POTENTIAL PROBLEMS WITH ETHYLENE-VINYL ACETATE FOR PHOTOVOLTAIC PACKAGING

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Abstract

Photovoltaic (PV) devices are typically encapsulated using ethylene-vinyl acetate (EVA) to provide mechanical support, electrical isolation, optical coupling, and protection against environmental exposure. Under exposure to atmospheric water and/or ultraviolet radiation, EVA will decompose to produce acetic acid, lowering the pH and increasing the surface corrosion rates of embedded devices. Even though acetic acid is produced at a very slow rate it may not take much to catalyze reactions that lead to rapid module deterioration. Another consideration is that the glass transition of EVA, as measured using dynamic mechanical analysis, begins at temperatures of about -15ºC. Temperatures lower than this can be reached for extended periods of time in some climates. Due to increased moduli below the glass transition temperature, a module may be more vulnerable to damage if a mechanical load is applied by snow or wind at low temperatures. Modules using EVA should not be rated for use at such low temperatures without additional low-temperature mechanical testing beyond the scope of UL 1703.

Materials and Methods

(1) EVA was obtained from a commercial source and was well formulated for use in photovoltaic applications.

(2) EVA acetic acid formation was evaluated by collecting the effused gases from the thermal decomposition of EVA using a heating apparatus and an ion chromatograph (IC) vial that contained a weighed amount of 4.8-mM KOH. This collection solution was tested using IC analysis to determine the acetic acid formation rate.

(3) Aluminum mirrors were produced in the sputtering chamber of a Pernicka multichamber vacuum deposition system. The final Al thickness was approximately 800±25 Å.

(4) Dynamic mechanical analysis was performed on a TA Instruments Ares Rheometer using a rectangular torsional testing fixture.

(5) A TA Instruments DSC Q1000 was used for differential scanning calorimetry (DSC).

EVA Decomposes to Produce Acetic Acid

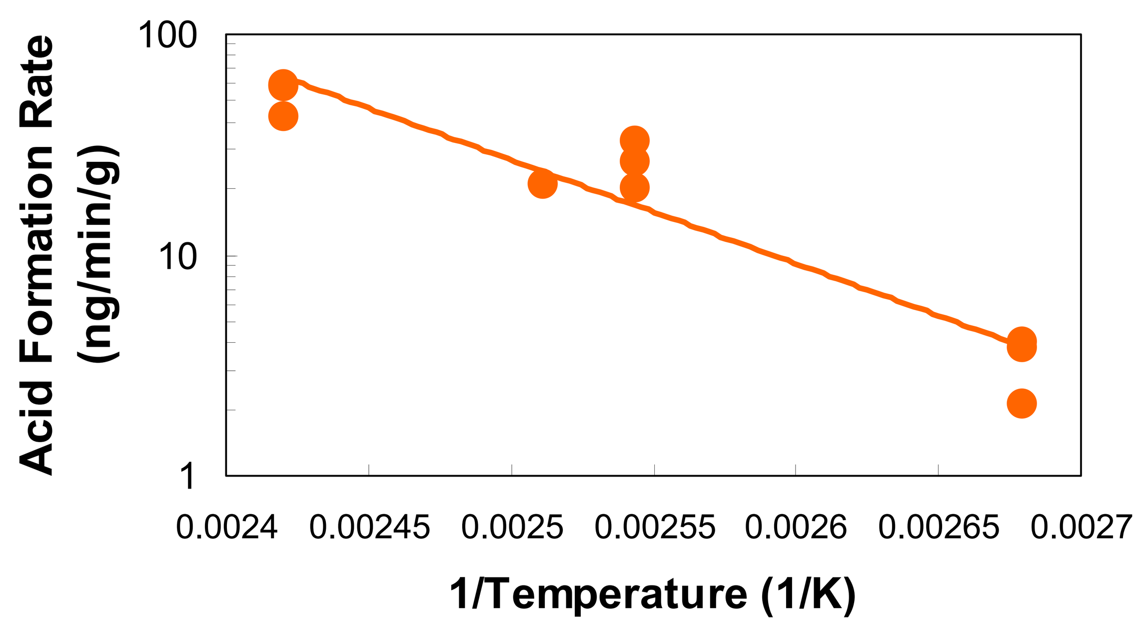

Figure 1. Nanograms Acetate per minute per gram EVA. Acetate was also detected at 80°C (1/K=0.00283) but was not quantified. This test was performed using a humidified N_2 carrier gas.

EVA Produces Acidic Environments in Non-Breathable Packaging

Acetic acid has a pKa of 4.76 so it will tend to buffer solutions to pH~4.76 corresponding to a hydronium ion concentration of 1.74×10^{-5} mol/L. As an order of magnitude estimate of the time necessary to reach pH~4.76, we extrapolate down to 27ºC where EVA will produce 3.31×10^{-12} g_{Acid}/g_{EVA}/min and assume that the ratio of acetic acid to water in the polymer is the same as would be found for a solution in equilibrium with the polymer. This assumption provides a relationship between the chemical potential of the acetic acid in the polymer as compared to an aqueous solution. At 27ºC EVA has at most 0.00223 g_{H_2O}/g_{EVA} [1], and at pH~4.76 there will be equal amounts of acetic acid and acetate ions (or 2.136×10^{-6} g_{Acid}/g_{H_2O}). Under these conditions it will take about 1 day to approach a chemical potential for acetic acid roughly equivalent to pH=4.76.

A module constructed using EVA will quickly equilibrate to a pH less than 4.76 (probably around 2 to 3) if it has an impermeable back-sheet, and to a pH between 4.76 and 7.0 if it has a breathable back-sheet.

[1] M. D. Kempe, Modeling of rates of Moisture Ingress Into Photovoltaic Modules, Solar Energy Materials and Solar Cells, Accepted 00 (2006) 000-000

Aluminum Mirrors Oxidize When Acetic Acid is Trapped

(A)

(B)

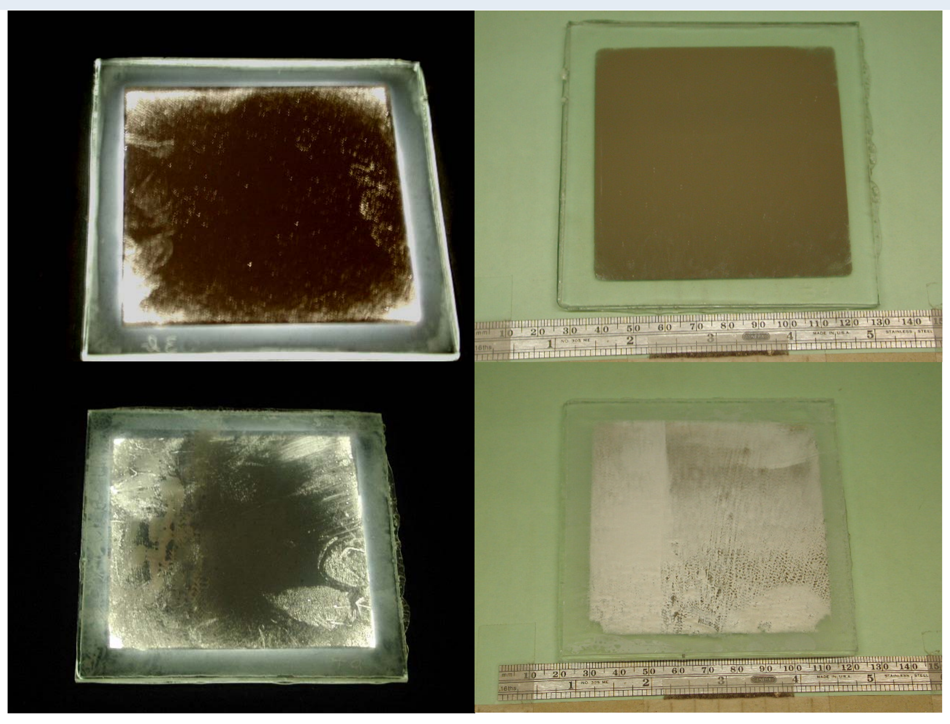

Figure 2. Aluminum mirror laminated with EVA and a glass back-sheet after 1003 hours of 85°C with (A) 85% RH exposure and (B) 100% RH exposure.

Breathable Back-Sheet Allows Acetic Acid to Escape

(A)

(B)

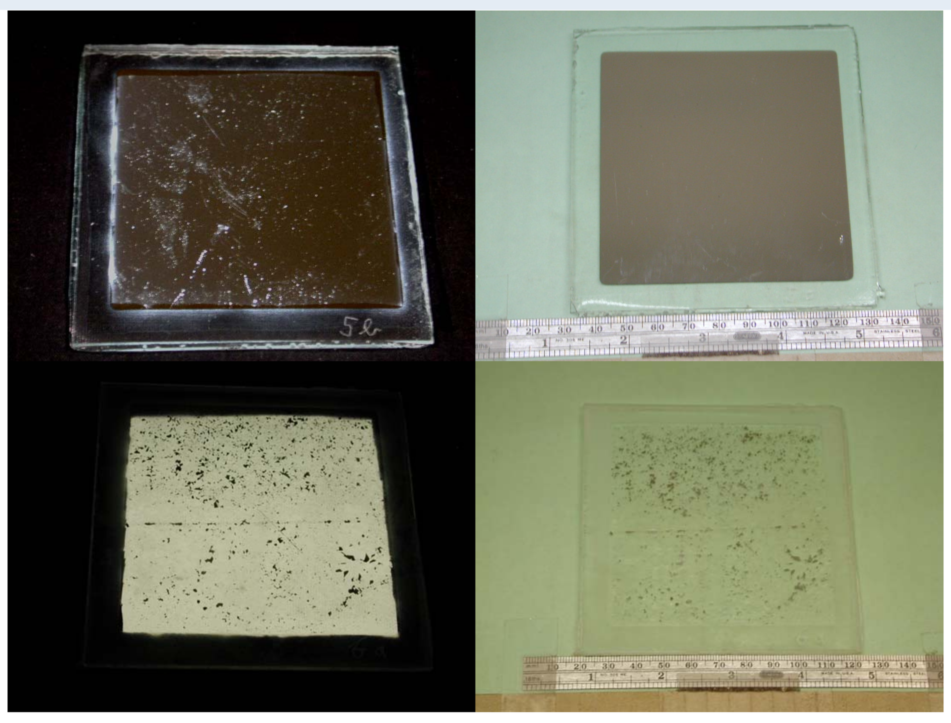

Figure 3. EVA on an Al mirror without a back-sheet, (A) 1003 h at 85ºC/85% RH and (B) 357 h at 85ºC/100% RH. Acetic acid escape is beneficial, but saturated water is very detrimental.

Alternative Encapsulants Reduce Rather than Accelerate Corrosion

(A)

(B)

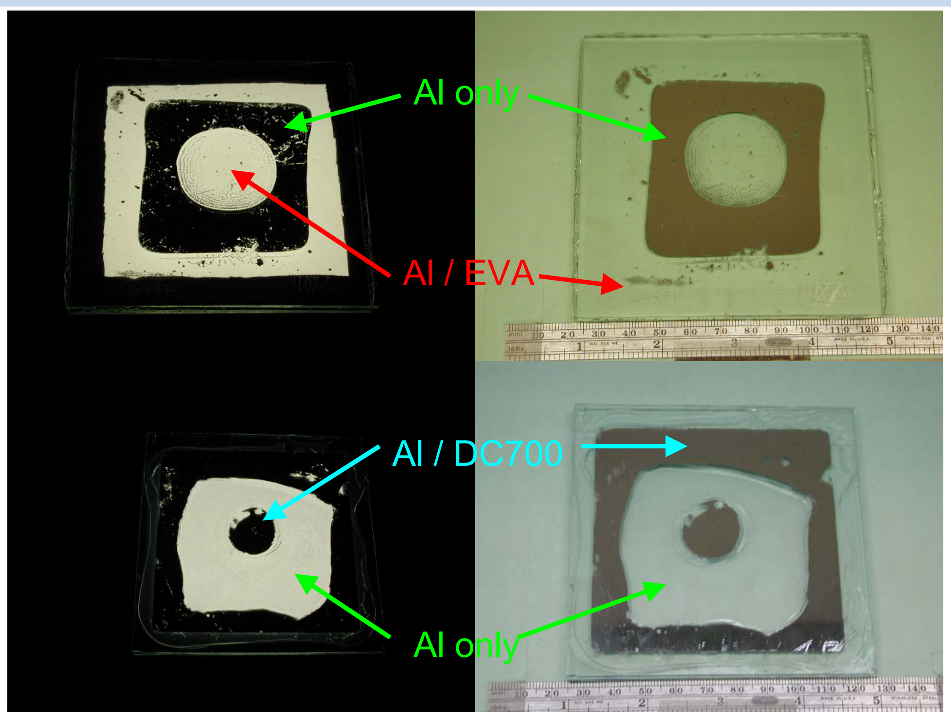

Figure 4. Aluminum mirror laminated with (A) EVA (B) DC 700 acetic acid cure silicone after 1000 hours of 85°C and 85% RH exposure with a soda-lime glass back-sheet having polymer located only in the center and the outer ~25mm.

Exposure to Acidic Solutions Quantifies Acetic Acid Exposure

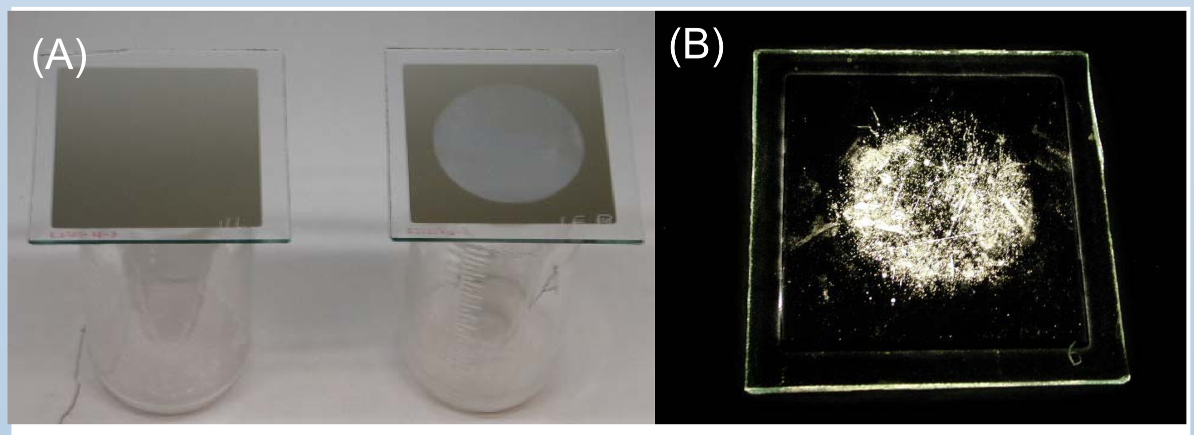

Figure 5. (A) Aluminum mirror laminated using EVA without a back-sheet. The sample on the left was placed on top of a jar (mirror/EVA side down) with a saturated salt solution. The sample jar on the right contained 20% acetic acid. (B) Backlit photo of an aluminum mirror after 1024 hrs at 85ºC exposure on top of a jar containing a saturated KCl with 1% acetic acid (pH ~ 3). At 85ºC this produced a vapor at approximately 79% RH.

A Low pH is Required to Oxidize the Aluminum Mirrors

The pH was estimated using BAKER-pHIX pH indicator strips. At 1%, 4%, and 7% acetic acid a pH of approximately 3, 2.5, and 2.5 was obtained. For higher concentrations, the pH was at least 2 or lower. The control solutions (no acetic acid) did not oxidize significantly and had an appearance similar to Fig. 3a after 1024 hrs. Solutions containing 10%, 15% and 20% acetic acid experienced severe corrosion after about a 1 day exposure at 85ºC (e.g. Fig. 5a Right Side). At 4% and 7%, 200 to 300 hours were necessary to produce severe corrosion. Finally, the 1% solution experienced a small but significant amount of oxidation after 1024 hrs exposure at 85ºC (Fig. 5b). The amount of corrosion seen at 1% is similar to that experienced at the perimeter of the samples with impermeable glass back-sheets (e.g. Fig. 2a). Therefore, as a first order approximation, the 10.2 cm square samples with glass back-sheets can trap enough acetic acid at 85ºC to produce an acid environment with a chemical potential approximately equal to a solution at pH~3.

These findings are consistent with the fact that Al oxides become highly soluble in water at pH~2.4 and are only slightly soluble at pH~4 [2]. This analysis demonstrates the large potential for EVA to produce a corrosive environment in a sealed package where acetic acid can not escape. More experimentation is necessary to determine the specific relevance to PV devices.

[2] T. E. Graedel, Corrosion Mechanisms for Aluminum Exposed to the Atmosphere, J. Electrochem. Soc., 136(4) (1989) 204-212.

Thermally Deduced T_g is Significantly Lower than the Mechanical T_g

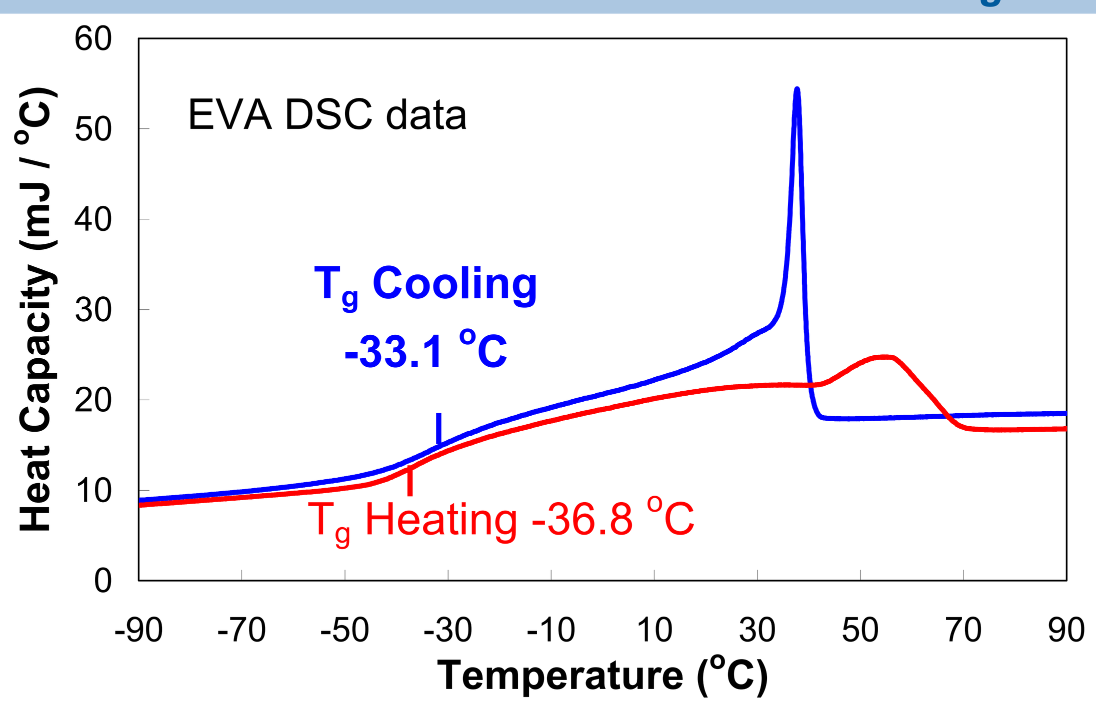

Figure 6. Heat capacity of cured EVA measured by DSC at a heating/cooling rate of 10ºC/min. This is the usual method for determining the glass transition temperature (T_g) even though mechanical methods are more relevant.

Low Temperature Mechanical Testing of Modules is Needed

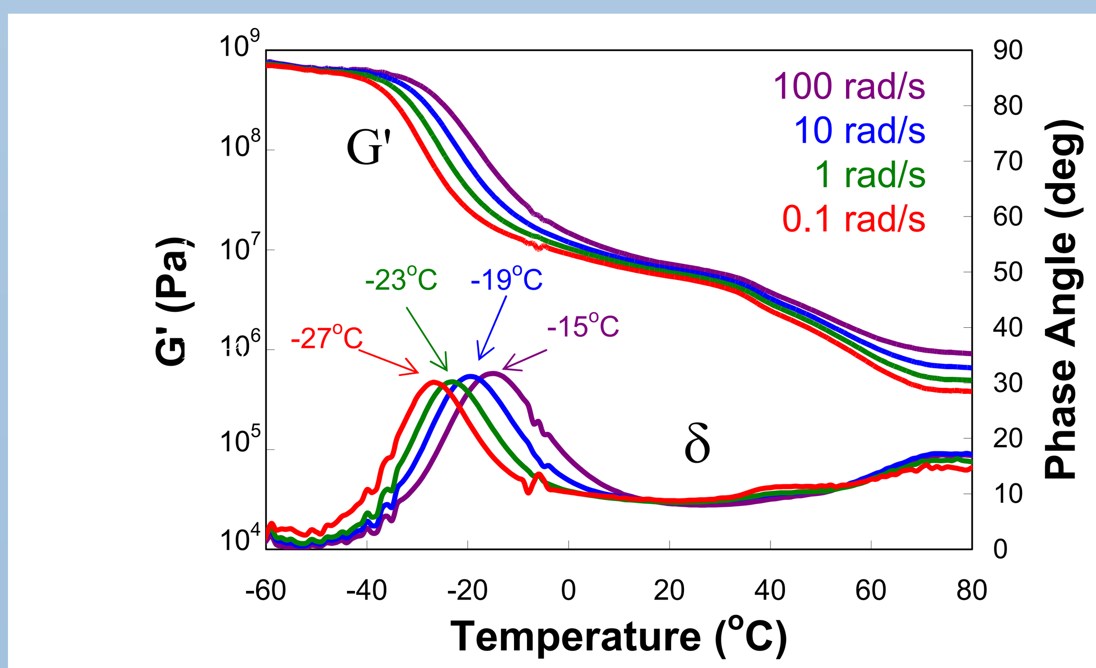

Figure 7. Dynamic mechanical analysis of cured EVA. The moduli increased by a factor of about 500 because of the presence of both a melting point and a glass transition. For many environments, a temperature of –15°C is often reached, making cells in EVA-based modules significantly more susceptible to breakage from sudden impacts and rapid flexing.

Conclusions

(1) During exposure to water and/or UV radiation EVA will decompose to produce acetic acid, thereby lowering the pH and generally increasing surface corrosion rates.

(2) Thin film PV technologies are more likely to be sensitive to acetic acid induced corrosion than are crystalline wafer based technologies.

(3) EVA goes through a T_g beginning at about -15°C, making its use at lower temperatures a significant concern.

(4) Without low temperature mechanical testing, a temperature rating of –15°C may be appropriate for modules constructed using EVA.

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