Predictive and Semi-gSEM Models of Poly(Ethylene-Terephthalate) under Multi-Factor Accelerated Weathering Exposures

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Motivation

Degradation Science\(^1\)
Of Complex Materials Systems
Under Multi-factor Exposures

Develop Data-driven Analysis and Modeling
• Exploratory Data Analysis
• Predictive Modeling
• Diagnostic Modeling for Degradation Mechanisms and Pathways

Using Un-biased Analysis, based in Statistical Significance
• That Complements Hypothesis-driven Physical & Chemical Modeling

PET Films Case Study
• Longitudinal Weathering Study
• Under 4 Accelerated Exposure Conditions

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Degradation science: Mesoscopic evolution and temporal analytics of photovoltaic energy materials

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ABSTRACT

Based on recent advances in nanoscience, data science and the availability of massive real-world data-streams, the temporal evolution of mesoscopic energy materials can now be more fully studied. The temporal evolution is vastly complex in time and length scales and is fundamentally challenging to scientific understanding of degradation mechanisms and pathways responsible for energy materials evolution over lifetime. We propose a paradigm shift towards mesoscopic evolution modeling, based on physical and statistical models, that would integrate laboratory studies and real-world massive datastreams into a stress/mechanism/response framework with predictive capabilities. These epidemiological studies encompass the variability in properties that affect performance of material ensembles. This mesoscopic evolution modeling is shown to encompass the heterogeneity of these materials and systems, and enables the discrimination of the fast dynamics of their functional use and the slow and/or rare events of their degradation. We delineate paths forward for degradation science.
Longitudinal Weathering Study of PET Grades

The three PET grades used:

- **Unstabilized** (Dupont-Teijin Melinex 454, 3 mil)
- **UV stabilized** (Dupont-Teijin Tetoron HB3, 2 mil)
- **Hydrolytically stabilized** (Mitsubishi 8LH1, 5 mil)

A lab-based, completely randomized, longitudinal study design

- Followed over time with repeated measurements.
  - **Step size is one week (168 hours) for a total of 7 weeks (1176 hours)**
  - Retained Sample Library: Retain one sample at each time step

More Generally:

For One grade
In One Exposure

<table>
<thead>
<tr>
<th>Exposure Time</th>
<th>168 hours</th>
<th>336 hours</th>
<th>504 hours</th>
<th>672 hours</th>
<th>840 hours</th>
<th>1008 hours</th>
<th>1176 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
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</tbody>
</table>
Exposure Conditions

Heat and humidity exposures

- Environmental test chambers
- Temperature and humidity control

1) DampHeat
- Constant exposure at 85°C and 85%RH per IEC 61215

2) FreezeThaw
- 20 hrs of 70 °C at 85% RH plus 0.5 hrs of -40 °C at 0 % RH

UVA light exposures

- Fluorescent weathering tester
- Outfitted with UVA 340 lamps and water spray

3) ASTM G154 Cycle 4 (CyclicQUV)
- 8 hrs of 1.55 W/m² @ 340 nm light at 70 °C plus 4 hrs of condensing humidity in dark at 50 °C

4) ASTM G154 Cycle 4 without the condensing humidity (HotQUV)
- Constant UVA light at 1.55 W/m² @ 340 nm at 70°C
Performance Response: Yellowness Index (YI)

Humidity only, did not result in significant yellowing.

In UV stabilized grade, change point in YI after first exposure step.
Performance Response: Haze (%)

Humidity only did not result in significant hazing.
No hazing observed with light only
  • Even with high level of yellowing.

Marked Hazing in CyclicQUV exposure in presence of light & moisture.
  • Increased hazing in unstabilized grade than in UV stabilized grade.

Hazing Requires
Moisture
Increased by
Precursor Yellowing

Follow UV-Stabilized
Under
HotQUV & Cyclic QUV
Exposures
## Mechanistic: PET UV-Vis Spectral Features

<table>
<thead>
<tr>
<th>Abs (nm)</th>
<th>Feature</th>
<th>Mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>312</td>
<td>Fund. abs. edge</td>
<td>( \pi \rightarrow \pi^* ) transition of the terephthalate unit and ester carbonyl on the PET backbone</td>
</tr>
<tr>
<td>325</td>
<td>carboxylic acid end groups</td>
<td>photo-oxidation</td>
</tr>
<tr>
<td>340</td>
<td>hydroxylated species</td>
<td>hydroperoxide formation ( \rightarrow ) photolysis of hydroperoxides ( \rightarrow ) hydroxyl radicals ( \rightarrow ) substitution reactions ( \rightarrow ) mono- or dihydroxy terephthalate unit ( \rightarrow ) hydroxylated species ( \rightarrow ) increase in absorbance</td>
</tr>
<tr>
<td>340</td>
<td>UV Stabilizer(^2)</td>
<td>UV stabilizer bleaching</td>
</tr>
<tr>
<td>375-425</td>
<td>quinones(^1)</td>
<td>( \text{photolysis} \rightarrow \text{chain scissions} \rightarrow \text{hydroperoxides} \rightarrow \text{hydroxylated species} \rightarrow \text{fluorescence} \rightarrow \text{increased yellowing} )</td>
</tr>
</tbody>
</table>

Choose 2 UV Mechanisms

- 312 nm: Fundamental Absorption Edge
- 340 nm: UV Stabilizer Bleaching For Stabilized PET

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\(^1\) From UV Spectra of the UV stabilizer (Cyasorb 3638)

Mechanistic: PET FTIR Spectral Features

Unstabilized - CyclicQUV

<table>
<thead>
<tr>
<th>cm⁻¹</th>
<th>Band</th>
<th>Mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1711</td>
<td>C=O carbonyl</td>
<td>Chain scission</td>
</tr>
<tr>
<td></td>
<td>broadening</td>
<td></td>
</tr>
<tr>
<td>1675</td>
<td>C=O</td>
<td>Formation of carboxylic acid</td>
</tr>
<tr>
<td>975</td>
<td>trans O-CH₂</td>
<td>Crystallization</td>
</tr>
<tr>
<td>1340</td>
<td>trans CH₂</td>
<td></td>
</tr>
<tr>
<td>1125</td>
<td>trans C-O</td>
<td></td>
</tr>
<tr>
<td>775</td>
<td>new formation</td>
<td>Photo-oxidation</td>
</tr>
</tbody>
</table>

Normalized to the internal reference band at 1410 cm⁻¹

Changes in the rotational isomers
Formation of end groups and degradation byproducts

<table>
<thead>
<tr>
<th>Time</th>
<th>975</th>
<th>1125</th>
<th>1340</th>
<th>1675-1711</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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</tbody>
</table>

Note: The table contains data and visualizations for different time periods and conditions.

- Red circles highlight specific data points or areas of interest.
Statistical Modeling Approaches

1. Multi-Level Predictive Modeling

And

2. Semi-Supervised Generalized Structural Equation (semi-gSEM) Diagnostic Modeling
Multi-Level Predictive Modeling

Multi-Level Modeling for a longitudinal weathering study
• Repeated measurements on multiple samples
• Of various grades
• Under different exposures

Model Definition and Selection
• Overfitting & Predictive R²
• Model Validation using Leave-one-out Cross-validation
Overfitting & Predictive $R^2$

Overfitting When
- Complexity of your model increases
  - Too many predictors to obtain the best fit
- You Train model without testing on new data

Optimism Needs to be Small for
- Smaller “true” prediction error
- Greater prediction power

Always Check Assumptions on Error Terms
- Homoscedasticity, Linearity, Normality

Model Validation Is Essential

Using Leave-one-out Cross-validation
Apply your model to both
- training data and testing data

Predictive $R^2$ gives model fit to testing data
- Spanning the cross-validation datasets
Multi-Level Predictive Modeling

Yellowing & Hazing
Under
HotQUV and CyclicQUV Exposures
### Yellowing Model: under HotQUV & CyclicQUV Exposures

#### Fixed Effects Modeling approach

- **Yellowing: Fixed Scale**

<table>
<thead>
<tr>
<th>Yellowing Index (Y)</th>
<th>Exposure Step</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CyclicQUV</td>
</tr>
<tr>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

- **Variable Power Transformation** ($y \rightarrow y^\lambda$)
  - Toward linearity or normality
  - Log-likelihood vs. power ($\lambda$)

- **Model Equation**
  
  $YF^{0.5} \approx (\beta_0 + \beta_{01}M_1 + \beta_{02}M_2 + \beta_{03}X + \beta_{04}M_1X + \beta_{05}M_2X) + (\beta_1 + \beta_{11}M_1 + \beta_{12}M_2 + \beta_{13}X + \beta_{14}M_1X + \beta_{15}M_2X)t + (\beta_2 + \beta_{21}M_1 + \beta_{22}M_2 + \beta_{23}X + \beta_{24}M_1X + \beta_{25}M_2X)t^2 + (\beta_3 + \beta_{31}M_1 + \beta_{32}M_2 + \beta_{33}X + \beta_{34}M_1X + \beta_{35}M_2X)t^3$

- **Power of 0.5 is in 95% conf.int.**

- **Fixed Effects Modeling**
  - Small variation in-between samples
  - Similar trend for all samples
  - Yellowing $\rightarrow$ uniform formation of chromophores
  - Smaller measurement uncertainty
Yellowing Model: under HotQUV & CyclicQUV Exposures

Diagnostics: Residuals vs. Fitted and Normal Quantile-Quantile

- Model satisfies the regression assumption reasonably well.

Two Exposures and Three Materials in One Model

\[ Y^{0.5} \approx (1.170 - 0.626M_1 - 0.122M_2 + 0.078X - 0.100M_1X - 0.035M_2X) \]
\[ + (0.377 + 0.330M_1 - 0.349M_2 + 0.073X - 0.042M_1X - 0.032M_2X)t \]
\[ + (-0.046 - 0.067M_1 + 0.092M_2)t^2 + (0.003 + 0.004M_1 - 0.007M_2)t^3 \]
Yellowing Model: under HotQUV & CyclicQUV Exposures

Model Superimposed on the data

Adjusted $R^2 = 0.98$
- To training dataset

Predicted $R^2 = 0.95$
- To testing dataset
- In cross-validation
Hazing Model: Hazing under CyclicQUV Exposure

Mixed Effects Modeling approach: Fixed Effects + Random Effects

- Account for between sample variability
- Individual trends for each sample
- Hazing $\rightarrow$ localized growth of features
- Larger measurement uncertainty

Modeling based on each individual sample’s trend
No power transformation

\[
Haze_{ijkl} \approx (\beta_0 + \beta_{01}M_1 + \beta_{02}M_2) + (\beta_1 + \beta_{11}M_1 + \beta_{12}M_2 + b_{1i})t_{ijkl} \\
+ (\beta_2 + \beta_{21}M_1 + \beta_{22}M_2 + b_{2i})t_{ijkl}^2 + (\beta_3)t_{ijkl}^3 + \epsilon_{ijkl}
\]
Hazing Model: Hazing under CyclicQUV Exposure

Model Superimposed on the data
Fitted $R^2 = 0.95$
Predictive $R^2 = 0.82$

Mixed effects = Fixed + Random

- Marginal $\rightarrow$ variance explained by the fixed effects
- Conditional $\rightarrow$ variance explained by both fixed effects and random effects

Marginal $R^2 = 0.88$
Conditional $R^2 = 0.94$

Including random effects increased the variance explained by the fixed effects
Statistical Modeling Approaches

2. Semi-Supervised, Generalized Structural Equation (semi-gSEM)

Diagnostic Modeling
Diagnostic Modeling: Degradation Pathways Using semi-gSEM

**Stress | mechanism | response framework (S|M|R)**

- Stressors (applied)
- Mechanistic (intermediate, observed-measured or latent) variables
- Performance level responses

**Functional Forms among Variables**

- Simple linear: \( y \sim b_0 + b_1 x \)
- Simple quadratic: \( y \sim b_0 + b_1 x^2 \)
- Quadratic: \( y \sim b_0 + b_1 x + b_2 x^2 \)
- Logarithmic: \( y \sim b_0 + b_1 \log(x) \)
- Exponential: \( y \sim b_0 + b_1 \exp(x) \)

**Combination of Metrics for Statistically Significant Relationships**

- \( R^2 \), Adjusted-\( R^2 \)
  
  Goodness & quality of fit of the observed relationships between variables

**Principles in semi-gSEM**

- Principle 1: Univariate relationships (Markov. spirit, prior events don’t affect current variables)
- Principle 2: Multivariate relationships (additive model that accounts for variable interactions)
## Variables & Statistical Significance in semi-gSEM Analysis

<table>
<thead>
<tr>
<th>Variables</th>
<th>Mechanisms</th>
<th>In semi-gSEM analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>As a proxy to exposures</td>
<td>Main stressor</td>
</tr>
<tr>
<td>abs/cm at 312 nm</td>
<td>Degradation of the polymer backbone</td>
<td>Mechanistic variable</td>
</tr>
<tr>
<td>abs/cm at 340 nm</td>
<td>UV stabilizer bleaching</td>
<td>Mechanistic variable</td>
</tr>
<tr>
<td>IR band at 975 cm⁻¹</td>
<td>Change in morphology</td>
<td>Mechanistic variable</td>
</tr>
<tr>
<td>IR band at 1711 cm⁻¹</td>
<td>Chain scissions</td>
<td>Mechanistic variable</td>
</tr>
<tr>
<td>Yellowness index (YI)</td>
<td>Photolytic and hydrolytic degradation</td>
<td>Performance level response</td>
</tr>
<tr>
<td>Haze (%)</td>
<td>Hydrolytic degradation</td>
<td>Performance level response</td>
</tr>
</tbody>
</table>

### Two adjusted R² cutoffs to rank order relationships

- D-a-s-h-e-d < 0.5 adj. R²
- 0.75 adj. R² < Solid < 0.5 adj. R²
- Thick > 0.75 adj. R²
semi-gSEM Degradation Pathway Models

UV stabilized PET

1) yellowing under HotQUV
2) yellowing under CyclicQUV
3) hazing under CyclicQUV
Yellowing sgSEM: UV stabilized PET under HotQUV Exposures

Crystallization and Chain Scission
• Produce Yellowing

Confirmatory Evidence
• From DCS and IV
Yellowing sgSEM: UV stabilized PET under CyclicQUV Exposure

Important Role of
- Fund. Abs. Edge
- UV Stabilizer Bleaching

Crystallization and Chain Scission
- Produce Yellowing
- But at Reduced Rate
Hazing sgSEM: UV Stabilized PET under CyclicQUV Exposure

Crystallization Induced Hazing

• Complex interactions due to cyclic conditions is evident

UV Stabilizer Consumed
Confirmatory Results: 
Direct Measures of Mechanistic Variables

Catalyst trace analysis
Change in crystallinity via DSC
Intrinsic viscosity and molecular weight
Carboxyl end group (CEG) analysis
Change in Crystallinity via DSC (UV Stabilized)

Degradation Causes

• Decrease in melting point ($T_m$)
• Decrease in intrinsic viscosity and Mw
• Increase in chain scission
• Increase in CEG content

Crystallinity increased from 36%

• to 42% During UV Exposure
• to 45% During UV+Humidity Exposure
M<sub>w</sub> & CEG analysis: Incr. Chain Scission, CEGs, Decr. M<sub>w</sub>

Intrinsic viscosity (IV) to determine molecular weight (M<sub>w</sub>)

- The degree of degradation
  i.e., increased chain scission, formation of end groups, and reduced molecular weight
- IV measurement via glass capillary viscometer (ASTM 4603-03)

  - Decrease in IV and Molecular Weight (M<sub>n</sub>)
  - Increase in total end groups and chain scission per molecule

<table>
<thead>
<tr>
<th>Grade - Exposure</th>
<th>IV(η)</th>
<th>M&lt;sub&gt;n&lt;/sub&gt;</th>
<th>Total end groups</th>
<th>Chain scissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyd. stabilized - Baseline</td>
<td>0.648</td>
<td>20,635</td>
<td>97</td>
<td>0</td>
</tr>
<tr>
<td>Hyd. stabilized - HotQUV*</td>
<td>0.593</td>
<td>18,544</td>
<td>108</td>
<td>0.11</td>
</tr>
<tr>
<td>Hyd. stabilized - CyclicQUV</td>
<td>0.495</td>
<td>14,917</td>
<td>135</td>
<td>0.38</td>
</tr>
<tr>
<td>Unstabilized - Baseline</td>
<td>0.564</td>
<td>17,457</td>
<td>115</td>
<td>0</td>
</tr>
<tr>
<td>Unstabilized - HotQUV*</td>
<td>0.375</td>
<td>10,676</td>
<td>188</td>
<td>0.64</td>
</tr>
<tr>
<td>Unstabilized - CyclicQUV</td>
<td>0.457</td>
<td>13,548</td>
<td>148</td>
<td>0.29</td>
</tr>
<tr>
<td>UV stabilized - Baseline</td>
<td>0.573</td>
<td>17,793</td>
<td>114</td>
<td>0</td>
</tr>
<tr>
<td>UV stabilized - HotQUV</td>
<td>0.503</td>
<td>15,208</td>
<td>132</td>
<td>0.17</td>
</tr>
<tr>
<td>UV stabilized - CyclicQUV</td>
<td>0.497</td>
<td>14,990</td>
<td>136</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Carboxylic acid end group (CEG) analysis

- CEGs play a major role in PET’s hydrolytic stability
  i.e., autocatalytic effect of CEGs in hydrolysis reactions
- Direct measure of CEG conc. (ASTM D7409-15)

  - Increase in CEG concentration under both UV and UV+Humidity
Conclusions

Longitudinal Weathering Study of PET in 4 Exposures: Epidemiology

• Yellowing most strongly induced by UV light
  Moisture enhanced yellowing was evident
• Hazing was predominantly from hydrolysis

Develop Data-driven Analysis and Modeling

• Using Un-biased Analysis, based in Statistical Significance

Multi-Level Modeling Predicted Experimental Responses Very Closely

• Predictive $R^2$ aides Model Selection and Cross-validation

In the semi-gSEM pathway Models, Mechanistic Contributions

• Chain scission common mechanism under HotQUV & CyclicQUV exposures.
• Change-points along the Temporal Degradation Pathway
  UV Stabilizer Bleaching
  Hazing Onset under Humidity, After Chromophore Development

Multi-variate and Multi-stressor semi-gSEM Development is in Progress.
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3M

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