

CORRELATION OF DEGREE OF EVA CROSSLINKING WITH FORMATION AND DISCHARGE OF ACETIC ACID IN PV MODULES

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ABSTRACT: Ethylene vinyl-acetate (EVA) encapsulated crystalline silicon PV modules see encapsulant related degradation such as the hydrolysis of EVA which leads to generation of acetic acid that corrodes cells and cell metallisation. The formation and discharge of acetic acid in PV modules during an extended damp-heat test are studied in this work in dependence of the EVA crosslinking degree. To achieve different degrees of EVA encapsulation, mini-modules were laminated under different curing temperatures. The thermogravimetric analysis (TGA) is used to estimate the vinyl acetate (VA) content of the EVA before and after damp-heat ageing, from which the formation of acetic acid is evaluated. The net accumulation of acetic acid within modules is evaluated by corrosion induced power losses. Results show mini-modules with highly cross-linked EVA form less acetic acid under damp-heat stresses, however, accumulated the highest amount of acetic acid leading to the most severe corrosion. Therefore, highly cross-linked EVA is not favoured in terms of long-term degradation due to DH stresses as it may trap the generated acetic acid within module

Keywords: EVA, vinyl acetate, VA, acetic acid, damp-heat, stress testing, lamination, curing, TGA

1 INTRODUCTION

PV modules rely on their packaging to provide durability. Typical c-Si modules consist of a number of interconnected solar cells encapsulated into two layers of EVA, and then sandwiched between a front glass layer and a back polymeric sheet. The outer layers of the front glass layer and the backsheets minimise encapsulant related degradations such as encapsulant decomposition (e.g. hydrolysis) and interconnect and cell surface corrosion [1-5]. However, when modules exposed to hot and humid environment, moisture can permeate through backsheets and interact with vinyl acetate (VA) leading to hydrolysis of EVA, where the acetic acid is formed as a by-product. The generated acetic acid can either diffuse out from the backsheets or accumulate within the module. Different types of EVA and backsheets will influence the diffusion behaviour of acetic acid and has been reported [6].

Lamination of PV modules is typically with a flat-bed laminator where the lamination temperature, pressure and duration are controlled carefully to ensure good encapsulation quality. Variation in any of the factors may lead to changes in chemical reaction rates and alterations of phase transition of polymers. The lamination process can influence the crosslinking degree of EVA [7], which will be shown in this paper has a significant impact on net accumulation of the generated acetic acid. This will then influence the module degradation behaviour, e.g. corrosion, and thus affect the performance of PV modules [8-9].

A number of mini-modules were laminated in-house and subjected to an extended damp-heat (DH) stress testing. All materials used for the laminated mini-modules are commercially available in the PV market. Lamination temperature was set between 125°C and 150°C in order to obtain samples with optimal and sub-optimal crosslinking degrees of EVA. The EVA crosslinking was characterised by gel content measurements. The module power performance and degradation was characterised by I-V measurements during the course of DH test. The DH test is designed to drive humidity into module package. The humidity

causes hydrolysis and acidification of EVA and ultimately corrodes busbars, fingers and cell surface [10-11]. The curing temperature in the lamination process influences the EVA crosslinking as well as the stability of the materials. The thermogravimetric analysis (TGA) was carried out for the unaged and aged EVA samples, respectively, from which the VA content of the unaged and aged EVA can be estimated. This is then used for evaluation of the acetic acid formation rate. Based on the power and material measurements, correlations between the VA content and the formation and discharge of acetic acid were established.

2 EXPERIMENTAL SETUP

2.1 Sample preparation

The structure and specifications of the laminated single cell mini-module used in this work is shown in Figure 1. It contains a glass front layer (2.9mm thick low iron float, un-tempered glass), two layers of encapsulant (460µm thick fast cure EVA) and a backsheets layer (tri-layer insulating polymer consisting PET/PET/primer layer). A 1.8W multi crystalline Si cell is laminated in between the two EVA layers. Lamination temperatures were set to different levels at 125°C, 135°C, 145°C, and 150°C, while the curing time was fixed at 10 minutes (These samples are referred to in the following as L125, L135, L145 and L150, respectively). Laminator was pre-heated to 120°C before placing samples on the flat bed. Vacuum time was 4 minutes and followed by 10 minutes curing under 1 Bar. Samples were taken out immediately after curing and left to cool in ambient environment.

At each lamination condition, four samples were fabricated for DH testing. No aluminium frame was fixed onto the mini-modules, but a large distance left to the boundaries of the module, so that edge diffusion should not change the experiment unduly.

2.2 Extended stress testing

The mini-modules were placed in an environmental chamber (see Figure 2) and subjected to extended damp-heat testing at 85°C and 85% relative humidity (RH) for a

total exposure of 11000 hours. It might not be realistic for PV modules to experience 11000 hours DH equivalent stress in the field, but this overstressing allows an investigation of the acetic acid formation and discharge behaviours as well as the corresponding degradation mechanism, i.e. the corrosion of cells and metallisation.

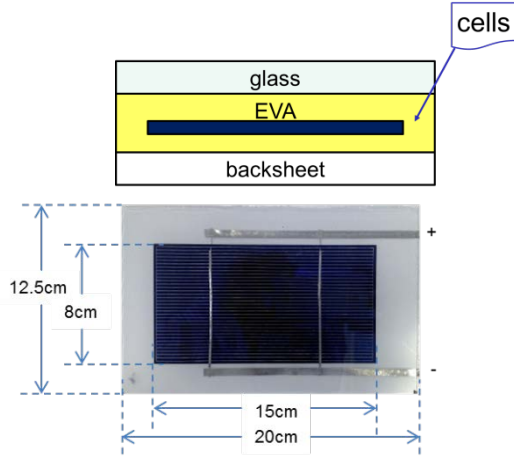


Figure 1: Specifications of the mc-Si mini-module laminated at CREST.

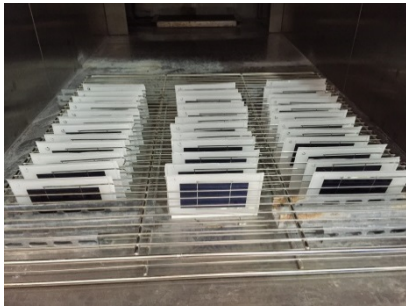


Figure 2: Testing samples in an environmental chamber.



Figure 3: Thermogravimetric analysis of EVA.

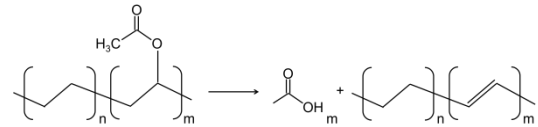
The prolonged DH test is designed to drive humidity into EVA from module backsheet. Once the moisture inside the module permeates into EVA it will form acetic acid which will attack the electric circuitry and, in the saturated case, free water may corrode cells as well. This will cause power reduction due to losses of passivation, electrochemical corrosion and ultimately lead to module failure.

Measurements of gel content were taken for EVA cured at different temperatures before ageing by the solvent extraction method. Module I-V characteristics were measured indoors using the Pasan IIIb solar simulator at the standard testing condition (STC).

2.3 Thermogravimetric analysis of EVA

The dependence of thermal degradation behaviour on VA content of EVA copolymers can be studied by TGA.

As shown in Figure 3, each TGA measurement uses about 5mg EVA sample extracted from the unaged or aged mini-modules. The sample is left in ambient environment for a few hours before measuring. This assumes no generated acetic acid remains in the tested sample of EVA. Then the sample is heated from 30°C to 600°C at the heating rate of 10°C per minute while the weight loss is monitored. It has shown the maximum rate of weight loss at the stage of evolving acetic acid exhibits a linear relationship with VA content and is independent of molecular weight and heating rate [12]. When temperature is at 350-380°C, the chemical reaction of EVA evolving acetic acid is expressed below:



where n and m are the numbers of ethylene monomers and vinyl acetate monomers, respectively.

3 EFFECTS OF EVA CROSSLINKING ON WATER PERMEATION AND HYDROLYSIS

The lamination temperature has a significant impact on curing and crosslinking degree of EVA. The curing rate of EVA increases with the increasing temperature. If the temperature is too high, curing may occur too quickly without completely removing the gases within the module structure and the gases generated during crosslinking. If the temperature is too low, curing rate may become too slow and cannot achieve a good curing state during lamination. The crosslinking also converts a thermoplastic material into a network format thermosetting material so that the material will not flow under heat.

Figure 4 plots the averaged values of gel contents for EVA samples L125, L135, L145 and L150. The L125 shows gel content less than 60%. Samples of L135, L145 and L150 show a linear increase in gel contents from 72% to 85%. It has been reported in [13], for the EVA studied in this work, samples with lower degrees of crosslinking (gel content <60%) show water diffusion rate of about 35 g/m²/day under 23°C and 1 bar. The diffusion rate reduces with the increasing crosslinking degree and reaches about 10 g/m²/day for samples of gel content >80%. Higher curing temperature ensures good crosslinking of EVA, which has better resistivity to moisture ingress.

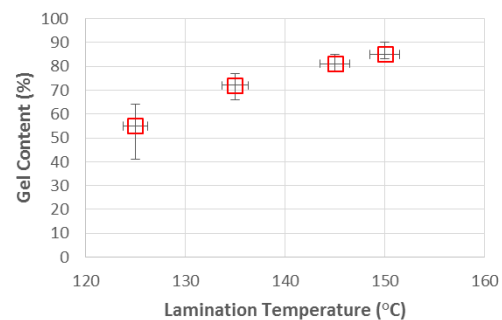
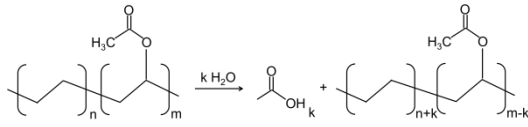


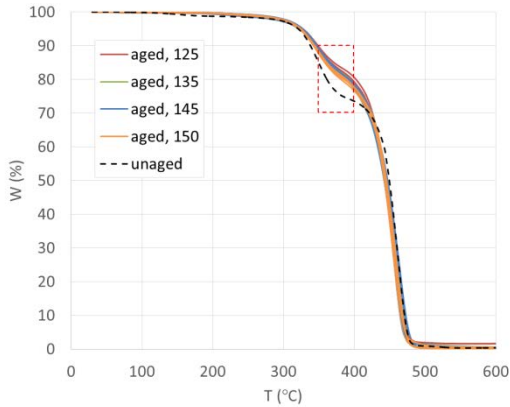
Figure 4: Averaged gel content of EVA versus lamination temperature.

Hydrolysis of EVA is a typical degradation mechanism due to DH stresses. The chemical reaction is expressed below:

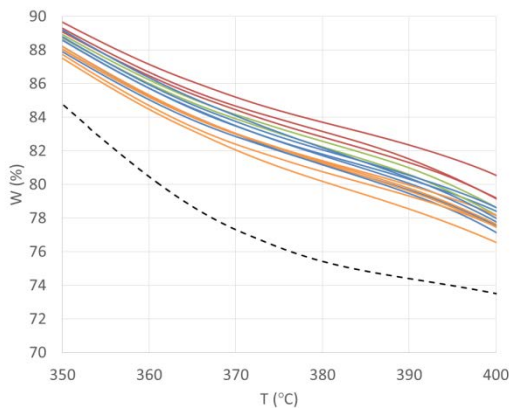


where k is the number of acetic acid generated due to hydrolysis during the DH test, n and m are the original numbers of ethylene monomers and vinyl acetate monomers, respectively.

The acetic acid is formed in the presence of water when the VA content of EVA is decomposed. Applying TGA technique for the unaged and aged EVA samples, the differences in weight loss curves were observed and shown in Figure 5. According to the method in [12], the VA content can be estimated based on the TGA measurements and the averaged values are summarised in Table I for mini-modules L125, L135, L145 and L150. By comparing the VA contents before and after DH ageing, it is possible to estimate the amounts of VA content of EVA decomposed to produce acetic acid, which is equivalent to the amounts of acetic acid was formed. The result shows that L125 samples generated more acetic acid than others as 31.3% of VA was decomposed, whereas L150 samples led to the least generation with only 20.8% of VA hydrolysed during the 11000 hours of DH test. This indicates that lower cross-linked EVA tends to produce more acetic acid than higher cross-linked EVA.



(a)



(b)

Figure 5: TGA curves for unaged and aged EVA samples extracted from mini-modules L125, L135, L145 and L150.

Table I: Evaluation of consumption of VA and formation of acetic acid.

	$\Delta W\%$ - Unaged EVA sample	VA% - before DH ageing	$\Delta W\%$ - Aged EVA sample	VA% - after DH ageing	Percentage of VA hydrolysed
L125	24	34.4	16.5	23.7	31.3%
L135	24	34.4	17.3	24.8	27.9%
L145	24	34.4	18.2	26.1	24.2%
L150	24	34.4	19	27.3	20.8%

4 EFFECTS OF EVA CROSSLINKING ON POWER DEGRADATION AND CORROSION

The mini-module power degradations due to DH stresses are reported in this section and their dependencies on EVA crosslinking degree are discussed.

Visual inspection saw all samples suffering from the same type of degradation mode, i.e. corrosion of busbars, fingers, cell surface and yellowing of EVA (see Figure 6), which are the expected degradation mechanisms in DH test.

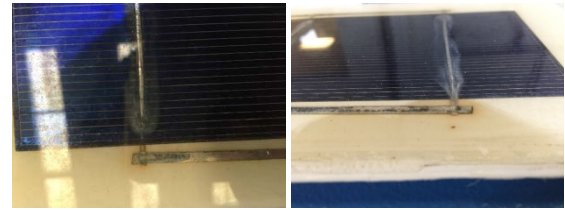


Figure 6: Observed corrosion of mini-modules.

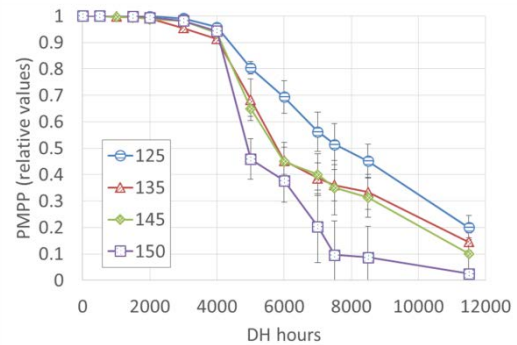


Figure 7: P_{MPP} degradation over time.

The averaged module power (P_{MPP}) of mini-modules L125, L135, L145 and L150 over DH testing time is plotted in Figure 7. Clear difference in the pattern of power degradation is observed for mini-modules with higher and lower cross-linked EVA encapsulation. Most of the samples started to degrade after 4000 hours in DH test. L125 samples saw the slowest deterioration, whereas L150 samples saw the fastest degradation in power. As the degradation is solely due to the mechanism of corrosion, which the acetic acid plays an important role, the accumulation of acetic acid within the module is lower in L125 samples and higher in L150 samples. This implies that lower cross-linked EVA tends to discharge more acetic acid than higher cross-linked EVA.

5 CONCLUSIONS

An extended DH stress test was carried out for EVA encapsulated mini-modules, whose EVA encapsulant exhibits different degrees of crosslinking with gel contents between 50% and 90%. The L150 samples with the highest crosslinking degree of EVA encapsulant producing the least acetic acid, however, showed the most severe corrosion and power degradation during the extended DH test.

The formation of acetic acid under DH stresses is evaluated by analysing the VA content in the EVA through TGA measurements for unaged and aged EVA samples extracted from the mini-modules. The formation rate appeared to be of positive dependence on the water diffusion behaviour in EVA as the amount of VA content hydrolysed increases with the increasing water diffusion rate in EVA.

The generated acetic acid either diffused out through backsheet or accumulated within module at e.g. EVA/cell interface and eventually the concentration saturated after about 4000-5000 hours DH test for this type of mini-modules, where corrosion led to rapid degradation in power. The EVA crosslinking degree appeared to be of negative dependence on acetic acid discharge rate. The L125 samples with the most acetic acid produced during the DH test had the least amount of acetic acid accumulation, which means acetic acid discharge rate for the L125 samples is the highest. Highly cross-linked EVA is not favoured in terms of long-term degradation due to DH stresses as it may trap the generated acetic acid within module leading to severer corrosion effect.

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