Service Life Prediction of Field-Exposed Units Based on Laboratory Accelerated Degradation Test Data

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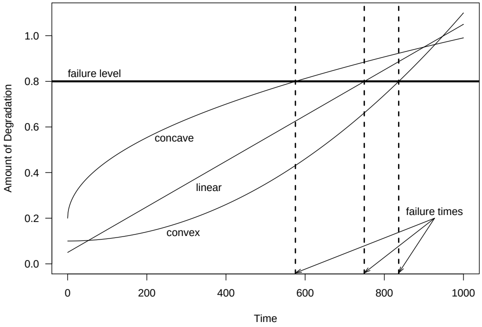
Outline

- Background and Motivation
- NIST accelerated test experiments and data collection
- Statistical model for photodegradation
- Statistical modeling and data analysis
- Using the accelerated test model to predict outdoor weathering
- Conclusions and future work

Background and Motivation

- Service life prediction is of high interest in the coating industry.
- Failures of coatings/paints are mainly caused by photodegradation, driven by ultraviolet (UV) radiation.
- Temperature and humidity also affect the degradation process.
- Traditional outdoor exposure testing takes too much time
- Some previous attempts at indoor accelerated testing gave misleading results
- Need a reliable, scientifically-based, indoor accelerated test methodology

General Degradation Path Model



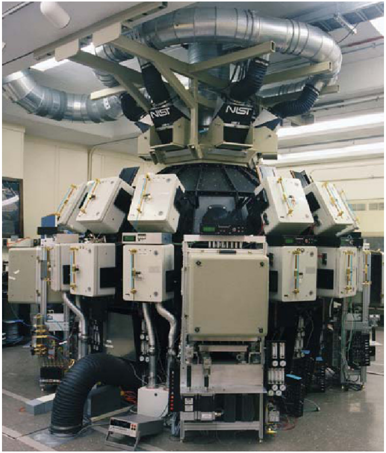
- Degradation models provide tools for service life prediction
- The service life is $T = \inf\{t : D(t) \text{ reaches } D_f\}$
- The cdf $F(t)$ is obtained based on the degradation model
- Service life prediction can be based on the estimated $F(t)$

NIST Objectives

- Develop a scientifically-based accelerated test methodology for organic paints and coatings
- Use indoor accelerated tests to develop a photodegradation path model as a function of explanatory variables
  - For indoor tests, explanatory variables are at fixed levels
  - Desire to have physical/chemical-based model components
  - Otherwise use empirical fitting
- Verify that indoor testing can be used to predict outdoor weathering
  - Verify that both indoor accelerated tests and outdoor weathering share the same degradation mechanism (i.e., same chemical changes by comparing FTIR spectra)
  - Drive the accelerated-test photodegradation path model with time-varying explanatory variables to predict outdoor degradation
  - Compare predictions with actual outdoor exposure experiments

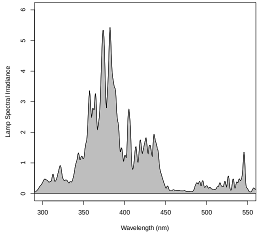
NIST Indoor Experiment

- Studied the degradation of a model epoxy coating system.
- Both indoor and outdoor experiments were done at NIST from 2002 through 2006.
- Indoor experiments were done using the NIST SPHERE (Simulated Photodegradation via High Energy Radiant Exposure).
- The SPHERE can control precisely the UV exposure, temperature and relative humidity.
- Accelerating variables are UV spectrum, UV intensity, temperature, and humidity.



Indoor Experiment Setup

- To study the effect of UV spectrum, UV intensity, temperature, and humidity
- The UV light source for indoor experiments is from high intensity light lamps, made approximately spatially uniform by the integrating sphere



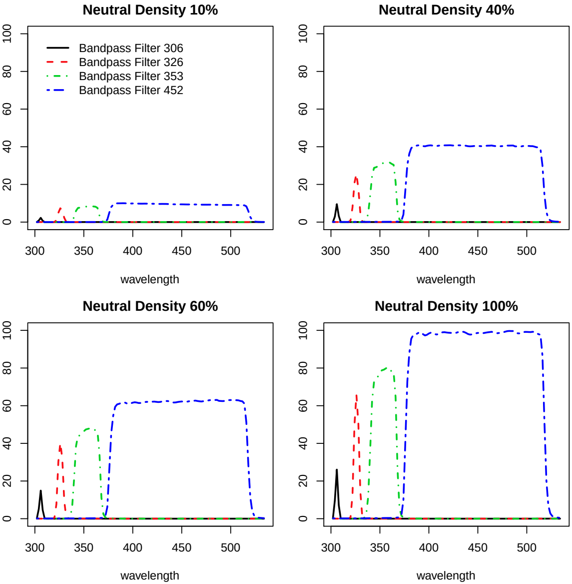
Bandpass Filter

- BP filter only passes UV with wavelengths within a given range.
- Four filters: 306 nm ($\pm$3), 326 nm ($\pm$6), 353 nm ($\pm$19), 452 nm($\pm$80)
- UVB: 280-315nm, UVA: 315-400nm, Visible light: >400nm

BP and ND Filter Combinations

Neutral Density Filter

- Four BP filters with centers at 306, 326, 353, 452 nm, control the UV spectrum shape
- Four ND filters: 10%, 40%, 60%, 100% UV intensity



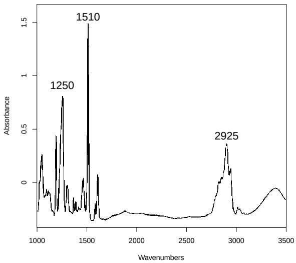
Experimental Design

- Four BP filter levels with centers at 306, 326, 353, 452 nm
- Four ND filter levels: 10%, 40%, 60%, 100%
- Four temperature levels: 25°C, 35°C, 45°C, 55°C
- Four relative humidity (RH) levels: 0%, 25%, 50%, 75%

Temp \ RH	0%	25%	50%	75%
25	4×4			
35	4×4	4×1	4×1	
45		4×1	4×1	4×4
55				4×4

Degradation Measurements

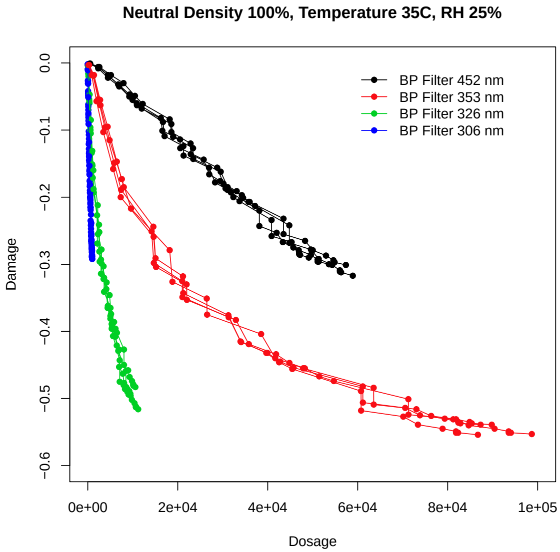
- Chemical degradation was measured automatically every few days by Fourier transform infrared (FTIR) spectroscopy.
- Spectral structure of compounds absorb the energy of the infrared at different wavelengths.
- The location of a peak corresponds to a unique chemical compound or structure.
- The height of a peak is proportional to the concentration of a particular chemical compound.



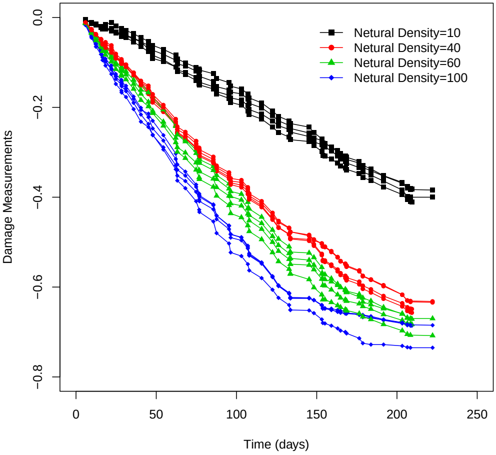
Damage numbers

- 1250 $\leftrightarrow$ aromatic C-O bonds
- 1510 $\leftrightarrow$ benzene ring mass loss
- 2925 $\leftrightarrow$ CH mass loss

Example Indoor Degradation Paths for Damage Number 1250 for Different BP filters



Example Indoor Degradation Paths for Damage Number 1250 for Different ND filters



Dosage Time Scale

- The time scale is dosage: proportional to the number of photons absorbed into the material
- The dosage up to time t is computed by $d(t) = \int_0^t \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} E(\tau, \lambda) \left[1 - e^{-A(\lambda)}\right] d\lambda d\tau$
- $E(\tau, \lambda)$ the spectral irradiance at wavelength λ and time τ after the BP and ND filters
- $[1 - e^{A(\lambda)}]$ is the proportion of photons absorbed into the material

Effective Dosage

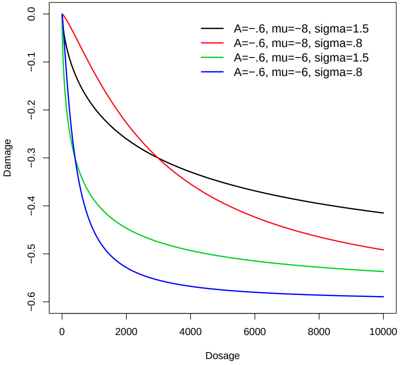
- The effective cumulative dosage is defined as $d_{\mathrm{eff}}(t) = \int_0^t \int_{\lambda_{\min}}^{\lambda_{\max}} E(\tau, \lambda) \left[1 - e^{-A(\lambda)}\right] \phi(\lambda) d\lambda d\tau$
- $\phi(\lambda)$ is the quasi-quantum yield function allowing that a shorter wavelength photons have a higher probability of causing damage
- To allow for the environmental effects, consider

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

- We initially use a **categorical model** to provide guidance for finding the functional forms of f, g, h, and ϕ

Degradation Path Model

$$\mathcal{D}(t) = \frac{\alpha}{1 + \exp\left\{-\frac{\log[d(t)]+\mu}{\sigma}\right\}}$$



Categorical Effect Model

- For indoor data, explanatory variables held constant during the experiments.
- Consider nonlinear mixed effects model for unit i:

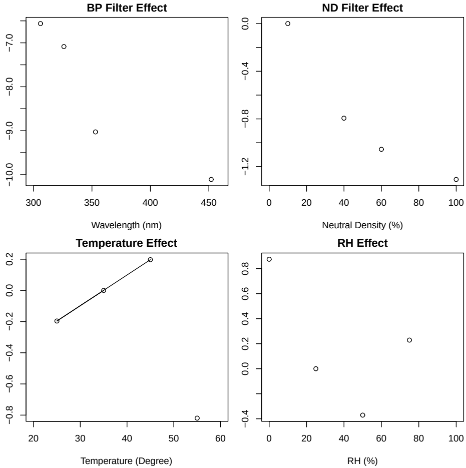
$$y_i(t_{ij}) = \frac{\alpha \exp(\nu_i)}{1 + \exp(-z_{ij})} + \epsilon_{ij}$$

  - where $\nu_i \sim \mathrm{N}(0, \sigma_\nu^2)$ is the exposure-to-exposure random effect and $\epsilon_{ij} \sim \mathrm{N}(0, \sigma_\epsilon^2)$ is the error term and

$$z_{ij} = \frac{\log[d(t_{ij})] + \log[b(BP_i)] + \log[f(Temp_i)] + \log[g(RH_i)] + \log[h(ND_i)]}{\sigma_{\lambda_i}}$$

  - $\log[b(BP_i)], \log[f(Temp_i)], \log[g(RH_i)]$ and $\log[h(ND_i)]$ are categorical effects for BP, temperature, RH, and ND.
- `nlme` in R used to do the estimation.

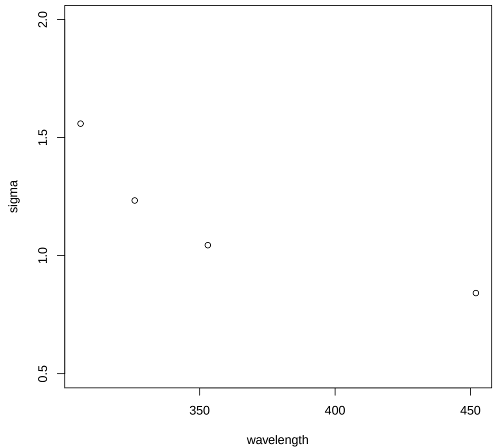
Categorical Variable Effects



Modeling Explanatory Variable Effects

- The Arrhenius relationship is used to describe the acceleration effect of temperature: $r(\text{Temp}) = \gamma_0 \exp(\frac{-E_a}{R \times \text{Temp}K})$ where Temp$K$ is a Kelvin temperature (Celsius+273), R is a gas constant, and E_a is an effective activation energy
- The RH effect is decreasing and then increasing, suggesting a convex relationship: $\log[g(\text{RH})] = \beta_{\text{RH}} \times (\text{RH} - \text{rh}_0)^2$
- BP effect (effect of UV spectrum) is modeled by a log linear relationship: $\phi(\lambda) = \exp(\beta_0 + \beta_1 \lambda)$
- The ND effect is modeled by power law relationship: $h(\text{ND}_i) = (\text{ND}_i)^p$
- The unexpected behavior at 55C and 75% modeled as an interaction effect

Functional Form for σ_λ



- The curve of categorical estimates of the path-model slope parameter σ shows an exponential relationship with wavelength.
- We take $\sigma_\lambda = \sigma_0 + \exp(\sigma_1 + \sigma_2\lambda)$.

Nonlinear Mixed Effects Model with Continuous Factors Held Constant

- Nonlinear mixed Effects model:

$$y_i(t_{ij}) = \frac{\alpha \exp(\nu_i)}{1 + \exp(-z_{ij})} + \epsilon_{ij}$$

- $\nu_i \sim \mathrm{N}(0, \sigma_\nu)$ is the random effect and

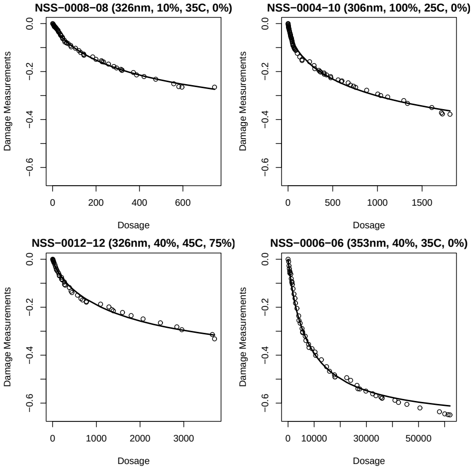
$$z_{ij} = \frac{\log[\int_0^{t_{ij}} \int_{\lambda_{\min}}^{\lambda_{\max}} D(\tau, \lambda)] \exp(\beta_0 + \beta_1 \lambda) d\lambda d\tau] + p(\log[ND_i]) + \frac{-\frac{E_a}{R}}{\mathrm{Temp}K} + \beta_{\mathrm{RH}}(\mathrm{RH} - \mathrm{rh}_0)^2}{\sigma_0 + \exp(\sigma_1 + \sigma_2 \times \lambda)}$$

- The parameters are
  $\theta = (\alpha, \beta_\lambda, p, E_a/R, \beta_{\mathrm{RH}}, \mathrm{rh}_0, \eta_0, \sigma_0, \sigma_1, \sigma_2, \sigma_\nu)$
- `nlme` in R was used to do the estimation.

Model Parameter ML Estimates

Parameter	Value	Std.Error	*p*-value
α	-0.6191	0.0101	< 0.0001
β_λ	-0.0297	0.00026	< 0.0001
p	-0.5606	0.0078	< 0.0001
E_a/R	1945.6234	75.8383	< 0.0001
β_{RH}	-0.0005	0.00001	< 0.0001
rh_0	45.4761	0.2875	< 0.0001
η_0	13.4159	0.2539	< 0.0001
σ_0	0.8019	0.0066	< 0.0001
σ_1	7.6784	0.1876	< 0.0001
σ_2	-0.0260	0.0006	< 0.0001

Fitted Degradation Path for Selected Indoor Units

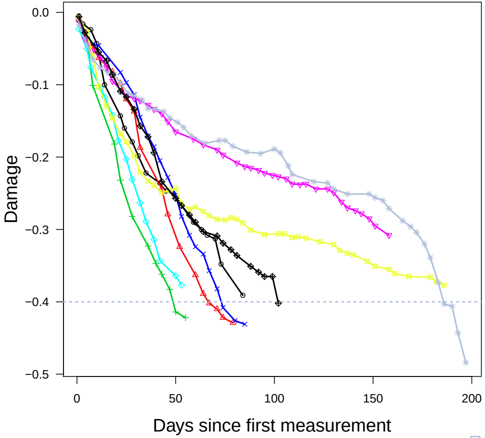


Outdoor Experiments

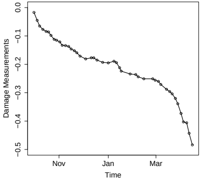
- Objective: verify that the accelerated tests and outdoor weathering have the same degradation mechanism
- Outdoor UV exposures were conducted on a roof at NIST.
- Different groups of units were exposed, each for several months, between 2002 and 2006
- UV exposure, temperature, and RH were uncontrolled, but recorded by sensors, at a 12-minute interval.
- FTIR degradation measurements were taken every three to four days.

Degradation Paths for Nine Specimens Exposed at Different Times of the Year

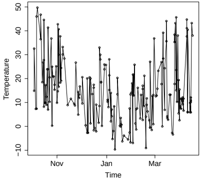
- FTIR wavenumber 1250 cm^{-1} (aromatic C-O bonds)
- Failure threshold is $D_f = -0.4$ (level where there would be customer perceivable loss of gloss)



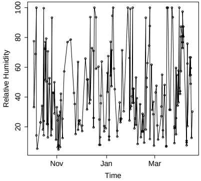
Sample Data from a Single Outdoor Unit



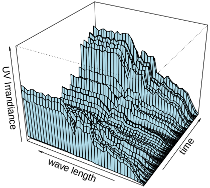
(a) Damage



(b) Temperature



(c) Relative humidity



(d) UV

Model for Outdoor Prediction

- We use the cumulative damage model, based on the indoor experiments, to generate predictions for the outdoor units
- The prediction is conditional on the observed time varying explanatory variables.
- Basic idea: compute damage predictions over short time intervals (one hour) and for a given wavelength 2 nm λ intervals, according to the nonlinear mixed effects model
- The damage is then accumulated over wavelengths and time to compare with the actual observed damage

Calculation of Incremental Cumulative Damage

- The incremental effective dosage for 2 nm and one-hour intervals is computed from the reported dosage $\mathrm{D}(\tau, \lambda)$ as

$$\Delta S^*(\tau, \lambda) = \int_{\tau}^{\tau + 60\,\text{min}} \int_{\lambda - 1\mathrm{nm}}^{\lambda + 1\mathrm{nm}} \mathrm{D}(\tau, \lambda) \exp(\beta_\lambda \lambda) d\lambda d\tau.$$

- The slope of the degradation curve at time τ is

$$g'(\tau, \lambda) = \frac{d\mathcal{D}[\tau, S^*(t), \mathrm{Temp}(\tau), \mathrm{RH}(\tau)]}{dS^*(\tau, \lambda)} = \frac{1}{S^*(\tau, \lambda)\sigma_\lambda} \times \frac{\alpha \exp(z)}{(1 + \exp(z))^2}$$

where

$$z = \frac{\log\left(S^* |\beta_\lambda|\right) + \eta_0 + p[\log(\mathrm{ND})] - \left(\frac{\frac{E_a}{R}}{\mathrm{temp}K}\right) - \beta_{\mathrm{RH}} \left(\mathrm{RH} - \mathrm{rh}_0\right)^2}{\sigma_0 + \exp\left(\sigma_1 + \sigma_2 \bar{\lambda}\right)}$$

- The predicted instantaneous damage for the hour beginning at τ and 2 nm interval centered at λ is

$$\Delta\mathcal{D}(\tau, \lambda) = g'(\tau, \lambda) \Delta S^*(\tau, \lambda)$$

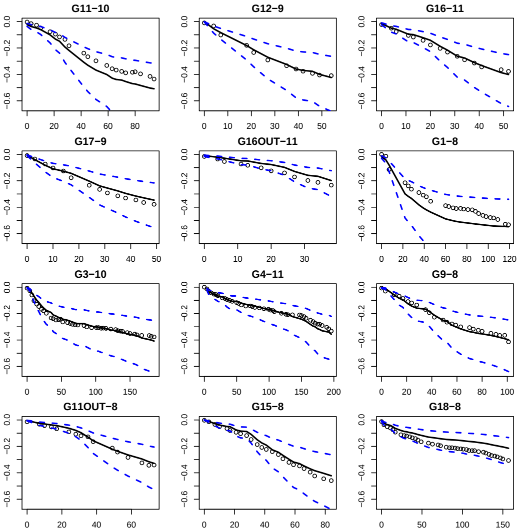
Calculation of Cumulative Damage Predictions and Prediction Intervals

- The predicted cumulative damage across all wavelength is $\Delta\mathcal{D}(\tau) = \sum_{\text{range of } \lambda} \Delta\mathcal{D}(\tau, \lambda)$
- The predicted cumulative damage is up to time t is

$$\mathcal{D}(t) = \sum_{\tau=0}^{t} \Delta\mathcal{D}(\tau) \tag{1}$$

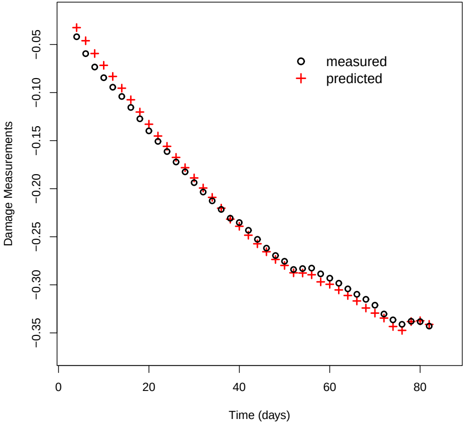
- Prediction intervals are computed with a bootstrap procedure, accounting for the random effect and sampling variability

Predicted Outdoor Damages

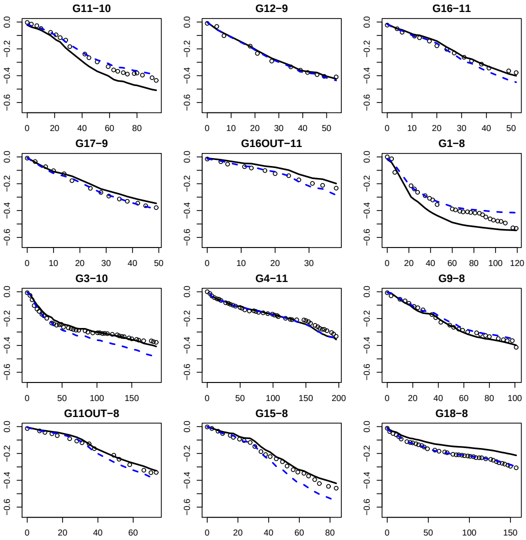


Predicted vs Observed

- Average of outdoor predictions versus average of observed



Predicted vs Observed After Adjustment for Random Effects Estimated from the 5th to 10th Data Points



Conclusions and Areas for Future Research

- We identified a physically motivated model incorporating effects of UV spectrum, UV intensity, temperature, and RH that adequately describes photodegradation paths
- A time series model for the environmental variables at a particular location could be used to make predictions and prediction intervals that account for weather uncertainty.
- Could make similar predictions for other geographical locations or for "typical" locations
- The methodology can be applied to paints and coatings that are designed to last many years
- Some examples of other application areas are
  - Loss of light output from an LED array
  - Power output decrease of photovoltaic arrays
  - Corrosion in a pipeline
  - Vibration from a worn bearing in a wind turbine