NREL
NATIONAL RENEWABLE ENERGY LABORATORY

"The Durability of Poly(Methyl Methacrylate) Lenses Used in Concentrating Photovoltaic Technology"

David C. Miller[1]*, Joseph D. Carloni[2,3], Joel W. Pankow[1], Erica L. Gjersing[1], Bobby To[1], Corinne E. Packard[2], Cheryl E. Kennedy[1], and Sarah R. Kurtz[1]

ATLAS/NIST Workshop on Photovoltaic Materials Reliability

2011/10/27 (Thurs)
12:00 – 12:35 pm
Green room (Administrative Bldg)

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[3]Binghamton University, SUNY

***Presenter:**
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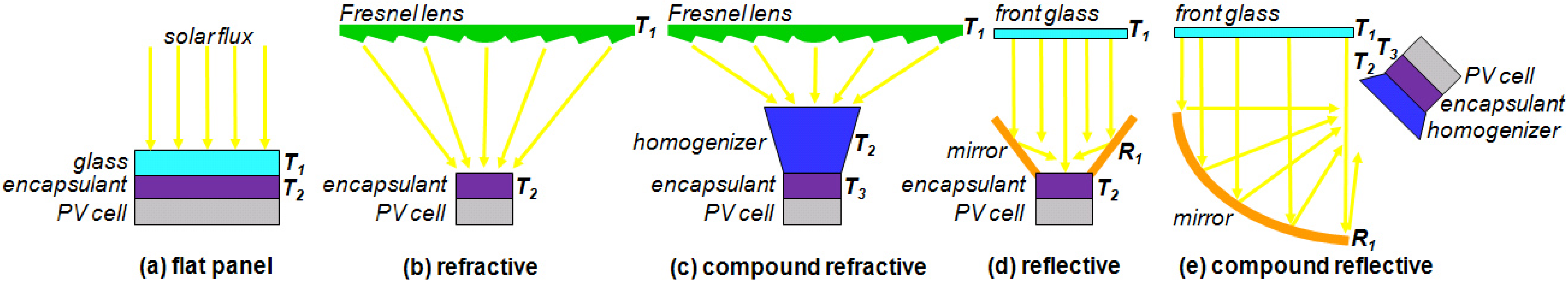
The Use of Fresnel Lenses in CPV

- Concentrating Photovoltaic (CPV) modules use cost effective optics ($) to focus light onto high efficiency (η=43%) multijunction cells ($$$$$)
- Many present CPV implementations use refractive optics (Fresnel lenses)



Implementations of CPV , including refractive and reflective, shown relative to flat-panel technology

*Miller et. al., Optical Engineering, **50**, 2011, 013003.*

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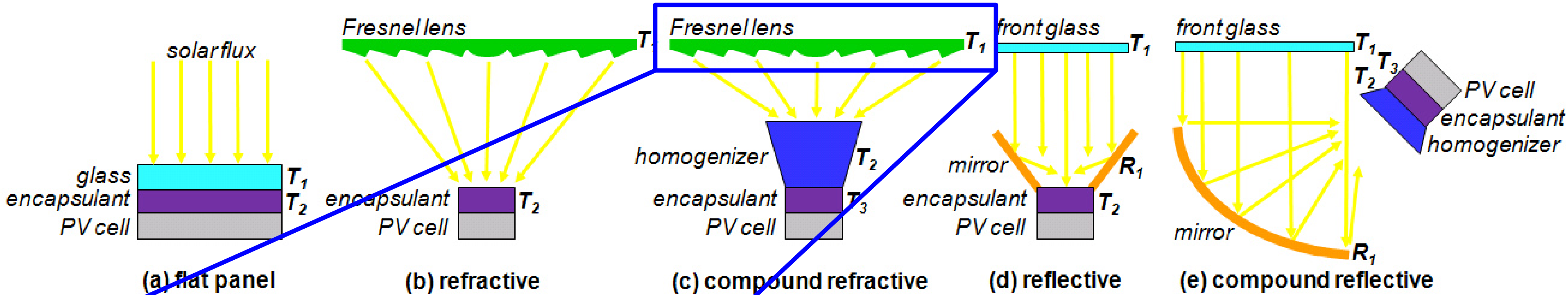

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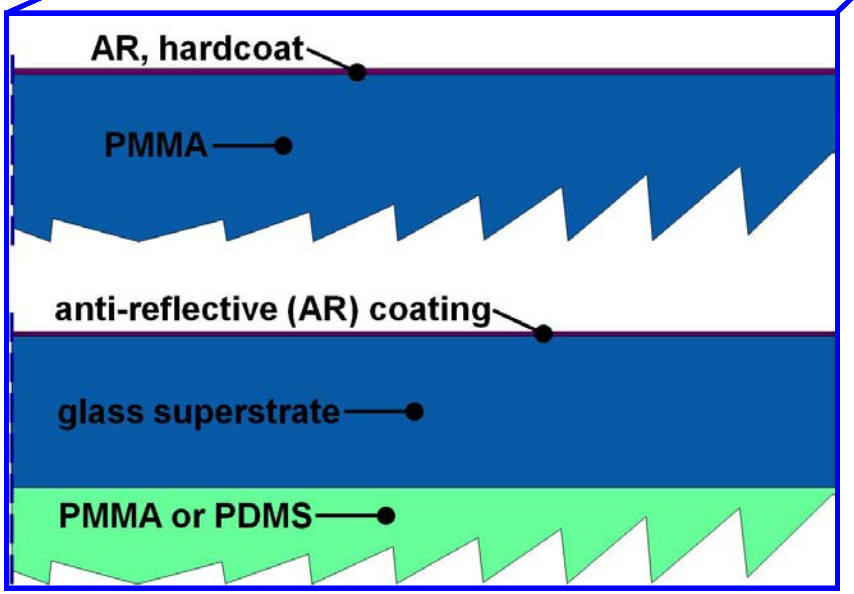

Cross-sectional schematics of monolithic PMMA and SoG lenses

- Monolithic PMMA is the most cost effective, lightweight lens implementation (vs. silicone on glass)
- The durability (expected life) for lenses is unknown for the CPV application

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Purpose- and Details- of Screen Test at NREL

- Literature ⇒ studies initiated ≥20 years ago
- Goal here: characterize the durability of a broad range of ***contemporary*** specimens subject to indoor HAST

DESCRIPTION	SPECIMEN TYPES
stock (unpatterned)	11
linear focus lens	1
spot focus lens	8
veteran (fielded) lens	5

- Veteran specimens on tracker in desert site, seldom cleaned (8, 22, 27 yrs)

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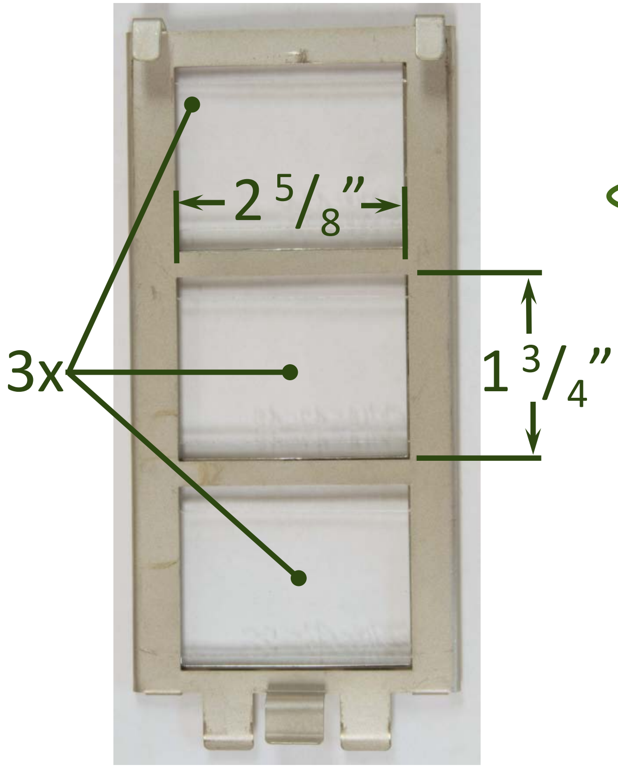

Test specimens (4.4 x 6.7 cm^2)

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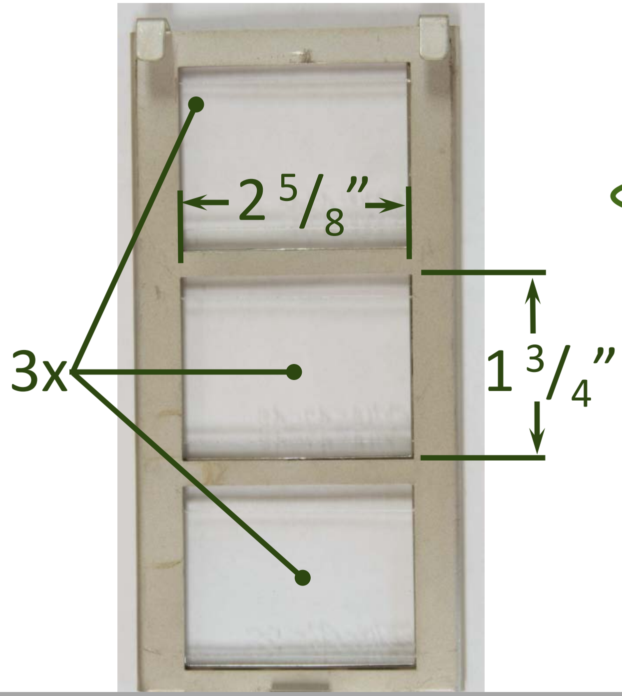

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Now also "round 2": (38) PMMA , SoG specmens. Indoors and FL, AZ, CO.

- Test instrument: ATLAS Ci4000 Weather-ometer (Xenon-arc lamp @ 2.5x UV suns. Chamber @ 60°C/60%RH)

Details of the NREL Screen Test

- Measurands:

  Periodic

  optical appearance (photograph)

  → optical transmittance (hemispherical & direct)

  mass

  → contact angle (sessile drop, H_2O on 1st surface)

  "End of life"

  haze (from direct transmittance)

  prism facet geometry (lenses: section then SEM)

  → surface morphology (SEM or AFM)

  → indentation (Berkovich hardness, toughness)

  → XPS (surface chemistry, before & after cleaning)

  → fluorescence spectroscopy

  MALDI (M_w)

  NMR (bulk chemistry)

- Test schedule:

  0, 1, 2, 4, 6, 12, **18**, 24, 30, 36 months

  ≥8 acceleration factor (irradiance and 24 hour operation)

  pull 1 of replicates every 12 months

Summary of Trends Observed to Date

Transmittance:

- Reduced with age, especially purple & blue wavelengths
- Effects similar for degradation & soiling
- H_2O affects IR wavelengths only (*e.g.*, 1415, 1910, 2700 nm)

Contact Angle:

- Reduced with age (66 ° $\rightarrow$ 57 ° [12 months] $\rightarrow$ 43° [veteran])
- Significant restoration with cleaning

Mechanical Fracture:

- Radial cracks on injection molded lens

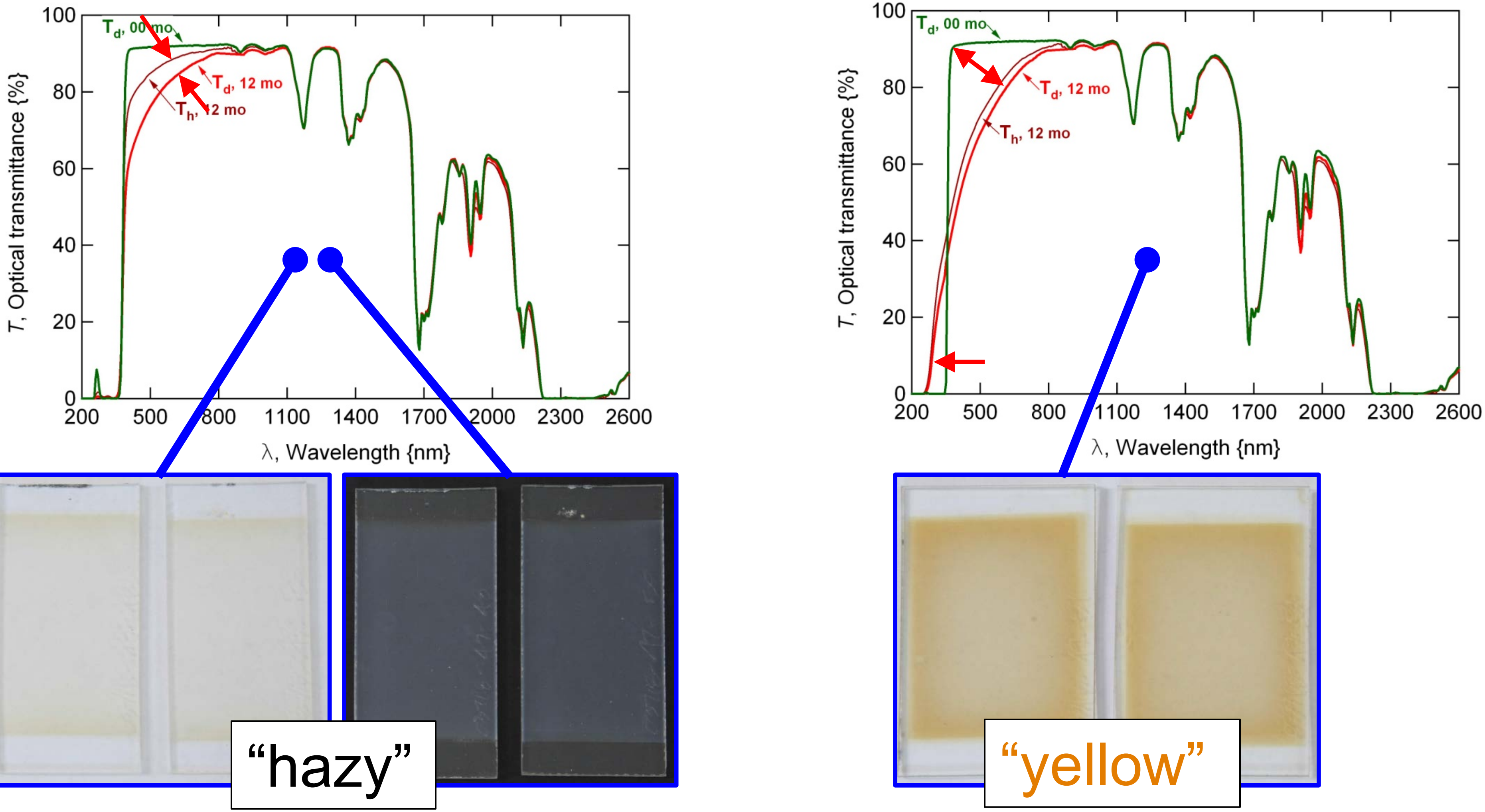
Surface Roughness:

- Solid erosion, scratches, embedded material

@ 6 months: Miller et. al., Proc. SPIE, 2010, 7773-02.

2 Different Damage Morphologies Have Emerged!

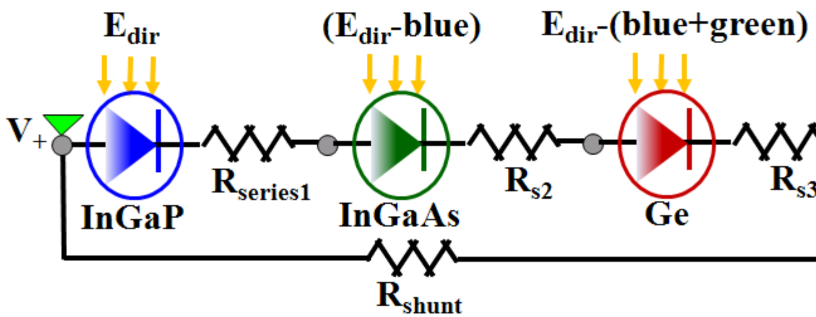
Transmittance characteristics and visual appearance of the two damage morphologies



- Specimens have a hazy (scattering) or yellow (attenuating) appearance
- Both examples are "solar grade" material, same manufacturer
- What are the significance and cause?

Electrical Interconnection in Multijunction and Si CPV Cells

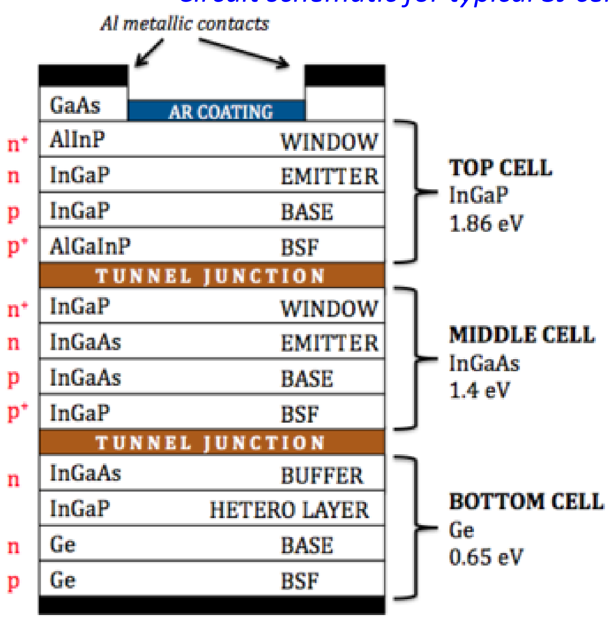
- Because 3J cells are connected in series, the characteristics of the optical system have increased importance
- Optical degradation & soiling are critical reliability issues



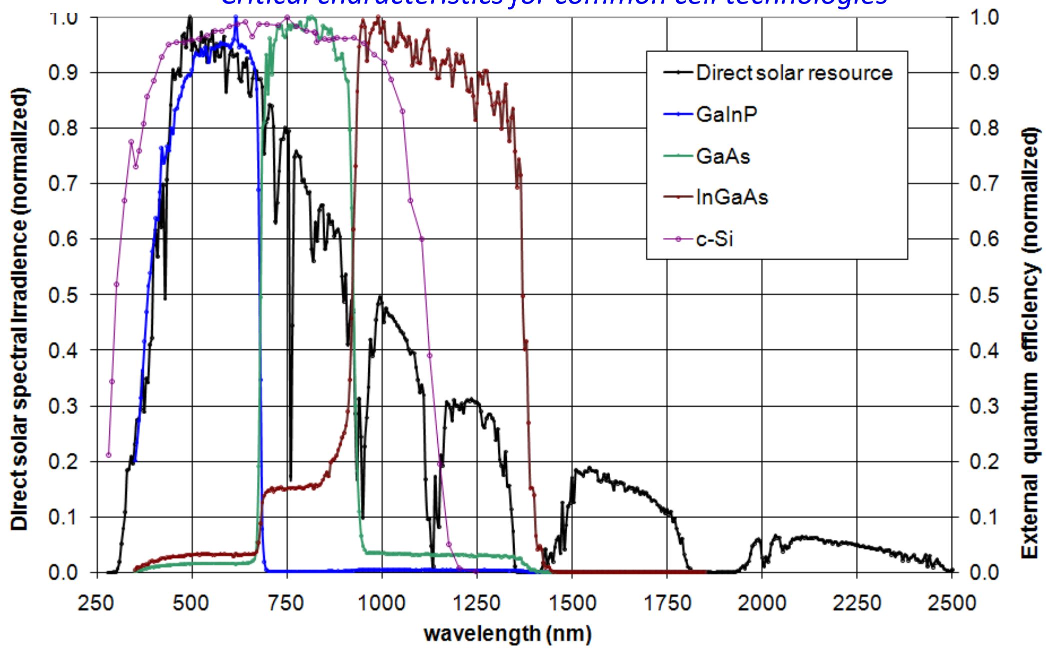
Circuit schematic for typical 3J cell

λ, @peak {nm}	E_g {eV}	E_g identity
664	1.87	GaInP, direct bg
881	1.41	GaAs, direct bg
1850	0.67	Ge, direct bg
1107	1.12	Si, intrinsic

Critical characteristics for common cell technologies

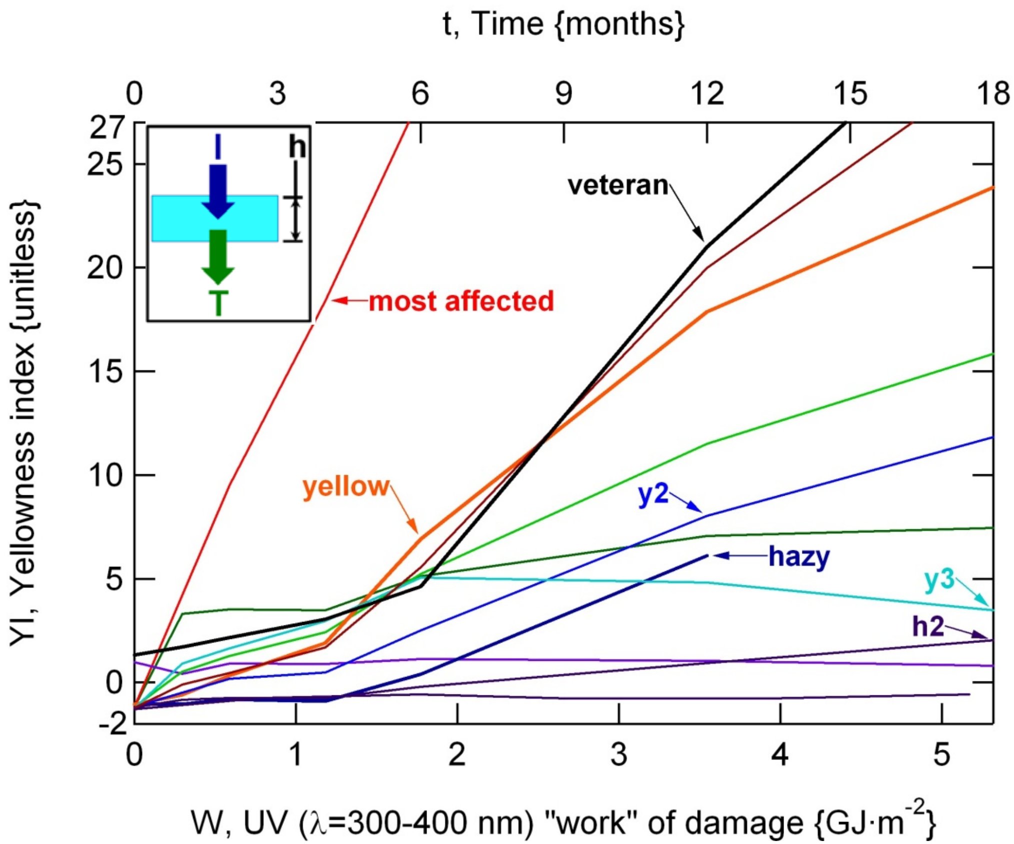


Cross-section of typical commercial 3J cell
http://en.wikipedia.org/wiki/Multijunction_photovoltaic_cell (2011/10/10)



External quantum efficiency for terrestrial 3J and c-Si cells
*Nann and Emery, Solar Energy Mats Solar Cells, **27**, 1992, 189-216*
*Green et. al., Prog Photovoltaics, **18**, 2010, 346-352.*

YI Distinguishes the Aged PMMA Formulations

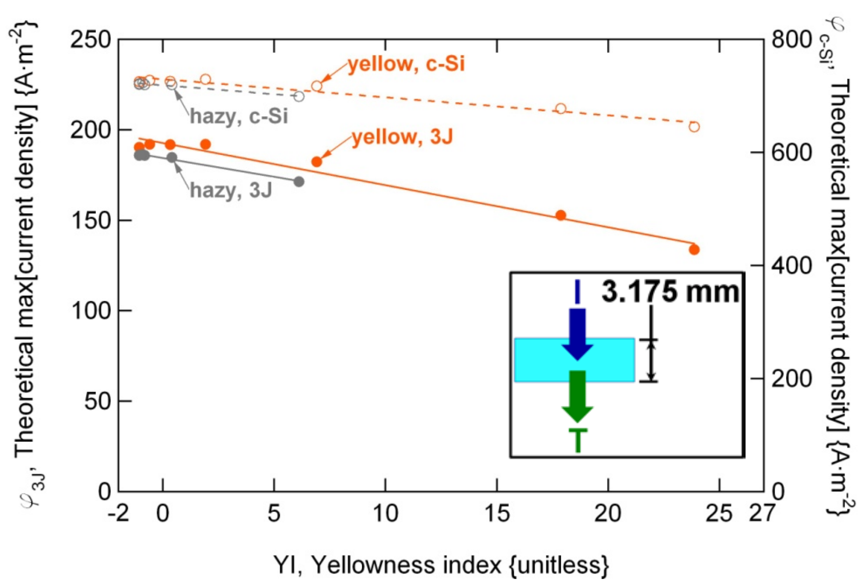


YI determined from raw hemispherical transmittance measurements (proportional to visual appearance) for sheet specimens. Veteran lens fielded 8 years

YI: ASTM E313 & E308

[D65 source, 10° observer]

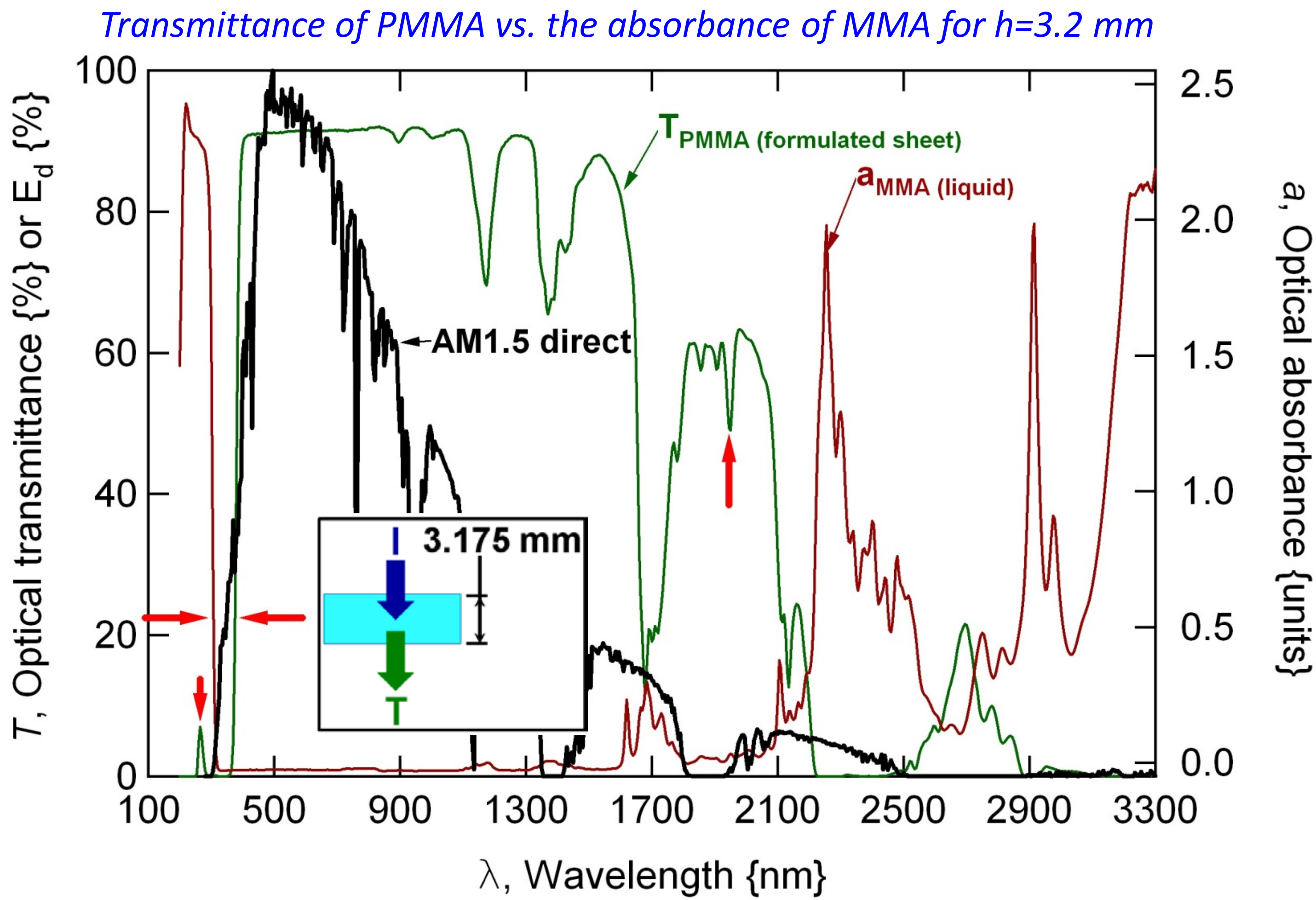
- A broad variety of results follows for the sheet specimens
- 5/11 shown were CPV or PV marketed materials, including (2) "hazy" and (3) "yellow"



YI vs. T (300-650 nm or 300-1220 nm)

- YI correlates well with transmittance! (*i.e.,* expected module performance)
- Single quantitative figure of merit

Differences in the Optical Transmittance of PMMA & MMA



- The transmittance of (unaged) PMMA polymer follows from MMA monomer
- Differences: T at 265 nm, absorption from 300-380 nm in PMMA
- MMA & unformulated PMMA have similar spectra

  $\Rightarrow$ differences from additives, co-polymer

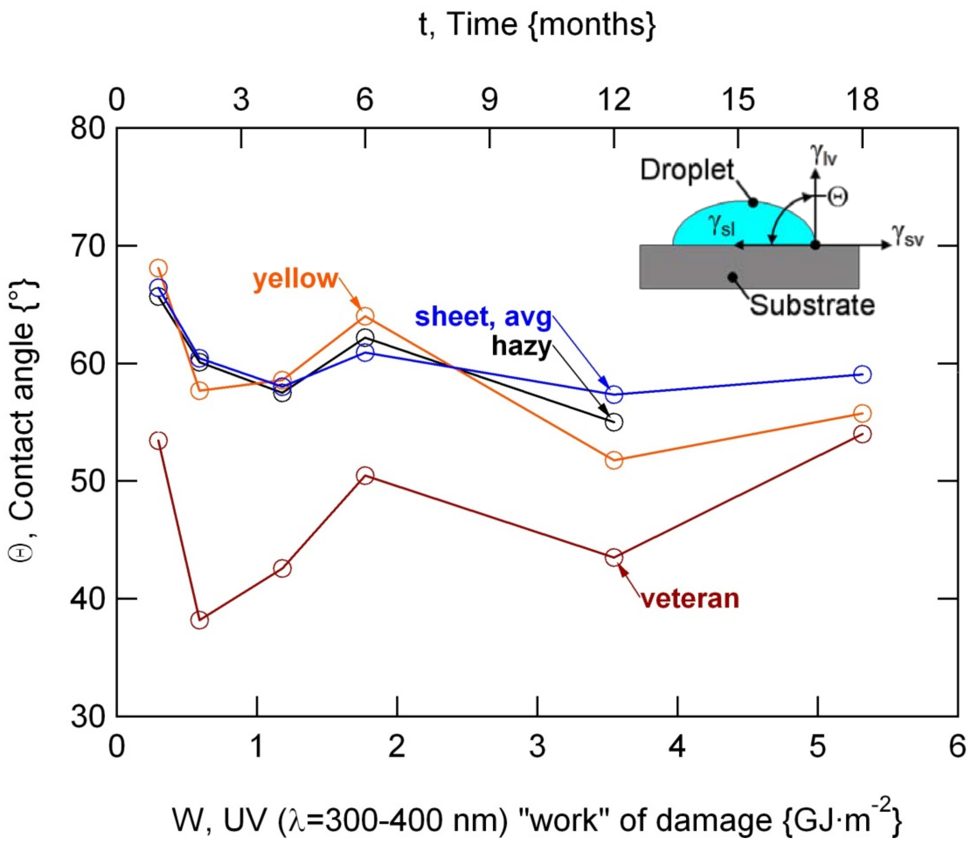
Contact Angle Is Affected By Age

•Contact angle relates to the accumulation and retention of particulate matter

•Contact angle decreased with time for hazy & yellow specimens
•Both similarly restored when cleaned at 6 months

•Decreasing Θ, with no distinction between h & y specimens

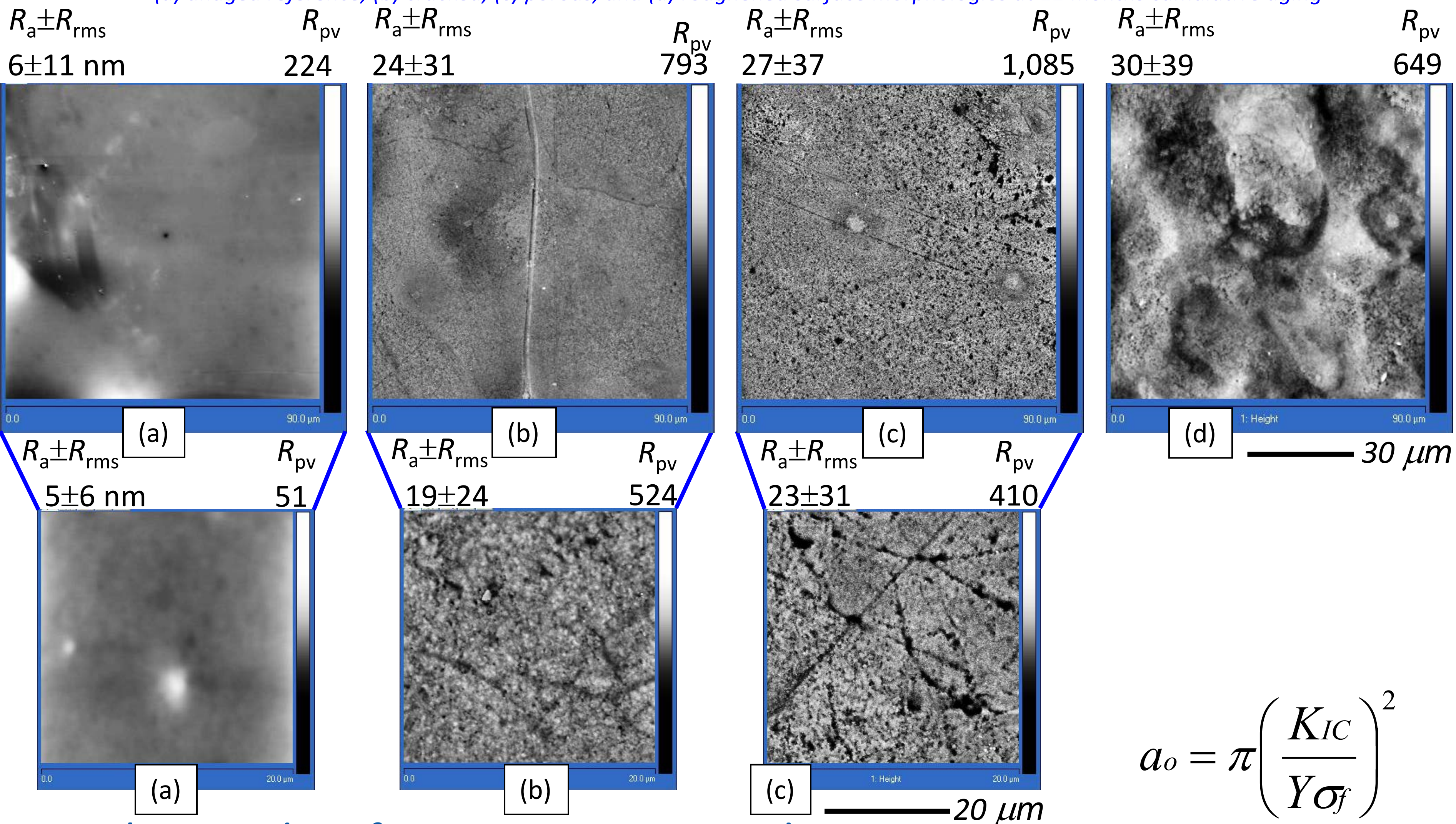
Helpful: measure after desiccating



Contact angle for hazy and yellow specimens.
average Θ shown for sheet specimens
veteran lens fielded 8 years

Surface Features of the Indoor Aged Specimens

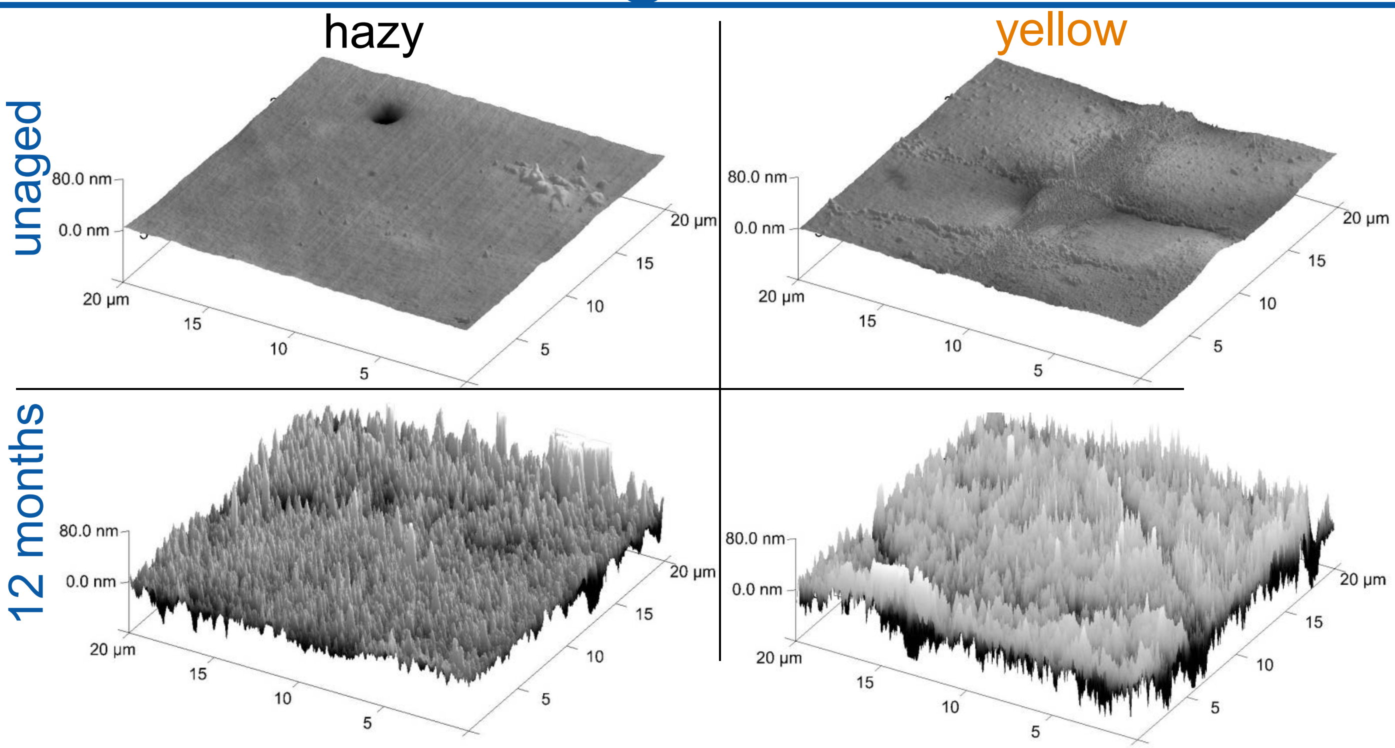
(a) unaged reference, (b) cracked, (c) porous, and (d) roughened surface morphologies at 12 months cumulative aging



$$a_o = \pi \left(\frac{K_{IC}}{Y \sigma_f} \right)^2$$

- Cracking and surface porosity are evident
- A defect size of 35-75 μm, however, is implied for unaged PMMA from its fracture strength (70-105 MPa)

Surface Roughness Increases With Aging



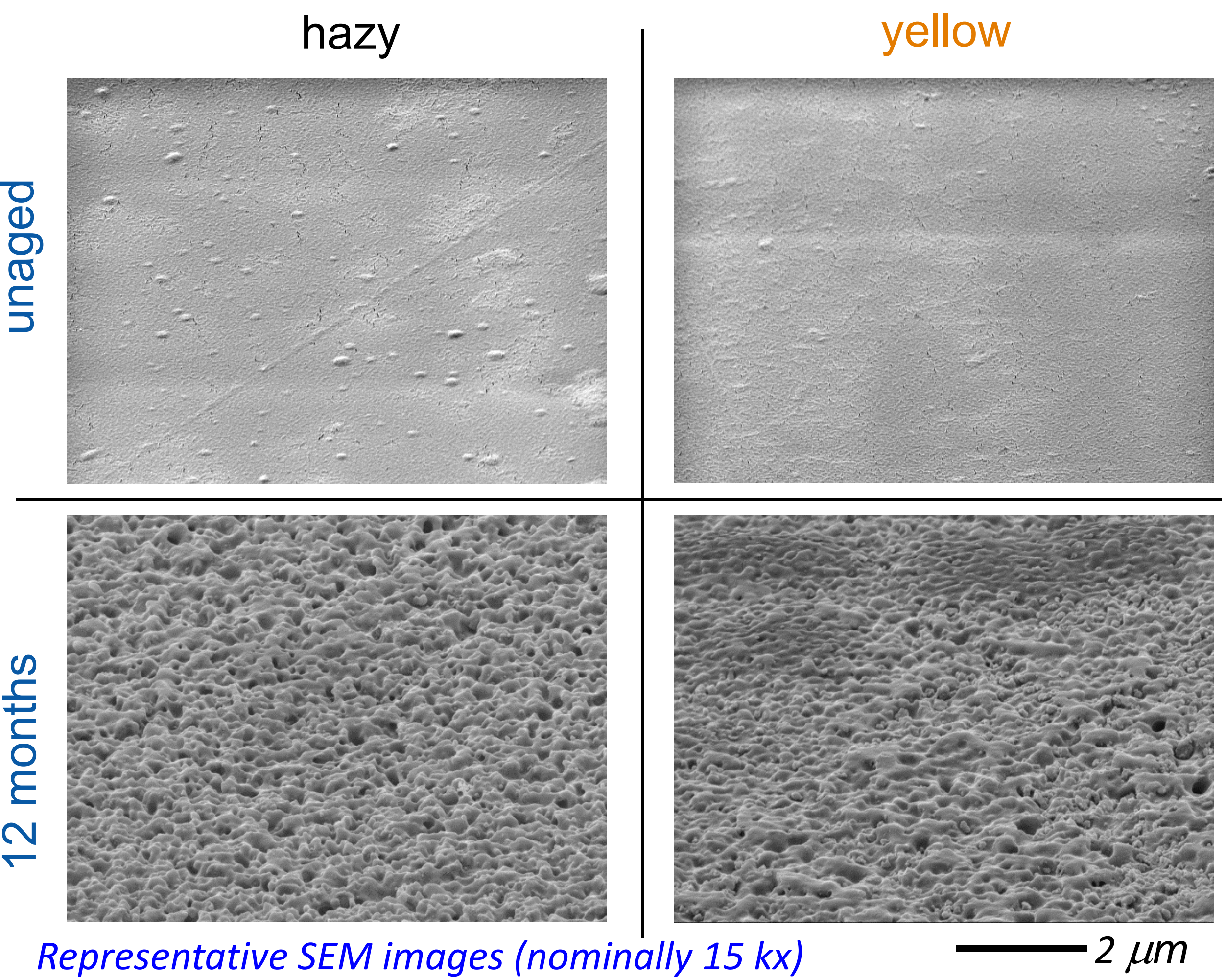
Representative isometric representation of hazy & yellow specimens

SPECIMEN SET	HISTORY	R_a {nm}	R_{rms} {nm}
hazy	unaged	3.1	4.4
hazy	aged	26.0	38.8
yellow	unaged	2.6	3.5
yellow	aged	21.9	28.1

Summary of AFM measurements

- Roughness increased significantly (10x) with age
- No overt distinction, hazy vs. yellow
- Outdoor deployment also includes surface abrasion (solid erosion) & particle implantation
- Increased roughness should scatter light (increase haze) and reduce contact angle
- Crazing/cracking could relieve stress

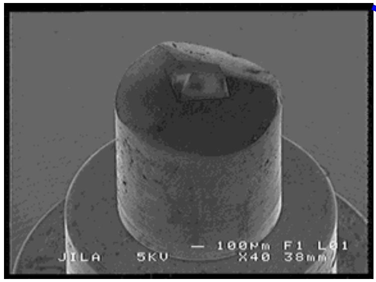
Surface Roughness Increases With Aging (SEM)



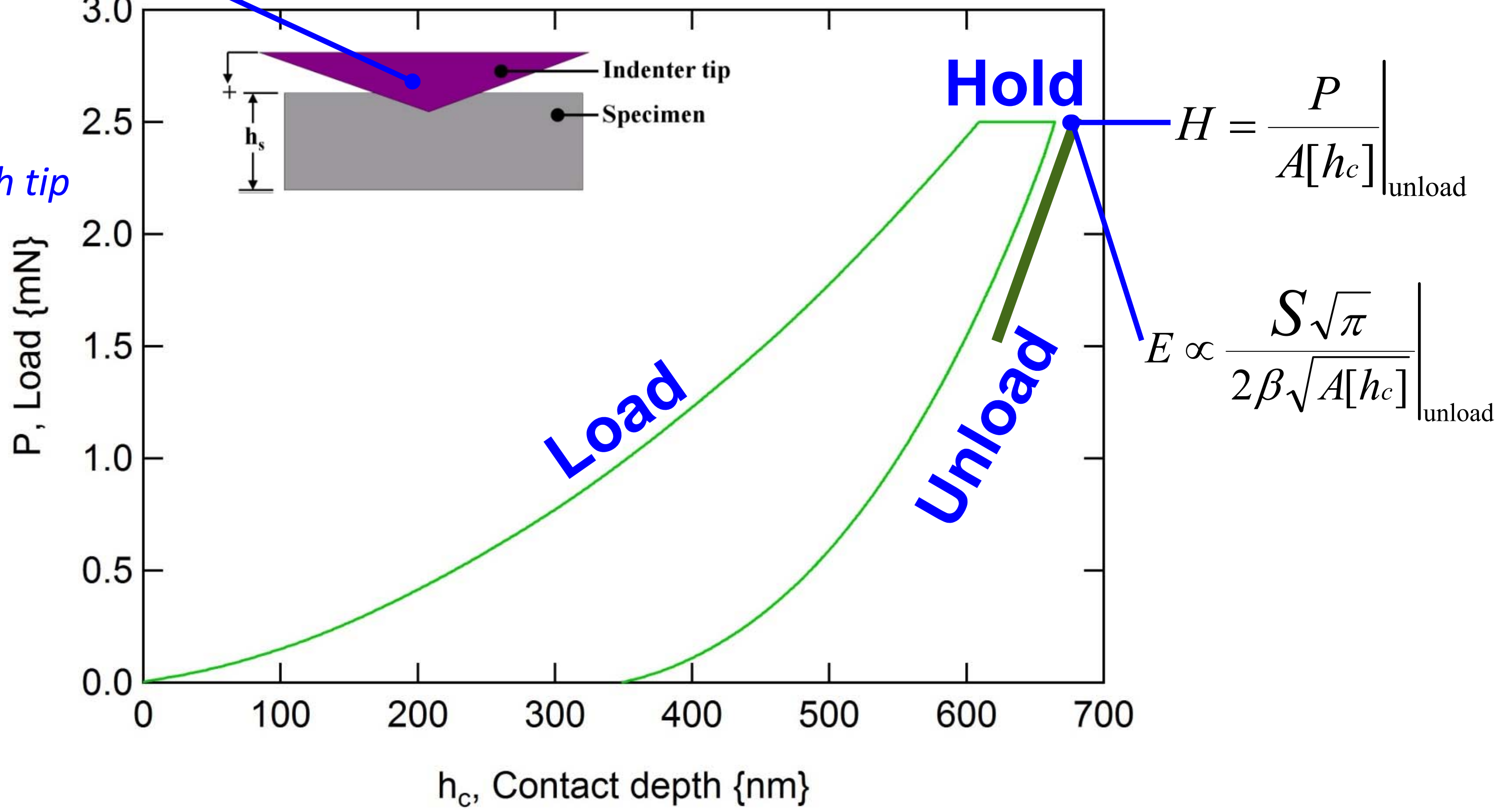
Representative SEM images (nominally 15 kx)

- Morphology qualitatively similar in SEM
- Some irregular features (including spikes) for unaged materials
- Morphology porous (varied ∅) across aged

"Nanoindentation" Quantifies Mechanical Properties



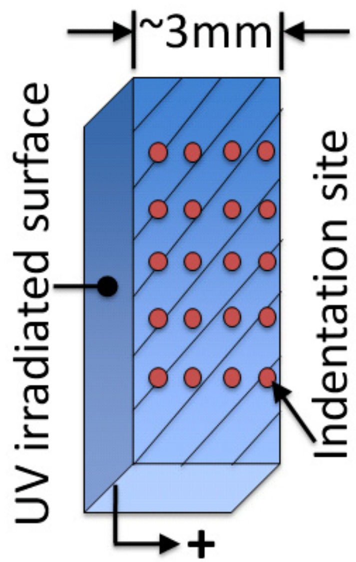
SEM image of Berkovich tip



Load/displacement profile for PMMA

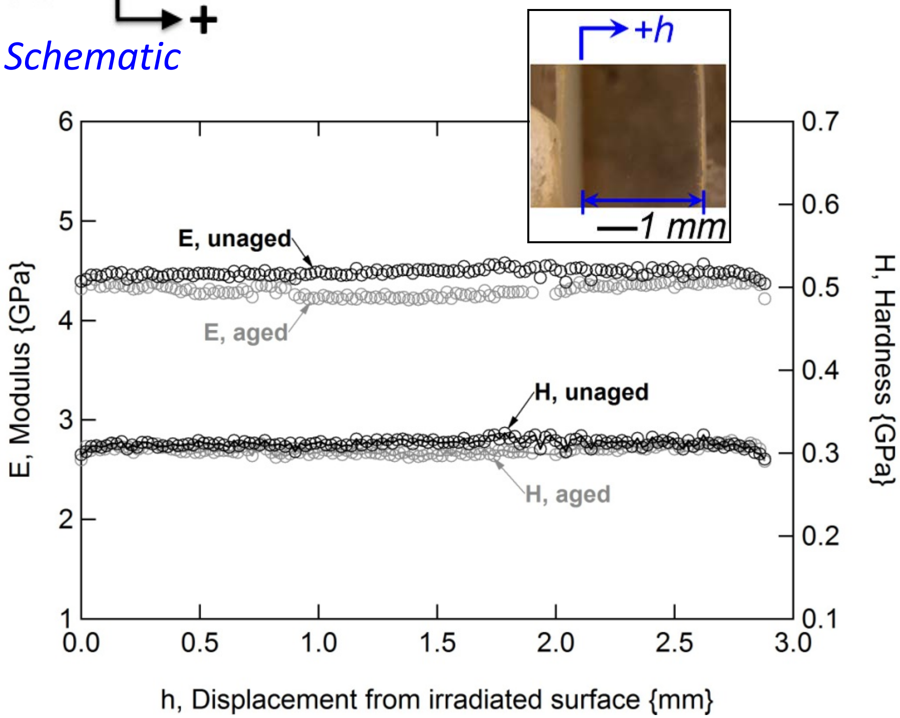
- A prescribed diamond tip is pressed into the specimen
- Elastic recovery of strain occurs at the instant of unloading the tip
- The key tribological characteristics (*E*,*H*) can be determined locally from the load/displacement data

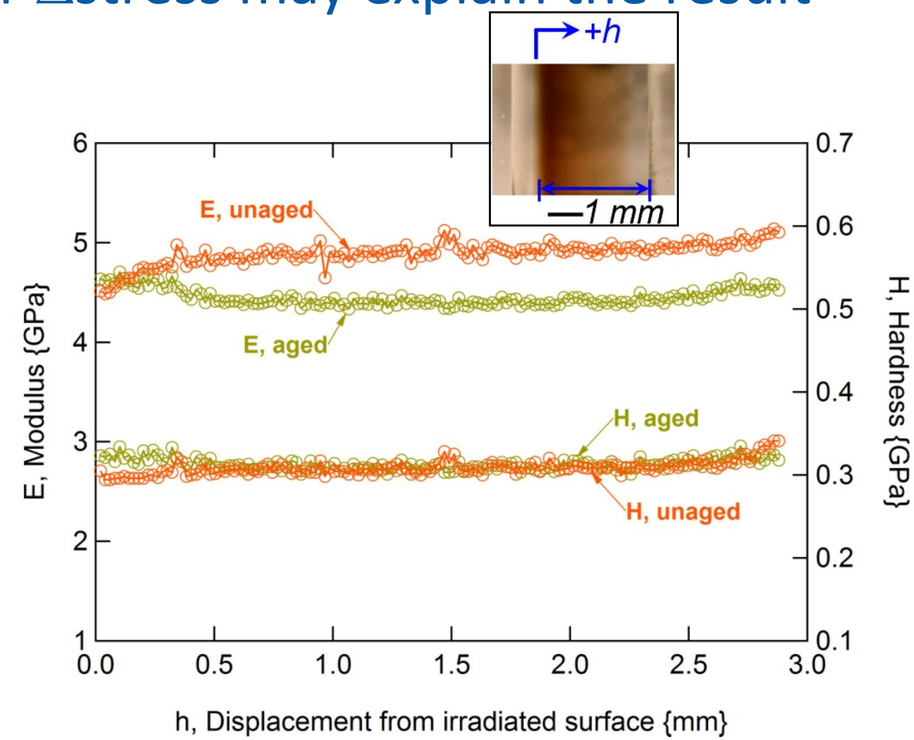
Indentation Distinguishes the Aged PMMA Formulations



Schematic

- Specimens potted & x-sectioned for indentation (150 x 5 matrix) in the thickness direction
- Little effect observed near the surface
- Little effect observed for hazy (aged vs. unaged)
- E affected for yellow (aged) through the thickness
- Degradation and/or Δstress may explain the result

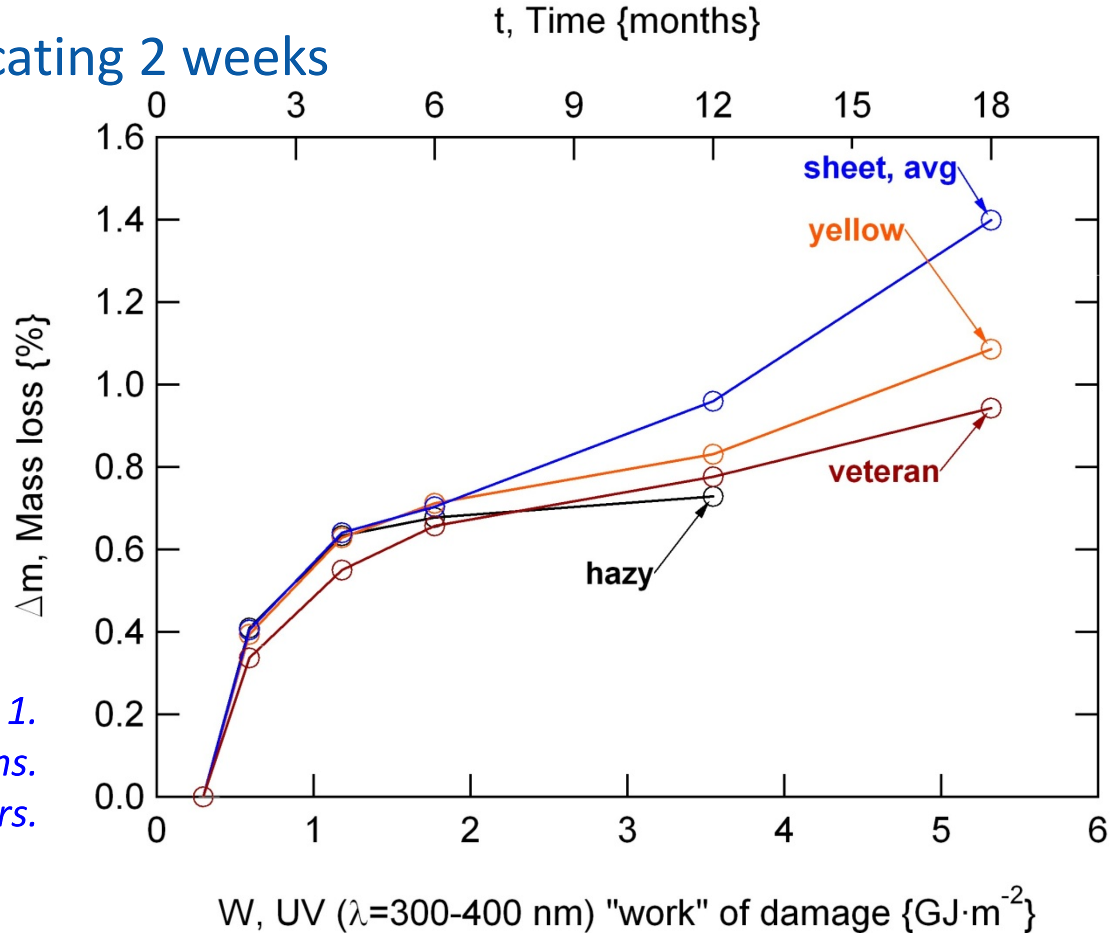




Indentation results (elastic modulus and Berkovich hardness)

Mass Loss Resulting From Aging

- Resembles asymptotic diffusion process. Degradation products? Additives?
- Δm of hazy and yellow specimens not readily distinguished
- Δm similar for veteran and contemporary specimens
- Δm from lost volatile content would be proportional to cumulative damage
- Critical: measure after desiccating 2 weeks



Specimen mass, relative to that at month 1.
Average Δm shown for sheet specimens.
Veteran lens fielded 8 years.

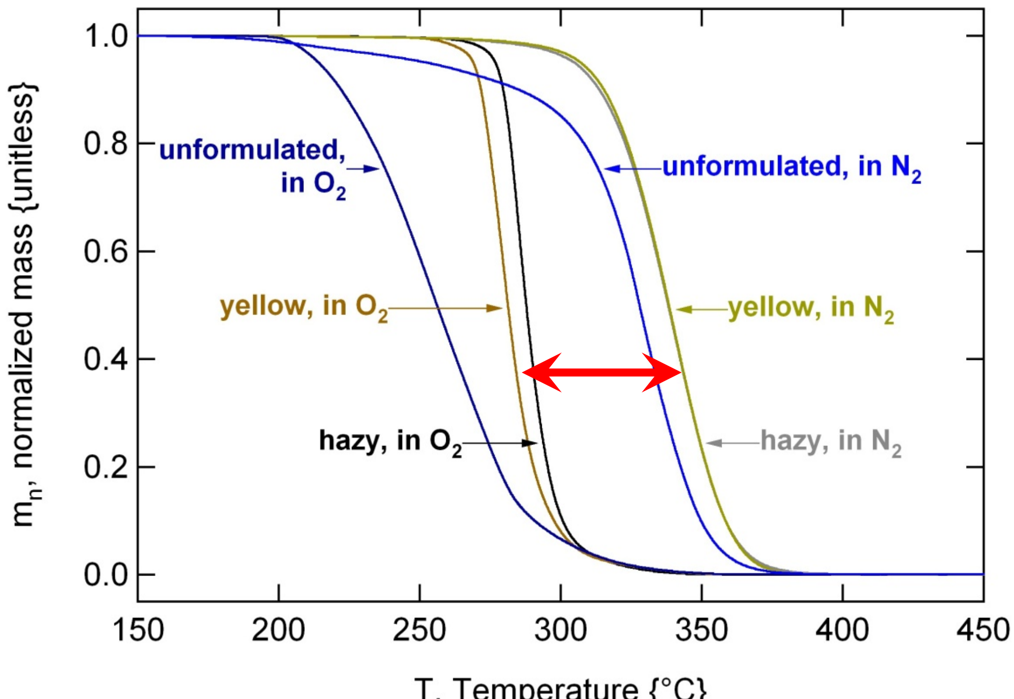
Thermometric Gravitational Analysis (TGA) Does Not Distinguish the Hazy and Yellow Formulations

SPECIMEN	ATMOSPHERE	T, 0.5% mass loss {°C}	T, 50% mass loss {°C}	FREQUENCY FACTOR: $c_{1, avg}$ (s^{-1})	$E_{a, avg \pm SD}$ (kJ/mol)
unformulated	O_2	201	256	2.1E+07	108±8
unformulated	N_2	185	328	4.7E+13	194±44
hazy	O_2	256	288	8.3E+07	115±6
hazy	N_2	258	338	7.7E+15	223±15
yellow	O_2	250	281	2.0E+07	108±6
yellow	N_2	257	338	5.0E+16	232±15

Table and figure: modulated TGA results for the specimens

$$k_r = c_1 \exp\left[\frac{-E_a}{RT}\right]$$

- O_2 facilitates thermal degradation



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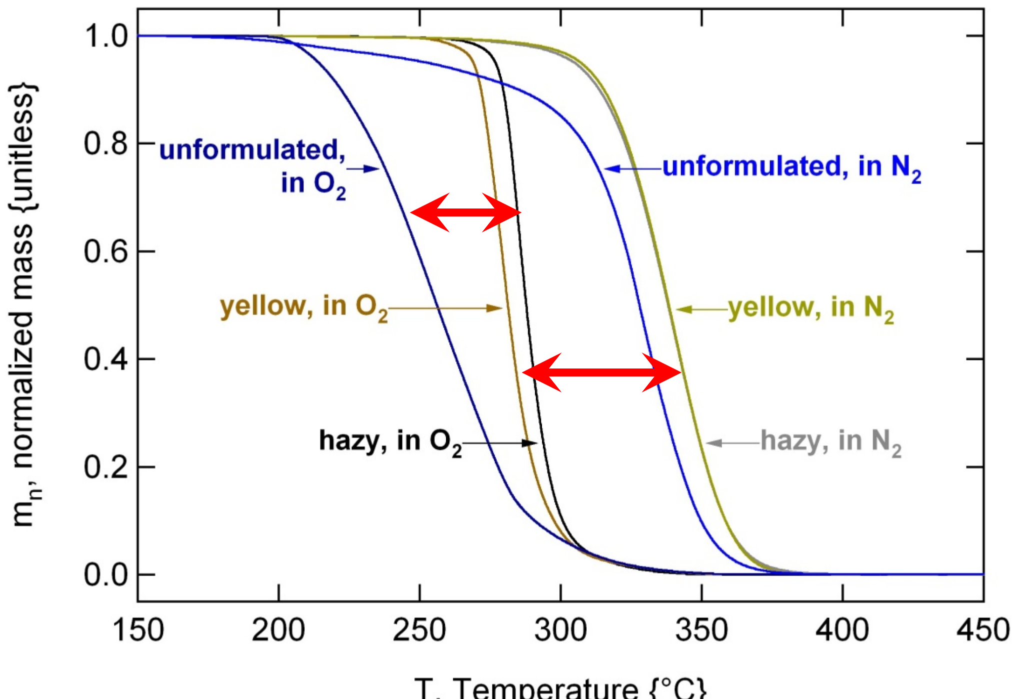

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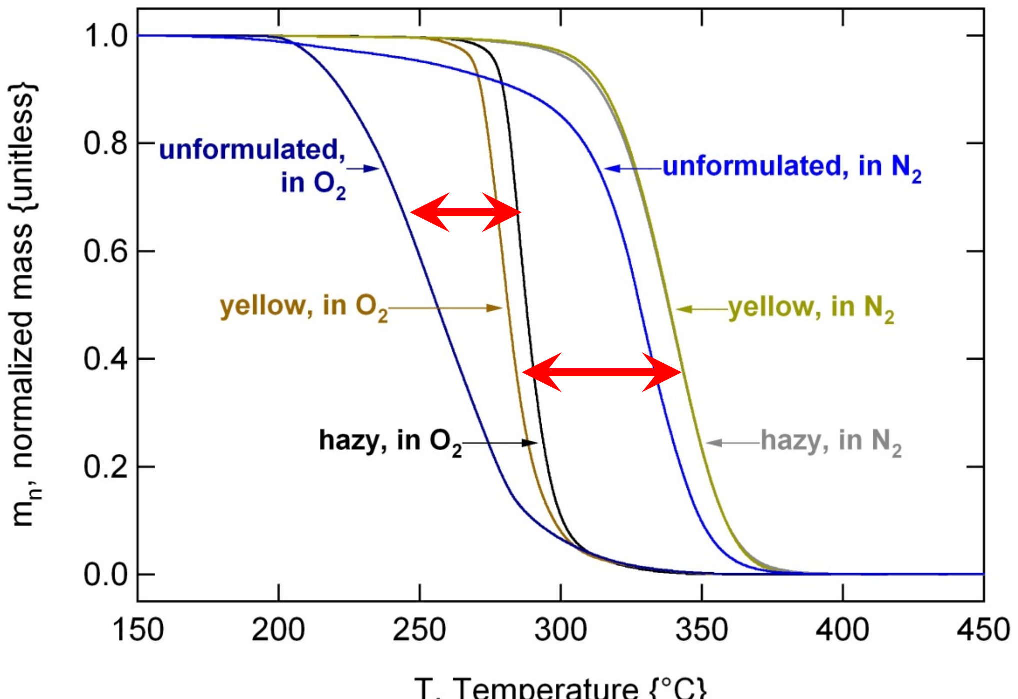
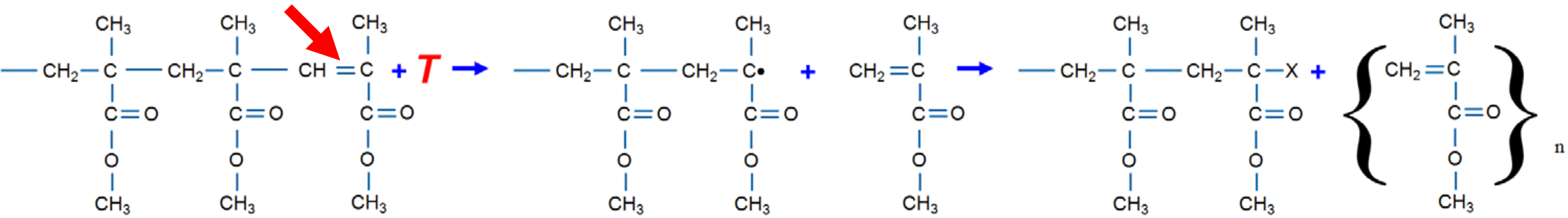
- O_2 facilitates thermal degradation
- Formulation improves stability (co-polymer, additives)
- Depolymerization is a high E_a process (60 °C in Ci4000 vs. ≥250 °C in TGA)



Thermal Decomposition … Not Suspected Here

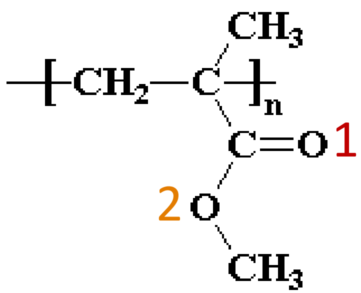
- Unzipping of main chain into methyl methacrylate (monomer)
- Autocatalytic process (zip length on order of 1000)
- Significant weight loss (100% vs. minimal for chain scission)



*Miller et. al., Solar Energy Materials and Solar Cells, **95**, 2011, 2037.*
(after Aboulezz and Waters, “Studies on the Photodegradation of Poly(Methyl Methacrylate)”, 1978)

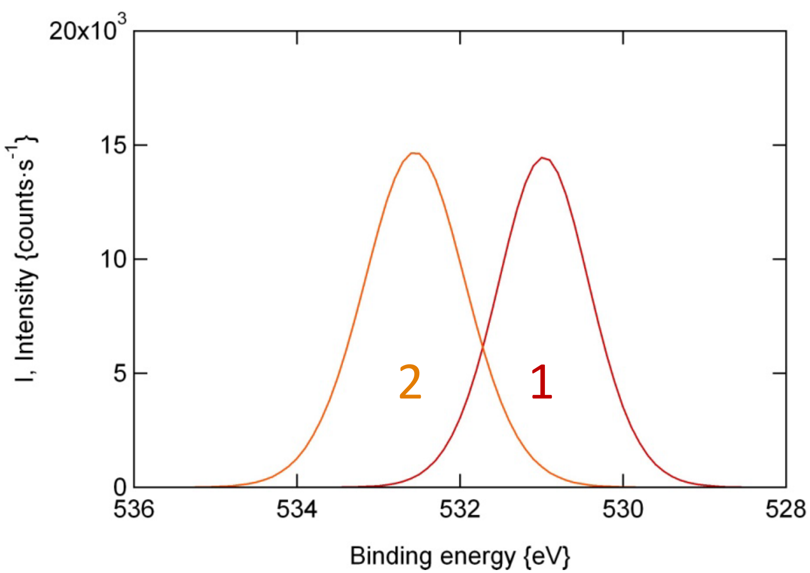
- Synergistic effect w/ irradiation (UV)⇒occurs at T<200°C
- Unlikely to explain distinction between hazy and yellow specimens (similar Δm and E_a characteristics)

X-Ray Photoelectron Spectroscopy (XPS) Quantifies Composition



Schematic and XPS data:
O and C peaks distinguished for clinical PMMA

- Surface ($h \leq 10$ nm) analysis technique
- Technique distinguishes valence and/or chemical state:
  →O=C (carbonyl oxygen) is distinct from O-CH_3 (ester oxygen)



←positive charge/environment negative charge/environment→

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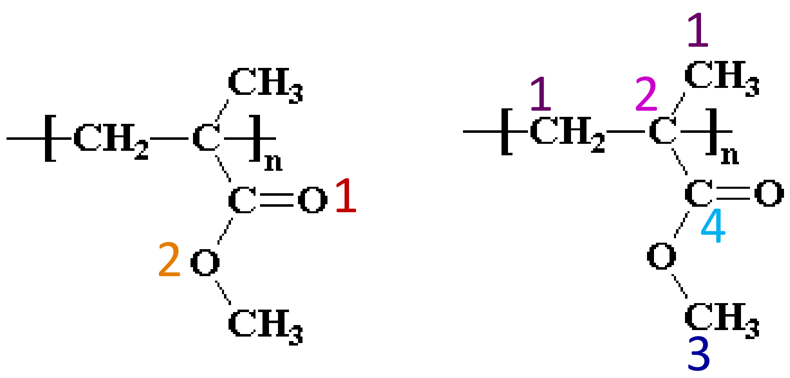

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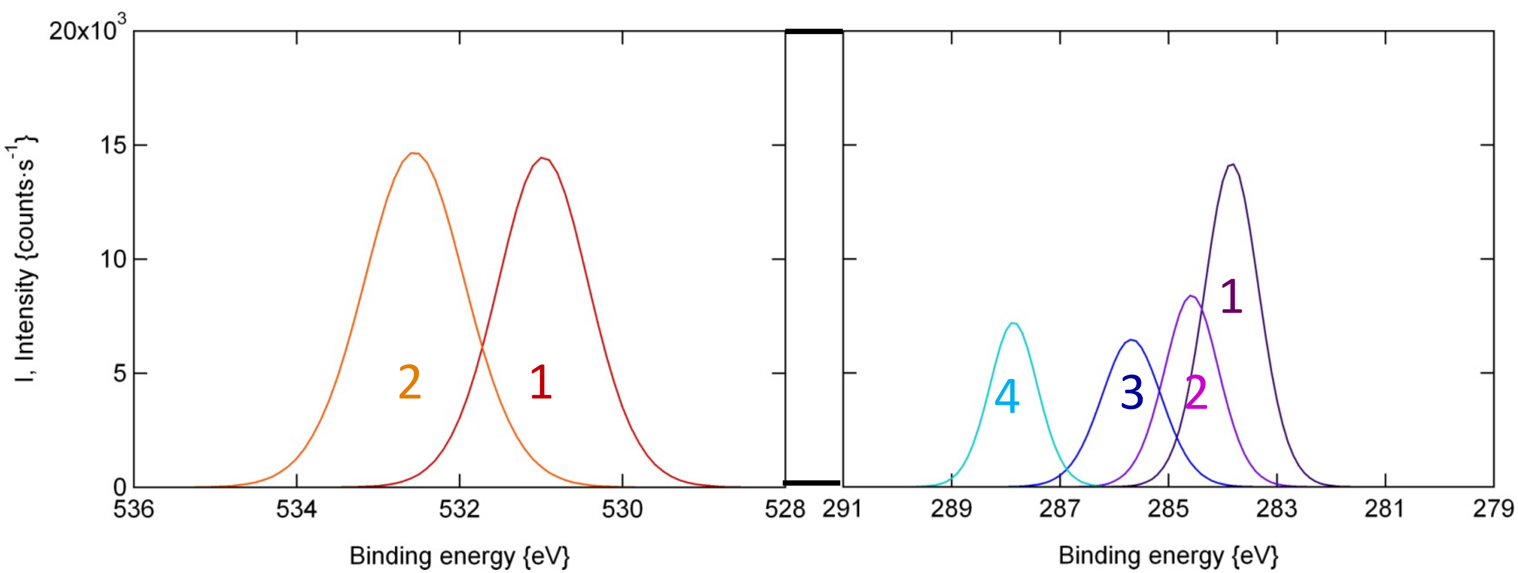

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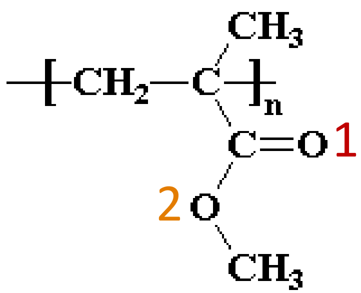

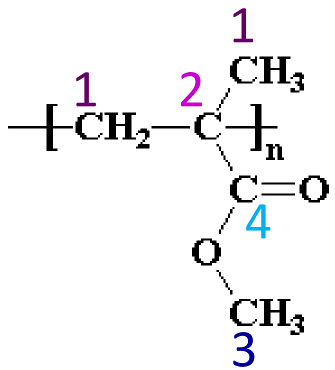

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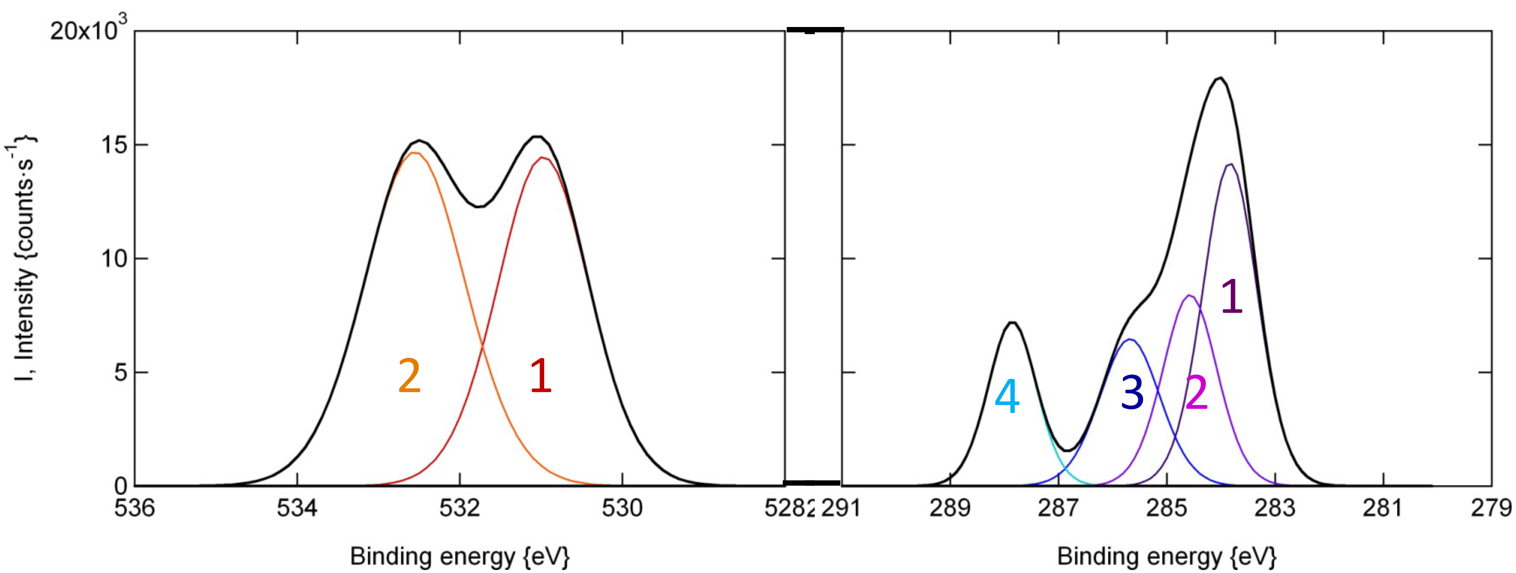
  - →CH_2 (methylene *C*) and CH_3 (methyl *C*) look the same. But 4c's!
  - →*O* and *C* peaks deconvoluted via fit model for O1s and C1s
- ~1 mm^2 X-ray spot used here



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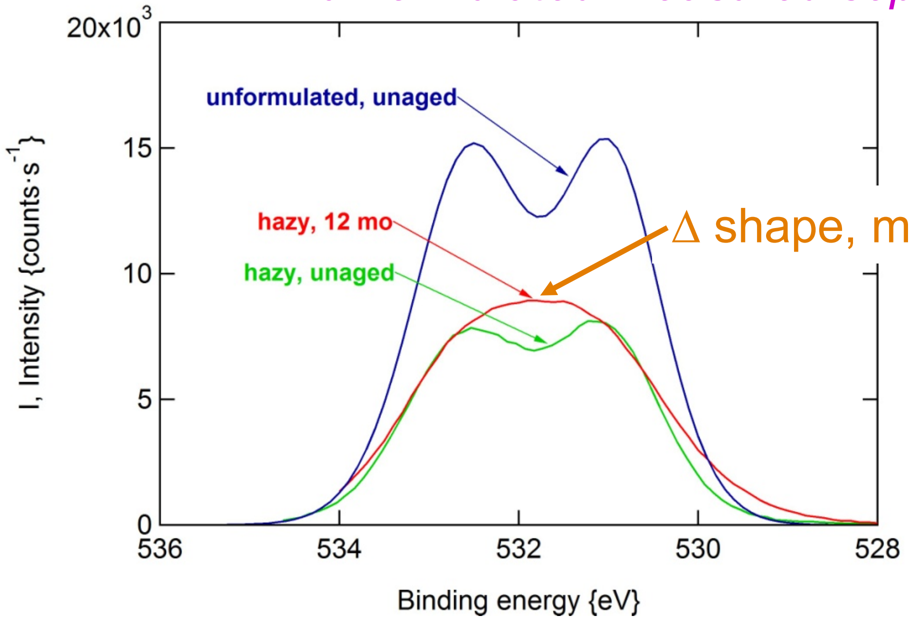
XPS Spectra Identify Chemistry Changes (O↑, C↓)

unformulated measured separately, shown for reference



Δ shape, magnitude O

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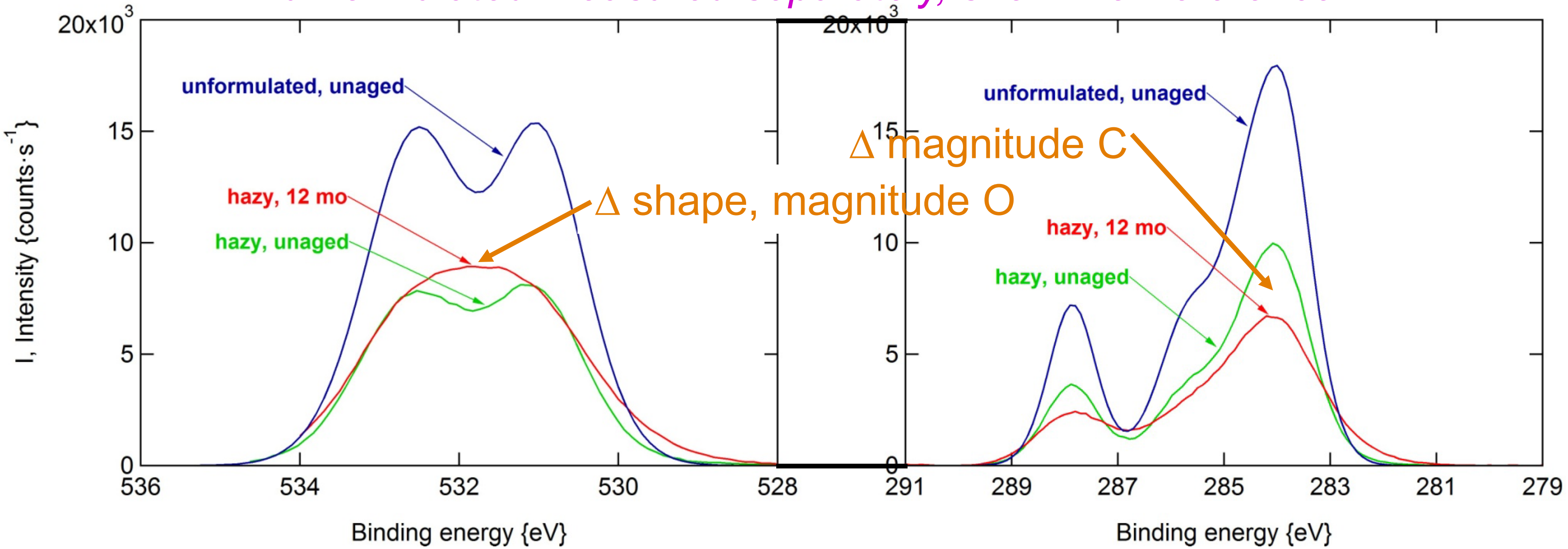

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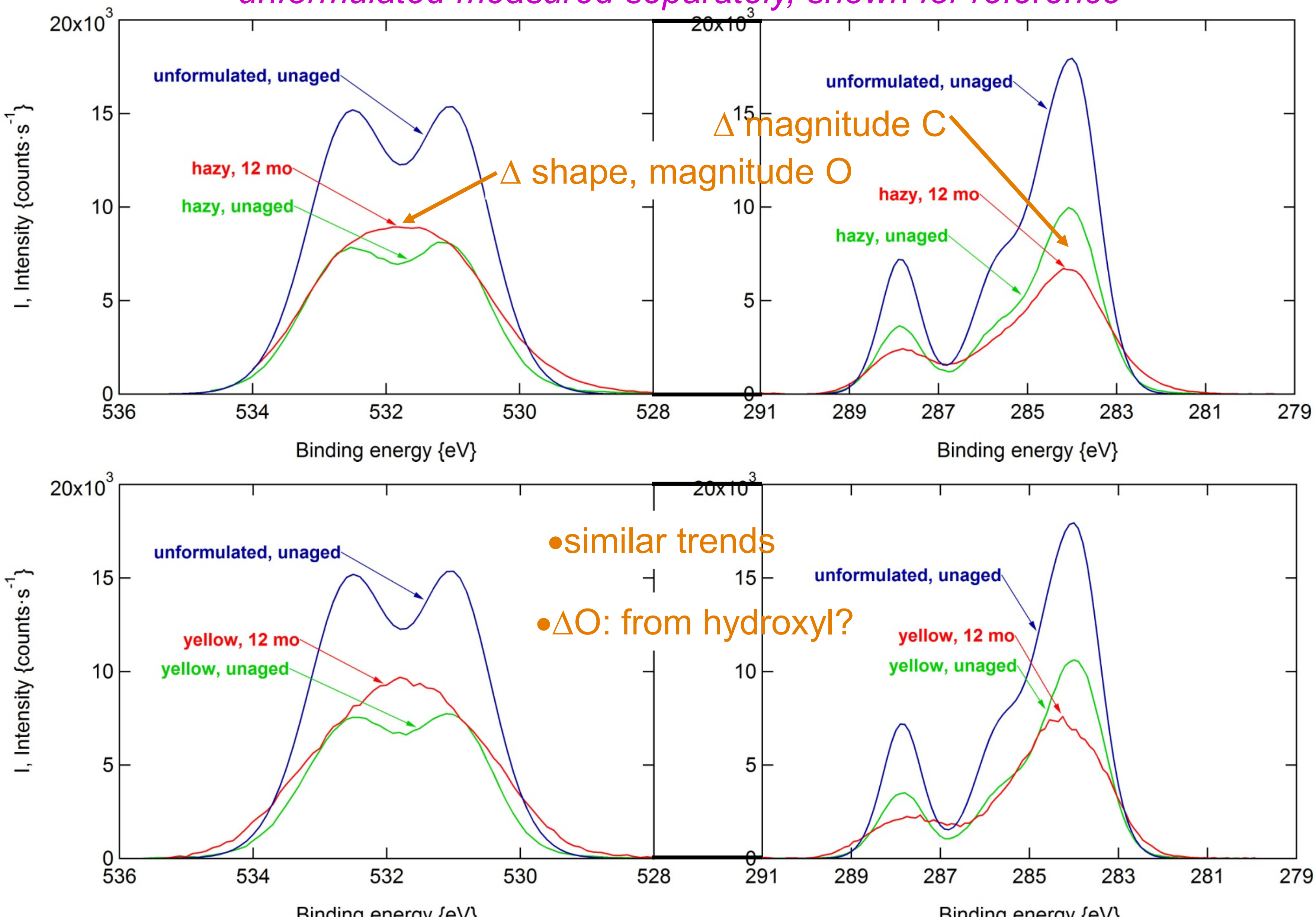

XPS: Quantification of Changes at the Surface

- Oxygen content increased, carbon decreased

		COMPOSITION (IDENTIFYING PEAK) {% at. concentration}				
SPECIMEN	HISTORY	C (1s)	O (1s)	N (1s)	F (1s)	Si (2p)
unformulated	unaged	72.4	27.6	0.0	0.0	0.0
hazy	unaged	73.5	26.2	0.0	0.0	0.2
hazy	aged	62.6	32.0	1.1	1.2	2.9
hazy	aged, cleaned	64.3	32.4	0.0	1.2	2.0
yellow	unaged	71.9	27.8	0.0	0.0	0.3
yellow	aged	61.8	33.7	0.7	1.2	2.5
yellow	aged, cleaned	65.1	31.8	0.2	1.0	1.9

XPS: Quantification of Changes at the Surface

- Oxygen content increased, carbon decreased
- N, F, Si evident after aging. Removable by washing

→N corresponds to removable polar species expected from $\Delta\Theta$

→N from "blooming" or decomposition of UVA

(*e.g.*, benzotriazole: $C_6H_4N_3H$)?

→F, Si from release paper, typically fluorinated?

(Maybe from additive… more likely lubricant/mold release)

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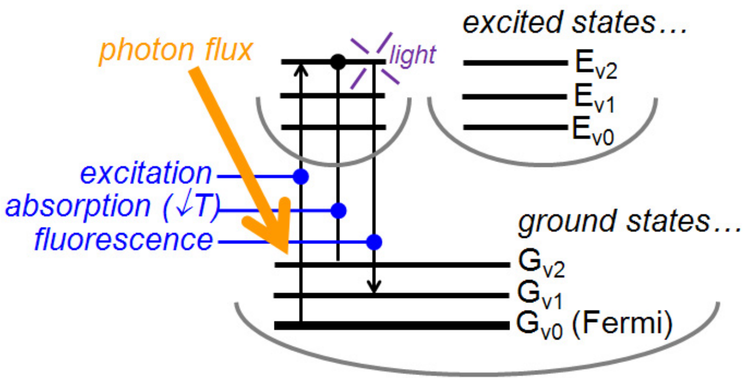
The "Mechanics" of Fluorescence



- In polymers, illumination can generate optical absorption and **fluorescence** where:

  intensity ∝ lumophore concentration

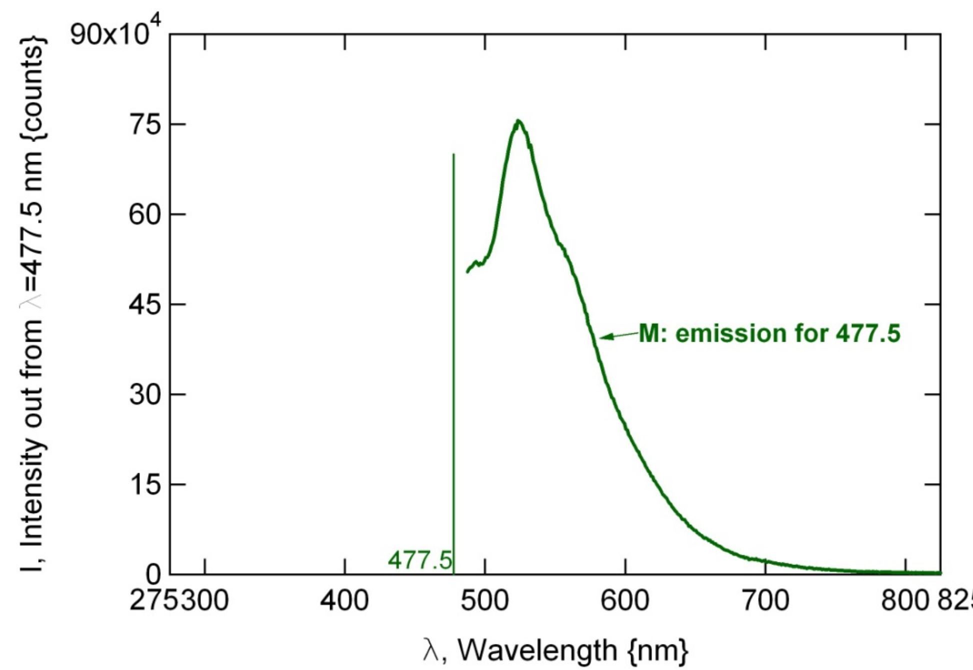
  wavelength ∝ lumophore composition

lumophore sites: UVA, impurities, chromophores

1. Excite at 477.5 nm, measure emission from 487.5-825 nm

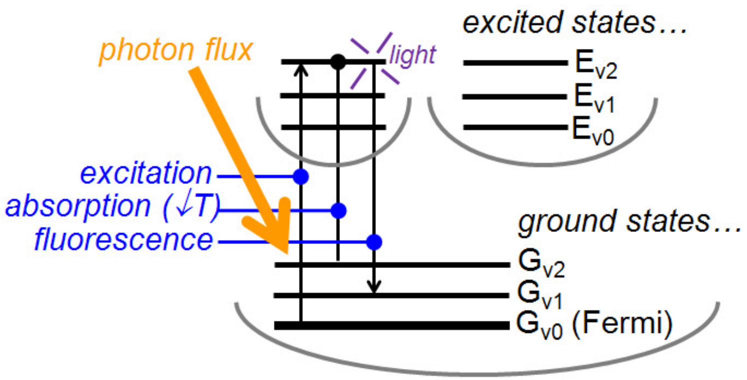
**there is a peak @ 525 nm!*

**avoid harmonics (λ_h=2λ) e.g., 955 nm*



M and X fluorescence spectra for "yellow" specimen

The "Mechanics" of Fluorescence



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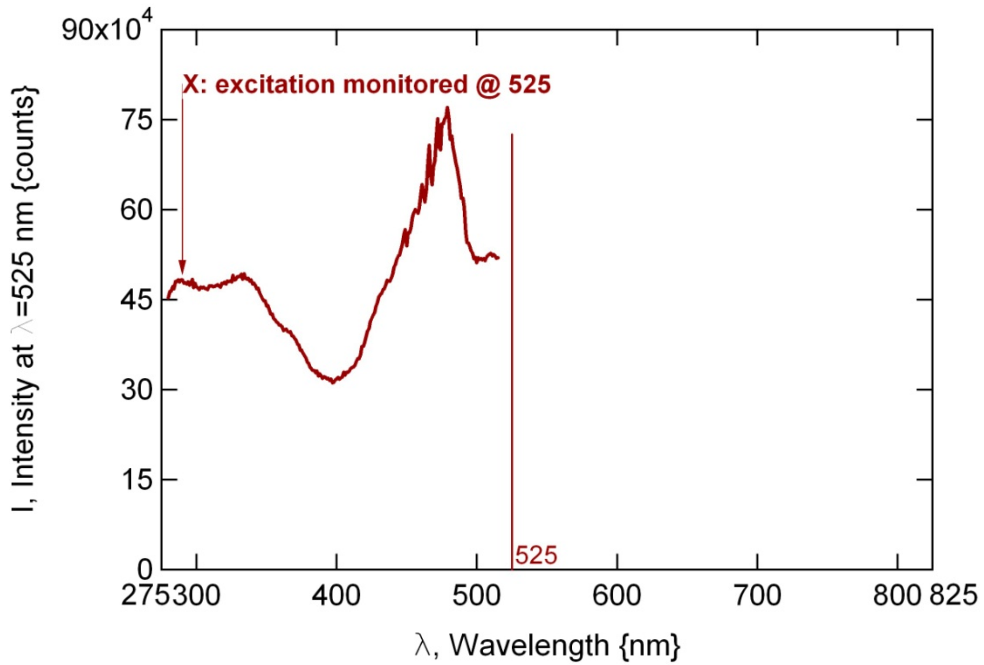


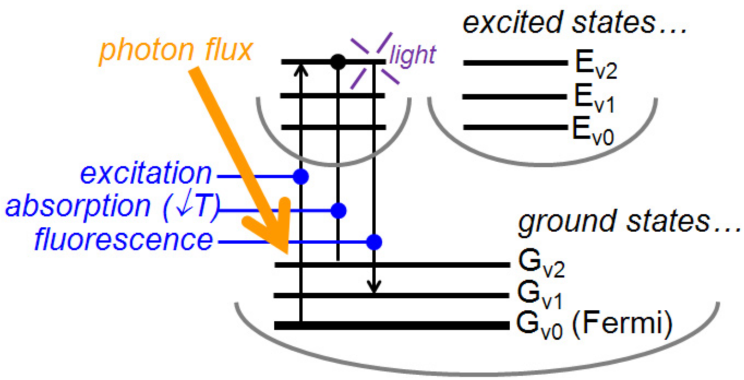
2. Measure at 525, excite from 280-515

M and X fluorescence spectra for "yellow" specimen

**there are peaks at 285, 330, and 477.5 motivating emission @ 525 nm*

**iterate for excitation peaks @ 280, 330 nm (emission spectra)*

The “Mechanics” of Fluorescence



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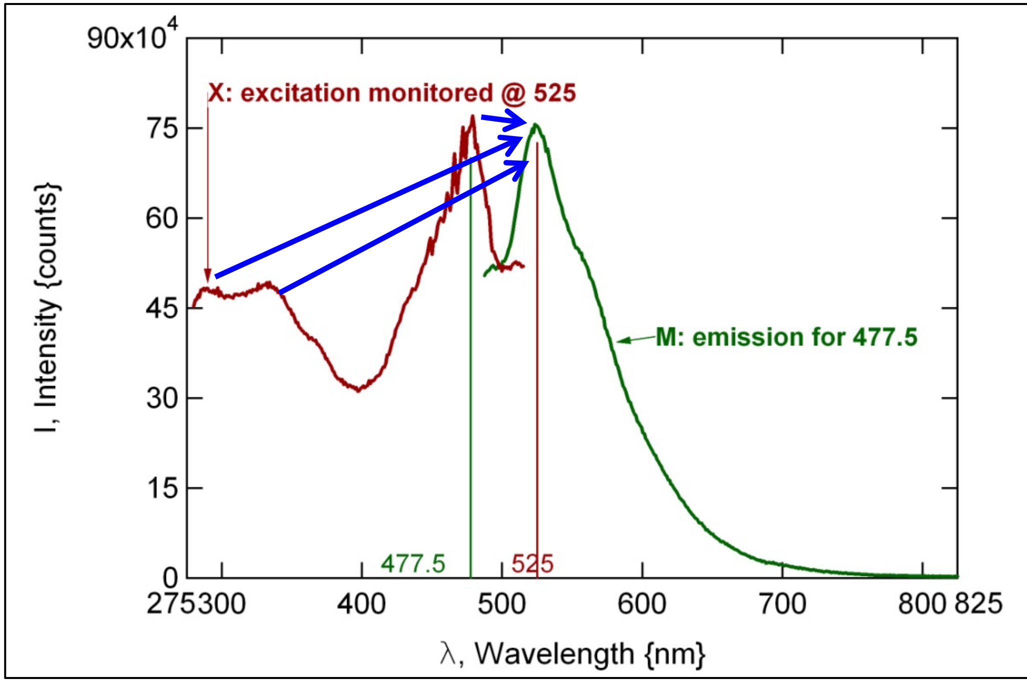

M and X fluorescence spectra for “yellow” specimen

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**there are peaks at 285, 330, and 477.5 motivating emission @ 525 nm*

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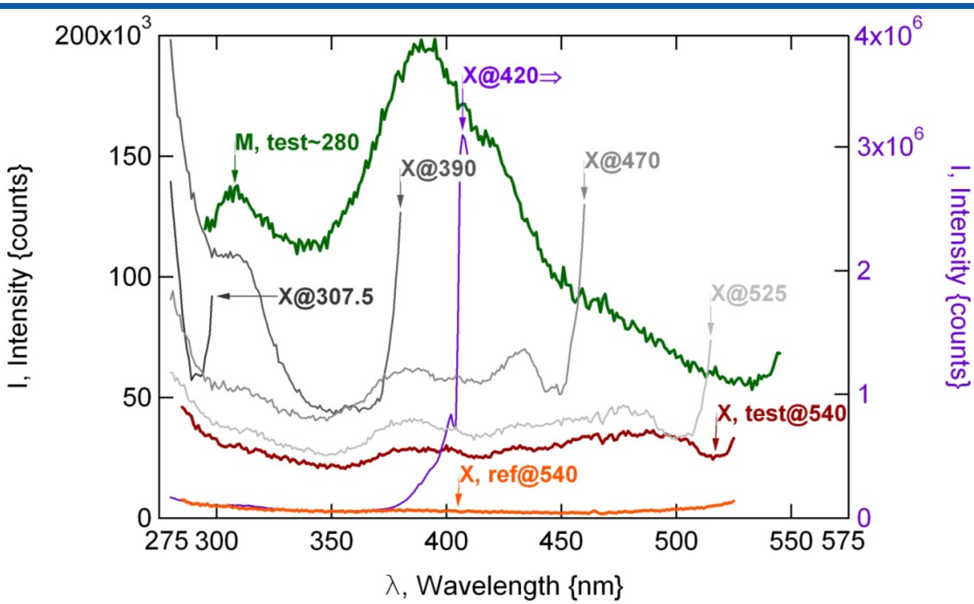
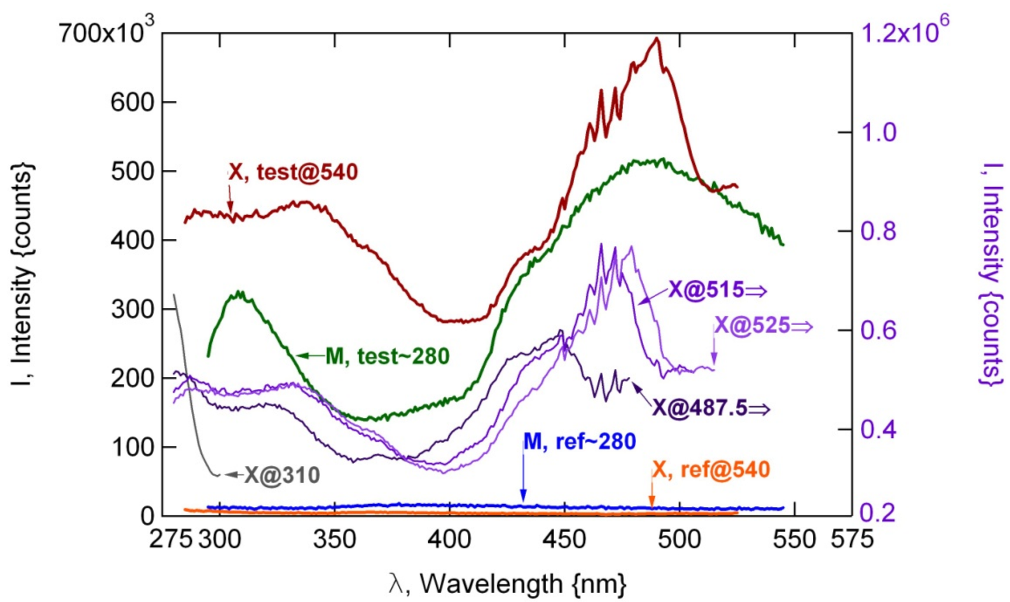
Fluorescence Suggests Additives Distinguish Formulations



Emission (M) and excitation (X) spectra for "hazy" specimen

- Modest fluorescence observed in test relative to unaged reference-specimens
- Different fluorescent spectra were observed for (2) "hazy" and (10) "yellow" specimens
- Different spectra suggest change in electronic structure … is there a connection to degradation mechanism?

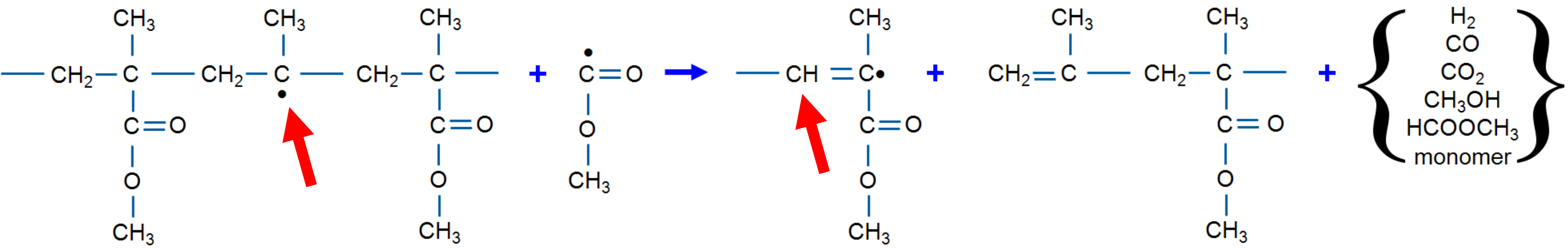
- In particular the excitation @ 310nm is correlates to the action spectrum for PMMA identified in the literature
- No fluorescence is observed for MMA from 250-550 nm



M and X fluorescence spectra for "yellow" specimen

The Degradation Mechanism of Photolysis

- Dominant mechanism suggested in literature & suspected here



(after Aboulezz and Waters, "Studies on the Photodegradation of Poly(Methyl Methacrylate)", 1978)

- Random main chain scission by UV (photolysis) $\Rightarrow M_w$ therefore T_g reduced

- T_g reduced ↓~5°C after 18 years outdoors

L.G. Rainhart & W. P Schimmel, SAND 74-0241, 1974.

- $M_w \downarrow$ likewise affects mechanical durability: $K_{IC}\downarrow \Rightarrow \sigma_f \downarrow$ … $\partial a/\partial N \uparrow$

- E could be affected if M_w severely compromised

Details of Future Work (2nd Round of Study)

Goals:

- Quantify the acceleration factor: aging indoors vs. outdoors (FL, AZ, CO)
- Identify the expected life of PMMA in these key locations
- Understand the degradation mechanism(s) [if lifetime can be improved]

Noteworthy specimens:

- With & without UV stabilizer (compare to academic literature)
- Residual monomer (suspected to facilitate degradation)
- High vs. low M_w (mechanism of photolysis)
- Fabrication method (cast vs. extruded vs. molded)
- Co-monomer content (methyl acrylate and ethyl acrylate)
- Polycarbonate (benchmark a competing material)
- SoG (benchmark a competing technology)

Summary of Results

Weathered PMMA for CPV: 2 specimen morphologies have emerged

Not distinguished by:

- surface morphology (roughness increased in both)
- contact angle (decreased for both)
- mass (decreased for both)
- thermogravimetry (depolymerization not suspected)
- XPS (O↑ [hydroxyl formed], C↓; removable N, F, Si)

Distinguished by:

- transmittance & YI ("hazy" vs. "yellow")
- indentation (modulus decreased for yellow)
- fluorescence (distinction motivated by additives)

Consistent with random chain scission for formulated PMMA

(will verify contributing factors)

Acknowledgements

•NREL: Mike Kempe, Lynn Gedvilas, Daryl Myers, John Pern, Dan Ruddy, Matt Beach, Christa Loux, Marc Oddo, Bryan Price, Kent Terwilliger, Robert Tirawat

•Others: Ralf Leutz, Hans Philipp Annen (Concentrator Optics Inc.), John Wiedner, Michael Longyear, Scott Steele (Arizona Public Service, S.T.A.R. facility)

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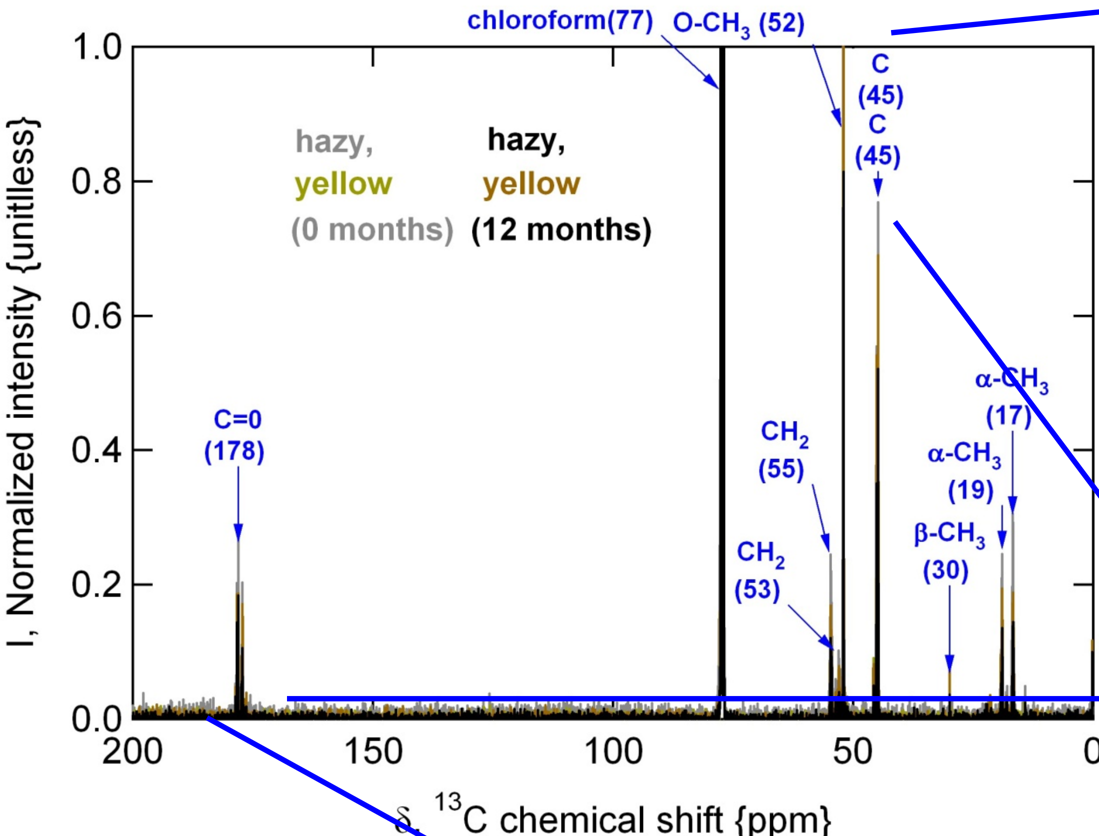
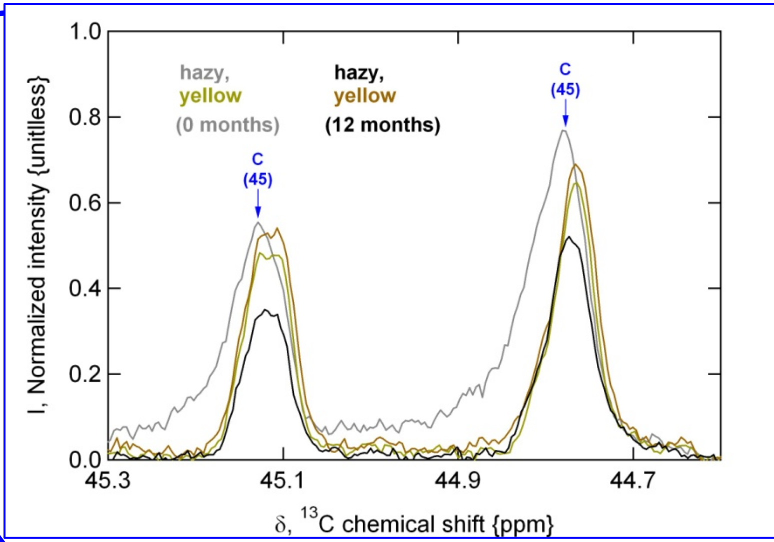
NSF National Science Foundation WHERE DISCOVERIES BEGIN

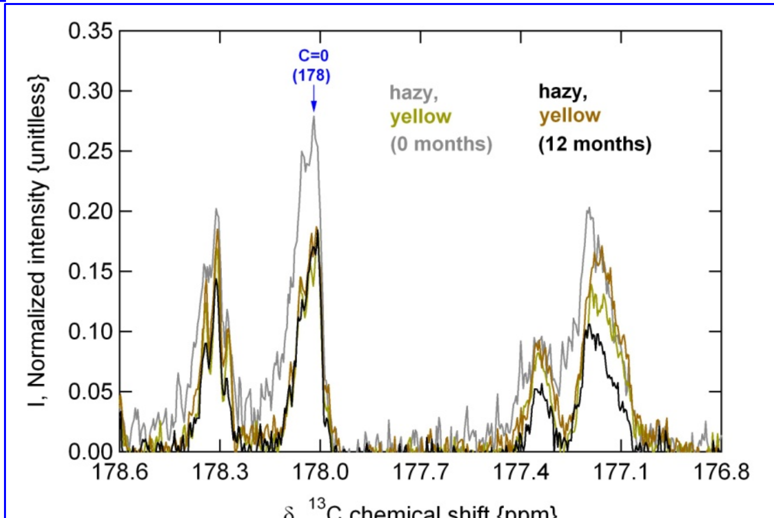
Nuclear Magnetic Resonance (NMR): ^{13}C Data





Close-up of C region

Close-up of C=O region

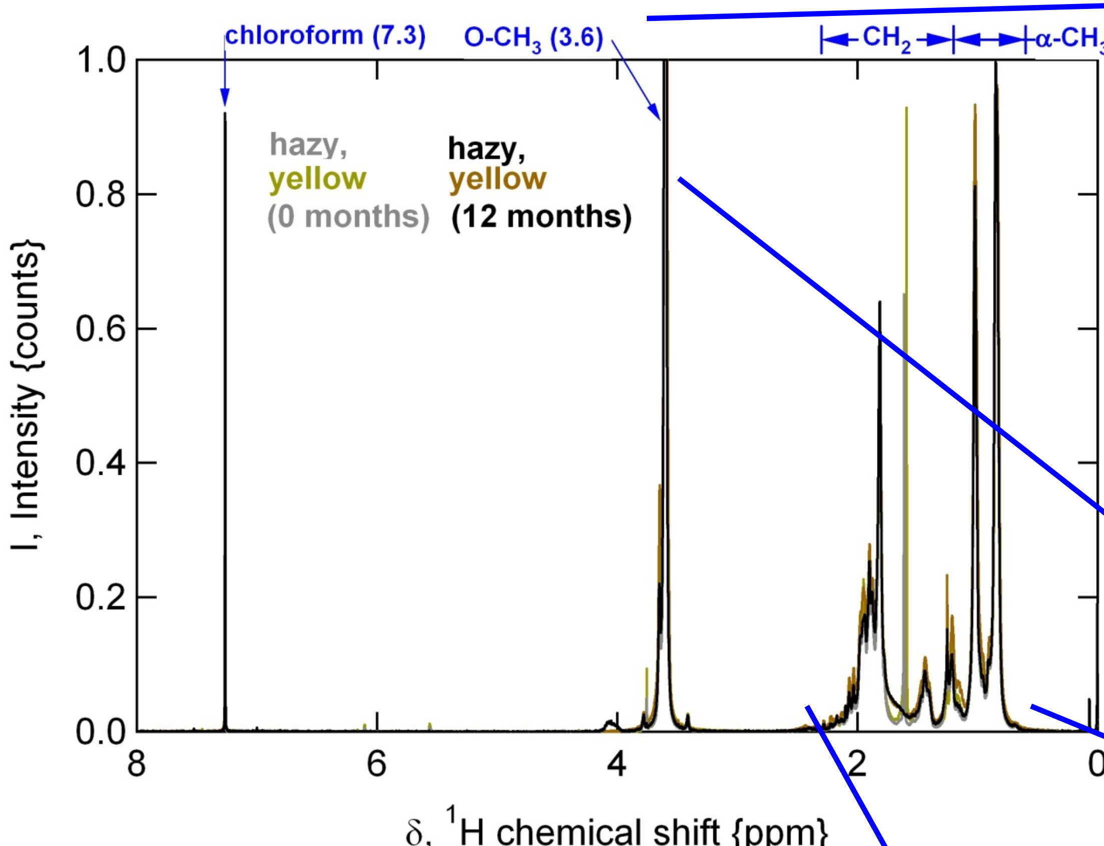


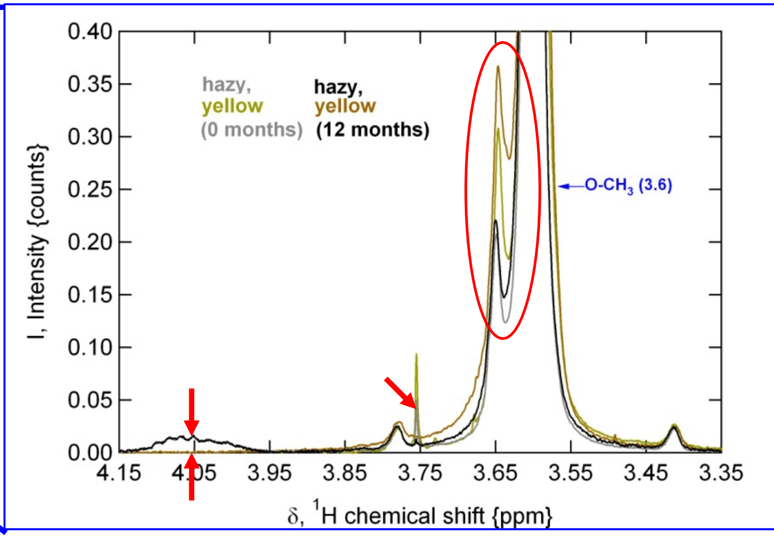
- Solvent: deuterated chloroform
- hazy: -appears- δ shifted right (smaller ppm);

yellow: no δ shift

No real shift for hazy, rather…
accuracy of the lock to the marker species

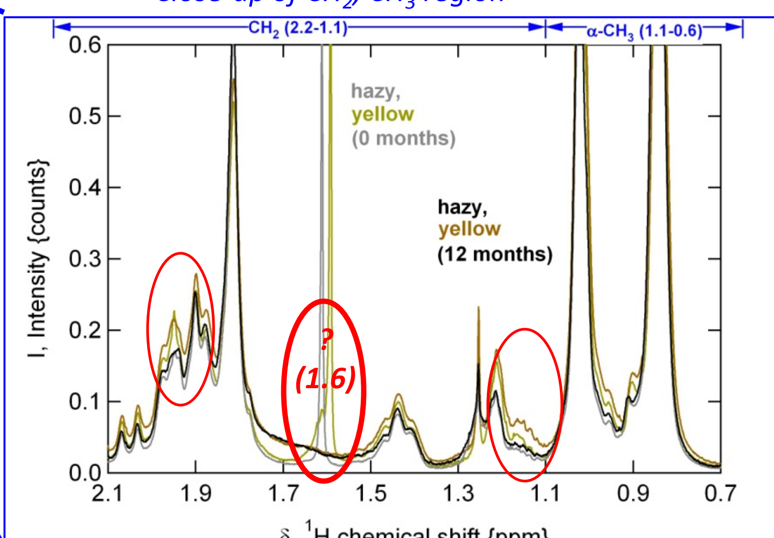
Nuclear Magnetic Resonance (NMR): ^{1}H Data





Close-up of O-CH_3 region

Close-up of CH_2, CH_3 region



- CH_2, CH_3 region: random tacticity
- no major new peaks: no cross-linking
- hazy only: additive peak @ 4.05 ppm
- h & y: additive peak @ 3.75 ppm lost by aging
- h & y: @1.6 ppm, lost w/ aging
  from formulation additive
- y: broader peaks suggest shorter chains