LONG-TERM PHOTOTHERMAL/HUMIDITY TESTING OF PHOTOVOLTAIC MODULE POLYMER INSULATIONS AND COVER FILMS

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ABSTRACT
The life expectancies of Tedlar and other polymer films considered for use as cover materials in terrestrial photovoltaic modules were investigated by exposing them for more than 13,000 hours on an outdoor test stand and for up to 10,000 hours in several accelerated multi-stress environments. Visual observations, and diagnostic analyses of weight and mechanical strength losses, were periodically conducted to assess the nature and rate of degradation of mechanical properties and to assess the effects of film thickness and UV stabilizer content. Spectroscopic analyses of pristine and degraded materials linked weight and mechanical properties losses to the underlying photo-thermal/photo-oxidation chemistry.

Heavy doses of UV stabilizers prolong, and elevated temperatures shorten, the useful life of these materials; humidity plays only a minor role. The most heavily UV-stabilized films are expected to usefully operate in a PV module front-cover application for only 5 to 10 years. The performance of none of the tested films appears consistent with the 20-30 year life goals of the PV industry.

INTRODUCTION
A number of polymeric films are in use or are under consideration for use as front and/or back cover materials for terrestrial PV modules. These include transparent front-cover candidate films such as Tedlar, i.e., poly(vinyl fluoride) - PVF, and assorted other translucent and opaque back-cover candidate films such as polyesters, poly(vinyl chlorides), and acrylics.

Prior field experience with crystalline-silicon (C-Si) cell modules has taught that, in as little as 18 months of exposure to combined ultraviolet and thermal environments, polymeric film materials may degrade by discoloration (yellowing, browning), embrittlement, and cracking. Cracking and embrittlement compromise the structural and protective features of the material; in a front-cover application, discoloration lowers optical transmission, thereby reducing the solar energy available for conversion to electricity.

Because module cover materials are susceptible to environmentally induced degradation, it is important to subject candidate materials to accelerated environmental stress testing in order to examine the interplay of environmental and material synergisms and to determine, in a relatively short time, failure mechanisms and degradation rates that may become apparent only after long-term exposure in the applications environment. This requires testing with combinations of environments -- thermal, UV, and humidity -- and with material combinations and constructions that contain the materials synergisms of real PV modules. Additional single-environment and single-material tests are often useful to allow detailed property characterization that is difficult or impossible to accomplish in a combined environment or in a composite sample.

TEST PROGRAM
Environments
In recognition of these issues, a comprehensive parametric test program was structured based on temperature/ultraviolet/humidity (T/UV/RH) combined-environment testing and using parametric test levels to provide quantitative data on the acceleration factors associated with each environmental ingredient. The three combined environments -- 65°C/85%RH/1sunUV, 85°C/10%RH/1sunUV, and 85°C/85%RH/1sunUV -- were achieved using a 3' x 3' x 3' temperature/humidity-controlled Bemco oven retrofitted with a water-cooled, 2000 watt medium-pressure mercury vapor lamp capable of emitting 1-sun of UV irradiance at the sample plane, Figure 1.

Fig 1. Controlled Environment Test Facility.
Elevated temperature provided the principal accelerating environment. Previous experience with polymer materials reveals that many chemical reaction rate increases with temperature in accordance with the classical Arrhenius relationship -- log reaction rate inversely proportional to inverse absolute temperature \[\text{reaction rate} \propto \frac{1}{T}\]. Often this rate dependence is well approximated as a rate doubling for each 10°C increase in temperature [2-4]. In this test program, however, the rate dependence was determined to be an increase by a factor of 1.6 per 10°C increase in temperature. Since the relevant temperature acceleration factor is dependent on the relationship between the nominal operating cell temperature (NOCT) for PV modules in the field, and the exposure temperature (T) in the test chamber, the thermal acceleration factor for exposure at temperature T can be estimated as \(1.6^{(T - \text{NOCT})/10}\). Parametric test levels of 65°C and 85°C were chosen to provide a modest acceleration of the reaction rates, while trying to avoid spurious reactions that might occur at higher temperatures. Using two temperatures allowed the actual thermal acceleration factors of the observed degradation to be determined.

Because previous JPL studies had shown that dependence on UV flux level can be highly non-linear and complex [4-6], it was decided to conduct most testing at a nominally unaccelerated UV flux level of \(I_{\text{sunUV}}\), defined as the amount of UV present in 100 mW/cm² of total solar irradiance on a clear day. This quantity is approximately 4 mW/cm² or 4% of the total solar irradiance. A constant 24-hour-a-day exposure at this flux level has been correlated, in a previous JPL study [4,5], to the total dosage of UV at various U.S. sites by processing site-specific SOLMET weather data on an hourly basis [7]. For this study, however, we shall be content to assume that 24 hours of \(I_{\text{sunUV}}\) exposure represents a time (t) acceleration of 5.

To allow explicit diagnosis of the UV dependence of certain reactions, such as weight loss, a number of samples were also aged in dark, dry, "non-UV" ovens (85°C/3%RH, 100°C/2%RH, and 85°C/vacuum).

Because the synergistic effects of humidity were unknown, two broadly spaced humidity levels were used -- 10%RH and 85%RH. In hindsight this proved fortunate, as very little humidity sensitivity was observed: hence, \(AC_{\text{RH}} = 1\).

In summary, Equation 1 lists the nominal acceleration factors to serve as a basis for estimating experimental run times and field longevity:

\[
AC = 1.6^{(T - \text{NOCT})/10}
\]

\[
AC_{\text{UV}} = 1 \quad AC_{\text{RH}} = 1 \quad AC_t = 5 
\]

If the individual degradation mechanisms are mutually independent, then the Arrhenius formalism permits the multiplication of the corresponding acceleration factors:

\[
AC_{\text{TOTAL}} = AC_t \cdot AC_{\text{UV}} \cdot AC_{\text{RH}} \cdot AC_t
\]

Test Specimens

The various polymer film materials tested, along with their added UV stabilizer contents and thicknesses, are enumerated in Table 1.

The raw PVF films were cut into two geometric configurations -- 0.75" x 4" samples for weight loss determinations, and "dog-bone"-shaped samples with 2" x 0.40" test sections for monitoring mechanical properties (force-elongation data).

To understand material synergisms, a set of module-like test coupons was fabricated by laminat-

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Table 1

<table>
<thead>
<tr>
<th>Manufacturer's Designation</th>
<th>UV Screen Weight Percent</th>
<th>Thickness (mils)</th>
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<tr>
<td>200-XRB-165-PT</td>
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<td>4</td>
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<tr>
<td>400-GS-20-SE</td>
<td>1.0</td>
<td>4</td>
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<table>
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<th>Manufacturer's Designation</th>
<th>Generic Polymer</th>
<th>Thickness (mils)</th>
</tr>
</thead>
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<td>A. Mylar</td>
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</tr>
<tr>
<td>B. Metallized Mylar</td>
<td>terephthalate</td>
<td>2/1</td>
</tr>
<tr>
<td>C. Fasson 890</td>
<td>poly(vinyl)</td>
<td>3</td>
</tr>
<tr>
<td>D. Fasson 1900</td>
<td>chloride</td>
<td>3</td>
</tr>
<tr>
<td>E. Fluorex</td>
<td>acrylic copolymer</td>
<td>3</td>
</tr>
<tr>
<td>F. Korad 63000</td>
<td>acrylic</td>
<td>3</td>
</tr>
</tbody>
</table>
ing the PVF test films with ethylene vinyl acetate (EVA) on a 4" x 4" piece of glass. Additional samples consisted of small sections of a 2' x 4' amorphous-silicon (a-Si) PV module with a PVF front cover, and of a glass-superstrate a-Si module over-covered with clear Tedlar/EVA. To provide a calibration of the test environment, small samples were also included from an available unweathered Tedlar-covered batten-and-seam module identical to those field weathered at the Southwest Residential Experiment Station several years ago. In this rooftop weathering environment, this module type failed in 18 months due to severe cracking of the Tedlar.

The last group of specimens consisted of assorted film/adhesive systems under consideration as rear cover materials for photovoltaic modules. The UV test environments used here represent a significant acceleration for these materials that are normally only exposed to reflected UV from surrounding surfaces. Rear cover samples consisted of both 4" x 4" module test coupons with polymer back covers, and a variety of self-adhering films laminated on 4" x 4" square aluminum substrates.

Diagnostic Tests

Three types of diagnostic tests were performed on the 0.75" wide samples. Weight loss measurements were made on the samples exposed in the 85°C/vacuum, 85°C/10%RH/1sunUV, and 100°C/2%RH environments. These tedious measurements were not conducted on samples exposed to the 65°C/85%RH/1sunUV and 85°C/85%RH/1sunUV environments. Rather, these "dog-bone"-shaped specimens were subjected to a pull test, in which the elongation-to-break and the peak force exerted to achieve rupture were measured, Figure 3.

Because of the inability to directly measure the mechanical and optical properties of the 4" x 4" laminated Tedlar/EVA/glass specimens, a special ball-detent test was developed to qualitatively measure the onset of brittleness, Figure 4. The ball "push test", developed at JPL, uses a steel-ball tip (0.0625" diameter) through which a known force is applied to the PVF film. A pristine sample responds by forming a depression in the laminate as the forced ball depresses the PVF film into the EVA. An exposed sample will form a smaller depression and will exhibit concentric cracks around and into the circular depression. The degree of sample degradation was measured by the amount of force required to cause the cracking.

TEST RESULTS

Visual Observations

The bare films in the 85°C/10%RH/1sunUV environment exhibited curling, cracking, and discoloration. The 4" x 4" laminated samples and module coupons exhibited cracking and crazing of the PVF-film front covers, Figure 5. Among the back cover film candidates, puckering of the metallized Mylar film and cracking of the Fasson 1900 PVC film has occurred in the 85°C/10%RH/1sunUV environment after 2952 hours. After 4080 hours at 85°C/85%RH/1sunUV, the Fasson 890 exhibited obvious cracking and the Fluorex acrylic copolymer film has delaminated from its substrate. The films exposed outdoors for 13056 hours were dirty but otherwise exhibited no obvious signs of embrittlement.

Weight Loss Measurements

In the 85°C/10%RH/1sunUV and 85°C/85%RH/1sunUV environments the PVF-film samples steadily lost weight at approximately the same rate, while in the non-UV ovens, an initial weight loss was followed by a long period of no weight loss, as typically depicted in Figure 6. The performance of the candidate back-surface films was similar -- samples in the UV environments lost considerably more weight than did samples in the non-UV environments. In
Fig 5. Laminated 4"x4" Tedlar/EVA/a-Si/Aluminum Coupon with Surface Cracks and Crazing after Test-Chamber Exposure.

Fig 6. Weight Loss vs Exposure Time for 0.75"x4" Tedlar Samples.

For each PVF material the pull-test data were reduced to graphs of rupture force and elongation-to-break versus time; the variation of these parameters with time was approximately linear but the data scatter was considerable. From these graphs, plots of rupture stress versus strain-at-break at the various exposure times were generated. Typical plots for the samples in the 85°C/85%RH/1sunUV environment are presented in Figures 7 and 8. We see that for fixed exposure conditions, the rupture stress and strain-at-break decrease with time, i.e., the energy to rupture decreases as the exposure time increases, but the ratio of rupture stress to strain-at-break, i.e., the rupture modulus, remains constant. Figure 7 shows the variation of mechanical strength with thickness (thinner films embrittle more rapidly with exposure than their thicker counterparts), and Figure 8 its variation with UV content (the higher the UV stabilizer content the slower the rate of embrittlement). The data in Figure 7 may also suggest that thinner films have larger rupture moduli than thicker films. It has additionally been observed that the rupture modulus is larger at higher temperatures.

Push-Test Measurements

An unexposed laminated Tedlar/EVA/glass module—like test coupon, when push-tested, shows a smooth depression with a gently-rolling edge. Samples exposed briefly, when push-tested, exhibit faint concentric rings (cracking) within the depression. The longer the exposure, the more numerous and noticeable are the cracks, now running in every particular, the poly(vinyl chloride) films experienced the greatest weight loss and, in fact, exhibited the most obvious visual deterioration.

Pull-Test Measurements

stress to strain-at-break, i.e., the rupture modulus, remains constant. Figure 7 shows the variation of mechanical strength with thickness (thinner films embrittle more rapidly with exposure than their thicker counterparts), and Figure 8 its variation with UV content (the higher the UV stabilizer content the slower the rate of embrittlement). The data in Figure 7 may also suggest that thinner films have larger rupture moduli than thicker films. It has additionally been observed that the rupture modulus is larger at higher temperatures.

Fig 7. Rupture Stress vs Strain-to-Break at Various Exposure Times for 5% UV-Stabilized Tedlar Films of Various Thicknesses.

Fig 8. Rupture Strength vs Strain-to-Break at Various Exposure Times for 0.004" Tedlar Films of Various UV Screening Levels.
direction, and the more cliff-like become the walls of the depression. In summary, the visual effects noted are a function of both sample exposure time and the amount of force exerted.

Figure 9 provides, for each UV exposure environment, a time line of observed effects of the push test on the Tedlar/EVA/glass samples, including the first observation of natural cracking, i.e., cracking not induced by the push-test apparatus.

In summary, the Tedlars that contain the least amount of UV screening agent (400-SG-20-SE and 400-XRB-177-SA, Table 1) are the same ones that exhibit the greatest weight loss and the greatest loss of mechanical strength.

Photodegradation of Tedlar

Pure PVF has very low UV absorbance; however, manufacturing impurities and the thermal formation of double bonds result in UV absorbing groups. These groups then participate in reactions involving UV and oxygen that chemically alter the polymer structure [9]. These reactions result in the breaking of polymer bonds, followed by embrittlement, and the formation of free radical catalysts. These chemical processes may also reverse the discoloration seen in thermally degraded films due to oxidation of the double bonds.

Typically, loss of tensile elongation is the first mechanical symptom of aging, which is then followed by cracking.

Photostabilization of Tedlar

Unscreened Tedlar degrades rapidly in a UV environment [10]. Most unpigmented Tedlar films incorporate a UV screening agent, typically a low molecular weight polymer containing hydroxybenzophenone absorbing groups, to absorb UV energy and dissipate it as heat before any degradation reactions can occur.

UV stabilizer levels in PVF films typically range from 0.1% to 0.5% by weight. The particular PVF films investigated in this research featured unusually high levels of UV stabilizer (1% - 5% by weight) added to them during the fabrication process.

INTERPRETATION OF EXPERIMENTAL RESULTS

Visual Observations

The observed curling in partially delaminated or free-standing films is caused by shrinkage of PVF induced by exposure to high temperature. Because thermal stresses differ in the machine and transverse directions, an unsupported sample will tend to curl.

The thermally induced dehydrofluorination and autocatalysis reactions in PVF films produce conjugated double bonds on the polymer main chain which, as previously explained, are responsible for the observed discoloration.

Embrittlement and cracking are due in part to photo-oxidation that results in polymer chain scission and in part to differential shrinkage. As the totally edge-clamped or fully bonded film heats, it shrinks and, not being free to curl, will crack instead.

Typical observed response of PVF material to a thermal-only environment is initial weight loss followed by a long period of no weight loss, which indicates that a volatile component, most likely the residual processing solvent, is being removed early in the heat exposure. Samples in the 85°C/10%RH/IsunUV environment undergo continual weight loss, Figure 6, suggesting that either humidity- and/or UV-induced effects are occurring. Humidity-related weight loss effects were not ob-
served, so we conclude that the observed weight loss profile is most probably the result of initial loss of residual extrusion solvent followed by photo-oxidative loss of UV absorber.

On the other hand, the observed first occurrences of various loss-of-mechanical-strength indicators for materials exposed to the 85°C/10%RH/1sunUV and 85°C/85%RH/1sunUV environments, as recorded in the timeline of Figure 9, shows a significant humidity contribution to the mechanical degradation of Tedlar 300-XRB-165-PT (5% UV stabilizer), a modest effect upon Tedlars 400-XRB-177-SA (2.5% UV stabilizer) and 400-SG-20-SE (1% UV stabilizer), and no effect on Tedlar 400-XRB-165-PT (5% UV stabilizer). There may be some humidity degradation, perhaps hydrolysis of the UV stabilizer, but there seems to be no solid correlation of humidity and loss-of-mechanical-strength indicators; hence, we adopt ACC_{\text{ST}} \approx 1.

Loss of Mechanical Properties

Pull Test - Arrhenius Analysis. The degradation chemistry induced in the accelerated test environments leads to the steady, linear decline of rupture strength and strain-to-break, as depicted in Figures 7 and 8. Tedlar 400-SG-20-SE, the material with the least amount of UV stabilizer, exhibited this behavior up to 2600 hours in the 85°C/85%RH/1sunUV environment and up to 6400 hours in the 65°C/85%RH/1sunUV environment, after which it ruptured at a mere touch. This film shows an "induction period" phenomenon -- clearly, two degradation rates are being observed. The first relates to gradual photo-oxidative loss of UV stabilizer; the second to thermal and photo-oxidative degradation of the PVF itself.

Such chemical reactions as these can generally be modelled as Arrhenius rate reactions. Arrhenius plots (log time versus inverse absolute temperature) of the pull-test data [11] shows that embrittlement occurs more rapidly the lower the material UV stabilizer content. The slopes of the Arrhenius plots reflect changes in time by factors ranging from 1.4 - 1.7 per 10°C, somewhat below the approximation engendered in the factor-of-two-per-10°C rule.

Push Test - Arrhenius Analysis. Arrhenius plots for the following three loss-of-mechanical-strength indicators observed during the push tests -- (1) the observation of the formation of concentric cracks at 20 lbs push-test force; (2) the observation of the formation of concentric cracks at 2 lbs push-test force; and (3) the observation of surface cracks and crazing without applied force -- reveal slopes corresponding to time acceleration factors ranging from 1.2 - 1.8 per 10°C, again below the approximation engendered in the factor-of-2-per-10°C rule.

SPECTROSCOPIC ANALYSIS AND RESULTS

Examination by UV/visible spectroscopy (300-700 nm) of pristine and aged PVF films reveals that the exposed films suffer a decrease in absorbance, clearly indicating loss of UV stabilizer, Figure 10.

Although difficult to quantify, the areas under the absorbance curves relate to the amounts of stabilizer present, which in turn correlates with the degrees of weight loss and mechanical failure.

Aged and unaged films were also examined by infrared spectroscopy (FTIR). The UV screening agent is known to be an acrylate polymer with a substituted hydroxybenzophenone group, and consequently has two characteristic ketone bands; the phenyl ketone band at 1624 cm^{-1} (benzophenone) and the ester ketone band at 1737 cm^{-1} (acrylic). Absolute absorbance varies with film thickness; consequently, changes are indicated by calculating the absorbance ratios. Comparison of the absorbance band ratios \( \frac{A_{\text{1624}}}{A_{\text{1737}}} \) in aged and unaged films shows that the phenyl ketone decreases in proportion to the ester ketone with continued exposure to the controlled environments, Figure 11. This suggests that scission of the protective hydroxybenzophenone group is occurring, which is followed by volatile loss from the film. These results are consistent with observations of weight loss, de-
creases in UV absorptance and deterioration of physical properties. Table 2 compares sample weight losses with the decreases in absorbance ratios.

**PERFORMANCE EVALUATION**

**Back-Cover Films**

Among the various back-cover films tested, only the Mylar polyester and the Korad 63000 acrylic polymer films appeared to weather unscathed the various exposures. The remaining films either embrittled and cracked or delaminated from their substrates in varying degrees.

**Tedlar PVF Films**

We consider here the utility of PVF films in a PV module front-cover application. What is desired in the way of performance from such a material is: (1) high transmission of energy across the wavelength band within which the underlying PV cells are strongly absorbing; (2) good environmental isolation characteristics; and (3) reliability and durability. The first criterion is compromised by the color-forming reactions that occur during the thermal decomposition of PVF films. PVF films are recognized as being good moisture barriers [12], but reactions leading to embrittlement and cracking will eventually compromise this property. The third criterion, reliability and durability, essentially imposes a useful lifetime requirement on the material for the intended application; in the case of PV modules, the commonly quoted design lifetime of a PV power generation station is 30 years.

In order to determine the lifetime of PVF films in a front-cover PV module application, it is necessary to assess the results of diagnostic tests performed on these materials in order to judge when these films have lost the ability to perform their intended function. For example, we may adopt as a criterion the loss of mechanical properties suggested by the observation of obvious surface cracks in the push-test diagnostics. In this case the films would no longer be able to keep moisture from contacting the module circuitry. In the 85°C environment, this occurs from about 8000 - 9600 hours. For an NOCT of 60°C (approximately the NOCT of PV modules in a free-standing application), the respective acceleration factors (Equations 1 and 2) are 16.2 and 6.3, which translates into about 6 - 8 years at a field site where the only environmental stresses are temperature, UV, and relative humidity.

If the performance loss criterion is the first observation of mechanical property loss (push test: 20 lbf), the exposure times are 2700 hours (85°C environment) and 5000 hours (65°C environment), corresponding to projected field lifetimes of 3 1/2 to 5 years. In the 85°C environments, serious weight losses occurred after approximately 2700 hours of exposure; thus these projected lifetimes may be regarded as correlating to loss of UV stabilizer with associated discoloration (reduction of transmittance) of the PVF films.

As previously stated, the particular PVF films investigated in this research featured unusually high levels of UV stabilizer (1% - 5% by weight); hence commercial films with normal additive levels will fail in correspondingly less time. A good stabilizer will effectively inhibit UV degradation only so long as the stabilizer itself is not degraded.

Comparison of the time it takes to reach the same level of visual degradation in a module-like chamber test coupons it does in an deployed module, such as at the Southwest Residential Experiment Station, brackets the acceleration factor of the chamber at from about 1.5 to 14, depending upon the normal operating temperature of the material in its intended application. These numbers are in accord with factors determined from an Arrhenius analysis of the push-test and pull-test data.

**REFERENCES**


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**Table 2**

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<tr>
<th>Tedlar No.</th>
<th>Initial Weight</th>
<th>Stabilizer Loss</th>
<th>Absorbance Ratio</th>
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<td></td>
<td>Weight %</td>
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Exposure: 4100 hours @ 85°C/85%RH/1sunUV


This report presents the results of one phase of research conducted at the Jet Propulsion Laboratory, California Institute of Technology, for the U.S. Department of Energy, and Solar Energy Research Institute, through an agreement with the National Aeronautics and Space Administration.