Accelerated UV Weathering
of Polymeric Systems:

RECENT INNOVATIONS AND
NEW PERSPECTIVES

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Outline

Paradigm Shift In Accelerated Aging of Materials
New Technologies
Lifetime prediction
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

“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
“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*
Have these issues been considered in other fields???

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

Service Life Prediction

Biology Medicine Agriculture
Total Effective Dosage Model

\[ D_{\text{total}}(t) = \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \int_{0}^{t} E_o(\lambda, t)(1 - e^{-A(\lambda)}) \phi(\lambda) \, d\lambda \, dt \]

- \( D_{\text{total}}(t) \) = 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
- \( \lambda_{\text{min}}, \lambda_{\text{max}} \) = min. and max. photolytically effective wavelengths
Total Effective Dosage Model

- Total Effective Dosage: $D(t)$
- Total Effective Dosage Model

- $E_o$: Incident Energy
- $E_{absorbed}$: Absorbed Energy
- $E_{transmitted}$: Transmitted Energy
- $E_{reflected}$: Reflected Energy

- DAMAGE: Energy Dissipated

- TOTAL EFFECTIVE DOSAGE: $D(t)$
Reliability-Based SLP Methodology

Outdoor Exposure

Time Series
Temperature
RH, UV Dosage

Cumulative Damage Model

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

Laboratory Exposure

Light
Heat
Moisture

Databases
SLP Models

Basis for Coatings Service Life Prediction Consortium, 1994 - 2007
Integrating Sphere Technology

**LIGHT** (can be internal or external to sphere)

- scattered, collected
- highly reflective diffuse coating

**ILLUMINATION:**
- uniform light source

**OUTPUT**

**MEASUREMENT:**
- power
- transmittance
- reflectance
Integrating Sphere-based UV Chamber

**NIST SPHERE**

- Simulated Photodegradation via High Energy Radiant Exposure
- 2 m integrating sphere
- 8400 W UV $\rightarrow$ 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
Integrating Sphere-based UV Chamber

Environmental Chamber
“Dark Side”
T and RH Chambers

Outdoor Exposure Apparatus
Integrating Sphere-based UV Chamber

Test geometry ASTM C719

Sealant Test Chamber
Thin polymer films spin-coated on CaF$_2$ windows.
SPHERE Sample Holder

Neutral density (ND) filter

coating

CaF$_2$

UV
### Coatings Service Life Prediction

Laboratory Exposure – unfilled, amine-cured epoxy

<table>
<thead>
<tr>
<th>Temp</th>
<th>RH</th>
<th>0%</th>
<th>25%</th>
<th>50%</th>
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<td>4 bandpass filters: 306, 326, 354, 452 nm</td>
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<td></td>
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<tr>
<td>35°C</td>
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<td></td>
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<td>45°C</td>
<td>0%</td>
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<td></td>
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</tr>
<tr>
<td>55°C</td>
<td>0%</td>
<td>1024 specimens</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>25%</td>
<td></td>
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</tr>
</tbody>
</table>

4 bandpass filters: 306, 326, 354, 452 nm
4 neutral density filters: 10, 40, 60, 100 %
4 replicates
1024 specimens
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.
- $G_1, G_2, G_3 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots G_{20}$
  (4 replicates, $t_1 \ldots t_n$ exposure times for each group)
**Effect of Light Intensity on Chemical Degradation**

Chain Scission (1510 cm\(^{-1}\))

- Absorbed Dosage (KJ/m\(^2\))
- Loss In 1510 cm\(^{-1}\)
- 10 %
- 40 %
- 60 %
- 100 %

Amide Formation (1658 cm\(^{-1}\))

- Increase In 1658 cm\(^{-1}\)

Ketone Formation (1728 cm\(^{-1}\))

- Increase In 1728 cm\(^{-1}\)

Chain Scission (1250 cm\(^{-1}\))

- Loss In 1250 cm\(^{-1}\)

Reciprocity law is obeyed.
Effect of Wavelength on Chemical Degradation

Aromatic Ring Loss, 1510 cm$^{-1}$

Total Dosage (KJ/m$^2$)

25 °C, 100% ND, Dry

452 nm

306 nm

326 nm

354 nm
Nano-morphological Changes during Outdoor Exposure using AFM

- **6 d**: ablation
- **38 d**: protuberance formation
- **69 d**: organized pit formation
- **77 d**: pits increasing in width and depth
- **84 d**
Relationship Between Chemical Changes and Nano-Morphological Changes

Absorbance, 1658 cm$^{-1}$ (amide formation)

Exposure Time (days)
Comparing Laboratory to Outdoor Exposure Data

Indoor: 25°C, 100% ND (16)
35°C, 4RH, 4WL, 100% (64)
45°C, 2RH, 4WL, 100% (32)
55°C/75%RH, 60% ND (16)

Outdoor: G4-17 (56)

Same degradation mechanism
Relating Indoor Data to Outdoor Results:

Three Strategies

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

- 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
  
Comparing Predicted Damage to Observed Damage for Specimens Exposed Outdoors

![Graph showing the comparison between outdoor data and predicted damage models.](image-url)
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.

\[
D_{tota}(t) = \int_{\lambda_{min}}^{\lambda_{max}} E_{\lambda}(\lambda, t)(1 - 10^{A(\lambda)}) d\lambda dt
\]
Total Effective Dosage Model

Synthetic polymers and biological materials
→ both carbon-based systems ↔
Similar in UV response