

EFFECT OF ENCAPSULANT STORAGE CONDITIONS ON THE LONG-TERM PHOTO-INDUCED DEGRADATION OF EVA IN DOUBLE-GLASS SOLAR PV MODULES.

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ABSTRACT: Double glass PV modules are expected to be more durable on the long term with respect to modules in a conventional glass/back-sheet configuration. The combination of a rear and front glass cover can in fact delay or completely prevent moisture ingress into the module structure. However, water can be absorbed from the environment by the virgin encapsulant so that storage conditions can be relevant in ensuring the long-time performance of the encapsulant and the PV module. Additionally, in a glass/glass configuration products formed during the aging of the polymeric encapsulant will remain trapped inside the module, affecting the long-term performance of the module. The encapsulant choice is then an important aspect to consider for the encapsulation scheme of bifacial modules. In this work, we investigate the effect of non-optimal storage conditions of EVA and its impact on long-term UV aging. After a total UV dose of 165 kWh/m² (corresponding to an outdoor exposure of ~2.2 years in a temperate climate the performance of 1-cell mini-modules does not vary. However, preliminary signs of chemical degradation are detectable by means of Raman and FTIR spectroscopy for the non-properly-stored polymer, suggesting that carefully controlling the storage conditions of the polymer may be critical if EVA is used in double glass structures.

Keywords: Bifacial module, glass-glass, EVA, UV degradation, storage, reliability

1 INTRODUCTION

During the last decade, the PV market share is evolving quite rapidly [1]. The rise of the Passivated Emitter and Rear Cells (PERC) and Silicon Hetero Junction (SHJ) cell technologies has boosted the efficiency, meanwhile offering the possibility to fabricate bi-facial devices. To take advantage of this type of cells, the module design needs to be adapted by replacing the standard white back-sheet with, for instance a glass rear cover. In addition, the rear glass improves the mechanical stability and prevents moisture ingress from the rear cover [2]. This last aspect can be particularly beneficial to mitigate or delay the degradation of the encapsulant and modules performance. On the other hand, when photo-degradation occurs the insulating double glass structure traps by-products (such as acetic acid and other volatile species) inside the module, which would normally be outgassed from the breathable back-sheet. The choice of the encapsulant material is therefore a relevant aspect when considering the long-term performance [3]. The PV community is still divided on the practicality of using Ethylene Vinyl Acetate (EVA) in a glass-glass structure. Advantages are the relatively low cost, widespread availability and proven track record; disadvantages are related to possible photo-induced degradation and potentially to the inability for some detrimental species to out diffuse. However, a suitable and comprehensive data record from field installations is largely lacking.

In this work, we investigate the impact of the presence of residual water trapped inside laminated double glass PV modules. We assess in particular the role of the encapsulant storage conditions. Uncured EVA is usually provided in sheet form. The EVA manufacturers recommend an optimum temperature of 22°C (generally below 30°C) as a storage temperature and a relative humidity (RH) below 50%. The virgin EVA should not be exposed to direct sunlight and should generally not be stored for more than 6 months [4]. However, due to poor storage conditions, such as temperature or humidity variations, water can be absorbed by EVA and can remain

trapped inside the encapsulant even after the lamination process. During outdoor exposure, UV radiation may then trigger a photo-degradation of EVA. The photochemical degradation processes of EVA leads to the formation of conjugated polyenes and unsaturated carbonyl groups, which may exhibit fluorescence. Furthermore, volatile compounds such as acetic acid and hydro-peroxides are formed [5].

2 EXPERIMENTAL

Uncured EVA films are stored under optimal and non-optimal conditions, then laminated and exposed to accelerated UV weathering. 1 cell mini-modules with c-Si PERC solar cells are manufactured and tested. Module performance are assessed by means of current-voltage (I-V) measurements, electroluminescence (EL) images, fluorescence images, and visual inspection.

The physical and chemical degradation of the encapsulant is assessed at regular intervals by means of optical transmittance spectroscopy (UV-vis-NIR), Raman spectroscopy, and Fourier transform Infrared (FTIR) spectroscopy.

2.1 Sample design and fabrication

A commercial EVA roll is used in this work, with a UV cut-off at 322 nm. The high UV transmission EVA demonstrated to be more stable under long-term UV exposure [6]. The virgin (uncured) encapsulant is subjected to three different pre-conditioning regimes for five days (Table I) to simulate seasonal humidity variations or non-optimal storage conditions, which can affect the relative humidity inside the storage room. EVA is first -cut and then stored to minimise the time between the removal from the storage room and the closing of the laminator. This time interval is controlled between 30 and 50 seconds.

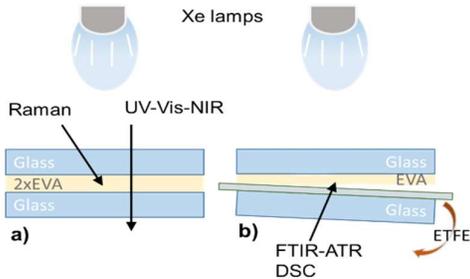
For each of the three EVA storage conditions, 1 cell mini-modules with c-Si PERC solar cells are manufactured in a glass/glass structure. Additionally, 7x7 cm² samples are prepared in order to check the degradation of the EVA.

Table I: EVA storage conditions.

Temperature [°C]	Relative Humidity [%]	Time [days]	ID code
20	30	5	<i>EVA-30</i>
30	65	5	<i>EVA-65</i>
20	100	5	<i>EVA-100</i>

The specimen structure most closely matched to a PV module is glass/EVA/EVA/glass. However, this configuration is not suitable for some characterization tools, which require physical contact with the EVA (FTIR-ATR). Therefore, to exploit multiple characterization techniques two different sample structures were prepared (see Figure 1):

1. glass/2xEVA/glass (*G/G*): it reflects a real module stack. This sample type is used to investigate the optical properties in transmittance of the encapsulant (see Figure 1, a)).
2. Front glass/1xEVA/ETFE/rear glass (*extracted-EVA*): it is used to investigate the chemical changes of the polymer during degradation. The insertion of an ETFE foil allows to easily open the sample and have access to the internal surface of the encapsulant. The analysed polymer surface corresponds to the one in contact with the front side of the cell in a standard module (as shown in Figure 1, b)).

**Figure 1:** cross-sectional sketch of the sample structures used to characterise the encapsulant properties changes during aging.

The same lamination recipe (indicated in Table II) is used for all samples processed for this work

Table II: Samples lamination recipe.

Step sequence	Time [sec]	Temperature [°C]	Pressure [mbar]
Closing	-	ambient	atmospheric
Degassing	240	ambient to 150	0
Curing	720	150	1000
Opening	-	150 to ambient	atmospheric

2.2 Aging conditions

All samples are aged following the IEC 62788-7-2 [7] standard for a total duration of 3000 hours. A Q-Sun Xenon chamber (Q-Lab) is used with the following exposure conditions:

- Chamber air temperature: 65°C;
- Black panel temperature: 90°C;

- Irradiance: 0.8 W/m² at 340 nm;
- Relative humidity: 20%.

The Xe-arc lamp with daylight filter has a UV dose corresponding to 63 W/m² (295 to 395 nm range). This value is corrected by subtracting the front glass absorbance at low UV wavelength. The corrected UV intensity seen by the polymer behind a 3.2-mm-thick front glass is 55 W/m², corresponding to a glass attenuation factor of 0.87. After 3000 hours of aging test, a total UV dose of 165 kWh/m² is reached. This corresponds roughly to an outdoor exposure of ~2.2 years in a Central European temperate climate.

2.3 Sample characterisation techniques

Ultraviolet (UV)/visual (Vis)/near IR (NIR) spectroscopy is used to study the optical properties of the polymer. To verify the chemical degradation effects of EVA, we use Raman spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy in attenuated total reflection (ATR) mode. All samples are characterised at the centre, in order to avoid uncertainties in results due to oxygen diffusion effects at the edges of sample [8].

A regular characterization of the specimens are performed at time intervals (i.e. UV doses) corresponding to the values reported in Table III.

Table III: Samples characterization intervals during aging test.

Time [h]	UV dose [KWh/m ²]
0 (after lam)	0
250	13.8
1000	55
2000	110
3000	165

UV-Vis-NIR spectroscopy.

The UV-Vis-NIR measurements are carried out using a Lambda 950 spectrometer from Perkin Elmer (Waltham, USA). Spectra are recorded from 250 to 2500 nm with an integrating sphere from Labsphere (North Sutton, USA) in order to measure hemispherical transmittance and reflectance. The samples with configuration G/G are measured in transmittance mode.

Raman spectroscopy

EVA in the G/G samples types are used to record Raman spectra by using the MonoVista confocal Raman system. A green laser is used for excitation at 514.5 nm and scanning is conducted in the range 60-4000 cm⁻¹ with an exposure time of 10 seconds with an accumulation of 3 times. Results are normalised at 90 cm⁻¹ to compare the fluorescence peak at 1660 cm⁻¹.

FTIR-ATR spectroscopy

The ATR spectra are recorded by means of a Thermo Fisher Scientific Nicolet 6700 FTIR, over the range 650-4000 cm⁻¹. The measurements are obtained from an average of 32 scans. The peak at 2850 cm⁻¹ of methylene is used as normalisation value. For this measurement, *extracted-EVA* type of samples are analysed.

3 RESULTS

3.1 Modules' visual inspection and performance

After the lamination process, before aging, differences can be noticed along the edges of modules encapsulant with EVA-30, 65, and 100. Figure 2 (top row) shows the visual inspection images of not aged 1 cell mini-modules: when EVA-30 is used, no visible defects are visible. Increasing the relative humidity in the storage room affects the lamination quality with the formation of bubbles during the fabrication step [9]. After the first 13.8 kWh/m² of UV aging, as reported in Figure (bottom row), the properly stored EVA has no visible defects. The bubbles formed after lamination in the EVA-65 module are getting gattered and slowly degassed out the edges. Module encapsulated with EVA-100 shows complete delamination at the edges, a displacement of the front glass and the formation of bubbles also in the center of the module (not shown here). This morphology remained unchanged during the whole test duration (e.g. 3000 hours, 165 kWh/m²).

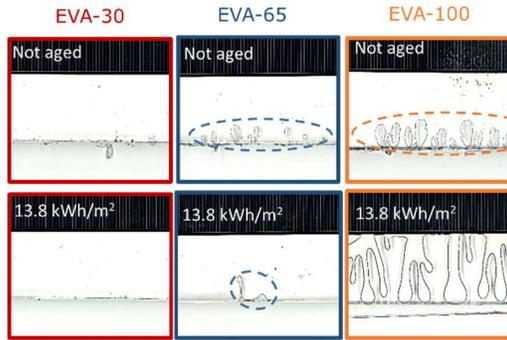


Figure 2: Visual inspection of 1 cell mini-module edges encapsulated with EVA-30, EVA-65, and EVA-100. The images on the top row correspond to unaged samples; Images on the bottom row have been taken after 13.8 kWh/m² of UV dose exposure.

In Figure 3a, the EL images show that the storage conditions or UV aging does not impact the cell/module stability. This result is also confirmed by the measured power from IV curves (see Figure 3b). Modules encapsulated with EVA-30 and EVA-65 did not show any visible defect. The good stability of cells during aging is also confirmed by I-V scans.

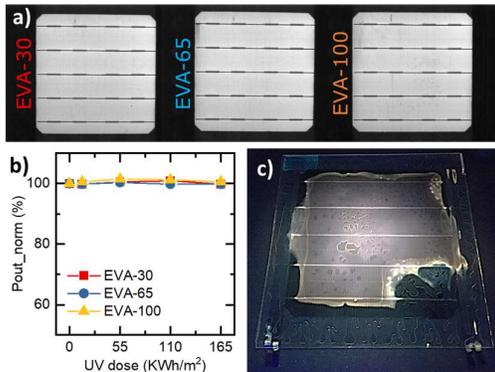


Figure 3: (a) electroluminescence images of 1 cell mini-modules after 165 kWh/m² of UV dose exposure; (b) power output (Pout) of modules during UV aging; (c) fluorescence images of EVA-100 after 165 kWh/m² of UV dose.

However, encapsulant degradation takes time to *translate* into module degradation. The use of a fluorescence lamp is a fast non-destructive method to check for polymer degradation. Under a fluorescent light source, the 1 cell mini-module encapsulated with EVA-100 clearly indicates that the encapsulant shows a degradation patterns particularly pronounced around the sample's edges (Figure 3c).

3.2 Encapsulant aging

The long lag-time between encapsulant and module degradation leads to the importance of investigating not only the module performance, but simultaneously the variation of the encapsulant properties during aging.

3.2.1 Optical transmittance

Storage influences on the optical properties of G/G samples during UV weathering are characterized via UV-Vis-NIR spectroscopy Figure 4 shows that the transmission decreases slightly in the UV range from 290 nm to 370 nm after the first 250 hours of exposure (e.g. 13.8 kWh/m² UV dose). This negligible variation is not accompanied by any visible yellowing. In addition, the transmittance in the Vis-IR range (not shown here) remains constant. This is observed for all the storage conditions. The same trend is reported by Morlier et al. [10] and by Jentsch et al [11] during aging of EVA formulations with low UV cut-off wavelength. It can be concluded that, up to this level of UV exposure, the storage

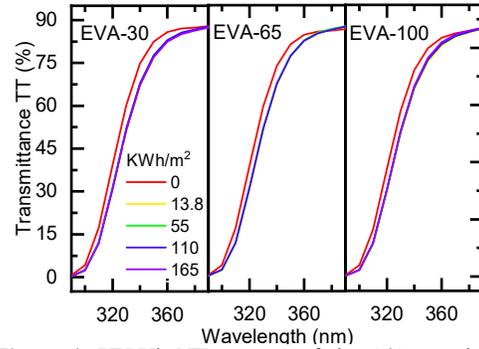


Figure 4: UV-Vis-NIR spectra of the G/G samples encapsulated with EVA-30, EVA-65, and EVA-100

conditions of the EVA do not influence the optical properties during UV aging.

3.2.2 Raman spectroscopy

Raman is a useful, non-invasive technique to study the degradation of the encapsulant [12]. Figure 5 shows Raman spectra recorded after 165kWh/m² UV dose, along with the reference spectrum of un-aged EVA (black curve in Figure 5a). Characteristic EVA peaks are shown: in the region between 3000 and 2830 (CH₂ and CH₃ stretching vibrations), 1740 (C=O stretching vibration), 1440 (CH deformation vibration), 1298 (CH deformation vibration), 1130 (CC stretching vibration) and 1064 cm⁻¹ (CC stretching vibration) [12].

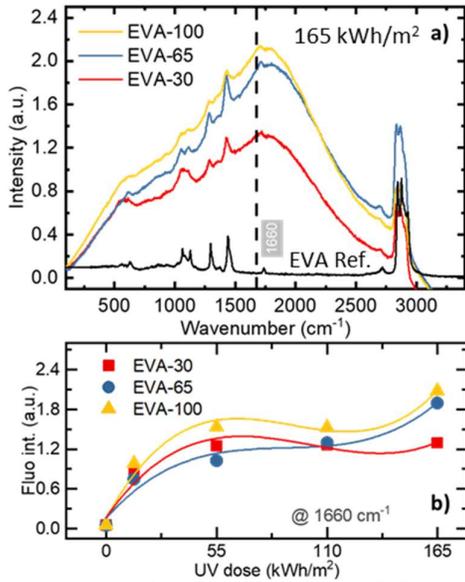


Figure 5: a) Raman spectra of the G/G samples collected after a UV dose of 165 kWh/m² (black curve corresponds to the unaged EVA); b) Fluorescence peak (at 1660 cm⁻¹) intensity trend during UV aging.

A fluorescent background appears and increases with the UV dose. The fluorescence intensity can be an indicator for polymer degradation since it is correlated to the amount of chromophores formed during degradation [13]. The fluorescence trend during UV aging is reported in Figure 5b. All investigated storage conditions (i.e. EVA-30, EVA-65, and EVA-100), show the same fluorescence trend up to 110 kWh/m² of UV dose. During the last measurement, after 165 kWh/m² of UV aging, the fluorescence peak of EVA-65 and EVA-100 start to increase sharper with respect to EVA-30.

3.2.3 FTIR spectroscopy

To understand the degradation impact of the storage conditions on the EVA, the idea is to study the chemical changes at the vicinity of the front cell. FTIR analysis in ATR mode are adopted. *Extracted-EVA* sample types are used and analysed in the central portion. The dry environment inside the climatic chamber allowed to use this type of samples structure (see Figure 1b) avoiding possible deviations with respect to a standard G/G sample [14]. The characterization of the chemical groups via FTIR spectroscopy for the three different stored EVA after lamination, revealed characteristic bands for the unaged samples. Typical peaks for EVA at 1370, 1463, 2848, and 2916 cm⁻¹ are assigned to the symmetric, asymmetric and deformation vibrations of the CH₂ and CH₃ groups of the ethylene segments. The absorption at 1740, 1238 and 1020 cm⁻¹ correspond to ester groups of the Vinyl Acetate segments [15]. During the complete aging time (e.g. 3000 hours, 165 kWh/m² UV dose) EVA-30 and EVA-65 spectra remain stable (not shown here). A small increase of the band at 1710 cm⁻¹ for the EVA-65 was detectable. Figure 6 shows the spectra recorded for the EVA-100 sample. After a UV dose of 110 kWh/m², an increase in the intensity signal is visible for three distinct regions. The

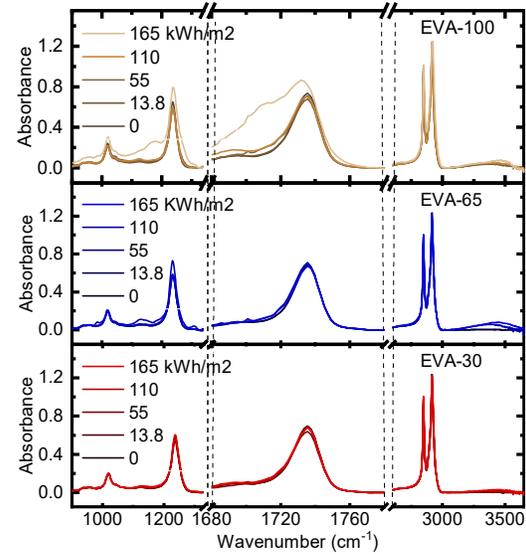


Figure 6: FTIR-ATR spectra recorded during UV aging for the different samples. Measurements are performed on *extracted-EVA* sample type.

appearance of the peak at 995 cm⁻¹ suggests the presence of =CH bonds formed after chain cleavage [16]. The peak at 1160 cm⁻¹ can be attributed to the influence of the C-O-C stretching in aliphatic ester obtained from chain scission [5]. Additionally, the peak at 1708 cm⁻¹ represents the formation of ketone groups [15]. It reveals a harder damage in the EVA stored in a highly humid environment after long-range UV aging.

4 CONCLUSIONS

The purpose of this work is the investigation of the influence of the EVA encapsulant storage condition on the long-term degradation of double glass PV modules. A high UV transmittance EVA formulation is used. Three type of storage conditions are tested with different relative humidity values (30%, 65%, and 100% RH). One cell mini-modules and laminated glass-EVA-glass samples are fabricated and exposed to UV aging up to a total UV dose of 165 kWh/m² (corresponding to approximately 2 years of operation in a Central European temperate climate). Up to this UV dose exposure, the module performance do not change during the whole duration of the test regardless of the storage conditions of the encapsulant.

However, the storage conditions of the polymer prior to the lamination process have clearly an impact on the polymer properties when exposing the samples to UV aging.

The optical characterization (UV/Vis transmittance) did not show remarkable differences. Preliminary signs of chemical degradation are detectable. Specifically, Raman spectroscopy shows a comparable fluorescence trend for all the tested conditions up to 110 kWh/m² of UV dose. The fluorescence background becomes higher in the measured spectra upon exposure to UV for the samples encapsulated with a poorly stored EVA. FTIR confirms the result: the polymer samples that are not correctly stored in a dry and dark environment started degrading after 110 kWh/m² with visible oxidation peaks.

These preliminary results suggest that carefully controlling the storage conditions of the polymer may be critical if EVA is used in double glass structures.

We are continuing this research activity and exposing the samples to higher UV doses in order to monitor the kinetics of the polymer degradation and to understand when this starts impacting the performance of the mini-modules.

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6 ACKNOWLEDGEMENTS

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