Durability of Poly (Methyl Methacrylate) Lenses Used in Concentrating Photovoltaics

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NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.
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

- Test instrument: ATLAS Ci4000 Weather-ometer (Xenon-arc lamp @ 2.5x UV suns. Chamber @ 60°C/60%RH); *1 exception

<table>
<thead>
<tr>
<th>DESCRIPTION</th>
<th>SPECIMEN TYPES</th>
</tr>
</thead>
<tbody>
<tr>
<td>stock (unpatterned)</td>
<td>11</td>
</tr>
<tr>
<td>linear focus lens</td>
<td>1</td>
</tr>
<tr>
<td>spot focus lens</td>
<td>8</td>
</tr>
<tr>
<td>veteran (fielded) lens</td>
<td>3</td>
</tr>
</tbody>
</table>

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

Test specimens (4.4 x 6.7 cm²)
Details of NREL Screen Test

- **Measurands:**
  - **Periodic**
    - optical appearance (photograph)
    - optical transmittance (hemispherical)
    - mass
    - contact angle (sessile drop, H₂O on 1st surface)
  - **“End of life”**
    - haze (from direct transmittance)
    - prism facet geometry (lenses: section then SEM)
  - surface morphology (SEM or AFM)
  - indentation (Vicker’s hardness, toughness)
  - rheometry ($E'$, $E''$, $T_g$)
  - XPS or ESCA (surface chemistry, before & after cleaning)

- **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
Transmittance is Reduced by Aging

- "Optical Durability" = transmittance as f[t]
- Lambda 900 (Perkin-Elmer) spectrophotometer (w/ integrating-sphere)

Measured transmittance at 0, 6 months for best and worst sheet stock specimens

#1 (least-affected):
- no UV absorber, other additives
- set#1 (YI=0.4)

#11 (most-affected):
- set#11 (YI=28.3)

#8 (increased T):
- loss of additive/chromophore production
- set#8 (YI=5.2)
Effect of H₂O on Transmittance

- Specimens maintained for >1 month in dry box (≤0.1 ppm H₂O) or DI
- Traditional λ’s to estimate H₂O dissolved in polymers: 1.9, 2.7 µm


- Verified in direct- & hemispherical-T measurements
- H₂O solubility (≤2.5 wt.% ) primarily affects unharvested IR λ’s
- UV & vis (PV) unaffected; weathering results are not H₂O absorption!
Transmittance is Reduced by Soiling

- Contamination absorbs, scatters, and back-reflects light
- Effect most significant as $\lambda \downarrow$ (Mie scattering: $0.6/n<\pi\varnothing/\lambda<5$)

*Remember also:

- Direct light (CPV) more severely affected than hemispherical (FP-PV)
- Optical durability & soiling affect color balance, e.g. top-cell limited I

Measured transmittance, as-received and after cleaning for 22, 8 year old Fresnel lens specimens

Optical durability $T \downarrow 6-29\%$

$\varphi_PV \downarrow 15, 2, 1\%$

$\varphi_{UV} \downarrow 29, 6, 2\%$
Yellowness Index (YI) Distinguishes Formulations, Aging Methods

- YI (ASTM E313 & E308 [D65 source, 10° observer]) quickly quantifies degradation

- **Range of results, depending on material formulation. Not all the same!**
- **Damage rate indoors/outdoors = 220x for same (unstabilized) material**
- **Suggests synergy between UV, temperature, and/or humidity**

*YI determined from raw hemispherical transmittance measurements (proportional to visual appearance). *Outdoor YI plotted for time only.*
Volatile Species (Mass Loss) Resulting From Aging

- Non-linear asymptotic trend (as great as 1.27%)
- Process of outward diffusion? (Degradation products and/or additives).
- Literature: 4.4% mass loss for chain scission (70 hours @ 300 nm)

*Abouelezz and Waters, Studies on the Photodegradation of Poly(Methyl Methacrylate), NBSIR 78-1463, (1978), 1-55.*

- If photolysis, then volatile content proportional to cumulative damage

mass loss determined, starting after 1 month indoor aging.
### The Expected Correlation Between YI, and UV/ PV Flux

- Table summarizes the 9 *standard* transmitting stock specimens

<table>
<thead>
<tr>
<th>CHARACTERISTIC</th>
<th>UNIT</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV photon flux</td>
<td>γ⋅m⁻²⋅s⁻¹</td>
<td>723±3</td>
<td>724±3</td>
<td>721±4</td>
<td>725±3</td>
<td>719±6</td>
</tr>
<tr>
<td>UV energy flux</td>
<td>W⋅m⁻²</td>
<td>14±8</td>
<td>17±8</td>
<td>17±7</td>
<td>17±8</td>
<td>16±9</td>
</tr>
<tr>
<td>IR energy flux</td>
<td>W⋅m⁻²</td>
<td>7±0</td>
<td>7±0</td>
<td>7±0</td>
<td>7±0</td>
<td>7±0</td>
</tr>
<tr>
<td>YI</td>
<td>unitless</td>
<td>-1.2±0.1</td>
<td>0.2±1.4</td>
<td>0.6±1.4</td>
<td>1.2±1.7</td>
<td>3.3±2.9</td>
</tr>
<tr>
<td>λₖₑᵤₜ⁻₀</td>
<td>nm</td>
<td>363±36</td>
<td>369±28</td>
<td>370±28</td>
<td>364±33</td>
<td>379±24</td>
</tr>
<tr>
<td>Δm, MASS LOSS</td>
<td>%</td>
<td>N/A</td>
<td>0.000±0.000</td>
<td>0.408±0.048</td>
<td>0.646±0.059</td>
<td>0.705±0.074</td>
</tr>
<tr>
<td>Θ, CONTACT ANGLE</td>
<td>degrees</td>
<td>N/A</td>
<td>66±1</td>
<td>60±1</td>
<td>58±2</td>
<td>61±4</td>
</tr>
</tbody>
</table>

#### Contact Angle is Reduced by Aging

- Θ relates to accumulation and retention of particulate matter
- Θ: 66 → 58 → 43° (for unaged → aged → veteran)
- More easily cleaned, but more rapid to accumulate soil
- Partially restored by cleaning at 6 months ... surface accumulation?
Mechanical Damage from Aging: Cracks and Haze

Cracks:
- Radial cracks in domed spot-focus lens (85°/85%RH)
- Cracks could motivate failure on impact; could grow via fatigue

Haze:
- As-received veteran specimens demonstrate haze
- Surface erosion or microcracks detrimental to direct solar flux
Surface Roughness Identifies the Causes of Haze

- 90x90 & 20x20 $\mu$m² topography atomic force microscopy (AFM) scans
- Largest features (width/depth): 3850/340, 1540/88, 2350/72 nm
- Veteran specimens:
  - (a) abrasion/erosion,
  - (b) scratches from cleaning,
  - (c) embedded material (Si) in set-B
- Erosion much less significant for mounting $\geq 2$ m (less airborne PM).


\[ \begin{align*}
R_a - R_{\text{rms}} & \quad 3 \pm 4 \\
R_{\text{pv}} & \quad 66 \\
R_a - R_{\text{rms}} & \quad 116 \pm 149 \\
R_{\text{pv}} & \quad 1,108 \\
R_a - R_{\text{rms}} & \quad 46 \pm 68 \\
R_{\text{pv}} & \quad 1,178 \\
R_a - R_{\text{rms}} & \quad 16 \pm 27 \\
R_{\text{pv}} & \quad 733
\end{align*} \]

(a) set#1  
(b) set-B  
(c) set-C  
(d) set-D

Roughness of unaged stock specimen relative to as-received (but cleaned) veteran specimens (27, 8, 8 years service)
A Summary of Photolysis From the Literature

- Dominant mechanism suggested in literature & suspected here

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

- \( T_g \) reduced \( \downarrow \sim 5^\circ C \) after 18 years outdoors

- \( M_w \downarrow \) likewise affects mechanical durability: \( K_{IC} \downarrow \Rightarrow \sigma_f \downarrow \ldots \partial a/\partial N \uparrow \)
Innovation for Our Energy Future

Fourier Transform Infrared (FTIR) Spectroscopy

* May identify changes in the molecular structure, but not vulnerability

- Magnitude major peaks reduced, consistent with chain scission
- All major peaks related to ester (C=O), (C-O), or methylene (-CH₂-)
- Technique not recommended for regular diagnosis of PMMA

Surface spectra of unaged and aged specimens (set#11) obtained using FTIR-ATR relative to reference spectrum for PMA monomer.
The Progress Report ... (Summary)

- Transmittance:
  - UV cut-on $f$, spectral bandwidth compromised by aging
  - Notable IR absorption @ 1415, 1907, 2697 nm from H$_2$O
  - Soiling $\Rightarrow$ trends as in optical durability. (Blue) current limited?
- Y1: This figure of merit may imply a synergy between UV, T, and/or RH
- Mass loss (on order of x%) may result from photolysis
- $\Theta$ decreases with time. Formation of water soluble surface layer?
- Erosion, scratching of surface quantified for veteran specimens
- FTIR: changes after 6 months consistent with chain scission... will verify

"Theme": from change in characteristics examined, photolysis suspected from the literature ... will verify in future with “end of life” (12 month) measurements

*Future: Work with a SOG lens? Your participation solicited for round 2!
Acknowledgements

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See also:

Questions

• Have you specifically studied the affects of cleaning (abrasion)?
• What about acid rain (the chemistry of outdoor rain)
• What can be learned/said about the (chemistry/additives/mW) most durable formulations
• Is there a change in the refractive index?
• XXX
• XXX
• XXX
• XXX
• XXX
Thermal Decomposition

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

(Chemical structure and text)

- Occurs readily for T>200°C
- Synergistic effect w/ irradiation (UV) ⇒ occurs at T<200°C
- Many classic studies of $E_a$ vs. heating rate, atmosphere
  - $O_2$ suppresses decomposition

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