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Investigating the Impact of Reciprocity on High-Irradiance Weathering Tests

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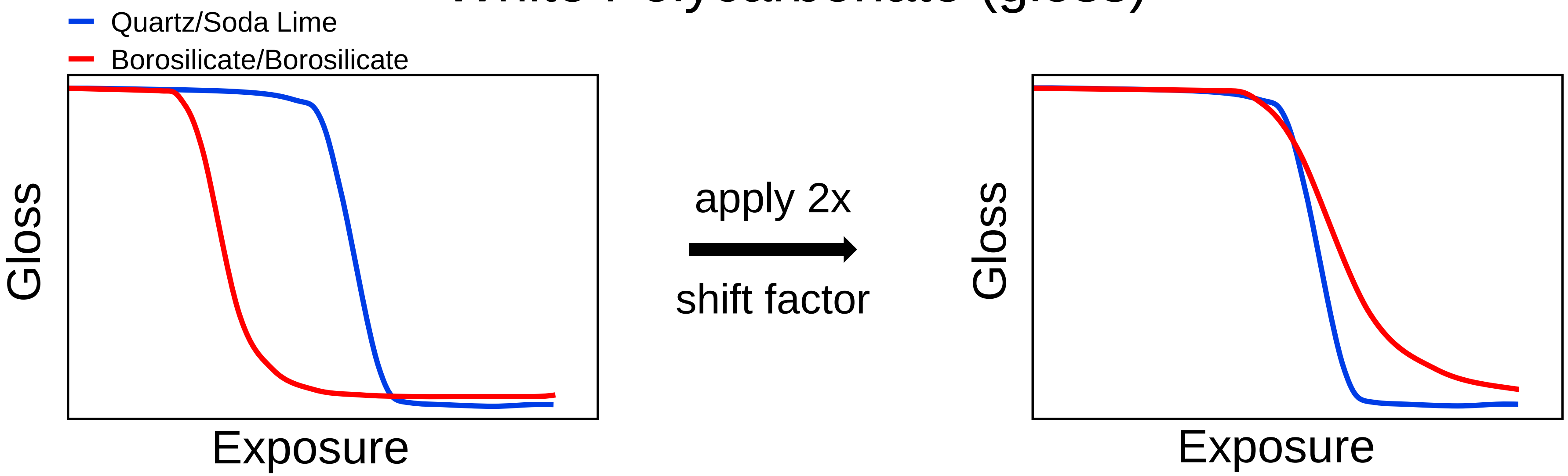
Effect of Light Source
- Filtered Xenon Arc

White Polycarbonate (gloss)



Degradation rate changes

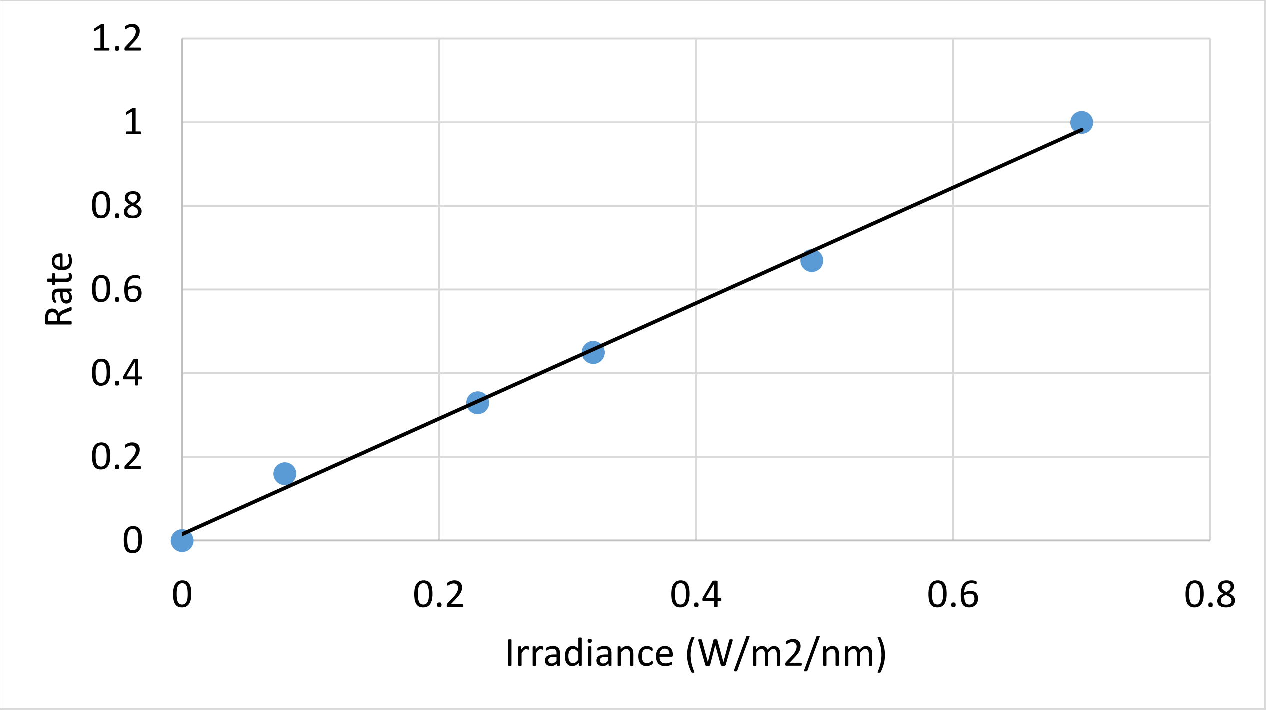
Degradation mechanism changes

J. E. Pickett *et al.*, Polymer Degradation and Stability 93 (2008) 1597–1606

Effect of Irradiance - Linear

- Near-perfect overlay of shifted degradation curves
- Linear increase in rate of yellowing with irradiance
- Law of Reciprocity obeyed

White Polycarbonate
(yellowing index)



I = 0.75 W/m^2/nm (340)

J. E. Pickett *et al.*, Polymer Degradation and Stability 93 (2008) 1597–1606

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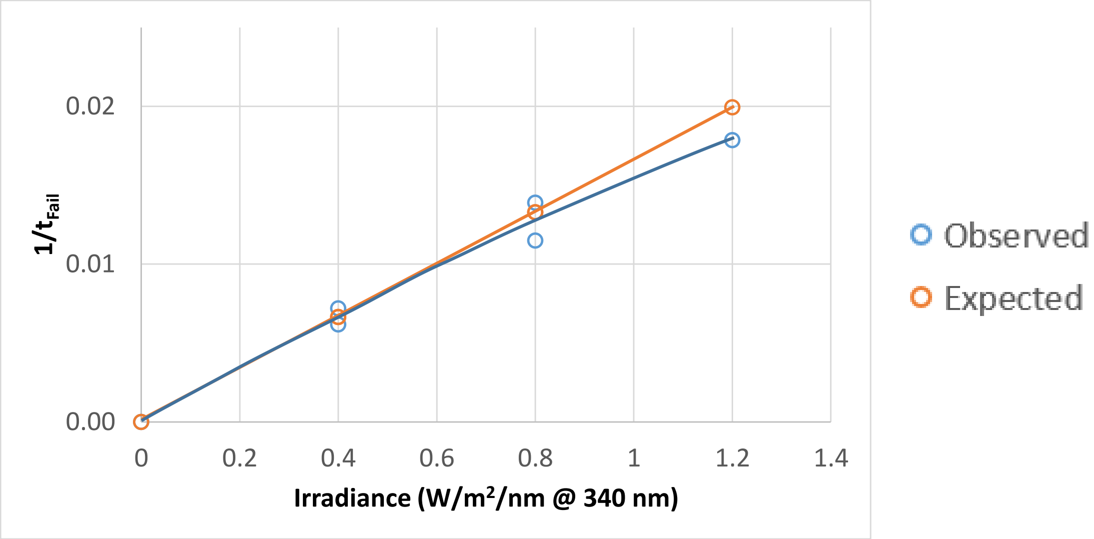
Law of Reciprocity

- $I \times t = \text{constant}$
- Equivalent degradation for equal doses of radiation
- Implications:
  - Degradation rate increases linearly with irradiance
  - Intermittent exposures give the same results as continuous exposures

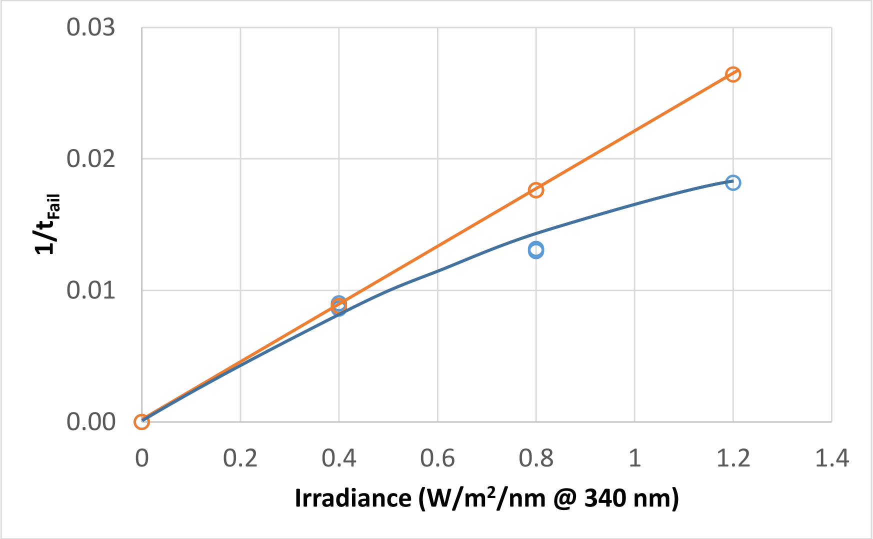
- Schwarzschild's Law: $I \times t^{p} = \text{constant}$
- Application to weathering exposure: $I^{q} \times t = \text{constant}$
  - $q = 1$: Reciprocity obeyed
  - $q < 1$: Reciprocity failure

Effect of Irradiance – Non-Linear

Polycarbonate



Polystyrene



$1/t_{Fail} \sim x^{0.91}$

$1/t_{Fail} \sim x^{0.63}$

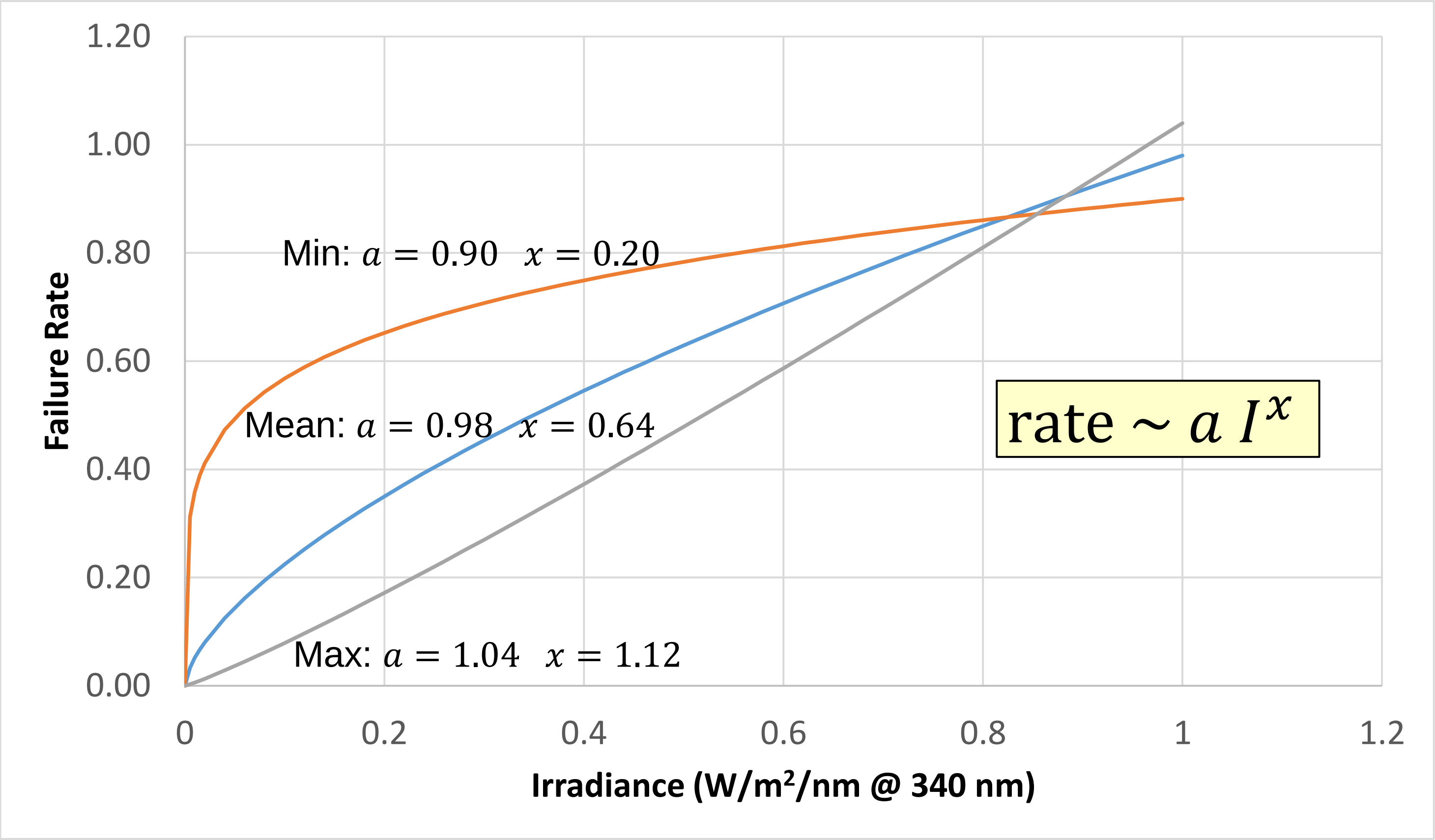
$1/t_{Fail} \sim x^{0.65}$
[accelerated outdoor]

K. P. Scott and H. K. Hardcastle III, in Service Life Prediction of Polymeric Materials: Global Perspectives, J. W. Martin *et al.* (Eds.), Springer, New York, pp. 83-91 (2009).

H. K. Hardcastle III, in Service Life Prediction: Challenging the Status Quo, J. W. Martin *et al.* (Eds.), Federation of Societies for Coatings Technology, Blue Bell, PA, pp. 217-226 (2005).

Effect of Irradiance – Survey of Materials

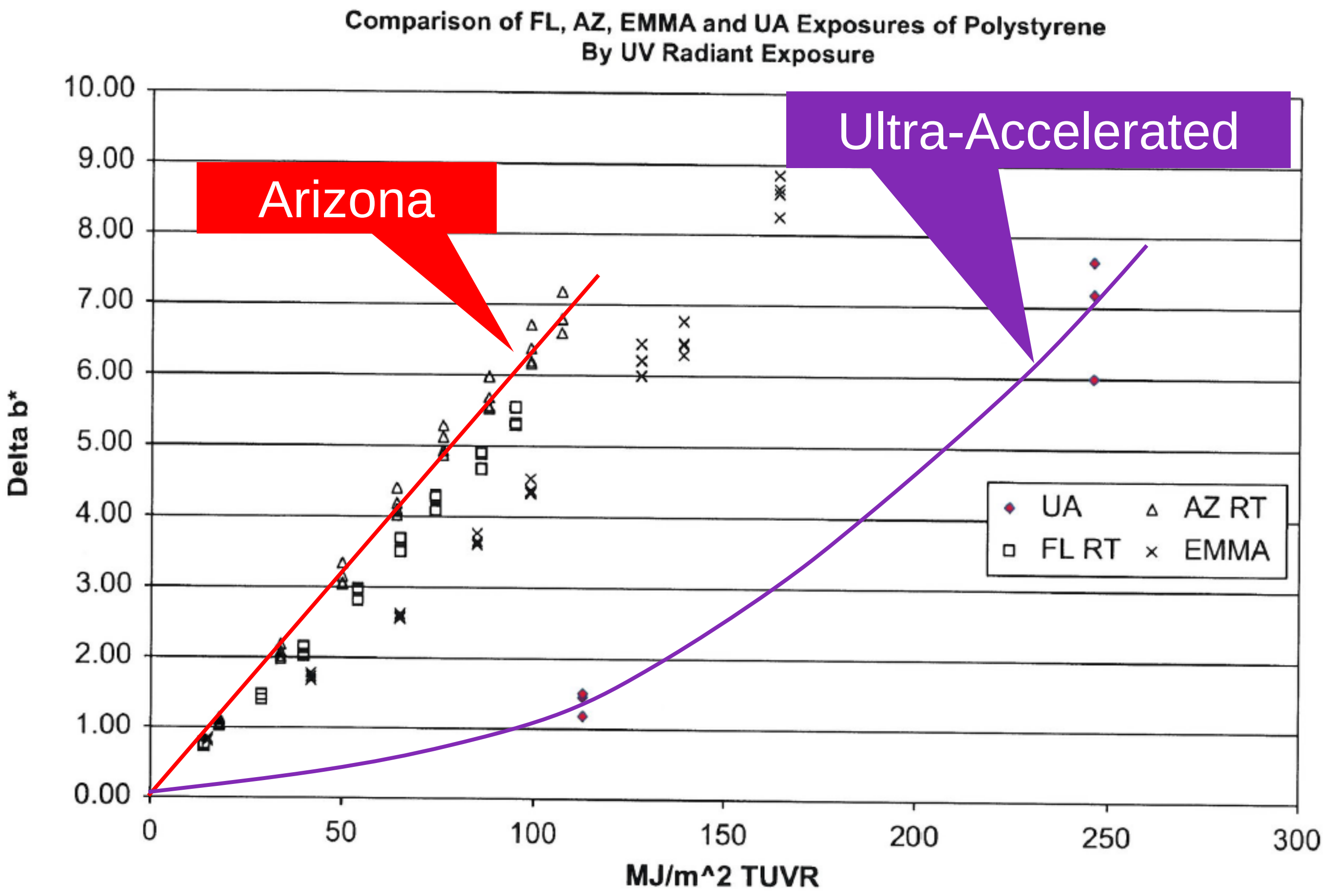
Minimum, Mean, and Maximum for 50 Weathered Materials



x	# Materials
= 1	3
< 0.5	14
< 0.3	3

R. M. Fischer and W. D. Ketola, in Service Life Prediction: Challenging the Status Quo,
J. W. Martin *et al.* (Eds.), Federation of Societies for Coatings Technology, Blue Bell, PA, pp. 79-92 (2005).

Effect of Irradiance – Very High Acceleration



H. K. Hardcastle III, in Service Life Prediction of Exterior Plastics: Vision for the Future, C. C. White *et al.* (Eds.), Springer, New York, pp. 165-184 (2015).

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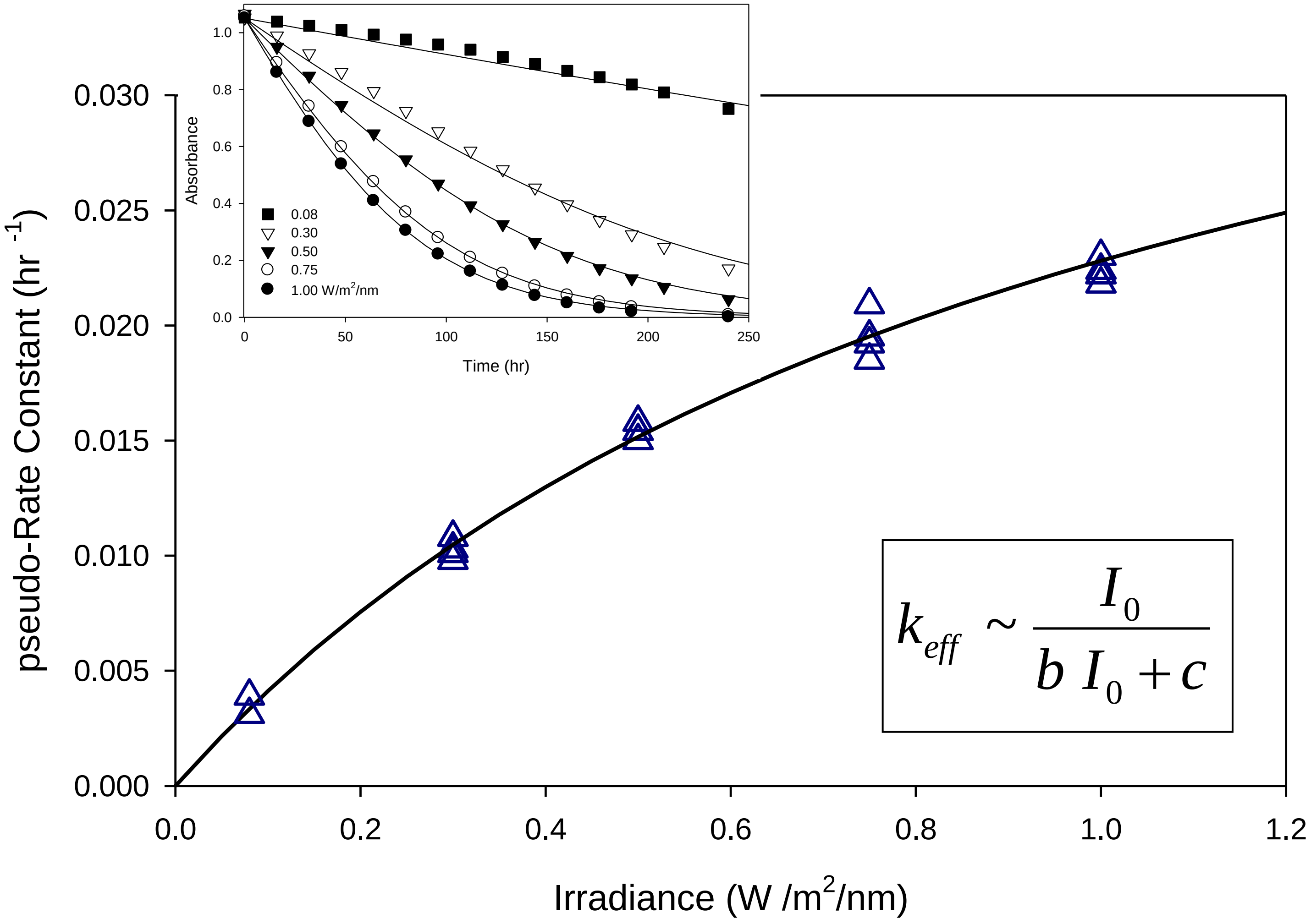
Accounting for Reciprocity Failure: Model Study

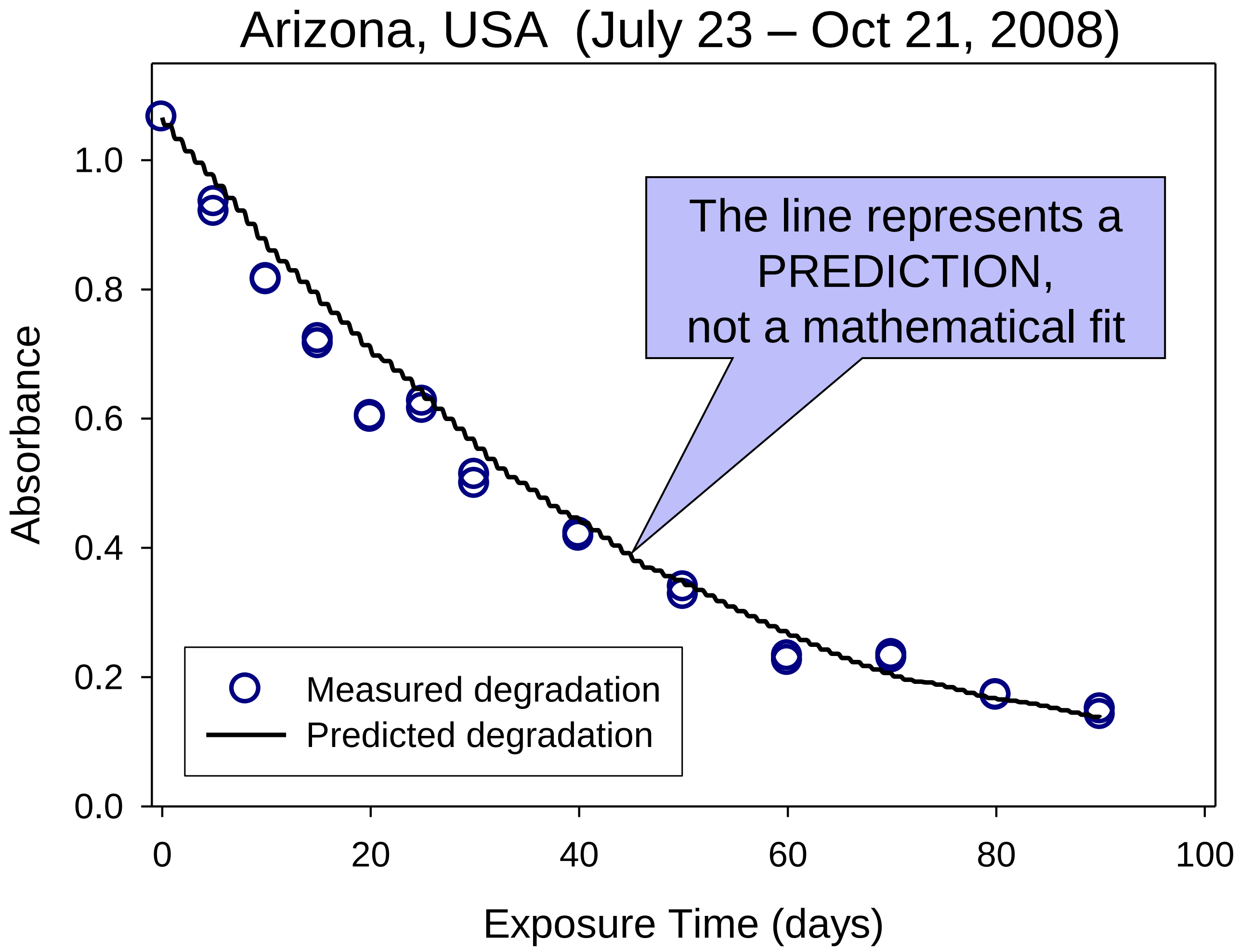


<u>Fluorescent dye in vinyl film</u>

- Transparent color enabled quantitative study
- Fades under exposure to visible radiation
- Measured response: absorbance of visible radiation
- Model for irradiance dependence consistent with photophysics of degradation

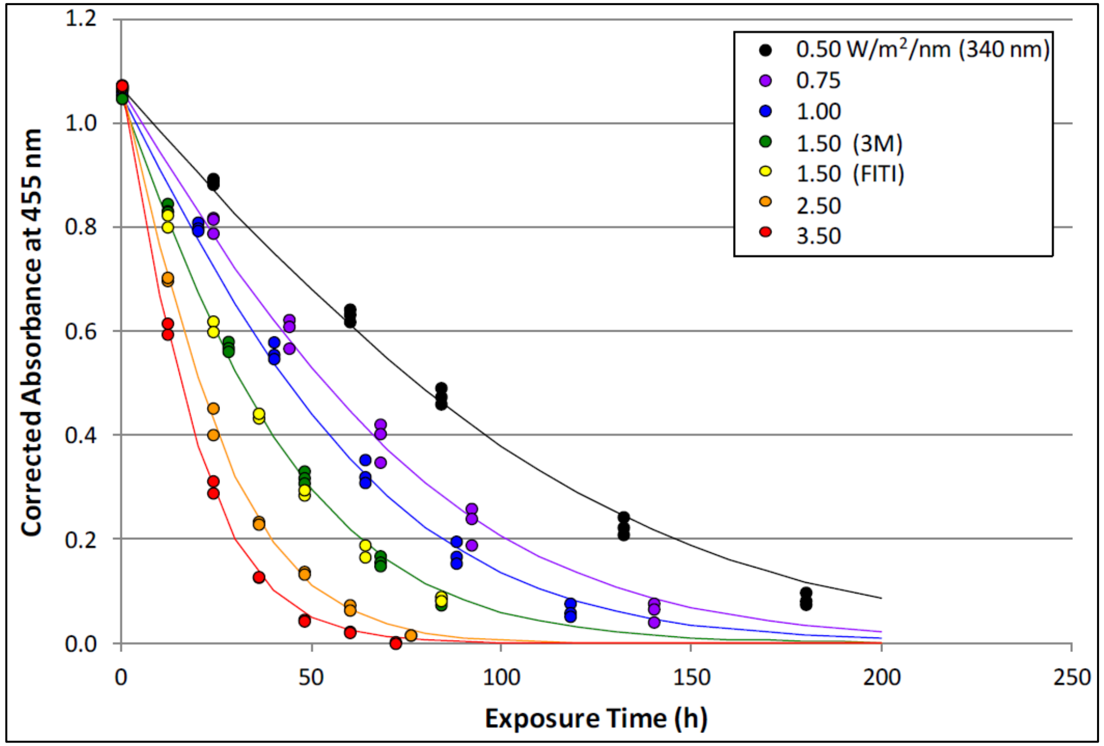
K. M. White *et al.,* in Service Life Prediction of Polymeric Materials: Global Perspectives, J. W. Martin *et al.* (Eds.), Springer, New York, pp. 71-82 (2009).

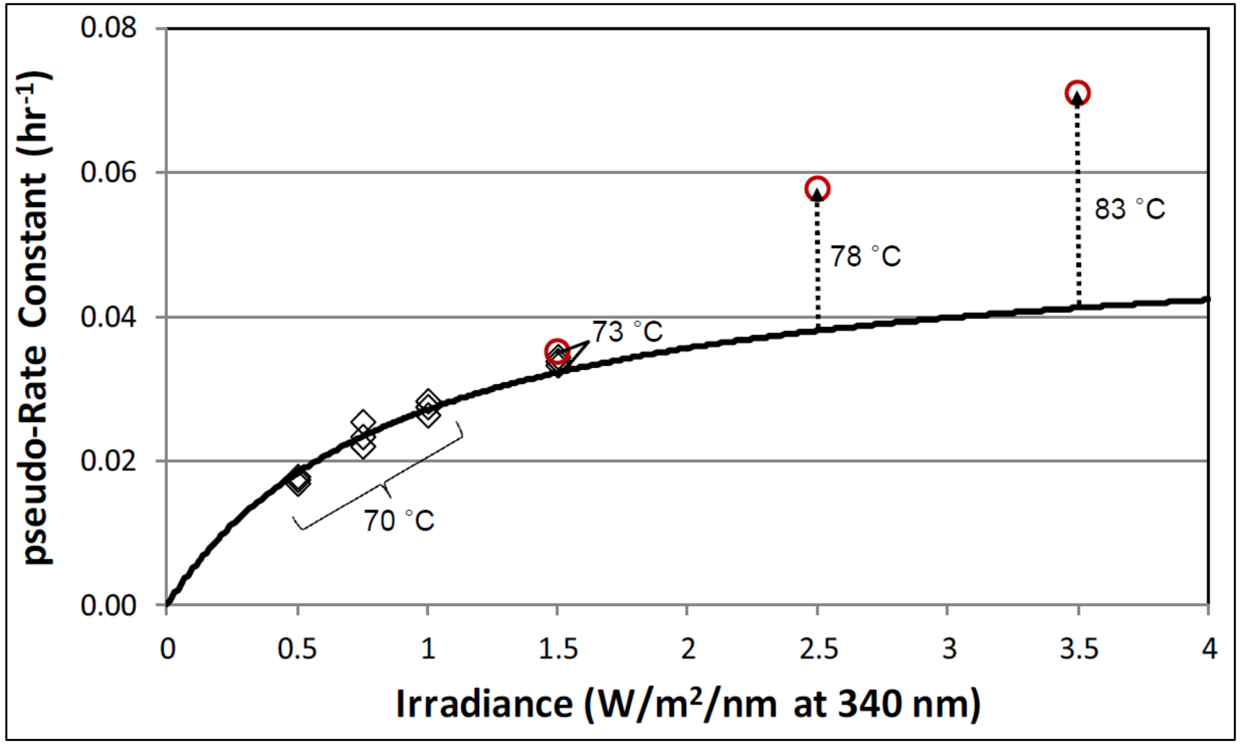
Accounting for Reciprocity Failure: Service-Life Prediction



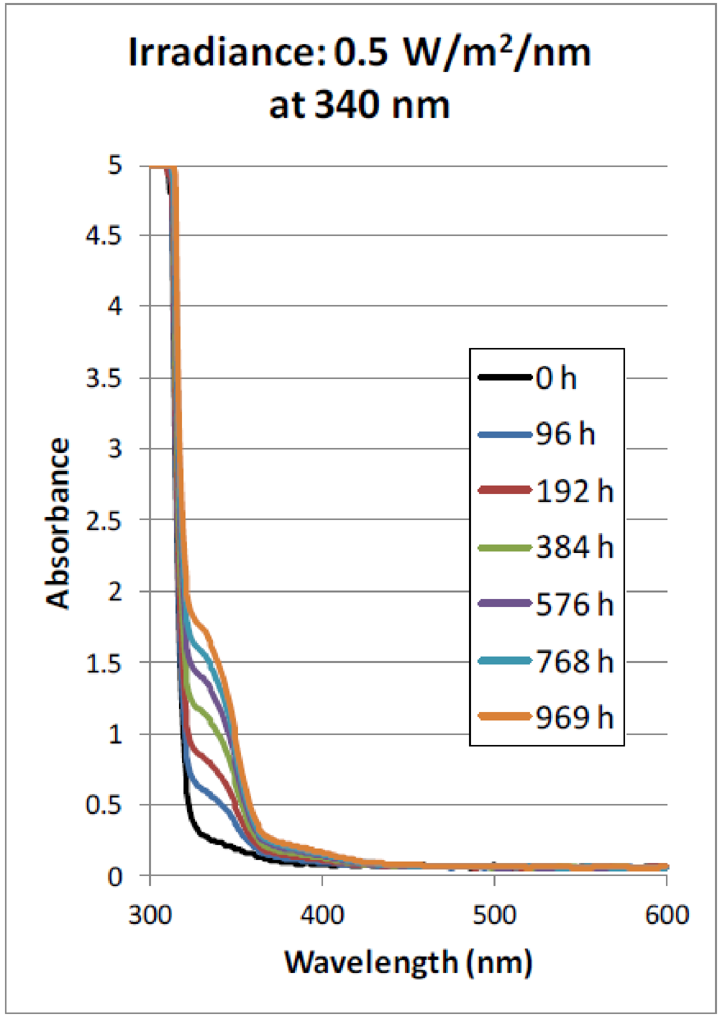
K. M. White *et al.,* in Service Life Prediction of Exterior Plastics: Vision for the Future, C. C. White *et al.* (Eds.), Springer, New York, pp. 21-40 (2015).

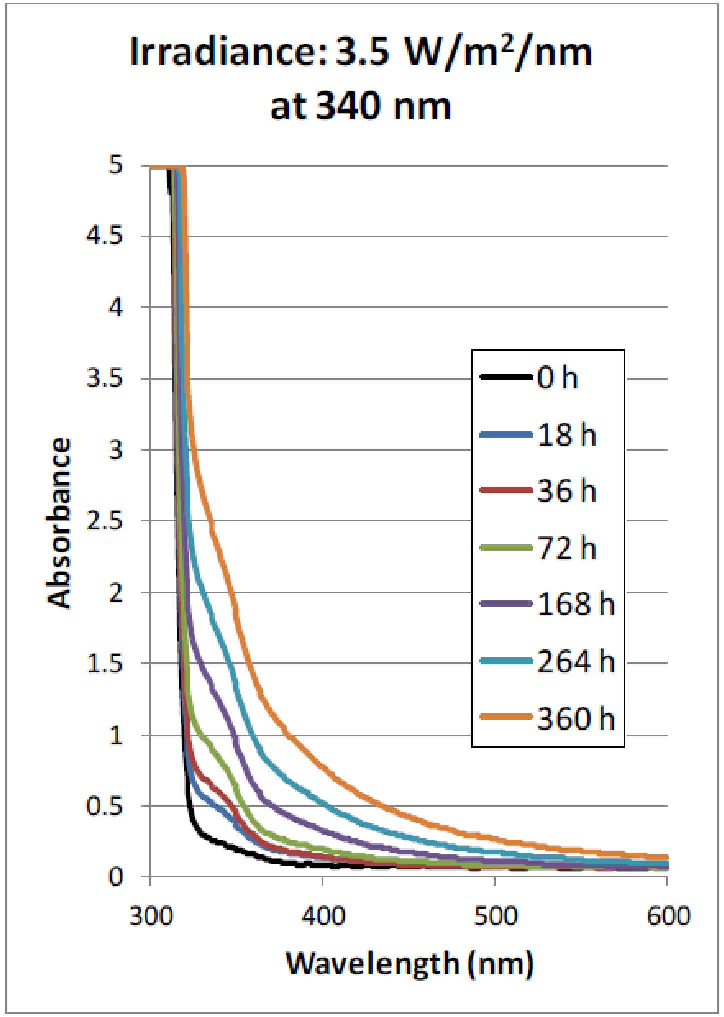
Extrapolation to High Irradiance
- Temperature Effects

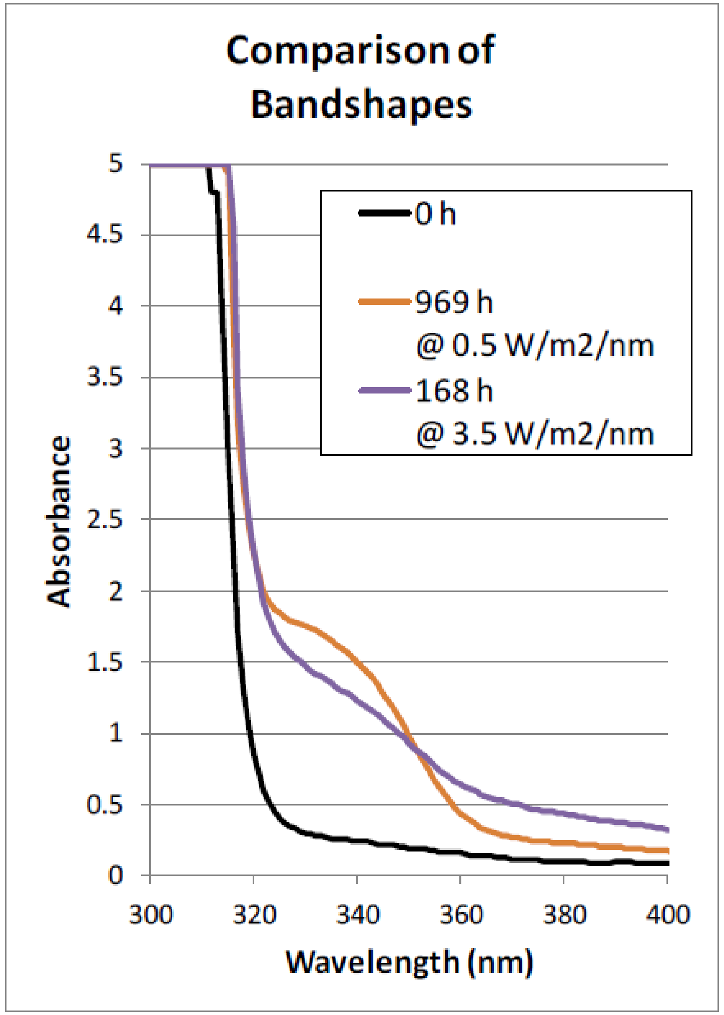




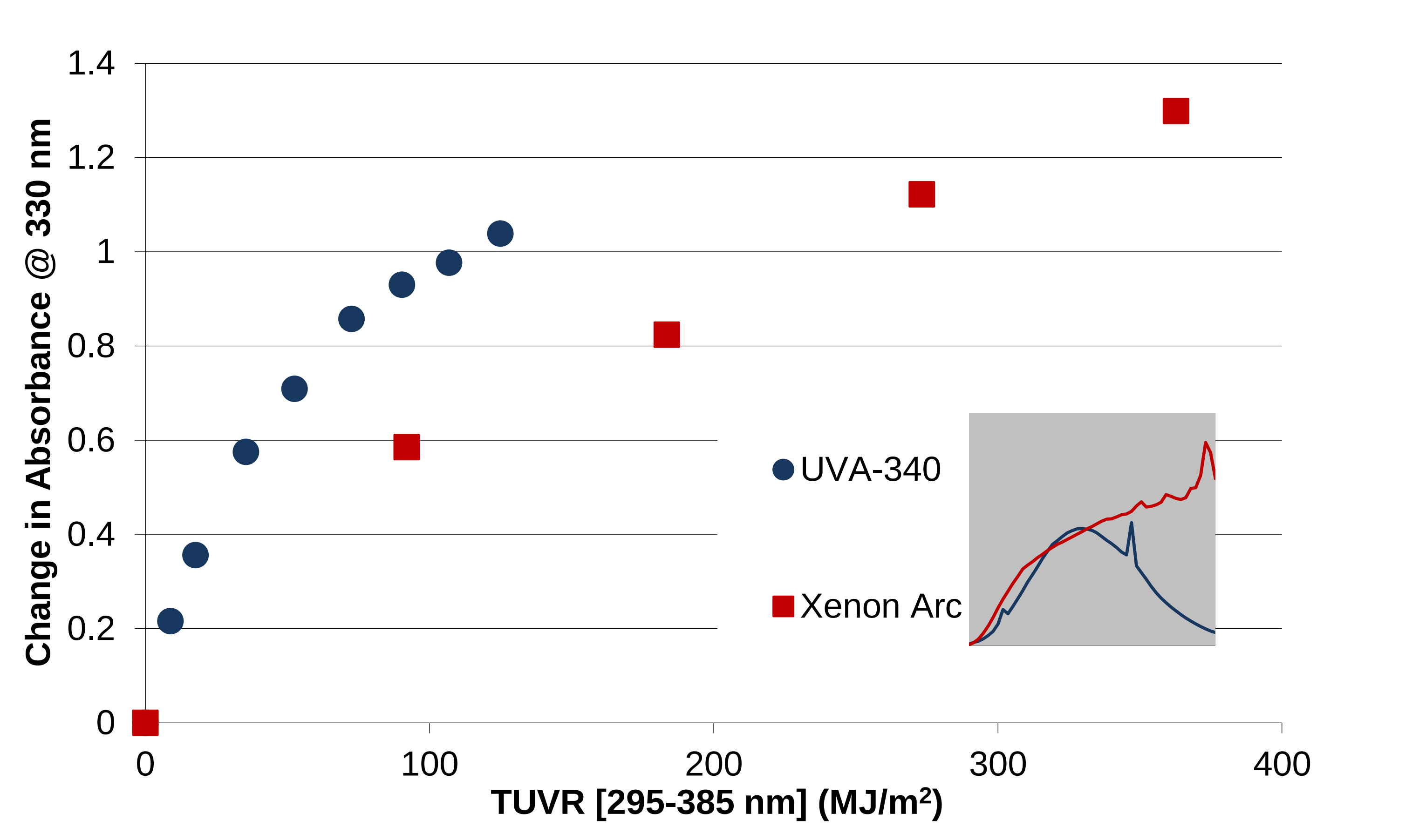
Effect of Irradiance on Degradation Pathway
- PET Film







Effect of Spectral Distribution on Degradation
- PET Film



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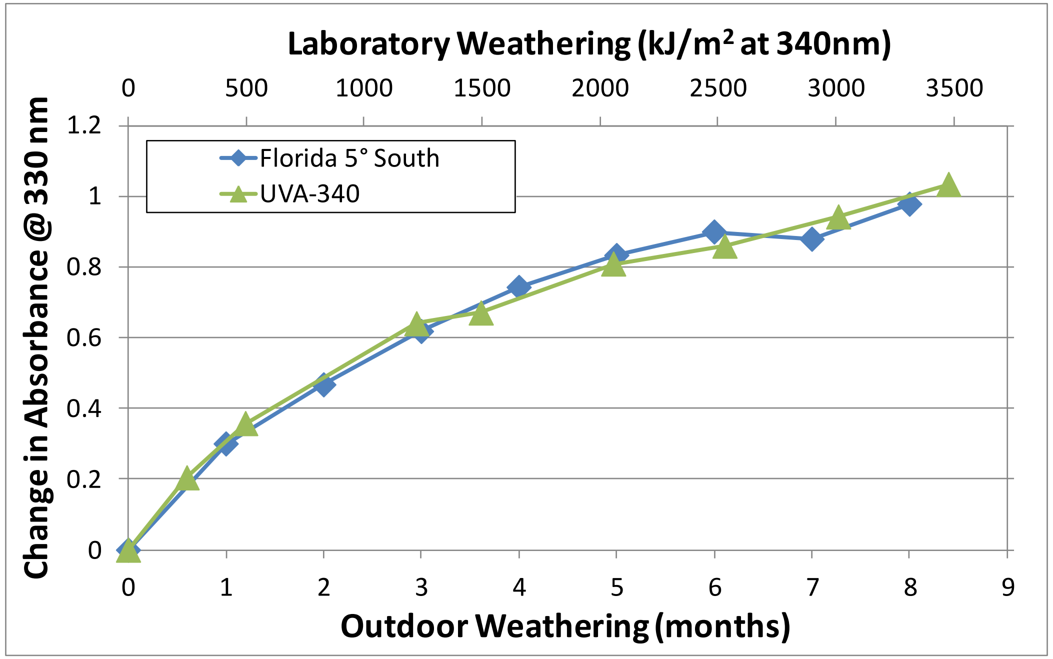
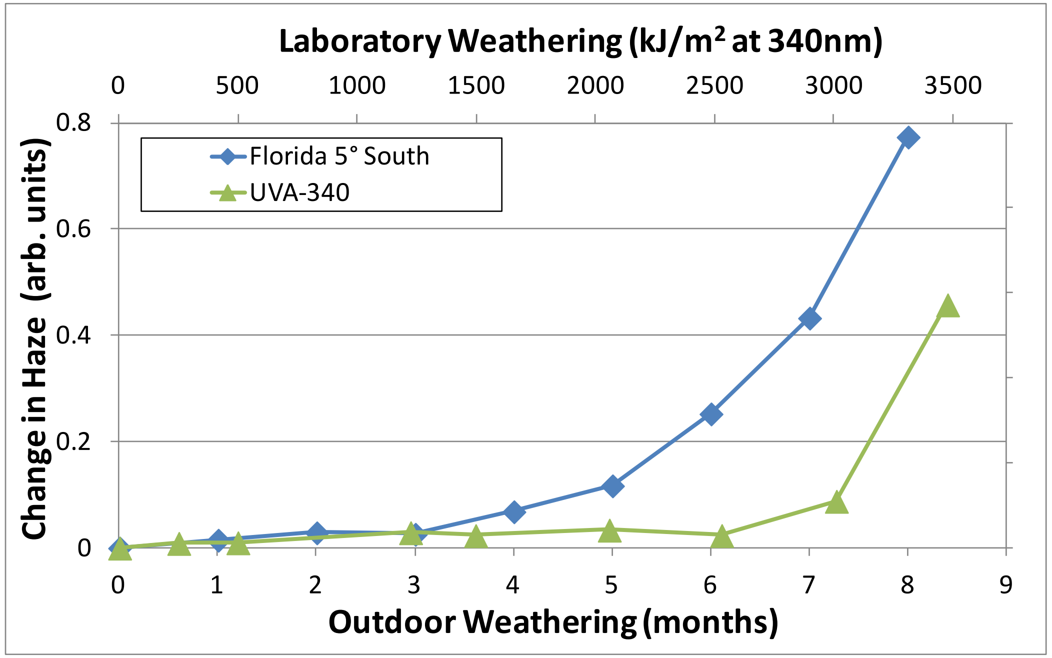
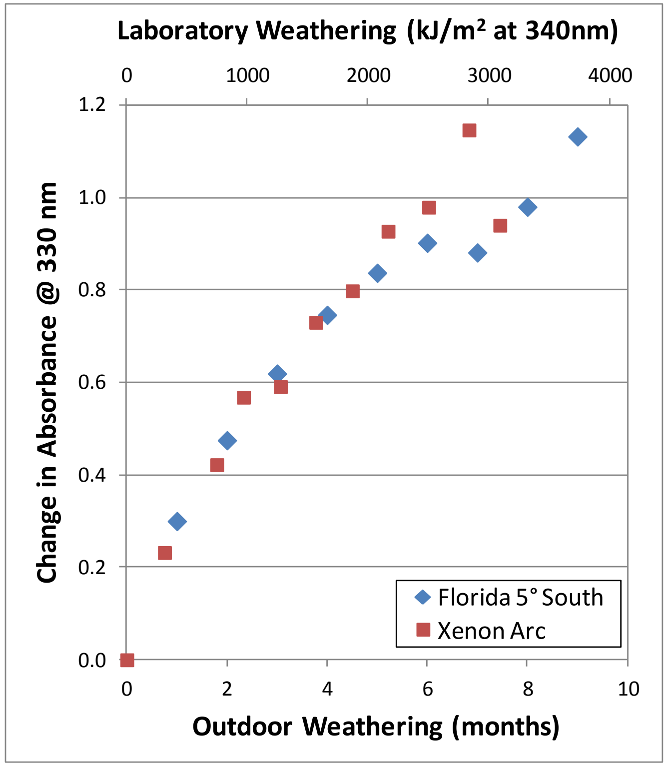
Multiple Modes of Degradation
- PET Film



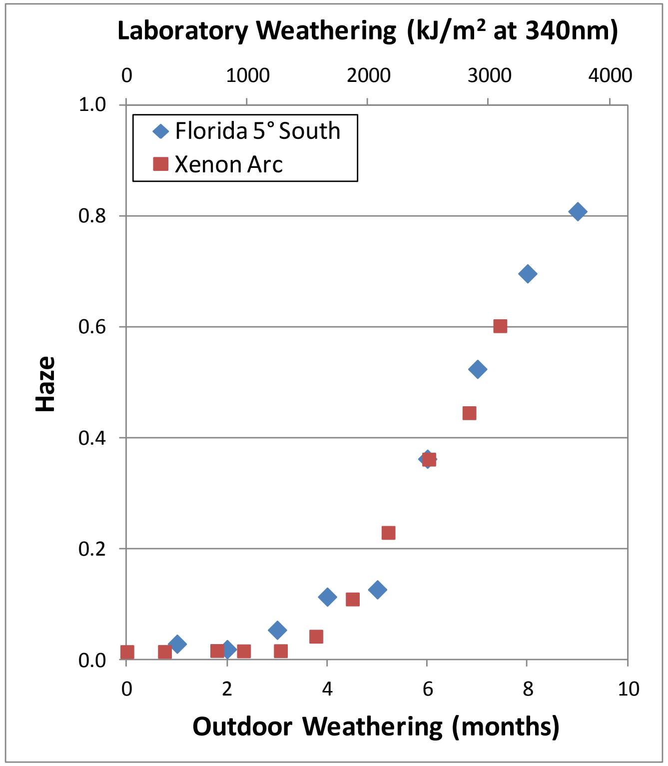


Synchronizing the Degradation
- PET Film

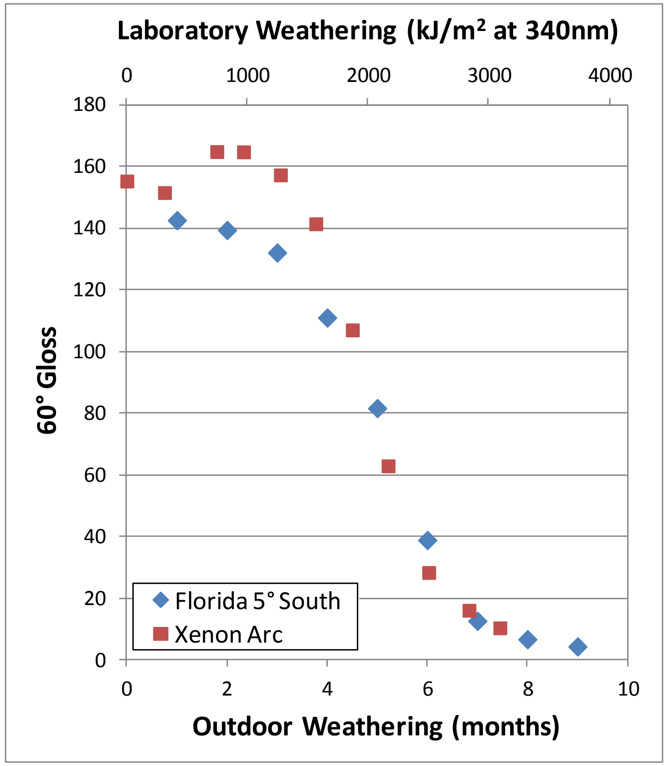
Yellowing



Haze



Gloss



Summary

- Reciprocity failure
  - Observed for numerous films and material properties
  - Onset may occur near irradiance level of peak sunlight
  - High-irradiance exposure can promote degradation modes that are not consistent or synchronous with real-world weathering
  - Lifetimes based on high-irradiance exposures may be overestimated
  - Service-life prediction can be achieved only when appropriately accounting for non-linearity in irradiance and temperature dependence
- Spectral distribution of light source
  - Observed to affect both degradation rates and degradation pathways
  - Impact is highly dependent on material under test
  - Service-life comparisons necessitate accounting for wavelength range of irradiance