# Determination of Acetic Acid Content in Ethylene-Vinyl Acetate (EVA) Based PV Modules

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## ABSTRACT

The acetic acid formation in EVA as one of the major products caused by thermal or photothermal degradation has been described in several papers.[1-3] Deacetylation and hydrolysis of vinyl-acetate monomers in EVA resulted in generating acetic acid that could accelerate the corrosion of electrical interconnects and deteriorate the transparency coating of the cells and then result in the eventual reduction in module performance.[4] Recently, ion chromatograph (IC), Infra-Red (IR) and Hot Water Extraction Method (HWEM) were used to evaluate the amount of free acetic acid desorbed in EVA.[3-5] In this study, more dedicated analytical technique of Thermal Desorption GC-MS was applied to quantitatively determine the acetic acid content within the full size PV modules with and without exposure. The correlation between the extent of acetic acid formation and the module performance was also investigated.

## 1. INTRODUCTION

Ethylene (vinyl acetate), EVA, is a copolymer that can be hydrolyzed under the presence of high temperatures and moisture as illustrated in Fig.1. The formation of acetic acid in aged PV modules has been investigated, and it was used as a good indicator to the reliability degradation of PV modules exposed in the field.
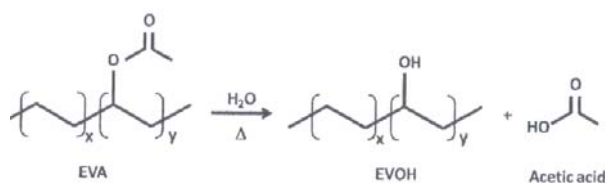


**Fig. 1** EVA hydrolysis reaction mechanism [6]

## 2. EXPERIMENTS

### 2.1 Samples and Aging Conditions

Eighteen commercially available polycrystalline 60-cell PV modules made with PVDF/PET/EVA type of backsheets were fabricated and used for two different conditions of accelerated exposures. Eight PV modules were exposed to UV, eight modules were subjected to damp heat aging, and two modules were not exposed and used as control samples. The accelerated aging conditions under laboratory-controlled exposure chambers including: (1) Damp Heat (DH) exposure: $85^{o}C$ ambient temperature and 85% relative humidity, described as in the test 10.13 of IEC 61215 Ed.2., and (2) UV exposure similar to test 10.10 of IEC 61215 Ed.2 but with higher light intensity about 80 $W/m^2$ UV plus additional 15% of the total irradiance at the back of the modules. The I-V performance of the modules were tested with every 500

hours exposure, and two of the eight modules were removed and disassembled, and the EVA/backsheet laminates were collected and tested up to 3000 hours exposure. The EVA/backsheet laminates were cut from the back surfaces of the PV modules into pieces around 5 mg, and then the entire EVA/backsheet pieces were directly injected into the furnace of the Thermal Desorption-GC/MS.

## 2.2 Instrument and Parameters

Thermal Desorption GC/MS analyses were performed via a Pyrolyzer of PY-2020iD (Frontier Lab, Japan) connecting with a GC-7890A and MS-5975C (Agilent, USA) equipped with an Ultra Alloy-FFAP capillary column (Frontier Lab, Japan, 30 m × 0.25 mm × 0.25 μm) made by Stainless Steel as shown in Fig. 2. The GC column temperature conditions were programmed as follows: initial temperature 50 °C, hold for 0 min, and then increased by 20 °C/min up to 150 °C. The helium gas flow was set at 1 mL/min, in split mode: split ratio is 1:30 and mass spectra were recorded under electron impact ionization at 70eV.
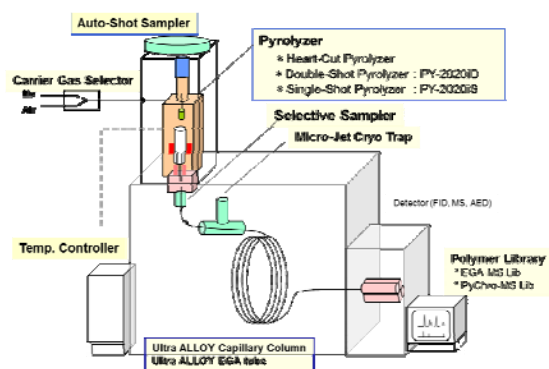


**Fig. 2** Multi-functional Pyrolysis System

## 3. RESULTS AND DISCUSSIONS
### 3.1 Module Performance Measurement

Electrical current vs. voltage (I-V) test was conducted for the modules at every 500 hour exposure, and the results were plotted

in Fig. 3. It showed that the power output of the DH-exposed modules was sharply declining right after 2000 hrs., but UV-exposed modules remained pretty constant for all exposures.
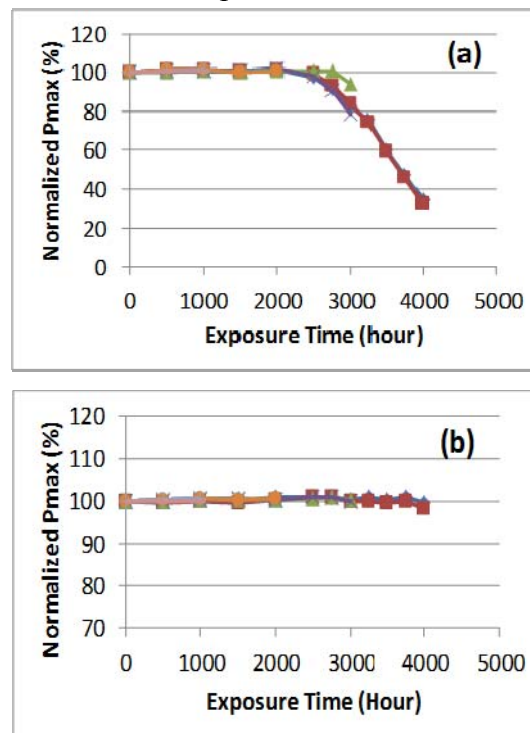


**Fig. 3** Module power degradation under (a) Damp Heat (DH), (b) UV conditions as a function of exposure time in hours.

### 3.2 Acetic Acid Investigation

Two of the aged modules were withdrawn from the chambers at every 1000 hours exposure, and six samples were randomly collected on each module for acetic acid measurements. The results were plotted in Fig. 4: (a) For damp heat aged samples, the desorbed acetic acid was sharply increased from 5 ppm to 56 ppm, 619 ppm and 1348 ppm at 0 hr, 1000 hrs., 2000 hrs. and 3000 hrs., respectively, and (b) For UV irradiation, it showed that the acetic acid was slightly increased, and it had much less aging effect on the generation of acetic acid than in damp heat. It was slightly increased from 5 ppm to 11 ppm, 40 ppm and 152 ppm at 0 hr, 1000 hrs., 2000 hrs. and 3000 hrs. exposure,

respectively. The formation of acetic acid amount may be a good indicator for estimating the degree of materials/polymers degradation in the exposed modules, and it could be correlated to the power efficiency of PV modules as described in 3.3.
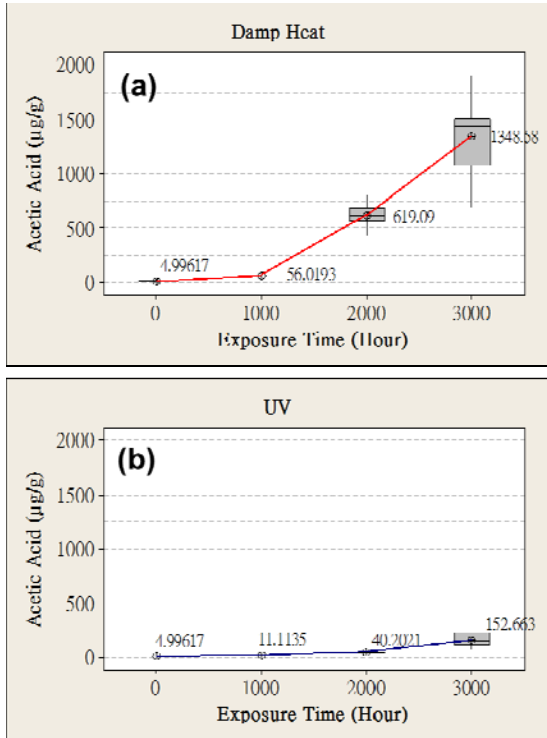


**Fig. 4** The amount of free acetic acid desorbed in the modules exposed with (a) damp heat aged EVA, (b) UV aged EVA
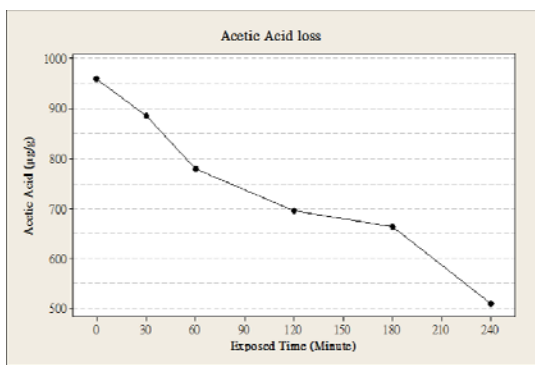


**Fig. 5** The amount of free acetic acid was decreased as a function of time after the sample exposed to air

It was noted that the free acetic acid could be quickly evaporated at ambient environment, so, the test must be conducted immediately after the sample was obtained from the modules. Otherwise the level of acetic acid might be underestimated as exhibited in Fig. 5.

**3.3 Correlation of Power reduction and Acetic Acid**

The linear degradation model was extended to a nonlinear degradation one proposed by Peng and Tseng [7] as follows:

$$Y(t) = g(t;\lambda) + \sigma B(t),$$

Where, $Y(t)$ denotes the power loss of a PV module under Damp Heat condition at time $t$, $g(t;\lambda) = \lambda_1 t^{\lambda_2}$ ; $\lambda' = (\lambda_1, \lambda_2)$ is a fixed unknown parameter vector; $\sigma$ is a diffusion coefficient; $B(t)$ is the standard Brownian motion. Fig. 6 shows the degradation paths for power loss of PV modules. By using the maximum likelihood method, the estimated mean degradation paths is obtained as

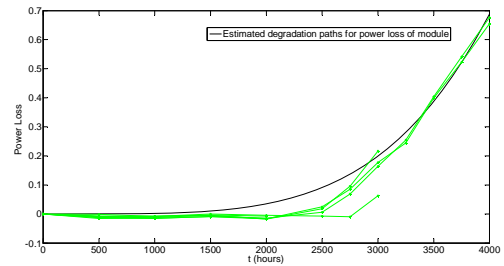$$\hat{g}(t;\hat{\lambda}) = 0.001757623 \times \left(\frac{t}{1000}\right)^{4.305979194}.$$



**Fig. 6** The degradation paths for power loss of PV modules

With regard to the acetic acid formation, a power-law destructive degradation model [8, 9] is given by

$$X(t) = f(t;\theta) + \varepsilon_t,$$

where $X(t)$ denotes the desorbed acetic acid under damp heat condition at time $t$,

$f(t;\boldsymbol{\theta}) = \theta_1 t^{\theta_2} + \theta_3$ ; $\boldsymbol{\theta}' = (\theta_1, \theta_2, \theta_3)$ is a fixed unknown parameter vector; $\varepsilon_t$ is measurement error and follows $N(0, \sigma_t^2)$; $\sigma_t^2$ is an unknown parameter. Fig. 7 shows the box plot of destructive degradation data at each measurement for desorbed acetic acid. By using the least squares method, the estimated mean destructive degradation paths is obtained as

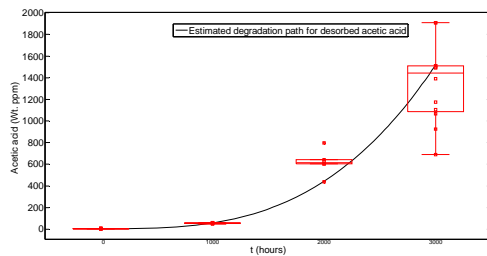$$\hat{f}(t;\hat{\boldsymbol{\theta}}) = 3.542441115 \times 10^{-8} \times t^{3.057203877} + 4.599427952.$$



**Fig. 7** The box plot of destructive degradation data for the desorbed acetic acid

The correlation between the mean power loss and mean acetic acid is 0.9916, which is a positive correlation. In other words, the mean desorbed acetic acid increases, the mean power loss of PV modules increases.

## 4. CONCLUSIONS

The increasing trend of acetic acid formation in the aged EVA modules was consistent with findings in other studies, and could serve as a good indicator for correlating to the power loss or degradation under the accelerated damp heat exposure. The Thermal Desorption GC-MS technique was believed to provide better detection sensitivity and a more accurate analysis for acetic acid. However, it was found that the free acetic acid could quickly be evaporated at ambient atmosphere. Therefore, in order to monitor the acetic acid content of exposed modules on the field, we need to develop a test method on how to directly obtain the sample without any loss of acetic acid right from the module. Several other degradation indicators such as EVA melting enthalpy, EVA glass transition temperature, EVA TGA weight loss, IR absorptions for certain functional groups, and EVA/glass interlayer adhesion strength were also identified and evaluated in the further studies.

**REFERENCES**

[1] A.W. Czanderna , F.J. Pern, *Solar Energy Materials and Solar Cells* **43,** 101 (1996).

[2] M.D. Kempe, G.J. Jorgensen, K.M. Terwilliger, T.J. McMahon, and C.E. Kennedy, *IEEE 4th World Conference on Photovoltaic Energy Conversion* (2006).

[3] Michael D. Kempe, Gary J. Jorgensen, Kent M. Terwilliger, Tom J. McMahon, Cheryl E. Kennedy, Theodore T. Borek, *Solar Energy Materials & Solar Cells* **91,** 315 (2007).

[4] T. Shioda, *NREL PV Module Reliability Workshop* (2012).

[5] Kaoru Ohshimizu, *NREL PV Module Reliability Workshop* (2012).

[6] Sinicco, T. Schuhmacher and K.Proost, *SPIE* (2011).

[7] Peng, C. Y. and Tseng, S. T., "Mis-specification Analysis of Linear Degradation Models." *IEEE Transactions on Reliability* **58**, 444-455 (2009).

[8] Tsai, C. C., Tseng, S. T., Balakrishnan, N., Lin, C. T., "Optimal Design for Accelerated Destructive Degradation Test." *Quality Technology and Quantitative Management* **10**, 263-276 (2013).

[9] Shi, Y., Meeker, W. Q., Escobar, L. A., "Accelerated Destructive Degradation Test Planning." *Technometrics* **51**, 1–13 (2009)