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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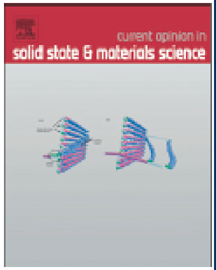

Degradation science: Mesoscopic evolution and temporal analytics of photovoltaic energy materials

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A B S T R A C T

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.

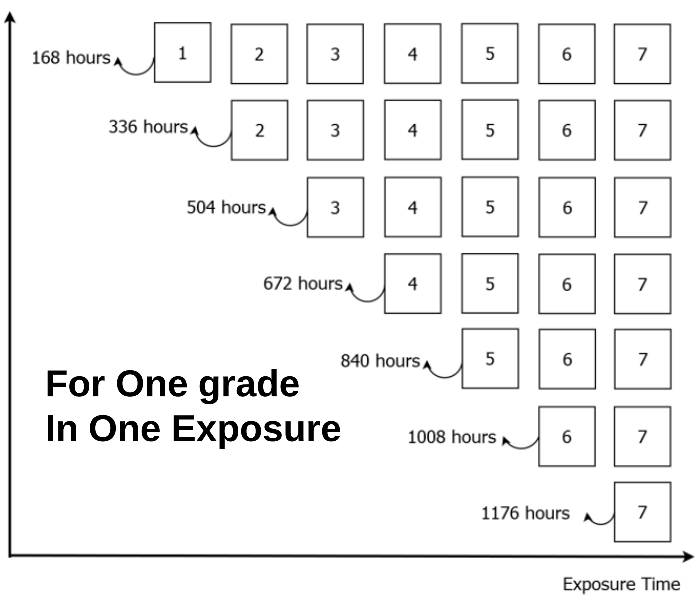
Longitudinal Weathering Study of PET Grades

The three PET grades used:

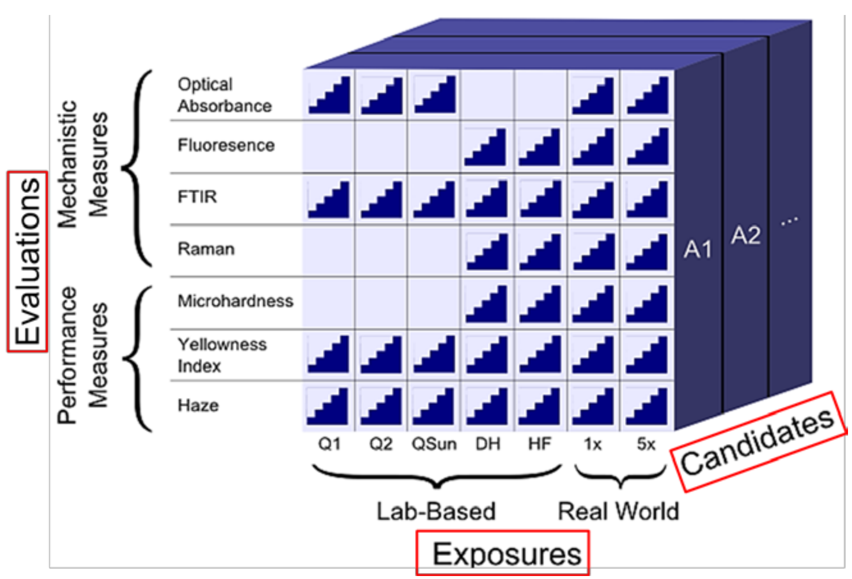
- **Unstabilized** (Dupont-Teijin Melinex 454, 3 mil)
- **UV stabilized** (Dupont-Teijin Tetoron HB3, 2 mil)
- **Hydrolytically stabilized** (Mitsubishi 8LH1, 5 mil)

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:



Exposure Conditions

Heat and humidity exposures

Environmental test chambers

Temperature and humidity control

1) DampHeat

Constant exposure at 85^{o}C and 85%RH per IEC 61215

2) FreezeThaw

20 hrs of 70 ^{o}C at 85% RH plus 0.5 hrs of -40 ^{o}C at 0 % RH

UVA light exposures

Fluorescent weathering tester

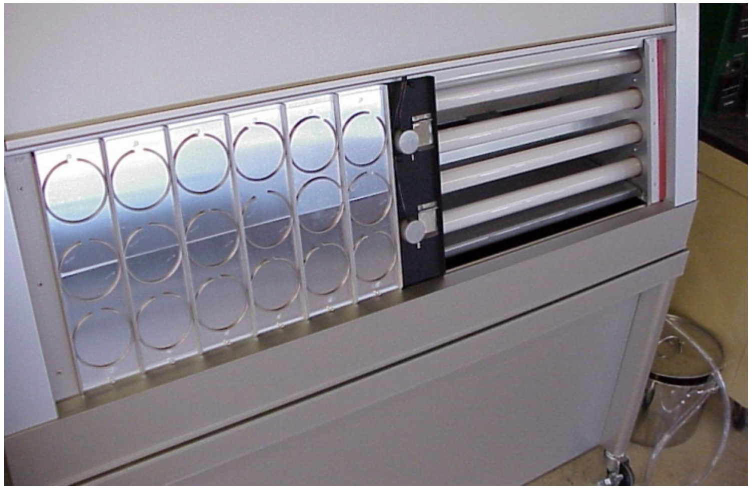
Outfitted with UVA 340 lamps and water spray

3) ASTM G154 Cycle 4 (CyclicQUV)

8 hrs of 1.55 W/m^2 @ 340 nm light at 70 ^{o}C plus 4 hrs of condensing humidity in dark at 50 ^{o}C

4) ASTM G154 Cycle 4 without the condensing humidity (HotQUV)

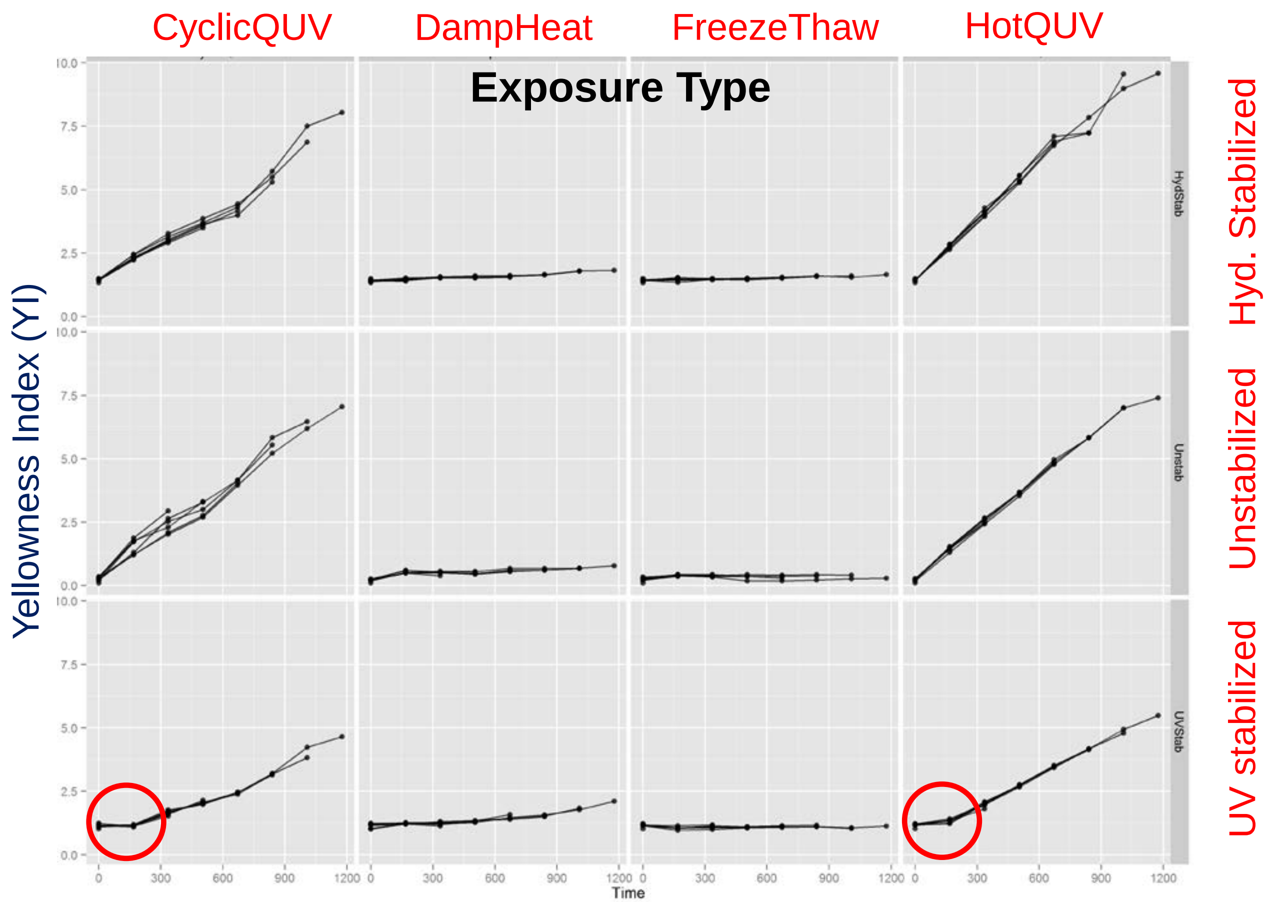
Constant UVA light at 1.55 W/m^2 @ 340 nm at 70^{o}C



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.



PET Grade

Yellowing Arises

With Photoexposure

Note Temporal Change Points

Performance Response: Haze (%)

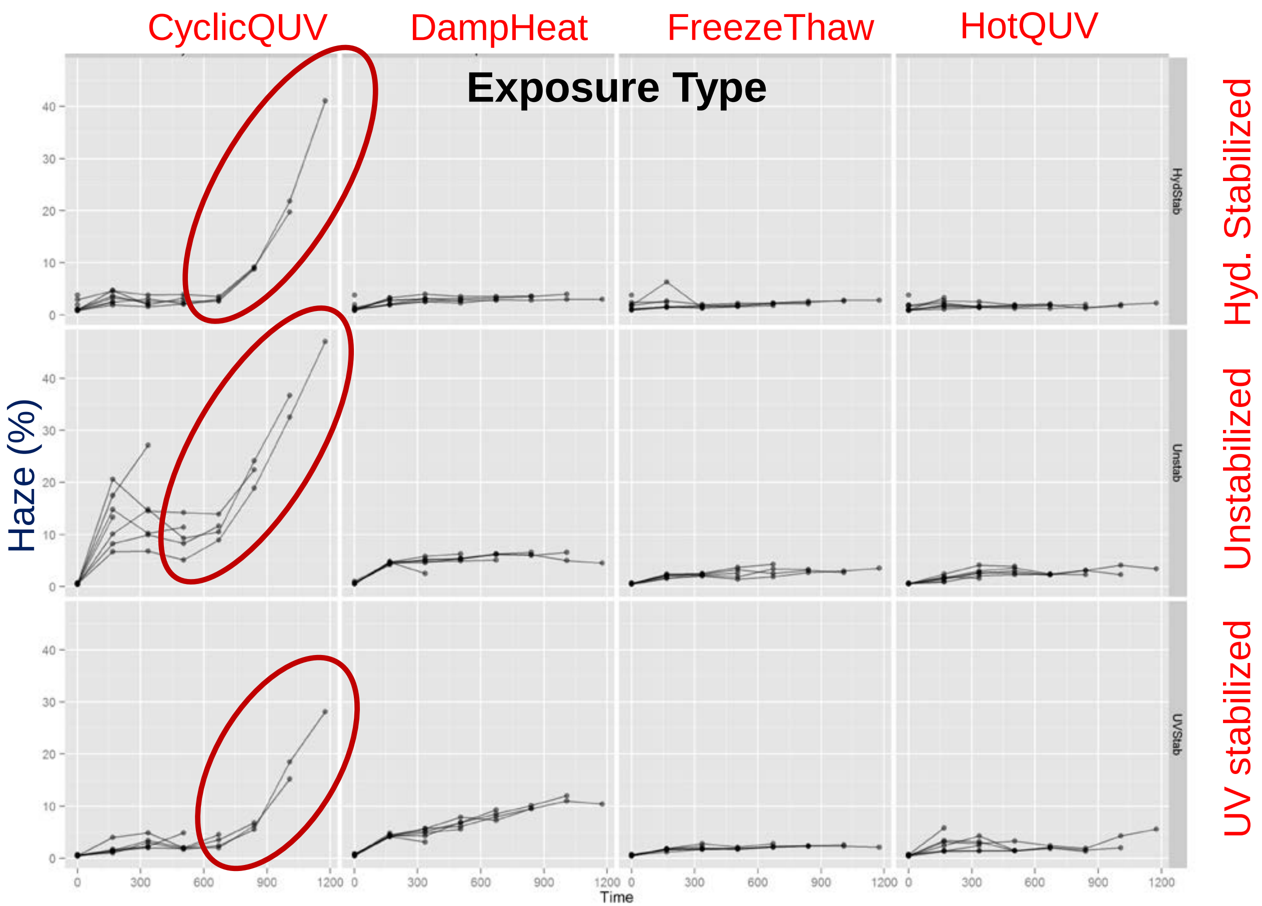
Humidity only did not result in significant hazing.

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.



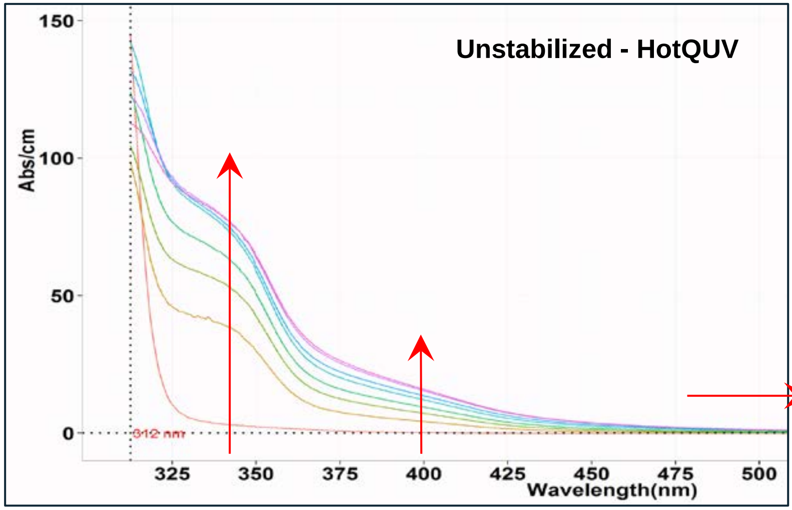
PET Grade

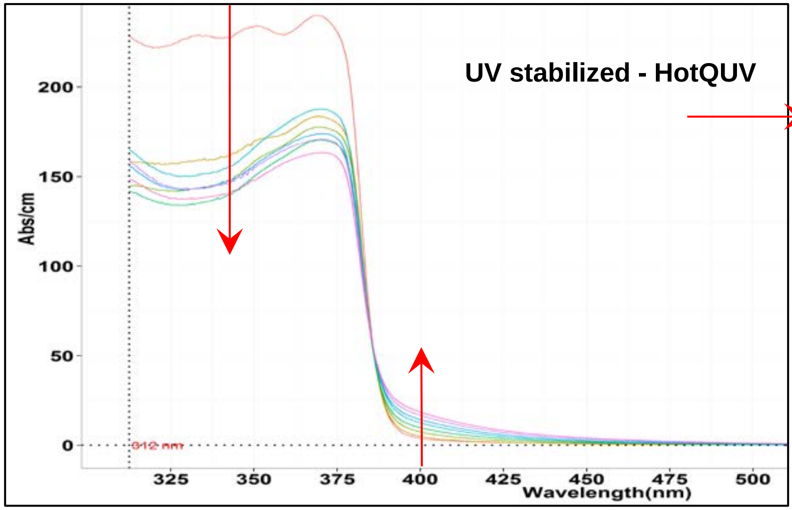
Hazing Requires Moisture

Increased by Precursor Yellowing

Follow UV-Stabilized Under HotQUV & Cyclic QUV Exposures

Mechanistic: PET UV-Vis Spectral Features





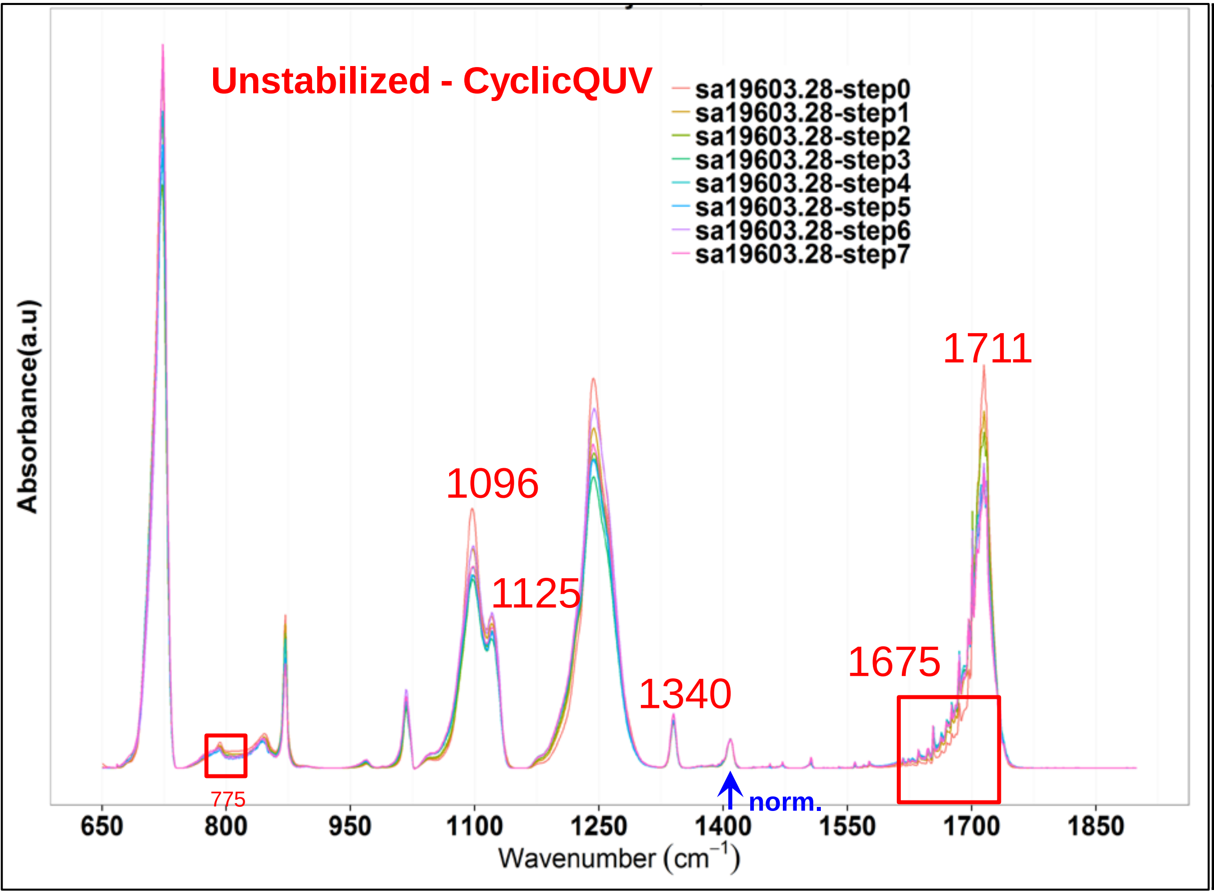
Abs (nm)	Feature	Mechanisms
312	Fund. abs. edge	π → π* transition of the terephthalate unit and ester carbonyl on the PET backbone
325	carboxylic acid end groups	photo-oxidation
340	hydroxylated species	hydroperoxide formation → photolysis of hydroperoxides → hydroxyl radicals → substitution reactions → mono- or dihydroxy terephthalate unit → hydroxylated species → increase in absorbance
340	UV Stabilizer[2]	UV stabilizer bleaching
375-425	quinones[1]	photolysis → chain scissions → hydroperoxides → hydroxylated species → fluorescence → increased yellowing photo-oxidation → chain scissions → hydroperoxides → hydroxylated species → oxidation → reduced fluorescence → increased yellowing

Choose 2 UV Mechanisms

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

[1] Yang, Poly. Degr.Stab., 95(1):53–58,2010, Tabankia, Poly. Degr,Stab., 14(4):351–365, 1986, Fechine, J. App. Poly. Sci.,104(1):51–57, 2007
[2]From UV Spectra of the UV stabilizer (Cyasorb 3638)

Mechanistic: PET FTIR Spectral Features

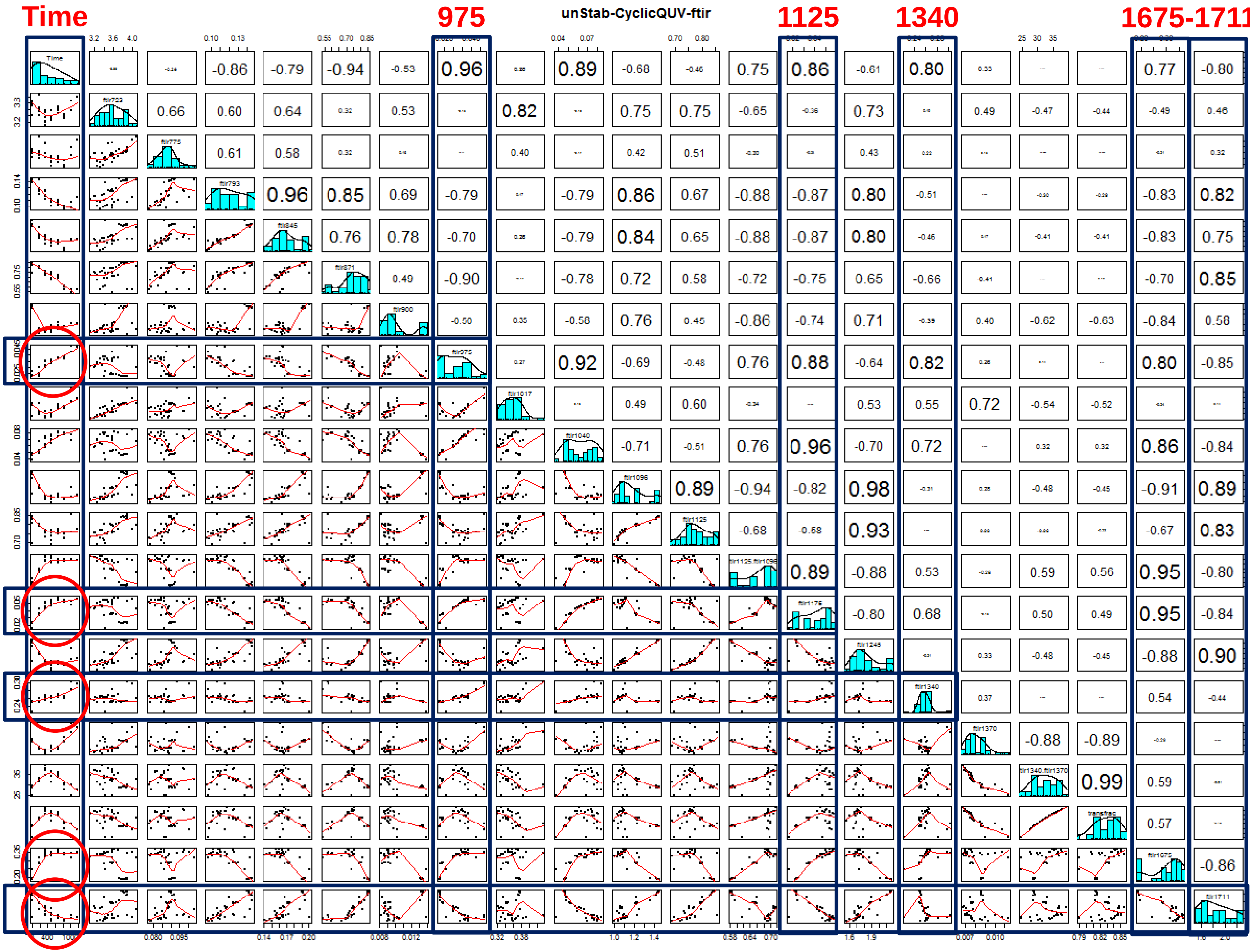


cm^{-1}	Band	Mechanisms
1711	C=O carbonyl stretching	Chain scission
1675	C=O broadening	Formation of carboxylic acid
975 1340 1125	*trans* O-CH_2 *trans* CH_2 *trans* C-O	Crystallization
775	new formation	Photo-oxidation

Normalized to the internal reference band at 1410 cm^{-1}

Changes in the rotational isomers

Formation of end groups and degradation byproducts



Time
975
unStab-CyclicQUV-ftir
1125
1340
1675-1711

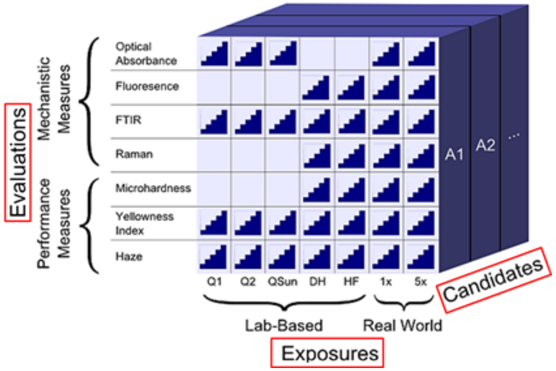
Statistical Modeling Approaches

1. Multi-Level Predictive Modeling

And

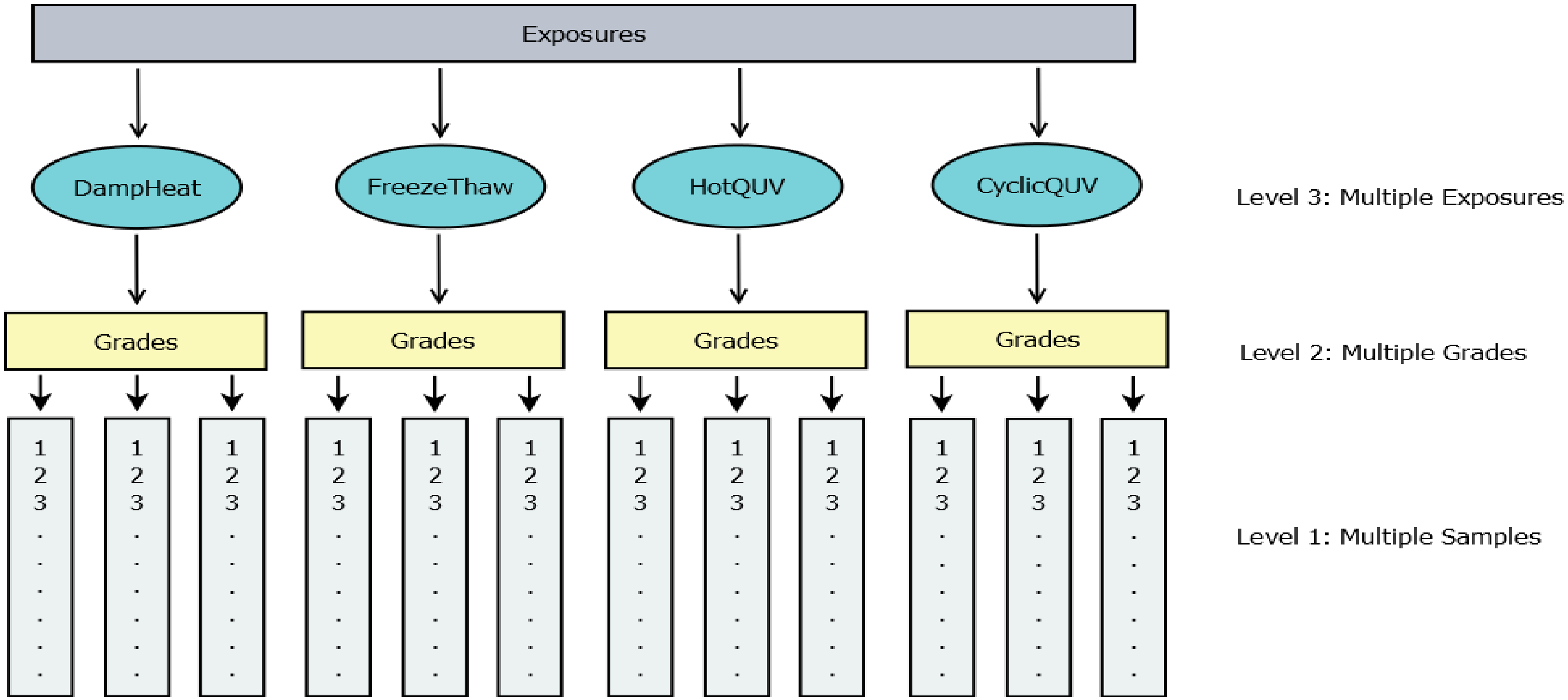
2. Semi-Supervised Generalized Structural Equation (semi-gSEM) Diagnostic Modeling

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 R^2
- Model Validation using Leave-one-out Cross-validation

Overfitting & Predictive R^2

Overfitting When

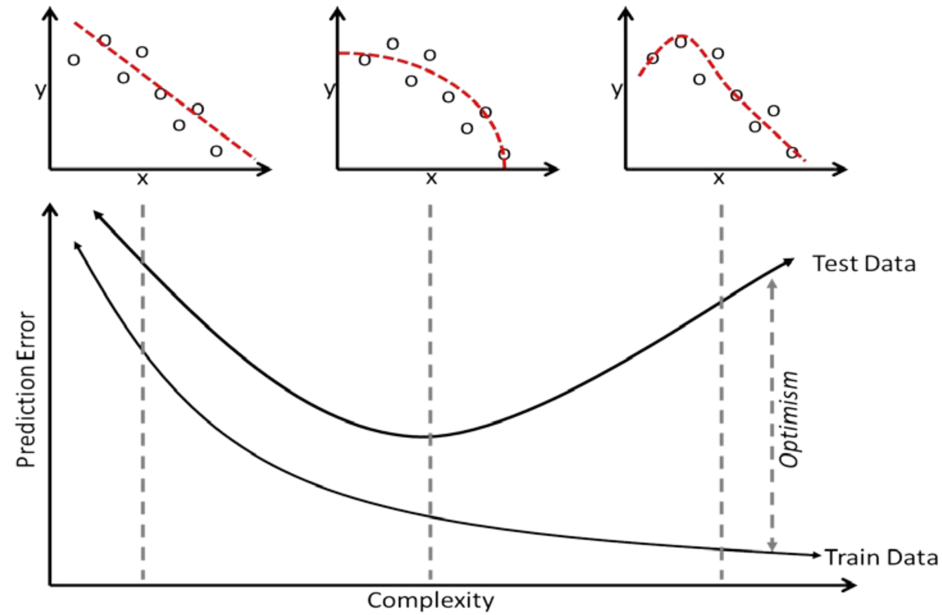
- Complexity of your model increases
  Too many predictors to obtain the best fit
- You Train model without testing on new data

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

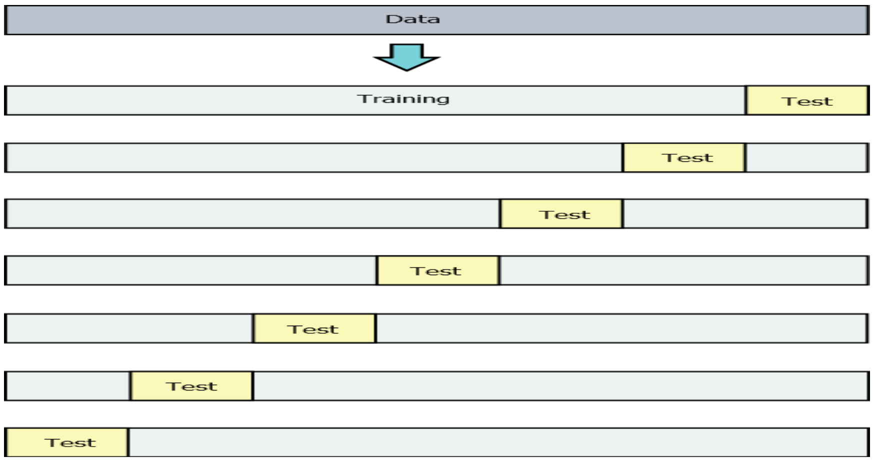
Using Leave-one-out Cross-validation

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

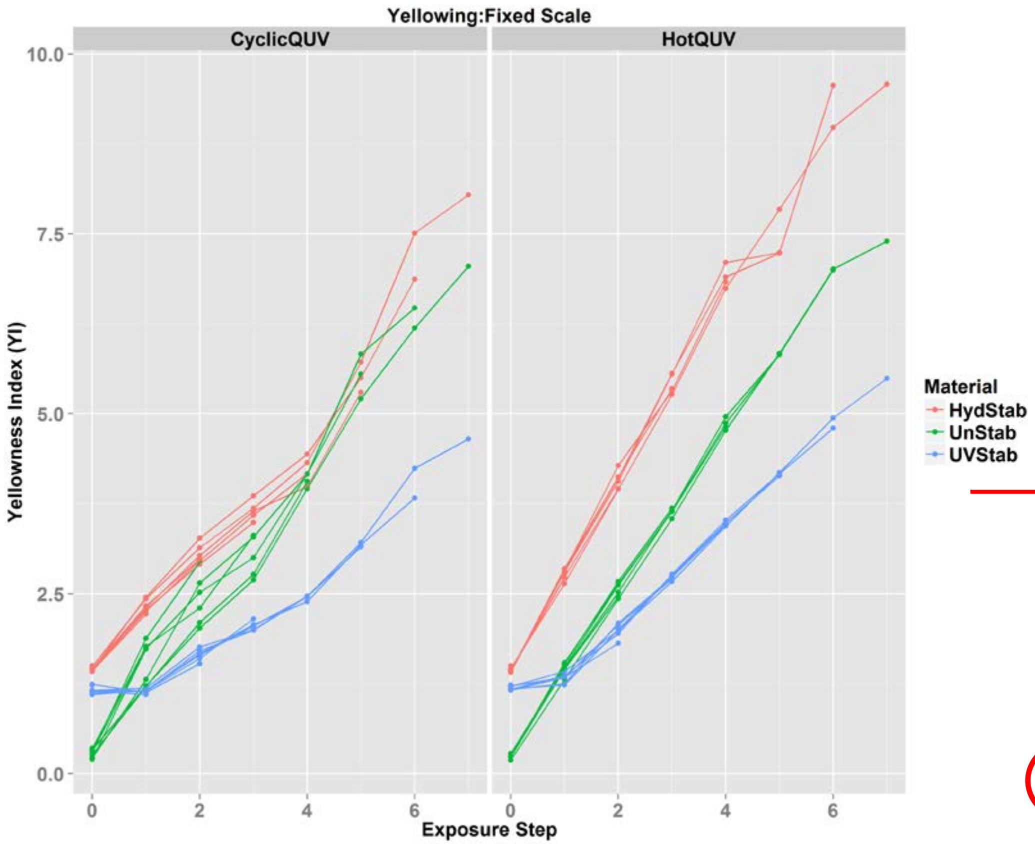
Yellowing & Hazing

Under

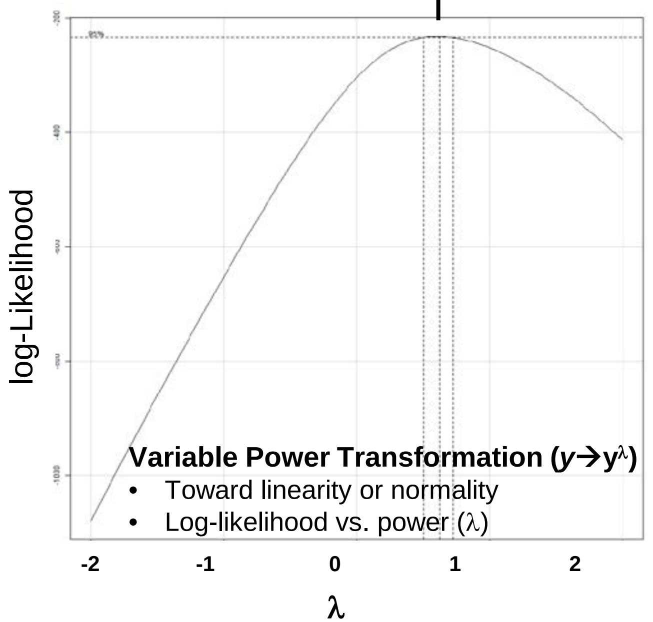
HotQUV and CyclicQUV Exposures

Yellowing Model: under HotQUV & CyclicQUV Exposures

Fixed Effects Modeling approach



Power of 0.5 is in 95% conf.int.



Variable Power Transformation (*y*→y^λ)

- Toward linearity or normality
- Log-likelihood vs. power (λ)

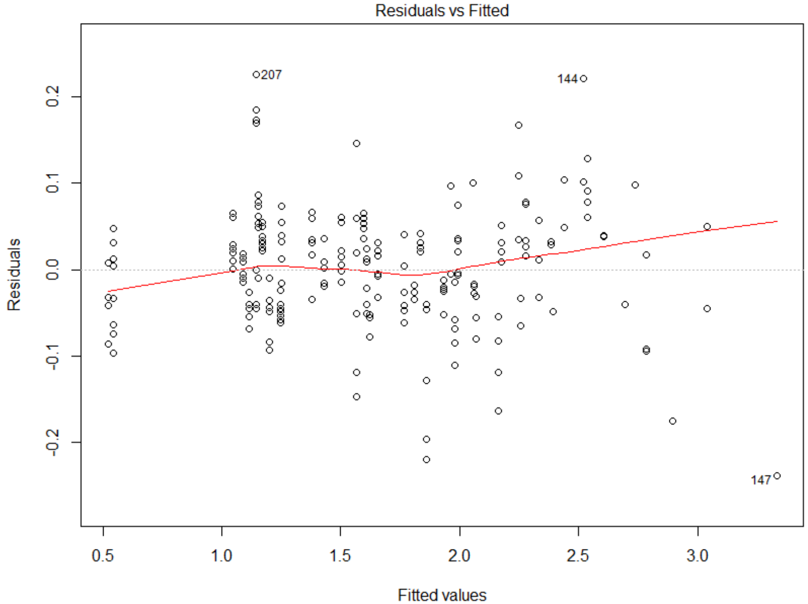
$$YI^{0.5} \approx (\beta_0 + \beta_{01}M_1 + \beta_{02}M_2 + \beta_{03}X + \beta_{04}M_1X + \beta_{05}M_2X)$$
$$+ (\beta_1 + \beta_{11}M_1 + \beta_{12}M_2 + \beta_{13}X + \beta_{14}M_1X + \beta_{15}M_2X)t$$
$$+ (\beta_2 + \beta_{21}M_1 + \beta_{22}M_2 + \beta_{23}X + \beta_{24}M_1X + \beta_{25}M_2X)t^2$$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

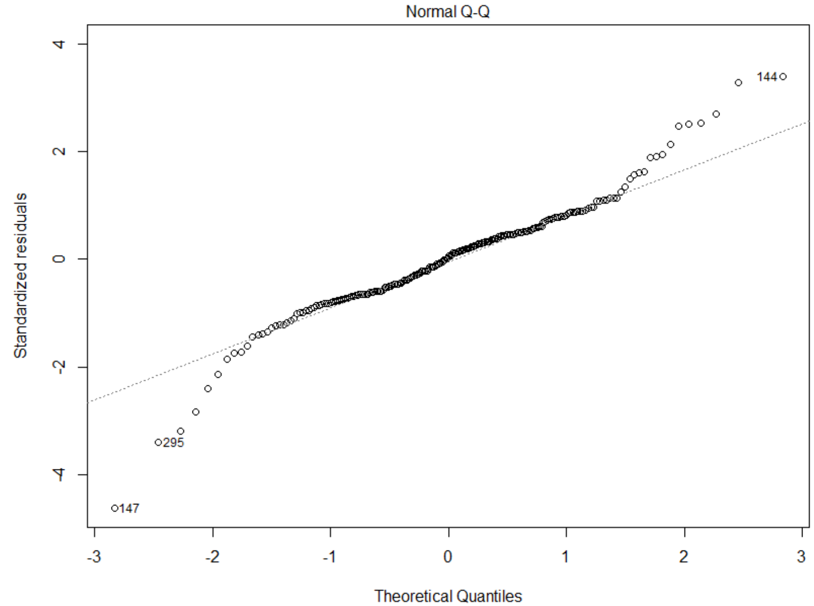
- Small variation in-between samples
- Similar trend for all samples
- Yellowing → uniform formation of chromophores
- Smaller measurement uncertainty

Yellowing Model: under HotQUV & CyclicQUV Exposures

Diagnostics: Residuals vs. Fitted and Normal Quantile-Quantile

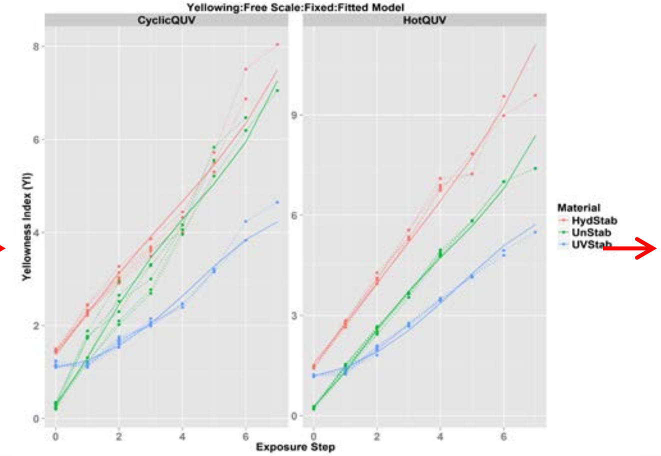
- Model satisfies the regression assumption reasonably well.





Two Exposures and Three Materials in One Model

$$YI^{0.5} \approx (1.170 - 0.626M_1 - 0.122M_2 + 0.078X - 0.100M_1X - 0.035M_2X)$$
$$+ (0.377 + 0.330M_1 - 0.349M_2 + 0.073X - 0.042M_1X - 0.032M_2X)t$$
$$+ (-0.046 - 0.067M_1 + 0.092M_2)t^2 + (0.003 + 0.004M_1 - 0.007M_2)t^3$$



Yellowing Model: under HotQUV & CyclicQUV Exposures

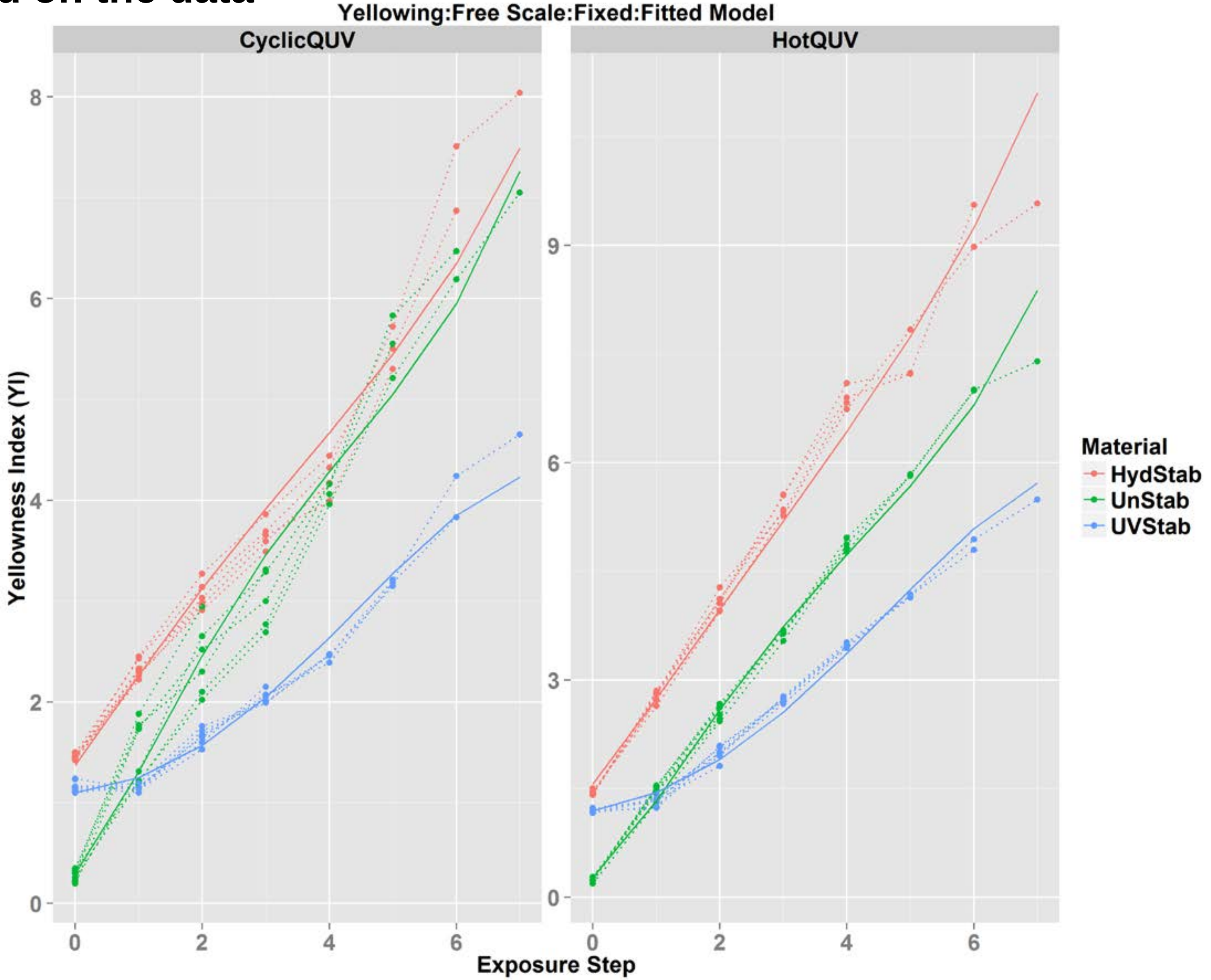
Model Superimposed on the data

Adjusted R^2 = 0.98

- To training dataset

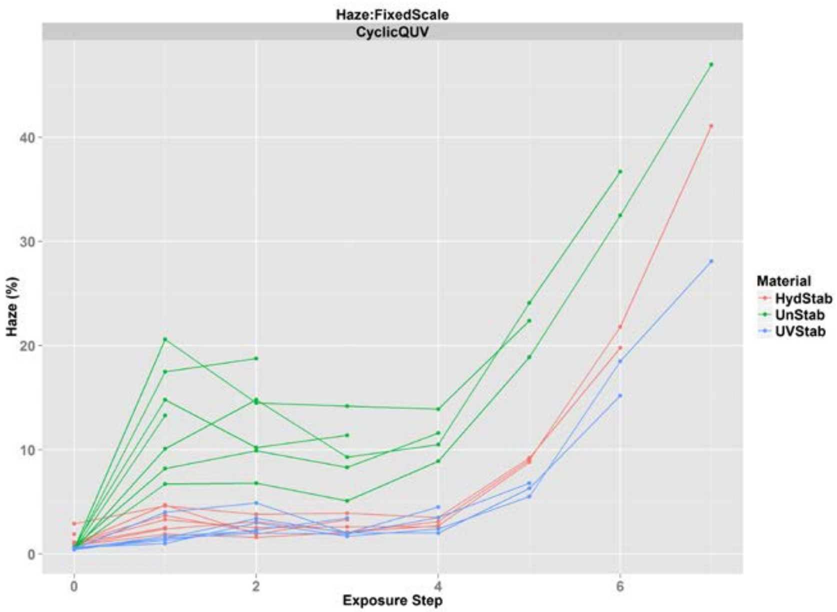
Predicted R^2 = 0.95

- To testing dataset
- In cross-validation



Hazing Model: Hazing under CyclicQUV Exposure

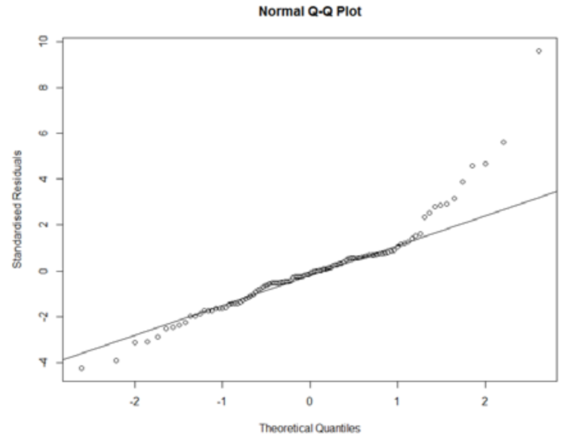
Mixed Effects Modeling approach: Fixed Effects + Random Effects

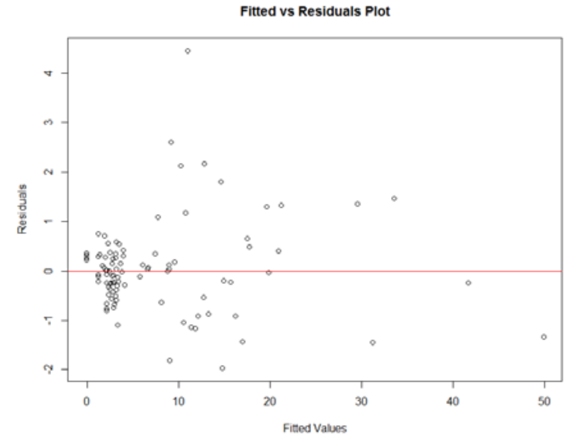


Modeling based on each individual sample's trend
No power transformation

$$Haze_{ijkl} \approx (\beta_0 + \beta_{01}M_1 + \beta_{02}M_2) + (\beta_1 + \beta_{11}M_1 + \beta_{12}M_2 + b_{1i})t_{ijkl}$$

$$+ (\beta_2 + \beta_{21}M_1 + \beta_{22}M_2 + b_{2i})t^2_{ijkl} + (\beta_3)t^3_{ijkl} + \epsilon_{ijkl}$$





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

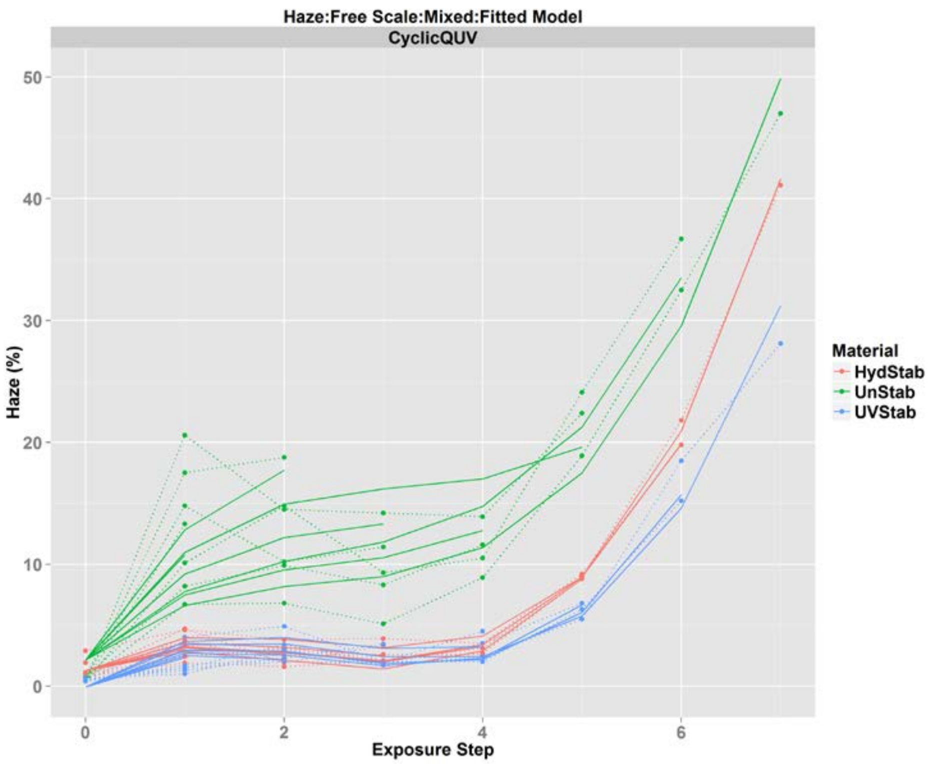
Hazing Model: Hazing under CyclicQUV Exposure

Model Superimposed on the data

Fitted R^2 = 0.95

Predictive R^2 = 0.82

$$Haze_{ijkl} \approx (1.267 + 0.876M_1 - 1.337M_2) + (\mathbf{3.985} + \mathbf{6.054}M_1 + 1.300M_2 + b_{1i})t_{ijkl}$$
$$+ (\mathbf{-2.349} - \mathbf{0.829}M_1 - 0.309M_2 + b_{2i})t^2_{ijkl} + (\mathbf{0.371})t^3_{ijkl} + \epsilon_{ijkl}$$



Mixed effects = Fixed + Random

- Marginal → variance explained by the fixed effects
- Conditional → 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

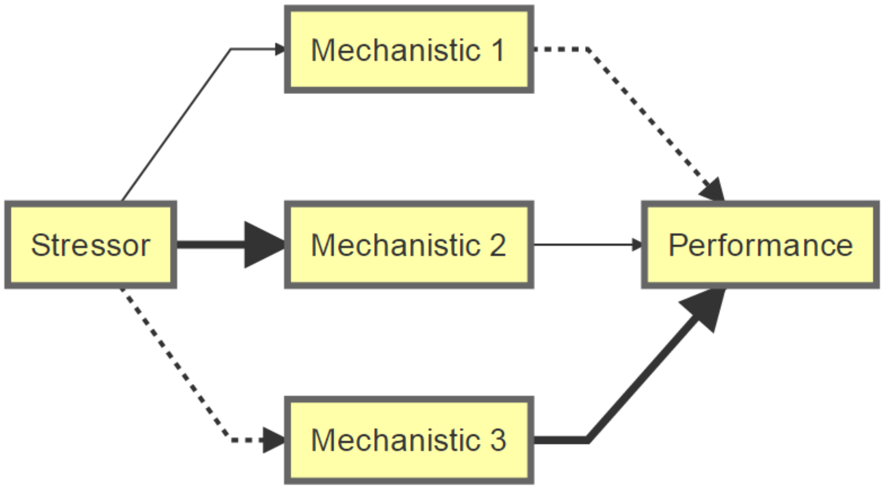
2. Semi-Supervised, Generalized Structural Equation (semi-gSEM)

<u>Diagnostic Modeling</u>

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

- Principle1: Univariate relationships (Markov. spirit, prior events don’t affect current variables)
- Principle2: Multivariate relationships (additive model that accounts for variable interactions)

Variables & Statistical Significance in semi-gSEM Analysis

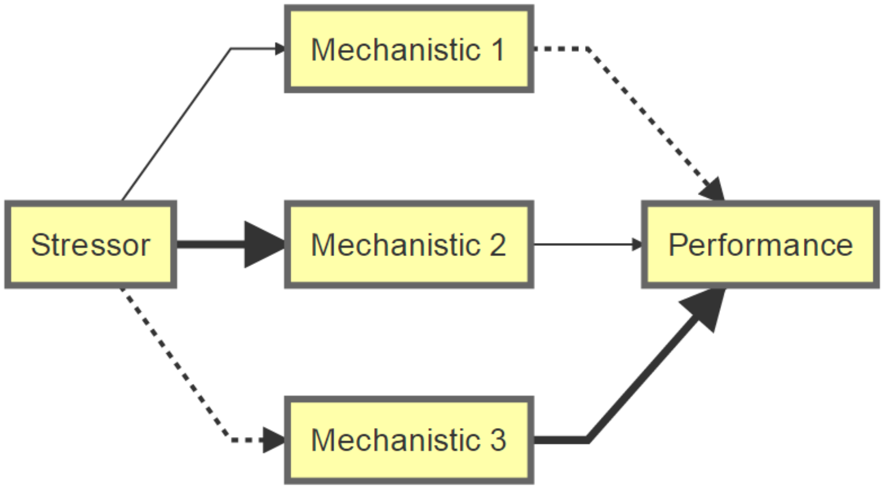
Variables	Mechanisms	In semi-gSEM analysis
Time	As a proxy to exposures	Main stresssor
abs/cm at 312 nm	Degradation of the polymer backbone	Mechanistic variable
abs/cm at 340 nm	UV stabilizer bleaching	Mechanistic variable
IR band at 975 cm^{-1}	Change in morphology (Crystallization)	Mechanistic variable
IR band at 1711 cm^{-1}	Chain scissions	Mechanistic variable
Yellowness index (YI)	Photolytic and hydrolytic degradation	Performance level response
Haze (%)	Hydrolytic degradation	Performance level response

Two adjusted R^2 cutoffs
to rank order relationships

D-a-s-h-e-d < 0.5 adj. R^2

0.75 adj. R^2 < Solid < 0.5 adj. R^2

Thick > 0.75 adj. R^2

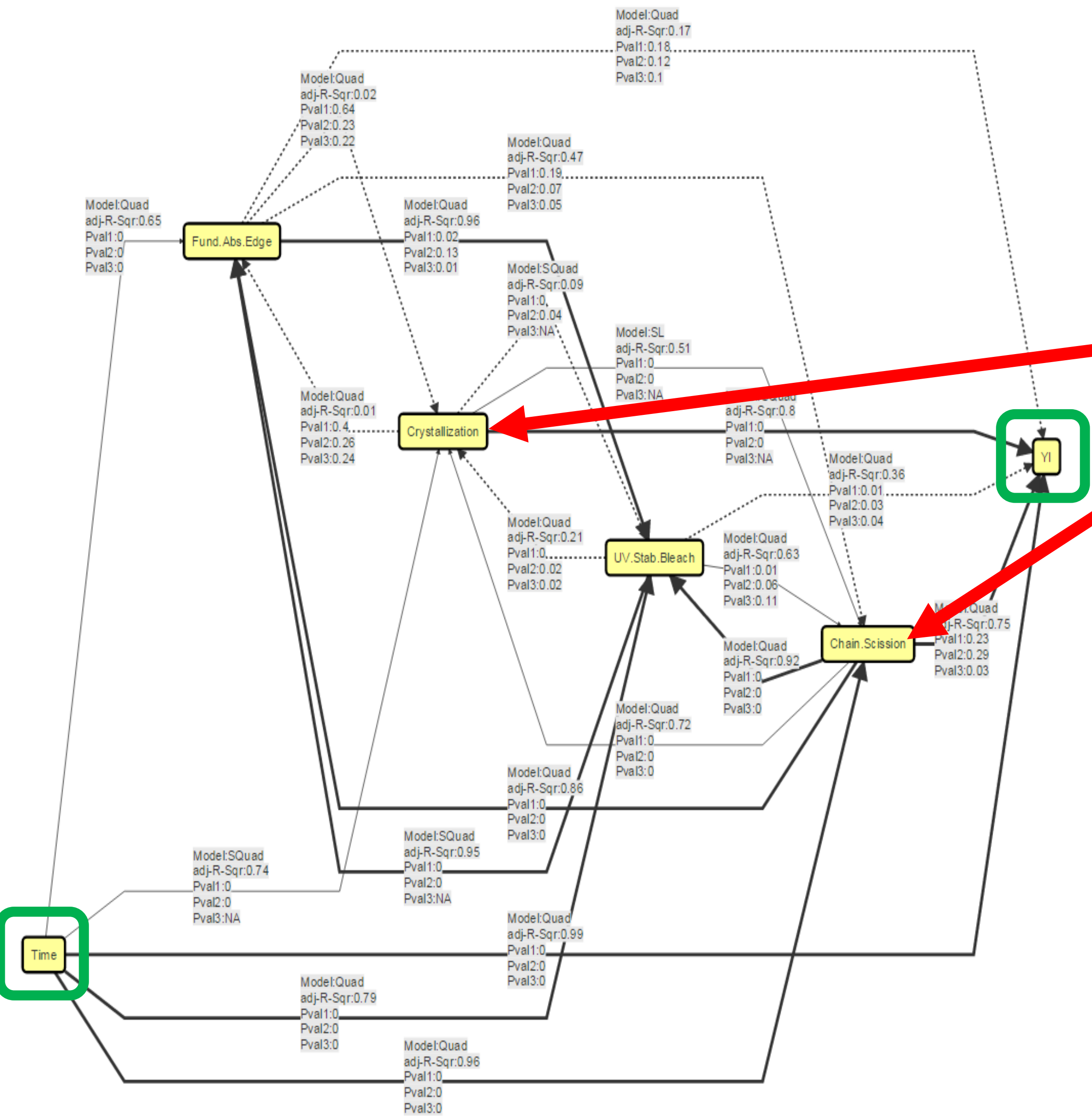


semi-gSEM Degradation Pathway Models

UV stabilized PET

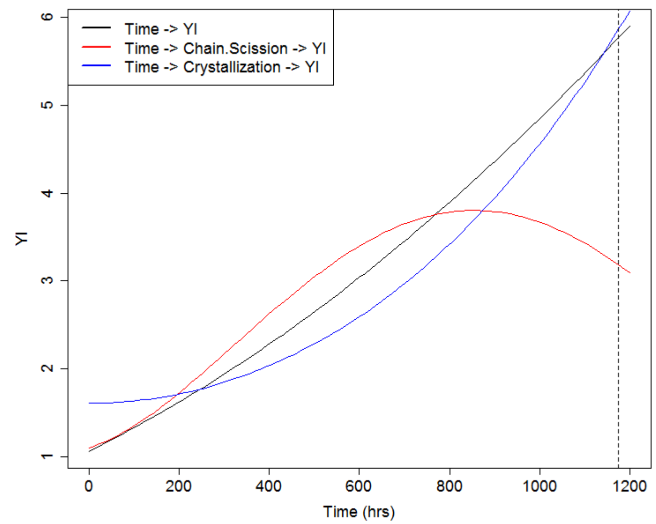
1) yellowing under HotQUV
2) yellowing under CyclicQUV
3) hazing under CyclicQUV

Yellowing sgSEM: UV stabilized PET under HotQUV Exposures



Crystallization and Chain Scission

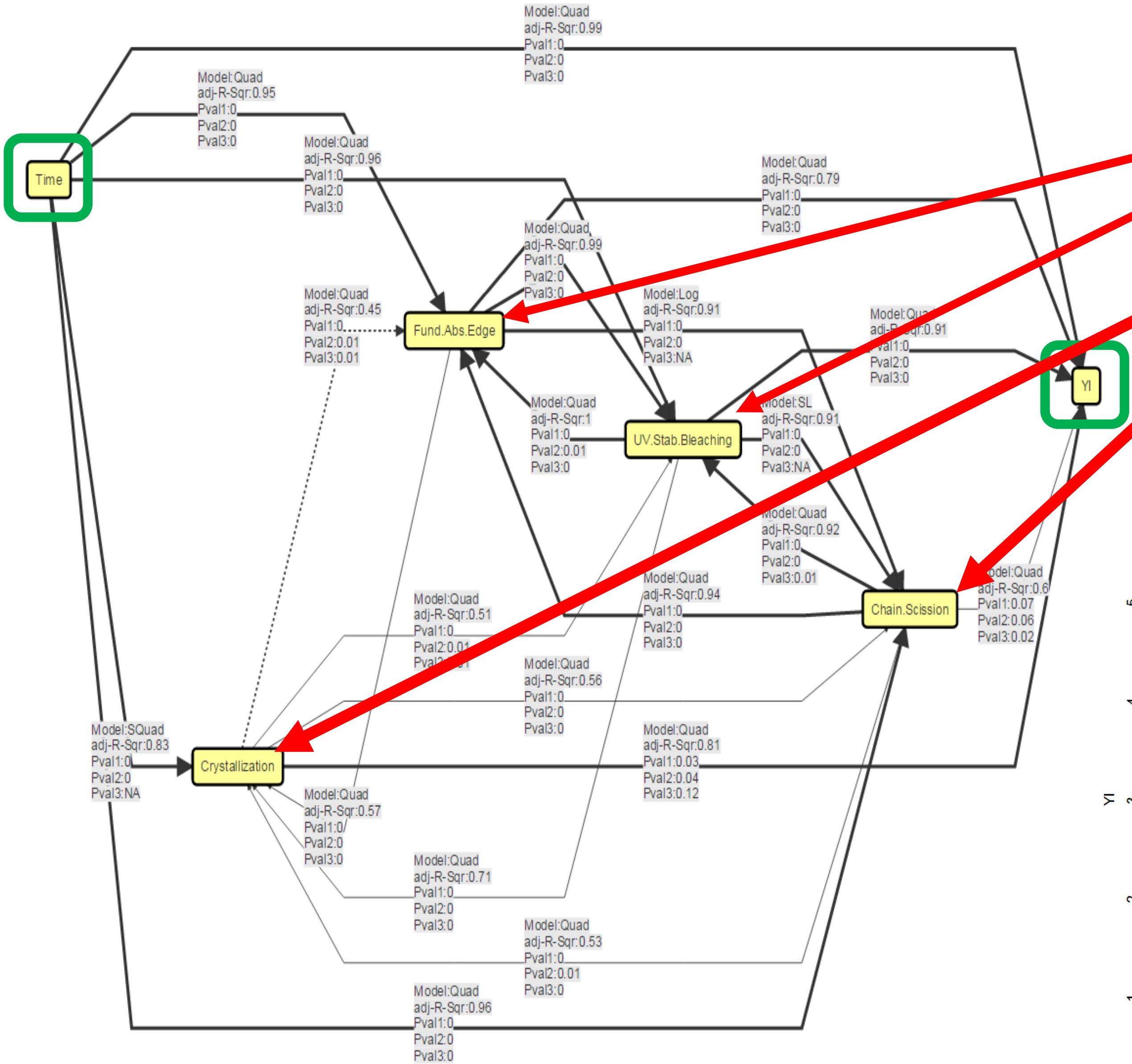
- Produce Yellowing



Confirmatory Evidence

- From DCS and IV

Yellowing sgSEM: UV stabilized PET under CyclicQUV Exposure

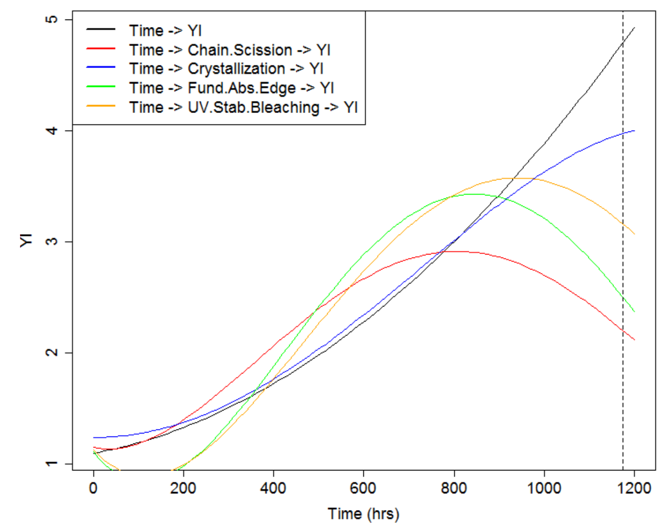


Important Role of

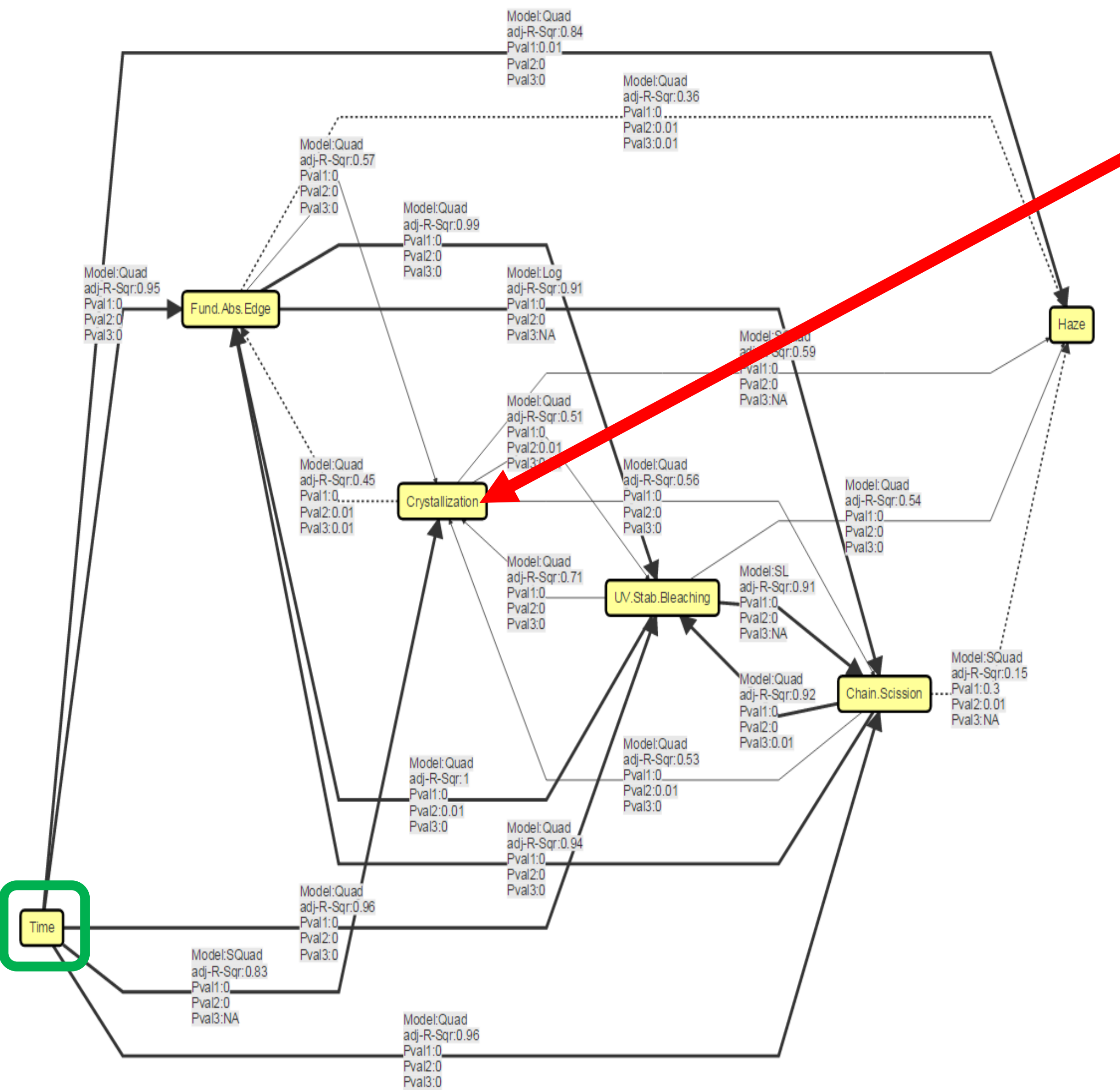
- Fund. Abs. Edge
- UV Stabilizer Bleaching

Crystallization and Chain Scission

- Produce Yellowing
- But at Reduced Rate



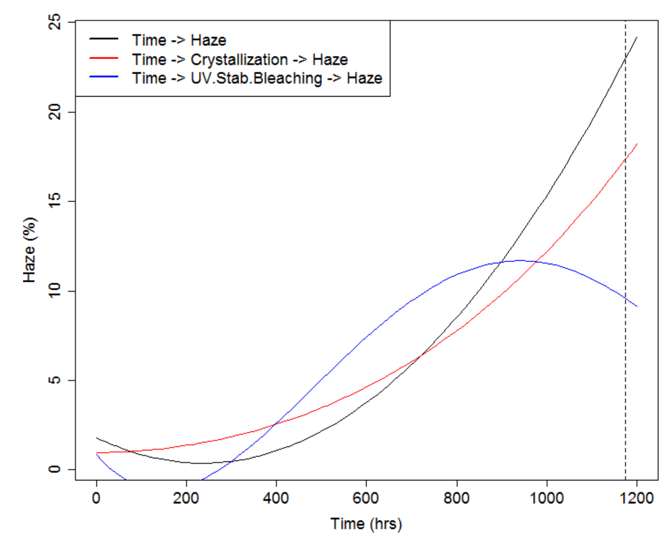
Hazing sgSEM: UV Stabilized PET under CyclicQUV Exposure



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

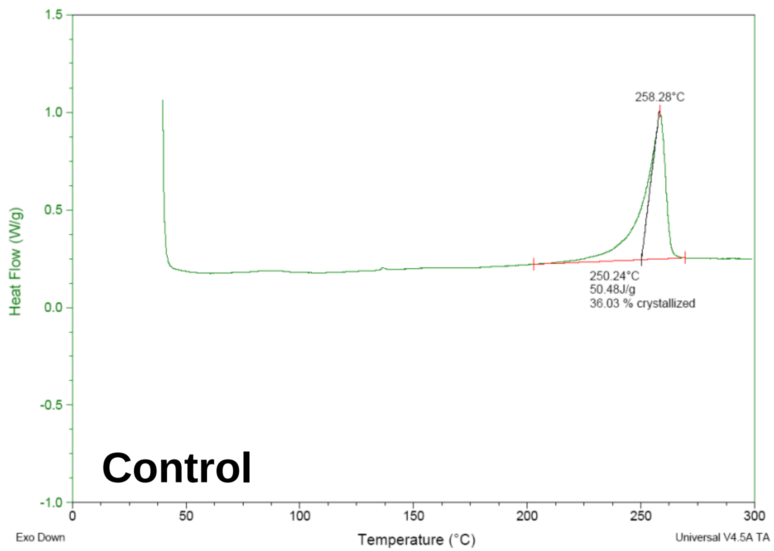
Change in Crystallinity via DSC (UV Stabilized)

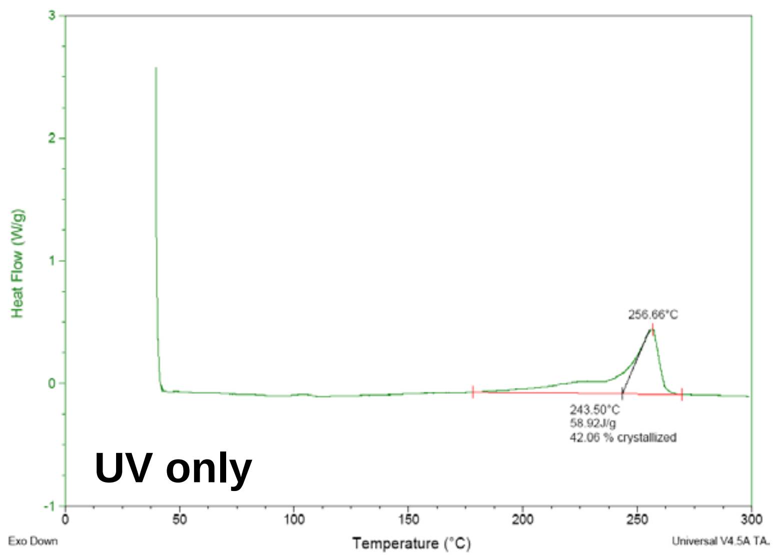
Degradation Causes

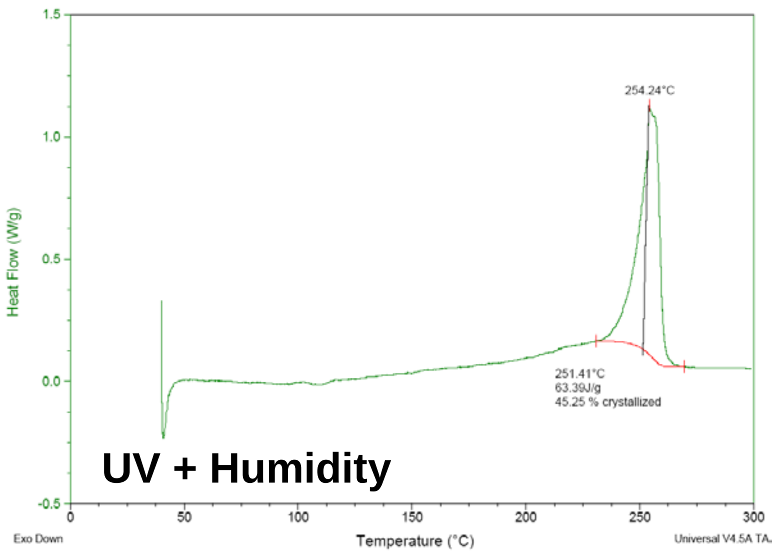
- Decrease in melting point (T_m)
- Decrease in intrinsic viscosity and Mw
- Increase in chain scission
- Increase in CEG content

Crystallinity increased from 36%

- to 42% During UV Exposure
- to 45% During UV+Humidity Exposure







M_w & CEG analysis: Incr. Chain Scission, CEGs, Decr. Mw

Intrinsic viscosity (IV) to determine molecular weight (M_w)

- 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_n)
- Increase in total end groups
  and chain scission per molecule

Grade - Exposure	IV(η)	$\overline{M}_n$	Total end groups	Chain scissions
Hyd. stabilized - Baseline	0.648	20,635	97	0
Hyd. stabilized - HotQUV*	0.593	18,544	108	0.11
Hyd. stabilized - CyclicQUV	0.495	14,917	135	0.38
Unstabilized - Baseline	0.564	17,457	115	0
Unstabilized - HotQUV*	0.375	10,676	188	0.64
Unstabilized - CyclicQUV	0.457	13,548	148	0.29
UV stabilized - Baseline	0.573	17,793	114	0
UV stabilized - HotQUV	0.503	15,208	132	0.17
UV stabilized - CyclicQUV	0.497	14,990	136	0.19

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

Grade - Exposure	KOH (ml)	CEG (mmol/Kg)	Ave. CEG (mmol/Kg)
Hyd. stabilized - Baseline	1.30 1.40	19.3 21.0	20.2±1.21
Hyd. stabilized - HotQUV*	9.85 9.80	192.6 192.5	192.6±0.05
Hyd. stabilized - CyclicQUV	8.55 8.65	166.7 165.3	166.0±0.94
Unstabilized - Baseline	1.70 1.75	27.6 28.5	28±0.69
Unstabilized - HotQUV*	10.75 10.85	214.8 211.4	213.1±2.43
Unstabilized - CyclicQUV	10.15 10.05	198.6 198.6	198.6±0.01
UV stabilized - Baseline	2.35 2.40	40.2 41.7	40.9±1.03
UV stabilized - HotQUV	7.50	146.6	146.6
UV stabilized - CyclicQUV	6.00	114.1	114.1

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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