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Solar cell UV-induced degradation or module discoloration: between the devil and the deep-yellow sea

Nicolas Pinochet^{1,2}, Romain Couderc¹, Sandrine Therias²

¹University of Grenoble Alpes, CEA, LITEN, DTS, LSA, INES, F-38000, France

²Université Clermont Auvergne-CNRS, ICCF, F-63000 Clermont-Ferrand, France

Corresponding author: Romain COUDERC | e-mail: romain.couderc@cea.fr |
phone: +33479792361

Abstract

For decades, photovoltaic (PV) modules yellowing caused by UV exposure has been observed on operating solar arrays. More than an aesthetic inconvenience, this phenomenon can severely impair the module performances and promote other degradation mechanisms through encapsulant photoprotection undermining. To better understand such reactions in current materials, HJT monocrystalline modules with either UV-cut or UV-pass commercial encapsulants were aged under UV irradiation and examined by visual inspection, fluorescence imaging and flash test. Only encapsulants that were stabilized by UV absorbers underwent discoloration. On one hand, UV absorbers photooxidation is responsible for the formation of yellow chromophores that affect the light transmission to the cell. Consequently, they caused a net decrease of the photogenerated current that reached up to 4% after 4200 hours of accelerated UV ageing. On the other hand, their photobleaching explains the lack of discoloration at the module edges. According to the behaviour of the current encapsulation formulations, stability of UV absorbing additives has to be improved to ensure the durability of the device over 30 years.

Introduction

To limit the most detrimental effects of global warming, major changes in our societies are expected. When it comes to power generation, the 1.5°C scenario requires a drastic increase of the renewable energy part in the global energy mix [1]. Solar photovoltaic (PV) output skyrocketed in the last decade, reaching 821 TWh in 2020. Such endeavour must continue as an 8-fold capacity is needed by 2030 to meet the net zero emissions by 2050, which is a 1.5°C scenario prerequisite [2]. Because of the high impact of a PV system durability on both its levelized cost of energy (LCOE) [3] and life cycle assessment (LCA) [4], the different degradation modes that affect PV modules have to be thoroughly investigated in order to secure the energy transition.

Despite an expected lifetime of 30 years, PV modules suffer from several degradation mechanisms [5] that affect differently their performance depending on its location [6] like discoloration, delamination, corrosion or cell breakage.

The encapsulant yellowing, which can be noticed after long time exposure to UV light [7], is the main topic of this article. Early in the history of large-scale PV power generation, the ARCO PV plant installed in California in 1982 allowed for one of the first observation of important EVA yellowing on the field [8]. Besides an esthetical issue, this phenomenon was then correlated to power losses that could reach 40 % [9], although maximal losses attributed to

discoloration alone are now estimated to be 15 % and due to a current generation decrease [10].

To have a better understanding of the involved phenomena, an imaging technique that precisely identifies where discoloration occurs was required. Some authors use the chromophores fluorescence emission to highlight the pattern of module yellowing or more pronounced browning [11]. To this end, they expose the samples to UV light in the 350-380 nm range and analyse the surface distribution of the module emission response [12]. Köntges *et al.* managed to show by UV fluorescence imaging that yellowing of glass-backsheet modules is particularly visible in the cells centre and lacks around their cracks [13]. Patel *et al.* noticed a different behaviour in the case of glass-glass modules which present a much more homogeneous yellowing [14].

Two hypothesis were formulated to explain the yellowing generation in outdoor conditions for EVA based modules: deacetylation and additives degradation. On one hand, Czanderna and Pern stated in 1996 that yellowing of a stabilized EVA was due to polymer matrix degradation and more specifically deacetylation caused by the photooxidation of carbon chains [9]. Relying on UV fluorescence measurements, they noticed a production of polyenes and α,β -unsaturated carbonyls in conjunction with module yellowing and identified these chromophores as being the ones responsible for the discoloration. On the other hand, after extensive tests of field-aged PV modules, Holley *et al.* showed no sign of EVA deacetylation nor unsaturation formation where yellowing appeared [15]. Based on this observation, they discarded the matrix degradation hypothesis. Instead, they raised a concern about additive reactions and more specifically curing agents such as peroxides. Jentsch *et al.* also supported the additives hypothesis by noticing a slight yellowing of unstabilized EVA that became more intense if the encapsulant contains either hydroxybenzophenone (common UV absorber), arylphosphite (secondary antioxidant) or both of them [16]. This result demonstrated the involvement of stabilizers in EVA optical degradation. Morse *et al.* showed in an International PV Quality Assurance Task Force (PVQAT) paper significant yellowing of all commercial encapsulants with embedded UV screeners [17]. Our article will add arguments for the additives degradation hypothesis.

In this article, monocrystalline modules with different contemporary commercial encapsulants were submitted to ageing tests under accelerated artificial UV light conditions. Visual inspection, fluorescence and I-V curve measurements highlight the UV absorbers role in the different polymer matrices.

Experimental

Five different encapsulants have been used to produce glass-glass monocrystalline modules with nHJT Si-cells with a rear-emitter. They are listed in Table 1.

Table 1 : Description of samples and aging test conditions

Batch number	Batch composition	Encapsulant	UV absorbance (300 – 400 nm)	Aging parameters
1	2 modules	EVA	negligible	Ci5000, xenon lamp, 100 W/m ² , 83 °C, under air
2		TPOA		
3		EVA-UV	high	
4		TPOA-UV		
5		TPOB-UV		

6	1 module			365 nm LEDs, 980 W/m ² , 83 °C, under air
7				305 nm LEDs, 28 W/m ² , 83 °C, under air

Among them, two are ethylene vinyl-acetate copolymers (EVA) and the others are thermoplastic olefinic elastomers (TPO). This designation describes a blend of polyolefin, like a polyethylene derivative, and an elastomer that is slightly crosslinked at the most [18]. EVA-UV, TPOA-UV and TPOB-UV, contain UV blockers. Moreover, EVA-UV and TPOA-UV share the same matrix as EVA and TPOA respectively. The absorption spectra presented in Figure 1a confirm the data provided by the manufacturer. The absorption bands either with two maximums at 314 nm and 356 nm for TPOA-UV or one maximum at 332 nm for EVA-UV and TPOB-UV (Figure 1a) in the UV region is the signature of UV screeners. The shape of TPOA-UV absorption band and the fact that it is substantially shifted compared to the other ones highlight its different nature. The slight UV absorption of encapsulants without UV blockers (EVA, TPOA) can be due to other additives like antioxidants.

Ten modules have been aged in an Atlas Ci5000 weatherometer with an AM1.5G emission spectrum [19] for 4200 hours. Two modules with TPOB-UV were exposed under UV LEDs to study the impact of UV light alone over discoloration phenomena. One was aged under UVB LEDs (305 nm) for up to 1300 h and the other was tested under UVA LEDs (365 nm) for 1000 h. The selection of ageing temperature (83 °C) as well as xenon lamp UV irradiance was made according to IEC 62788-7-2 standard draft to provide a high acceleration of degradation kinetics [20]. Ageing tests parameters (UV chamber, lamp type, UV irradiance, sample temperature, atmosphere) corresponding to each module are presented in Table 1. Figure 1b shows the emission spectra of the different lamps that are used during the tests.

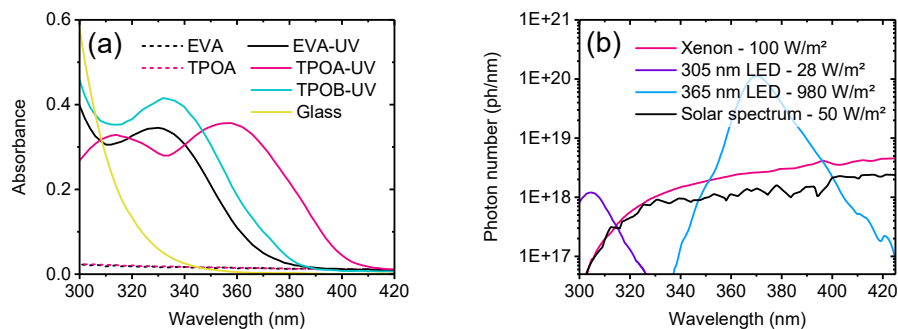


Figure 1: UV absorption spectra of the encapsulant materials (a) and UV emission spectra of the aging lamps (b)

Module samples yellowing is detected by visual inspection, fluorescence imaging and short circuit current loss. Unlike most of published works about PV module fluorescence measurement, our Greateyes LumisolarCell device does not emit UV but rather green light (510 nm) provided by LEDs. In fact, emissions of different UV-excited fluorophore species can overlap. It complicates the understanding of the implied mechanisms. For example, Adothu *et al.* [21] found comparable UV fluorescence emission in two UV aged modules whereas colorimeter measurements revealed a significant difference in modules yellowing. Such gap was however well depicted by Raman spectroscopy that highlighted the strong fluorescence of yellow chromophores under 532 nm emission. This can be explained by the 100 nm shifted

absorption of degraded stabilizers towards higher wavelengths compared to that of their pristine counterparts [22]. This difference may allow to better discriminate their fluorescence emission from that of their pristine counterparts when excitation is in the visible range instead of ultraviolet. As such, we take advantage of this phenomenon in our study. The fluorescent emission is received by a silicon-based CCD camera. Any radiation below 650 nm is also totally filtered to further reduce measure noise such as reflexion of LEDs emission.

To assess the discoloration impact over modules performance, I-V curves are collected under standard test conditions (AM 1.5G standard spectrum, 1000 W/m², 25 °C) [23] with a Spire 5600SPL flasher.

Results and discussion

Yellowing characterization

After 4200 hours of accelerated UV aging under a xenon arc lamp, some monocrystalline modules show yellowing with varying intensity as shown in Figure 2. In absence of polymeric backsheet, this phenomenon is attributed to encapsulant degradation. This is confirmed by a thorough visual inspection that enables a first yellowing mapping. The most affected is EVA-UV, which tends to a brown colouring (Figure 2c). TPOB-UV also exhibits minor discoloration (Figure 2e), followed by TPOA-UV of which yellowing is almost imperceptible to the naked eye (Figure 2d).

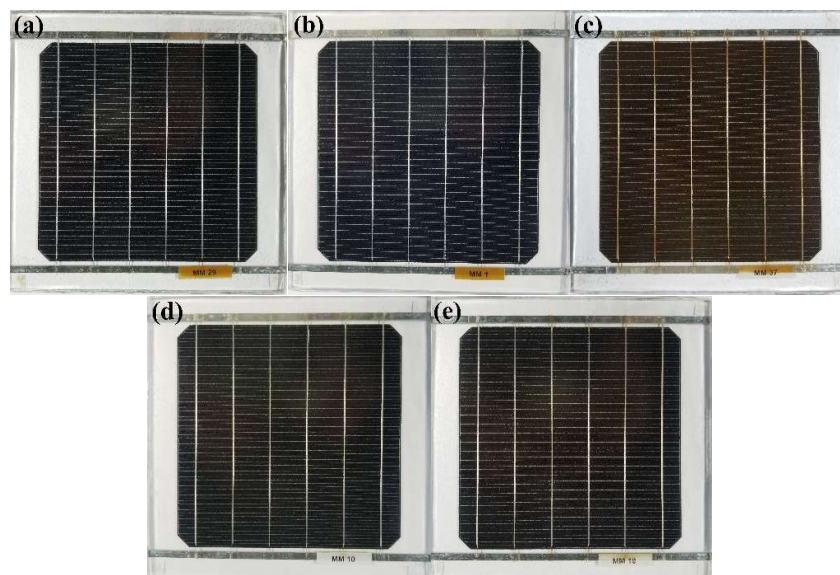


Figure 2: Comparison of monocrystalline modules with EVA (a), TPOA (b), EVA-UV (c), TPOA-UV (d) or TPOB-UV (e) encapsulant after 4200 hours long accelerated UV aging

More precisely, we detected discoloration in the front encapsulant parts that cover the cell and a part of output ribbons (Figure 3), with the notable exceptions of cell edges and gaps between ribbons and cell.

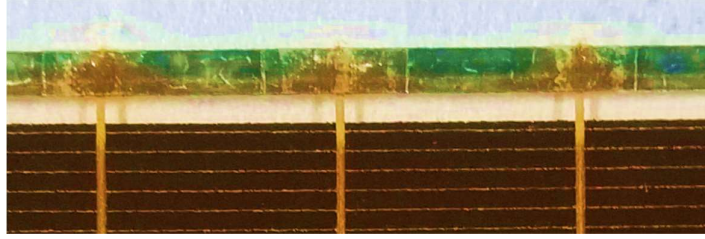


Figure 3: Output ribbon of an aged EVA-UV module. The colours are oversaturated to highlight the discoloration. A part of the output ribbon is partially yellowed, especially near the tab ribbons soldering points.

Finally, monocrystalline modules with the other encapsulation polymers, namely those without UV absorbers, as well as all back faces, did not display any sign of discoloration.

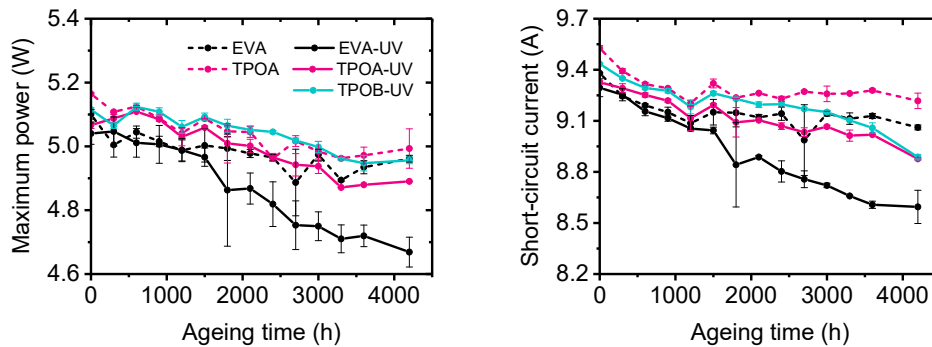
Ageing consequences on performances

More than an aesthetic issue, module yellowing is also a great concern in regard of performance. The performances of the modules enduring UV aging are monitored through recurrent flash tests. One can note in Table 1 that, before ageing, the maximum power (P_{max}) of the modules without UV absorbers is slightly higher (about 1%) than that of the modules with the same matrix and UV absorbers. Such difference comes from the higher I_{sc} allowed thanks to the contribution of the UV photons to the photogeneration in the cell.

Table 2: Initial parameters of monocrystalline modules

Encapsulant	P_{max} (W)	I_{sc} (A)	V_{oc} (V)	FF (%)
EVA	5.10 ± 0.01	9.38 ± 0.01	0.736 ± 0.001	73.9 ± 0.2
TPOA	5.16 ± 0.01	9.43 ± 0.01	0.738 ± 0.001	74.2 ± 0.1
EVA-UV	5.04 ± 0.03	9.29 ± 0.05	0.736 ± 0.002	73.7 ± 0.2
TPOA-UV	5.07 ± 0.01	9.23 ± 0.01	0.737 ± 0.001	74.5 ± 0.3
TPOB-UV	5.12 ± 0.01	9.34 ± 0.01	0.737 ± 0.001	74.3 ± 0.1

Figure 4 presents the evolution of the I-V parameters measured in figures of merit for all nHJT modules during UV aging.



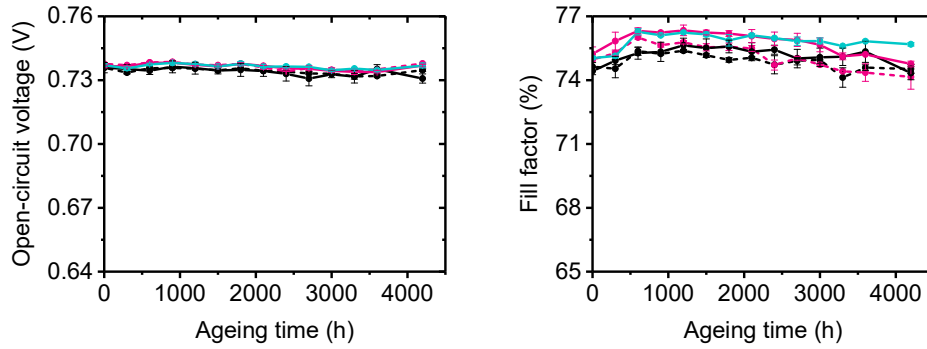


Figure 4: Evolution of the monocell modules performances during accelerated UV aging

The initial discrepancy between modules with and without UV absorbers rapidly shrinks and P_{\max} of the modules with the same encapsulant matrix are similar after only 300 h. After this initial stabilization, the maximum power of all modules are going down at the same rate until 1500 h of aging. After 1500 h, EVA-UV modules power drops at a much faster rate than that of the others. Moreover, if we compare the same matrix with and without UV absorbers, P_{\max} losses of TPOA-UV modules are slightly more important compared to those with TPOA. Such difference is even higher for EVA-UV and EVA modules, and P_{\max} of TPOB-UV modules follows a similar trend as EVA-UV modules' after its initial stabilization.

None of these losses comes from a V_{oc} loss. None of the modules, with or without UV absorbers, shows any V_{oc} loss after 4200 h of ageing. The stability of our nHJT passivation under UV is notable and contrasts with the observations of Sinha *et al* [24]. Such behaviour may be due to the emitter position. In our case, it is located in the rear part of the cell while the cited work touches on HJT cells with front emitter. The V_{oc} invariability means that the P_{\max} losses come from I_{sc} or FF degradations which are displayed in Figure 5.

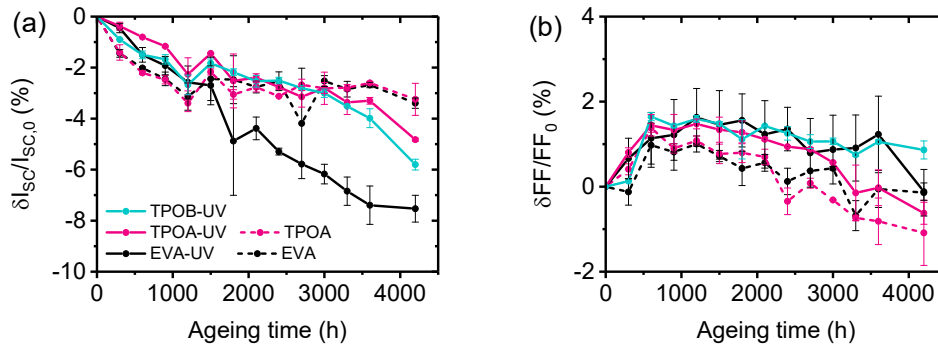


Figure 5: Evolution of the relative loss of modules short-circuit current (a) and fill factor (b) during the test

According to Figure 5a, the short-circuit current (I_{sc}) decreases for all modules. On one hand, after 1500 h, the modules without UV absorbers (EVA, TPOA) maintain their current with a I_{sc} loss of 3.3%. On the other hand, modules with UV-cut encapsulants (EVA-UV, TPOA-UV, TPOB-UV) show a continuous decline of their I_{sc} that reaches up to 7.5% in the case of EVA-UV. The initial I_{sc} decrease could be attributed to the opacification of the cell transparent conductive oxide (TCO) layer under high UV irradiance [25]. The long-term loss could be linked to the yellowing occurrence on modules with UV-cut encapsulants as such discoloration implies a reduced transmission of blue light that impairs the current generation of the cell. By comparing I_{sc} of modules with EVA-UV to that of modules with EVA, the net loss due to discoloration after 4200 h is at least 4.2%. If UV absorbers effectively slow the degradation

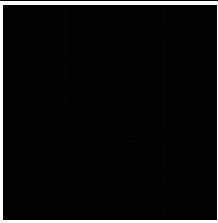
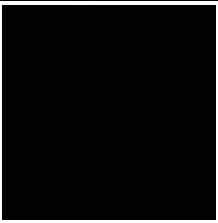
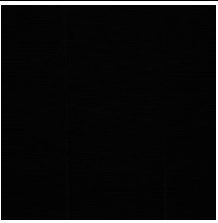
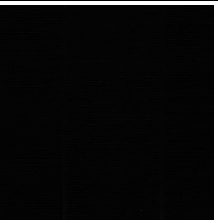
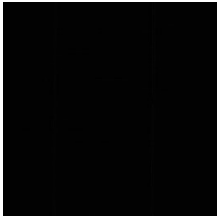
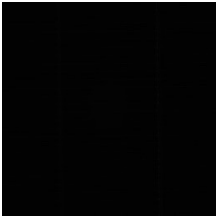
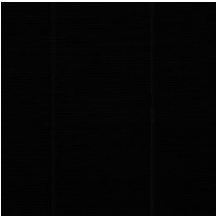
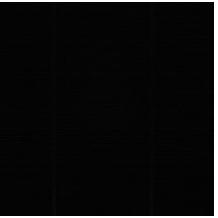
that seems to affect the TCO, the associated I_{sc} loss is reduced for UV-cut encapsulants. In that case, the I_{sc} loss due to yellowing is higher than the simple difference between short-circuit currents of modules with UV-cut and UV-pass encapsulants. The fact that these additional losses only concern encapsulants with UV absorbers indicate that these additives are involved in the degradation mechanism. Pickett and Moore [26] proposed a brief mechanism that could explain the destruction of the aforementioned UV screeners in polymethyl methacrylate (PMMA) that is exposed in the presence of air to wavelengths below 365 nm. According to their results, these molecules are excited by the UV light and decomposed in benzoic acid and phenol products. According to Jentsch *et al.* [16], these molecules can be responsible for the discoloration.

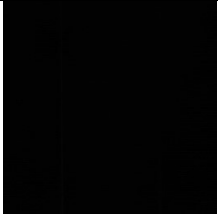
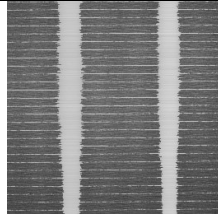

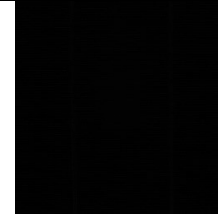
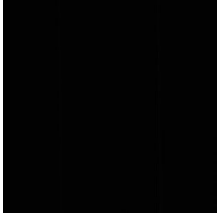
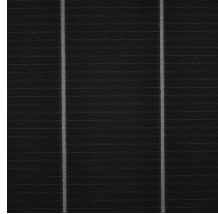
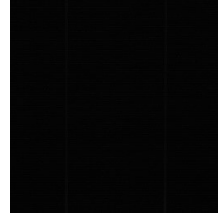
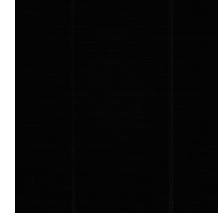
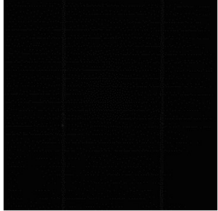
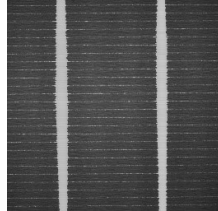
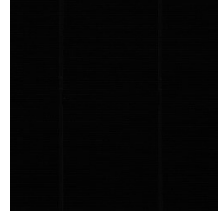
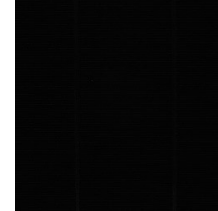
Figure 5b shows a fill factor (FF) increase after the first 600 hours of illumination. Furthermore, it also decreases in the long run for TPOA and TPOA-UV modules. The I-V curves reveal a notable increase of the series resistance R_{series} , which may explain the FF loss. However, for other modules, the FF variation does not follow the same trend as the decrease of their I_{sc} is more pronounced and consequently compensates for the R_{series} rise in the FF calculation. The early FF gain can be caused by the light soaking of the HJT cells involved by visible and infrared parts of the lamp spectrum [27]. The R_{series} increase could be attributed to the potential TCO photodegradation that would cause the aforementioned early I_{sc} loss.

Degradation of UV blockers under high UV irradiance

In order to get a more precise spatial localization of the observed yellowing after UV aging in the modules, fluorescence measurements with a 510 nm excitation were carried out. Table 3 presents fluorescence images of monocrystalline modules centre from the front and back sides with different encapsulation polymers (EVA, TPOA, EVA-UV, TPOA-UV, TPOB-UV) before and after accelerated UV aging for 4200 h.

Table 3: Fluorescence of monocrystalline modules centre from the front and back sides with different encapsulation polymers (EVA, TPOA, EVA-UV, TPOA-UV, TPOB-UV) before and after accelerated UV aging for 4200 h. Each picture was shot in the same conditions and covers a 5 x 5 cm² surface.

Encapsulant	Front – 0h	Front – 4200 h	Back – 0h	Back – 4200 h
EVA				
TPOA				

EVA-UV				
TPOA-UV				
TPOB-UV				

After ageing, the front side of modules with UV absorbers displays a fluorescence emission with higher intensity in the metallization vicinity whereas the backside images remain black. Other modules do not show any sign of fluorescence after ageing. The cell on top of the backside encapsulant protected the encapsulant from the UV light, explaining the differences between front and back faces. The absence of fluorescence emission for modules with UV-pass encapsulants suggests a degradation and transformation of the different UV absorbers into fluorescent chromophores [28]. The fact that ribbons and fingers seem brighter than TCO on images that depict fluorescence may be due to the reflexion of fluorophores emission on those metallic surfaces [29].

Figure 6 is a partial fluorescence mapping of a module of both front and back sides.

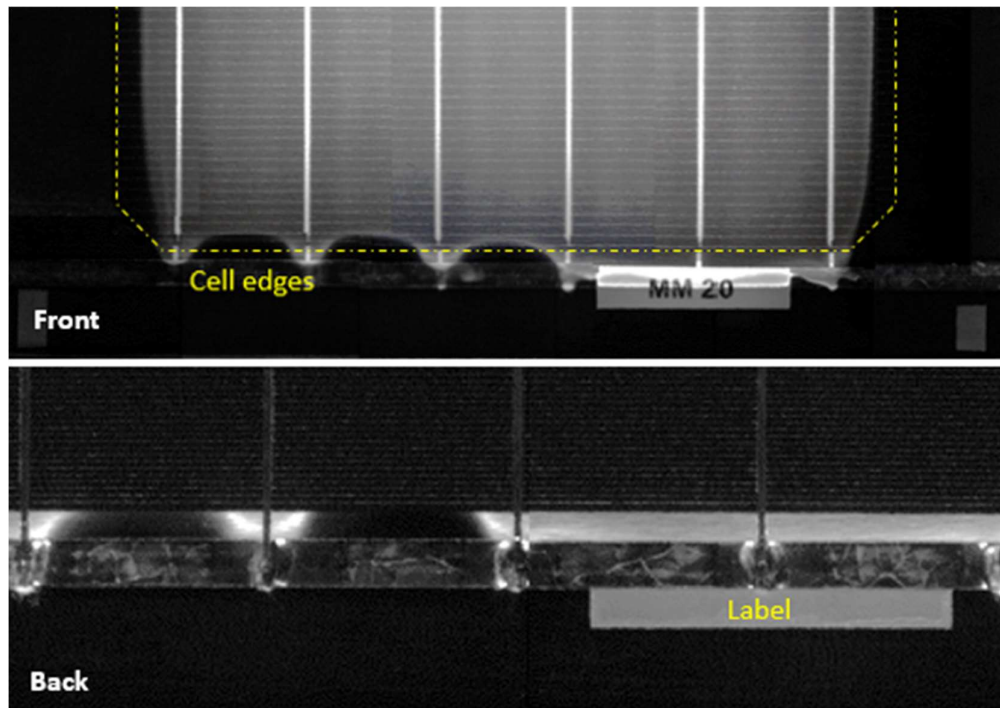


Figure 6: Partial fluorescence mapping of a monocell module with TPOB-UV encapsulant

On the front face, the module displays fluorescence with extended cell coverage while the edges remain dark. Over the cell, the intensity of the fluorescence emission becomes slightly higher toward the centre. The frontier between regions with and without fluorescence is very sharp and forms an arc-shaped front between the tab ribbons. Near the module tag, which is in between the front glass and the front encapsulant, the fluorescence front is smoother and irregular bright spots can be seen above the output ribbon. On its back face, fluorescence can be observed as well but output and tab ribbons obscure it. Then, the fluorescence emission seems to come from the upper part of the front encapsulant. Lyu *et al.* [30] also found that yellowing is mainly occurring near the glass-encapsulant interface. In fact, UV photons will be first absorbed in the encapsulant near the glass-encapsulant interface. It leads to a higher photoreactivity near the glass surface and thus a higher yellowing.

The sharp fluorescence gradient at the cell edges may be the consequence of a reaction-diffusion mechanism that arises from the competition between several chemical reactions. As soon as chromophore products are generated from UV absorbers, they can be destroyed through photobleaching (photooxydation mechanism) [21] that erases the discoloration. Strong photobleaching was expected at the edges of the module where oxygen concentration is kept high because of lateral diffusion. It explains the absence of fluorescence emission in this region. The fluorescent area is limited near the edges of the cell. Photobleaching seems limited because of the presence of obstacles. For example, the module label seems to favour fluorophores formation over photobleaching by acting as a mechanical barrier to oxygen diffusion. The same fluorescence patterns are visible with TPOA-UV and EVA-UV modules as shown in Figure 7.

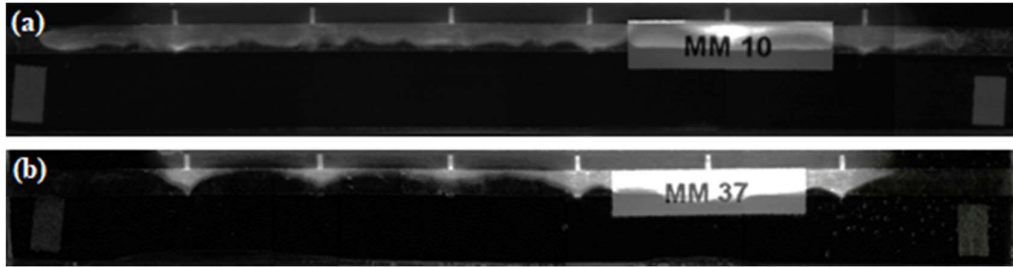


Figure 7: Fluorescence imaging of TPOA-UV (a) and EVA-UV (b) modules output ribbon.

Fluorescence emission can be detected on both modules and parts of respective fluorescence fronts are localized on the output ribbons. Because the fluorescent encapsulant part over the output ribbon is smaller, photobleaching seems more advanced in the case of EVA-UV compared to that of TPOA-UV. UV degradation in a given medium may differ relatively to their chemical nature [31] and the various polymer matrix can influence differently the behaviour and stability of such additives [32]. As such, the differences in UV-cut encapsulants formulation may explain the variability of fluorophores formation and photobleaching balance. Figure 3 and Figure 7b reveal similar patterns and location between yellowing and fluorescence emission, meaning that the visible chromophores and the fluorophores are the same species.

The role of UV light

Modules with TPOB-UV encapsulant has also been aged under UV LEDs that emit around either 365 or 305 nm. The emission spectra are much narrow than AM 1.5G or xenon-arc lamp's (Figure 1). As such, the specific role of UV irradiation on yellowing and photobleaching is investigated on an encapsulation polymer for which it has been proven that discoloration can happen under solar-like light during accelerating aging tests. Figure 8 presents the fluorescence shots of the modules with TPOB-UV module aged under 365 nm and 305 LEDs.

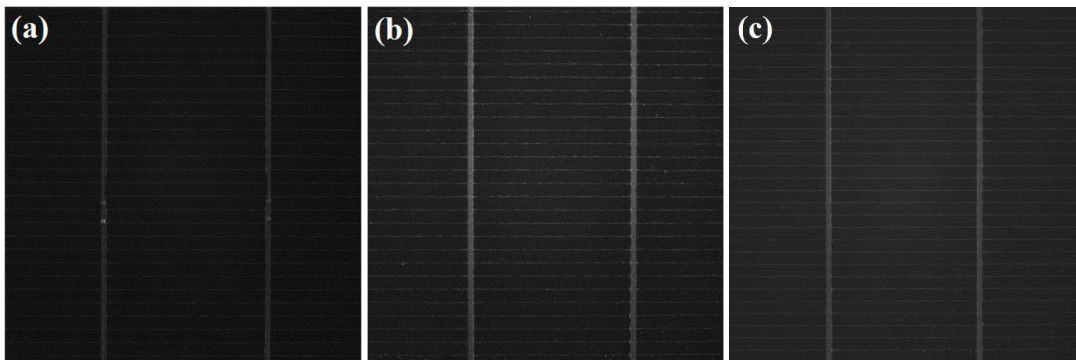


Figure 8: Fluorescence shots of unaged module (a), and modules aged under UVA (b) and UVB light (c). The three pictures were shot in the same conditions and covers a $5 \times 5 \text{ cm}^2$ surface.

A slight fluorescence can be noticed on both aged modules after 1000 and 1300 hours of accelerated aging test, respectively. Because of the lower intensity of fluorescence emission, the integration time we chose for imaging was five-fold higher than that of the previous study. It explains the brightness of the unaged sample that may be caused by the fluorescence emission of pristine additives. A sole UVA (*i.e.* 320 to 400 nm) exposure seems to be enough to cause fluorescence. Because of their massive UV absorption (Figure 1a), UV absorbers

degradation following their photoexcitation is likely responsible for the fluorescence.

Long irradiation time (1000 hours) under UVA LEDs (365 nm) seem to induce more fluorescence emission than 1300 hours of UVB LEDs (305 nm) irradiation while Figure 1 shows that UVA photons are less susceptible to be absorbed than their UVB counterparts. Furthermore, fluorescence is even higher after the aforementioned 4200 hours long ageing under a solar-like light. The UV photon dosage under UVB LEDs, UVA LEDs and xenon-arc lamp are 2.3×10^{22} , 1.8×10^{24} and 1.2×10^{23} ph.h.m⁻², respectively. While UVB irradiation may be more likely to degrade UV absorbers, the fact that UVA photons dosage is 2 decades higher may explain why fluorescence emission is brighter on Figure 8b compared to Figure 8c. According to Figure 1, the front glass strongly absorbs in the UVB range, which further reduce the amount of UVB photons that reach the encapsulant. The presence of UVB radiations in the xenon-arc lamp combined to a closer photon dosage may account for the more intense fluorescent emission of modules that were aged in Ci5000 test chamber. Failure of the reciprocity law (*i.e.* proportionality between degradation rate and UV light dosage) in that irradiance range could also lead to a higher fluorophore formation in the 4300 hours of ageing test under xenon-arc lamp.

Discussion

Although UV absorbers tend to degrade over time and impair PV modules performance, the protection they provide against polymer photodegradation may still justify their use in cell encapsulation. For instance, they may be used to shield high-efficiency cells like silicon heterojunction (HJT), passivated emitter rear totally diffused (PERT), passivated emitter and rear contact (PERC) [24] or even perovskite cells [33] from detrimental UV radiations as long as such technologies remain vulnerable.

Samples that have been discoloured underwent accelerated aging through high temperature and irradiance exposure in less than six months. Yellowing will not occur as early in outdoor conditions. An acceleration factor is yet to be determined to provide a reliable extrapolation of the actual degradation rate for outdoors modules. It requires an extensive study of each parameter effect on discoloration kinetics. For instance, higher temperatures may accelerate the reaction kinetics [28]. A simple Arrhenius law that is generally used in degradation rates modelling [34] can associate our last results (4200 h of accelerated aging) to an outdoor ageing that may go from 4 to 15 years depending on the apparent activation energy (30 [22] to 60 kJ.mol⁻¹ [35]).

On another hand, organic UV absorbers are still an efficient way to avoid or limit the UV induced damages on the cell and encapsulant despite their yellowing. Indeed, these damages can lead to catastrophic failures like delamination [36]. As such, it would be interesting to work on their stabilization to diminish the yellowing. This is particularly true for high UV irradiance environments like deserts. This might be done by increasing the photostabilisers concentration or replacing organic UV blockers by mineral ones [37]. Novel UV absorbing technologies such as quantum dots [38] may also become an alternative solution. Despite its slight impact on their initial performances [39], UV absorbing cerium oxide glass that was used in the 90's [40] could be reconsidered for the manufacturing of UV resilient PV modules. Finally, new encapsulation materials such as thermoplastic polyolefins (TPO) [41] are being developed and optimized in an attempt to improve the overall durability of the module. Diminishing the intrinsic discoloration potential stands among the goals of these studies [42].

Conclusion

The results obtained under accelerated artificial ageing of commercial encapsulants specially designed to provide high protection against UV are sensitive to yellowing. This phenomenon is not originating from the polymer matrix but rather from its additives and more particularly UV absorbers. Under UV exposure, they undergo a photoreaction and become chromophore species that can be detected through fluorescence measurement. The overall loss of photogenerated current is significant and reached 4% after 4200 hours of accelerated UV ageing for the most discoloured modules. Furthermore, the destruction of UV absorbers is an issue for the integrity of the whole PV module and can lead to accelerated delamination among other critical damages. There is then a challenge in finding new ways to bolster the photoprotection of the device, especially for the most stringent applications such as deserts.

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