Accelerated UV Weathering of Polymeric Systems:

RECENT INNOVATIONS AND NEW PERSPECTIVES

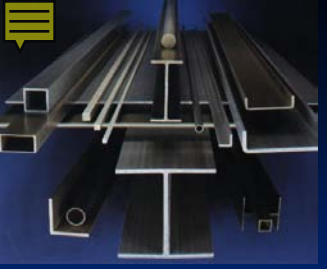
Joannie Chin, Eric Byrd, Xiaohong Gu and Chris White
Polymeric Materials Group
National Institute of Standards and Technology

Outline

Paradigm Shift In Accelerated Aging of Materials

New Technologies

Lifetime prediction



Polymeric Materials Group
Materials and Structural Systems Div.
Engineering Laboratory

- **Service life prediction of high performance polymers and composites**
- **Development of metrologies and methodologies for the characterization of high performance polymers and composites**

Service Life Prediction: Previous Reality

Outdoor Exposure

"Patience is the greatest of all virtues"

Cato the Elder

"A handful of patience is worth more than a bushel of brains"

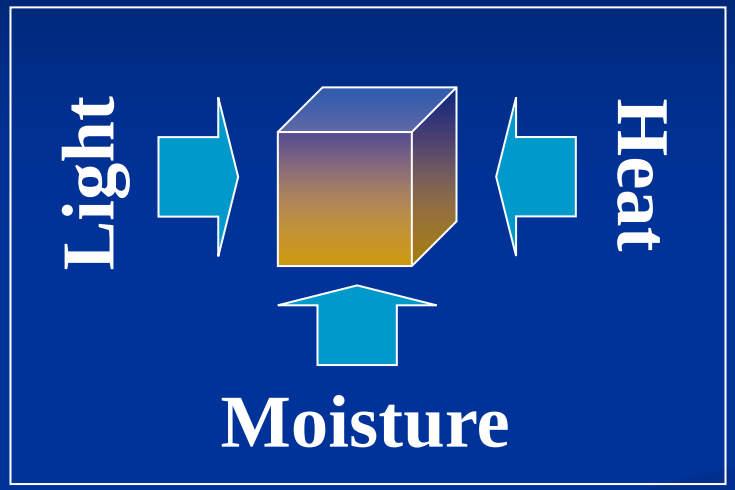
Dutch proverb

"The waiting is the hardest part…"

Tom Petty and the Heartbreakers

Service Life Prediction: Previous Reality

Laboratory Exposure



"Published literature report hundreds of attempts to duplicate and accelerate weathering effects and conclude that there is no substitute for natural weathering…" ***Dreger 1973***

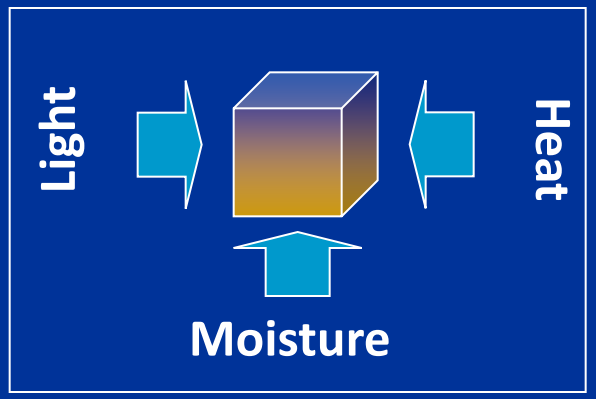
"…..variability both within and between accelerated devices is the primary reason for poor reproducibility in accelerated weathering testing" ***Fischer 1991.***

"The future ain't what it used to be…" ***Attributed to Yogi Berra***

Service Life Prediction: Previous Reality

Outdoor Exposure

Laboratory Exposure



RANK AND COMPARE
Outdoor exposure
vs.
Accelerated aging

No correlation; adjust acceleration factors

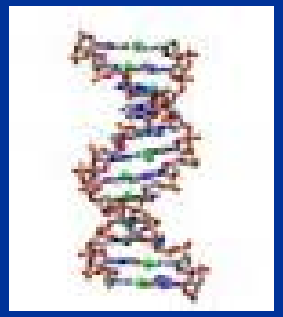
"Current estimates of service life are crude and there is little or no correlation between laboratory and field exposure." *Rilem State of the Art Report, 1999*

Service Life Prediction

INSIGHT

Defining the problem as *outdoor versus laboratory* makes the problem intractable

Have these issues been considered in other fields???



Biology
Medicine
Agriculture

Total Effective Dosage Model

$$D_{total}(t) = \int_0^t \int_{\lambda_{min}}^{\lambda_{max}} E_o(\lambda, t)(1 - e^{-A(\lambda)})\,\phi(\lambda)\,d\lambda\,dt$$

$D_{total}(t)$ = total effective dosage

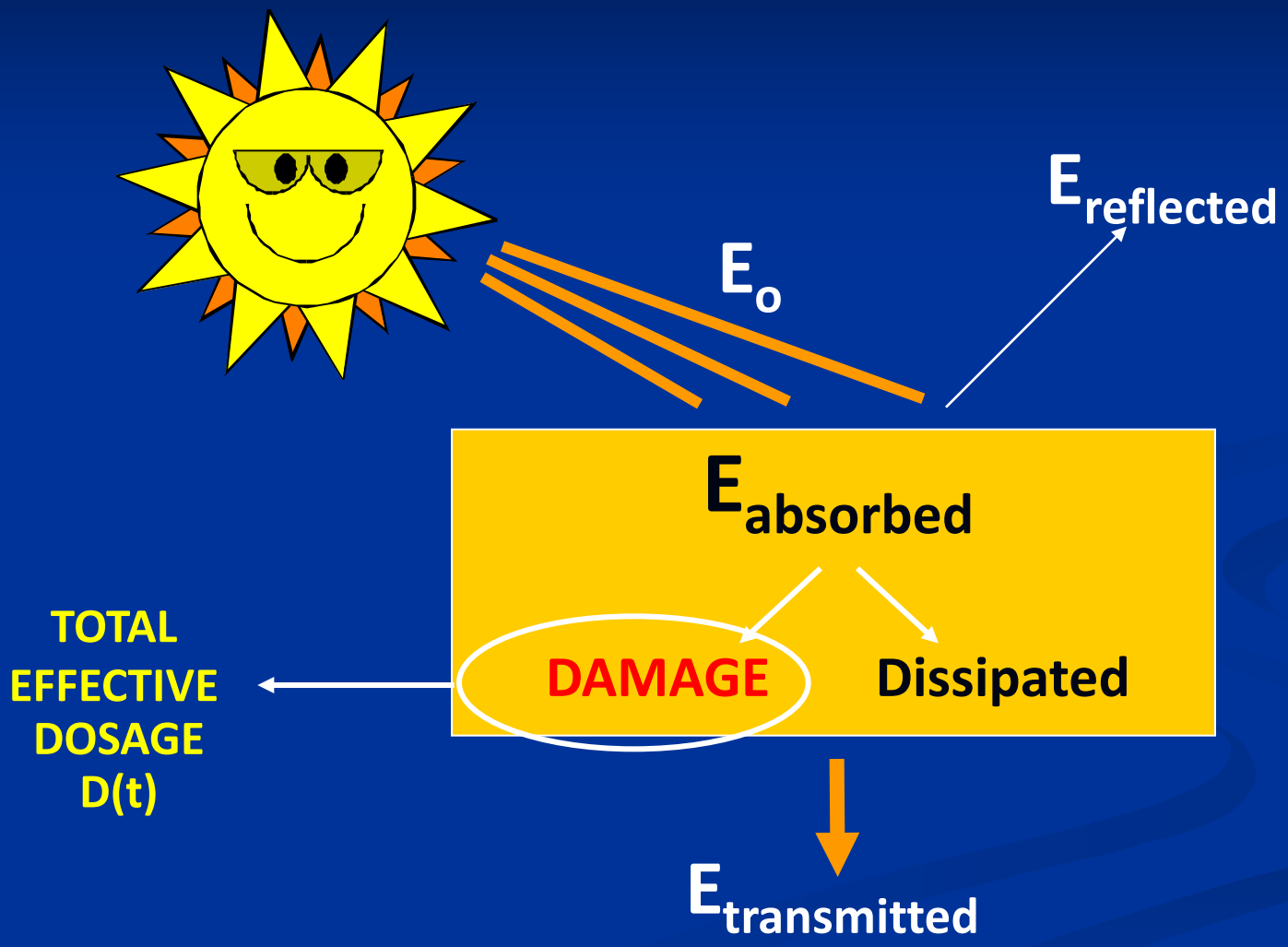
$E_o(\lambda,t)$ = spectral UV irradiance from light source

$1-e^{-A(\lambda)}$ = spectral absorption of specimen

$\phi(\lambda)$ = spectral quantum yield of specimen

λ_{min}, λ_{max} = min. and max. photolytically effective wavelengths

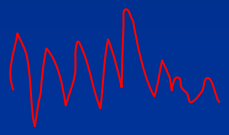
Total Effective Dosage Model



Reliability-Based SLP Methodology

Outdoor Exposure

Time Series

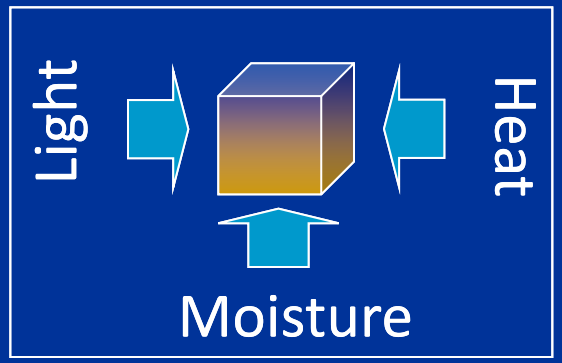


Temperature
RH, UV Dosage

Cumulative Damage Model

$$D_{total}(t) = \int_0^{\lambda} \int_{\lambda_{min}}^{\lambda_{max}} E_o(\lambda,t)\left(1-10^{-A(\lambda)}\right)\phi(\lambda)\, d\lambda\, dt$$

Laboratory Exposure

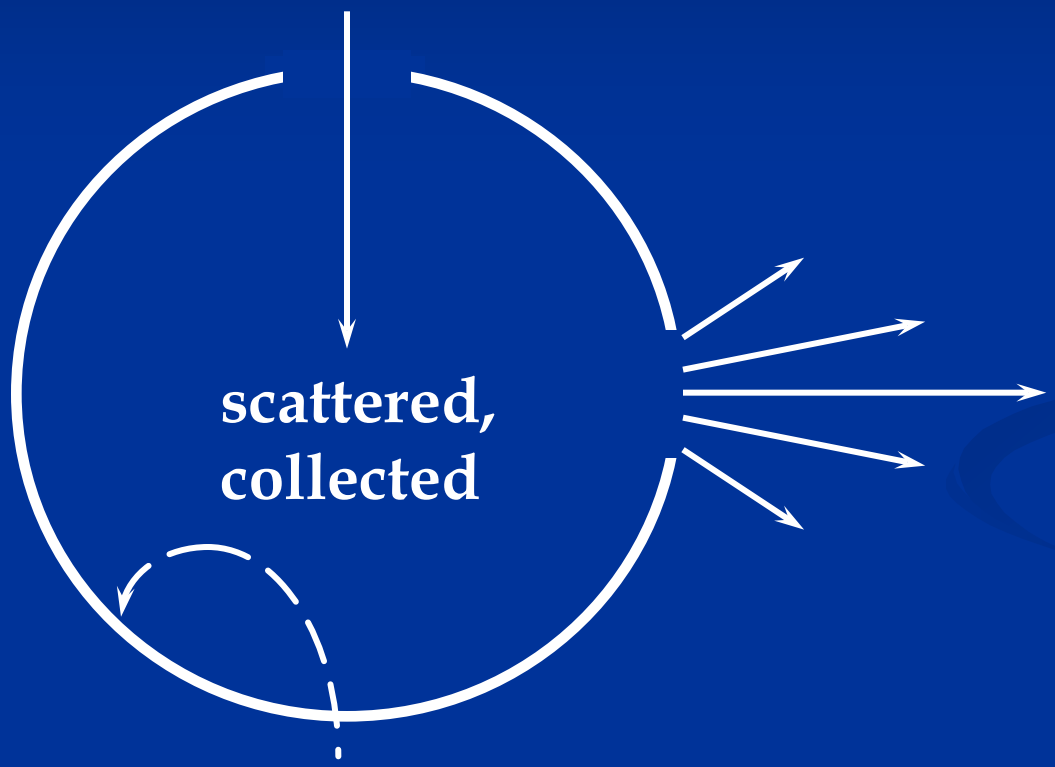


Databases
SLP Models

Basis for Coatings Service Life Prediction Consortium, 1994 - 2007

Integrating Sphere Technology

LIGHT (can be internal or external to sphere)



highly reflective
diffuse coating

ILLUMINATION:
uniform light source

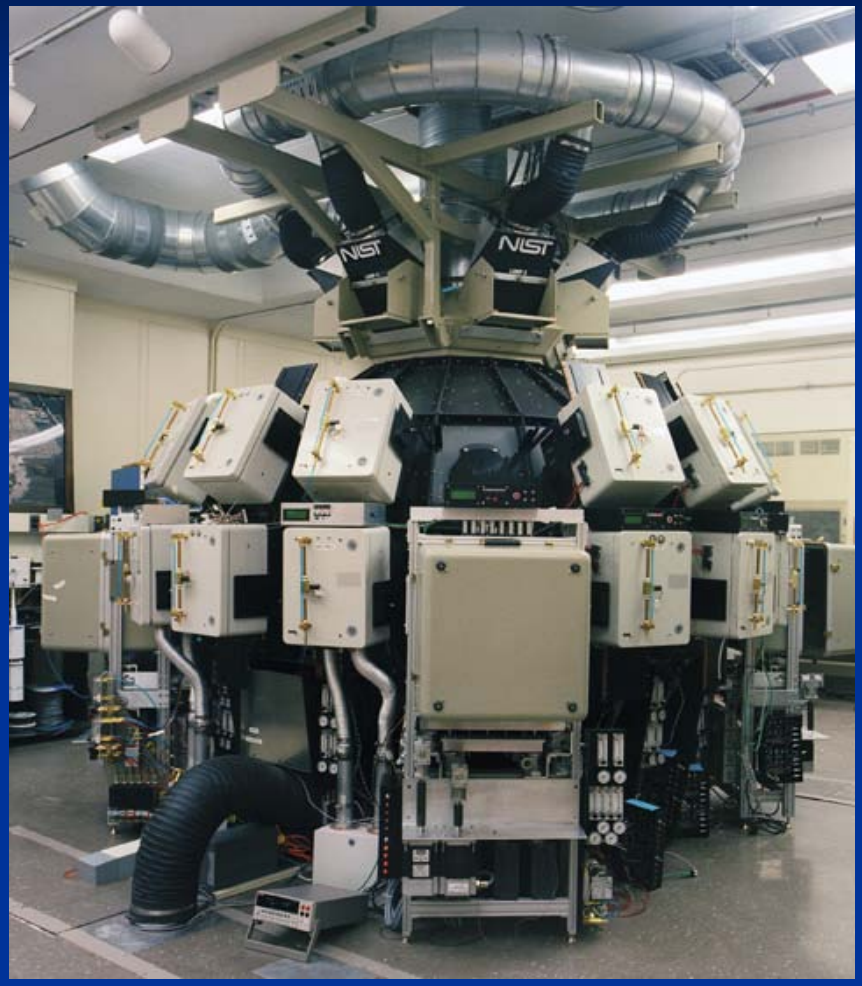
↑

OUTPUT

↓

MEASUREMENT:
power
transmittance
reflectance

Integrating Sphere-based UV Chamber



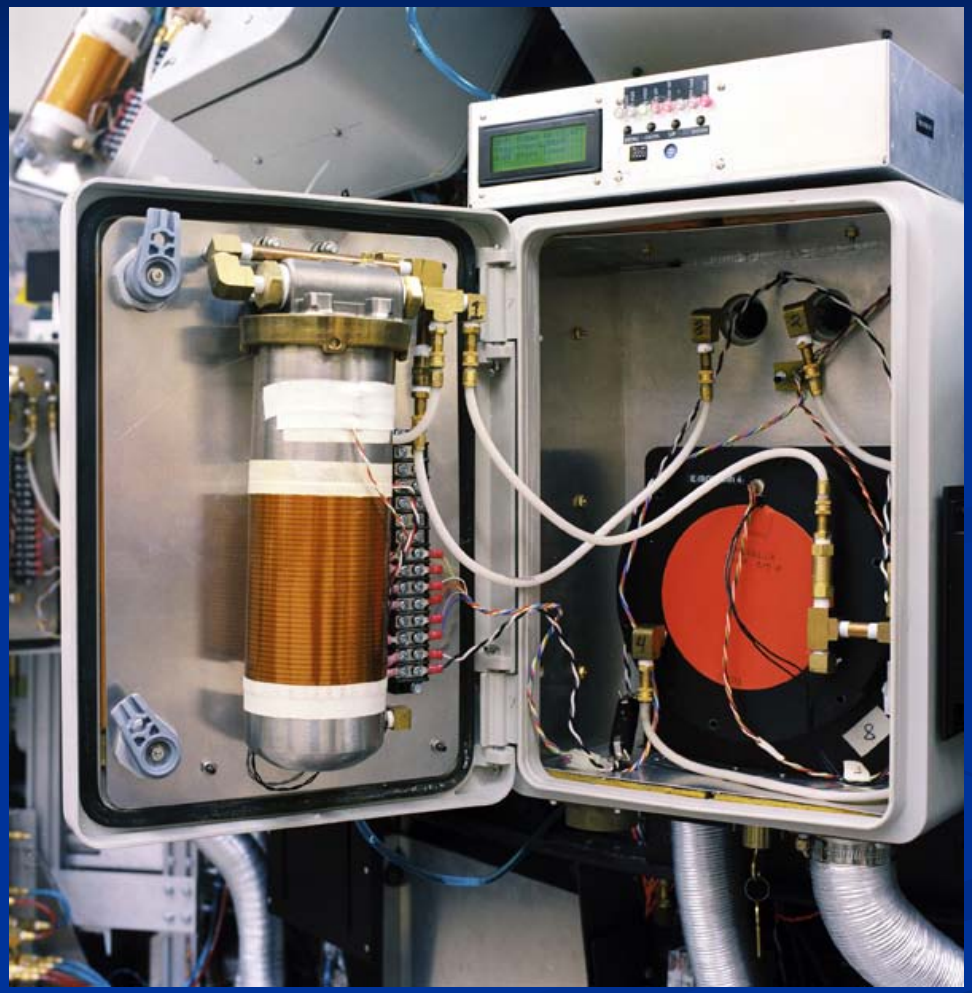
NIST SPHERE

- **S**imulated **P**hotodegradation via **H**igh **E**nergy **R**adiant **E**xposure
- 2 m integrating sphere
- 8400 W UV → 22 "SUNS"
- 95% exposure uniformity
- Visible and infrared radiation removed
- Temperature and relative humidity around specimens precisely controlled
- Capability for mechanical loading

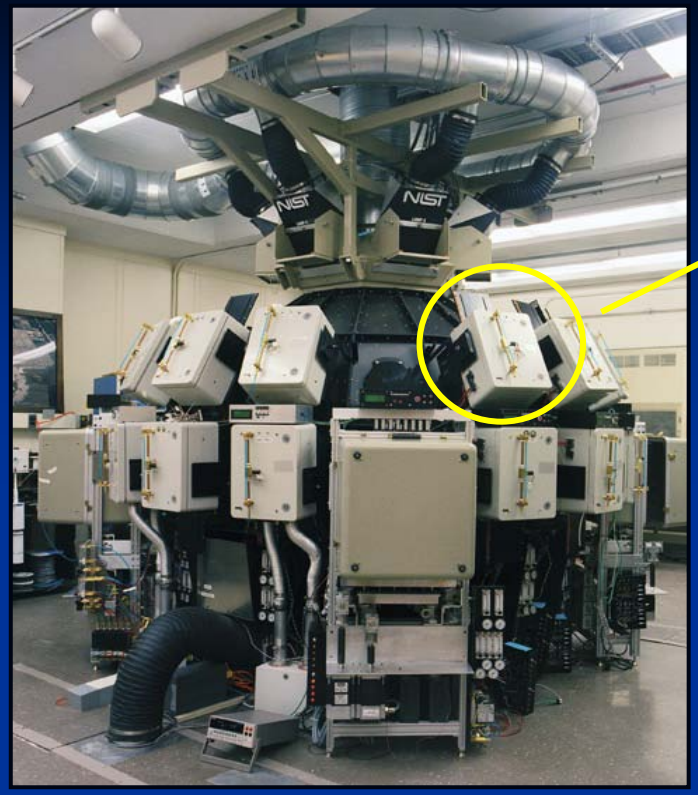
Martin and Chin, U.S. Patent 6626053

Chin et al, *Review of Scientific Instruments*, 75(11), 4951-4959, 2004.

Integrating Sphere-based UV Chamber



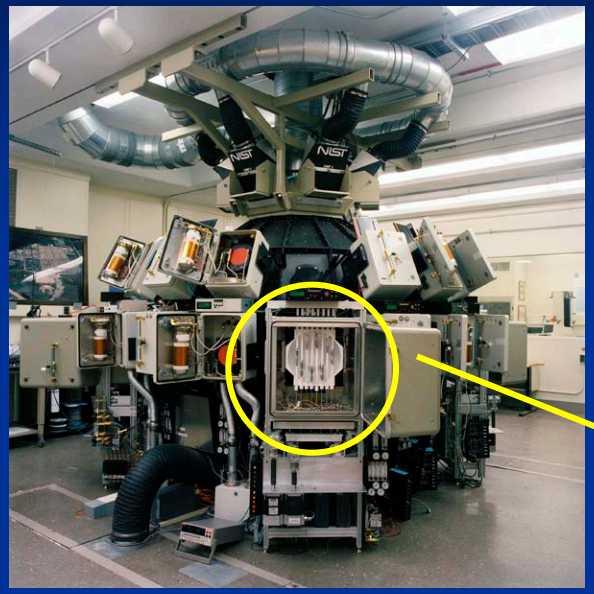
Environmental Chamber



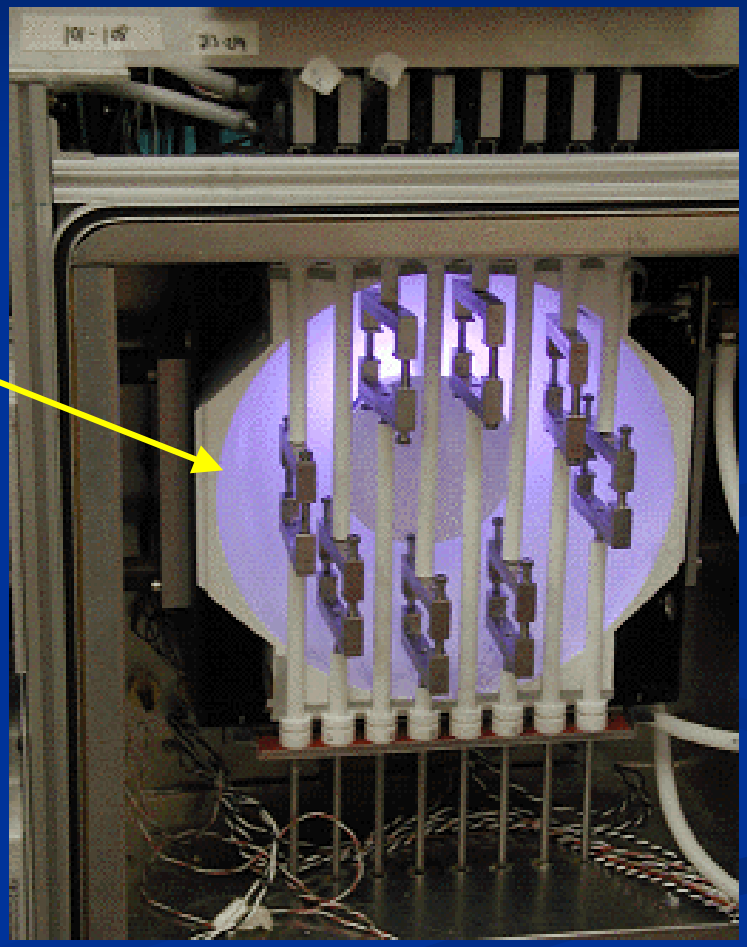
"Dark Side"
T and RH Chambers

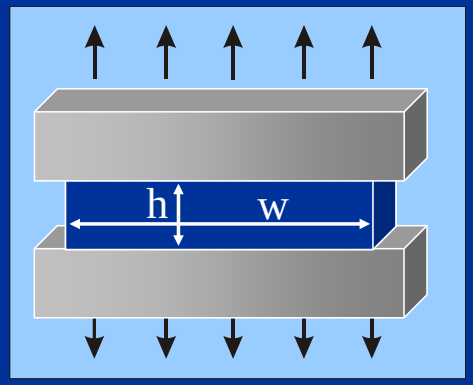
Outdoor
Exposure
Apparatus

Integrating Sphere-based UV Chamber



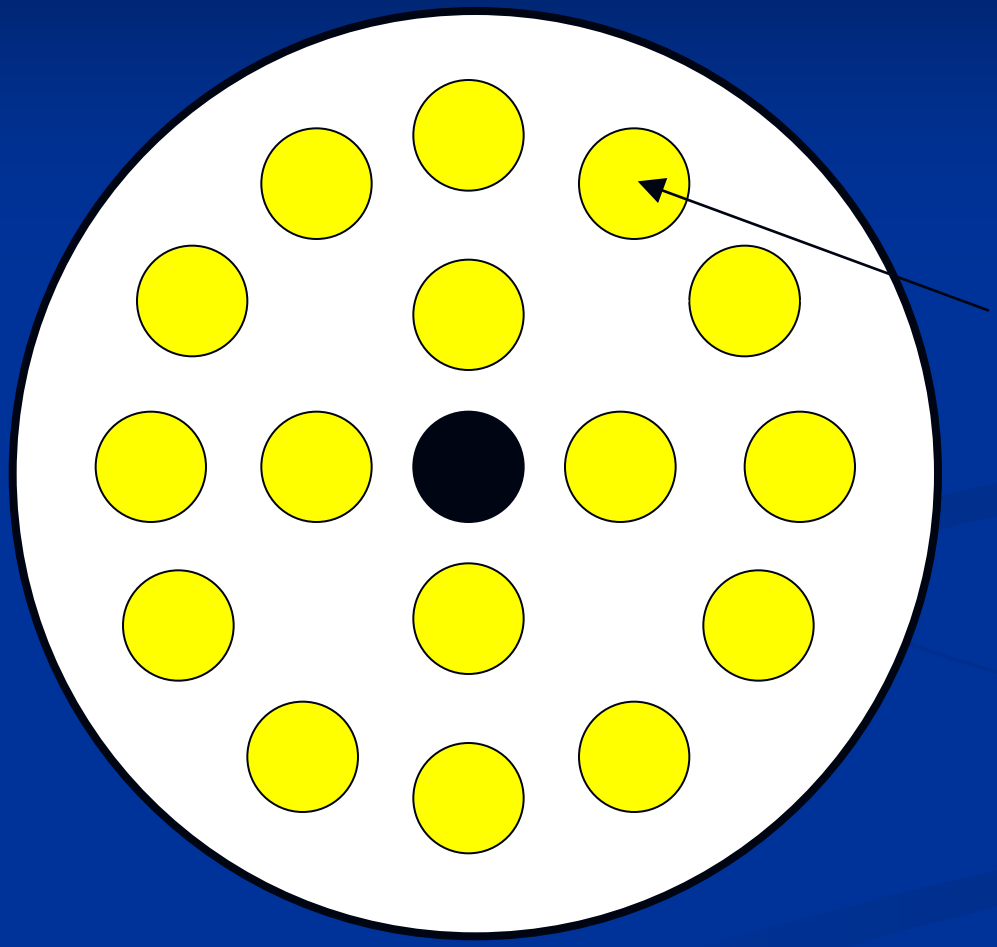
Sealant Test Chamber





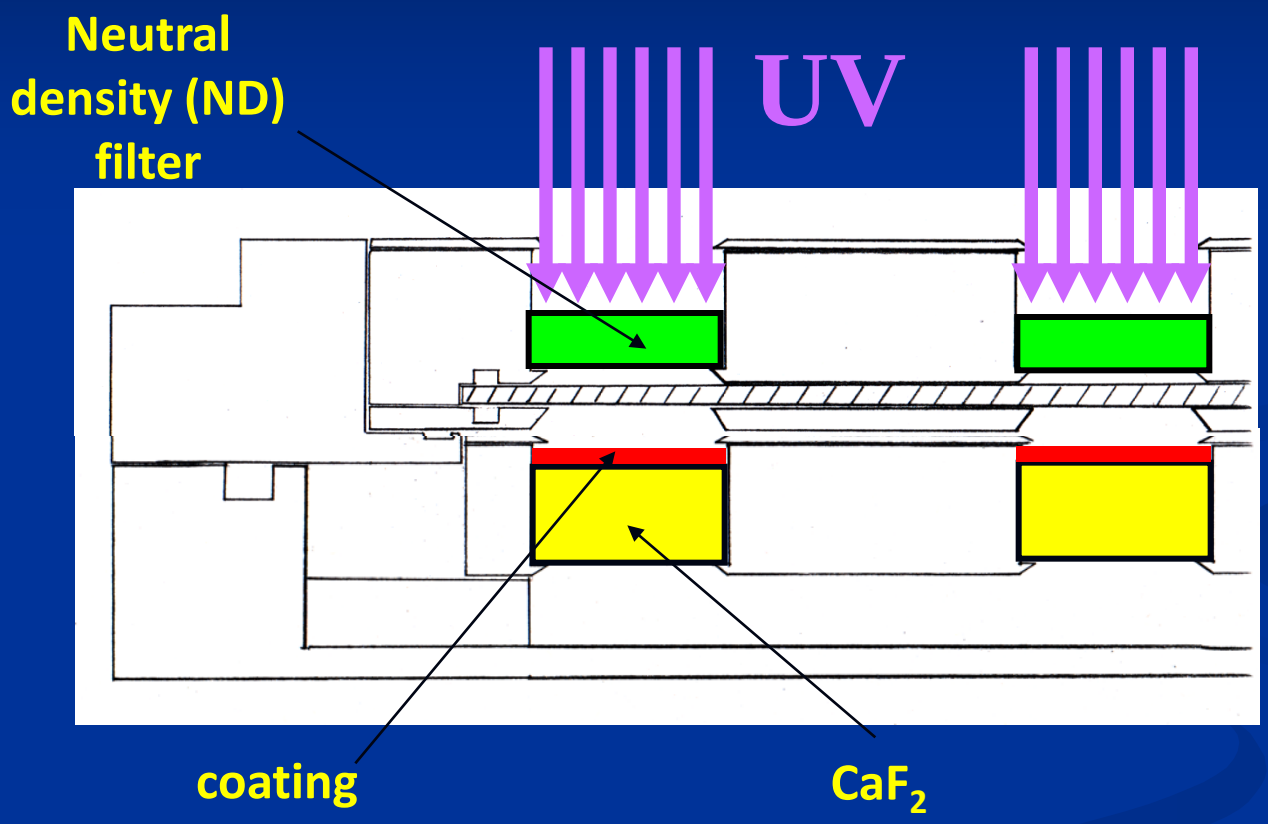
Test geometry ASTM C719

SPHERE Sample Holder



Thin polymer films spin-coated on CaF_2 windows.

SPHERE Sample Holder



Coatings Service Life Prediction

Laboratory Exposure – unfilled, amine-cured epoxy

Temp \ RH	0%	25%	50%	75%
25°C				
35°C				
45°C				
55°C				

4 bandpass filters: 306, 326, 354, 452 nm

4 neutral density filters: 10, 40, 60, 100 %

4 replicates

1024 specimens

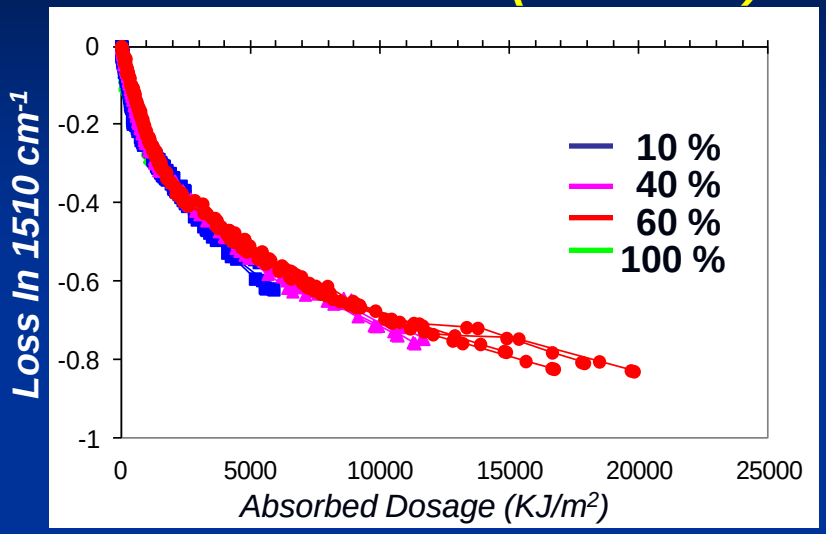
Coatings Service Life Prediction

Outdoor Exposure – unfilled amine-cured epoxy

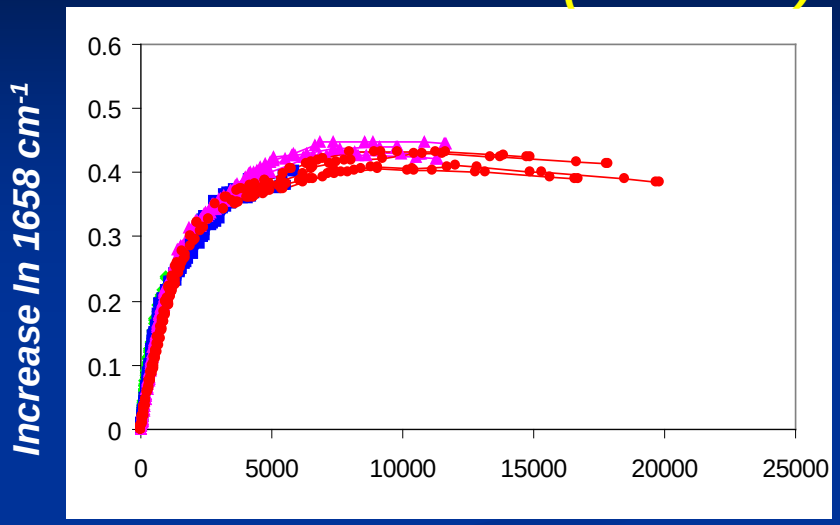
- Outdoor exposures were carried out on the roof of a NIST laboratory in Gaithersburg, MD.
- 20 groups of specimens were exposed in different months of different years.
- G_1, G_2, G_3 .....G_{20}
  (4 replicates, t_1.....t_n exposure times for each group)

Effect of Light Intensity on Chemical Degradation

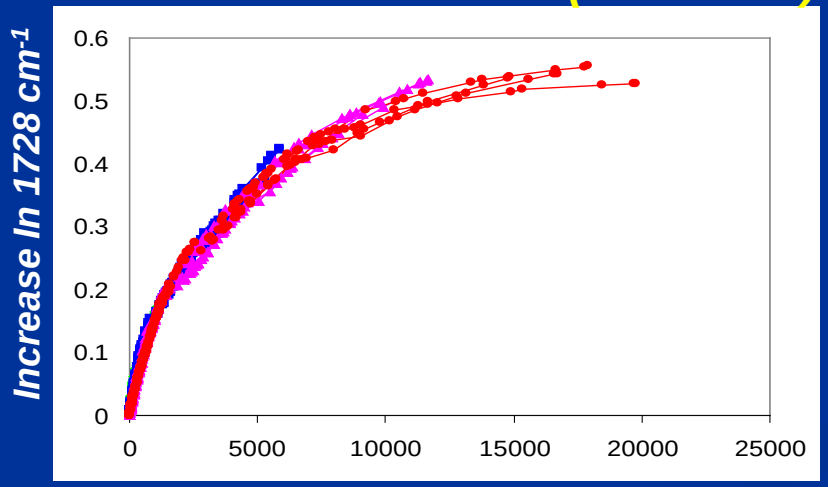
Chain Scission (1510 cm^{-1})



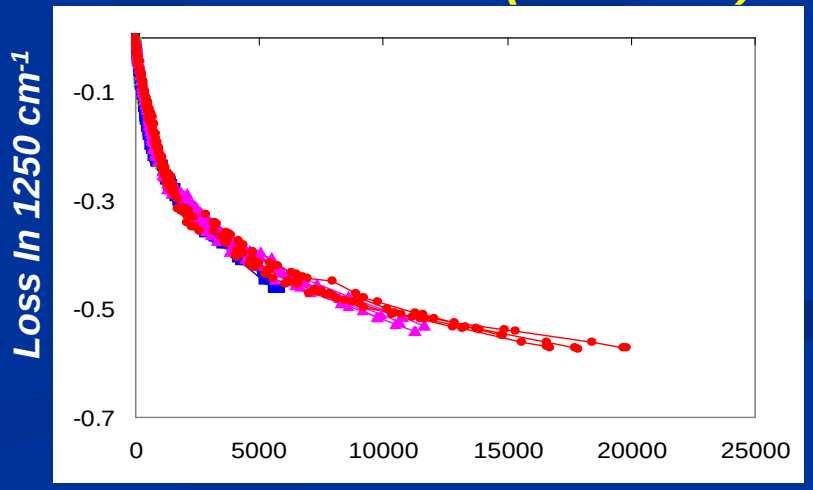
Amide Formation (1658 cm^{-1})



Ketone Formation (1728 cm^{-1})

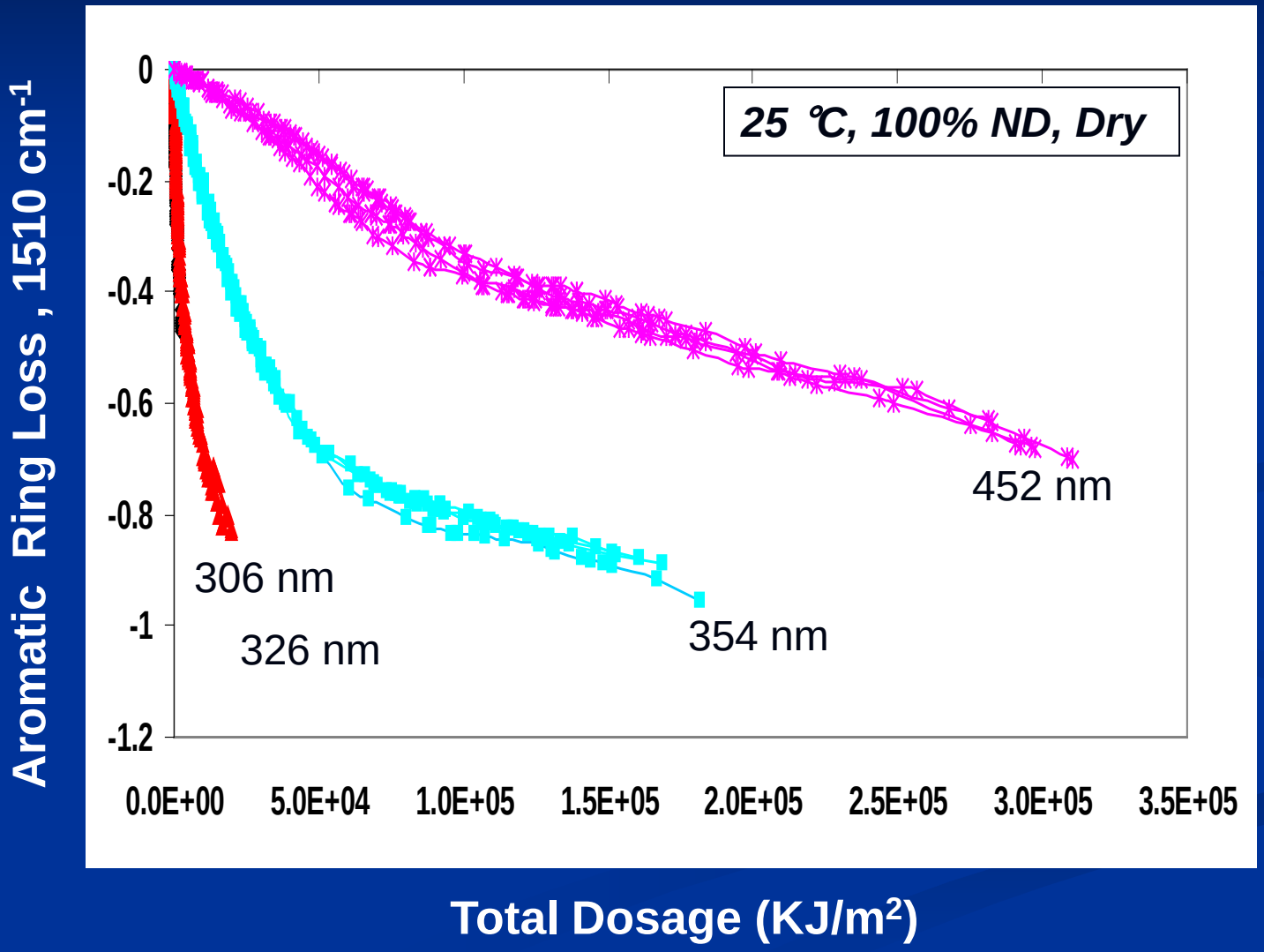


Chain Scission (1250 cm^{-1})



Reciprocity law is obeyed.

Effect of Wavelength on Chemical Degradation



Nano-morphological Changes during Outdoor Exposure using AFM

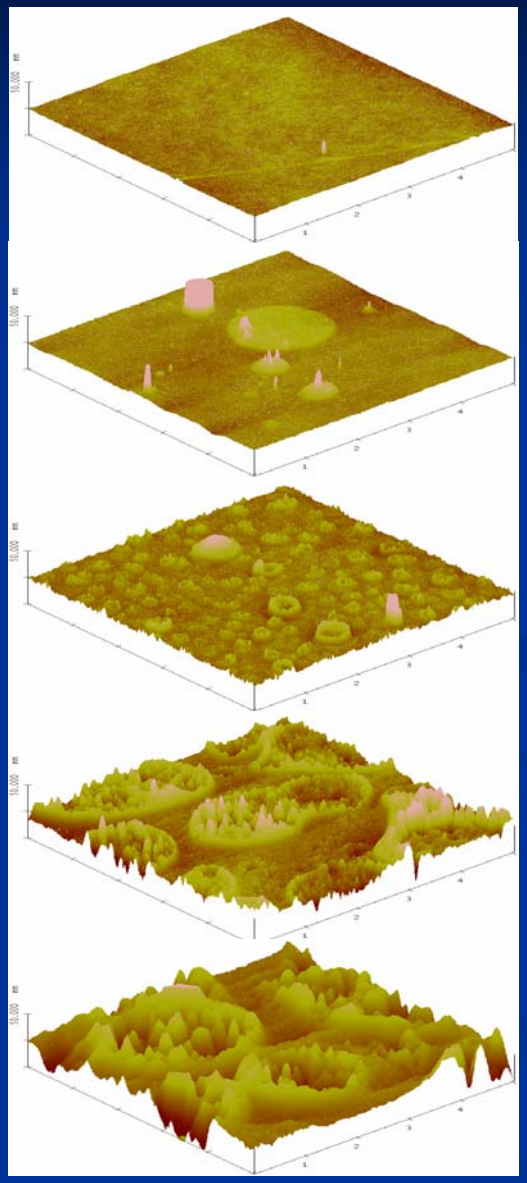
6 d

38 d

69 d

77 d

84 d



ablation

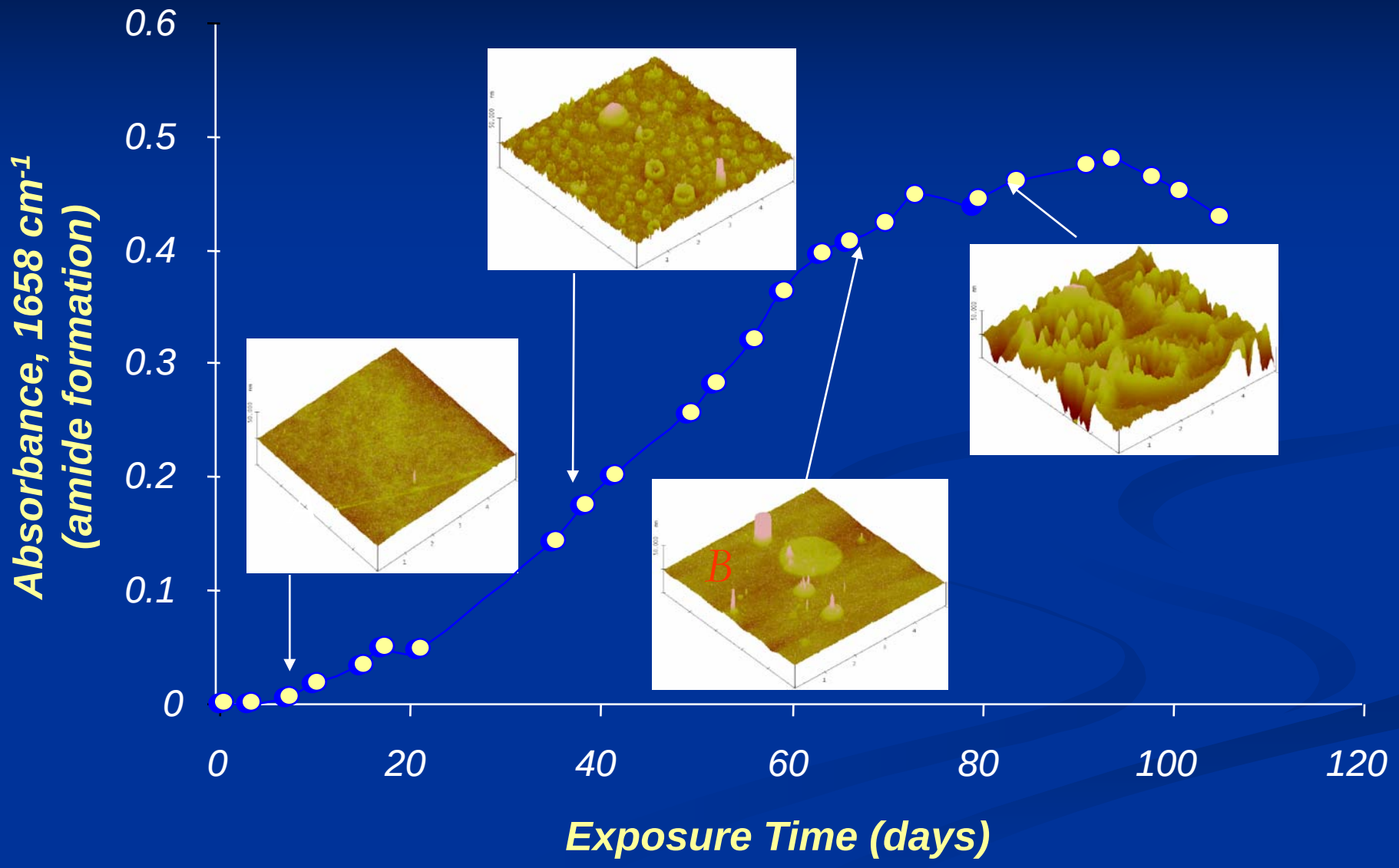
protuberance formation

organized pit formation

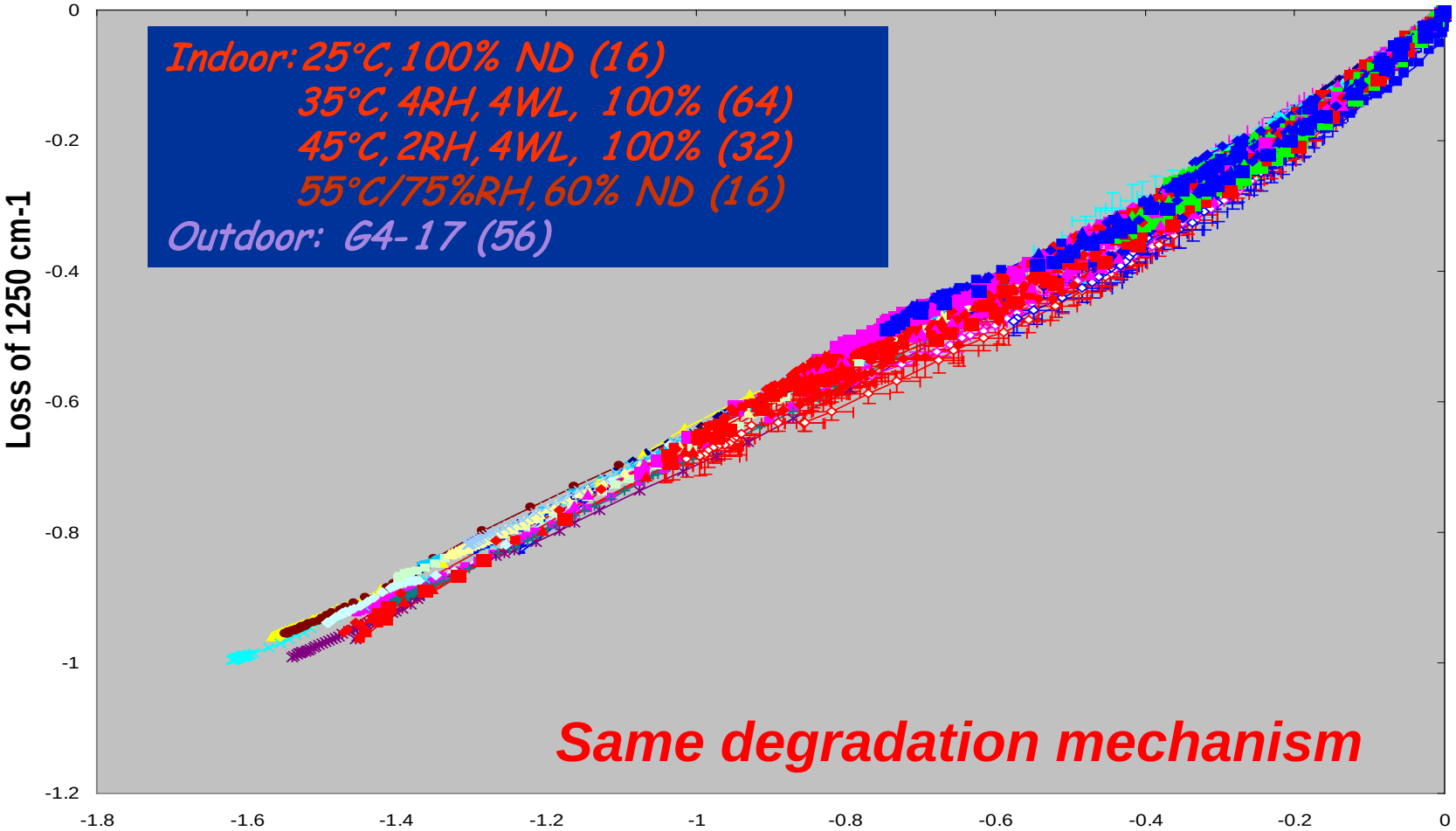
pits increasing in width and depth

5 mm x 5 mm

Relationship Between Chemical Changes and Nano-Morphological Changes



Comparing Laboratory to Outdoor Exposure Data



Relating Indoor Data to Outdoor Results:

Three Strategies

- **Using IR Ratios as a Chemical Metrics for Degradation Mechanism Comparison**

  Gu et al., "Linking Accelerated Laboratory Test with Outdoor Performance for a Model Epoxy Coating System" in Service Life Prediction for Polymeric Materials: Global Perspectives, Eds: J. Martin, R. Ryntz, J. Chin, R. Dickie, Springer Press, 2008.

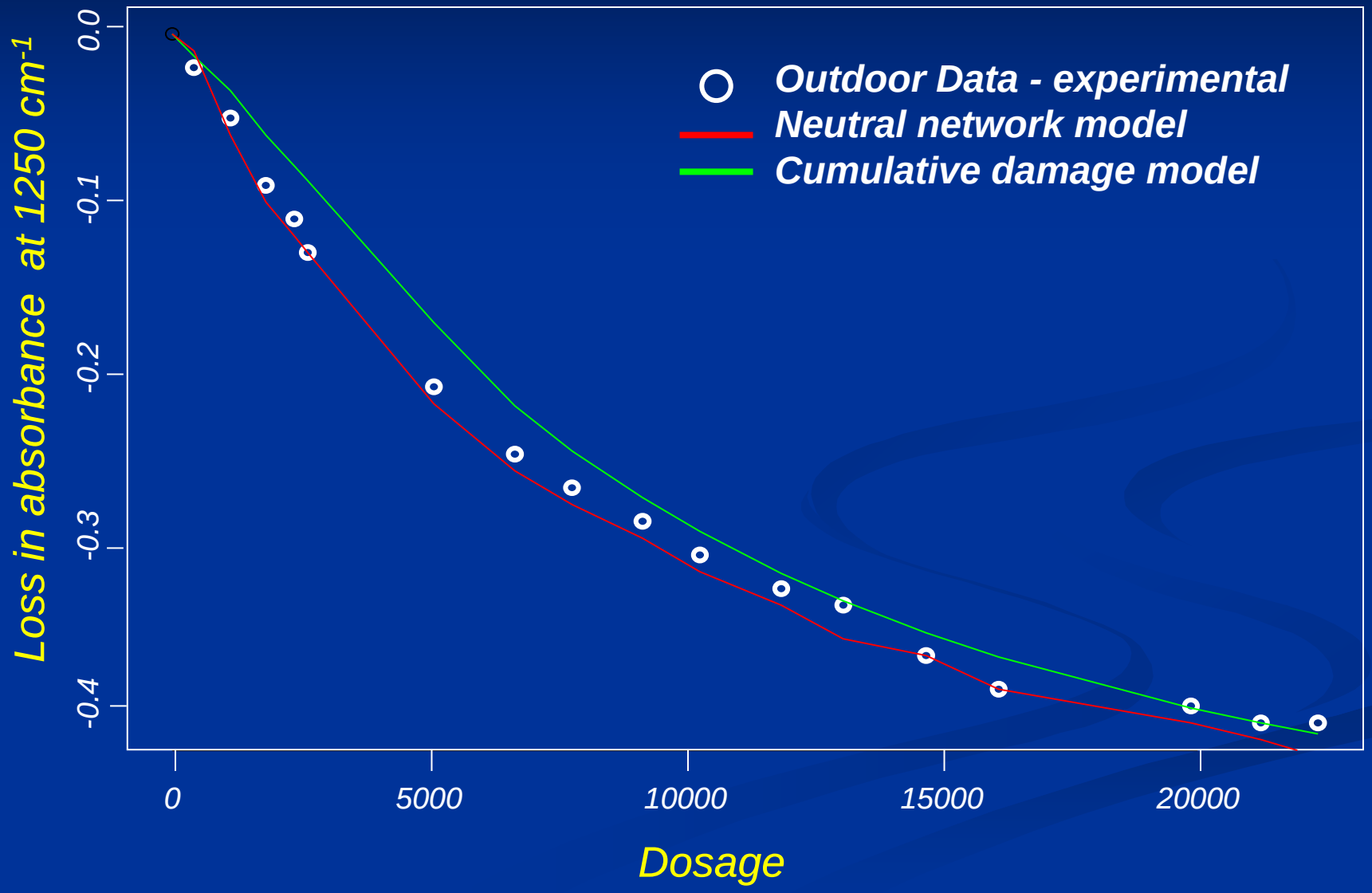
- **Model-Free Heuristic Approach (Neural Network model)**

  Dickens, B. "Model-free Estimation of Outdoor Performance of a Model Epoxy Coating System using Accelerated Test Laboratory Data", JCT Research (2009).

- **Cumulative Damage Prediction Model**

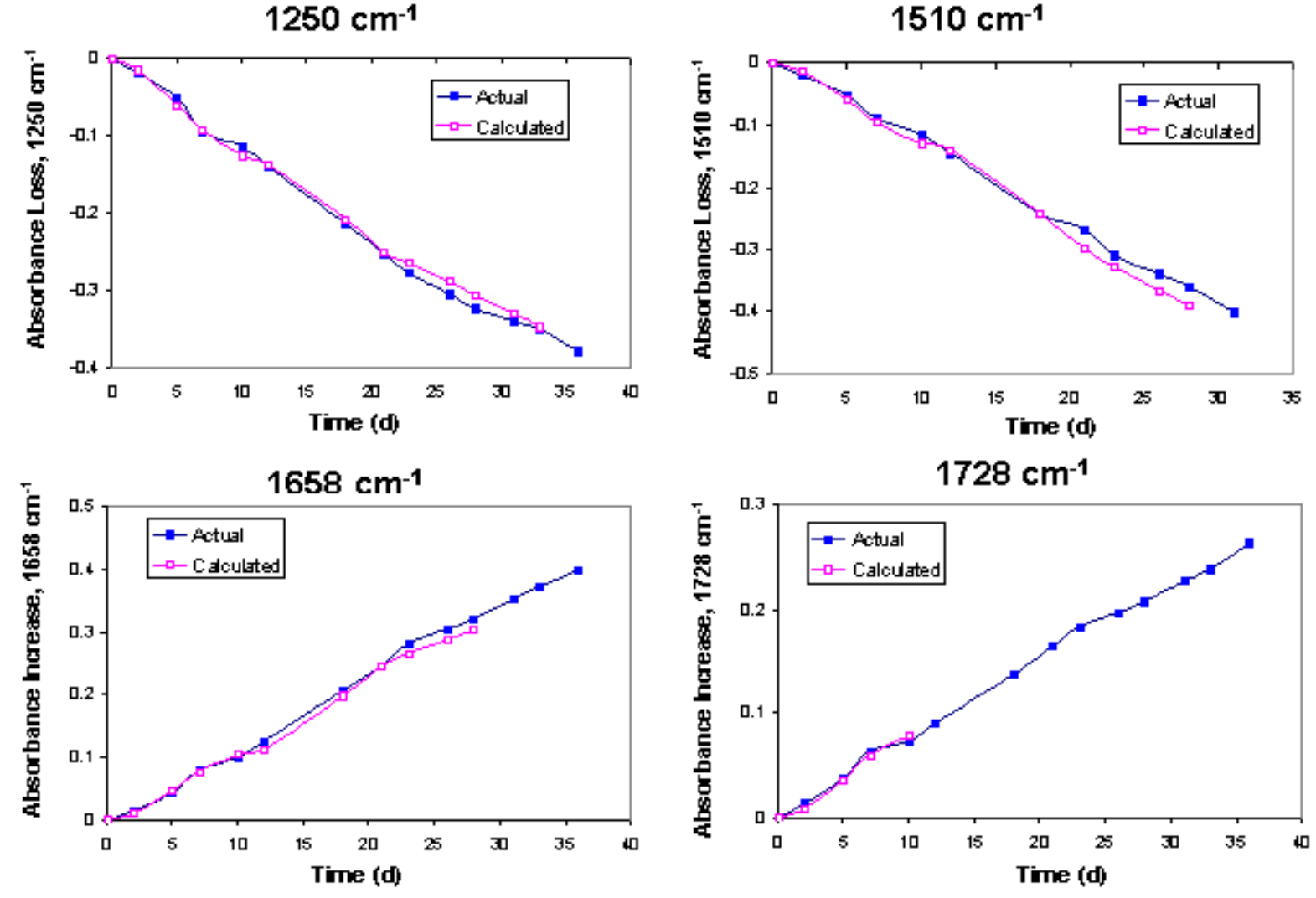
  Meeker, et al., "A Statistical Model for Linking Field and Laboratory Exposure Results for a Model Coating," Proceedings of 4th International Symposium on Service Life Prediction: Global Perspectives, Key Largo, Florida (2008).

Comparing Predicted Damage to Observed Damage for Specimens Exposed Outdoors



Predicted Damage vs. Observed Damage

Cumulative Damage Model

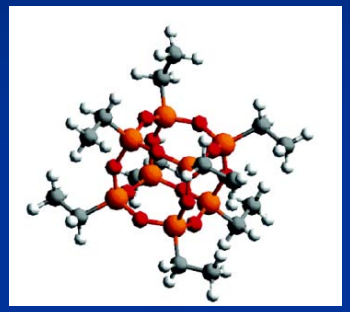


Summary and Future Work

- Feasibility of a service life prediction approach based on reliability methodology has been demonstrated for a model epoxy coating.
- Success of work on coatings indicates that this approach can also be applied to predicting service lives of polymeric materials used in other applications, such as sealants and photovoltaic polymers.
- Application of this methodology to sealants, nanocomposites, and photovoltaic polymers currently under study at NIST.

Program on Life Cycle and Sustainability of Polymers and Composites

- Develop and apply measurement science over a wide range of length (10^{-9} m to 10 m) and time scales to identify the critical fundamental material properties impacting performance and service life.



- Assess changes in critical fundamental properties via accelerated and real-time degradation studies on NIST SPHERE, “dark side” hygrothermal chambers, and outdoor testing devices.

- **Couple property measurements with reliability-based predictive models to enable quantitative prediction of service life.**

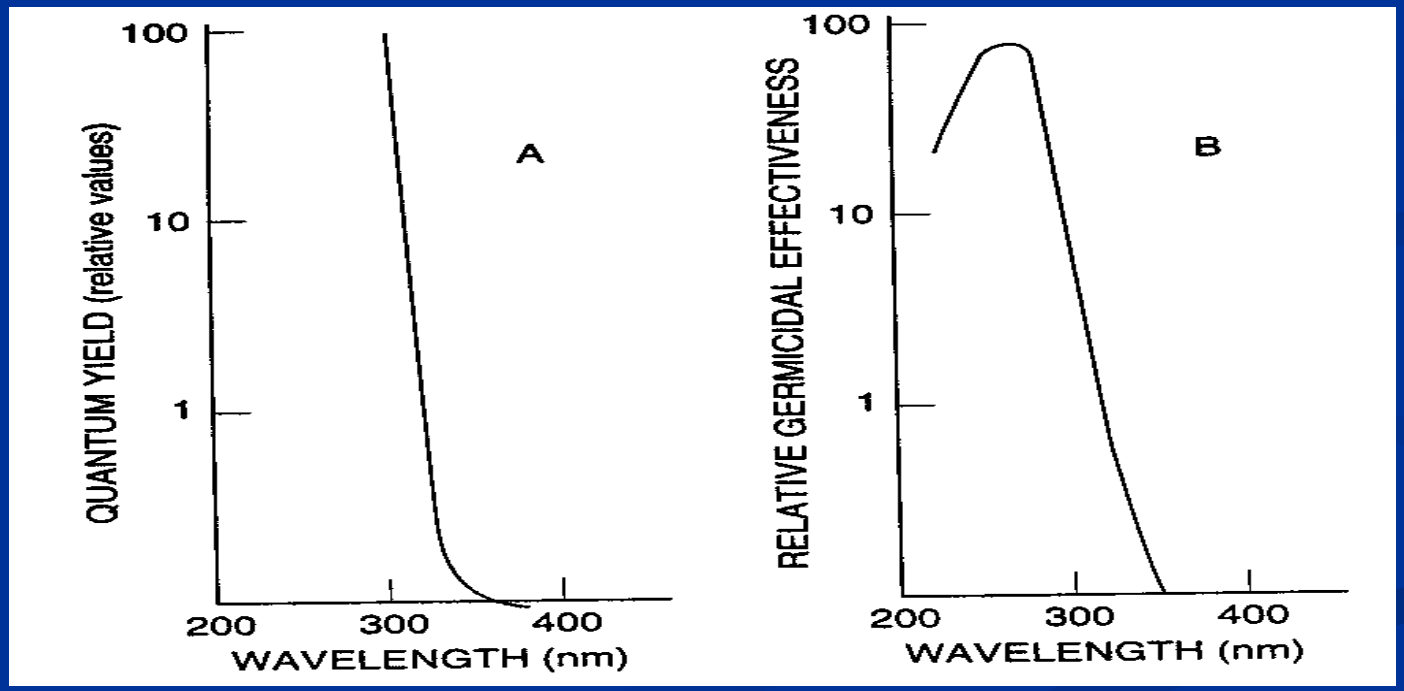
$$D_{total}(t) = \int_0^{\lambda} \int_{\lambda_{min}}^{\lambda_{max}} E_o(\lambda,t)\left(1-10^{-A(\lambda)}\right)\phi(\lambda)\,d\lambda\,dt$$

Total Effective Dosage Model

Synthetic polymers and biological materials

→ both carbon-based systems ←

Similar in UV response



Polymer DNA