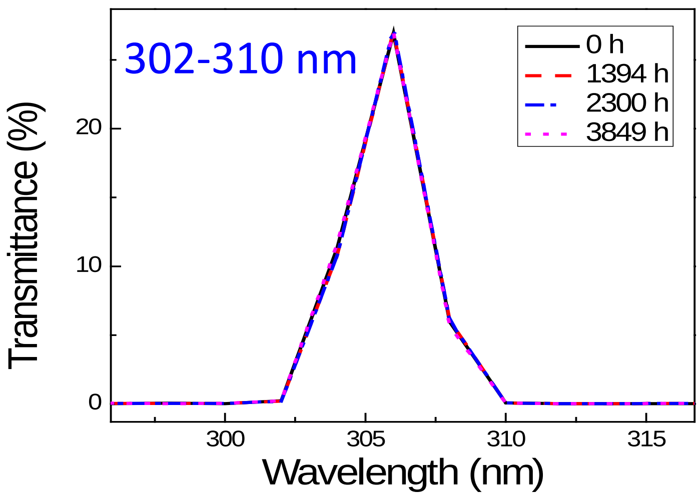
- ND filters are essentially stable during UV exposure at 85 °C/dry on the SPHERE so far.

Stability of Band Pass Filters during UV Exposure

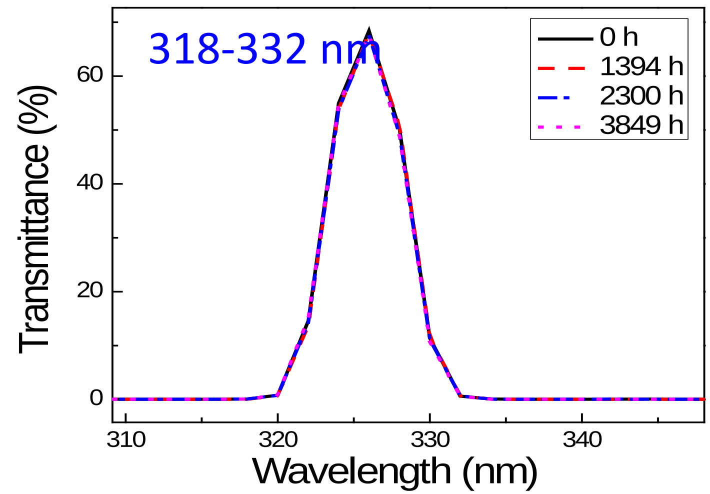
UV-Vis Spectra

85 °C, 0 % RH

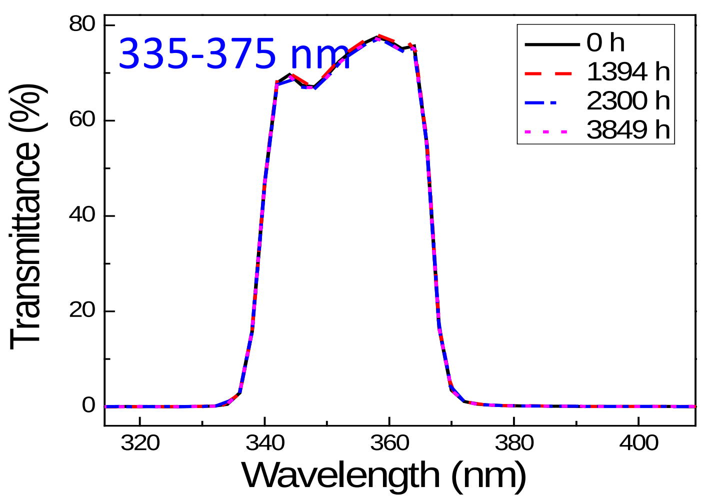
306 nm



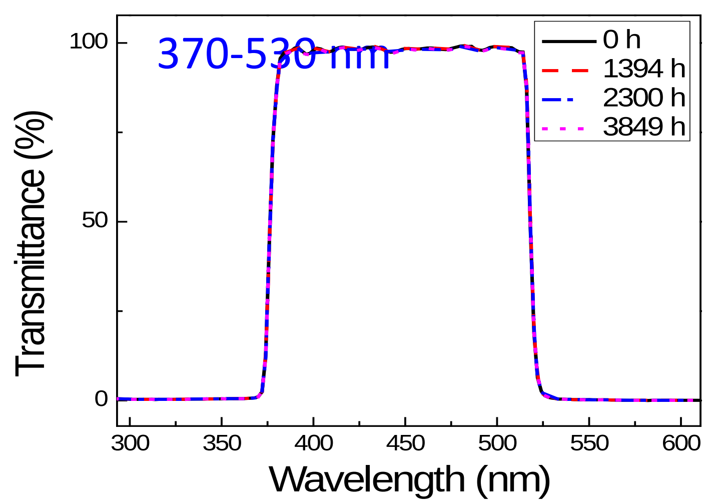
326 nm



354nm



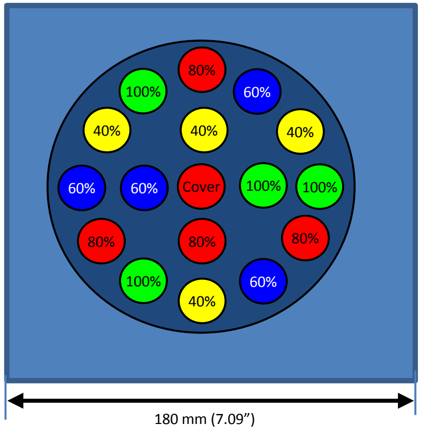
452 nm

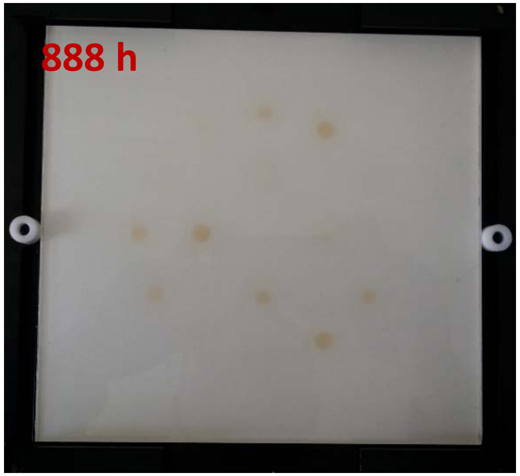


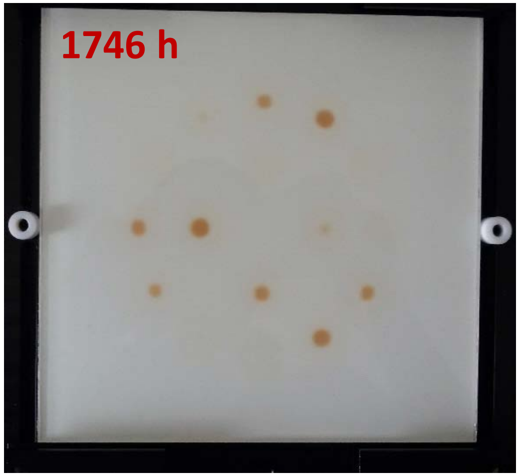
No obvious changes have been observed for these band pass filters at 85 °C/0 % RH on the SPHERE so far.

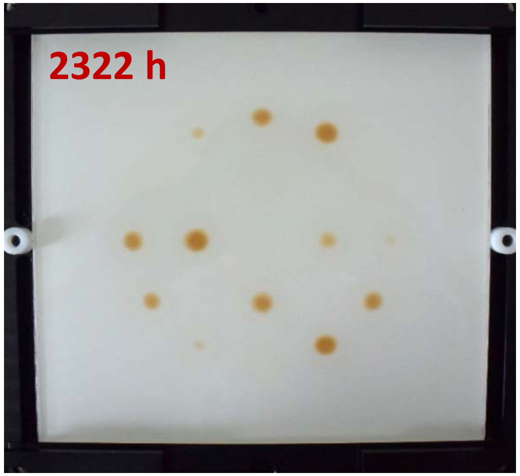
Photos of Samples Exposed to Different Light Intensities with Exposure Time

Reciprocity Study



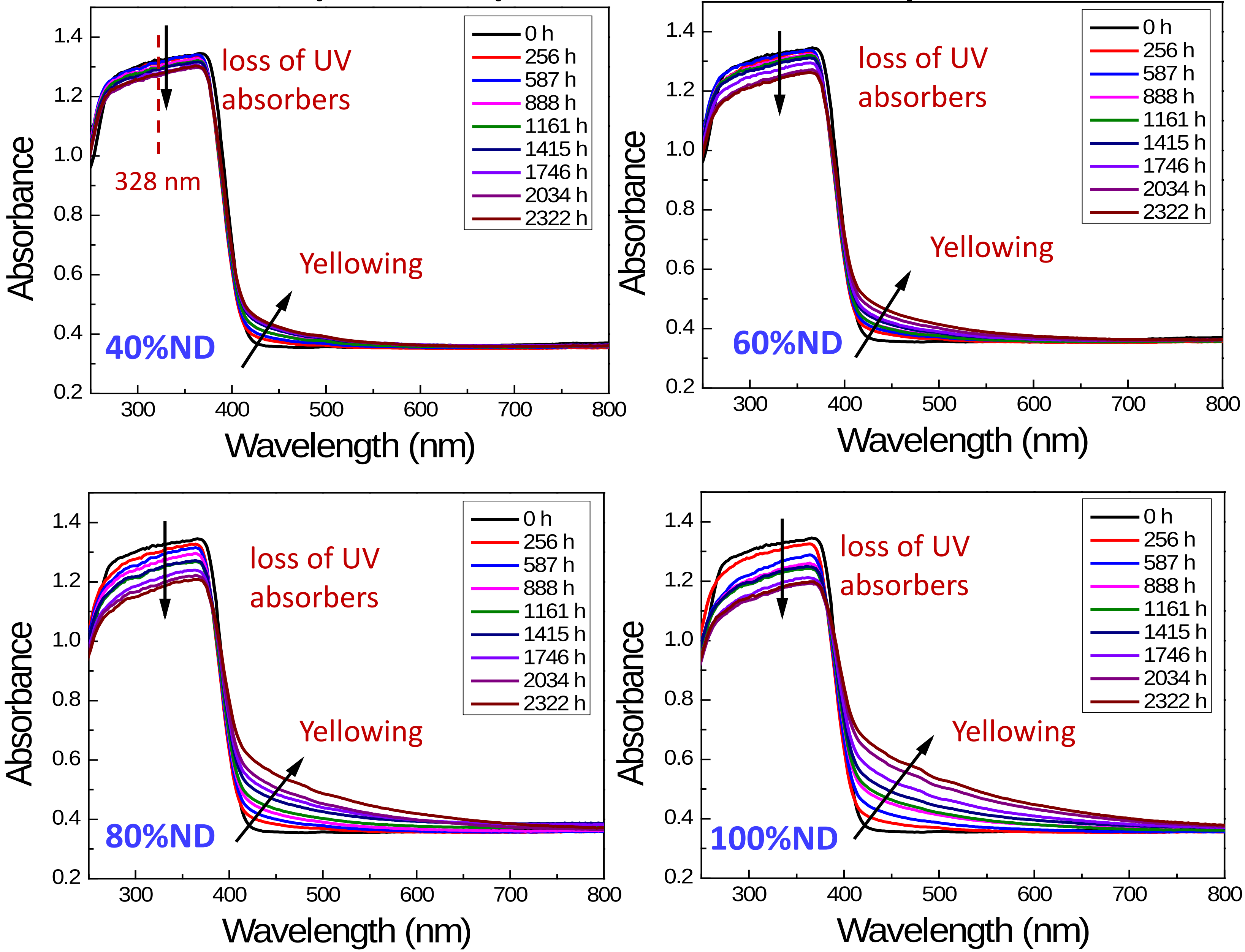






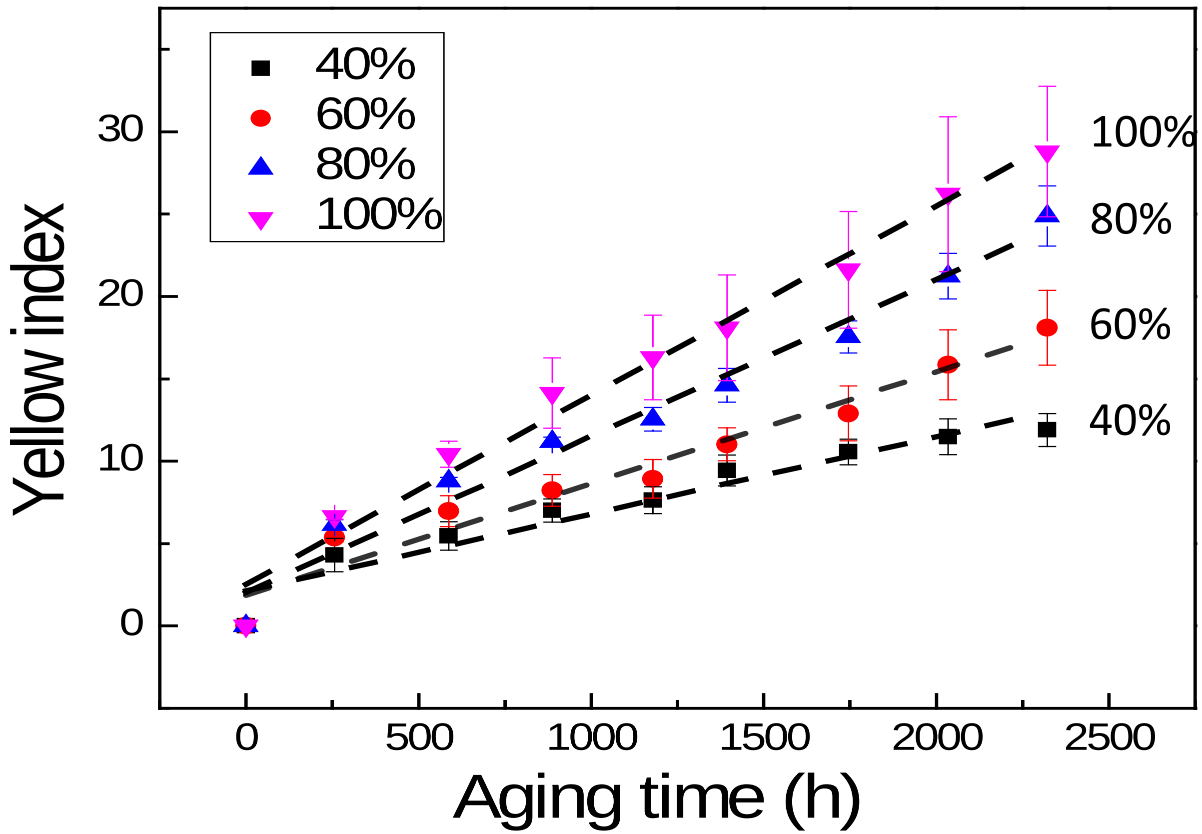
➢ The exposure regions gradually became yellow, while yellow areas basically kept similarly.

UV-Vis Spectra of Specimens at Different Exposure Time



The loss of UV absorbers and the increase in yellow index are observed.

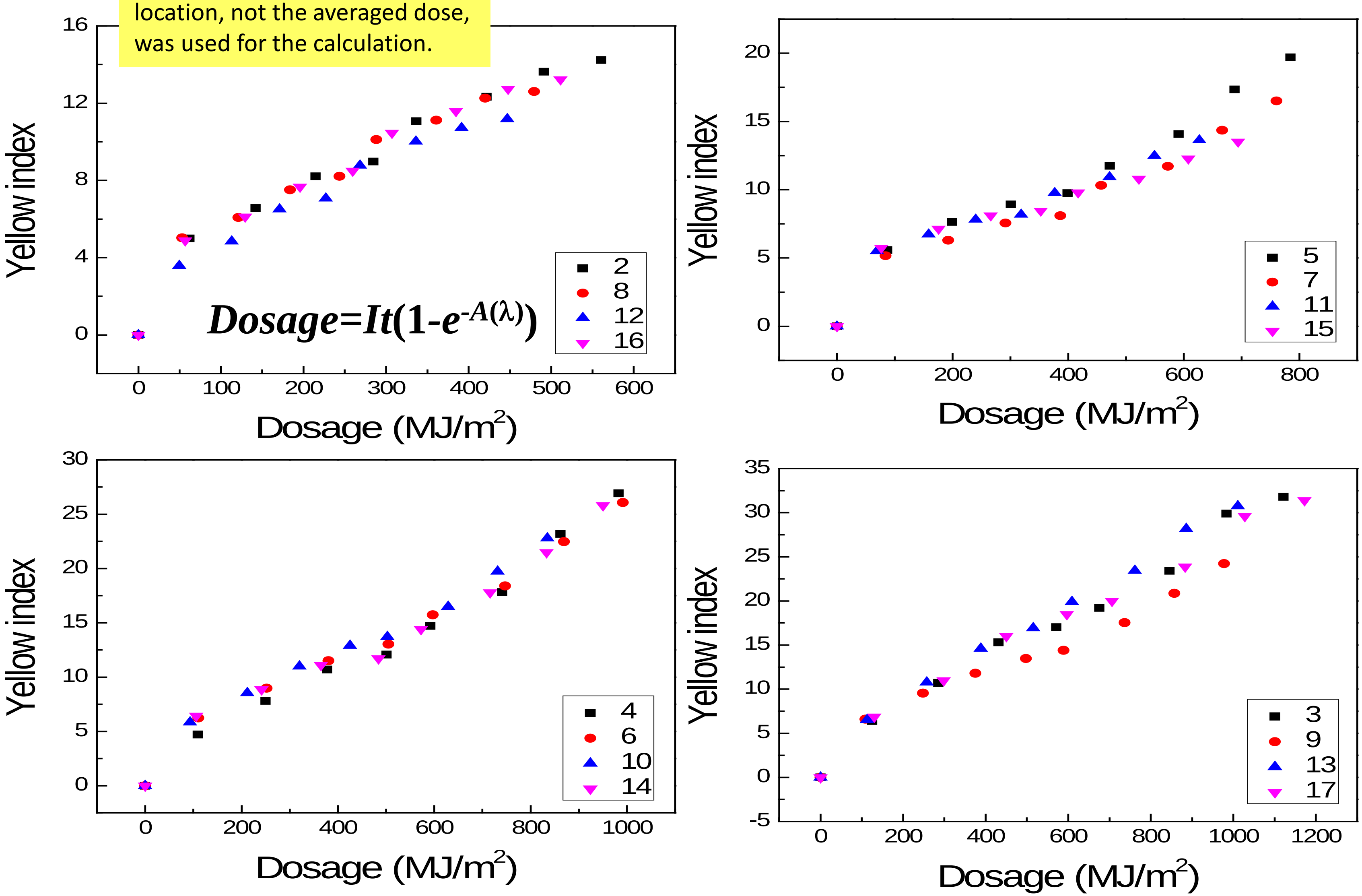
Effect of Light Intensity on Yellowing Index vs. Exposure Time



1) A higher light intensity led to a faster yellowing growth.
2) A quasi-linear relationship was observed for the yellow index-aging time plot.

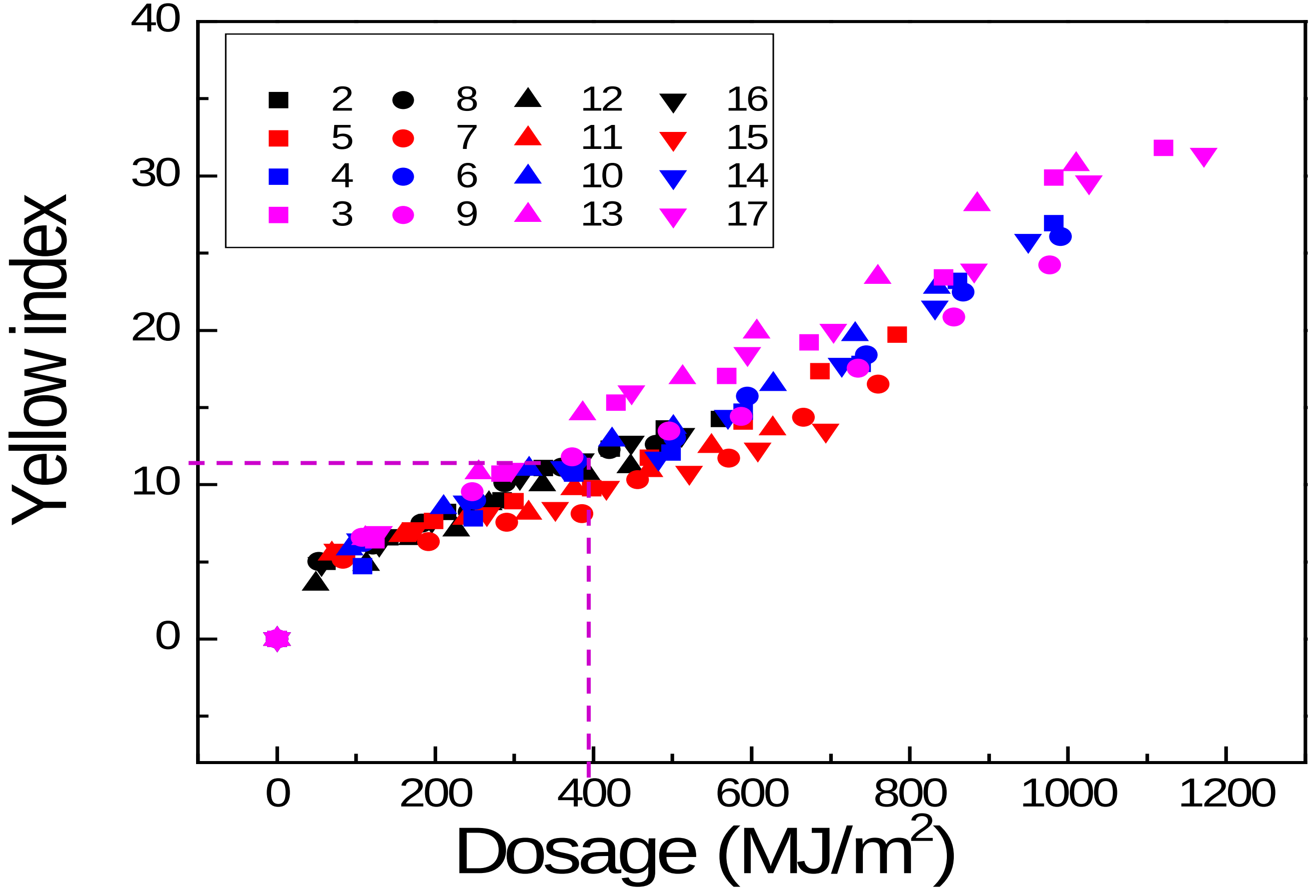
Yellowing Index as a Function of Dosage under Different Light Intensities

The dosage at each sample location, not the averaged dose, was used for the calculation.



The data from the replicates are generally consistent; the deviation could be due to the non-uniformity of the EVA curing and the EVA thickness.

Yellowing Index as a Function of Dose under Different Light Intensities



For a given damage, the required dosage is similar at different light intensities.
– Reciprocity Law seemed to be obeyed.

Validation and Failure of Reciprocity Law

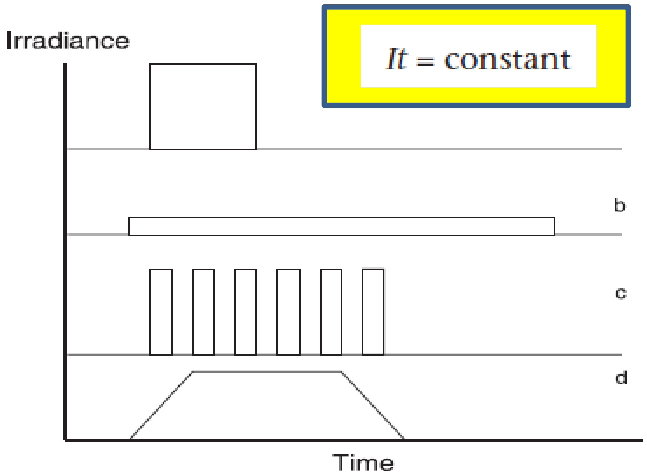


Figure 1—A selection of radiant flux versus exposure time regimes for testing the law of reciprocity in which the dose (integrated area on plot) for each exposure regime is identical. Assuming that the reciprocity law is obeyed, then the photoresponse for each of these exposure regimes should be the same (adapted from reference 6).

Schwarzschild's law and is given by

$$\boxed{It^{p} = \text{constant}} \qquad (2)$$

where p is the Schwarzschild coefficient, hereafter referred to as the p-coefficient. Note that when $p = 1$, Schwarzschild's law and the reciprocity law are identical and hence,

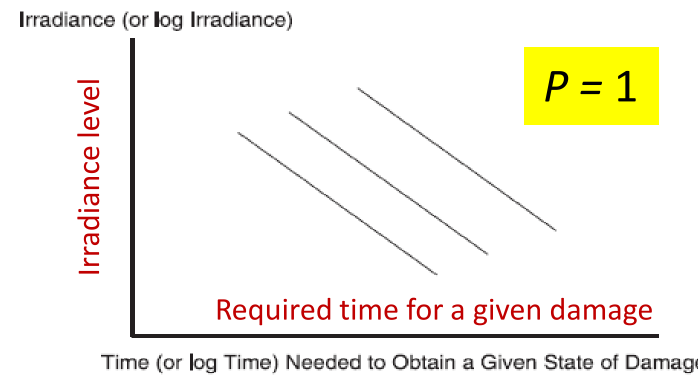


Figure 3—Plot of irradiance (or log irradiance) versus time (or log time) needed to achieve a given photoresponse (adapted from reference 17).

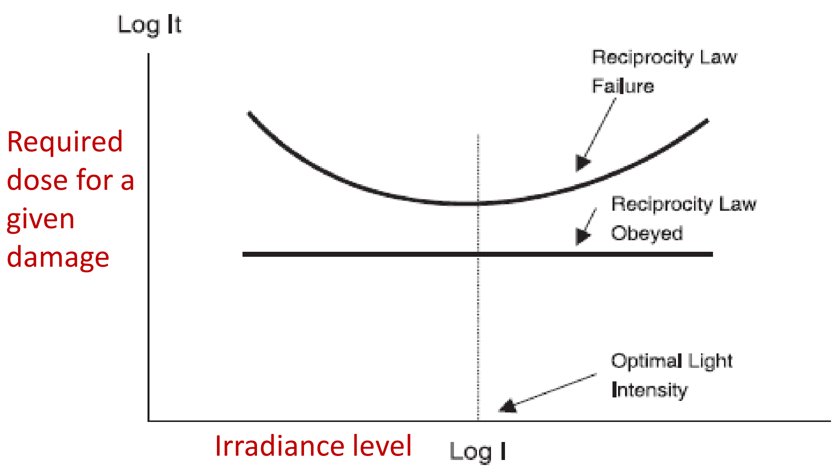
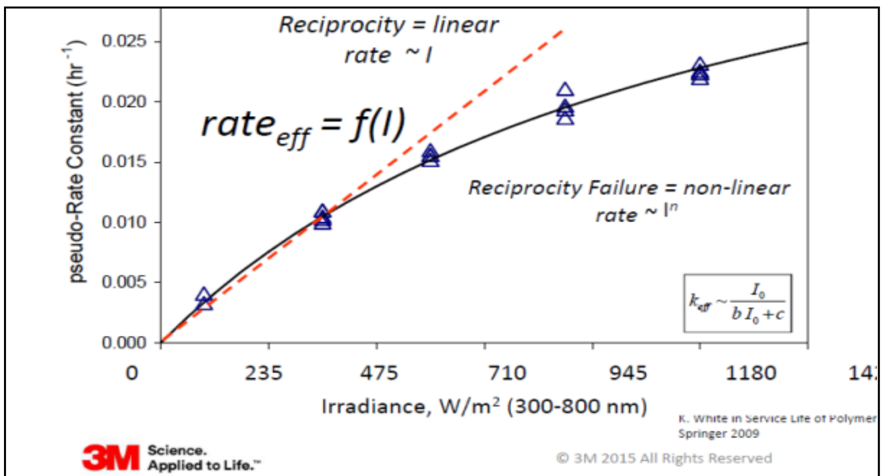


Figure 2—Kron's graphical method for presenting reciprocity data in which the logarithm of dose (irradiance x time) necessary to produce a given photoresponse is plotted against the logarithm of irradiance (adapted from reference 13).

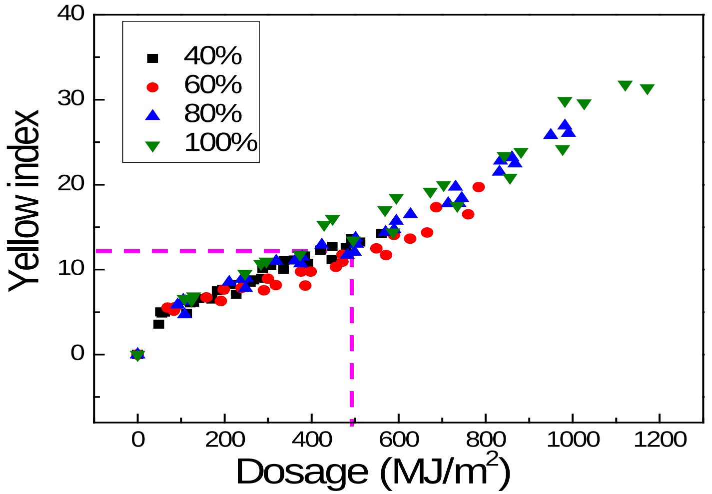


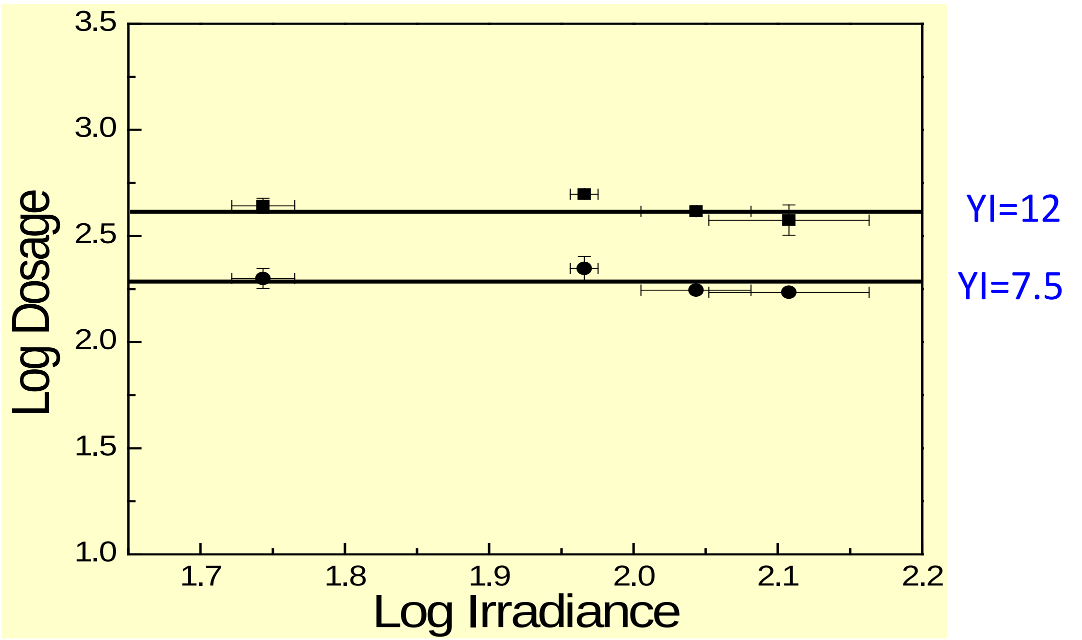
Burns, D. NIST SPI Workshop (2015)

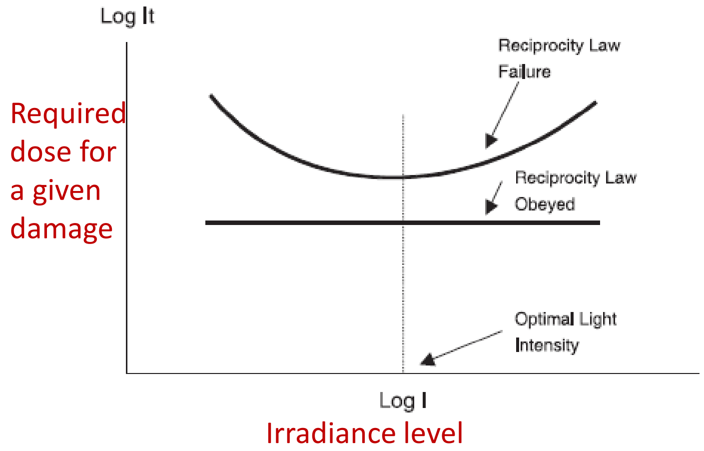
Validation of Reciprocity Law

Required Dose for a Given Damage vs. Irradiance Intensity

More degradation???



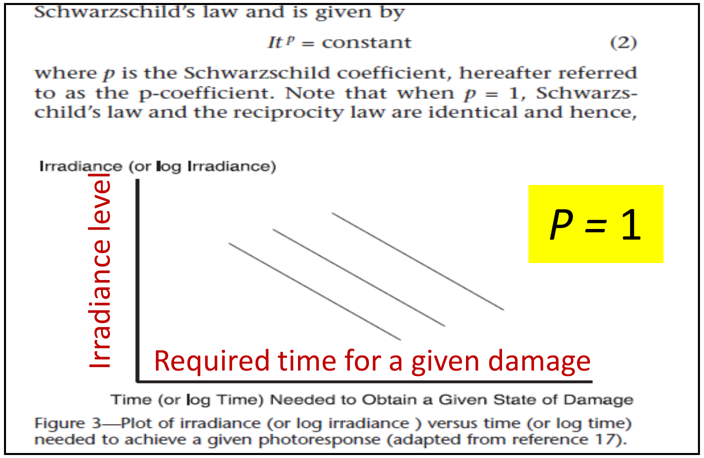


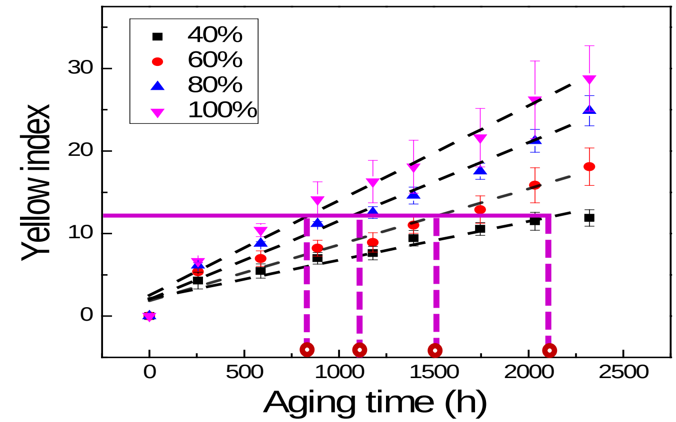


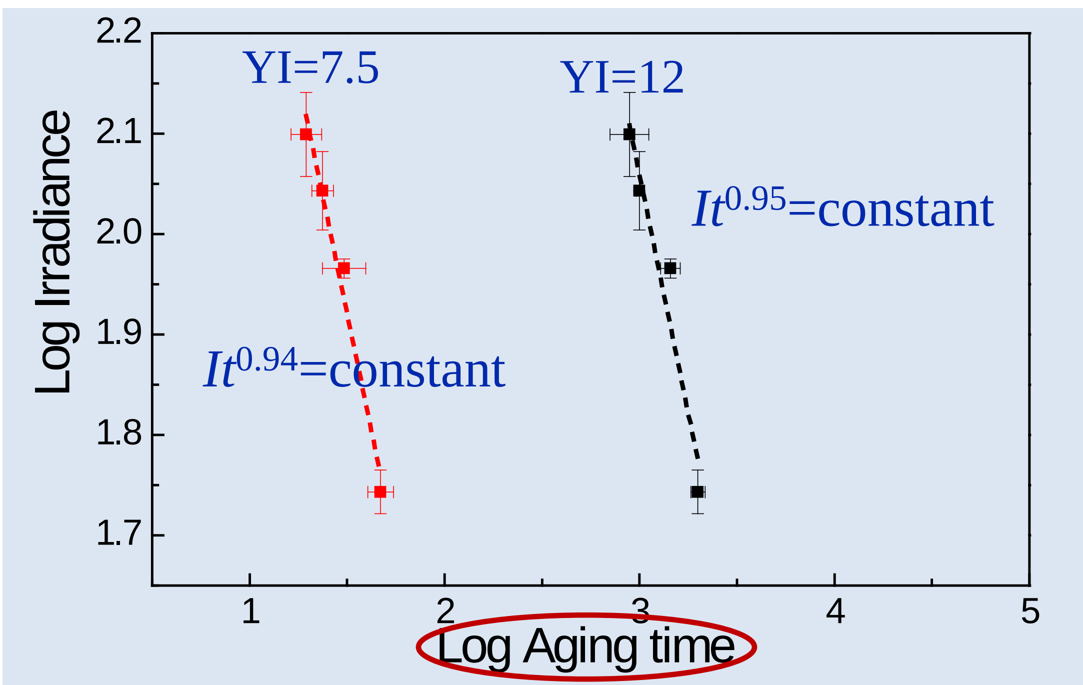
The needed dose appeared to be constant, regardless of light intensity.

Validation of Reciprocity Law

Irradiance vs. Time Required to Reach a Specific Change







It^p=constant

$P=0.94$

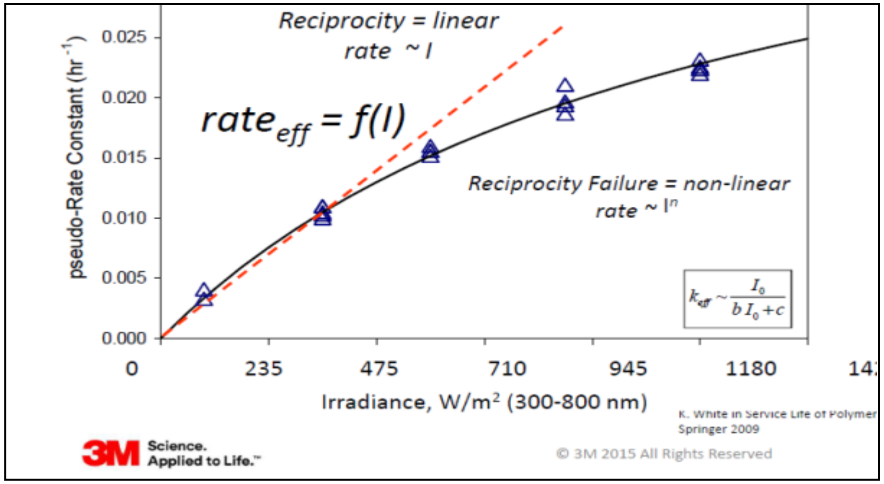
$P=0.95$

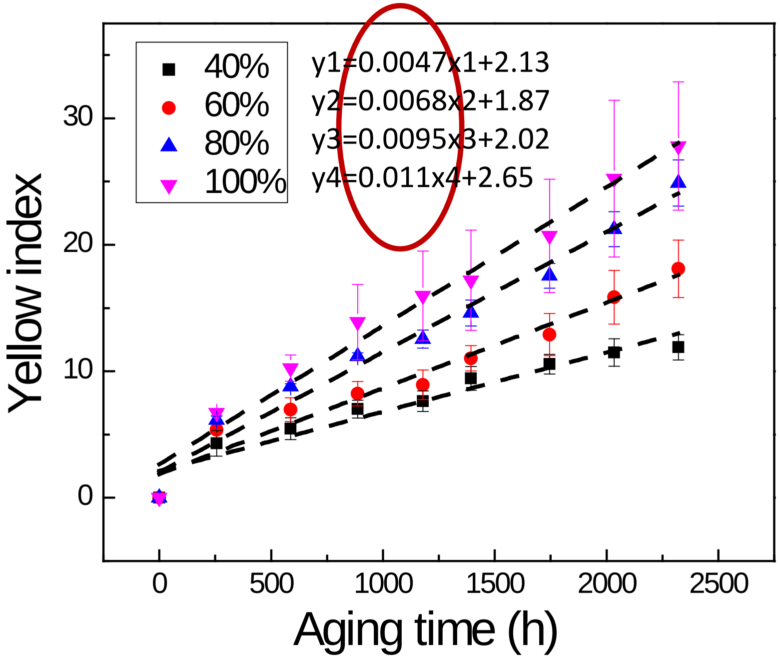
$p \approx 1$

Reciprocity Law appeared to be obeyed.

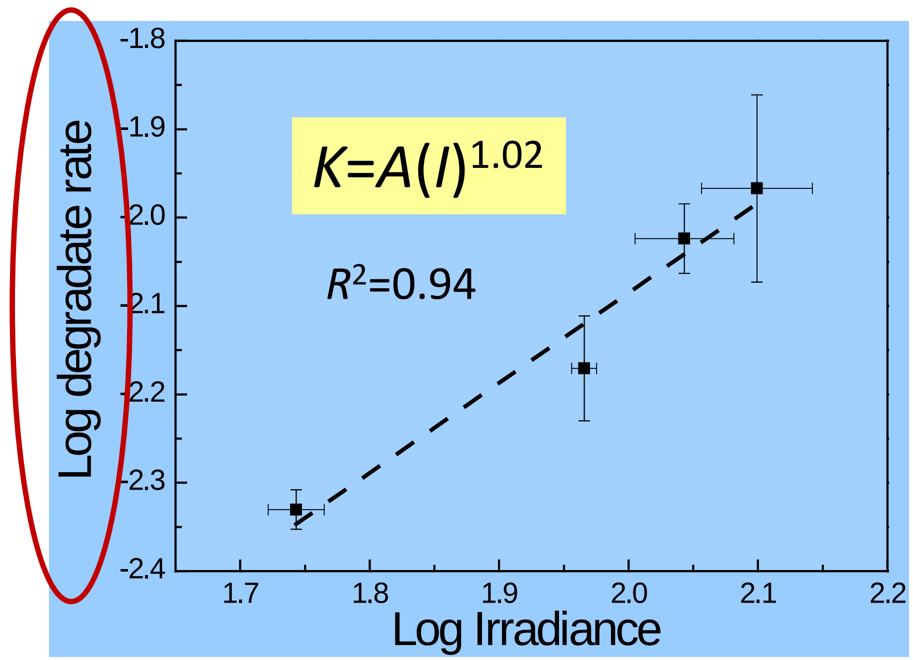
Validation of Reciprocity Law

Irradiance Dependence of Pseudo-rate Constant





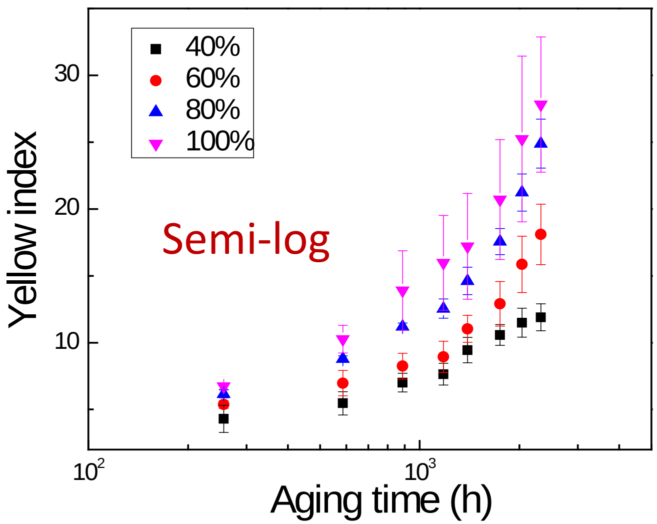
Pseudo-rate constant is defined as the slope of yellow index vs. time curve in this study (Assuming a linear relationship between yellow index and aging time)

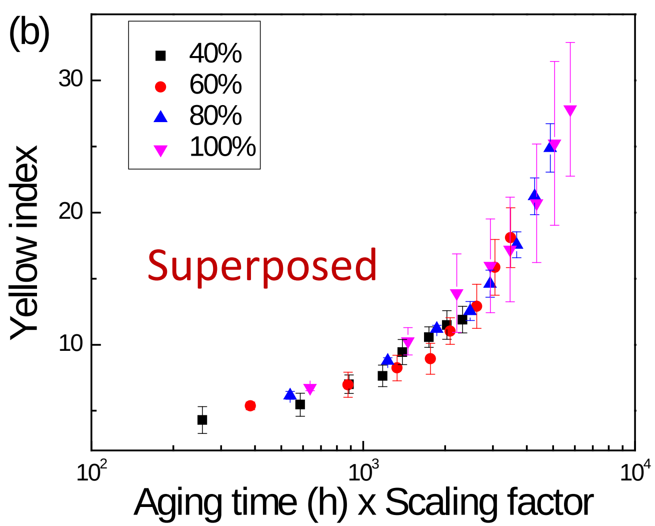


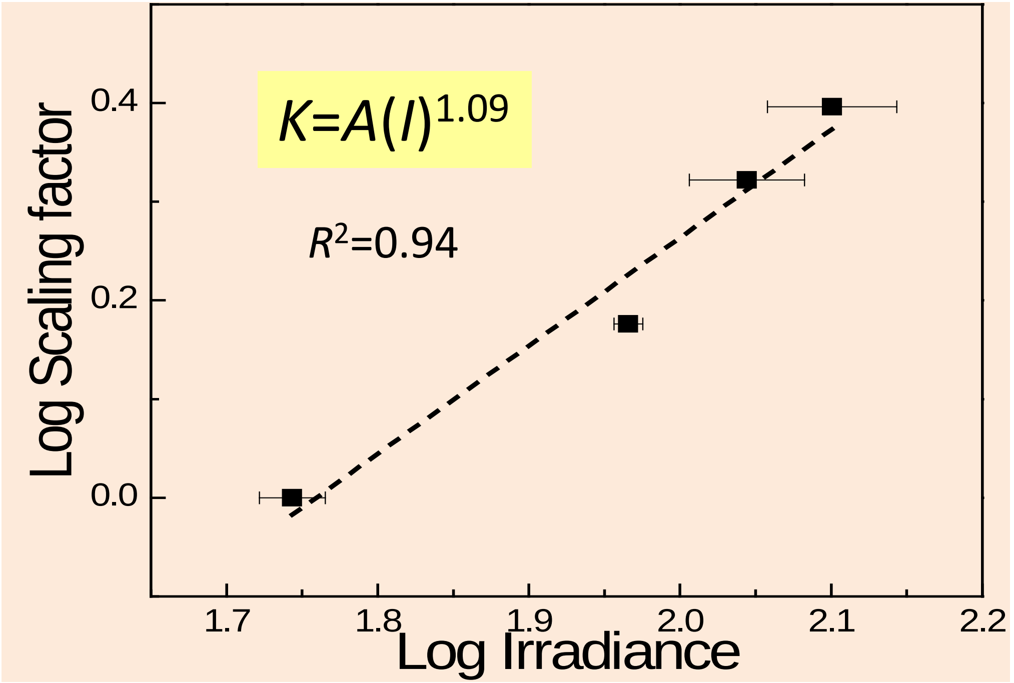
Reciprocity Law appeared to be obeyed.

Validation of Reciprocity Law

Irradiance Dependence of Scaling Factor



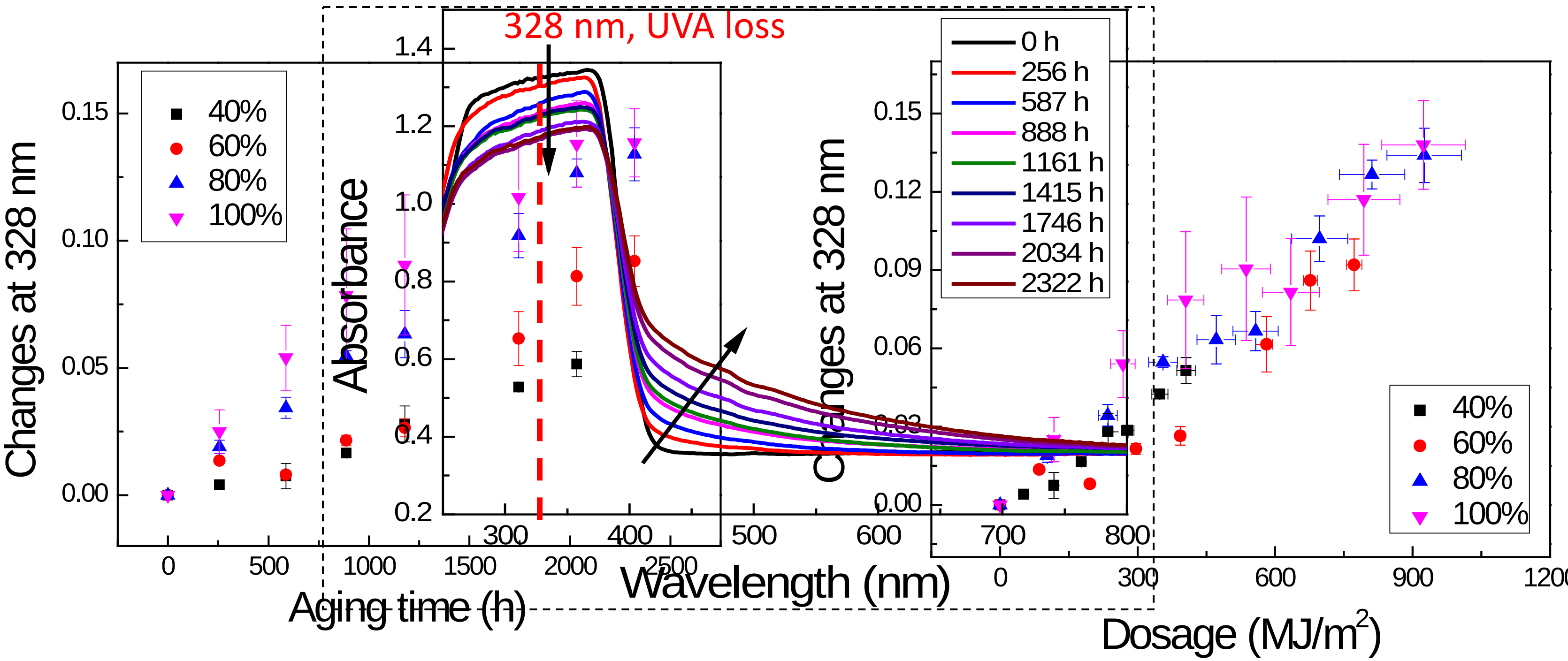




✓ **Reciprocity Law appeared to be obeyed.**

- Based on the current exposure data, the Reciprocity Law appeared to be obeyed for the growth of yellowing index of the Glass/EVA/PPE laminated system exposed to SPHERE at 85 °C/dry.

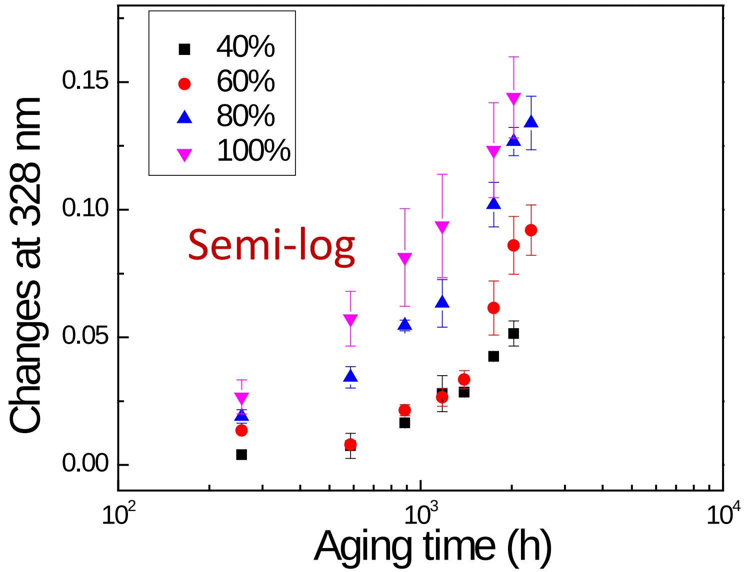
Effect of Light Intensity on the Loss of UV-absorbers (@328 nm)

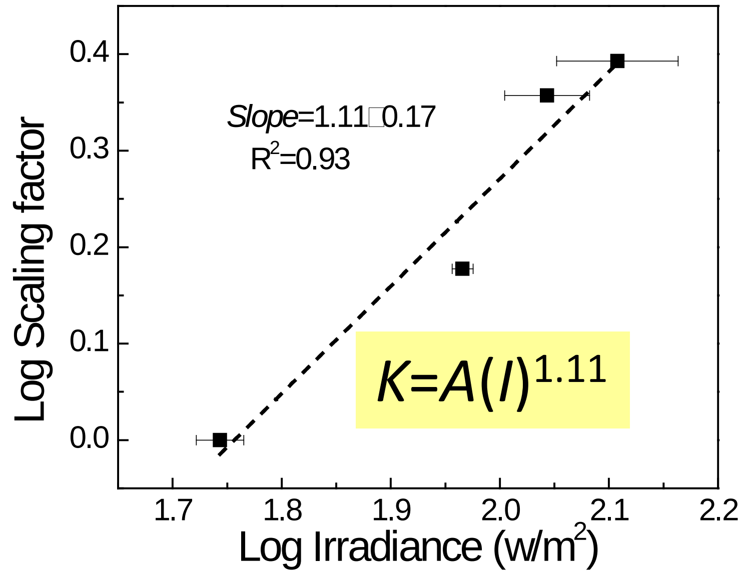


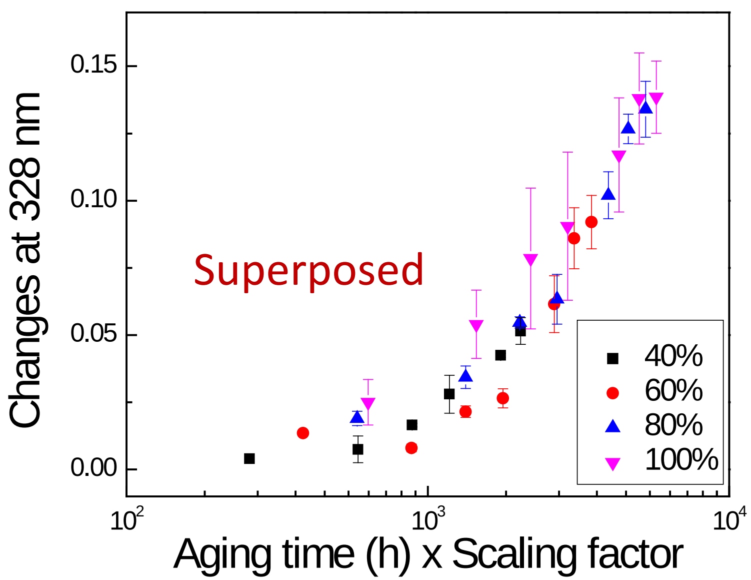
- Changes of UV absorption at 328 nm increased with longer exposure time.
- A higher light intensity led to a higher rate per time for the loss of UVA.
- When plotting absorbance with dosage, deviations became smaller between different light intensities.

Validation of Reciprocity Law

Irradiance Dependence of Scaling Factor

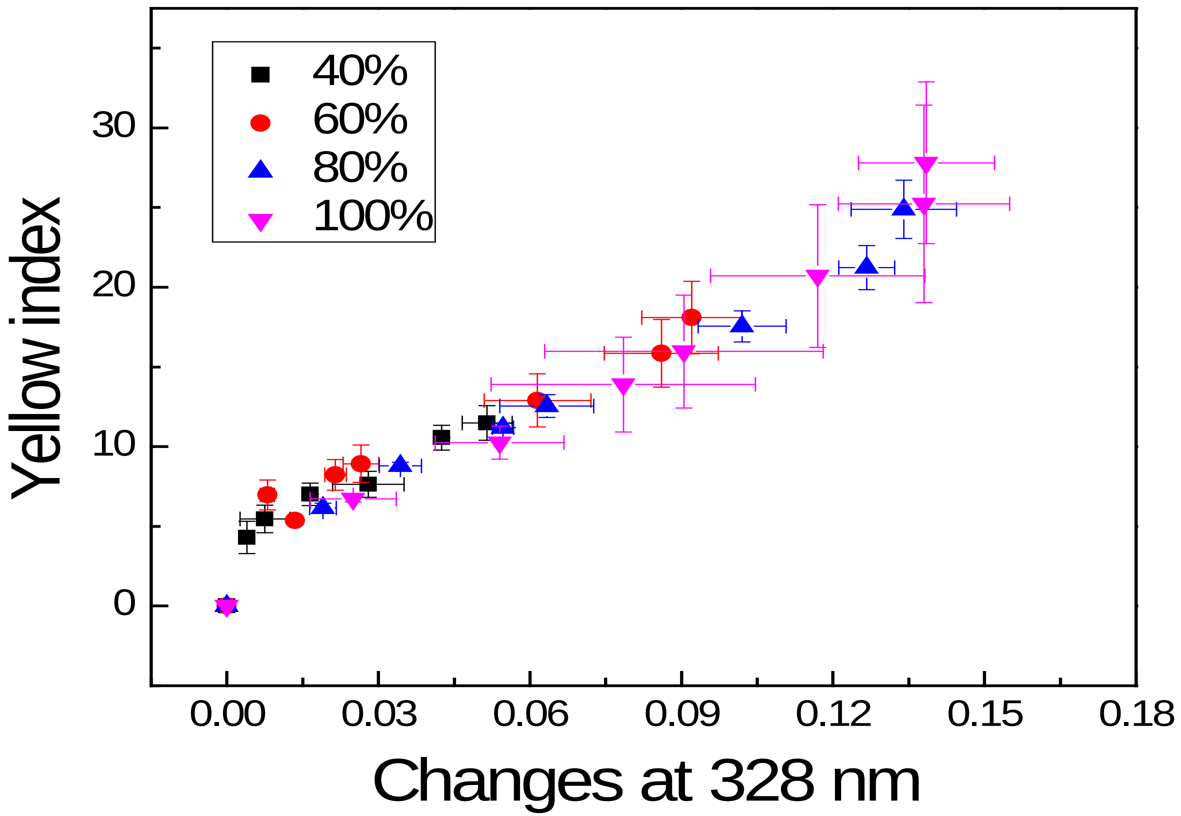






✓ **Reciprocity Law appeared to be obeyed for irradiance dependence of UVA loss.**

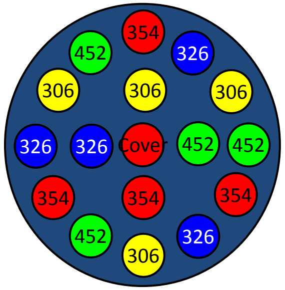
Correlation between Yellowing Index and Loss of UV Absorbers under Different Light Intensities

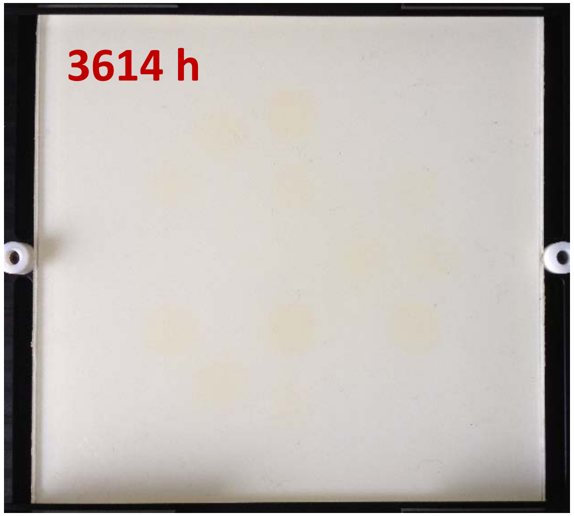


- **Increase in Yellow index is correlated well with loss of UV absorber, regardless of light intensities.**

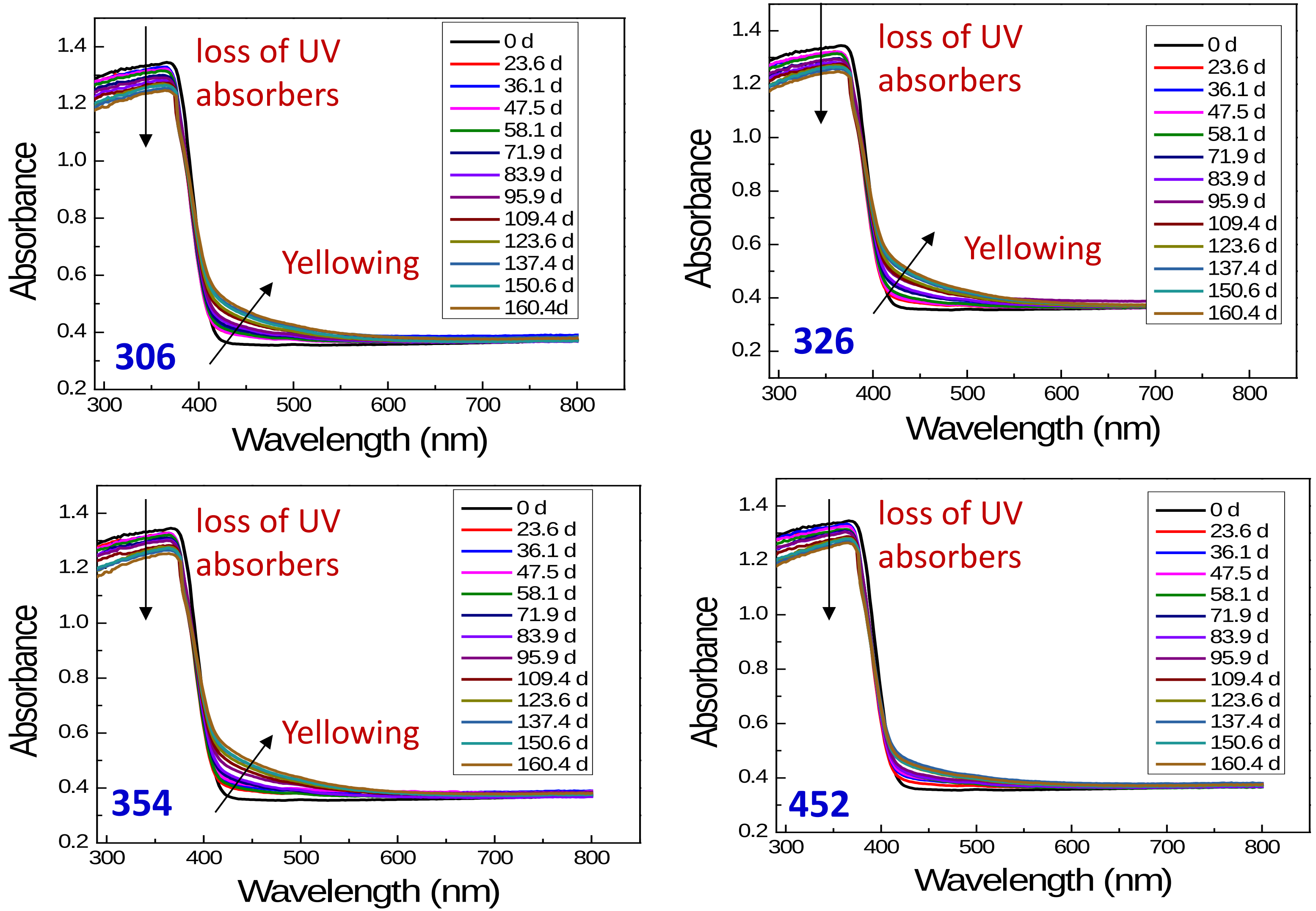
Photos of Samples Exposed to Different Wavelengths with Exposure Time

(306, 326, 354, 452 nm)





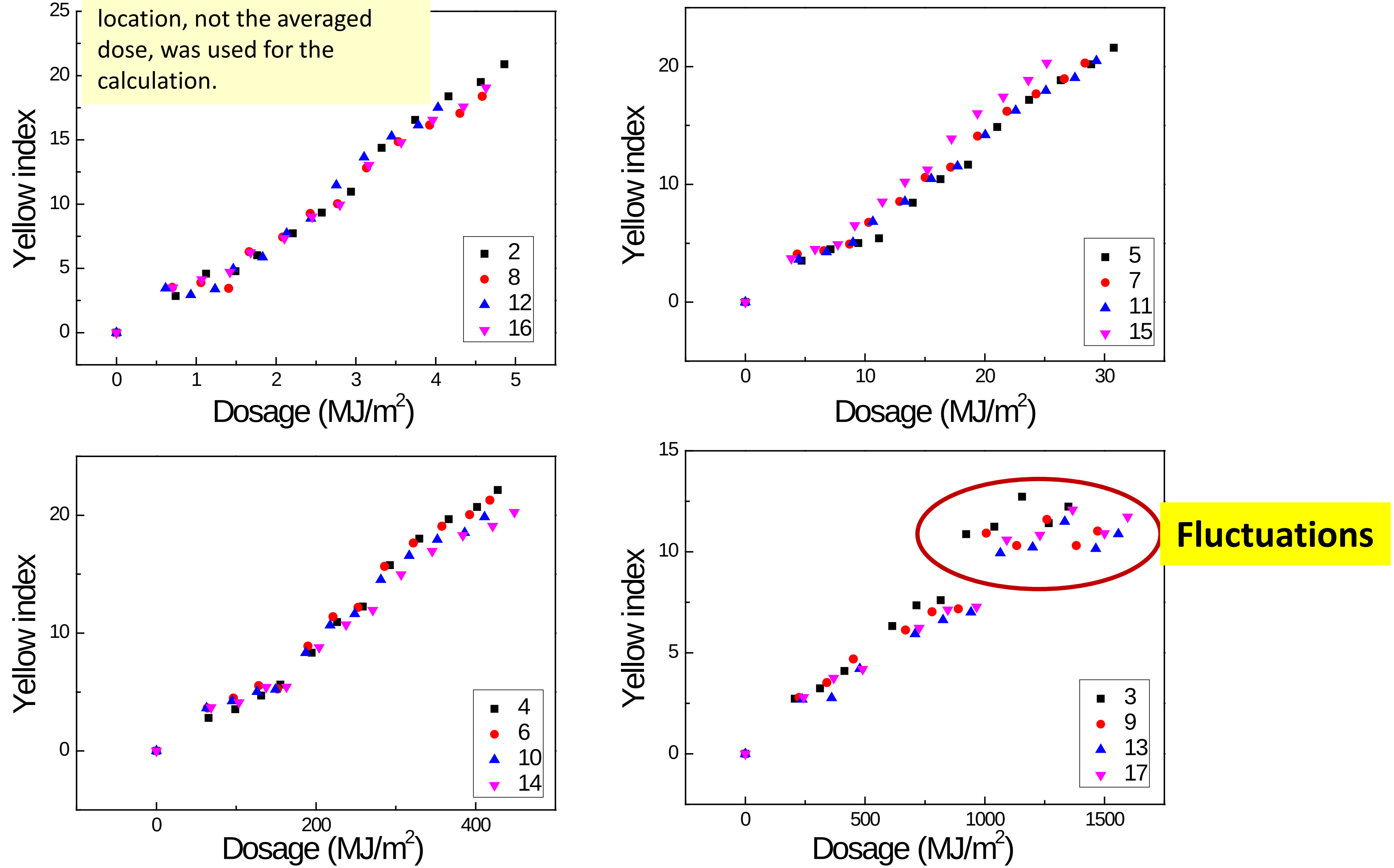
There was no distinguished change in the appearance at beginning ; regions under wavelengths of 306 nm, 326 nm and 354 nm gradually became yellow after 2500 h.



- Loss of UV absorbers and growth of yellowing increased over time under 306, 326 and 354 nm.
- The increase in yellowing index under 452 nm slowed down at late stage, probably due to the dominant photobleaching at longer wavelength.

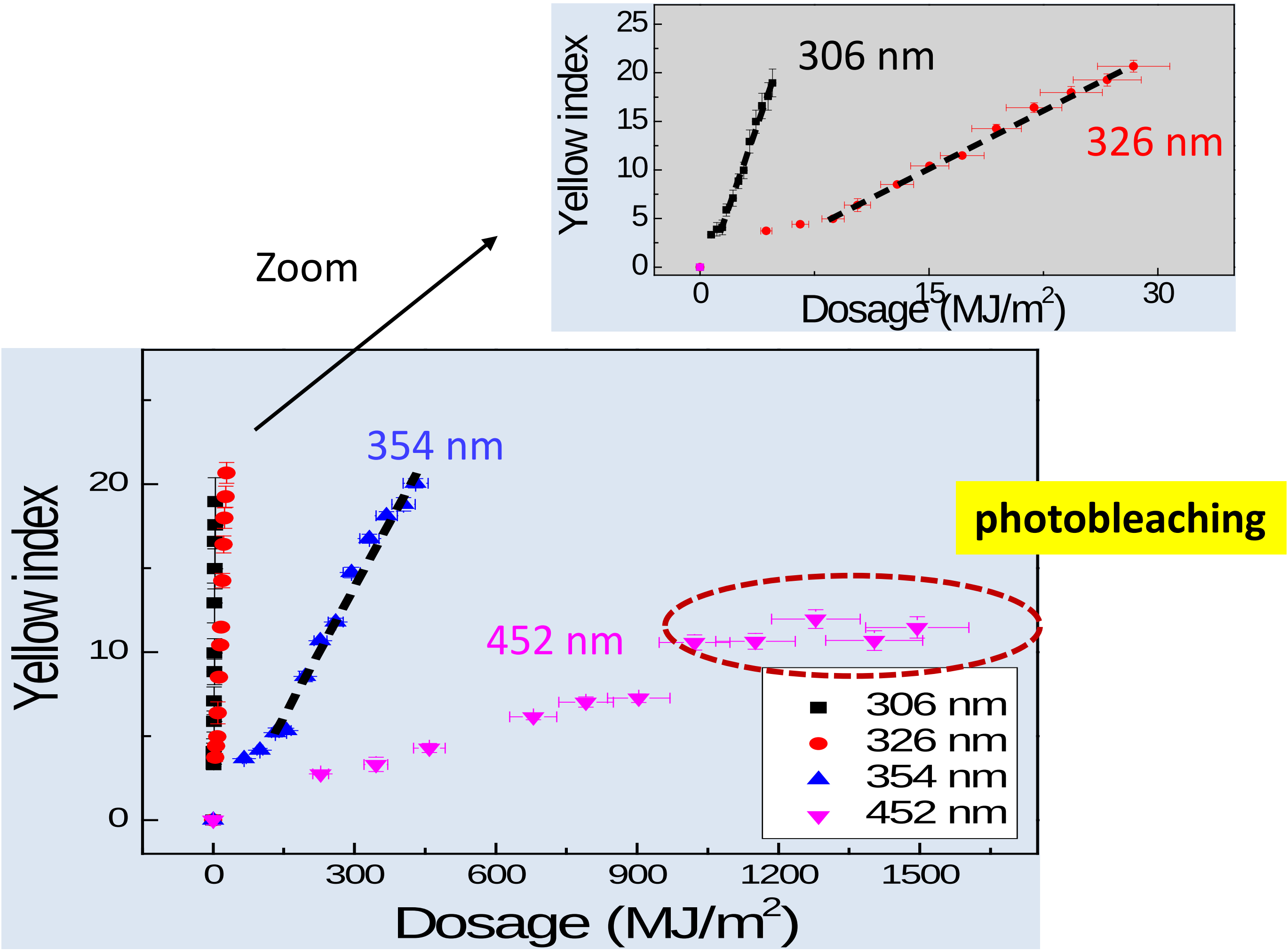
Yellowing Index as a Function of Dosage under Different Wavelengths

The dose at each sample location, not the averaged dose, was used for the calculation.



The data from the replicates are generally consistent; the deviation could be due to the non-uniformity of the EVA during curing.

Averaged Yellow Index vs. Dose For Different Wavelengths

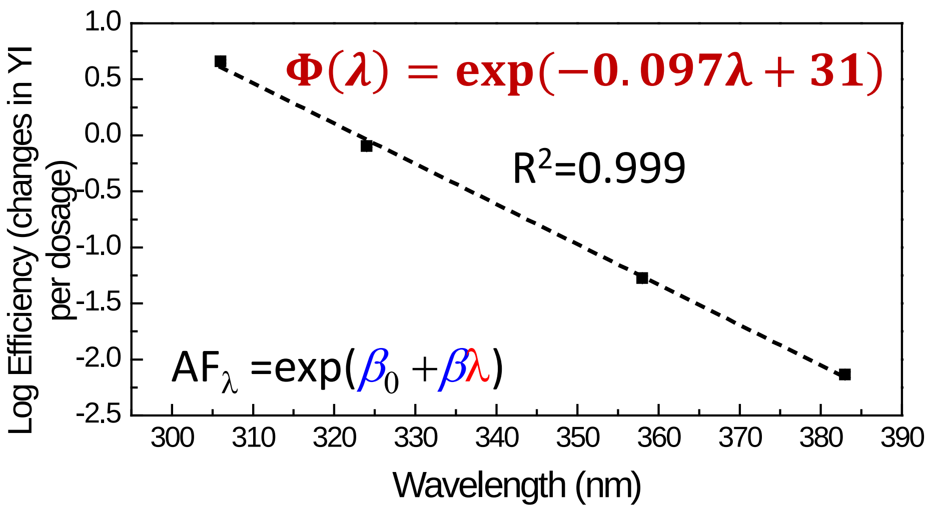


- ✓ Shorter wavelength leads to a higher yellow growth at same dosage.
- ✓ Increase of YI under 452 nm slowed down and then fluctuated at late stage, indicating a photobleaching effect.

Relative Efficiency of Different Wavelengths
(based on Yellowing vs. Dose)

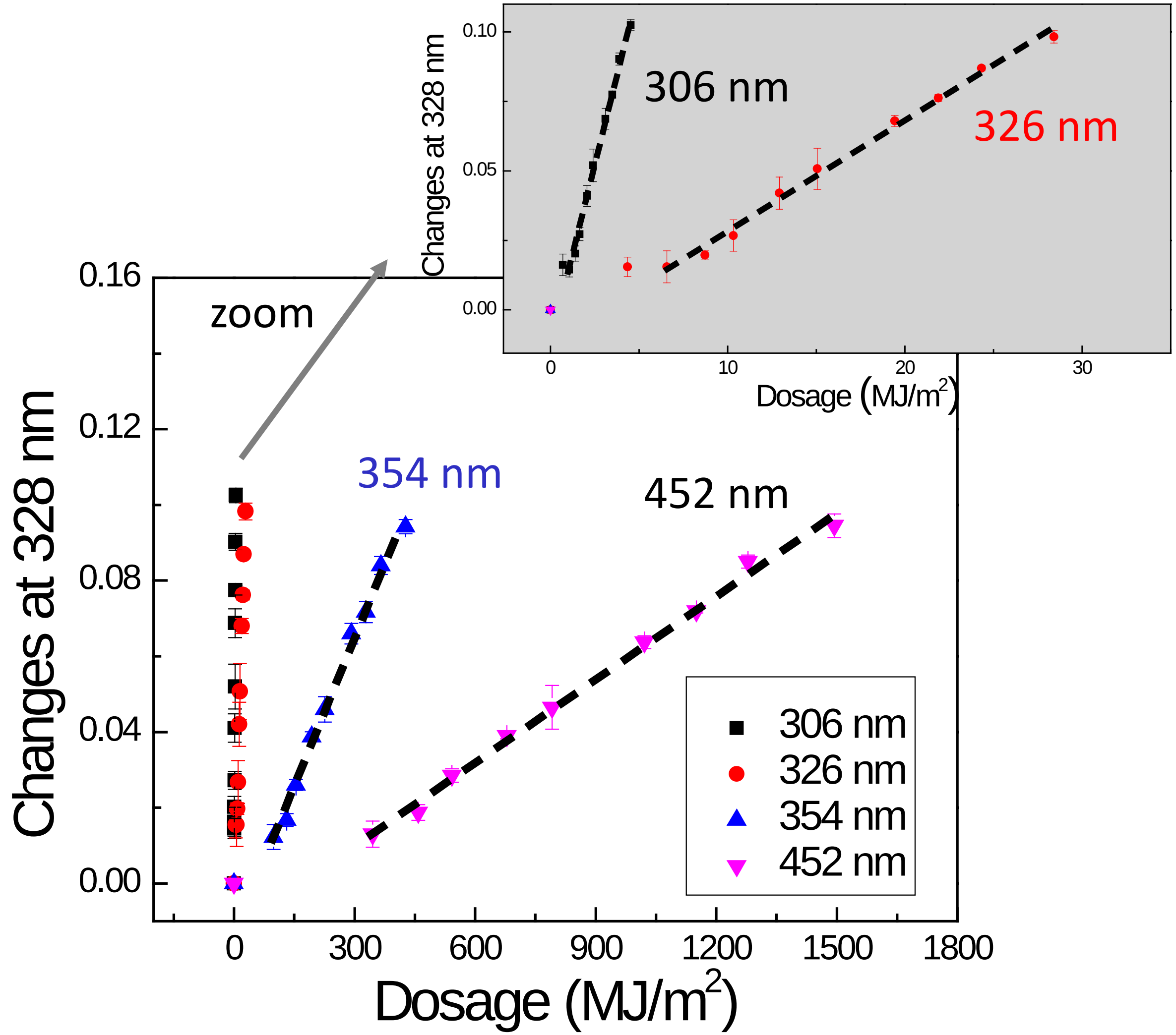
Wavelength (nm)	Pseudo-rate constant (m^2/MJ)	Relative Efficiency 1	Relative Efficiency 2
306	4.56	580.9	86.0
326 (324)	0.80	101.9	15.1
354 (358)	0.053	6.7	1
452 (383)	0.0079	1	-

Action Spectrum for increase in YI



- An exponential dependence between efficiency and wavelength was obtained.

UV Absorbance at 328 nm vs. Dosage for Different Wavelengths

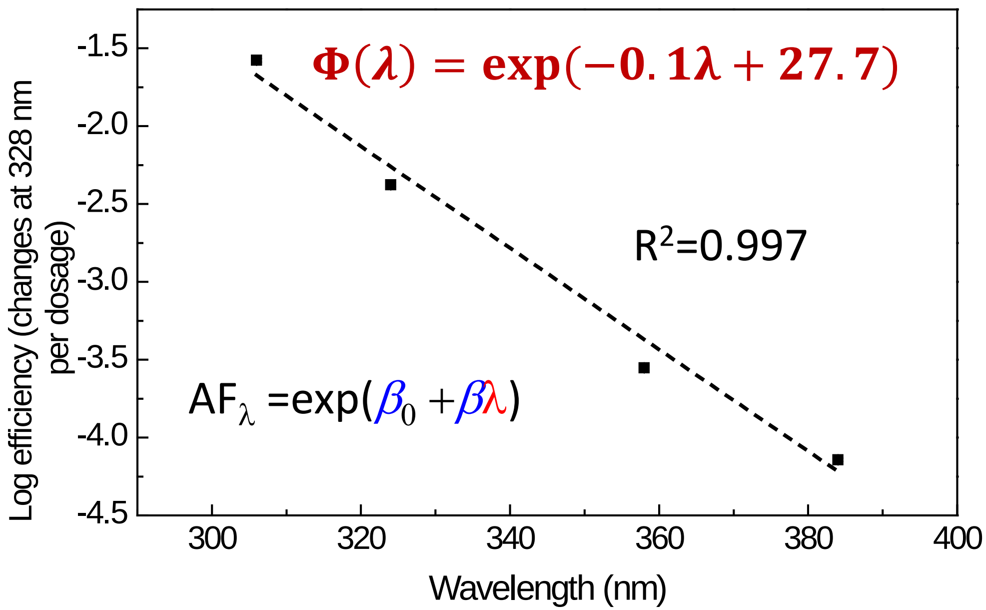


- UV loss increased with the increase in the UV exposure time.
- The rate of UV absorbance loss depended on the wavelength. The shorter wavelength, the higher rate per dosage.

Relative Efficiency of Different Wavelengths
(based on UV absorbance loss vs. Dose)

Wavelength (nm)	Pseudo-rate constant (m^2/MJ)	Relative Efficiency 1	Relative Efficiency 2
306	0.0265	368	94
326 (324)	0.0042	58	15
354 (358)	0.00028	3.9	1
452 (383)	0.000072	1	-

Action Spectrum for Loss of UVA



- The relative efficiencies of loss of UV absorptions in terms of 306 nm, 326 nm and 354 nm is consistent with those of YI.

Relative Efficiency of Different Wavelengths
(based on UV absorbance loss vs. Dose)

Wavelength (nm)	Pseudo-rate constant (m^2/MJ)	Relative Efficiency 1	Relative Efficiency 2
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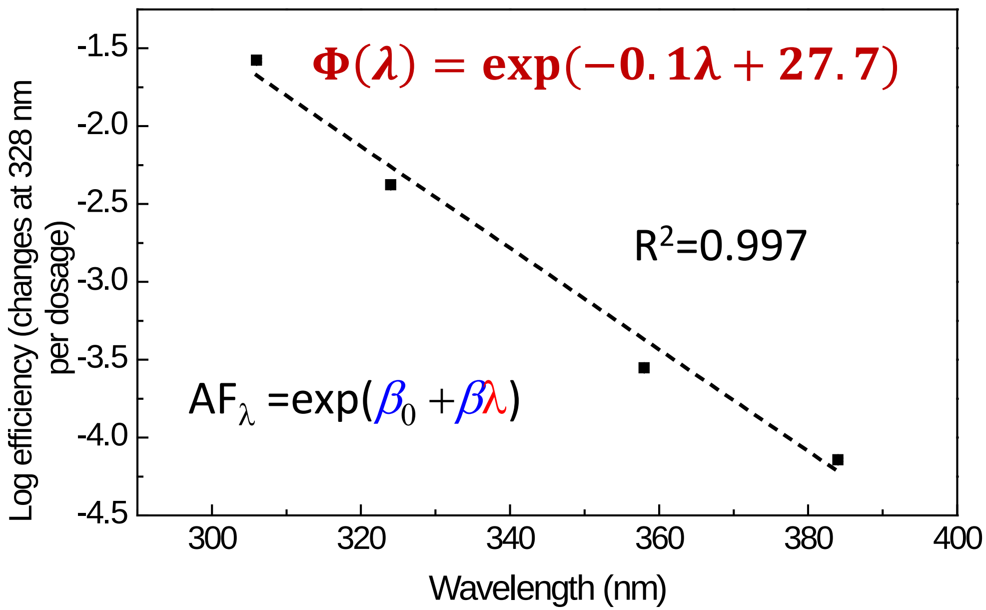
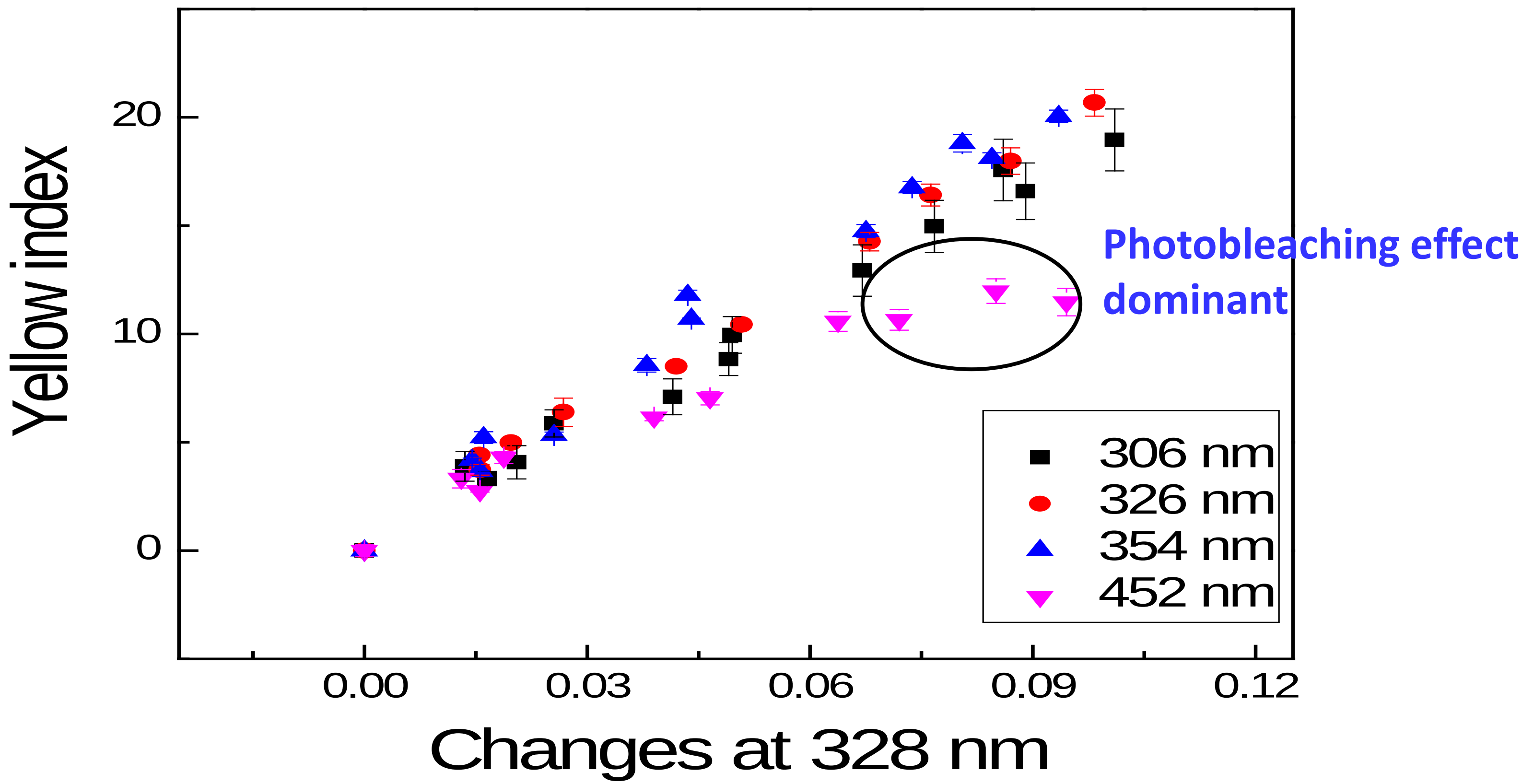
Action Spectrum for Loss of UVA



- The relative efficiencies of loss of UV absorptions in terms of 306 nm, 326 nm and 354 nm is consistent with those of YI.

Correlation between Yellowing Index and Loss of UV Absorbers under Different Wavelengths



- ✓ Curves for different wavelengths basically superposed initially (up to about 900 MJ/m^2), then deviation occurred for 452 nm, implying the photobleaching effect overpassed the yellowing growth then.

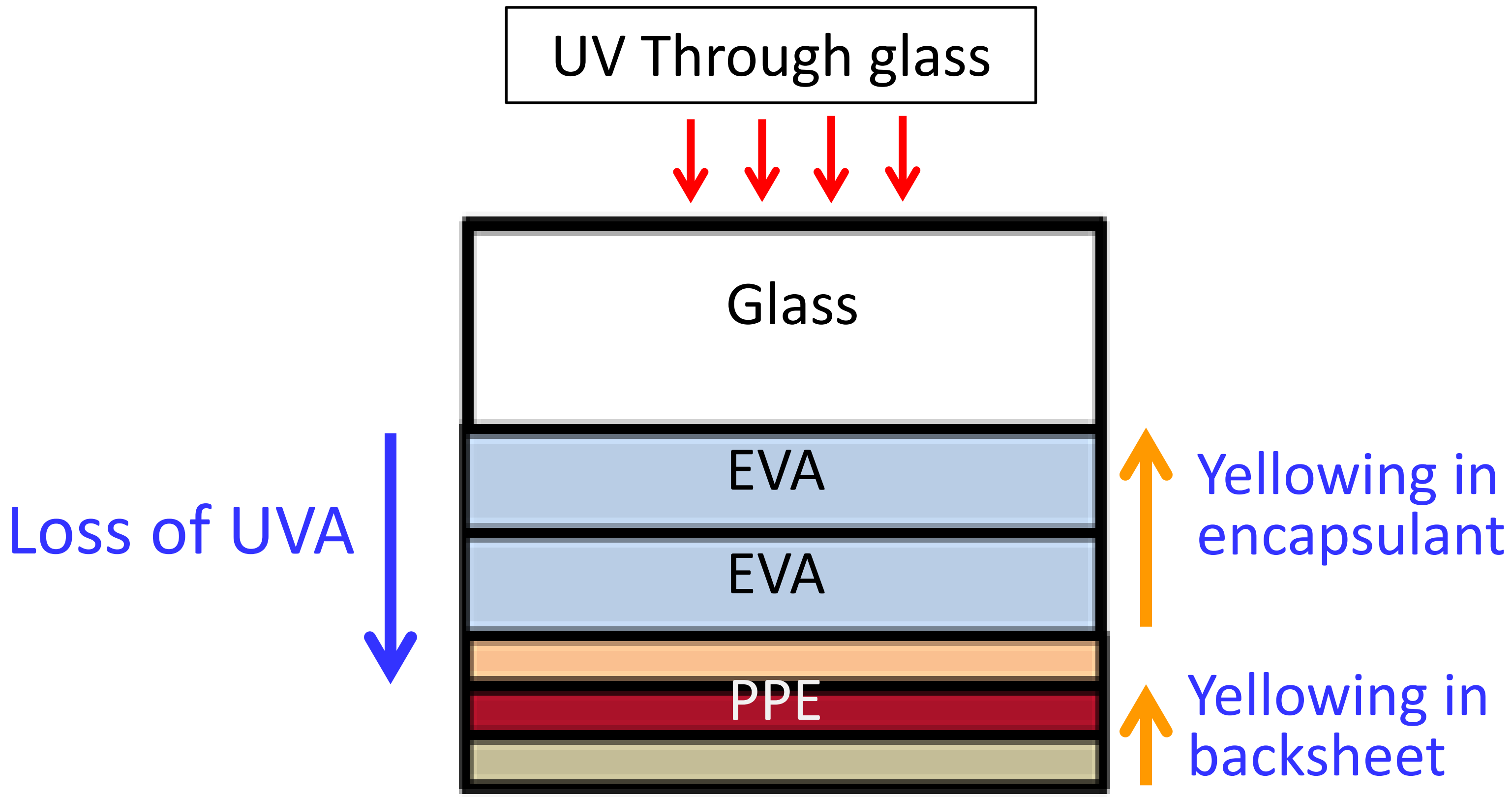
Launer. nature. 1968.
Pern. IEEE Photovoltaic Specialists Conference. 1994.
Hülsmann, P et al.. Progress in Photovoltaics: Research and Applications, 2014

- The loss of UV absorbers and the growth of yellowing are dependent on the wavelength of the UV light. The shorter wavelength, the higher efficiency of the UV light on those changes.

- A semi log linear function is observed between YI per dose and wavelength of UV light for the Glass/EVA/PPE laminated system exposed to SPHERE at 85 °C/dry. The Action Spectrum for changes in yellowing is obtained for this system.

- Same logarithmic dependence on wavelength was observed for the loss of UVA.

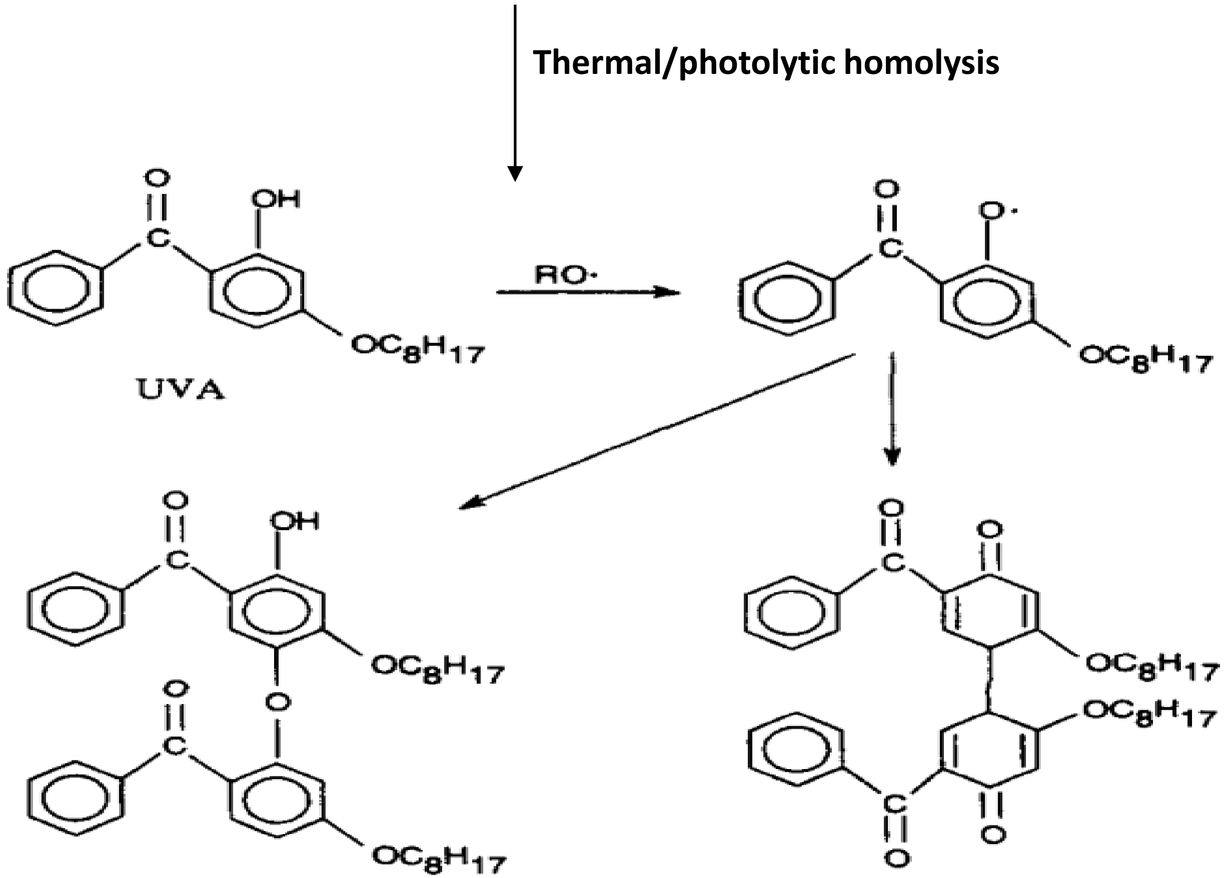
Possible mechanisms for the discoloration



- **Loss of UV absorber** permits UV penetration to a greater extent to encapsulant and backsheet, leading to further yellowing.
- It seems that yellowing is dominated by photoreaction, so the reciprocity law is obeyed for yellowing.
- The mechanism of yellowing will be further investigated by failure analysis of the laminate using a destruction way.

Possible Discoloration Reactions between UVA and Curing Peroxide in the Encapsulant Layer

Peroxides



These reactions are expected to give rise to chromophore precursors

Klemchuk *et al*.. Polym degrad stabil. 1997.

Summary

- Quantitative relationships between light intensity/wavelength and yellowing of Glass/EVA/PPE system have been established.
- The degradation rates for the growth of YI and the loss of UV absorbers are found to be proportional to the UV irradiance. Reciprocity law appears to be obeyed for both in the studied UV irradiance range.
- Wavelength effect is clearly seen for growth of YI and the loss of UV absorbers. The action spectrum is obtained for these changes. Photobleaching effect is observed at longer wavelength under 452 nm.
- It is found that the growth of yellowing correlates well with the loss of UV absorbers.
- The yellowing of the glass/ EVA/PPE system can be contributed to changes in encapsulant or/and backsheet.
- This study indicates that it is feasible to use a relative high light intensity (~2.5 suns) for the accelerating weathering testing of yellowing for this PV system. However, the wavelength and spectral distribution of the light source are very critical to the results.

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Debbie Stanley
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Li-Piin Sung
Stephanie Watson

new phase was just started.

NIST/industry PV Consortium on
Developing Reliability-based Accelerated Laboratory Tests for Service Life Prediction of PV Materials

Underwriters Laboratories
DU PONT
ARKEMA
3M
DAIKIN
First Solar
AGC BEYOND GLASS

Thank you for your attention!