New Concepts for Reliable Low-Cost Module Encapsulation and Barrier Technologies

Presenters: Patrick Thornton, Oliver Zhao and Reinhold H. Dauskardt (dauskardt@stanford.edu)
Graduated Students: Daisy Yuen, Yichuan Ding, Jared Tracy and Chris Delgado
Stanford University

Collaborators: Stephanie L. Moffitt*, Laura T. Schelhas* and Mihail Bora†
*SLAC National Laboratory, †Lawrence Livermore National Laboratory

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Outline

Scope: industrially-relevant new concepts in solar module encapsulation and moisture barrier technologies to accelerate state-of-the-art module performance, reliability and manufacturability with new module materials and interfaces demonstrated using accelerated testing and reliability models.

• Thrust 1: Encapsulant Degradation Mechanisms
  – Wide Angle X-ray Scattering and FTIR-ATR of delaminated EVA (with SLAC)
  – understanding and modeling fundamental degradation pathways

• Thrust 2: Advanced In-Situ Moisture Barrier Technology
  – open-air plasma-deposition of submicron multilayer barrier films
  – improved moisture barrier properties under accelerated aging conditions
Innovating Module Materials and Metrologies for Reliability

- new materials and cell packaging
- accelerated testing metrologies
- quantitative reliability models

Encapsulation delamination transparency WVTR
unexposed in shed 27 yrs
field exposed 27 yrs
28 μm
adhesion to metallized gridlines

backsheet blisters and lifetimes in fielded modules

Interfacial Adhesion Metrology for Solar Module Materials


Yuen, Moffitt, Novoa, Schelhas, Dauskardt, Prog. in Photovoltaics, 2019.
Debond energy decreased by 97% after 10 years in Florida sun.

**Debond Tip Viscoelastic Relaxation Models**

\[
\frac{da}{dt} = \frac{\pi}{8} \frac{\delta_c}{\epsilon_y (\delta_c \epsilon_y)^{\frac{1}{n}}} \left( \frac{G}{E_0(RH)} \right)^{\frac{1}{n}} \frac{E_h (1 - \nu^2)}{\tau R} \quad \text{Arhenius}
\]

\[
\frac{da}{dt} = \frac{\pi}{8} \frac{\delta_c}{\epsilon_y (\delta_c \epsilon_y)^{\frac{1}{n}}} \left( \frac{G}{E_0(RH)} \right)^{\frac{1}{n}} \frac{c_0 (\tau - \tau_f)}{10 (\tau - \tau_f) + (\tau - \tau_f)} \quad \text{Williams-Landel-Ferry}
\]

**Time and Temperature-Activated Backsheet Blistering Kinetics**

\[
t_{eq} = t_{Teq} e^{-G_a(RH)}
\]

**Blisters in fielded PV modules**
Time and Temperature-Activated Backsheet Blistering Kinetics


Degradation Mechanisms of Bulk Encapsulant and Interfaces

synergistic environmental stressors:

- sunlight (UV)
- heat
- humidity
- electrical bias (ion migration)
- thermomechanical strains

G_c ≈ 1,750 J/m^2 to 250 (27 yrs)…or to 1,170 (27 yrs no UV)

What are the detailed encapsulation degradation mechanisms?


Degradation Mechanisms of Bulk Encapsulant and Interfaces

synergistic environmental stressors:
- sunlight (UV)
- heat
- humidity
- electrical bias (ion migration)
- thermomechanical strains

specific EVA degradation reactions:

\[ \begin{align*}
& \text{I: } -\text{(C-C)}_n(\text{C-C})_y \xrightarrow{k_d} \text{deacetylation} \quad -\text{(C-C)}_n(\text{C}=\text{C})_y(\text{C-C})_{y-1} + \text{CH}_3\text{COOH} \\
& \text{II: } -\text{(C-C)}_n(\text{C-C})_y \xrightarrow{k_{\text{UV}}} \text{UV radical} \\
& \quad -\text{(C-C)}_n(\hat{\text{C}}-\hat{\text{C}})(\text{C-C})_{y-1} \\
& \quad -\text{(C-C)}_n(\hat{\text{C}}-\hat{\text{C}})(\text{C-C})_{y-1} + (\text{C-C})(\text{C-C})_{y-2} \\
& \text{III: } -\text{Si-O-Si} \xrightarrow{k_H} \text{hydrolytic depolymerization} \\
& \quad -\text{Si-OH} + \text{HO-Si} \\
\end{align*} \]

analytical adhesion mechanics model

\[ G_c(t) = \sum_{i} G_{c,\text{intr},i}(t) + G_{c,\text{PL}}(t) \]

intrinsic contribution  non-linear contribution

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Degradation Mechanisms of Bulk Encapsulant and Interfaces

**analytical adhesion mechanics model**

\[ G_c(t) = \sum_i^n G_{c,\text{intr},i}(t) + G_{c,\text{PL}}(t) \]

- **intrinsic contribution**
- **non-linear contribution**

- • depends on bond rupture
- • decreases with bond rupture events
- • superposition of \( n \) processes

\[ G_{c,\text{intr},i}(t) = G_{c,\text{intr},i}(0) f_i(t) \]

\[ f_i(t) = \exp \left( -a_i \left( 1 - \frac{b_i(t)}{b_i(0)} \right) \right) \]

- **intensity factor**
- **bonds rupture ratio**

\[ G_{c,\text{PL}}(t) = \sum_i^n G_{c,\text{intr},i}(t) d(t) \]

\[ d(t) = d(0) \left( 1 - \frac{t}{t_\infty} \right) \]

- **proportionality factor**

Tracy, D’hooge, Bosco, Delgado, Dauskardt, Prog. in Photovoltaics, 2018.

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Degradation Mechanisms of Bulk Encapsulant and Interfaces

**analytical adhesion mechanics model**

\[ G_c(t) = \sum_i^n G_{c,\text{intr},i}(t) + G_{c,\text{PL}}(t) \]

- contributions from each degradation process

\[ k_j = A_j \exp \left( \frac{-E_{Aj}}{RT} \right) \]

- \( f_i(t) = \exp \left( -a_i \left( 1 - \frac{b_i(t)}{b_i(0)} \right) \right) \)

- \( k_j = A_j \exp \left( \frac{-E_{Aj}}{RT} \right) \)

- \( \frac{dc_{VAc}(t)}{dt} = -k_{1c_{VAc}}(t) \)  
  - deacetylation (I)

- \( \frac{dc_{SiOSi}(t)}{dt} = -k_{2c_{SiOSi}}(t)c_n(t) \)
  - hydr. depolym. (III)

- \( \frac{dc_{CMCR}(t)}{dt} = k_{5c_{CMCR}}(t) \)  
  - radical formation and scission (II)

- \( \frac{dc_{CMF}(t)}{dt} = k_{4c_{CMF}}(t) \)

Tracy, D’hooge, Bosco, Delgado, Dauskardt, Prog. in Photovoltaics, 2018.
Sensitivity of adhesion to individual degradation processes varies temporally:

- deacetylation dominates initially
- UV radical formation and scission dominate at intermediate timeframes
- interface hydrolysis dominates at $t > 10$ yrs

Tracy, D’hooge, Bosco, Delgado, Dauskardt, Prog. in Photovoltaics, 2018.
Modular Description of Critical Degradation Pathways in EVA

**Degradation Pathways**

I. \( -\{\text{C}-\text{C}\}_x\{\text{C}-\text{C}\}_y \xrightarrow{k_1} -\{\text{C}-\text{C}\}_x\{\text{C}==\text{C}\}_y \xrightarrow{k_2} -\{\text{C}-\text{COOH}\} \) \\
   \text{deacetylation} \\
   \text{UV radical} \\
   \beta\text{-scission} \\
   \text{hydrolytic depolymerization}

**Advanced Characterization of EVA Degradation: WAXS**

- EVA is a semi-crystalline polymer...
- **Primary Crystalline Phases**
  - Orthorhombic
  - Monoclinic

- crystalline vol. frac. ~ 5%
- remainder amorphous

**Wide Angle X-ray Scattering**

- Exposure Conditions—
  - 10,000 Hours
  - "Dark" – 85°C, 13.5%RH, No UV,
  - "Light" – 65°C, 30%RH, with UV: 81 W/m²

With Laura Schelhas and Stephanie Moffitt, SLAC
Monoclinic crystallites form from shorter ethylene segments. The comparative increase of monoclinic phase evidences main polyethylene chain degradation.

Monoclinic Orthorhombic

Deacetylation: $k_1$

UV radical: $k_2$

$\beta$-scission: $k_3$

$\beta$-scission: $k_4$

Deacetylation: $k_1$

Wide Angle X-ray Scattering

Normalized Intensity

2 Theta (°)

- [110] (ortho)
- [200] (ortho/mono)
- [001] (mono)

Exposure Conditions—

"Dark" – 85°C, 13.5%RH, No UV,
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Advanced Characterization of EVA Degradation: WAXS

Advanced Characterization of EVA Degradation: FTIR-ATR

C-H (Chain Scission/ Cross Linking)

C-O (Acetic Ions/Salts)

C-O (Secondary Alcohol Shift)

(hydrolysis resulting in polyvinyl alcohol formation)

- OH

Absorbance (Counts)

Wavenumber cm$^{-1}$

4000 3500 3000 2500 2000 1500 1000 500
Advanced Characterization of EVA Degradation: FTIR-ATR

Formation of Polyvinyl Alcohol

Shift in C-O Stretch Peak

Main Chain C-H Absorption
~2920 cm⁻¹

-C-O-···-C-O-···- + CH₃COOH

Deacetylation

-Si-O-Si- + H₂O
-H₂O-···-Si-OH

Hydrolytic Depolymerization

--hydrolytic depolymerization catalyzed in acidic conditions--

FTIR-ATR: Interdependencies of Degradation Pathways

Neutral Hydrolysis
Protonated Hydrolysis

Energy barrier for acid catalyzed hydrolytic depolymerization of SiO bonds

Adapted from Cypryk and Apeloig, Organometallics, 2002

Location of key C-O stretching bands for Acetate Ions/Salts¹:

i. symmetric stretch – 1415 ± 20
ii. antisymmetric stretch – 1570 ± 20

i. low concentrations of acetate → weak split peaks at 1560 and 1577
ii. high concentrations of acetate → peaks merge and give higher intensity

Location of key C-O stretching bands for Acetate Ions/Salts¹:

1. symmetric stretch – 1415 ± 20
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**FTIR-ATR: Interdependencies of Degradation Pathways**

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**FTIR-ATR: Glass Interface Comparison**

0 Hour
10,000 Hour Light
10,000 Hour Dark

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**XPS at Glass/EVA Interface**

- O1s
- Si2p
- Ca2p
- Na1s

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**Acetate Salts**

- Glass/EVA

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**Deacetylation**

- (C=O)² \(\rightarrow\) (CO₂)²

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**Hydrolytic Depolymerization**

- Si-O-Si + H₂O → Si-OH + HO-Si

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**Hydrolytic depolymerization catalyzed in acidic conditions**

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**DuraMAT**
Outline

Scope: industrially-relevant new concepts in solar module encapsulation and moisture barrier technologies to accelerate state-of-the-art module performance, reliability and manufacturability with new module materials and interfaces demonstrated using accelerated testing and reliability models.

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Open-Air Spray Plasma Processing of In-Situ Barrier Films
Barrier Layers Markedly Improves Device Stability

![Graph showing the improvement in device stability with barrier layers.](image)

Barrier Properties – WVTR by Calcium Test

![Diagram showing the WVTR by Calcium Test with different barrier properties.](image)

5-layer barrier has a WVTR of 5.92 * 10^-3 g/m²/day which is more than 2 orders of magnitude lower than a single layer organosilicate barrier.
Barrier Properties – Moisture Transmission by IR Imaging

90% RH 70% RH 50% RH 30% RH 10% RH

Histogram

0.39% 0.37% 0.352% 0.347%

(a) (b) (c)

Blackbody source
Mounted sample
IR Camera

Barrier Properties – Moisture Transmission by IR Imaging

Polymide (75um)

1-layer Barrier (100nm) Polymide (75um)

Without Barrier With Barrier

With Mihail Bora (LLNL)
Conclusion: New Concepts in Module Reliability

**Scope:** industrially-relevant new concepts in solar module encapsulation and moisture barrier technologies to accelerate state-of-the-art module performance, reliability and manufacturability with new module materials and interfaces demonstrated using accelerated testing and reliability models.

**Thrust 1: Encapsulant Degradation Mechanisms**

1. $-\text{(C-C)}_3\text{(C-C)}_y\xrightarrow{\text{UV radical}} -\text{(C-C)}_x\text{(C-C)}_y$ deacetylation
2. $-\text{(C-C)}_x\text{(C-C)}_y\xrightarrow{\beta-\text{scission}} -\text{(C-C)}_x\text{(C-C)}_y$ hydrolytic depolymerization
3. $-\text{Si-O-Si...} + \text{H}_2\text{O}\xrightarrow{\text{H}_{2}\text{O}} -\text{Si-OH} + \text{HO-Si...}$

High resolution WAXS and FTIR-ATR explain the presence and interdependencies of degradation pathways.

**Thrust 2: Open-air In-Situ Moisture Barriers**

50% RH, 50°C

Low-cost barrier layers significantly improves solar cell stability in humid environments.

**Future Directions – Advancing Bifacial Modules**

Advancing Bifacial Solar Module Reliability and Manufacturability with New Module Materials and Light-Weight Transparent Back Lamination

**Emergence of Bifacial PV:** Bifacial panels have significant advantages over monofacial modules with increased power yield by up to 30%, and costs for bifacial PERC production are within $0.01—0.02/W of the costs for mono-facial PERC production*. Builds directly on capabilities developed in our current DuraMAT program, include advanced characterization and modeling of fundamental degradation pathways in module materials and our advanced in-situ moisture barrier technology.

Leverages the DuraMAT Materials Characterization and Forensics capability through our continued partnership with SLAC and collaboration with Dr. Matt Reese on WVTR characterization and Dr. Mike Woodhouse at NREL involving bifacial techno-economic analyses useful for U.S. PV manufacturing.

**Thrust 1** - Bifacial module materials degradation and interface reliability characterization.

**Thrust 2** – Develop and validate a transparent polymer back lamination technology comprising 1) a conformal, dense, multi-dyad thin-film barrier structure deposited directly onto the module backside using a scalable open-air spray plasma for pin-hole free barriers, 2) a high-quality transparent encapsulate, and 3) transparent polymer backsheet containing fluoropolymer which provides robust mechanical protection.