Project: Service Life Prediction of Polymeric Materials in Photovoltaics

Accelerated Laboratory Testing of PV Polymers using Simultaneous UV Radiation, Temperature and Moisture

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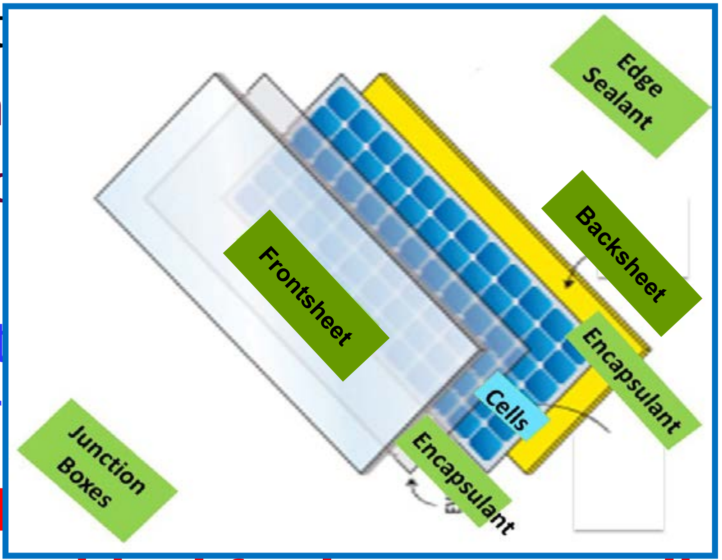
Outline

- **Motivation**
- **Study of degradation of PV polymeric materials under simultaneous multiple stresses (UV, T, RH)**
  - Encapsulant (EVA)
  - Backsheet (Fluoropolymer/PET/EVA)
  - Frontsheet Fluoropolymers
- **Summary**

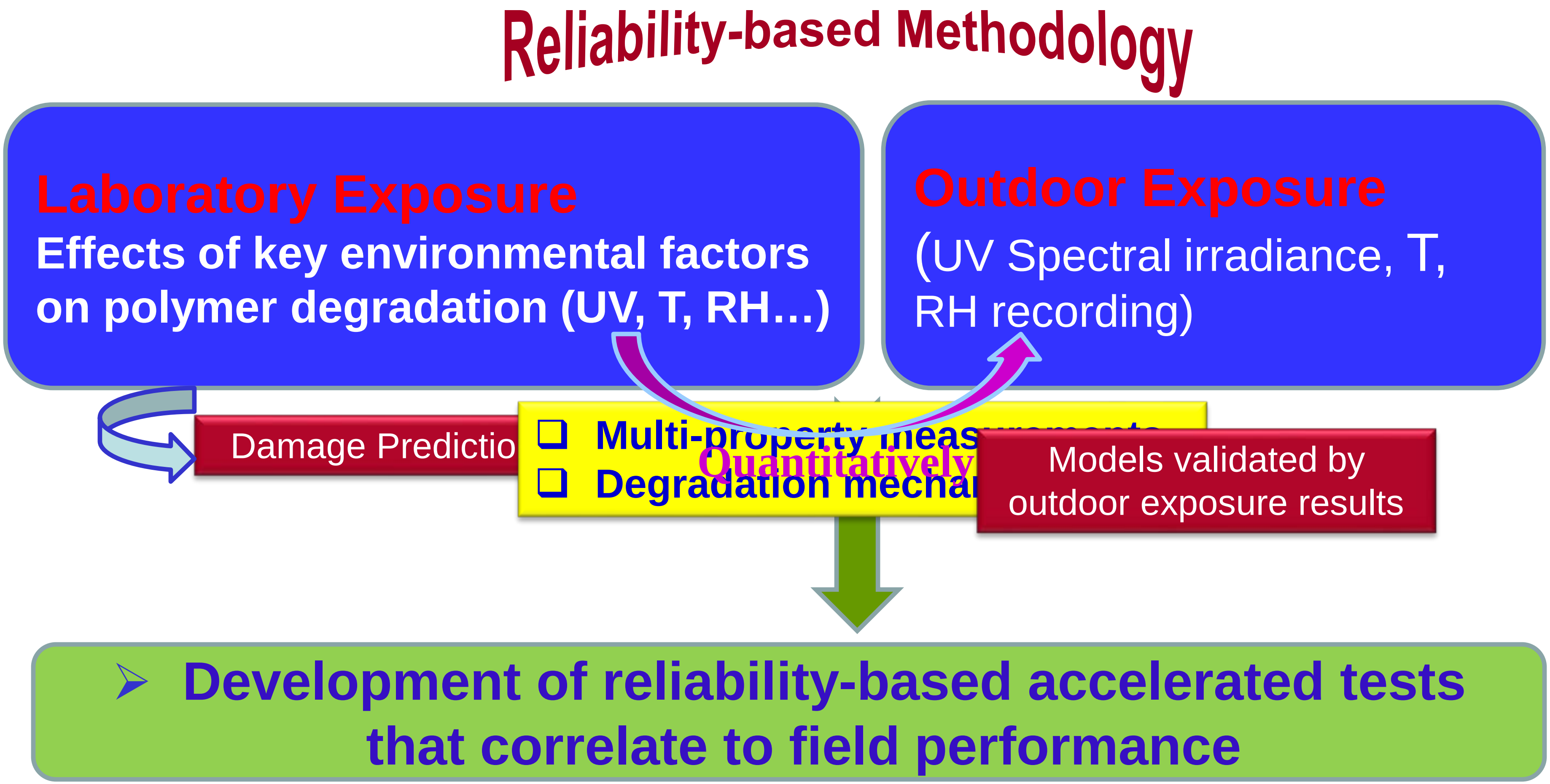
Motivation

- Success of PV technology strongly depends on a clear demonstration of long-term reliability of PV systems.
- PV systems contain **polymers**, susceptible to degradation (photo-, thermo-, hydrolysis, etc.), and polymers used in conjunction with other materials can also incur loss of adhesion at the interface.
- High competition of solar PV indust
  - Development of new materials → n
  - Emphasis on low cost → potential c quality/reliability?
- No validated accelerated aging test prediction of PV performance and r



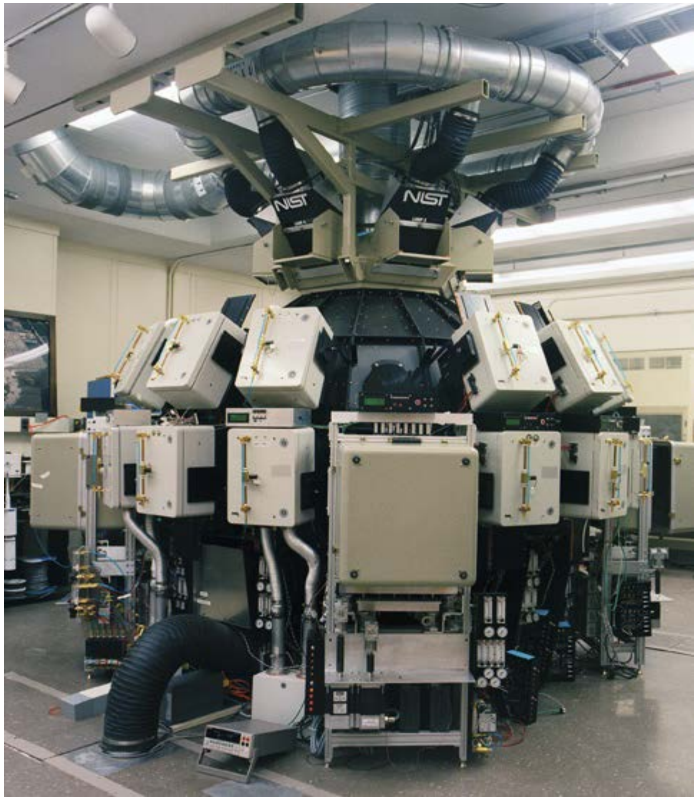
➤ **Development of reliability-based correlate to field performance is critical for long-term reliability of PV modules and systems.**

Service Life Prediction of Polymeric Materials used in PV System



* Successfully linked indoor and outdoor data for an epoxy system for coating industry.

NIST Integrating Sphere-based UV Chamber



NIST Patented

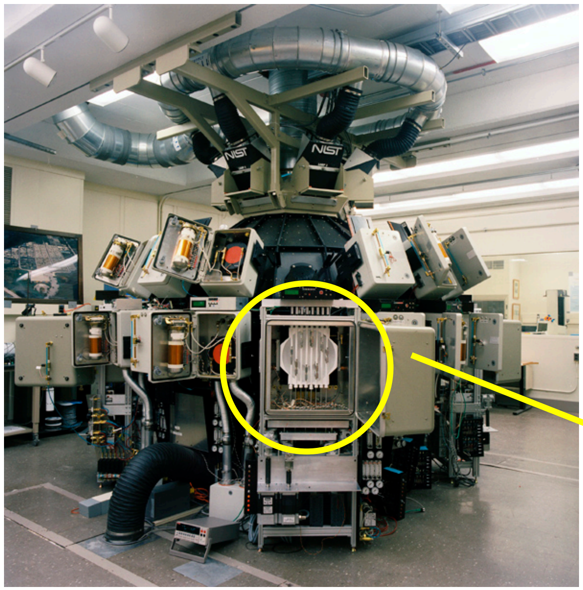
2m-Integrating SPHERE

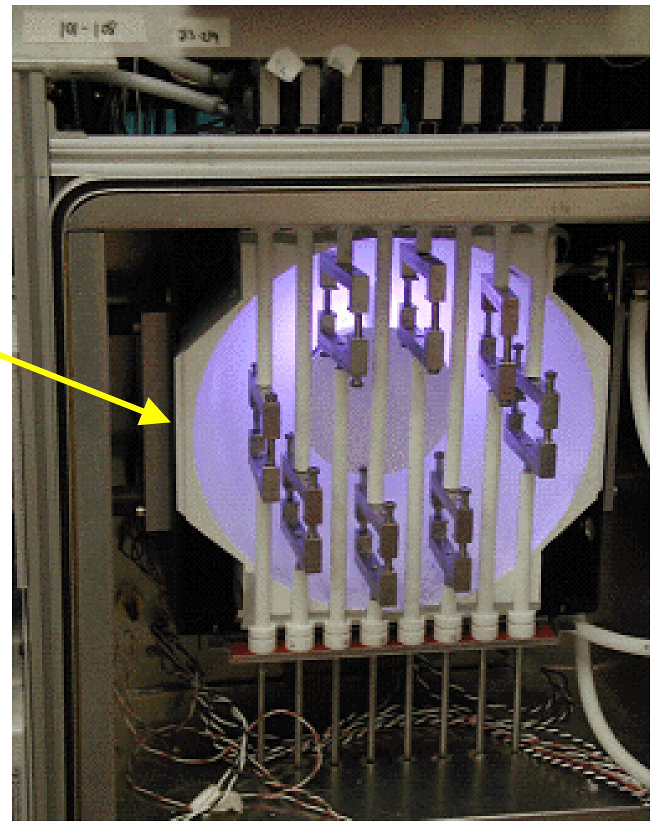
Simulated Photodegradation via High Energy Radiant Exposure

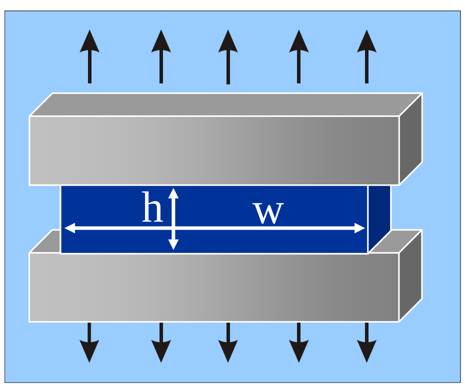
- 8400 W UV
- 95% exposure uniformity
- Visible and infrared radiation mostly removed
- Temperature and relative humidity around specimens precisely controlled (25-85 °C ± 0.1°C;
  0-95 % ± 0.2 % RH)
- Capability for mechanical loading
- Exposure conditions of 32 chambers can be individually controlled (UV, RH,T)

- ***Chin et al, Review of Scientific Instruments (2004), 75, 4951;***
- ***Martin and Chin, U.S. Patent 6626053***

Chambers with Mechanical Loading







Degradation of PV Polymers under Simultaneous UV Radiation, Temperature, and Moisture

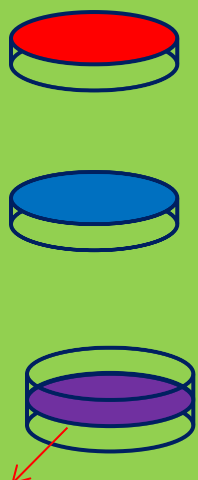
- **Materials**: Ethylene-Vinyl Acetate (EVA); Fluoropolymer/PET/EVA Backsheet; Frontsheet Fluoropolymers

- **Exposures:**
  - NIST SPHERE in a range of temperature, relative humidity. spectral UV intensity, and spectral UV wavelength
  - Outdoor roof on a NIST building, Gaithersburg, MD

- **Measurements:**
  - **Chemical Property:** FTIR and UV-Visible spectroscopies
  - **Physical Property:**
    Yellow index (UV-visible)
    Surface morphology (AFM and Confocal Microscopy)
  - **Mechanical Properties:** DMTA, Tensile Test, Nanoindentation

(1) Mechanistic Study of EVA Degradation under Simultaneous UV/T/RH

3 Types of Model Samples



Uncured EVA

TBEC-Cured EVA

Laminated EVA, Edge-sealed

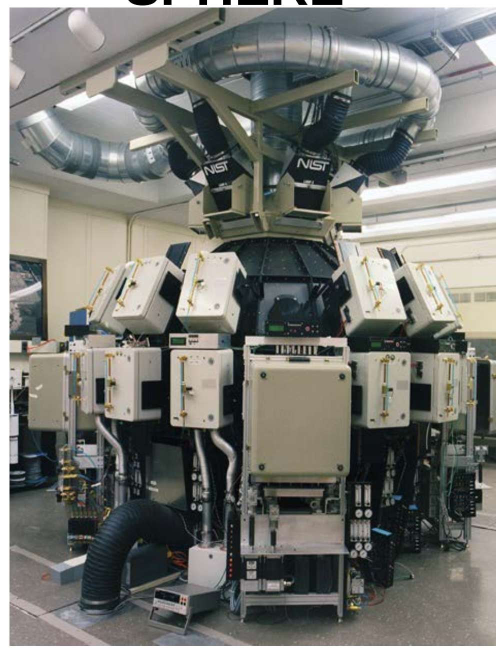
19 mm CaF_2 Substrate

(for T-FTIR, UV-visible and AFM)

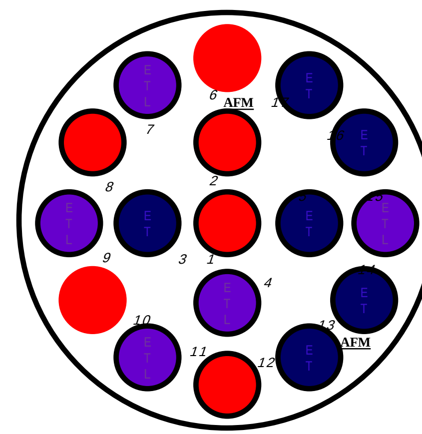
EVA: Unstablized

- To detect precursors of degradation using chemical and nanoscale characterization

SPHERE



55 °C, 75%RH, UV (wet)
55 °C, 0%RH, UV (dry)
55 °C, 75%RH, in Dark
55 °C, 0%RH, in Dark
UV: 200 W/m² (290-480 nm)

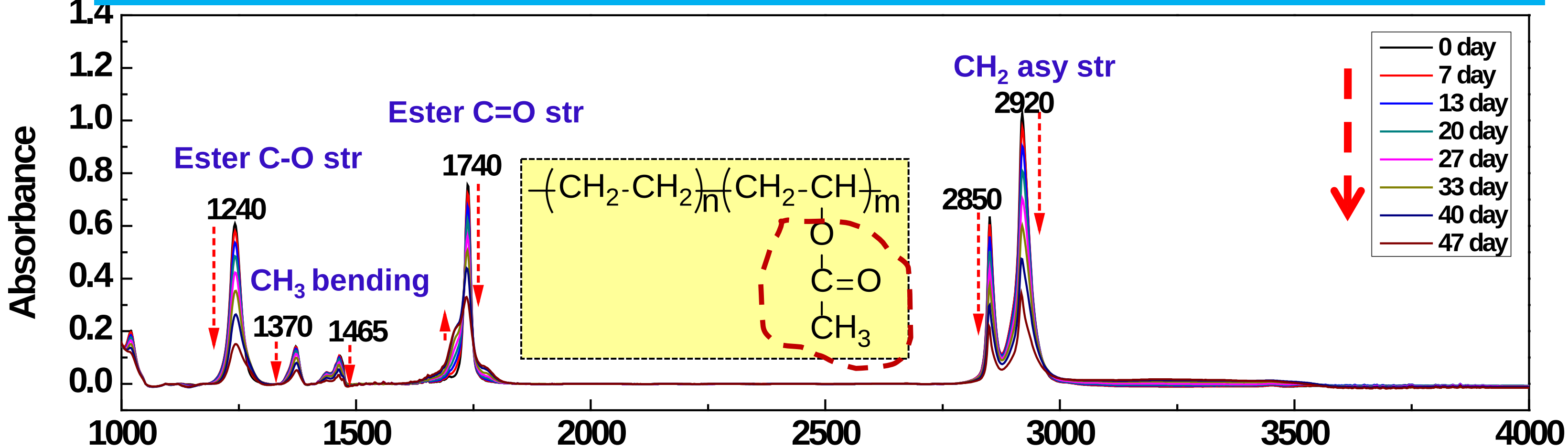


Outdoor Exposure

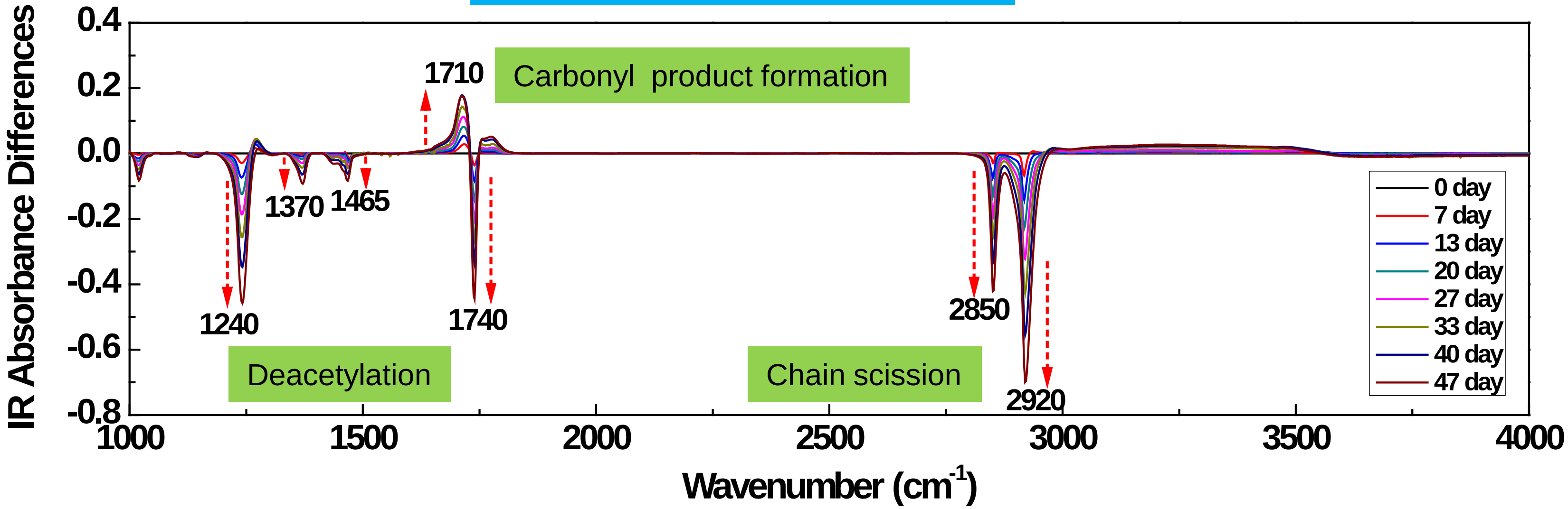
A. Laboratory Exposure Results

Chemical Degradation of EVA

Typical FTIR Spectra of EVA after UV Exposure for Different Time

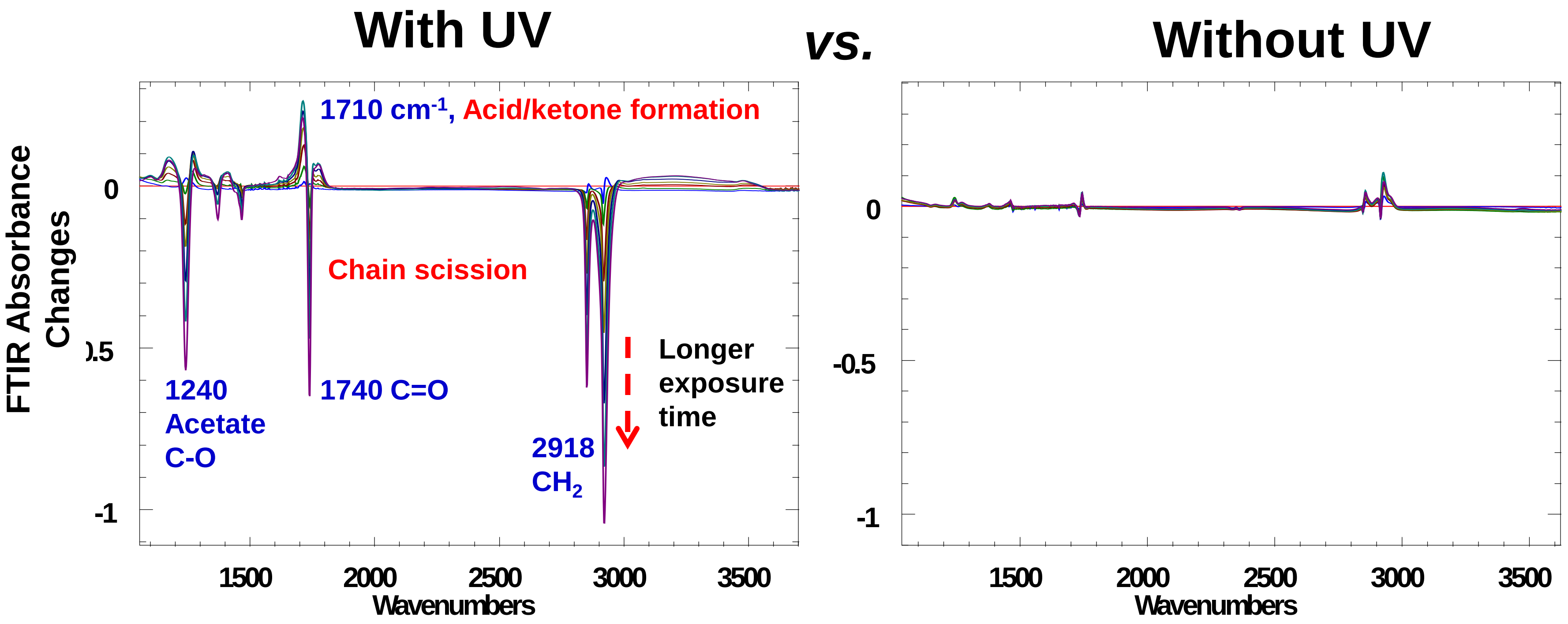


FTIR Difference Spectra



Effect of UV Light on Chemical Changes of EVA (55°C/75%RH)

Cured EVA, up to for 2 months

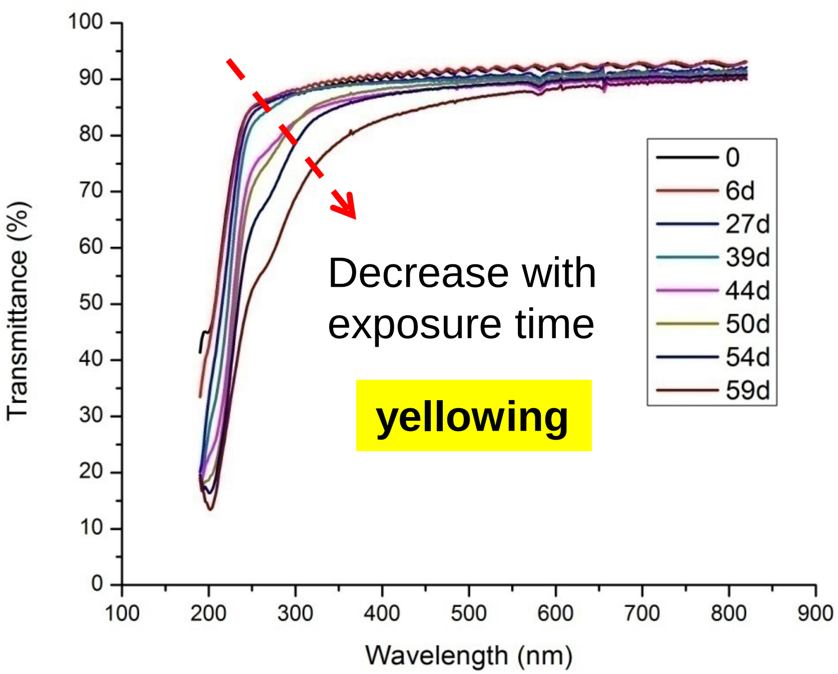


➢Importance of UV light on EVA chemical changes.

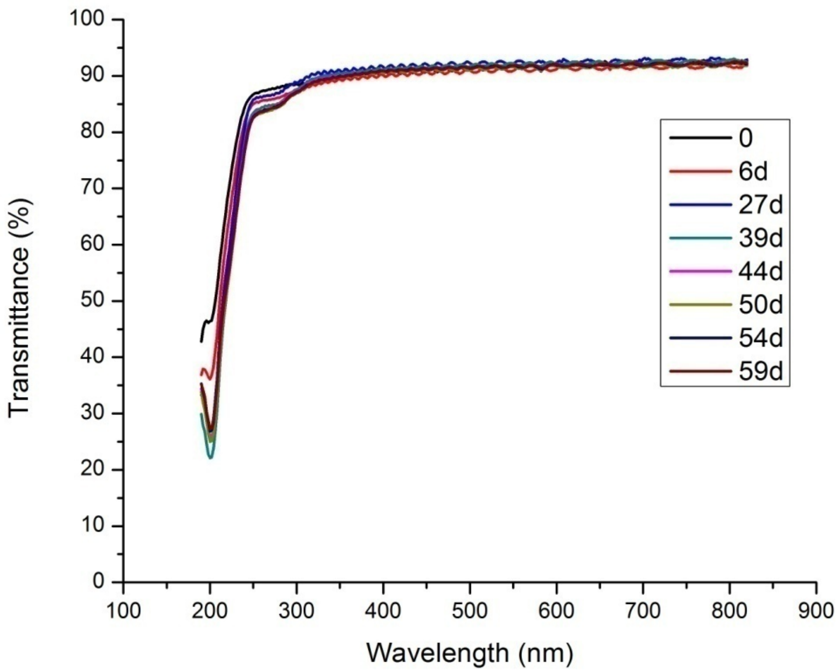
UV Transmittance Spectra for an EVA Exposed to 55°C/75%RH with and without UV Irradiation

Cured EVA, for 2 months

With UV Irradiation



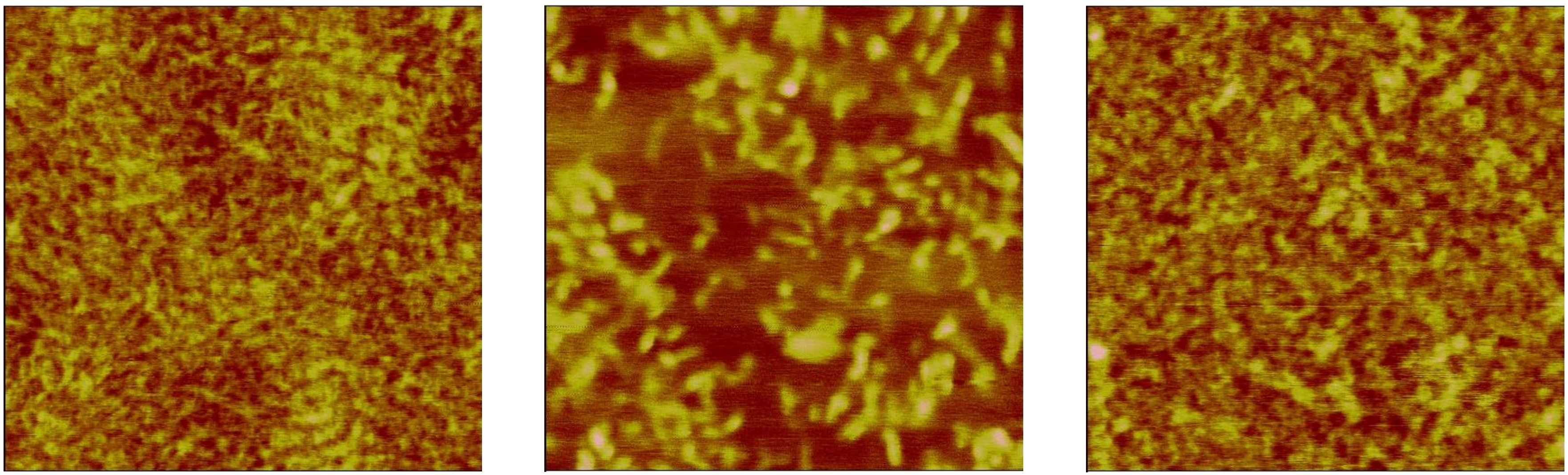
Without UV Irradiation



EVA Microstructural Changes Detected by AFM Phase Imaging after UV Exposure

Cured EVA, UV/55°C/75%RH, for 2 months

Before exposure   Exposed with UV   Exposed without UV



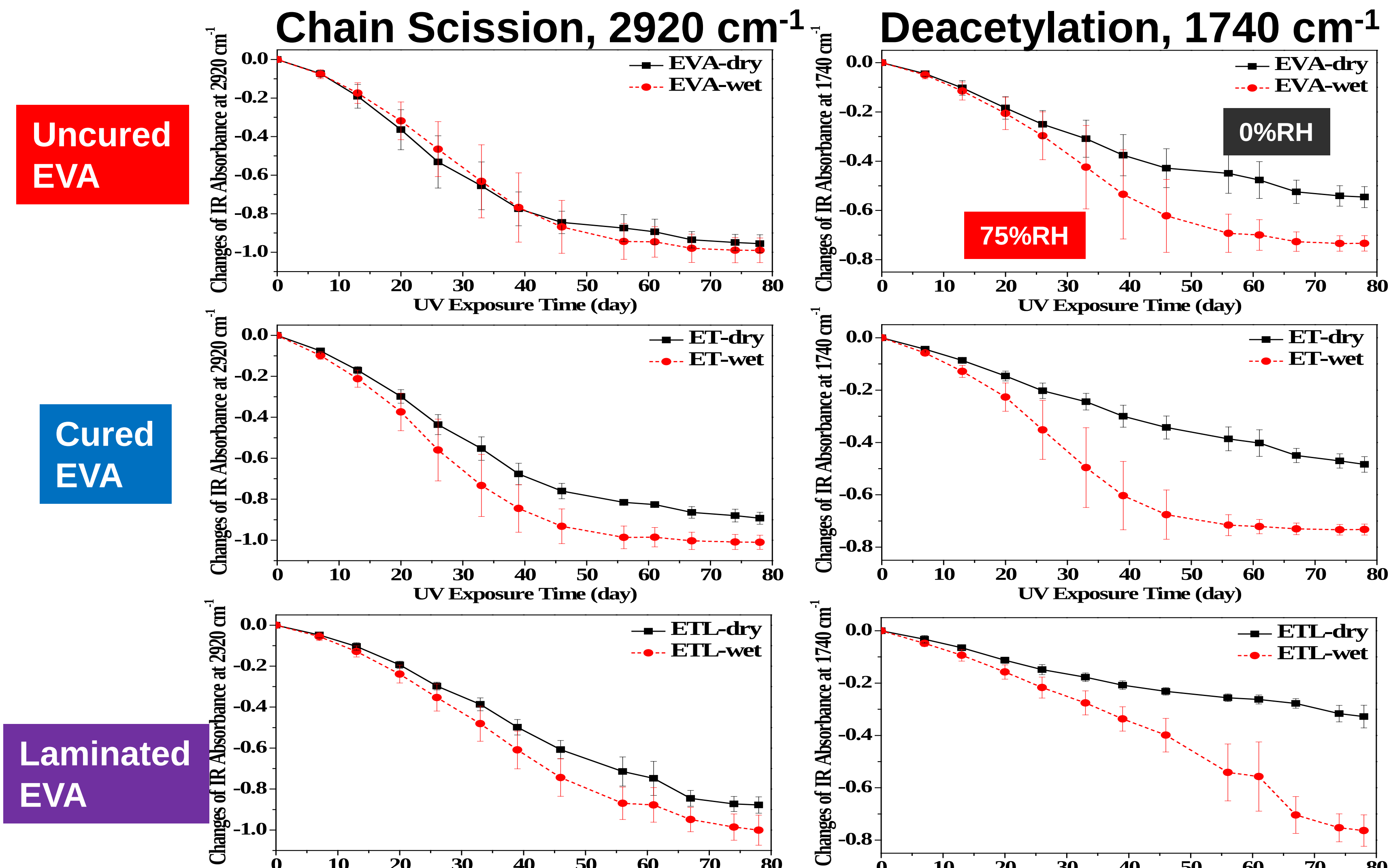
1 µm × 1 µm

- More district <u>lamellar </u>structures observed on the exposed samples indicate degradation of the amorphous regions and maybe some crystalline structures.

- UV light is an important factor for EVA degradation.

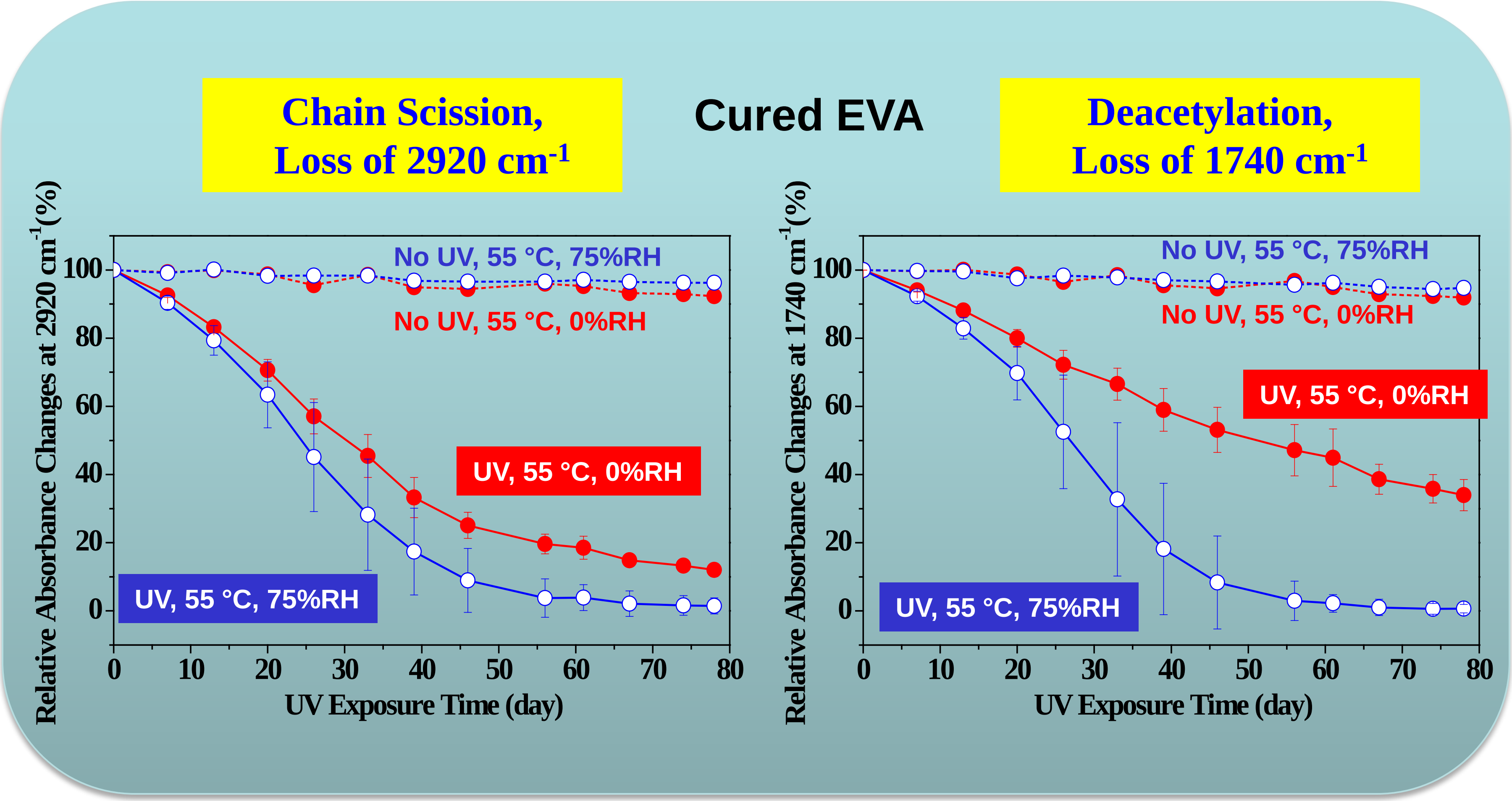
Effect of Relative Humidity on EVA Degradation

(UV, 55 °C, 0% RH (dry) *vs.* 75% RH (wet))



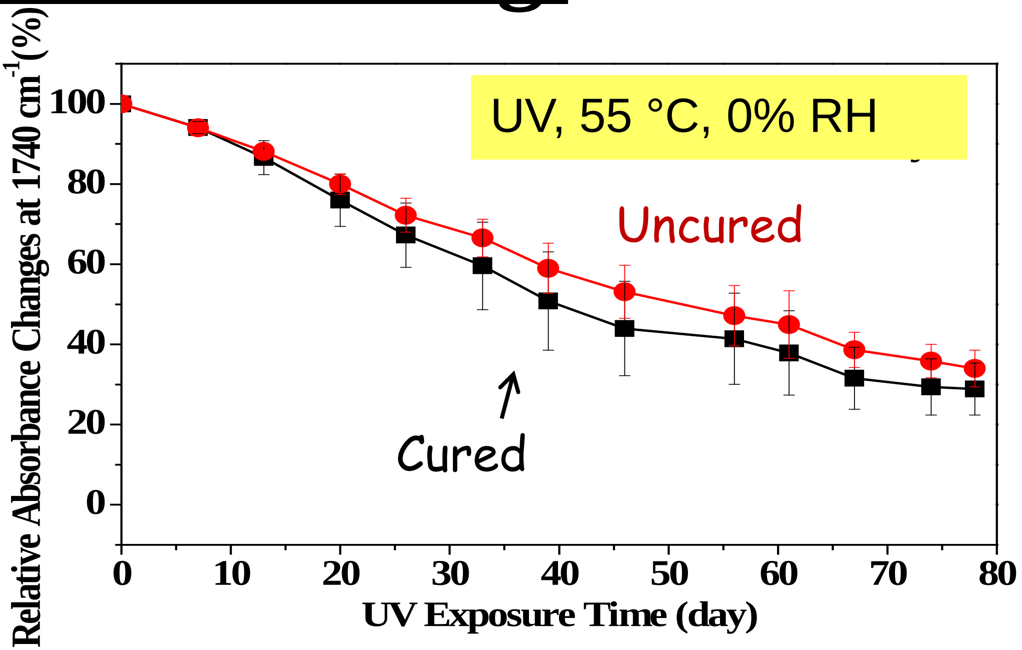
- ➢ Moisture accelerates the EVA chemical degradation, probably by promoting the formation of hydroperoxide free radicals during UV degradation.

Effect of Relative Humidity + UV Light



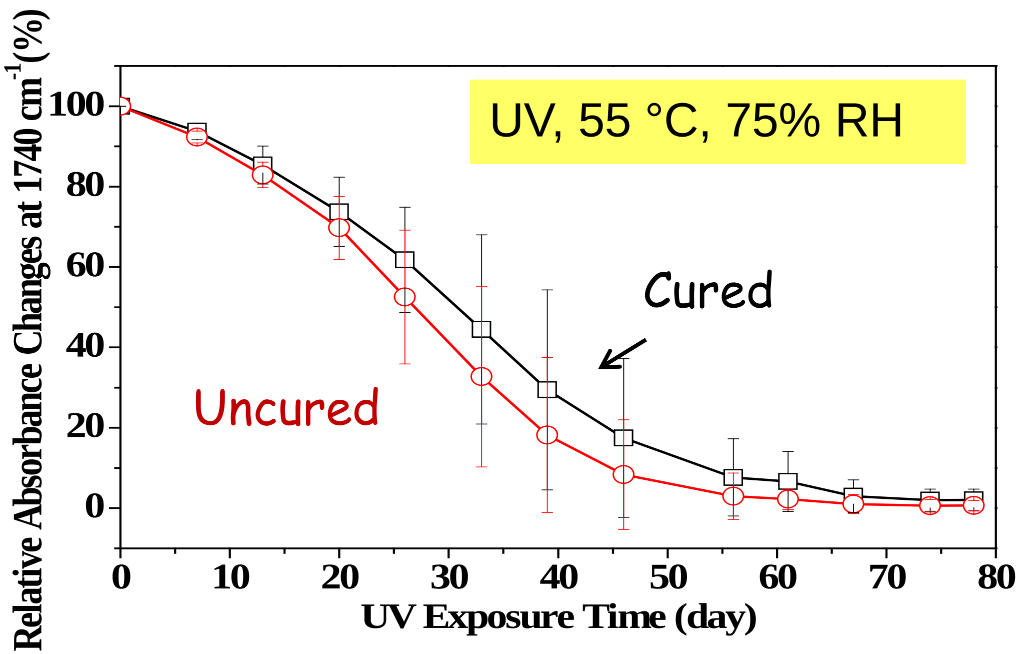
- Both UV and RH are important factors.
- Synergistic effect between UV and RH is observed.
- The degree of the effect depends on the chemical degradation mode.

Effect of Curing on Chemcal Degradation



Deacetylation,

Loss of 1740 cm^{-1}



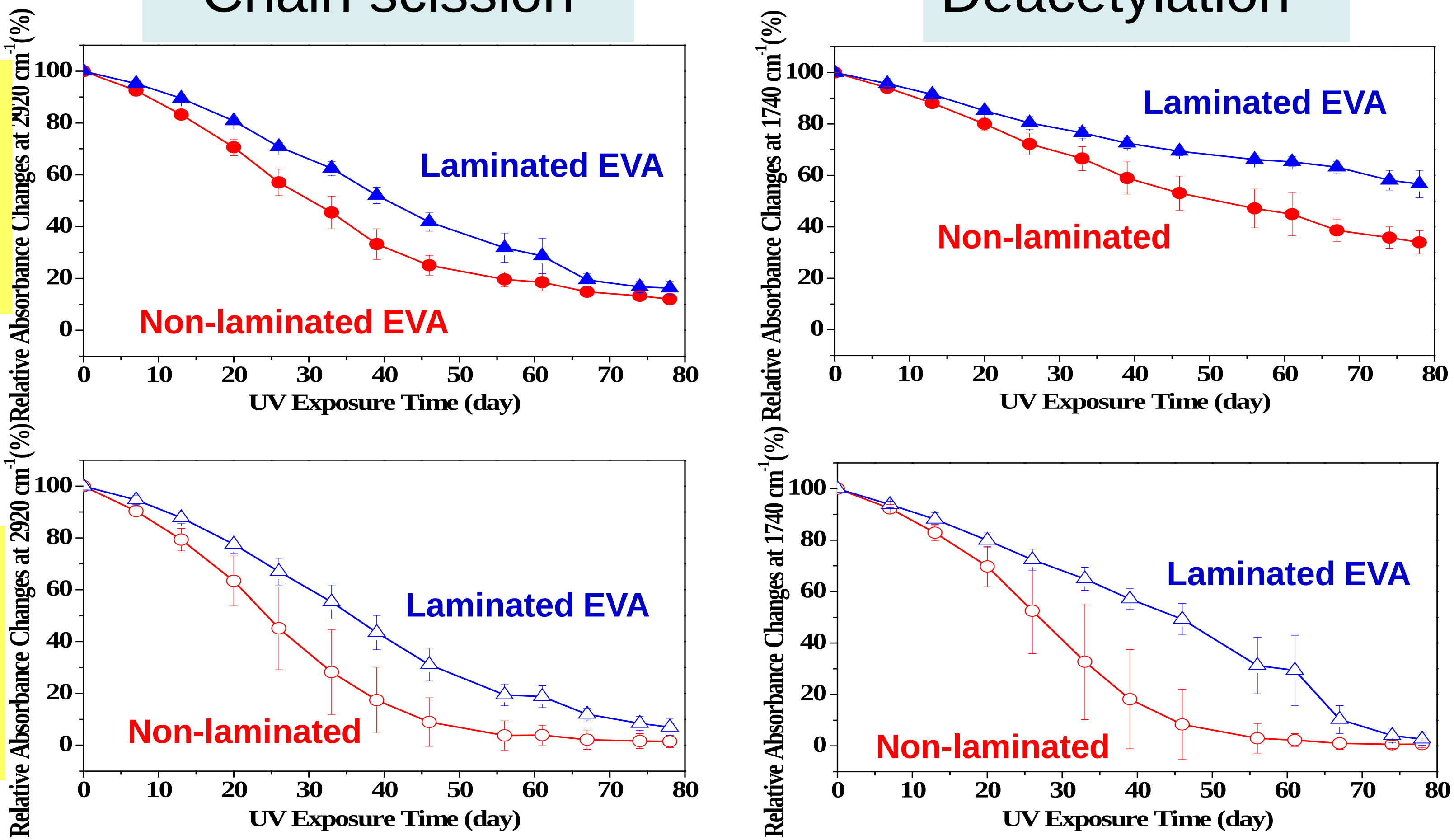
- Essentially no effect on chemical changes observed from curing.

Effect of Lamination on EVA Degradation

Chain scission | Deacetylation

UV, 55 °C, 0% RH

UV, 55 °C, 75% RH

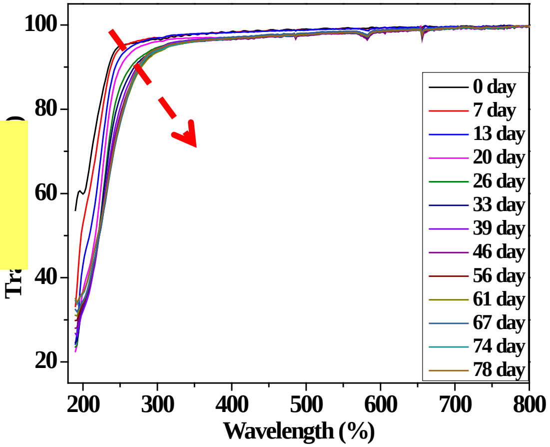


- **The degradation rate is lower for laminated EVA, probably because of limited diffusion of moisture and O_2 in the laminated system.**
- **Moisture and O_2 accelerate the chemical degradation.**

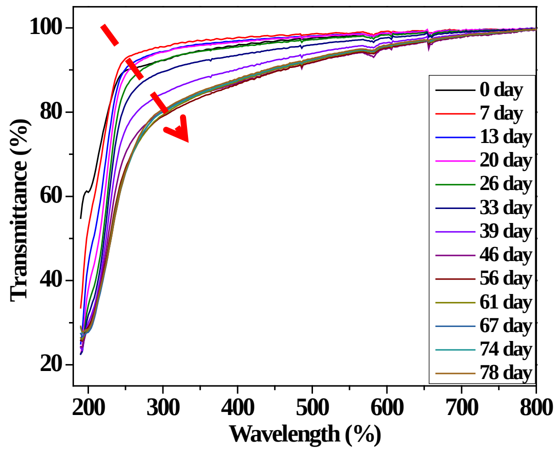
UV Transmission Spectra of 3 EVA Systems Exposed to SPHERE for Different Times (55° C, 0% RH)

With UV

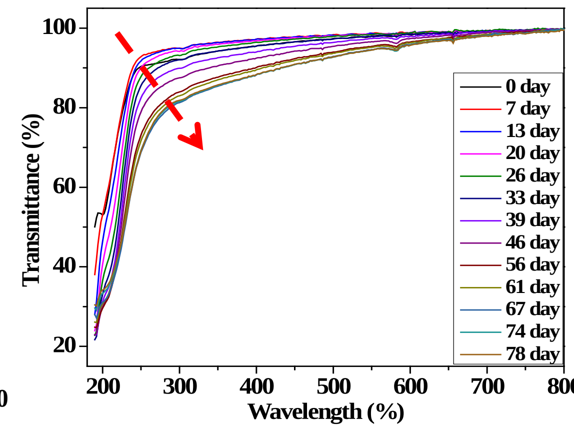
Uncured EVA



Crosslinked EVA

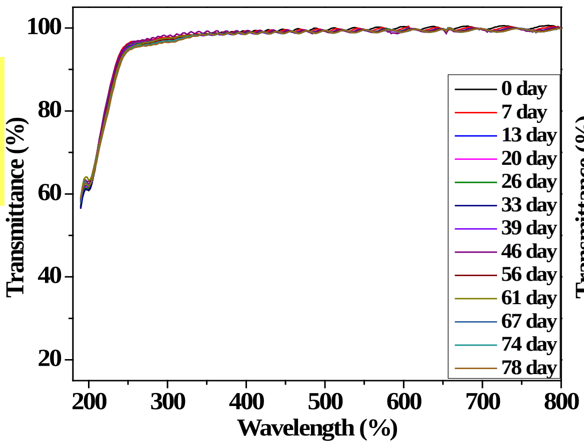


Laminated EVA

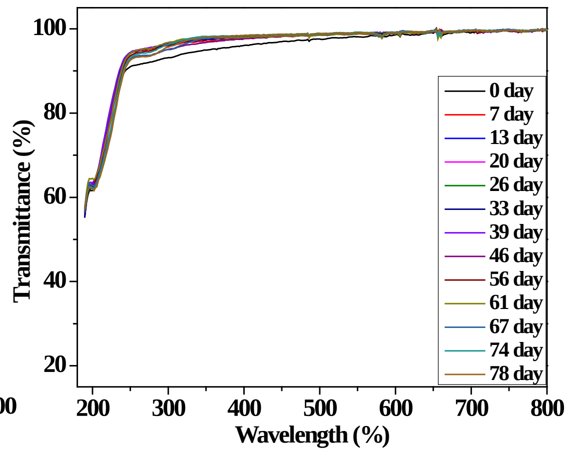


No UV

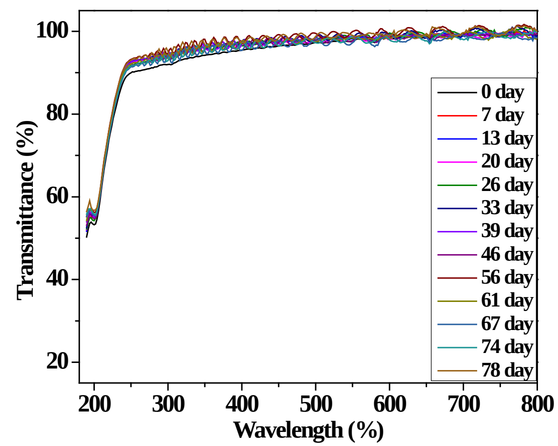
Uncured EVA



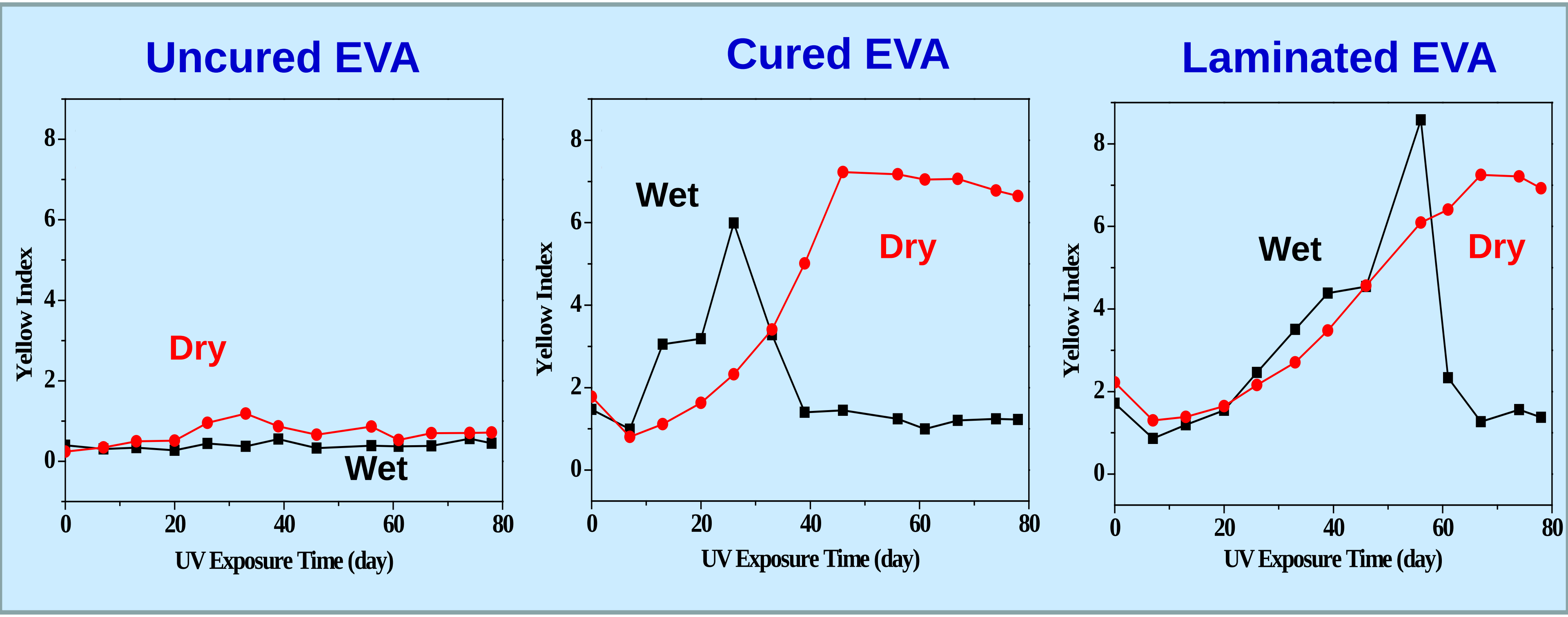
Crosslinked EVA



Laminated EVA

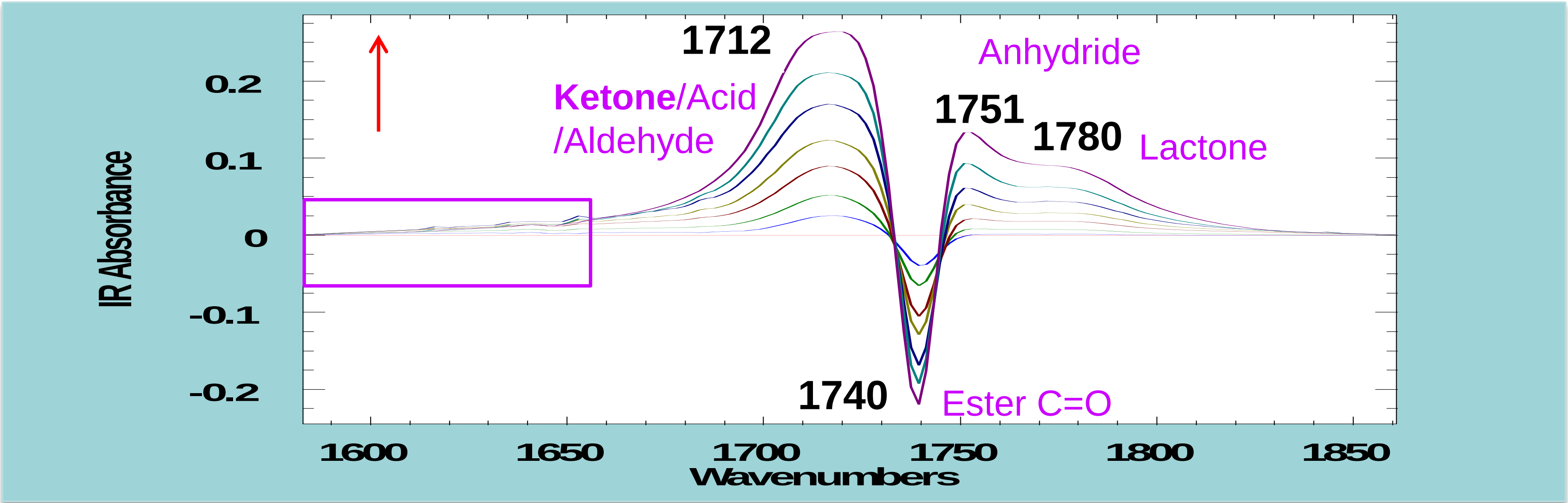


Preliminary Yellowing Index data for 3 EVA Systems
(SPHERE, UV/55° C, 75 % RH *vs.* 0% RH)

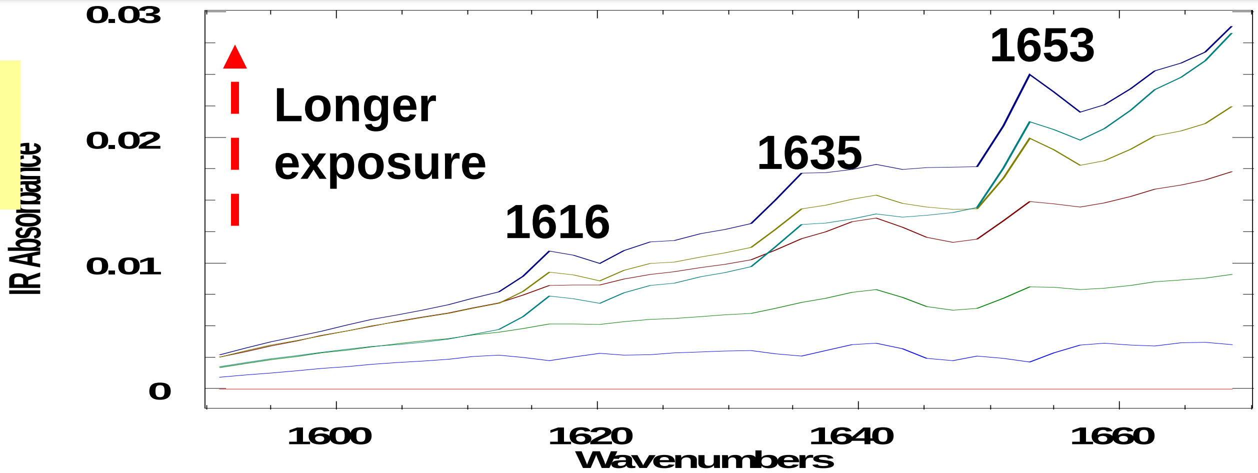


- The cured EVA system has higher yellowing than the uncured EVA.
- Decrease in yellowing is probably due to
  1) Photobleaching exceeds formation of yellowing (-O_2, H_2O)
  2) Physical erosion due to water (hydrophilic products)
- Less yellowing ≠ Less degradation (be cautious)

Complexity of Region 1600-1800 cm^{-1}

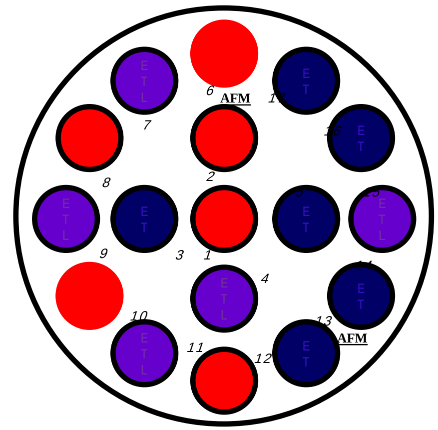


Laminated EVA



- **C=C** Conjugated (Polyene, but Raman didn't prove it.)
- **C=O,** α, β- Unsaturated ketone
- **Our data shows the yellowing is associated with the peroxide.**

(B) EVA Outdoor Exposure Results

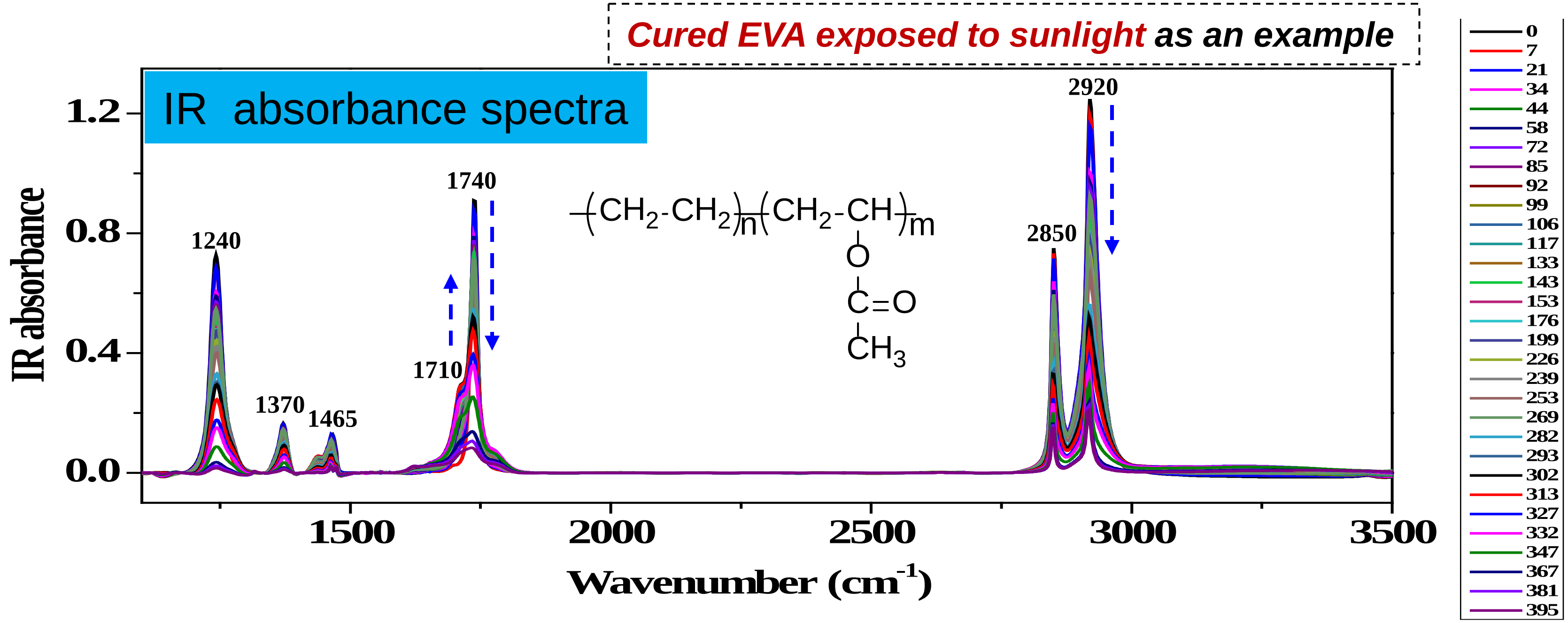


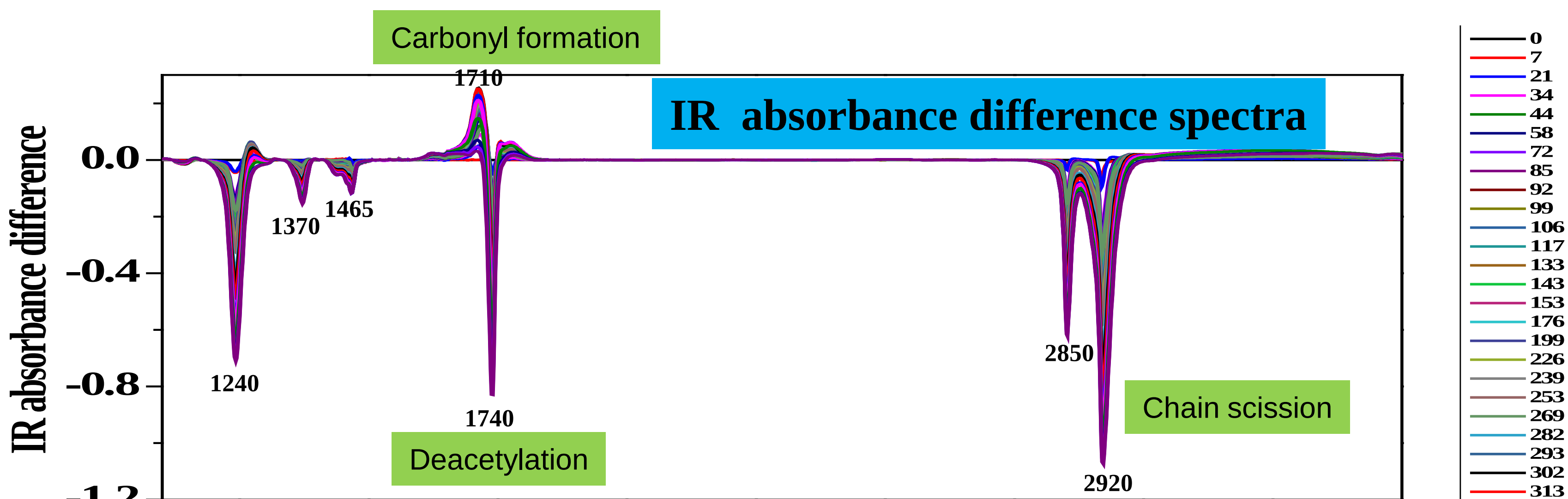
Outdoor Exposure Chamber

- Same samples as those for laboratory exposure
- The outdoor exposure was started from June, 2011
- Chemical and physical measurements performed weekly

Chemical Degradation

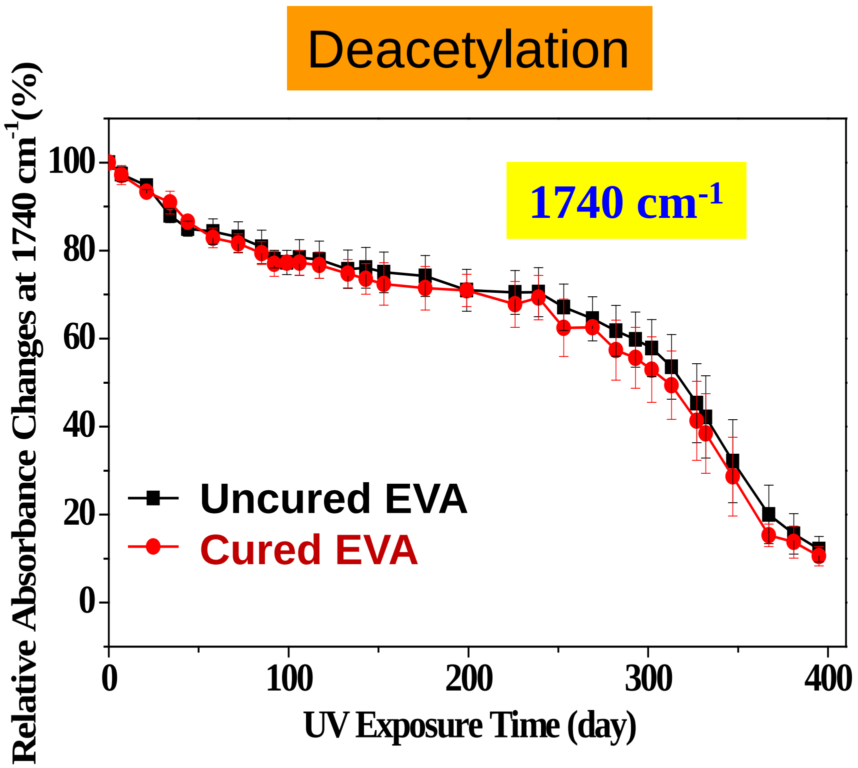
***Cured EVA exposed to sunlight* as an example**

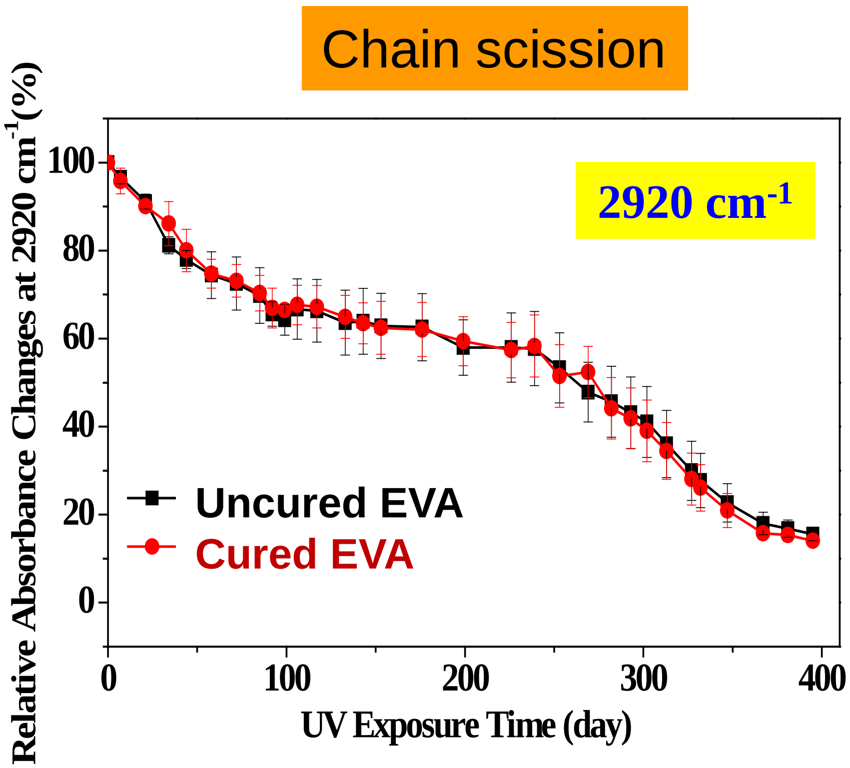




Same degradation modes observed between laboratory and outdoor exposures.

Effect of Curing on Outdoor Exposed EVA Degradation

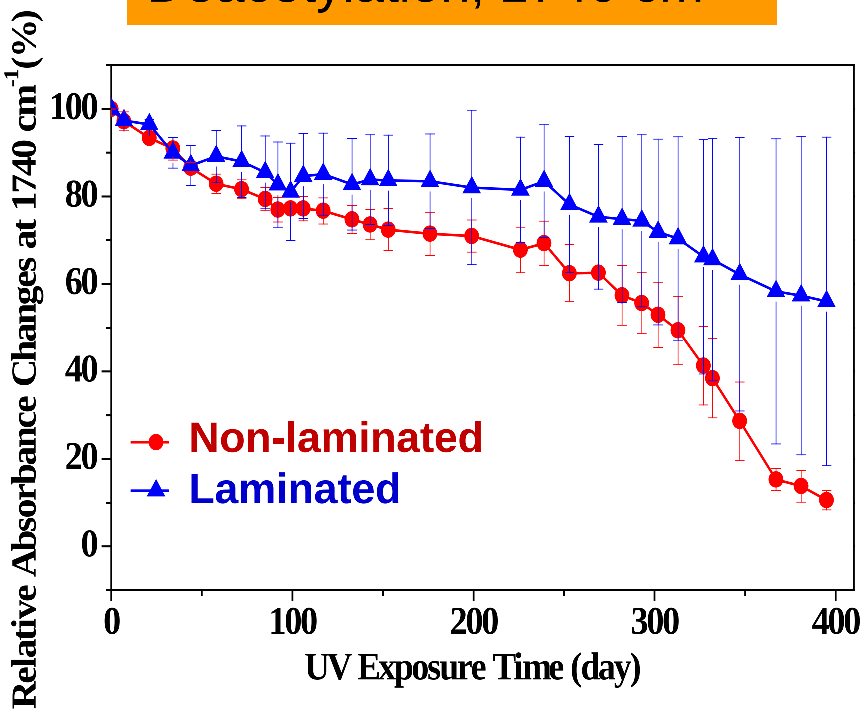




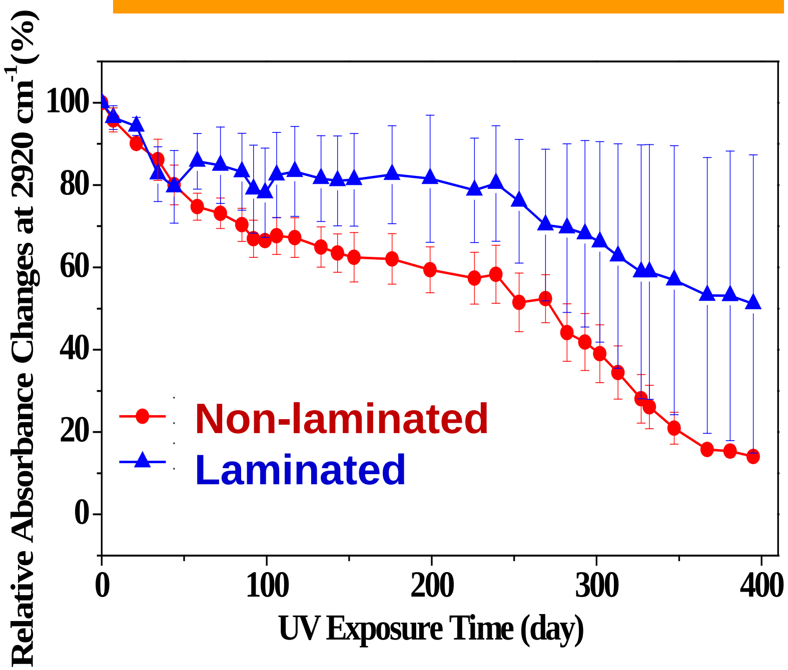
- Essentially no effect on chemical changes observed from curing.

Effect of Lamination on Outdoor Exposed EVA Degradation

Deacetylation, 1740 cm^{-1}



Chain scission, 2920 cm^{-1}

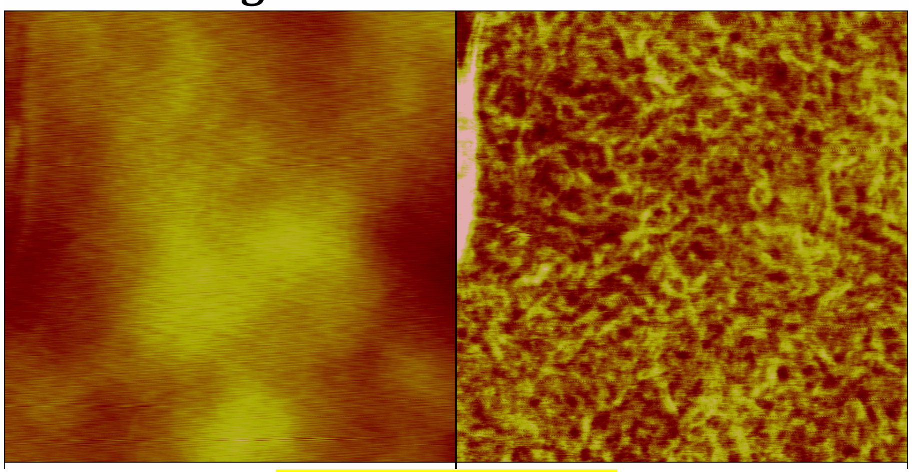


- **The degradation rate is lower for laminated EVA samples, because of limited diffusion of moisture and O_2.**

EVA Microstructural Changes after Outdoor UV Exposure (AFM)

Unexposed

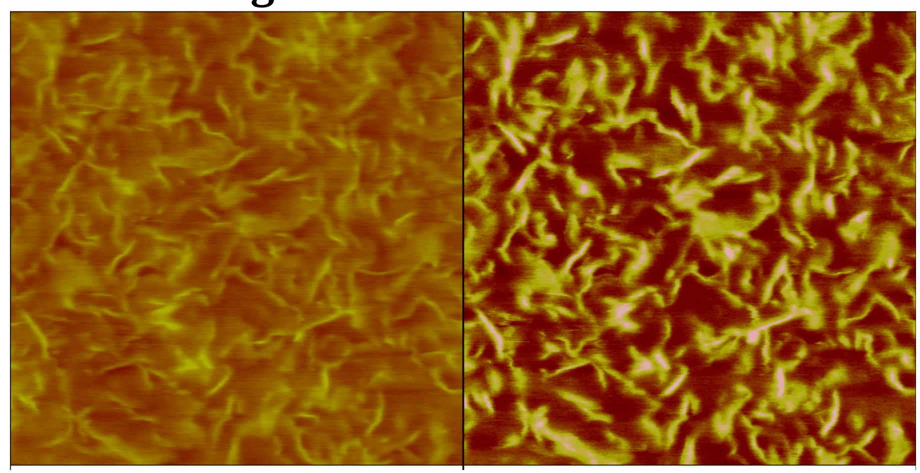
Height **Phase**



1 µm × 1 µm

Outdoor Exposed for 4 months

Height **Phase**

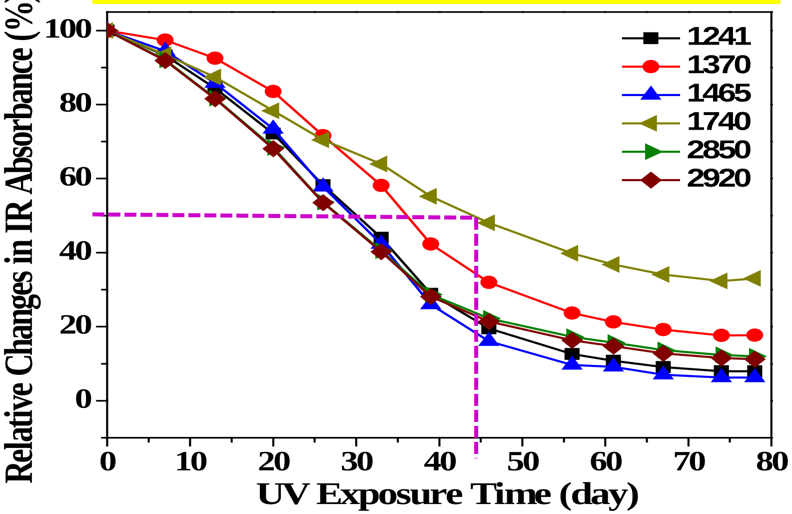


1 µm × 1 µm

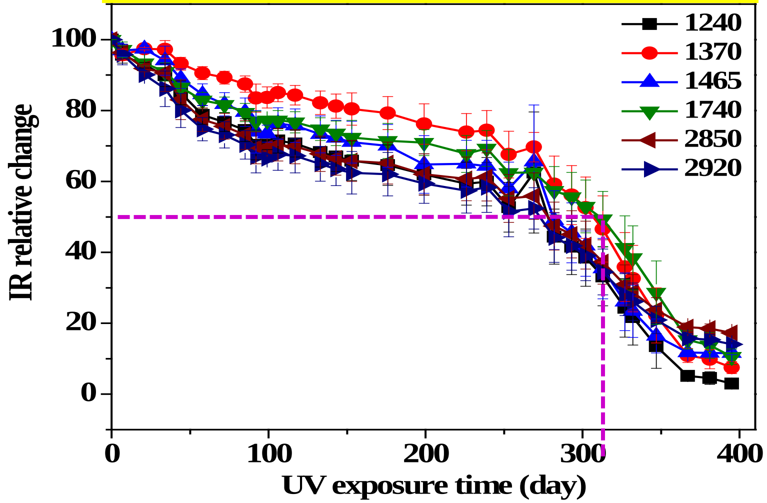
- More evident lamellar structures observed on the outdoor exposed samples indicate that degradation preferentially happened in amorphous regions, which is consistent with the indoor data.

Link Indoor and Outdoor Results based on Kinetic Study

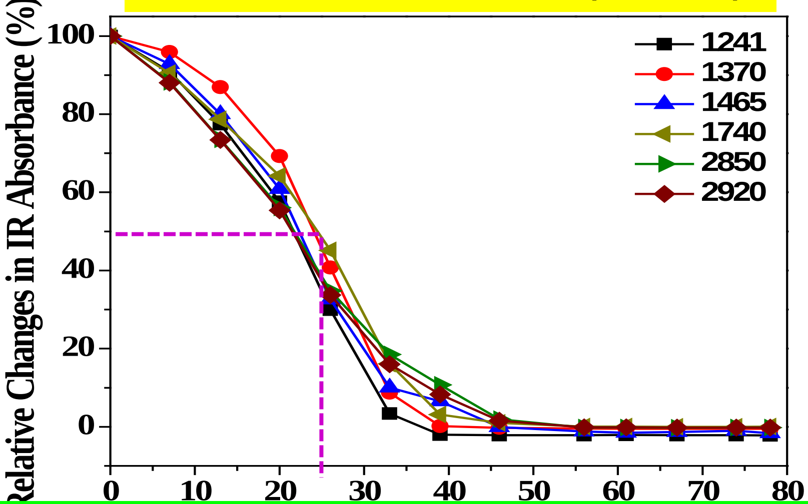
UV, 55 °C, 0% RH (Indoor)



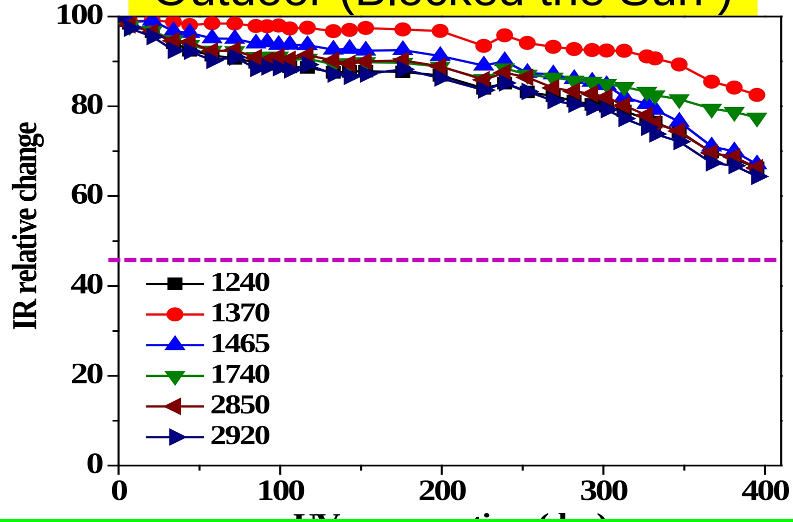
Outdoor (Gaithersburg, MD)



UV, 55 °C, 75% RH (Indoor)



Outdoor (Blocked the Sun)



- **A quantitative linkage needs a prediction model based on a more systematic indoor study and further outdoor validation. This is an on-going study.**

(2) Evaluation of Oxygen and Wavelength Effects on UV Degradation of EVA

➢ ***EVA Composition***

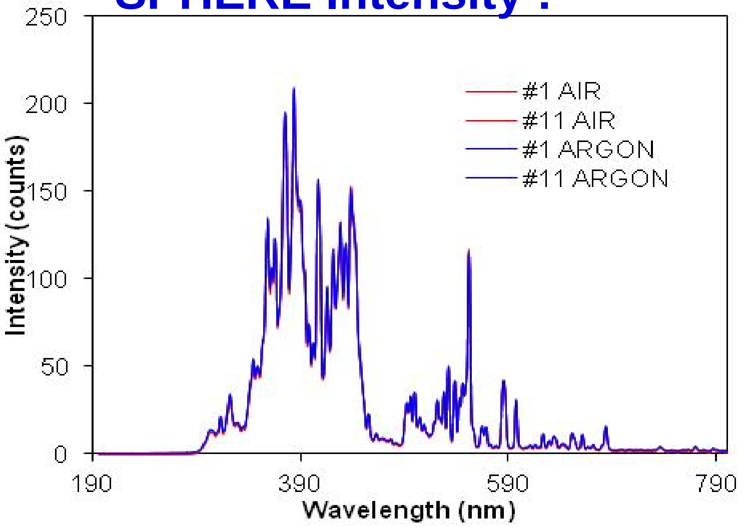
EVA	100 g
TBEC	1.50 g
Tinuvin 770	0.13 g
Chimassorb81	0.30 g

NIST SPHERE

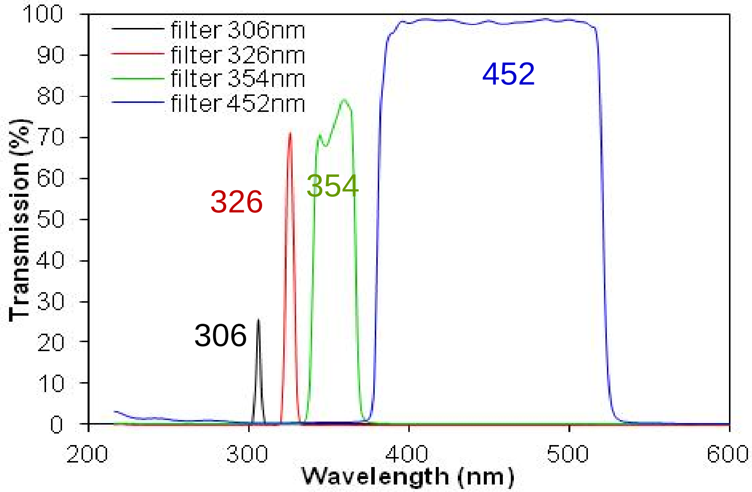
- 55°C and 0% RH
- Full (No filter), BP filters: 306nm, 326nm, 354nm, 452nm
- Air & Argon

❖ **pretest for QA-TG5 material aging test**

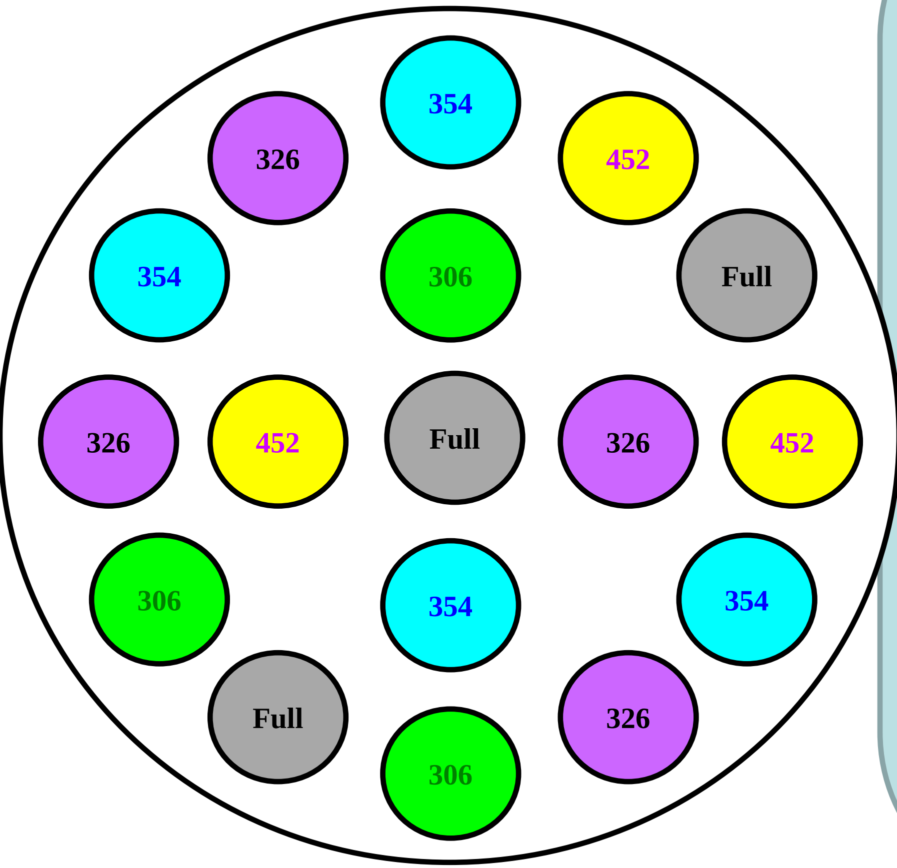
- **SPHERE Intensity :**

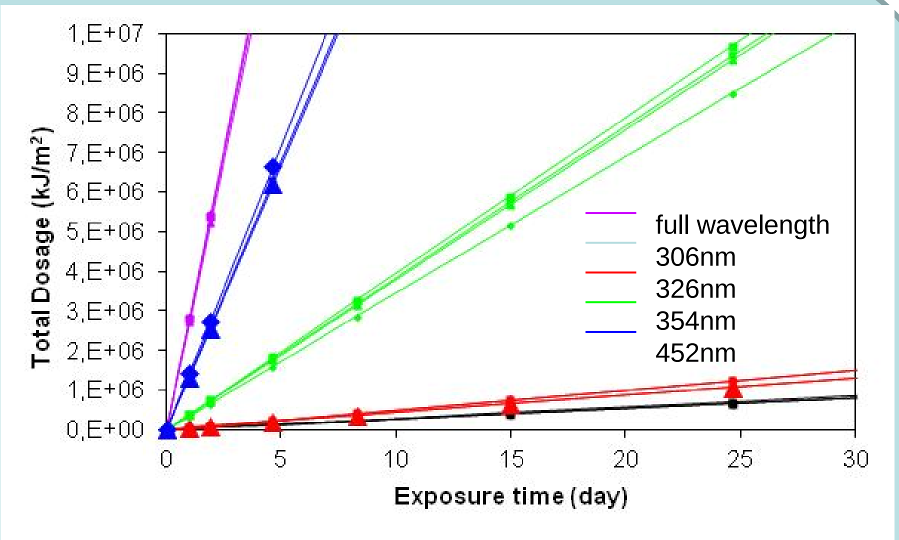


- **Filter transmission**



Total Dose for Samples Exposed through Different Filters



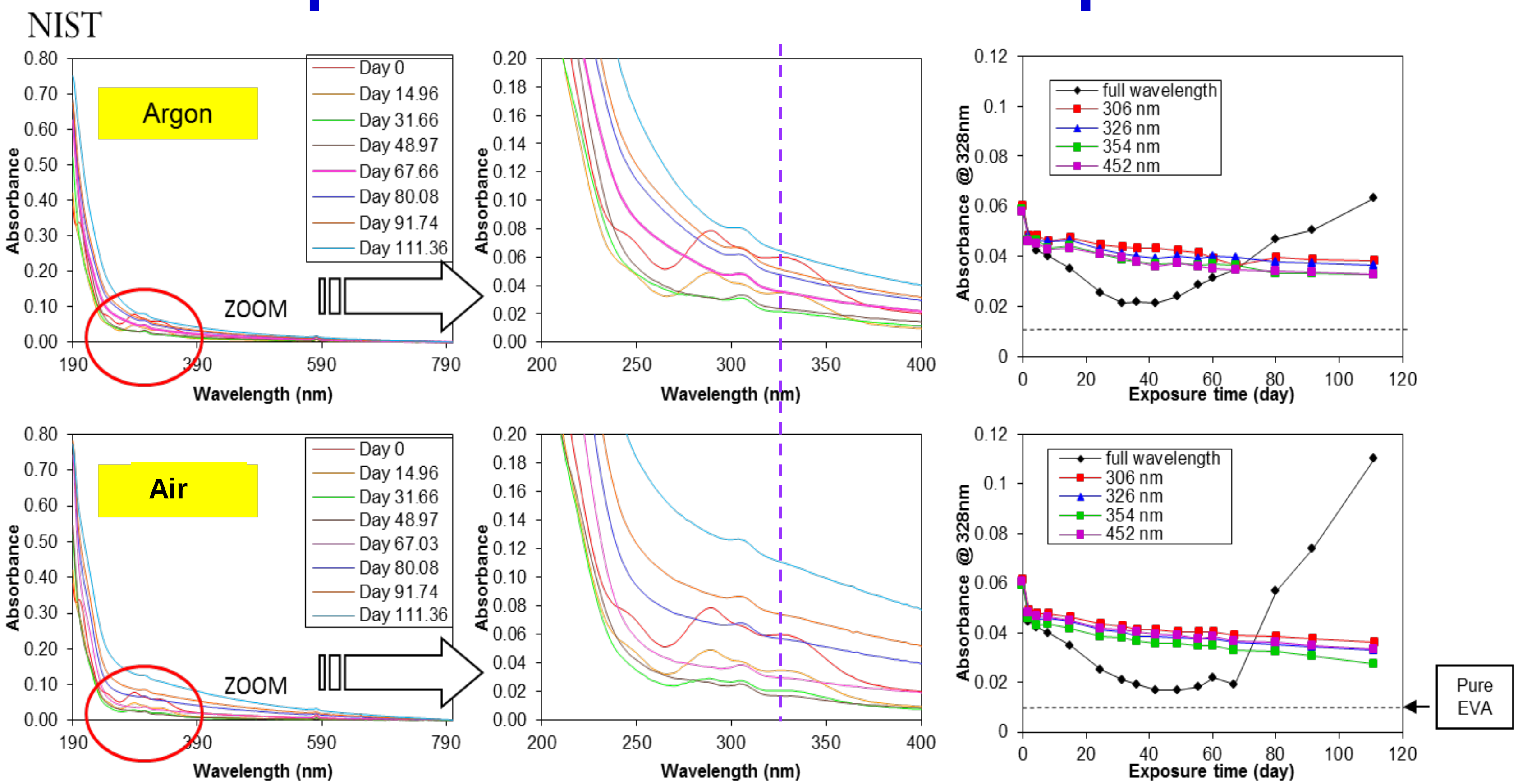


Equation of total dosage:

$$D = t\int_{\lambda} T(\lambda)I(\lambda)F(\lambda)d\lambda$$

with
- D : total dosage (kJ/m^2)
- λ : wavelength (nm)
- T : filter transmission (%)
- I : SPHERE UV intensity (counts)
- F : calibration factor ($\frac{W \cdot nm^{-1} \cdot m^{-2}}{counts}$)
- t : exposure time (s)

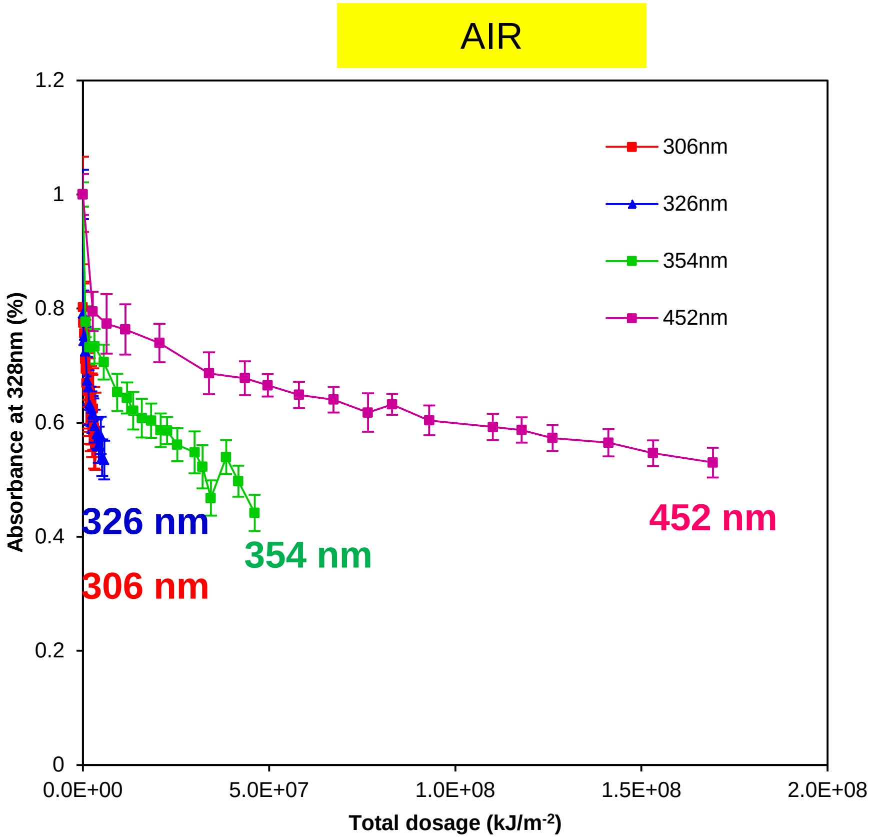
UV-Visible Spectra of Stabilized EVA Samples as a Function of Exposure Time

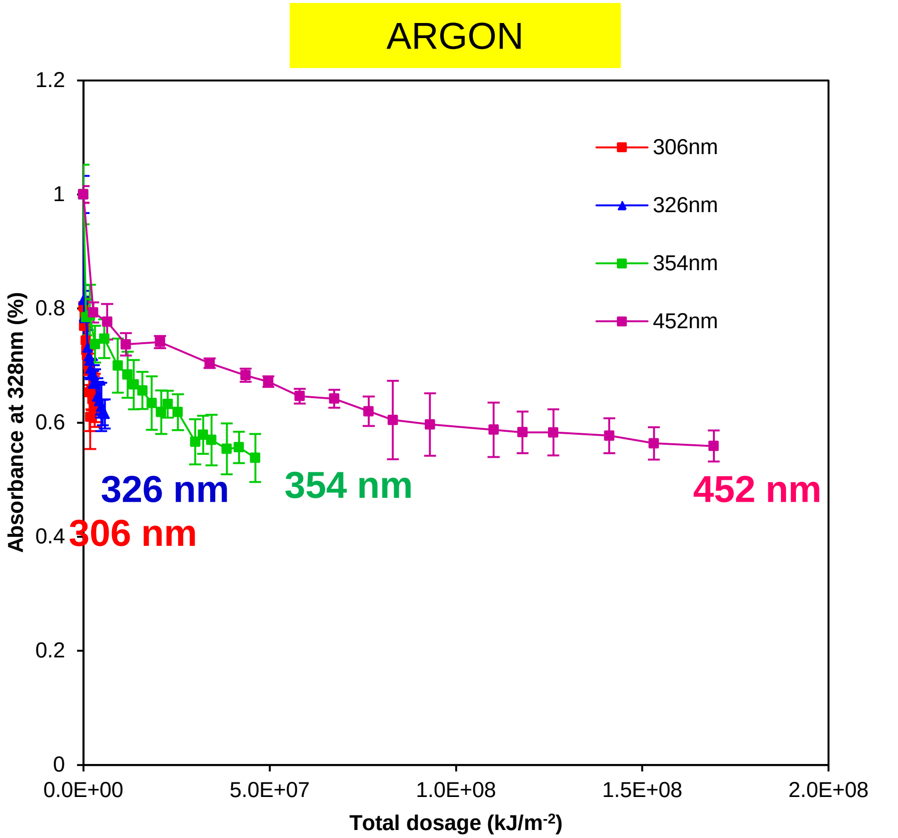


➢The trend of the UV absorbance change is determined by competition between the formation of yellowing products and the loss of UVA/HALS.

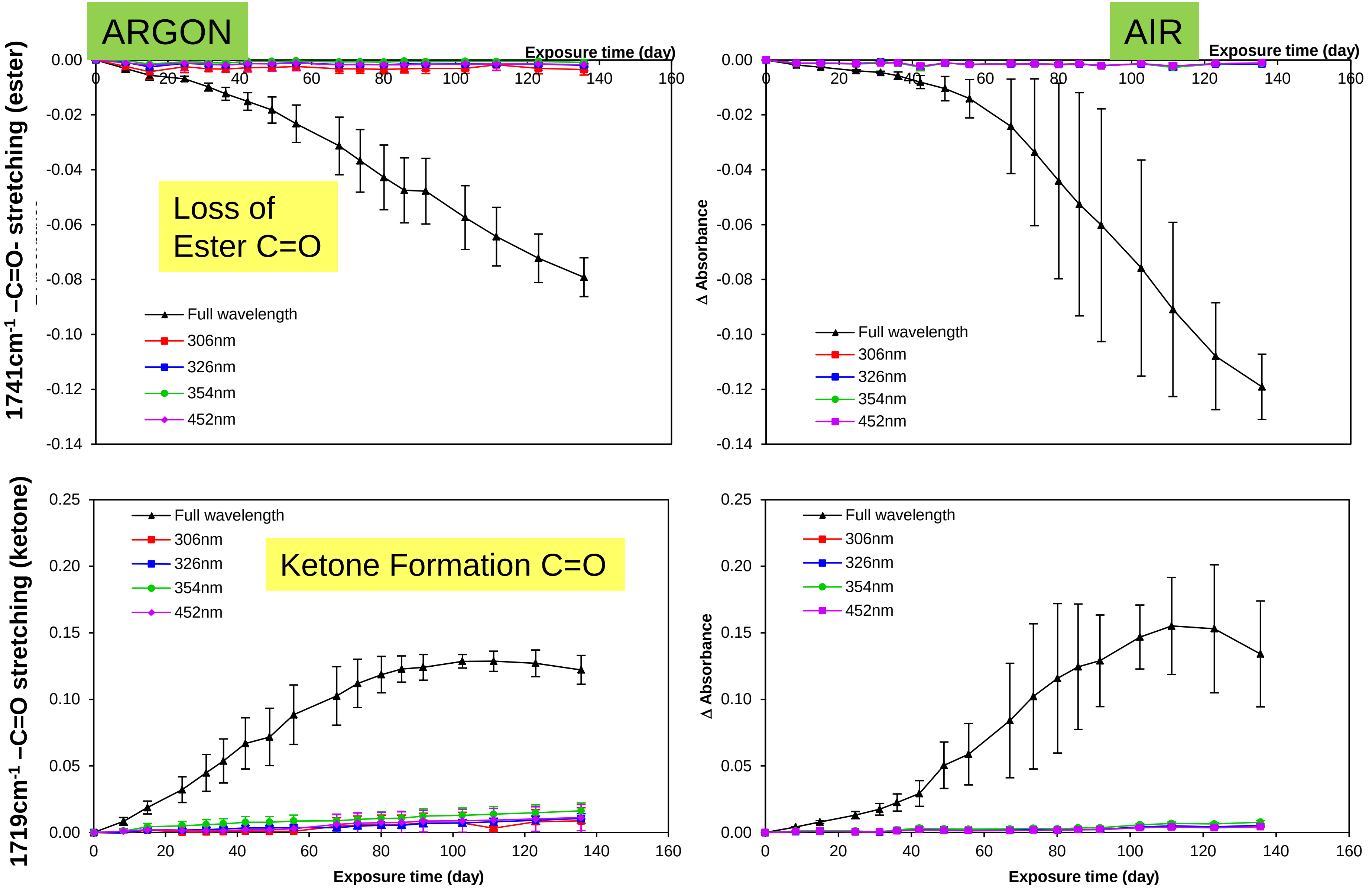
➢ In both Air and Argon atmosphere, the UV absorbance of EVA at 328 nm decreases first, then increases with exposure. However, samples exposed to UV in Air increases faster those in Argon.

Effect of Wavelength on Change of UV Absorbance at 328 nm for Stabilized EVA Samples





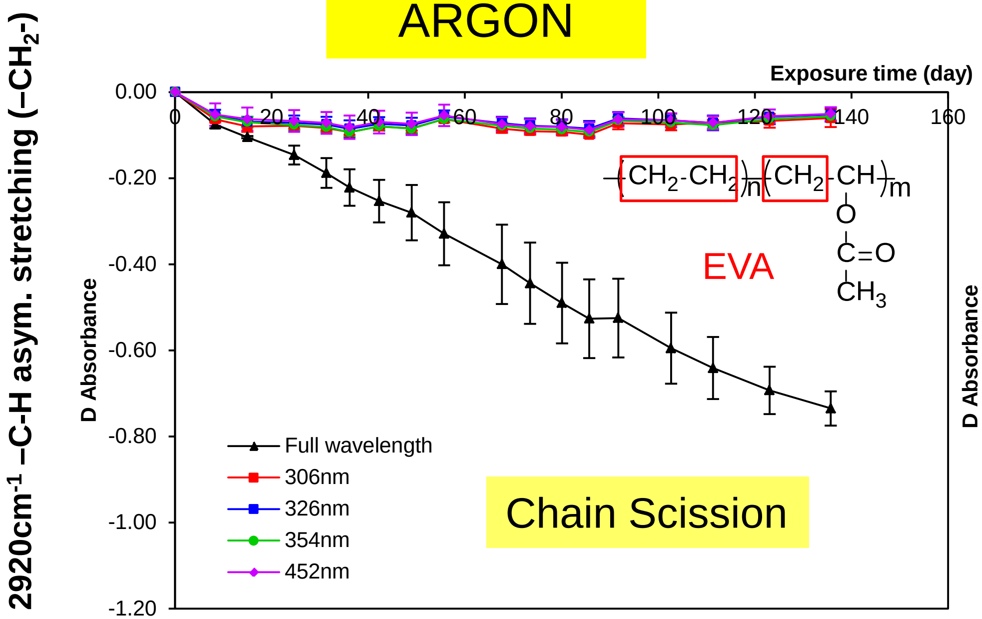
Chemical Degradation of EVA under Different Wavelengths (UV/55°C/0%RH) Air *vs.* Argon

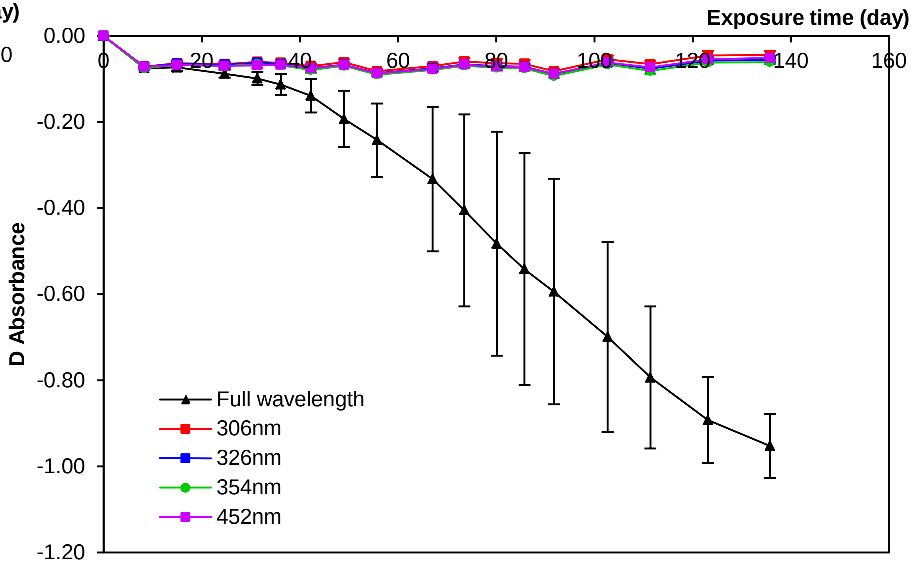


Degradation of EVA under Different Wavelengths (UV/55°C/0%RH) AIR *vs.* ARGON

ARGON

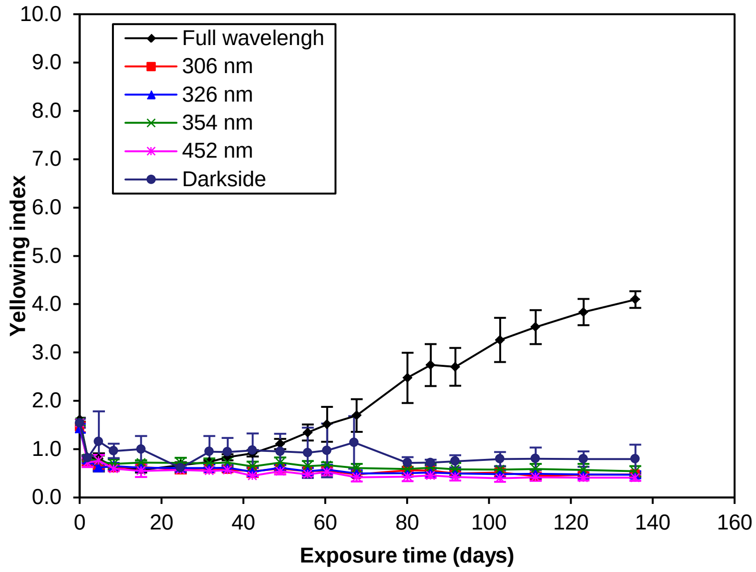
AIR



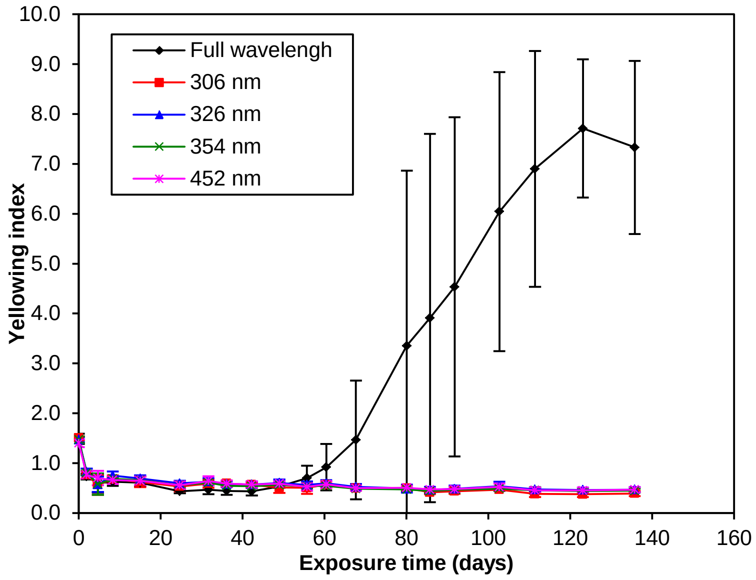


Yellowing Index of EVA as a Function of Exposure Time at Different Atmosphere

ARGON



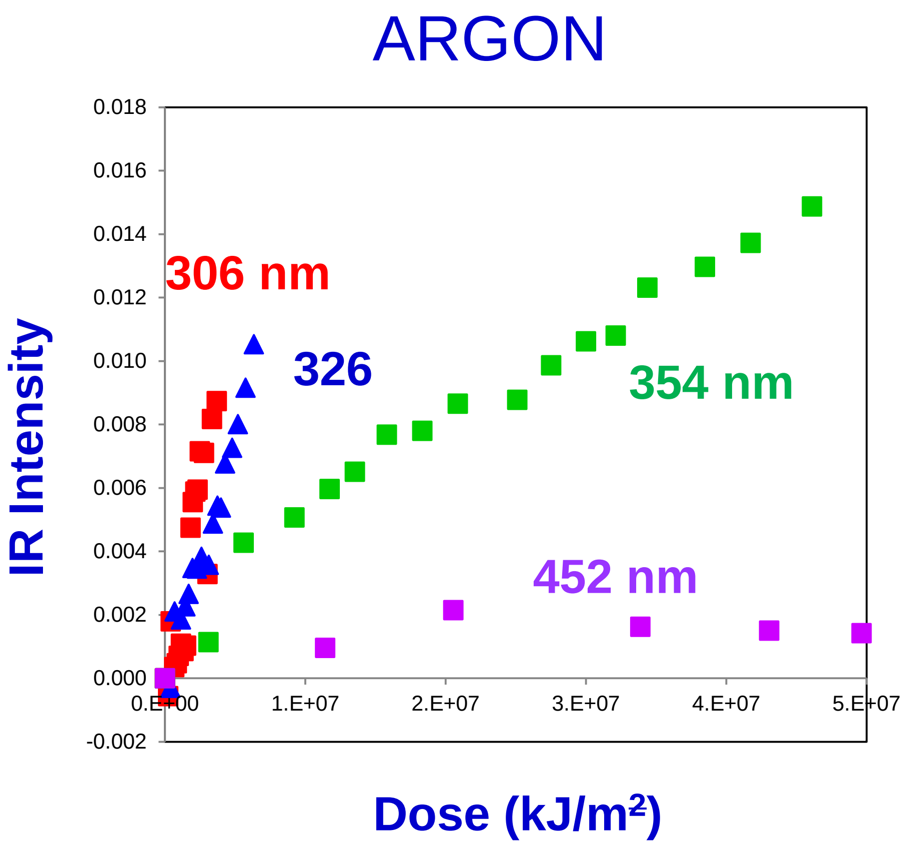
AIR

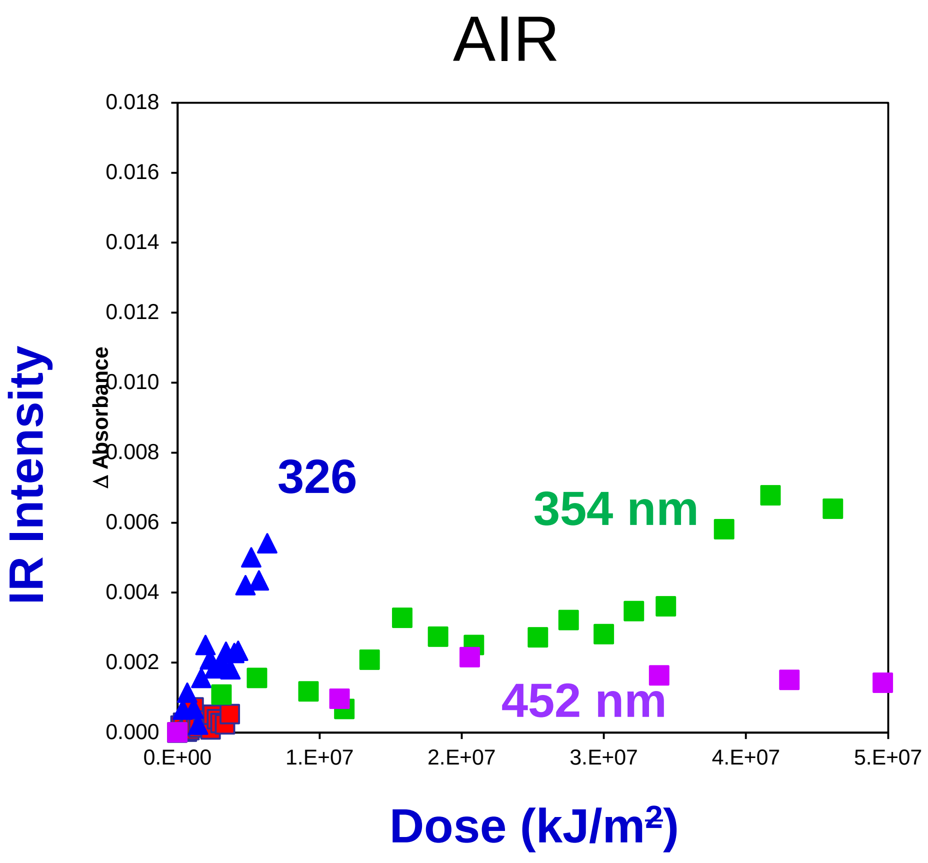


- Substantial degradation has been observed in both AIR and ARGON atmosphere for EVA when exposed to UV/55C/0% conditions
- However, it appears that the kinetics of EVA degradation in two conditions are different. In AIR condition, the yellowing started later, but increased faster than in ARGON.

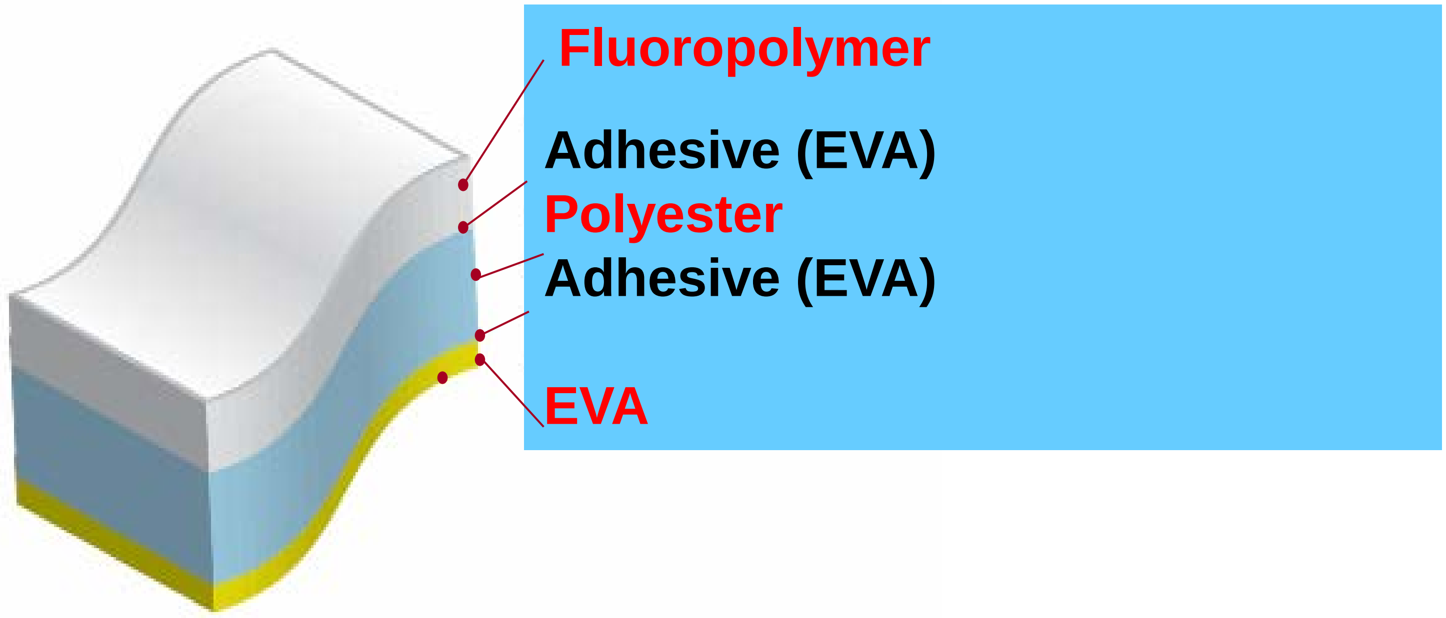
Effect of Wavelength on Carbonyl Formation

Carbonyl Formation at 1710 cm^{-1}



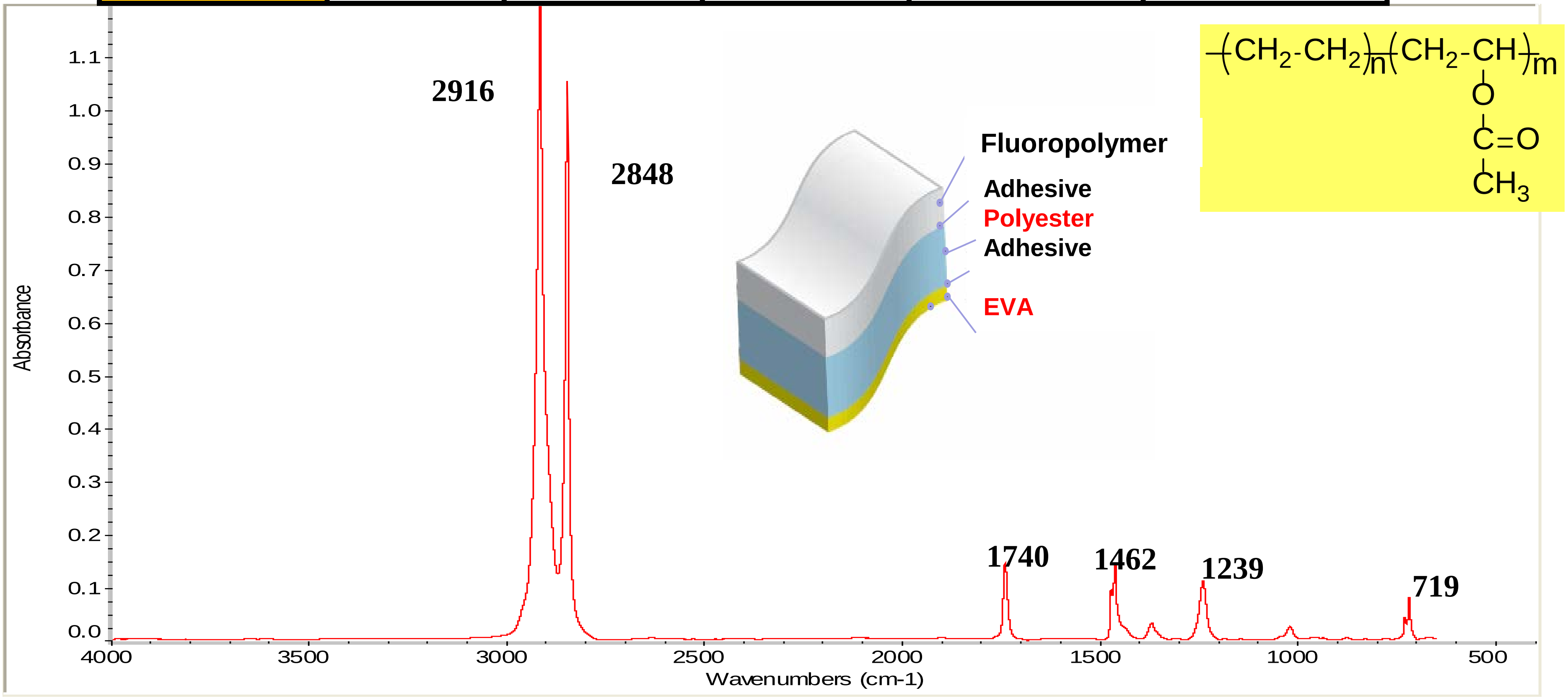


(3) Degradation of Backsheet Films



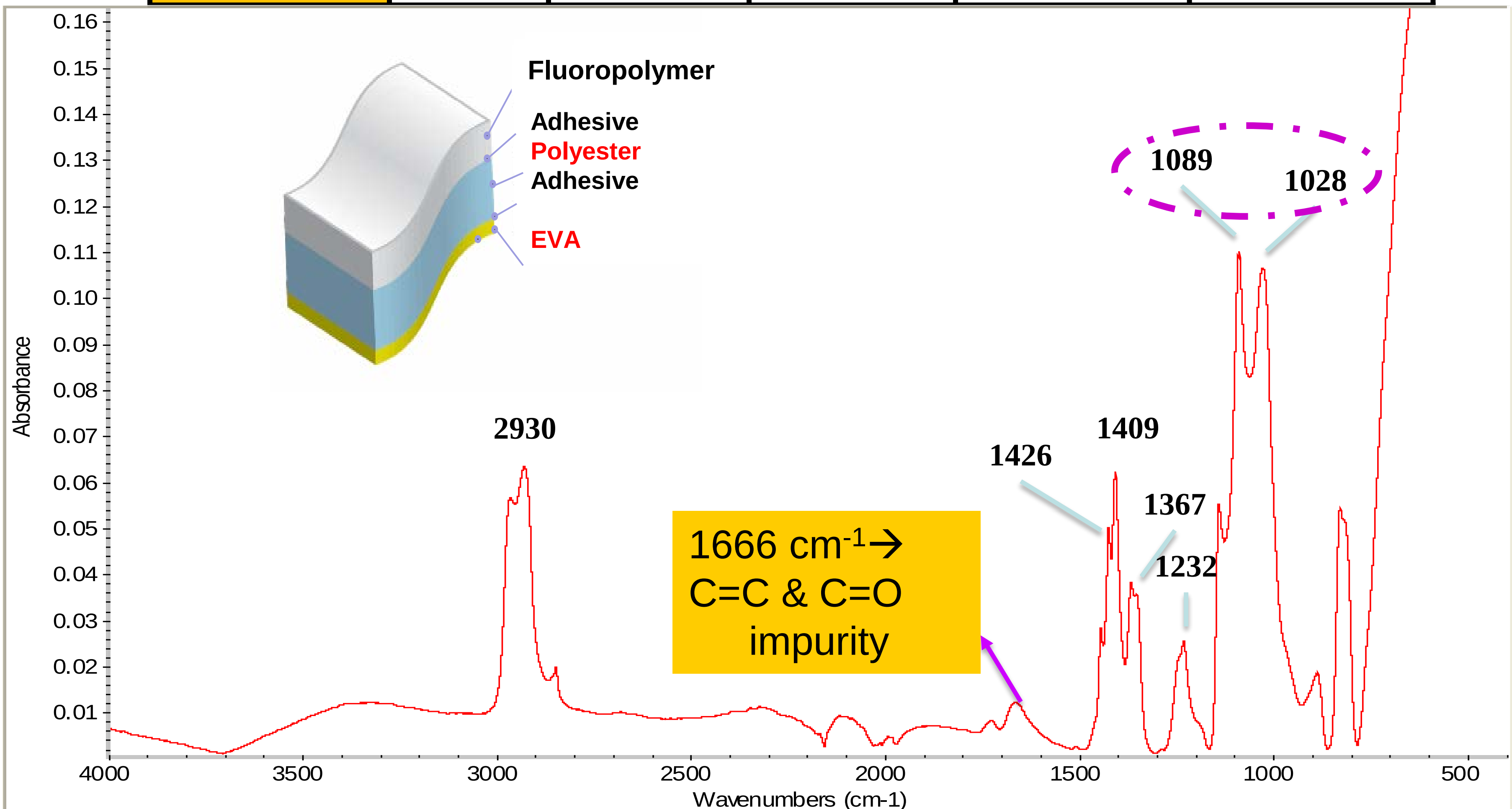
Typical ATR-FTIR Spectrum of EVA

Wavenumber (cm-1)	1239	1462	1740	2848	2916
Functional group	Ester C-O stretch	CH_2 bend	Ester C=O stretch	CH_2 asymmetric stretch	CH_2 asymmetric stretch



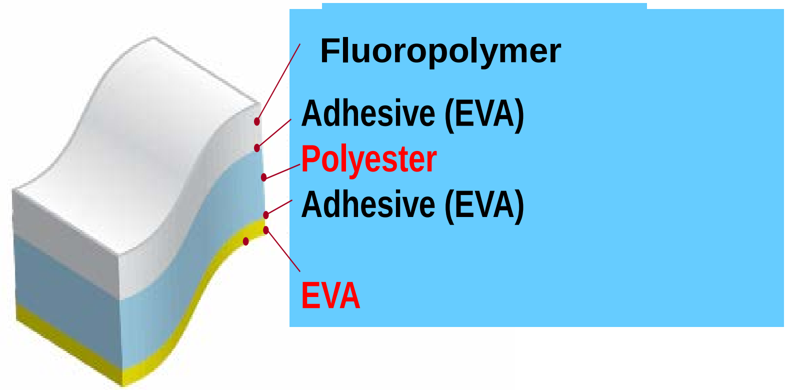
Typical ATR-FTIR Spectrum of Fluoropolymer

Wavenumber (cm^{-1})	1028	1089	1409	1426	2930
Functional group	C-F stretch	C-F stretch	CH_2 bend	CH_2 bend	CH_2 asymmetric stretch



Backsheet Experimental

- **Exposure:**
  1. Ovens
     85°C, 0% RH
     105°C, 0% RH
     120°C, 0% RH
  2. Environment Chamber
     85°C, 85% RH
  3. NIST SPHERE: UV irradiation
     UV, 55°C, 0% RH
     UV, 55°C, 75% RH



- **Measurements**

Chemical Property	Nano-, micro-scale Physical Property	Mechanical Property
FTIR-ATR	Confocal Microscopy AFM, Gloss, UV-R	Tensile Test Nanoindentation

Temperature Effect

- Exposure:
  1. Ovens

     85°C, 0% RH

     105°C, 0% RH

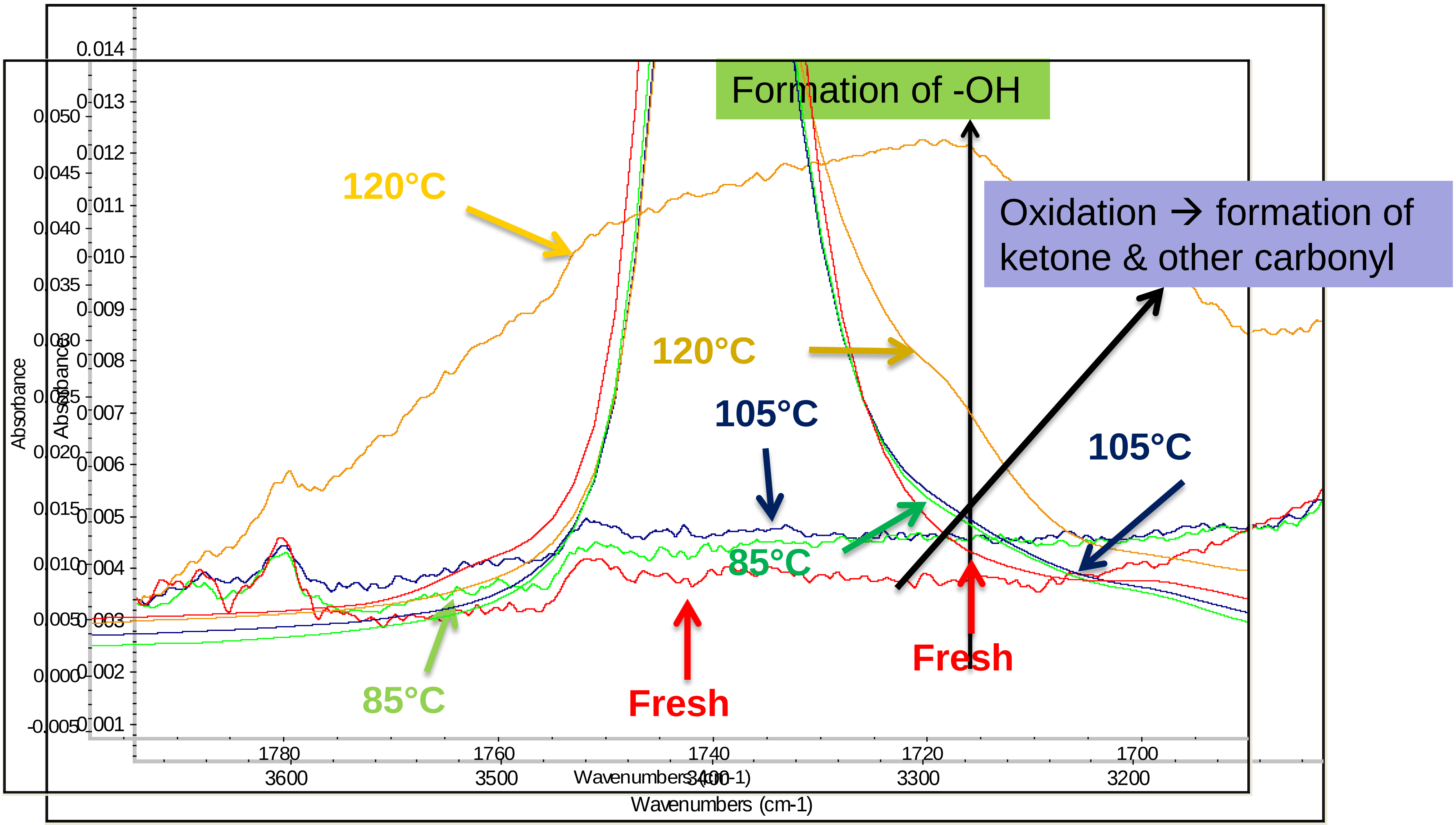
     120°C, 0% RH
  2. **Environment Chamber**

     85°C, 85% RH
  3. **NIST SPHERE: UV irradiation**

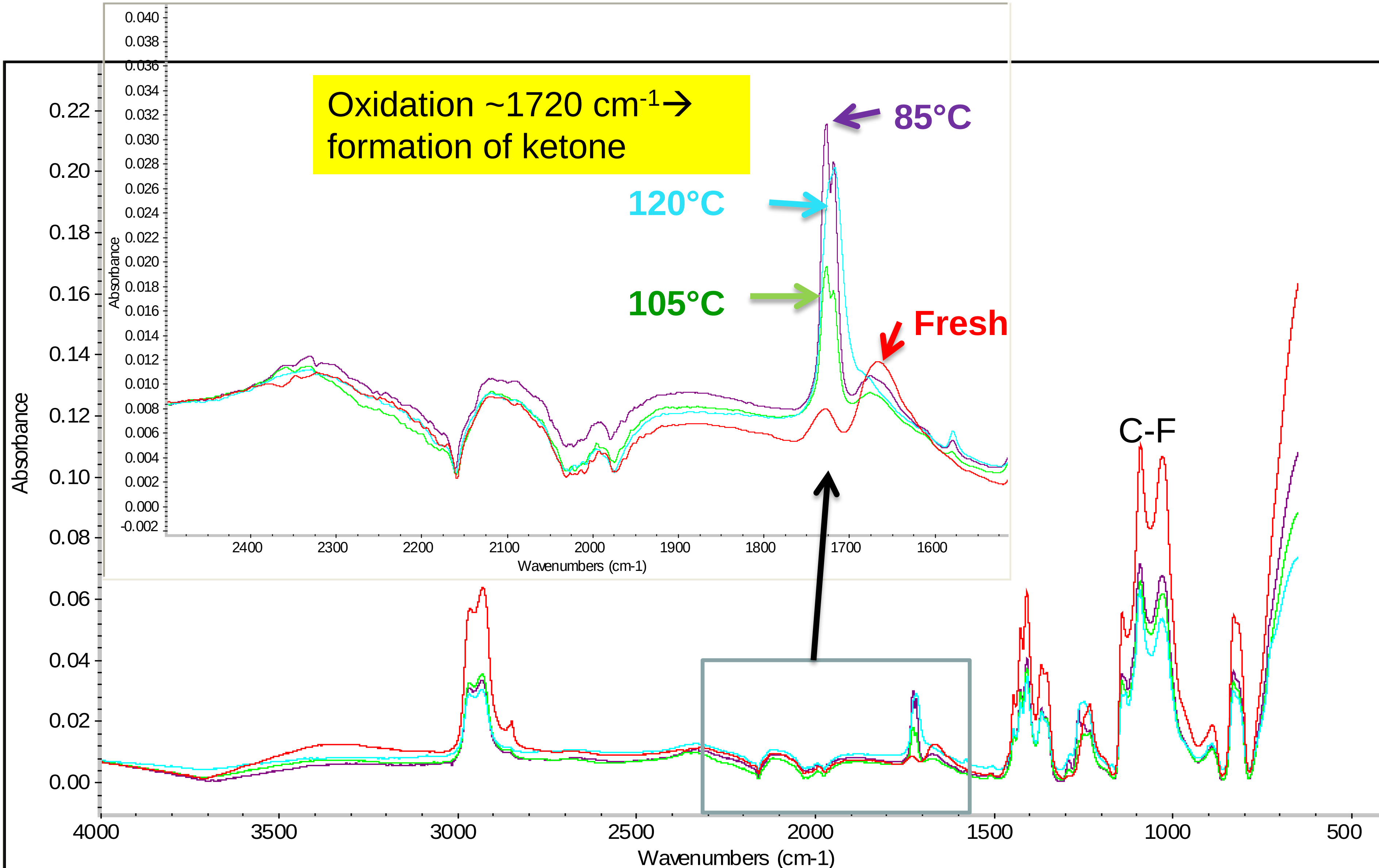
     55°C, 0% RH

     55°C, 75% RH

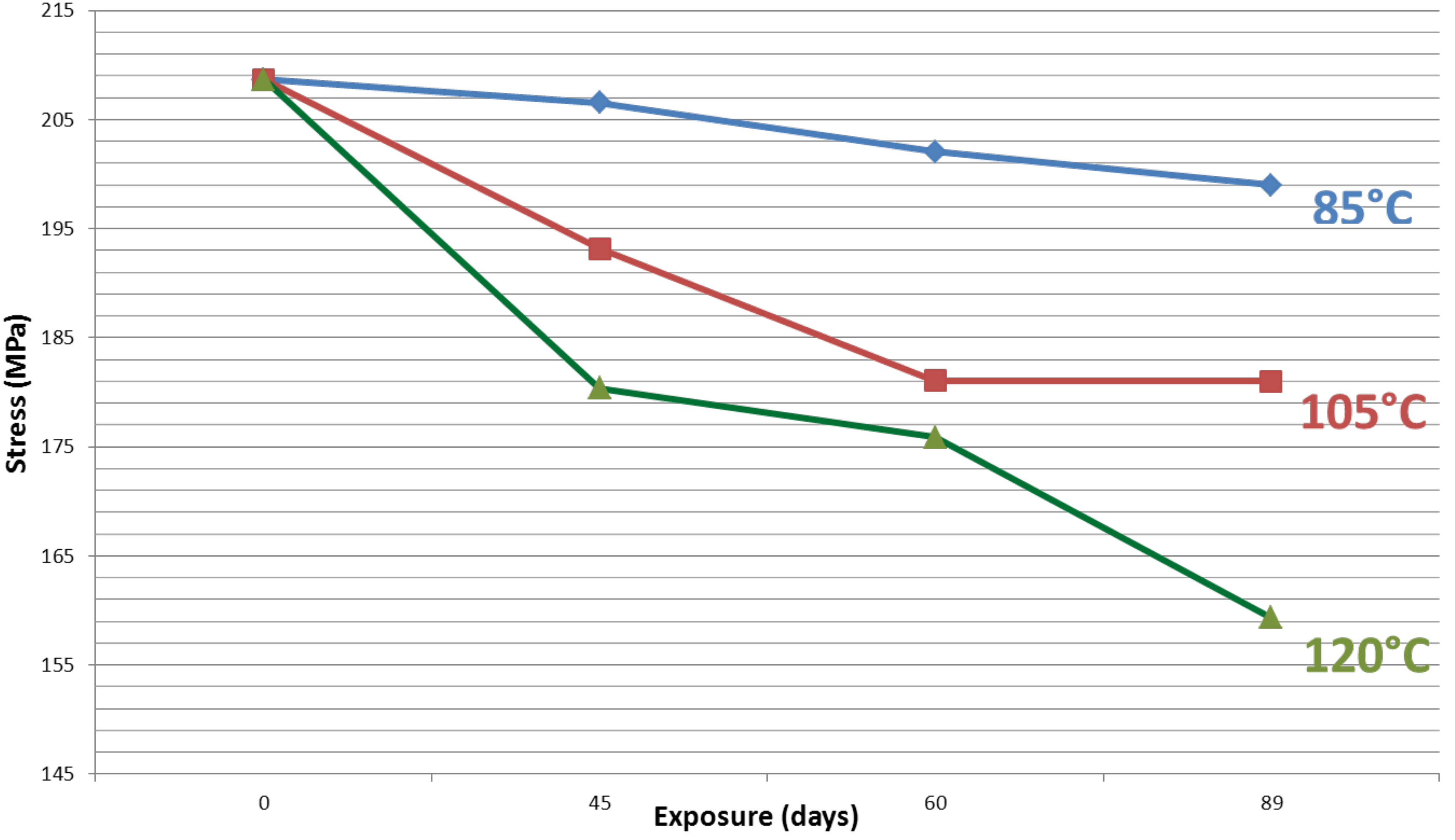
Chemical Change of EVA at Different Temperatures



Chemical Change of Fluoropolymer at Different Temperatures



Tensile Strength as a Function of Time at Different Temperatures

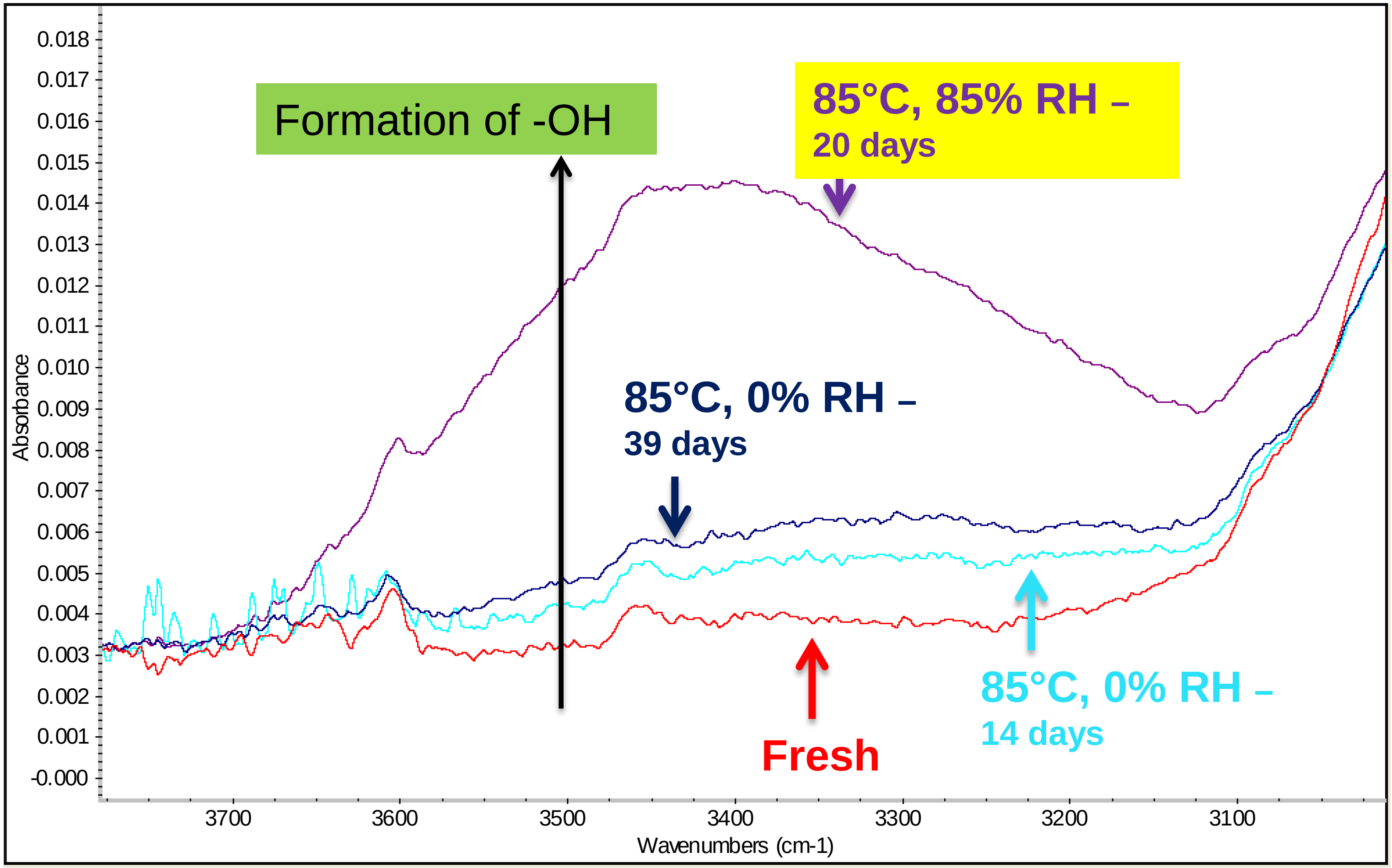


- Tensile strength decreases more rapidly at higher temperatures

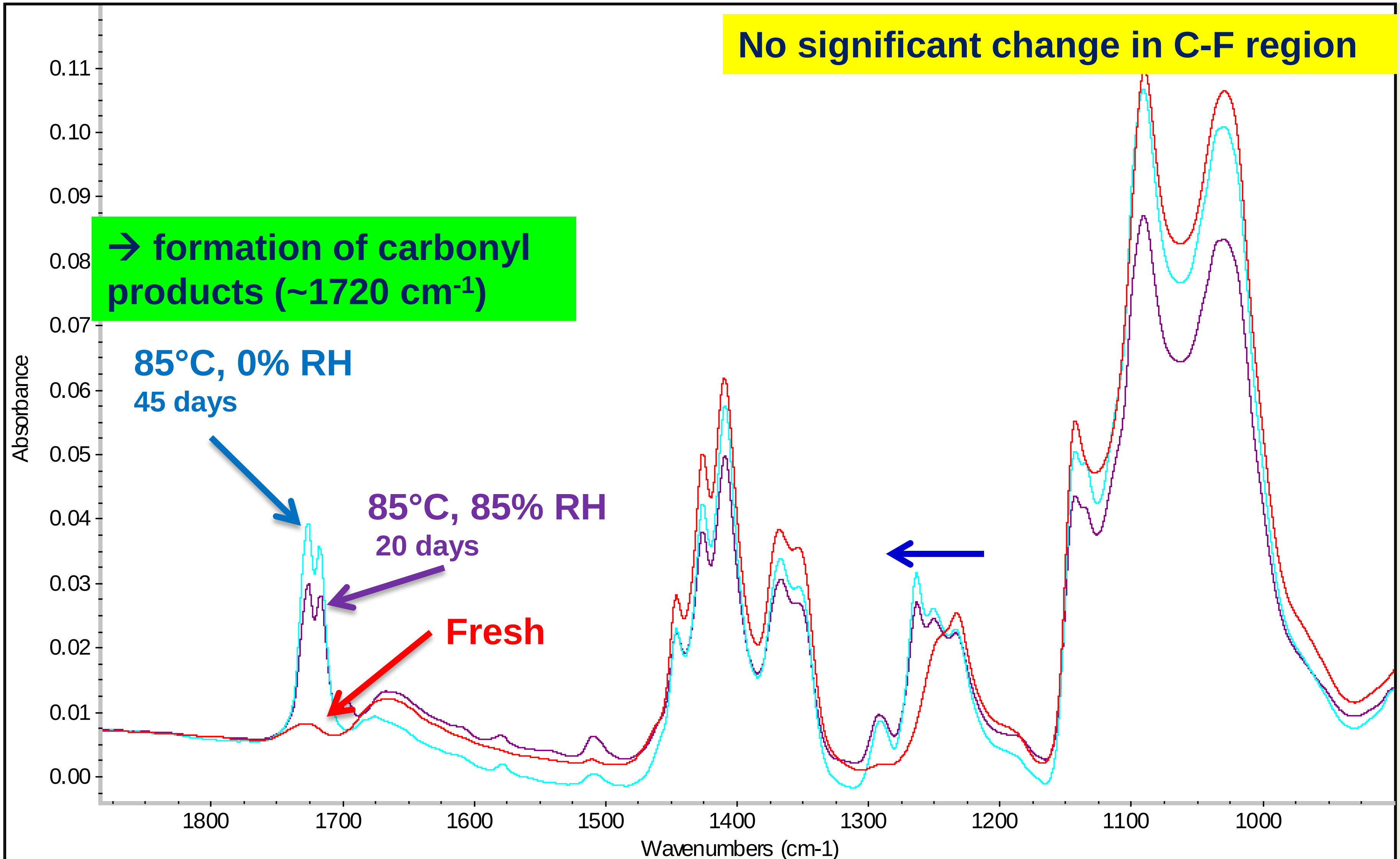
Humidity and Temperature Effect

- Exposure:
  1. **Ovens**
     85°C, 0% RH
     105°C, 0% RH
     120°C, 0% RH
  2. **Environment Chamber**
     85°C, 85% RH (Damp Heat)
  3. **NIST SPHERE:**
     UV, 55°C, 0% RH
     UV, 55°C, 75% RH

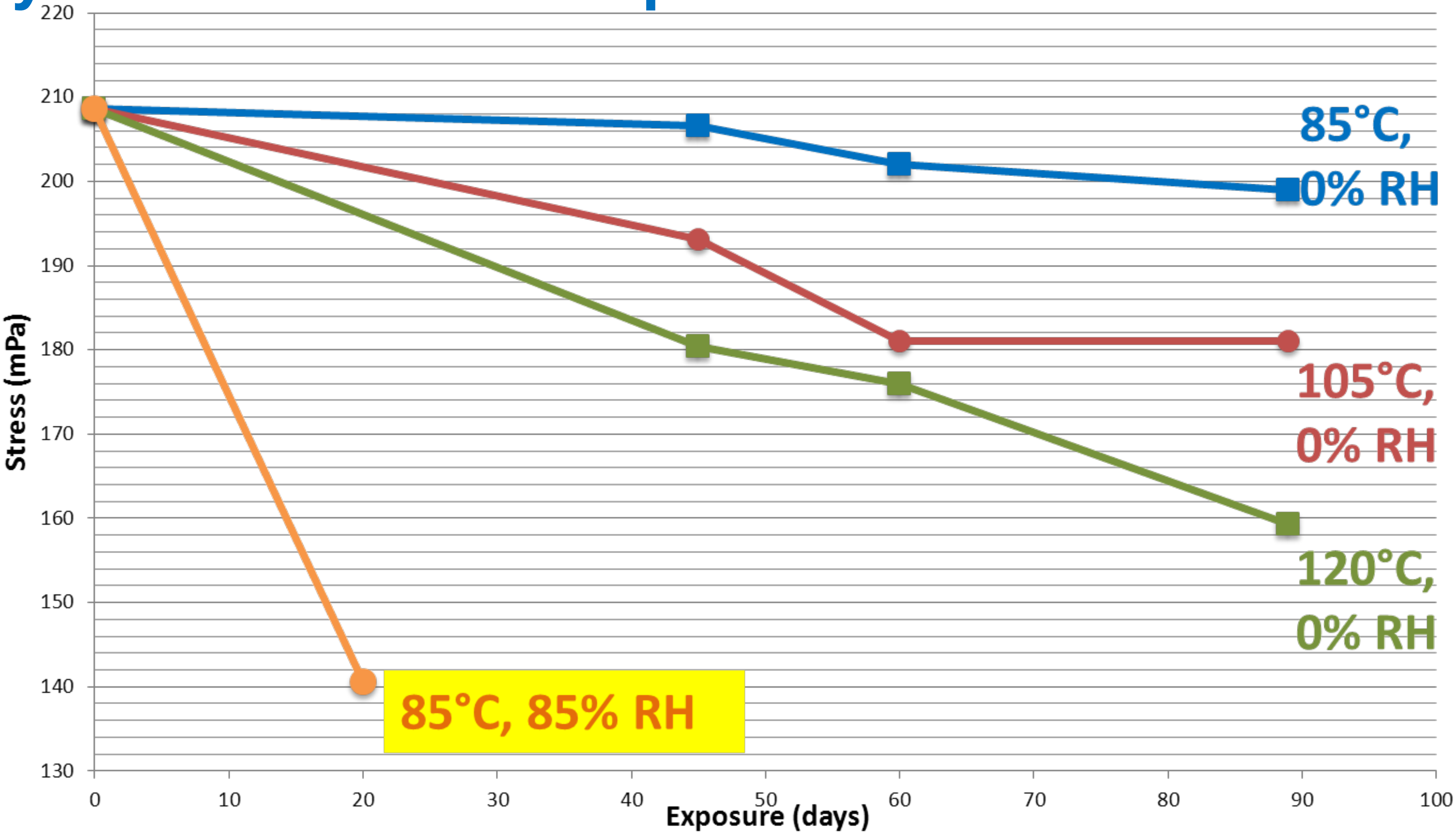
Chemical Change of EVA: Wet vs. Dry Conditions



Chemical Change of PVF: Wet vs. Dry Conditions



Tensile Strength as a Function of Time in Dry Conditions and Damp Heat



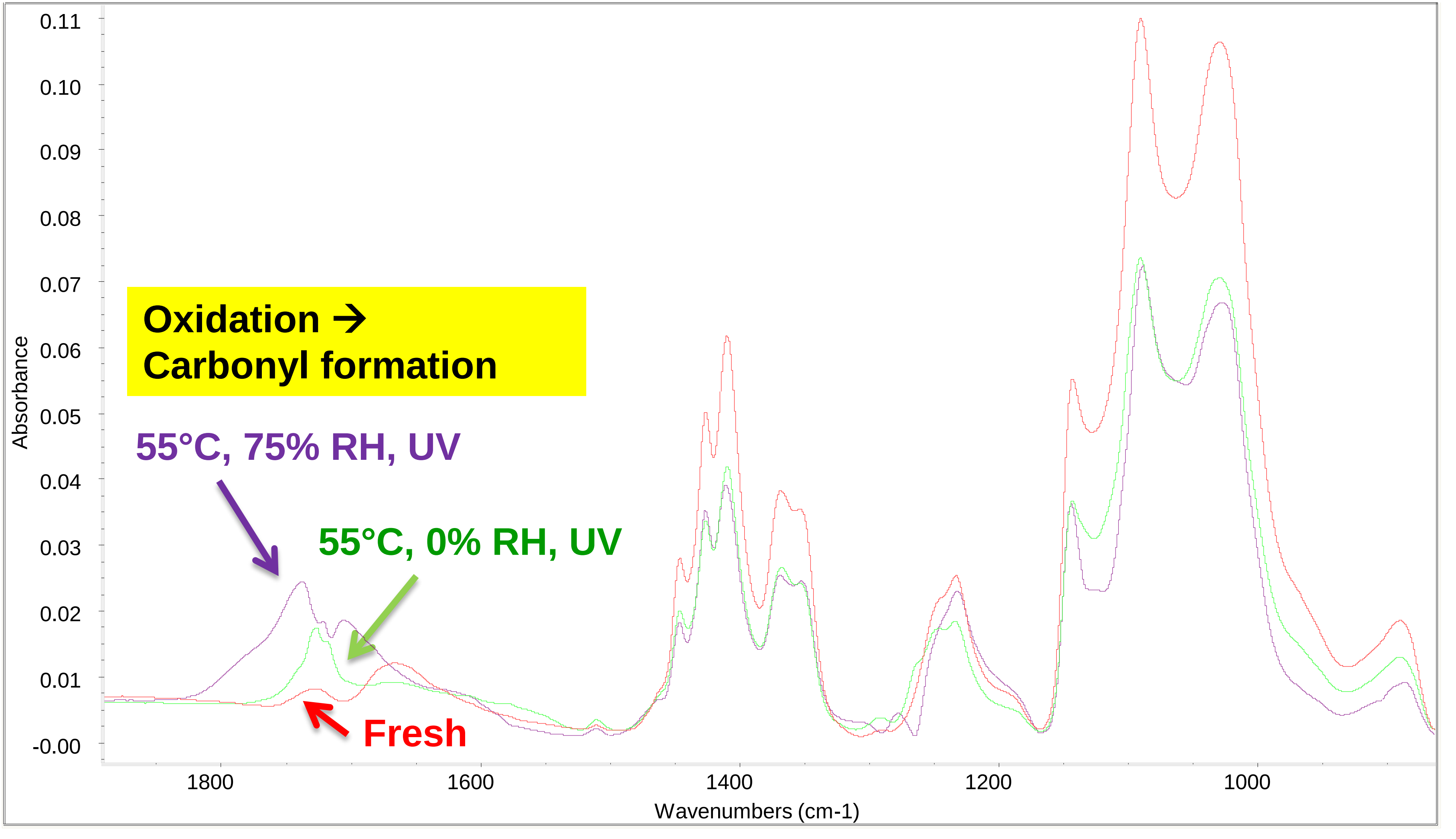
Tensile strength of backsheet greatly effected by simultaneous exposure to temperature and humidity

UV, Humidity, & Temperature Effect

- Exposure:
  1. **Ovens**
     85°C, 0% RH
     105°C, 0% RH
     120°C, 0% RH
  2. **Environment Chamber**
     85°C, 85% RH
  3. **NIST SPHERE:**
     UV, 55°C, 0% RH
     UV, 55°C, 75% RH

Chemical Change of Fluoropolymer Surface:

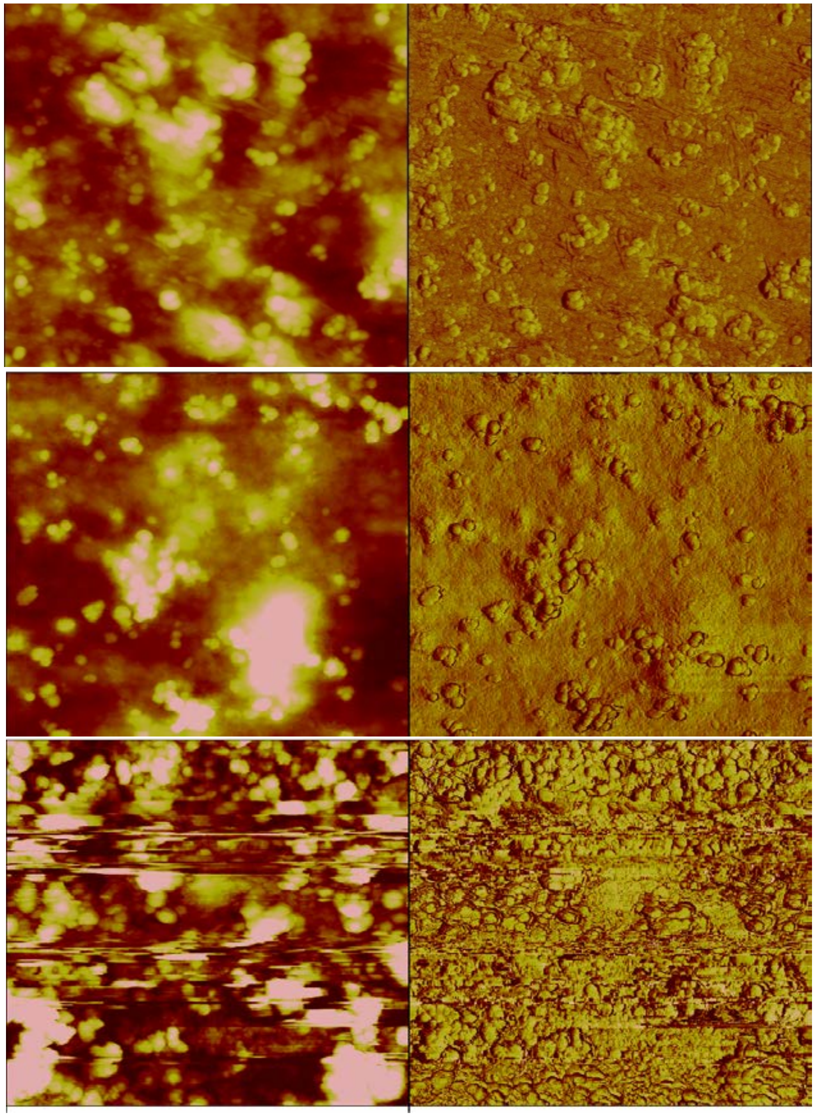
UV, 55°C, 75% RH vs. UV, 55°C, 0% RH



Morphological Changes of Fluoropolymer Surface (Imaged with AFM)

Height | Phase

10 µm x 10 µm



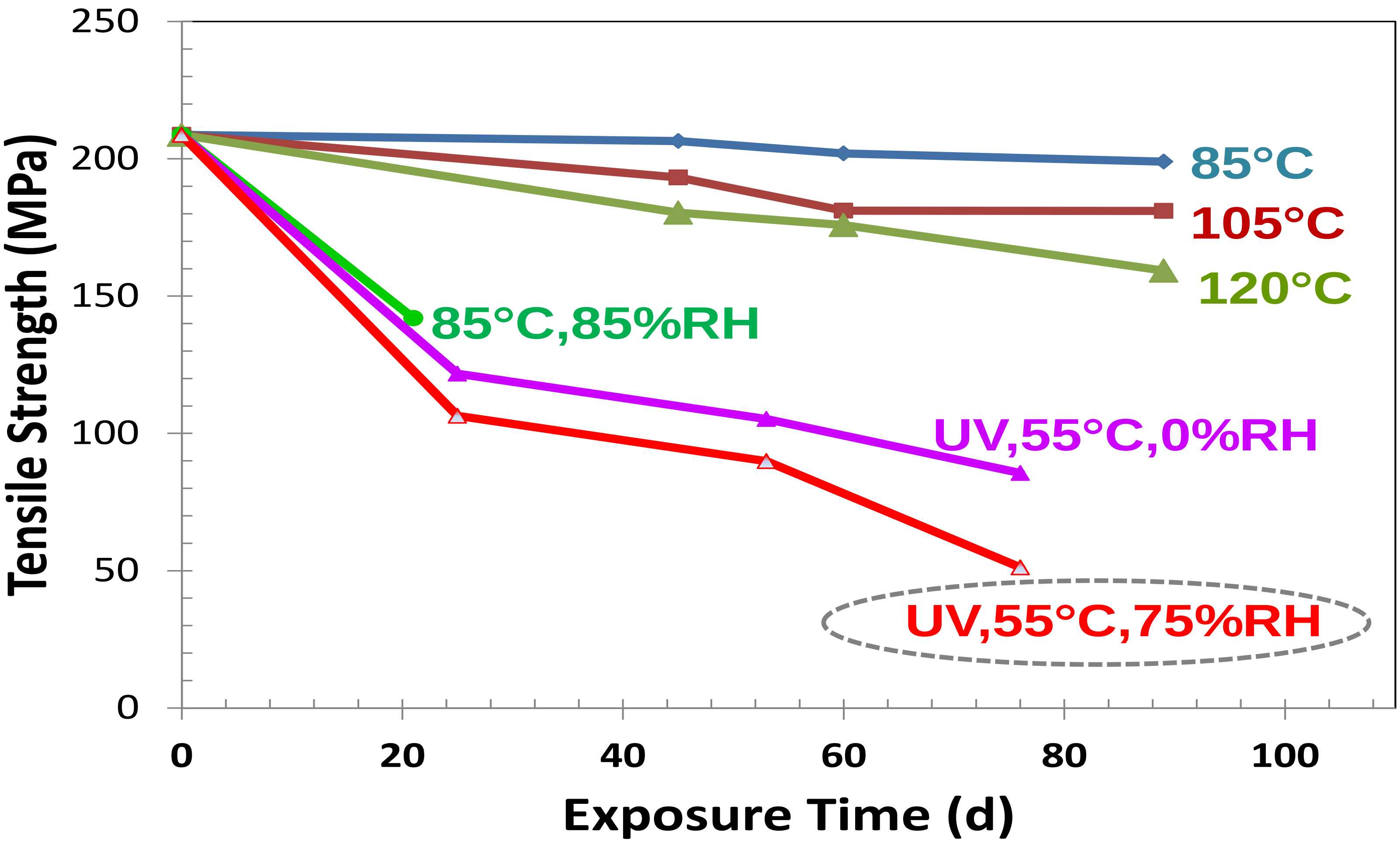
Unexposed

UV/55°C, 0%RH, 76d

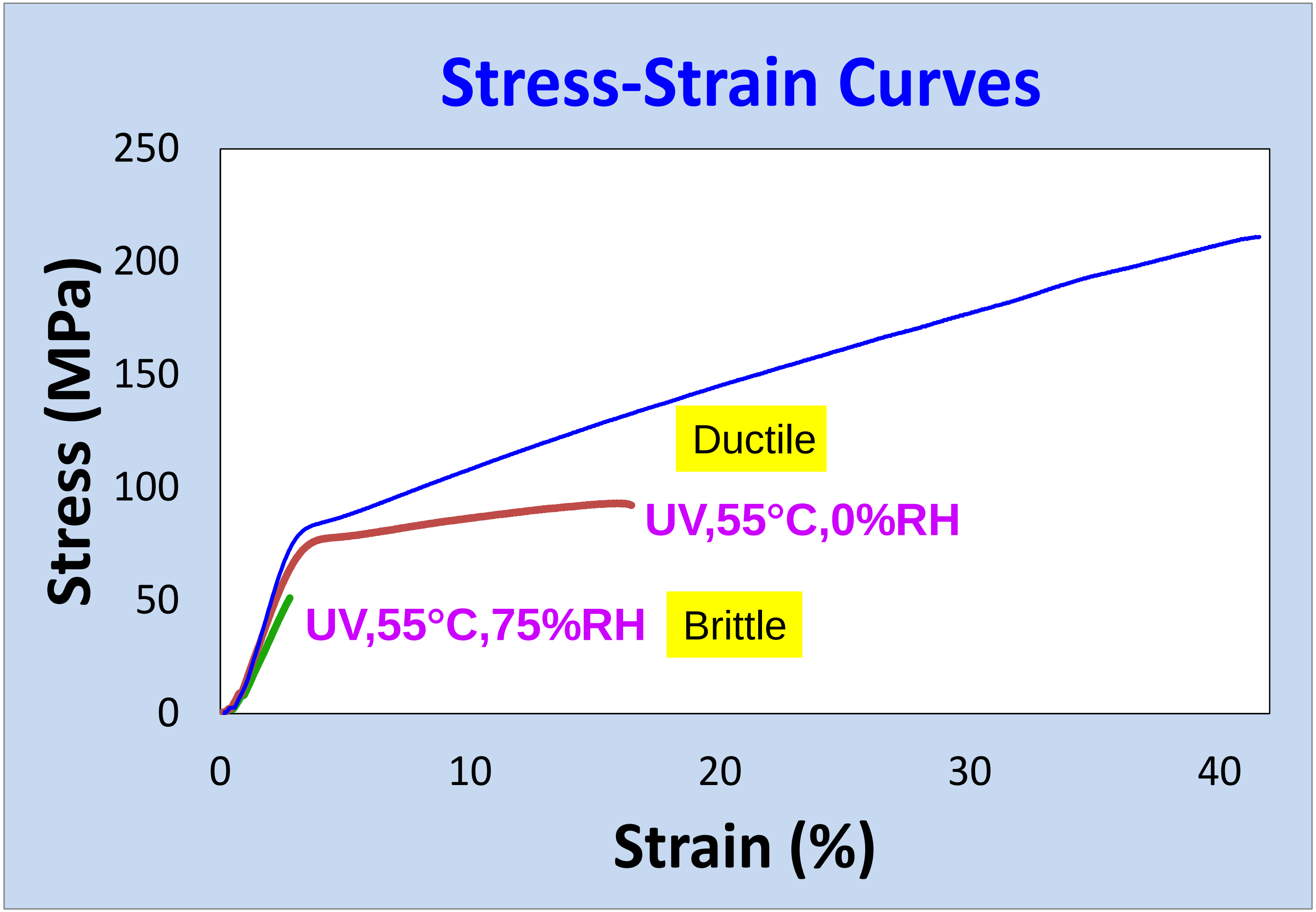
UV/55°C, 75%RH, 76d

Both chemical and morphological changes are more severe for fluoropolymer surface exposed to UV/55 °C/75% RH than UV/55°C/0% RH.

Tensile Strength Change as a Function of Time:



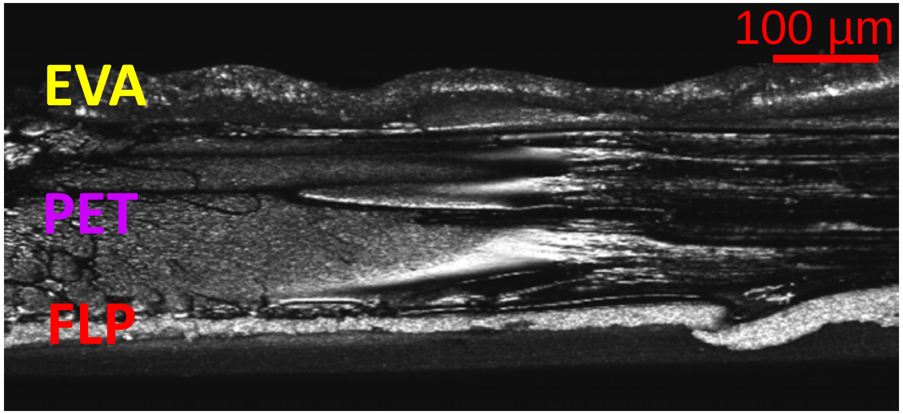
- Bulk mechanical strength decreased over time.
- Simultaneous exposure to **UV, Temperature, and Relative Humidity** results in greatest loss of tensile strength.



The tensile fracture modes of the studied backsheets change from ductile to brittle during exposure to UV/T/RH.

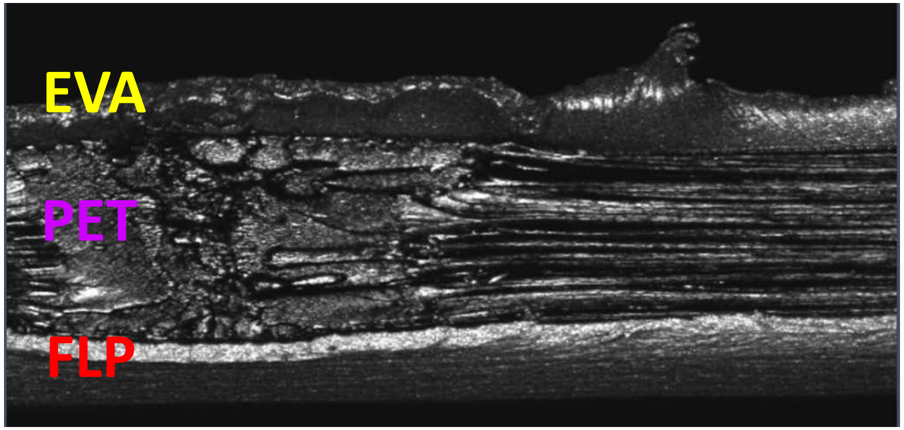
Confocal Images of the Fracture Surface after Tensile Testing

Unexposed



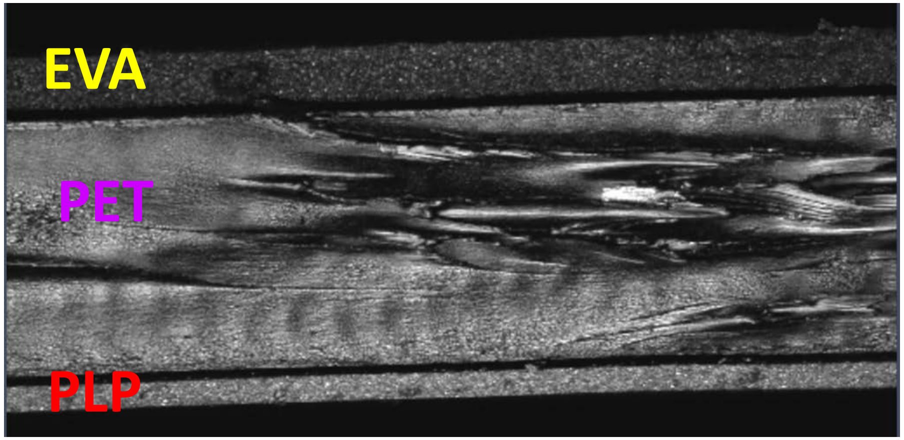
More Ductile

UV/55°C, 0%RH, 76d



More Ductile

UV/55°C, 75%RH, 76d

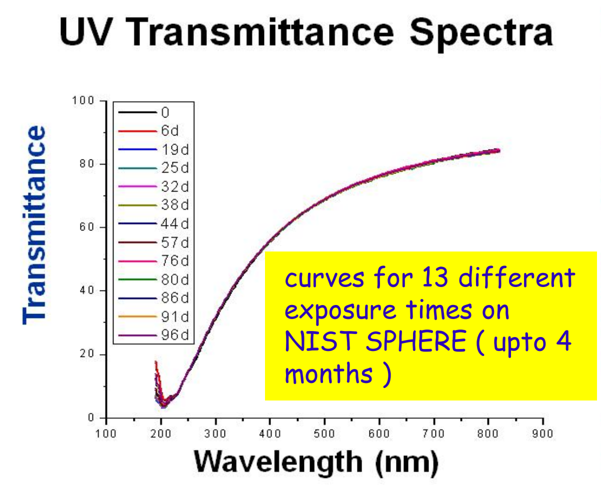


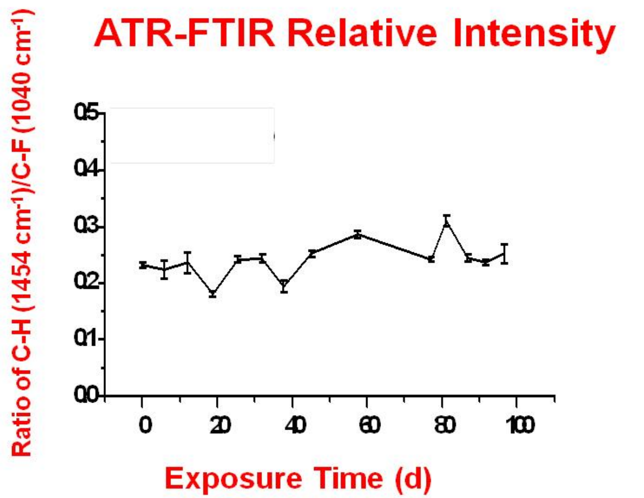
More Brittle

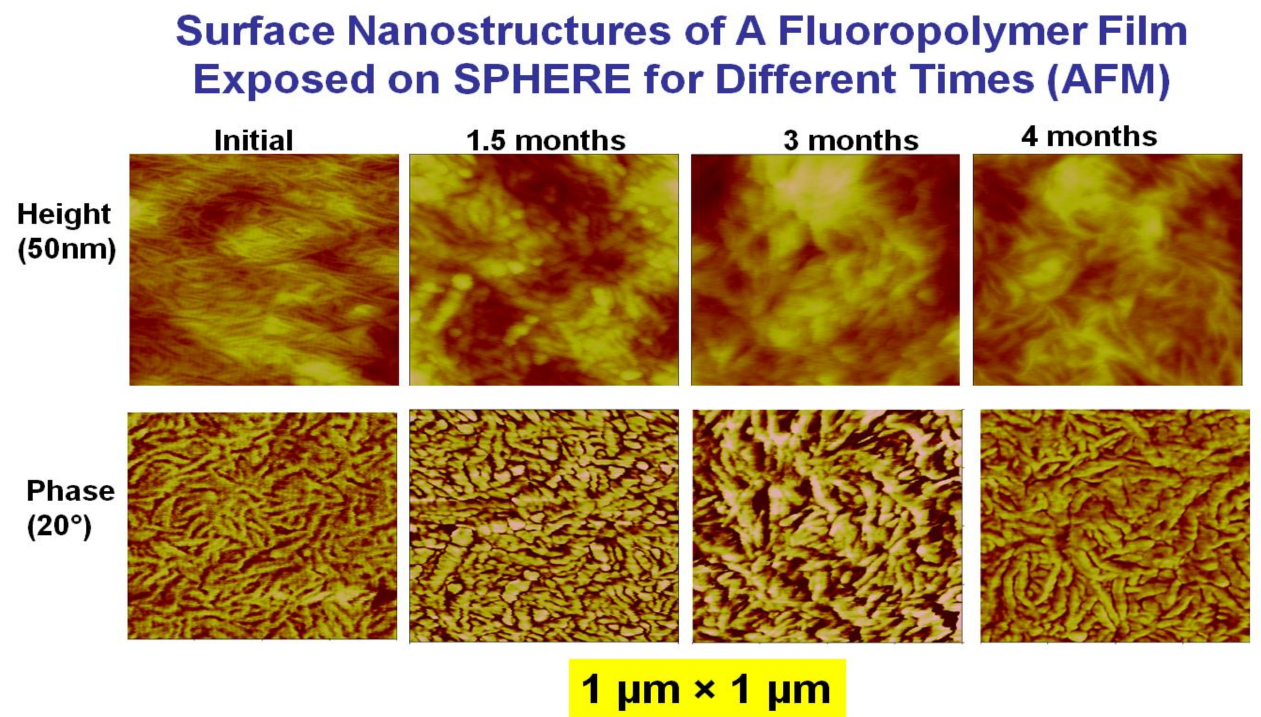
(3) Photostability of Frontsheet Fluoropolymer

(UV, 55 °C/75%RH For 4 months)

▪ETFE (-$CH_2CH_2CF_2CF_2$-)







❑ Essentially, no chemical, optical or nanostructural changes observed for fluoropolymers after UV exposure for 4 months on the SPHERE.

Summary

- **UV radiation is the most important factor for degradation of all studied materials. RH/UV synergistic effects have been observed for studied EVA and backsheet films. O_2 could be another key factor.**

- **A fundamental understanding of degradation mechanism of PV materials under simultaneous multiple stresses is important to develop reliable accelerated tests that correlate to field performance.**

Acknowledgements

People at NIST:

Eric Byrd	Stephanie Watson
Debbie Stanley	Lipiin Sung
Tinh Nguyen	Aaron Forste

NIST/industry PV Consortium

started from October, 2012

Part 3: Brief Introduction of NIST/industry PV Consortium on *Developing Reliability-based Accelerated Laboratory Tests for Service Life Prediction of PV Materials*

NIST/industry PV Consortium

started from October, 2012

Underwriters Laboratories

DUPONT

ARKEMA

3M

DAIKIN

First Solar

AGC BEYOND GLASS

Technical Objectives for Consortium

For PV polymers, components, and mini-modules, to develop:

- **Accelerated laboratory test for predicting service lives using the NIST SPHERE**
- **Measurement tools capable of discerning degradation mechanism(s) and failure mode(s)**
- **Mathematical models for linking field and laboratory exposure results**

What will be the impact?

Materials

- EVA
- PVB
- Fluoropolymers
- Polyesters
- PVC
- ABS
- Adhesives
- Sealants
- C-Si or A-Si
- CdTe or CIGS
- Glass

Components

- Superstrate
- Encapsulant
- Substrate
- PV Solar Cell
- Ribbon Cable
- Junction Box
- Frame
- Edge/Sealants

Modules/System

- Materials Process
- Interface
- Integrated Process
- Conversion Efficiency
- Circuit Design
- Uni- or Bi-facial
- Photoelectric process

Chemical, Optical, Mechanical, Electrical, Flammability, Adhesion Properties Before/After Environmental Aging

Scientific background

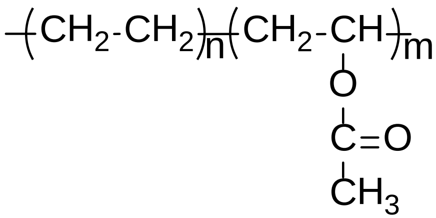
STANDARDS

Reliability and Safety

Courtesy of UL (Edwin Yang)

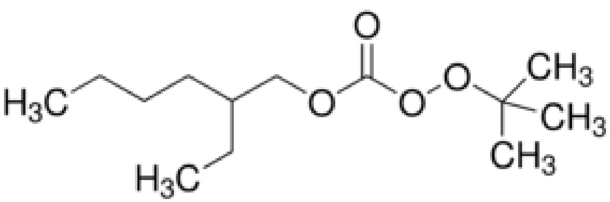
❑ MATERIALS

- **Polymer :** EVA



- Name: Evatane 33-45® made by Arkema®
- 32~34 wt% of VA

- **Polymerization agent :** Luperox TBEC (peroxide)



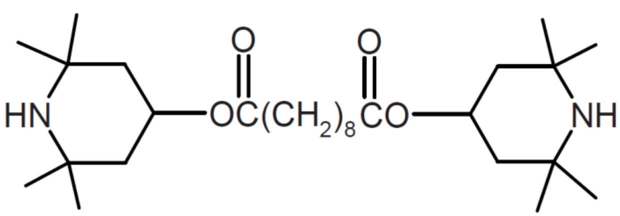
Allowing the cross-linking

➢ ***Composition:***

EVA	100 g
TBEC	1.5 g
Tinuvin 770	0.13g
Chimassorb81	0.3 g

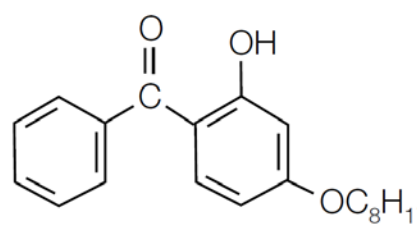
→ *Following BP® formulation*

- **UV stabilizer :** Tinuvin 770



Scavenging free radical

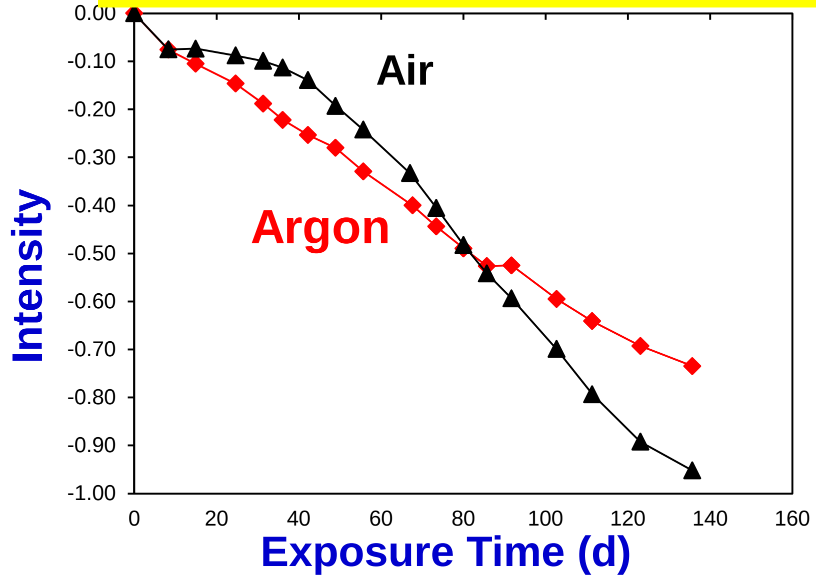
- **UV absorber :** Chimassorb 81



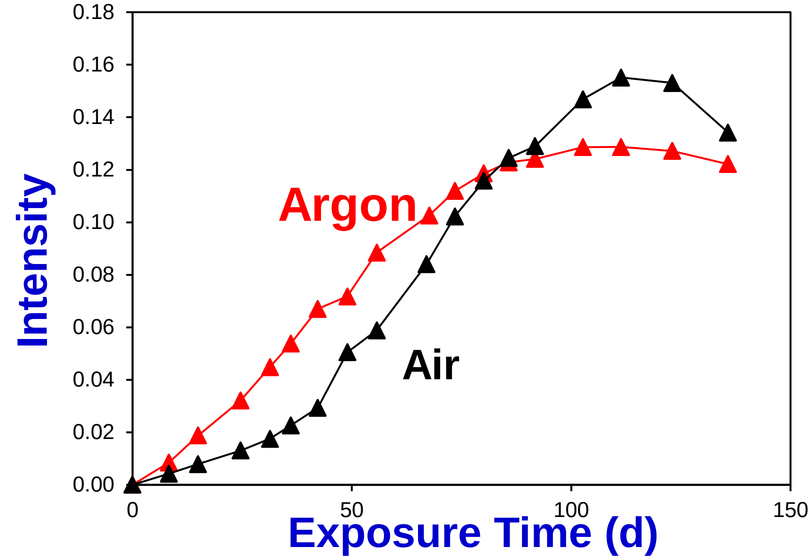
Quenching excited states

EVA Chemical Degradation at UV/55°C/0%RH Argon *vs.* Air

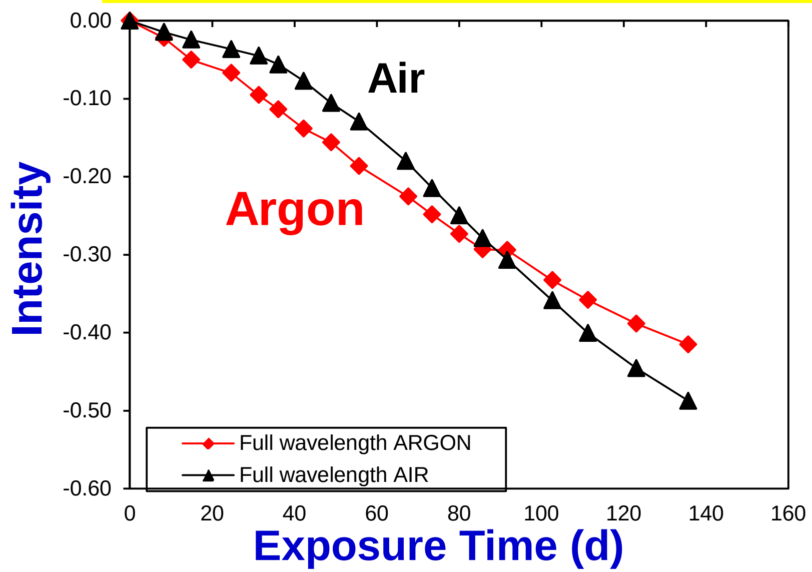
Loss of Intensity at 2920 cm^{-1}



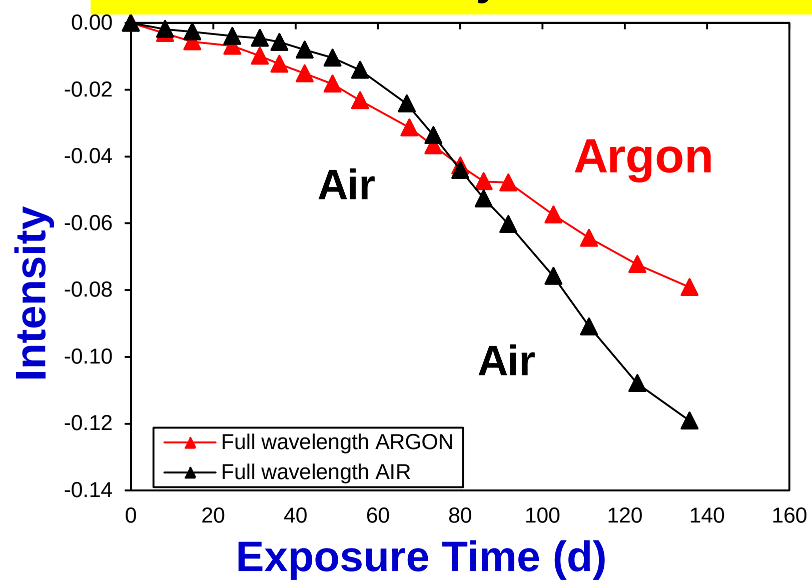
Formation at 1720 cm^{-1}



Loss of Intensity at 1740 cm^{-1}



Loss of Intensity at 1365 cm^{-1}



NIST

YI of EVA in function of time