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

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

¹Univ. Grenoble Alpes, CEA, Liten, INES, ITE INES.2S, 73375 Le Bourget du Lac, 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) module yellowing caused by UV exposure has been observed on solar arrays in operation. More than an aesthetic inconvenience, this phenomenon can severely impair module performance and promote other degradation mechanisms by undermining the photoprotection provided by encapsulation. To understand how this reaction may affect current encapsulation materials, silicon heterojunction (SHJ) monocrystalline modules with either UV-cut or UV-transparent commercial encapsulants were aged under UV irradiation and examined by visual inspection, fluorescence imaging and flash tests. Despite the photoprotection they provide, only the encapsulants that were stabilized by UV absorbers underwent discolouration. On the one hand, UV absorber photooxidation is responsible for the formation of yellow chromophores that affect light transmission to the cell, which could cause net decrease in the photogenerated current high as 4% after 4200 hours of accelerated UV ageing. On the other hand, UV-induced degradation of SHJ solar cells only accounts for a lower photogenerated current loss (3%), in contrast with previous observations in the literature. According to the behaviour of the current encapsulation formulation, the 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 needed. In regard to power generation, a drastic increase in the renewable energy part of the global energy mix is needed [1]. Solar photovoltaic (PV) output has skyrocketed in the last decade, reaching 821 TWh in 2020. This endeavour must continue, as an 8-fold capacity is needed by 2030 to meet the goal of net zero emissions by 2050, which is a prerequisite for the 1.5 °C scenario [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 must be thoroughly investigated to secure the energy transition.

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

Encapsulant polymer yellowing, which can occur after long term 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 observations of EVA

yellowing in the field [8]. In addition to being an aesthetical issue, this phenomenon was then correlated to power losses that could reach 40%[9], although maximal losses attributed to discolouration alone are now estimated to be 15% and due to a current generation decrease [10].

The following two hypotheses were formulated to explain the yellowing of EVA based modules in outdoor conditions: deacetylation and additive degradation. On the 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 the production of polyenes and α,β -unsaturated carbonyls in conjunction with module yellowing and identified these chromophores as being responsible for the discolouration. On the other hand, after extensive tests of field-aged PV modules, Holley *et al.* found no sign of EVA deacetylation or unsaturation formation where yellowing appeared [11]. Based on this observation, they discarded the matrix degradation hypothesis. Instead, they hypothesized that additive reactions may be blame and, more specifically, curing agents such as peroxides. Jentsch *et al.* also provided support for the additives hypothesis, stating that the yellowing of unstabilized EVA that became more intense if the encapsulant contained either hydroxybenzophenone (common UV absorber), arylphosphite (secondary antioxidant) or both [12]. This result indicated the involvement of stabilizers in EVA optical degradation. In an International PV Quality Assurance Task Force (PVQAT) paper, Morse *et al.* showed significant yellowing of all commercial encapsulants with embedded UV absorbers [13]. Our findings further support the additive 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 were used to highlight the roles of UV absorbers in different polymer matrices.

Experimental

Five different encapsulants were used to produce glass-glass monocrystalline modules with nSHJ Si-cells with a rear-emitter. These modules were manufactured in a 3S S1815E laminator at 160 °C. Depending of the encapsulation polymer, lamination time varies from 12 min (TPOA, TPOA-UV) to 22 min (EVA, EVA-UV, TPOB).The modules encapsulant and associated ageing test conditions are listed in Table 1.

Table 1 : Description of samples and ageing test conditions

Ageing test	Encapsulant	UV chamber	Lamp	UV irradiance (W.m ⁻² , 300-400 nm)	Module temperature (°C, front face)	Atmosphere
1	EVA	Atlas Ci5000	Xenon-arc with borosilicate filter	100	83	Air, 30 %RH
	TPOA					
	EVA-UV					
	TPOA-UV					
	TPOB-UV					
2	TPOB-UV	UWAVE UV chamber with	305 nm LEDs	28		

		heating plate				
3	TPOB-UV	UWAVE UV chamber with heating plate under air	365 nm LEDs	980		

Two of the encapsulants are ethylene vinyl-acetate copolymers (EVA) and the others are thermoplastic olefinic elastomers (TPO). This designation describes blends of polyolefins, such as polyethylene derivative, and elastomers that are only slightly crosslinked [14]. EVA-UV, TPOA-UV and TPOB-UV contain UV absorbers, as confirmed by their absorption spectra in Figure 1a. Moreover, EVA-UV and TPOA-UV share the same matrices as EVA and TPOA respectively, while TPOA and TPOB-UV are different polyolefins. The absorption bands either with two maxima 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 are the signatures of UV absorbers. The shape of the TPOA-UV absorption band and the fact that it is substantially shifted compared to the other bands highlight its different nature.

Five pairs of modules of each encapsulant were aged in an Atlas Ci5000 weatherometer with an AM1.5G emission spectrum [15] for 4200 hours. Two modules with TPOB-UV were exposed in two UWAVE chambers with UV LEDs to study the impact of either UVB (280-320 nm) and UVA (320-400 nm) light alone over discoloration phenomena. One was aged under 305 nm LEDs for up to 1300 h and the other was tested under 365 nm LEDs for 1000 h. The ageing temperature (83 °C) and xenon lamp UV irradiance were selected according to the IEC TS 62788-7-2:2017 standard to provide a high acceleration of degradation kinetics [16]. The ageing test 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.

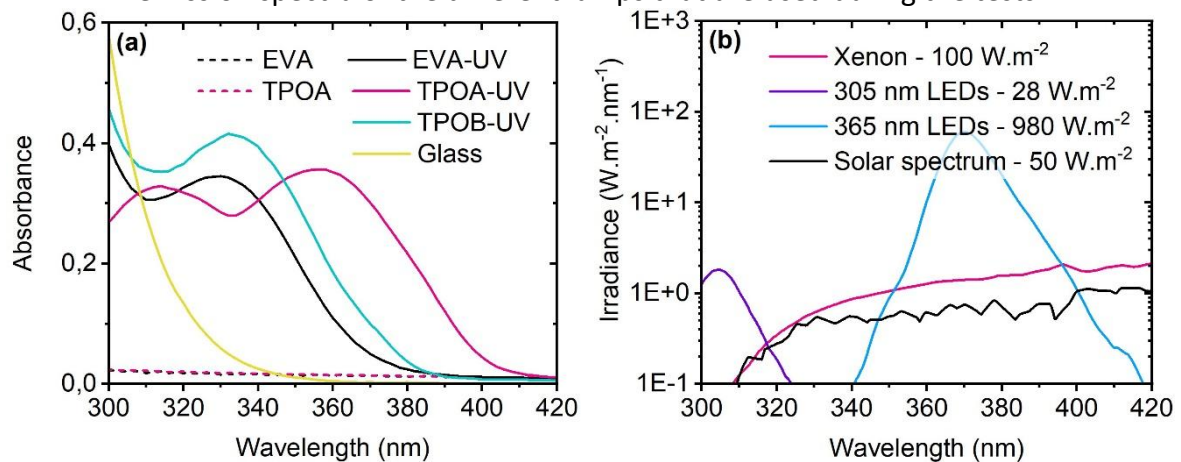


Figure 1: UV absorption spectra of the encapsulant materials (a) and UV emission spectra of the ageing lamps (b)

Yellowing of the samples is detected by visual inspection, fluorescence imaging and short circuit current loss. Unlike most published works on PV module fluorescence measurement, our Greateyes LumisolarCell device does not emit UV light but rather emits green light (510 nm) provided by LEDs. In fact, the emissions of different UV-excited fluorophore species can overlap. It complicates the understanding of the implied mechanisms. For example, Adothu *et al.* [17] found comparable UV fluorescence emission results in two UV-aged modules,

whereas the colorimeter measurements revealed a significant difference in the amount of yellowing of the modules. However, this gap was well depicted by Raman spectroscopy, which highlighted the strong fluorescence of yellow chromophores under a 532 nm emission. During its degradation, a 100 nm redshift of the UV absorber absorption spectrum occurs [18]. As such, the fluorescence response of the photostabilizers under visible light becomes much more probable in their degraded state. This difference may allow better discrimination of their fluorescence emission from that of their pristine counterparts when excitation is in the visible range instead of in the ultraviolet range. We take advantage of this phenomenon in our study. The fluorescent emission is captured by a silicon-based CCD camera. Any radiation below 650 nm is also totally filtered to further reduce measurement noise, such as reflexion of LED emission reflexions.

To assess the impact of discolouration on module performance, I-V curves are collected under standard test conditions (AM 1.5G standard spectrum, 1000 W/m², 25 °C) [19] with a Spire 5600SPL flasher.

Results and discussion

Yellowing characterisation

After 4200 hours of accelerated UV ageing under a xenon arc lamp, some monocrystalline modules show yellowing with varying intensity levels as shown in Figure 2. In the absence of a polymeric backsheet, this phenomenon is attributed to encapsulant degradation. This is confirmed by a thorough visual inspection that enables mapping of the occurrences of yellowing. The most affected is the EVA-UV encapsulated module, which tends to have a brown colour (Figure 2c). TPOB-UV also exhibits minor discolouration (Figure 2e), followed by TPOA-UV, of which almost no yellowing is perceivable by the naked eye (Figure 2d).

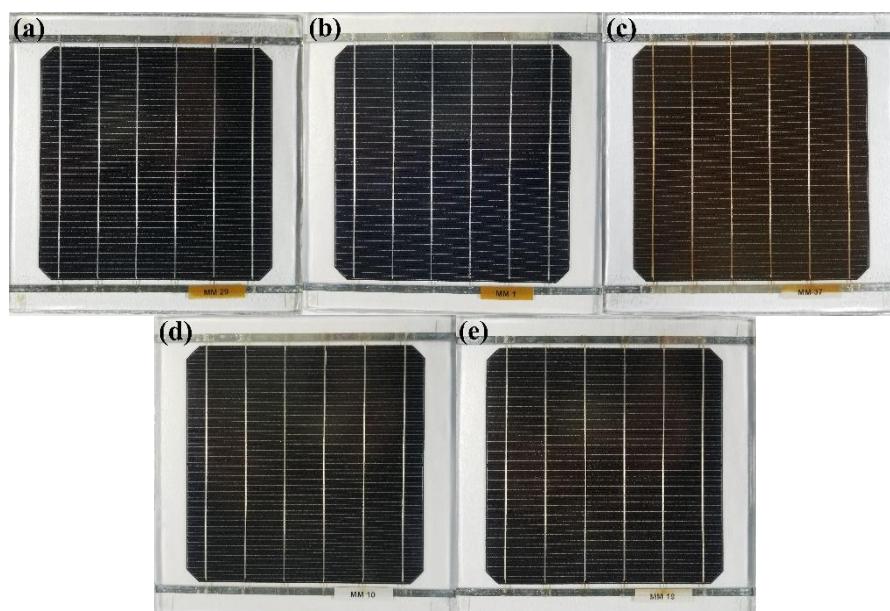


Figure 2: Comparison of monocrystalline modules with EVA (a), TPOA (b), EVA-UV (c), TPOA-UV (d) or TPOB-UV (e) encapsulants after 4200 hours of accelerated UV ageing

More precisely, we detected discolouration in the front encapsulant parts that cover the cell

and a part of cross connectors (Figure 3), with the notable exceptions being the cell edges and gaps between ribbons and cell.

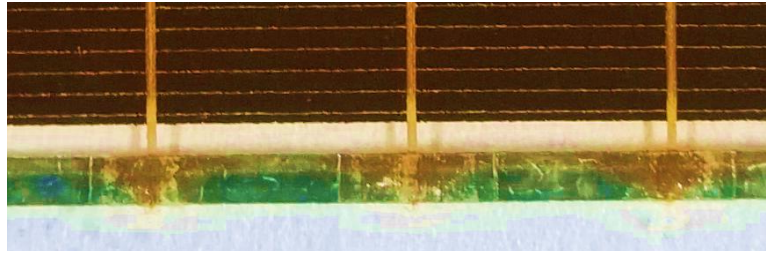


Figure 3: Output ribbon of an aged EVA-UV module. The colours are oversaturated to highlight the discolouration. A part of the cross connector is partially yellowed, especially near the tab ribbon soldering points.

Finally, none of the monocrystalline modules encapsulated with the other polymers (Figures 2a and 2b), namely, those without UV absorbers, displayed any signs of discolouration, nor did any of the rear faces.

Ageing consequences on performance

More than an aesthetic issue, module yellowing is also a great concern in regard to performance. The performances of the modules enduring UV ageing are monitored through recurrent flash tests. As Table 2 shows, before ageing, the maximum power (P_{max}) of the modules without UV absorbers is slightly higher (approximately 1%) than that of the modules with the same matrix and UV absorbers. This difference results from the higher short-circuit current (I_{sc}) allowed thanks to the contribution of the UV photons to the photogeneration in the cell.

Table 2: Initial parameters of the 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 of all nSHJ modules during UV ageing.

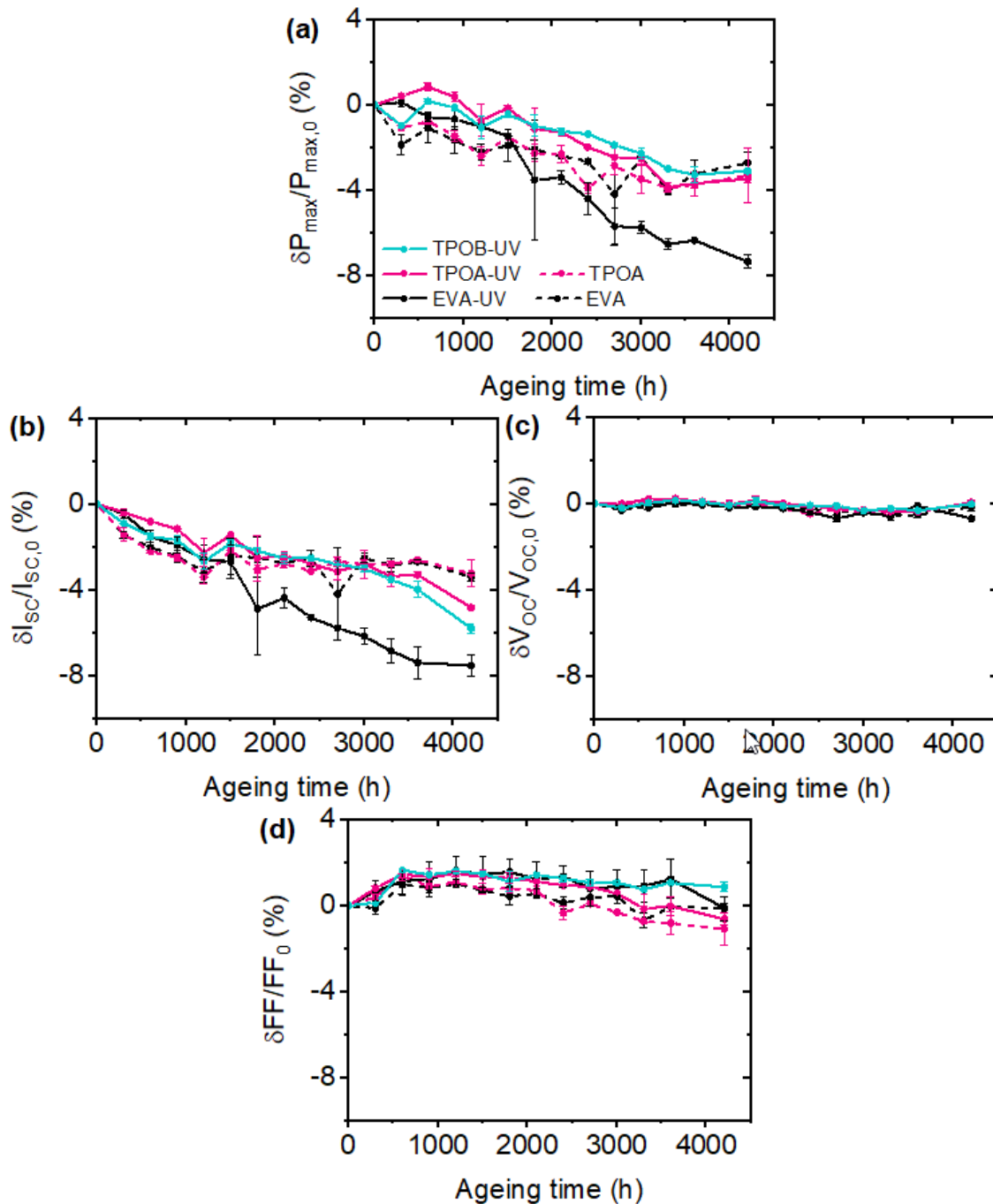


Figure 4: Evolution of the monocell module maximum power (a), short-circuit current (b), open-circuit voltage (c) and fill factor (d) during accelerated UV ageing

According to Figure 4a, the initial discrepancy between modules with and without UV absorbers rapidly shrinks, and the P_{max} values of the modules with the same encapsulant matrices are similar after only 300 h. After this initial stabilization, the maximum power of all modules decreases at the same rate until 1500 h of ageing. After 1500 h, the power of the EVA-UV modules drops at a much faster rate than that of the others. Moreover, if we compare the same matrix with and without UV absorbers, the P_{max} losses of the TPOA-UV modules are slightly more important than those of the TPOA modules. This difference is even more pronounced for the EVA-UV and EVA modules, and the P_{max} of the TPOB-UV modules follows a similar trend as that of the EVA-UV modules after its initial stabilization.

According to Figure 4c, these losses do not relate to the open-circuit voltage (V_{oc})

evolution. No module, with or without UV absorbers, shows any V_{oc} loss after 4200 h of ageing. The stability of our SHJ passivation under UV is notable and contrasts with the observations of Sinha *et al.* [20]. Such behaviour may be due to the emitter position. In our case, it is in the rear part of the cell, while the cited work focuses on SHJ cells with a front emitter. V_{oc} invariability means that the P_{max} losses come from I_{sc} or FF degradations.

According to Figure 4b, the I_{sc} values decrease for all modules. On the one hand, after 1500 h, the modules without UV absorbers (EVA, TPOA) maintain their current values with an 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 transparent conductive oxide (TCO) layer of the cell under high UV irradiance [21]. The long-term loss could be linked to the yellowing of the modules with UV-cut encapsulants, as such discolouration implies a reduced transmission of blue light, which impairs the current generation of the cell. By comparing the I_{sc} values of modules with EVA-UV to those of modules with EVA, the net loss due to discolouration 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 the short-circuit currents of modules with UV-cut and UV-transparent encapsulants. The fact that these additional losses only concern encapsulants with UV absorbers indicates that these additives are involved in the degradation mechanism. Pickett and Moore [22] proposed a mechanism that could explain the destruction of the aforementioned UV absorbers 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 UV light and decomposed into benzoic acid and phenol products. According to Jentsch *et al.* [12], these molecules may be responsible for the discolouration.

Figure 4d **Erreur ! Source du renvoi introuvable.** shows a fill factor (FF) increase after the first 600 hours of illumination. Furthermore, it also decreases in the long run for the TPOA and TPOA-UV modules. The I-V curves evolution, of which an example is given in Figure 5, reveals a notable increase in the series resistance R_{series} for all modules, which may explain the FF loss.

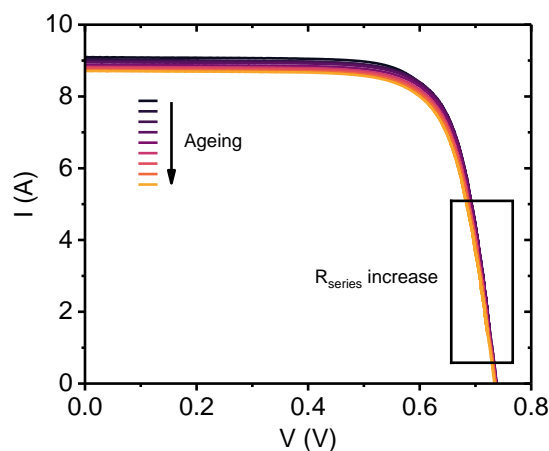


Figure 5: I-V curve evolution of module with TPOB-UV during accelerated UV ageing

However, for modules with UV-cut encapsulant, the FF variation does not follow the same

trend, as their I_{sc} values decrease dramatically more pronounced and consequently compensate for the increase in the R_{series} values in the FF calculation. The early FF gain can be caused by the light soaking of the SHJ cells involved in the visible and infrared parts of the lamp spectrum [23]. The R_{series} increase could be attributed to the potential TCO photodegradation that would cause the aforementioned early I_{sc} loss.

Degradation of UV absorbers under high UV irradiance

To obtain a more precise spatial localization of the observed yellowing in the modules after UV ageing, fluorescence measurements with 510 nm excitation were carried out. Table 3 presents fluorescence images of monocell modules centred from the front and back sides with different encapsulation polymers (EVA, TPOA, EVA-UV, TPOA-UV, and TPOB-UV) before and after accelerated UV ageing for 4200 h.

Table 3: Fluorescence of monocell modules centred from the front and back sides with different encapsulation polymers before and after accelerated UV ageing for 4200 h. Each picture was taken under the same conditions and covers a 5 x 5 cm² surface. The pictures are black when no fluorescence emission was detected.

Encapsulant	Front – 0 h	Front – 4200 h	Back – 0 h	Back – 4200 h
EVA				
TPOA				
EVA-UV				
TPOA-UV				
TPOB-UV				

After ageing, the front sides of the modules with UV absorbers display fluorescence emissions with higher intensity in the metallization vicinity, whereas the backside images remain black. The other modules do not show any signs of fluorescence after ageing. The cell on top of the backside of the encapsulant protected the encapsulant from UV light, explaining the differences between the front and rear faces. The absence of fluorescence emissions for modules with UV-transparent encapsulants suggests a degradation and transformation of the different UV absorbers into fluorescent chromophores [24]. The fact that the ribbons and fingers seem brighter than the TCO on the images that depict fluorescence may be due to fluorophore emission reflexions on those metallic surfaces [25]. Furthermore, the comparison of module picture and fluorescence shot (Figure 6) reveals similar patterns and locations of the yellowing and fluorescence emissions, meaning that the visible chromophores and the fluorophores are the same species.

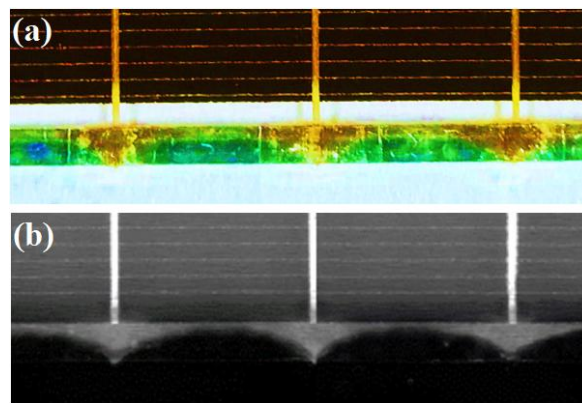


Figure 6: Comparison of yellowing (a) and fluorescence emission (b) patterns on an aged EVA-UV module

Figure 7 is a partial fluorescence mapping of a module of both front and back sides.

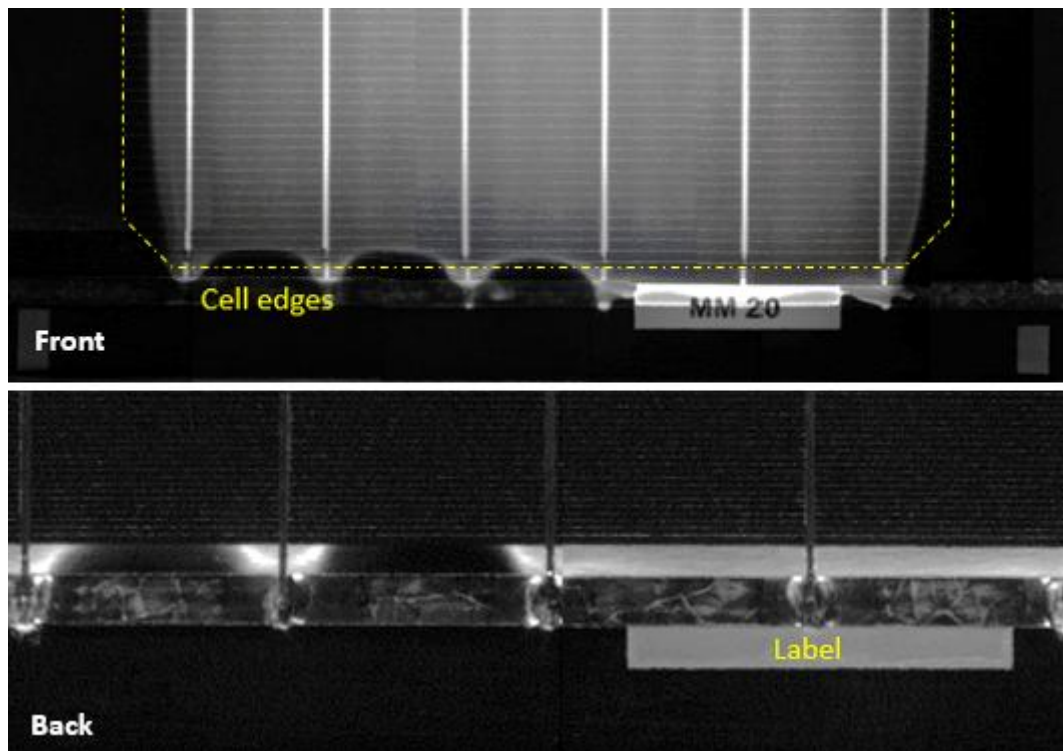


Figure 7: Partial fluorescence mapping of a monocrystalline module with a TPOB-UV encapsulant

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 towards 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 between the front glass and the front encapsulant, the fluorescence front is smoother and irregular bright spots can be observed above the cross connector. On its rear face, fluorescence can be observed as well, but the cross connector and tab ribbons obscure it. Then, the fluorescence emission seems to come from the upper part of the front encapsulant. Lyu *et al.* [26] also found that yellowing mainly occurs near the glass-encapsulant interface. In fact, UV photons will be first absorbed by the encapsulant near the glass-encapsulant interface. This leads to a higher photoreactivity near the glass surface and, thus, more pronounced 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 (photooxidation mechanism) [17], which erases the discolouration. Strong photobleaching was expected at the edges of the module where the oxygen concentration remained high because of lateral diffusion. This 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 fluorophore formation over photobleaching by acting as a mechanical barrier to oxygen diffusion. The TPOA-UV and EVA-UV modules display the same fluorescence patterns, as shown in Figure 8.

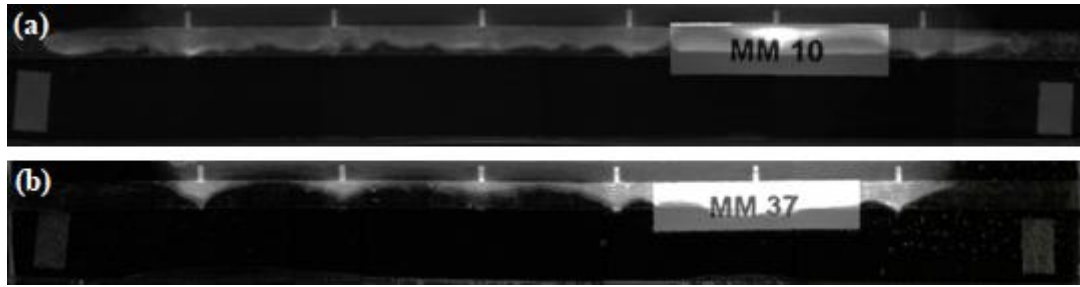


Figure 8: Fluorescence imaging of the TPOA-UV (a) and EVA-UV (b) module cross connectors.

Fluorescence emissions can be detected on both modules, and parts of the respective fluorescence fronts are localized on the cross connectors. Because the fluorescent encapsulant part over the cross connector is smaller, photobleaching seems more advanced in the case of EVA-UV compared to that of TPOA-UV. UV degradation in a given environment may differ relative to their chemical nature [27], and the various polymer matrices can differently influence the behaviour and stability of such additives [28]. As such, the differences in UV-cut encapsulant formulations may explain the variability of the fluorophore formation and photobleaching balance.

The role of UV light

Modules with TPOB-UV encapsulants have also been aged under UV LEDs with emissions of approximately either 365 or 305 nm. The emission spectra are much narrower than those of the AM 1.5G or xenon-arc lamp (Figure 1). As such, the specific role of UV irradiation in yellowing and photobleaching is investigated on an encapsulation polymer for which it has been proven that discolouration can occur under solar-like light during accelerated ageing tests. Figure 9 presents the fluorescence shots of the modules with the TPOB-UV encapsulation module aged under 365 nm and 305 LEDs.

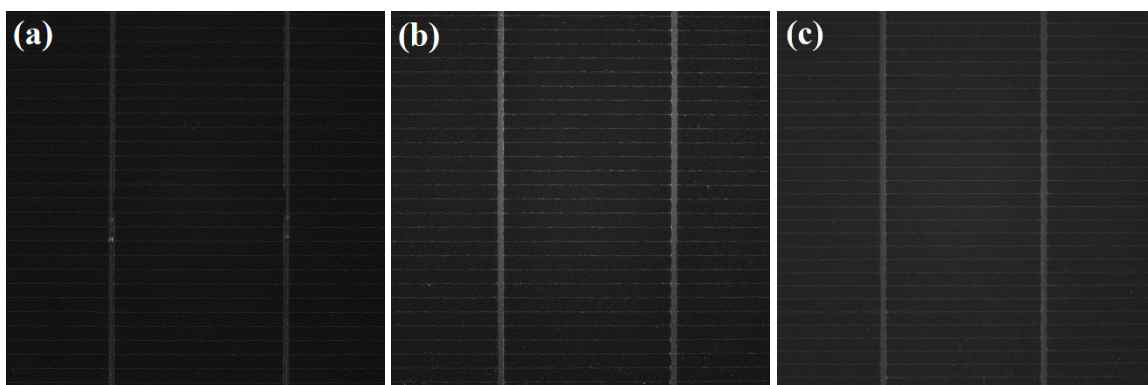


Figure 9: Fluorescence shots of unaged module (a), and modules aged under UVA (b) and UVB light (c). The three pictures were shot under the same conditions and cover a $5 \times 5 \text{ cm}^2$ surface.

Slight fluorescence can be noticed on both aged modules after 1000 and 1300 hours of accelerated ageing, respectively. Because of the lower intensity of fluorescence emission, the integration time we chose for imaging was fivefold higher than that of the previous study. This explains the brightness of the unaged sample, which may be caused by the fluorescence emissions 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 absorber degradation following photoexcitation is likely responsible for the

fluorescence.

A long irradiation time (1000 hours) under UVA LED (365 nm) irradiation seems to induce more fluorescence emissions than 1300 hours under UVB LED (305 nm) irradiation, while Figure 1 shows that UVA photons are less susceptible to absorption than their UVB counterparts. Furthermore, fluorescence is even higher after the aforementioned 4200 hours of ageing under solar-like light. The UV photon dosages under UVB LED, UVA LED and xenon-arc lamps 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 the UVA photon dosage is 100 times higher may explain why the fluorescence emission is brighter in Figure 9b than in Figure 9c. According to Figure 1, the front glass strongly absorbs in the UVB range, which further reduces the amount of UVB photons that reach the encapsulant. In case of reciprocity law failure (*i.e.*, sublinear relation between degradation rate and UV light dosage), the 4 times longer test under xenon-arc lamp may account for the more intense fluorescent emission of the modules that were aged in Ci5000 test chamber despite the 10-fold higher UV photon dosage of 365 nm LEDs.

Discussion

Although UV absorbers tend to degrade over time and impair PV module 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 such as SHJ, passivated emitter rear totally diffused (PERT), passivated emitter and rear contact (PERC) [20] or even perovskite cells [29] from detrimental UV radiation as long as such technologies remain vulnerable.

The samples that were discoloured underwent accelerated ageing by applying high temperature and irradiance exposure over less than six months. Yellowing will not occur so quickly in outdoor conditions. An acceleration factor is yet to be determined to provide a reliable extrapolation of the actual degradation rate for outdoor modules. This requires an extensive study of the effect of each parameter on the discolouration kinetics. For instance, higher temperatures may accelerate the reaction kinetics [28]. A simple Arrhenius law that is generally used in degradation rates modelling [30] associates our last results (4200 h of accelerated ageing) with outdoor ageing in desert that may range from 10 to 24 years depending on the apparent activation energy (30 [18] to 60 kJ.mol⁻¹ [31]).

On the other hand, the use of organic UV absorbers is still an efficient way to avoid or limit UV-induced damage to cells and encapsulants despite their yellowing. Indeed, this damage can lead to catastrophic failures such as delamination [32]. As such, it would be interesting to develop stabilization measures to diminish the occurrence of yellowing. This is particularly true for high UV irradiance environments such as deserts. This might be done by increasing the photostabilizer concentration or replacing organic UV absorbers with mineral absorbers [33]. Novel UV absorbing technologies such as quantum dots [34] may also become alternative solutions. Despite its slight impact on the initial performances of modules [35], UV absorbing cerium oxide glass, which was used in the 1990s [36], could be reconsidered for the manufacturing of UV resilient PV modules.

Conclusion

The results obtained under accelerated artificial ageing of commercial encapsulants specially designed to provide high protection against UV showed that they are sensitive to yellowing. This phenomenon does not originate 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 associated loss of photogenerated current is significant. It reached 4% after 4200 hours of accelerated UV ageing for the most discoloured modules, while the UVID of the SHJ solar cells only accounted for a 3% loss. Furthermore, the destruction of UV absorbers is an issue affecting the integrity of the whole PV module and can lead to accelerated delamination, among other critical types of damage. There is then a challenge to find new ways to bolster the photoprotection of the device, especially for the most stringent environments, such as those located in deserts.

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