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ETHYLENE-VINYL ACETATE POTENTIAL PROBLEMS FOR PHOTOVOLTAIC PACKAGING*

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ABSTRACT

Photovoltaic (PV) devices are typically encapsulated using ethylene-vinyl acetate (EVA) to provide mechanical support, optical coupling, electrical isolation, 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 -15°C . Temperatures lower than this can be reached for extended periods of time in some climates. Because of 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.

INTRODUCTION

Polymeric encapsulant materials are used in PV modules to provide electrical insulation and protect them from mechanical damage and environmental corrosion. A well bonded polymer can protect a surface by physically preventing the accumulation of water at its bonding interface. Water can enhance corrosion by providing a means by which by-products can more easily diffuse away from the surface to allow further corrosion. The presence of counter ions (such as Cl^- , Br^- , or acetate) similarly enhance corrosion by facilitating the diffusion of metal ions [1]. Furthermore, acidic materials can catalyze the oxidation of metals.

In some of the early work performed at the Jet Propulsion Laboratory in the 1980s [2,3,4] a number of encapsulant materials were investigated, and of those with

adequate mechanical and optical properties, EVA was chosen because it was inexpensive. EVA continues as the dominant encapsulant in the PV industry even though it suffers from non-ideal mechanical and thermal properties, a high diffusivity for water, the need for vacuum lamination in a semi-batch manufacturing process, and the production of acetic acid. As next-generation crystalline silicon wafers are manufactured thinner, the mechanical properties of EVA may not be sufficient, especially at low service temperatures [5].

Because of the success of EVA with silicon-wafer based technologies, it has often been assumed that the generation of acetic acid is not a problem [2]. Typical modules with “breathable” packages should be less affected by acetic acid than those built with impermeable front- and back-sheets (e.g., glass), which trap decomposition products within the package. This type of “non-breathable” package is commonly used in thin-film devices. This problem is exacerbated by the thinness of the device structures, enabling small amounts of surface corrosion to produce significant deleterious effects. Further experimentation is necessary to evaluate the effect of different encapsulants on the stability of thin-film devices to determine if the higher costs of other encapsulants can be justified by an increase in durability.

In this work, we demonstrate that the hydrolysis of vinyl-acetate monomers results in the production of acetic acid, which can accelerate corrosion. We further explain how the mechanical properties of EVA are non-ideal because of the presence of both a melting point and a glass transition temperature (T_g) within the operating limits of a module.

EXPERIMENTAL

The effused gases from the thermal decomposition of EVA were collected 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. Dynamic mechanical analysis was performed on a TA Instruments Ares Rheometer (equipped with an IGC Polycold Systems Inc. cryogenic refrigeration unit model #PGC-100 and the Ares forced convection oven) using a rectangular torsional testing fixture. A TA Instruments DSC Q1000 was used for differential scanning calorimetry (DSC). Damp heat (85°C and 85% relative humidity [RH]) exposure was conducted in a Blue M environmental

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chamber. Aluminum mirrors were produced in the sputtering chamber of a Pernicka multichamber vacuum deposition system. The final Al thickness was approximately $800 \pm 25 \text{ \AA}$.

RESULTS AND DISCUSSION

Acetic acid formation

The results for the measurement of acetic acid formation in EVA are summarized in Fig. 1. The slope of the curve indicates an activation energy of 90 kJ/mol and extrapolating to the typical average module temperature, 27°C [6], predicts 0.00331 (ng/min/g).

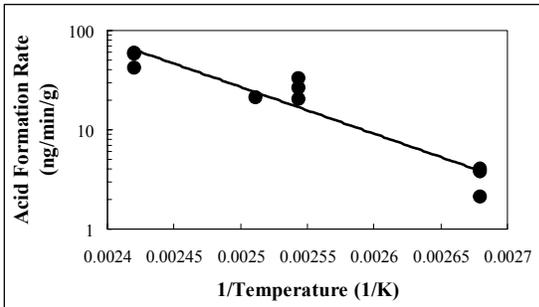


Fig. 1. Nanograms acetate per minute per gram EVA. Acetate was also detected at 80°C ($1/K=0.00283$), but was not quantified.

Acetic acid has a pKa of 4.76, so it will tend to buffer solutions to $\text{pH} \sim 4.76$ corresponding to a hydronium ion concentration of $1.74 \cdot 10^{-5} \text{ mol/L}$. As an order of magnitude estimate of the time necessary to reach $\text{pH} \sim 4.76$, we assume $3.31 \cdot 10^{-12} \text{ g}_{\text{Acid}}/\text{g}_{\text{EVA}}/\text{min}$ and 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 second assumption provides a relationship between the chemical potential of the acetic acid in the polymer as compared to an aqueous solution. At 27°C, EVA has at most $0.00223 \text{ g}_{\text{H}_2\text{O}}/\text{g}_{\text{EVA}}$ [6], and at $\text{pH} \sim 4.76$, there will be equal amounts of acetic acid and acetate ions (or $2.136 \cdot 10^{-6} \text{ g}_{\text{Acid}}/\text{g}_{\text{H}_2\text{O}}$). Under these conditions, it will take about 1 day to approach a chemical potential for acetic acid roughly equivalent to $\text{pH} = 4.76$. This estimation ignores the large acetic acid production during lamination at $\sim 140^\circ\text{C}$ and the affects of UV radiation. A module constructed using EVA will quickly equilibrate to a pH less than 4.76 if it has an impermeable back-sheet, and to a pH between 4.76 and 7.0 if it has a breathable back-sheet.

Aluminized glass

Because Al is often used for electrical interconnects in PV modules, the ability of EVA to protect it was investigated. In Fig. 2a, aluminized glass substrates were laminated with EVA using a soda-lime glass back-sheet and were exposed to 85°C and 85% RH for 1003-h. In the backlit photograph, some corrosion is visible primarily around the edges where the highest concentration of water was seen. In Fig. 2b, a similar substrate was exposed to 85°C and 100% RH for 1003-h and slightly

greater corrosion was seen. This demonstrates that corrosion rates with impermeable back-sheets are somewhat limited by moisture ingress rates from the sides.

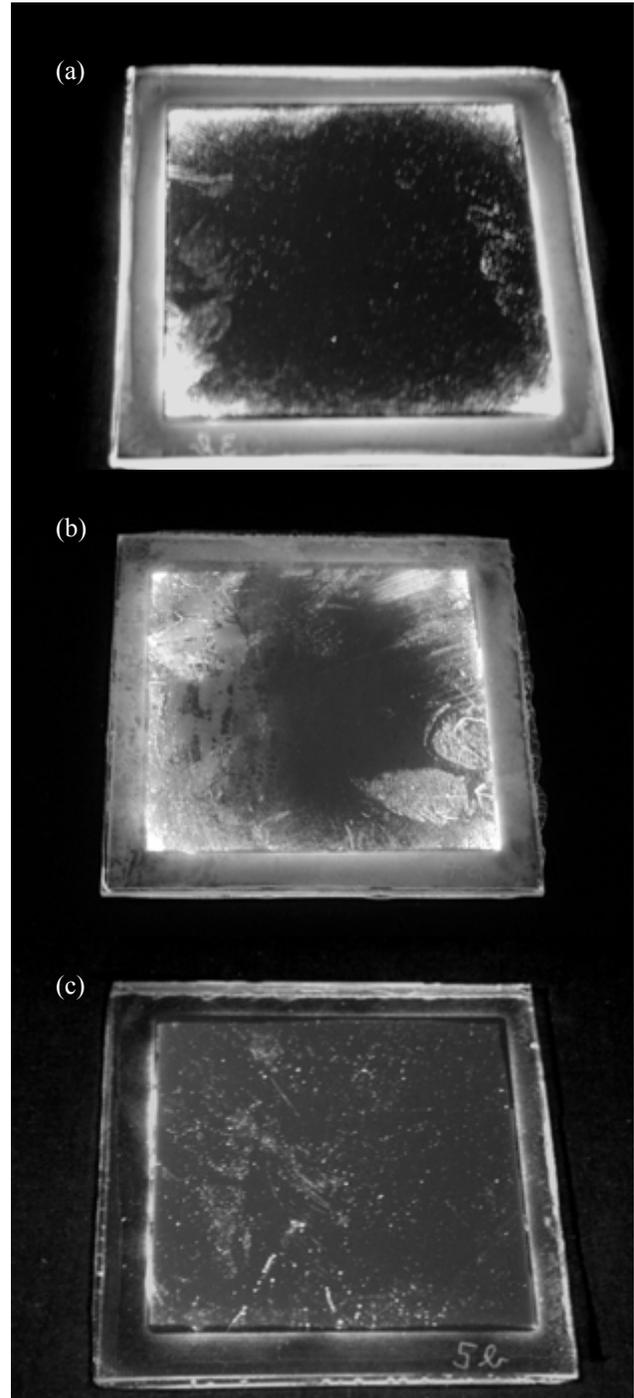


Fig. 2. Aluminum mirror laminated with EVA after 1003-h of 85°C (a) with a soda-lime glass back-sheet and 85% RH exposure, (b) with a soda-lime glass back-sheet and 100% RH exposure, and (c) without a back-sheet and 85% RH exposure.

Aluminized glass substrates were also encapsulated without a back-sheet material. When exposed to damp heat (85°C, 85% RH) for 1003-h, these breathable packages do not show significant corrosion of the Al (Fig. 2c). However, when this same breathable construction is exposed to 85°C and 100% humidity (not shown), the Al is completely oxidized in about 750-h. This indicates that saturation is far more corrosive than 85% RH.

When comparing Fig. 2a (impermeable back-sheet) with Fig. 2c (EVA only), it is apparent that the escape of a volatile component (presumably acetic acid) is enabling the Al coating to withstand damp heat much better. If acetic acid is allowed to escape easily as it is formed, then the pH of the encapsulant will remain between 4.76 and 7; but if it is trapped, the pH will be a little below 4.76, leading to faster corrosion rates.

Aluminized glass substrates were also encapsulated with an impermeable glass back-sheet with EVA located only at the center and the edges so that the effects of encapsulation could be directly compared to bare Al (Fig. 3). After 1003-h of exposure, the Al was almost completely removed in areas in contact with the EVA with very little corrosion detectable on the bare Al. In this configuration, the areas covered by EVA have a reduced barrier to corrosion relative to unencapsulated Al. EVA catalyzes corrosion processes presumably because of the presence of acetic acid and a low pH.

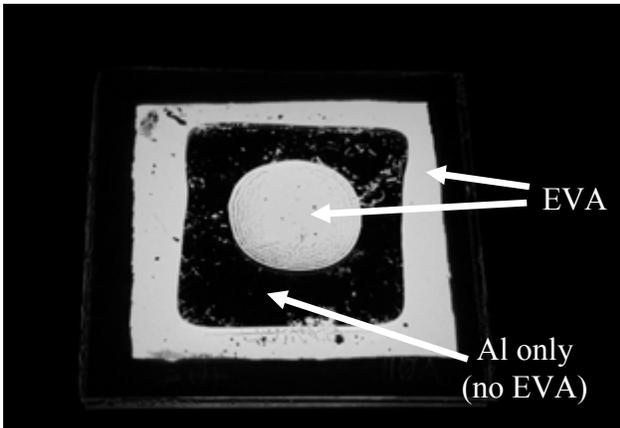


Fig. 3. Aluminum mirror laminated with EVA after 1003-h of 85°C and 85% RH exposure with a soda-lime glass back-sheet having EVA located only in the center and the outer ~25 mm.

To help quantify the effective chemical potential of the acetic acid produced in EVA, Al mirrors were exposed to the vapors coming off of saturated salt solutions containing varying amounts of acetic acid (Fig. 4a). This was accomplished using an excess of KCl in an aqueous solution containing up to 20% (by volume relative to the water content) acetic acid. At 85°C, this produced a vapor at approximately 79% RH.

The pH was estimated using BAKER-pHIX pH indicator strips. At 1%, 4%, and 7%, a pH of approximately 3, 2.5, and 2.5, respectively, 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. 2c after 1024-h.

Solutions containing 10%, 15%, and 20% acetic acid experienced severe corrosion after about a 1-day exposure at 85°C (Fig. 4a, right side). At 4% and 7%, 200 to 300 h were necessary to produce severe corrosion. Finally, the 1% solution experienced a small but significant amount of oxidation after 1024-h exposure at 85°C (Fig. 4b). 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 85°C to produce an acid environment with a chemical potential approximately equal to a solution at pH~3. However, the pH was measured at room temperature; the rate of acetic acid loss vs. its production rate changes with temperature, which may affect the final effective pH attained.

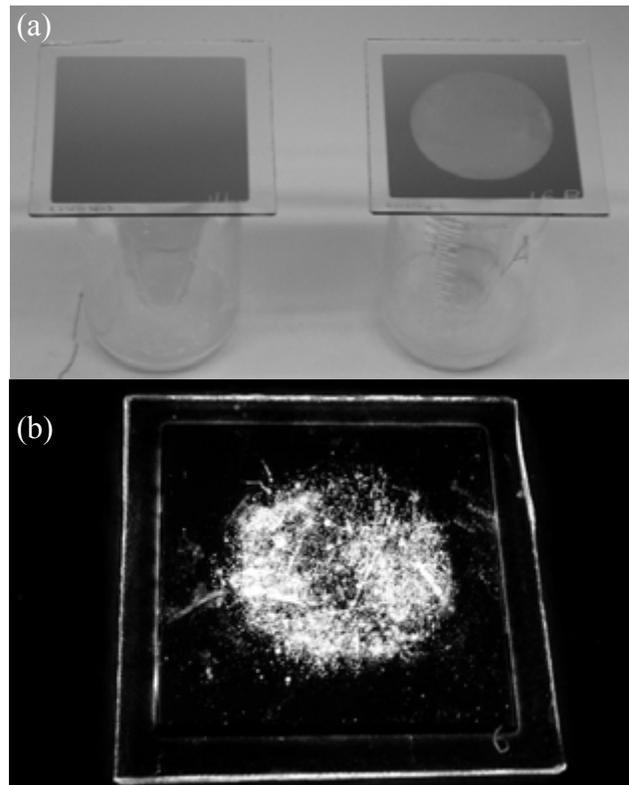


Fig. 4. (a) Aluminum mirror laminated with EVA only. Sample on left placed on top of a jar (mirror/EVA side down) with a saturated salt solution. The sample jar on the right contained 20% acetic acid. (b) Backlit photo of an aluminum mirror after 1024-h at 85°C exposure on top of a jar containing a saturated KCl with 1% acetic acid.

These findings are consistent with the fact that Al oxides become highly soluble in water at pH~2.4 and only slightly soluble at pH~4 [1]. This analysis demonstrates the large potential for EVA to produce a corrosive environment in a sealed package where acetic acid cannot escape.

Rheology

Because PV encapsulant materials provide mechanical support to the cells [2], rheological

measurements were made to determine where the phase transitions are and their effect on the dynamic mechanical moduli. In the temperature range of 80° to -40°C, the moduli increased by a factor of about 500 (Fig. 5). This large change in mechanical properties is due to the presence of both a melting point and a glass transition at or near temperatures that are commonly experienced by a module. For frequencies of 100-rad/s, the T_g was measured to be -15°C, which is much higher than the values of around -40°C frequently reported in the literature [2]. These other sources measured the T_g using DSC, therefore we performed DSC measurements (at a heating/cooling rate of 10°C/min) and found the center of the transition at -33°C and -37°C when cooling and heating, respectively (Fig. 6). This kind of a discrepancy is common for polymers, because the two methods are measuring very different phenomena associated with a second-order transition [7]. Because one of the primary purposes of using an encapsulant is to provide mechanical support, the T_g measured using dynamic mechanical analysis is more relevant.

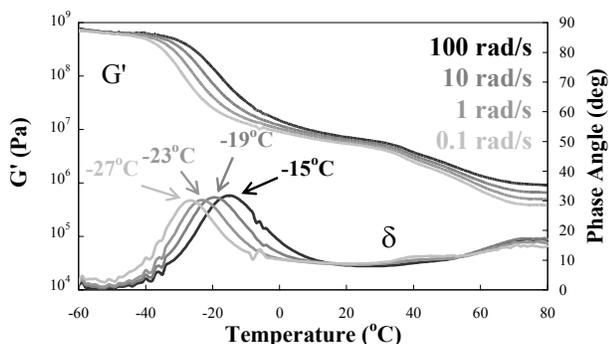


Fig. 5. Dynamic mechanical analysis of cured EVA while heating the sample.

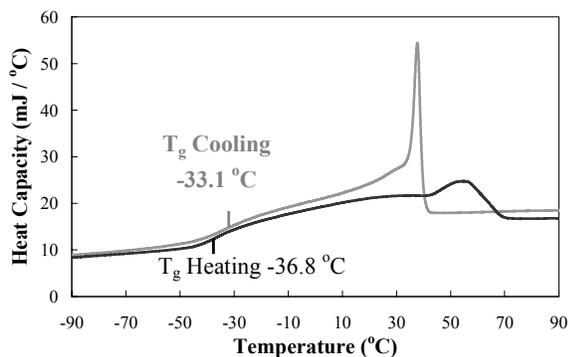


Fig. 6. Heat capacity of cured EVA measured by DSC at a heating/cooling rate of 10°C/min.

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. PV modules are typically rated for use in environments as low as -40°C, but this may be too extreme. This low temperature is often based on passing a qualification test (UL 1703 [8]) where the temperature of a module is cycled between 90°C and

-40°C. If high winds were experienced at such low temperatures, the flexing of a module could break the thin cells or debond interconnects. Inclusion of some mechanical bending at low temperatures would be a good addition to UL 1703. Without further testing, a low temperature rating of -15°C may be more appropriate for modules constructed using EVA.

CONCLUSIONS

Photovoltaic PV devices are typically encapsulated using EVA to provide them with mechanical support, electrical isolation, and protection against environmental exposure. During exposure to water, heat, and/or UV radiation, EVA will decompose to produce acetic acid, thereby lowering the pH and generally increasing surface corrosion rates. EVA also goes through a T_g beginning at about -15°C, making its use at low temperatures a significant concern. Despite these shortcomings, EVA has proven to be adequate for most terrestrial environments using silicon-wafer-based devices. Thin-film PV technologies, however, are constructed using layers that are only a few microns thick, making them potentially much more sensitive to surface corrosion than are silicon-wafer-based technologies.

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