Fluorescence imaging analysis of depth-dependent degradation in photovoltaic laminates: insights to the failure

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Abstract

Accurate evaluation of the reliability of photovoltaic (PV) packaging materials is critically important for the long-term safe operation of modules. However, the complexity of the laminated systems due to their multilayered and multicomponent structures and diverse aging mechanisms makes a thorough system evaluation very challenging, especially when the degradation is non-uniform through the thickness. In such a case, neither surface nor bulk measurements can present a clear picture of the degradation profile. In this study, fluorescence imaging was developed to visualize the degradation depth-profiles of an aged laminated PV system. A glass/ethylene vinyl acetate (EVA) encapsulant/poly(ethylene terephthalate) (PET)-PET-EVA (PPE) backsheets laminate was weathered with the glass-side facing an ultraviolet (UV) light source for 3840 h. Cross-sectional fluorescence images revealed a non-uniform distribution of degradation species across the thickness of the EVA encapsulant, providing greater insight into the mechanisms of degradation, which are unavailable by traditional bulk-based methods. In addition, strong fluorescence emissions were observed from the two thin adhesive layers of the aged backsheet, indicating severe degradation of the adhesives and a potential for interlayer delamination. This method is further confirmed with other microscale characterization techniques. The changes in optical (yellowness index), chemical (oxidation, UV absorber concentration), mechanical (Derjaguin-Muller-Toporov modulus), and thermal (melting enthalpy) properties of the EVA encapsulant were found to be related to fluorescence profiles, following the attenuation of UV light. This study highlights that fluorescence imaging is a spatially-resolved and sensitive method for rapid failure assessment and in-depth mechanism study for complex PV-laminated systems.

KEYWORDS

degradation, depth profile, fluorescence imaging, modulus, photovoltaic laminates, UV aging, yellowness index
INTRODUCTION

To ensure the long-term reliability of photovoltaic (PV) modules, a multilayer encapsulant system is used to create multiple physical barriers for the solar cell to prevent damage from UV light, moisture or oxygen. However, the polymeric materials used for encapsulants and backsheets are susceptible to degradation and their degradation or failures (such as discoloration, cracking or delamination) tend to initiate at their surfaces or weak interfaces. Gradual progression of such localized degradation to the whole packaging system would lead to non-uniform failure, which finally induces dramatic loss in the module power efficiency and the catastrophic failure of the whole system. Despite the great necessity to evaluate the inhomogeneous degradation behavior to predict the reliability and lifetime of PV systems, most studies are mainly confined to bulk property changes. Investigations on the inhomogeneity of degradation within the layers of aged packaging materials for PV application is still scarce.

Gradient degradation of polymers, induced by the ultraviolet (UV) light attenuation or the diffusion limited effects of oxygen and moisture exposure, is ubiquitous and has been studied extensively in past decades. Nevertheless, the complex construction of PV modules, with multiple layers and components, makes it especially challenging to quantify the structure and property degradation of individual components/layers during their service lifetime, and to correlate them with the likelihood of failure. Several spectroscopic imaging techniques, such as Fourier-transform infrared spectroscopy and Raman spectroscopy have been used to examine the degradation gradient of multilayer PV laminates. While these techniques are capable of mapping degradation, their limited spatial resolution, low signal-to-noise ratios, or time-consuming measurement procedures have hampered wider application of these techniques. For example, although Raman spectroscopy has superior lateral resolution compared to FTIR spectroscopy, significantly enhanced fluorescence background emitted from aged materials dominates Raman spectra and obscures spectroscopic information.

While fluorescence emission hinders the utility of Raman spectroscopy, it can provide valuable information on evaluating polymer degradation as it is sensitive to conjugated products which often form during degradation. Approaches using fluorescence emission are promising to determine the degree of degradation in an EVA encapsulant and identify cell cracks in PV modules. For example, Röder et al. successfully used fluorescence spectroscopy with a lateral resolution of about 1 mm to characterize the degradation of EVA from the edge to the center of PV modules after outdoor and accelerated aging (damp-heat and UV aging). Although their work did not provide depth-dependent information, it has laid groundwork for using fluorescence measurement as a tool for characterization of degradation of PV polymers.

In this study, we have extended the capability of fluorescence spectroscopy to a spatially-resolved and sensitive tool for rapid visualization of degradation depth-profiles of UV-aged PV laminates, thanks to its characteristics of high spatial resolution (hundreds of nanometers) and rapid acquisition (a few seconds to a few minutes for each image). Confocal fluorescence imaging was used to investigate the effects of UV intensity and wavelength on degradation depth-profiles of both EVA encapsulant and PPE backsheet in glass/EVA/PPE laminates aged on the NIST SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) at 85 °C/0 % RH with UV exposure. To validate and better understand the fluorescence results, the depth profiles of optical (yellowness index), chemical (oxidation, UV absorber concentration), mechanical (modulus), and thermal (melting enthalpy) properties of the EVA degradation were also characterized by UV-Vis-NIR microspectrophotometry (MSP), micro-Fourier-transform infrared spectroscopy (Micro-FTIR), quantitative nanomechanical mapping atomic force microscopy (QNM-AFM) and differential scanning calorimetry (DSC), which tend to be more destructive or more time-consuming in sampling. The correlation of fluorescence mapping to these techniques demonstrates its utility as an effective tool for depth-dependent degradation analysis of polymer laminates. Furthermore, the use of varying UV light conditions (intensity and wavelength) provides critical information on the light-induced non-uniformity and great insight into the mechanisms of degradation with the presence of UV light, which laid crucial groundwork for establishing the correlation between degradation under different laboratory UV-light sources and solar exposure.

2 EXPERIMENTAL*

2.1 Materials

Glass/EVA/backsheet laminates (as shown in Figure 1 (a)) made of commercial materials with dimensions of (180 mm × 180 mm) were designed for this study. The glass, with 3 mm nominal thickness, was polished fused silica with a transmittance of around 95% in the UV and visible range. The encapsulant was EVA Photocap 15420P/UF (STR), which contained a UV absorber and curing agent and a vinyl acetate content of 33 % mass fraction. The backsheet consisted of PPE, layers of PET (poly (ethylene terephthalate)), PET and EVA, respectively. The PPE backsheet was composed of pigmented PET outer layer, PET core layer and multiple EVA layers (Coveme). The laminates were prepared in a vacuum environment using a commercial process with a plate temperature of 150°C, evacuation time of 4 min, then pressing time of 1 min and crosslinking time of 13 min. Based on the topography image of the cross-section of the EVA/PPE backsheet laminate (shown in Figure 1 (b)) collected by laser scanning confocal microscope (LSCM) described later, the thickness of the EVA encapsulant layer was determined to be (920 ± 4) μm, and the entire PPE backsheet laminate to be (300 ± 4) μm. The backsheet (labeled PPE) was composed of five layers, from the EVA encapsulant side: an EVA outer layer (25 μm thick), pigmented EVA middle layer (55 μm), EVA inner layer (25 μm), PET core layer (126 μm), and PET...
In addition, there were two polyurethane-based adhesive layers between the EVA inner and PET core layers, and PET core and PET outer layers, with thicknesses of 8 μm and 6 μm, respectively.

2.2 Accelerated aging

Accelerated aging was performed with the glass-side of the laminates facing the UV light source in the NIST SPHERE at 85 °C/0 % RH under different light intensities and wavelengths for 3840 h. Relatively high temperature was used to simulate harsh climatic conditions of PV modules under hot conditions. For example, the maximum module temperature was used to simulate harsh climatic conditions of PV facing the UV light source in the NIST SPHERE at 85 °C/0 % RH. Accelerated aging was performed with the glass superstrate with thicknesses indicated. [Colour figure can be viewed at wileyonlinelibrary.com]

2.3 Sample preparation and characterization

Specimen cutting (1 mm x 5 mm) Strips of glass/EVA/PPE backsheet laminate from each exposure condition were cut from the larger laminate using a diamond saw. These were taken from the center of the laminates, to minimize oxygen diffusion effects from the sides. Then the EVA/PPE layers were mechanically peeled off from the glass with tweezers (as shown in Figure 1 (a)). Small strips of each laminate were used to avoid the deformation of polymeric materials during the peeling and to ensure a minimal amount of polymer residue remained on the glass. To conduct cross-sectional analysis, EVA/PPE strips were embedded in an epoxy molding to support the thin cross-sectional strip during cutting. A smooth, cross-sectional surface parallel to the film thickness was then obtained by cryo-microtomy along the interface between different layers using a diamond blade at -80°C on a Leica EM FC7 (Leica Mikrosysteme GmbH), as shown in Figure 2 (a). For characterization by GC/MS, slices of the EVA encapsulant were microtomed parallel to the exposed surface, as shown in Figure 2 (b).

Laser scanning confocal microscopy (LSCM) Morphology and fluorescence imaging were measured on a Zeiss LSM510 Meta (Carl Zeiss, Inc., Oberkochen, Germany) laser scanning confocal microscope. For cross-section morphology, an objective of Epiplan-Neofluar 10×/0.3 was used with field view of about (840 μm × 840 μm) and pixel size of 512 pixels by 512 pixels using a laser wavelength of 543 nm in reflection mode. The lateral resolution of this objective with a 543 nm laser is 0.9 μm for a pinhole size at 1 Airy unit providing optimal focus. A series of image planes (optical sections) of cross-sectional surfaces was collected by adjusting the focal plane in the Z-direction with a step size of 0.5 μm and was then used to build the topography image using intensity values. For fluorescence zmeasurements, an objective of 5x/0.15 was used with a diode laser (405 nm) to excite the sample. Only a single image plane was collected by adjusting the focal plane along the Z-axis to get the maximum intensity across the whole cross-section. The scanning area was about (1700 μm × 1700 μm) and the lateral resolution of this objective at 405 nm is 1.4 μm. Both integrated fluorescence intensity (obtained by channel mode) and corresponding fluorescence spectra (obtained by lambda mode) were measured. Channel mode was used to detect emission signals at all
wavelengths with a long pass filter to remove light with wavelength below 420 nm, while lambda mode could monitor individual emission spectra from 411 nm to 753 nm with 10.7 nm increments using a META detector. With this lambda mode, the overall emission from the sample is directed onto a wavelength-dispersive element and is imaged on a 32-channel photomultiplier (PMT) detector with each PMT spanning a 10.7 nm spectral range. The power was attenuated to 30% of the maximum laser power (25 mW).

**Micro-Fourier-transform infrared spectroscopy (Micro-FTIR)** Infrared analyses were performed by a Thermo Scientific Nicolet iN10 MX infrared imaging microscope purged by dry air, equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector. Chemical changes in the glass side of the EVA encapsulant were measured in Attenuated Total Reflection (ATR) mode using a germanium conical tip with an aperture size of 40 μm x 40 μm. ATR-FTIR is used as its penetration depth into the sample is typically between 0.5 and 2 μm, thus it is sensitive to surface changes compared with transmission mode FTIR. The depth profile of chemical changes of the EVA encapsulant across the cross-sectional direction was also measured in transmission mode using aperture size of (10 μm x 10 μm) with step size of 10 μm on the 5 μm thick cross-sectional slice (as shown in Figure S2 (a)). Spectra were recorded in the spectral range from 4000 cm⁻¹ to 650 cm⁻¹ at 8 cm⁻¹ resolution with 64 scans. Spectra were then processed with a baseline correction and normalization to the peak at 2851 cm⁻¹ assigned to the methylene (−CH₂−) symmetrical stretching. To ensure reproducibility, at least three different locations were measured for each data point.

**UV-Vis-NIR microspectrophotometry (MSP)** UV-Vis spectra were recorded in transmission mode using a microspectrophotometer (CRAIC Technologies, Model MSP 121i) in the UV-Vis range between 250 nm and 800 nm across the sample. The microscope objective was a Davin reflecting objective 36x, NA 0.5 with aperture size of (7.9 μm x 7.9 μm). UV-Vis spectra were collected along the cross-sectional direction from the exposed side to the back-side with a step size of 7.9 μm, as shown in Figure S2 (a). A cross-sectional slice of only EVA encapsulant, with a thickness of 2 μm, was mounted between quartz microscope slides and cover slips with a glycerin mounting medium. The corresponding yellowness index was calculated based on these spectra according to ASTM E308. To ensure reproducibility, at least three different locations were measured for each data point.

**Gas Chromatography Mass Spectrometry (GC-MS)** To determine the UV absorber (UVA) concentration as a function of depth, 10 slices of EVA encapsulant with each thickness of 5 μm were extracted by 100 μL methanol and taken as one sample at the nominal depth (as shown in Figure S2 (b)). The median depth is used as the nominal depth for each data point. The extracts were analyzed by an Agilent 7890B GC system coupled with a 5977B mass spectrometer. The GC was carried out on a Rxi5HT column (15 m, 0.25 mm ID, 0.10 mm film thickness) from Restek (Bad Homburg, Germany) with helium as the carrier gas. Injections (1 μL) were performed at 280°C with a splitless time of 0.5 min. The oven temperature was held for 5 min at 40°C, then ramped up to 300°C at a rate of 20°C/min and held for 4 min. Triphenylbenzene was used as the internal standard. The target compounds were quantified using the selected molecular ions: m/z (mass-to-charge ratio) = 151 for UVA and m/z = 306 for triphenylbenzene.

**Quantitative nanomechanical mapping atomic force microscopy (QNM-AFM)** QNM-AFM was performed on the cross-sectional surface (as shown in Figure 2 (a)) by a Bruker Dimension Icon AFM to obtain quantitative information on height, modulus, and deformation of samples at the nanoscale. A scan size of (35 μm x 35 μm) was used for the EVA encapsulant, while (15 μm x 15 μm) was used for the backsheet. A (512 x 512) pixel resolution with a scan rate of 0.5 Hz was used. The modulus was estimated using the Derjaguin-Muller-Toporov (DMT) model following the relative method. This model considers the adhesion force and is applicable when the deformation of sample is lower than the radius of tip. Silicon AFM probes and reference samples were selected based on the Young's modulus range of the samples. At least three locations were measured for each data point to evaluate the repeatability.

**Differential scanning calorimetry (DSC)** Melting curves of the EVA encapsulant were determined by TA Q2000 DSC. The aged EVA encapsulant samples were cut into two halves: the top part was from the peeled surface to the middle section of the encapsulant and the bottom part was from the middle section to the part near the backsheet, cutting in a similar way to that in Figure 2 (b). The thickness of the slices is about 400 μm. Samples from the top and bottom part with mass of about 5 mg were measured separately. Samples in the pan were heated from 15°C to 210°C with a heating rate of 10 °C/min under a nitrogen atmosphere with a flow rate of 50 mL/min. To ensure reproducibility, at least three samples were measured.
3 | RESULT AND DISCUSSION

3.1 | Depth-dependent degradation of EVA encapsulant in glass/EVA/backsheet laminate

Accelerated aging under intensified exposure conditions, especially enhanced UV light intensity or shorter wavelengths, is commonly used to simulate the field degradation of photovoltaic laminates in a shorter time. A thorough understanding of the UV light and wavelength response of materials is critical for reliable accelerated test design for lifetime prediction. Moreover, the attenuation of the UV light in samples could be the root cause for the heterogeneous degradation across the thickness, and requires that a microscopic level spatial analysis should be carried out. To address these problems, a detailed analysis on the effects of UV intensity and wavelength on the degradation depth-profiles of EVA encapsulant will be presented below based on cross-sectional fluorescence imaging.

3.1.1 | Fluorescence imaging for samples aged under different UV light intensities

Figure 3 shows the fluorescence emission intensity across the cross-section of the EVA encapsulant in the glass/EVA/PPE laminates before and after exposure to UV/85°C/0 % RH under different UV light intensities ((a)-(d)) and their corresponding line profiles (e). Using neutral density filters, the measured UV irradiances (295 nm to 385 nm) are 60.5 W/m² (40 %), 93.5 W/m² (60 %), and 142.5 W/m² (100 %). The gradual drop in the fluorescence intensity from the exposed surface across the thickness is most likely due to the attenuation of the UV light through the EVA encapsulant. Among the three UV light intensities, the specimen exposed under 60 % UV light has the highest fluorescence intensity near the surface, and reasons for this behavior will be discussed in the next paragraph. Substantial changes in the fluorescence intensity occur within 200 μm from the exposed side of the encapsulant, exceeding which level the intensity reaches the plateau gradually. The overall degradation depth under different UV light intensities is essentially similar, as confirmed by the normalized line profiles given in Figure S3.

Figure 4 shows the depth-dependent fluorescence spectra of the same regions shown in Figure 3. A broad fluorescence peak is observed at the exposed side of the EVA, which progressively shifts toward shorter wavelengths and decreases in intensity. No discernable peak is found in the fluorescence spectra of the fresh sample with very low fluorescence intensity (as shown in Figure S4). For 40 % UV light, the peak position shifts from 600 nm to 520 nm about halfway into the EVA layer, and no obvious shifts are observed thereafter. For 60 % UV light, the emission peak position shifts consistently from 617 nm to 520 nm throughout the entire EVA layer. And for 100 % UV light the peak position (around 635 nm) changes very slowly at first, and then a sharp shift to 520 nm is observed at about 100 μm. Also note that the peak position of the exposed side of samples under 100 % UV light possesses the longest wavelength (around 635 nm). These fluorescence emissions can be ascribed to the formation of α,β-unsaturated carbonyl species. The short chain α,β-unsaturated carbonyl species play an important role for emission at shorter wavelengths while the contribution of relatively long polyconjugated structures is dominant for emission at longer wavelengths. These results indicate the existence of different degradation species across the EVA layer thickness under different UV light intensities: shorter chain species are easier to form under lower UV dose, while longer chain species grow gradually with increasing UV dose. Figure 4 shows...
that the fluorescence intensity of the 60 % UV sample is higher than the 100 % UV sample. The reason for this drop for 100 % UV light could be due to secondary reactions related to the short chain α, β-unsaturated carbonyl species with more severe UV exposure. A similar peak intensity drop for severely discolored EVA encapsulant was also reported by Pern.20

3.1.2 | Fluorescence imaging for samples aged under different UV light wavelengths

The fluorescence images of the EVA encapsulant aged under different UV wavelengths (center wavelength: 306 nm, 326 nm, 354 nm, and 452 nm) are shown in Figure 5. The measured irradiances are 0.30 W/m² (306 nm ± 3 nm), 2.2 W/m² (326 nm ± 6 nm), 37.3 W/m² (354 nm ± 21 nm) and 36.0 W/m² (452 nm ± 79 nm). All samples show a successive decay in the fluorescence emission from the exposed side to the inner part of EVA encapsulant, regardless of UV wavelength. Quantitative changes in the fluorescence intensity are given by their line profiles and manifested by normalized profiles in Figure 5 (e) and (f). The fluorescence intensities near the exposed side for samples aged under 306 nm, 326 nm and 354 nm are much higher than those under 452 nm, indicating a wavelength dependence for the fluorescence intensity of the EVA encapsulant. It is known that the damage efficiency of light with wavelength of 306 nm should be much higher than that of 452 nm,35 which results in a higher fluorescence intensity for the sample exposed under 306 nm bandpass filter even with lower total UV dosage. It is interesting to find that a slight increase in the fluorescence intensity occurs in the regions near the backsheet, in the regions near the backsheet.
especially for samples aged under 354 nm. This rebound could be induced by the UV light passing through the EVA encapsulant layer and being reflected back by the backsheet. In fact, the pigmented EVA middle layer in the backsheet is designed to reflect the photons back to the cells. The reflectance of the backsheet (EVA layer side) is only about 9% below 340 nm while increases sharply above about 380 nm (as shown in Figure S5). Although the light centered at 452 nm is also strongly reflected, only a small increase in the fluorescence intensity on the backsheet side of the EVA encapsulant is observed. It is known that the degradation efficiency of light at this wavelength range is rather low, and more importantly, light with longer wavelengths could bleach the chromophores and reduce yellowing and fluorescence. The competitive reactions between formation and depletion of chromophores during degradation may be the reason that no obvious increase in the fluorescence intensity at the backsheet interface was observed for samples aged under broad band UV spectrum with neutral density filters (Figure 3).

The effect of UV wavelength on the rate of decay in fluorescence intensity as a function of depth can be clearly seen from the normalized curves (Figure 5 (f)), that is, a higher attenuation rate at a shorter wavelength. This relationship can be quantified by Lambert-Beer law, in which light intensity \( I(\lambda, x) \) decays exponentially in the material with the penetration depth \( x \):

\[
I(\lambda, x) = I_0 e^{-\alpha(\lambda)x}
\]

where \( I_0 \) is the incident intensity, \( \alpha(\lambda) \) is the absorption coefficient. The drop in fluorescence intensity \( F(\lambda, a) \) is then fitted using an exponential relationship

\[
F(\lambda, a) = a + be^{-R_0x}
\]

\( a \) and \( b \) are the offset and amplitude parameters, and \( R_0 \) determines the decay rate of fluorescence intensity. Here the decay of the fluorescence intensity can be well described by this function, as shown by fitted dash lines in Figure 5 (f). \( R_0 \) values were fitted as 0.018, 0.015, 0.009 and 0.004 for 306 nm, 326 nm, 354 nm and 452 nm, respectively. Samples under shorter wavelengths have a higher \( R_0 \), exhibiting a sharper decrease in the fluorescence intensity and a shallower degradation depth. The decay rate of fluorescence at different wavelengths is also consistent with the corresponding absorption of EVA encapsulant at each wavelength (See the absorption spectra of the EVA encapsulant in Figure 6 (a) below).

No obvious change in the shape of fluorescence spectra as a function of depth is observed (as shown in Figure S6). Compared with the degradation of samples under different light intensities, the degradation process under different wavelengths is still in the early stage, so the shift in peak position of the fluorescence spectra has not occurred yet.

3.1.3 Correlation between fluorescence and other material properties

The above results have demonstrated that fluorescence imaging is an effective and spatially sensitive tool to visualize the depth-dependent non-uniformity in degradation of the aged encapsulant EVA in the UV-exposed glass/EVA/PPE laminates. However, the quantitative identification of degradation products based on the fluorescence spectra is only in the early stage, as well as the correlation of the fluorescence to other properties and performance of PV packaging materials. To validate and better understand the fluorescence results, the relationship between fluorescence profiles and depth-dependent optical, chemical, mechanical, and thermal properties of the EVA encapsulant are examined for the glass/EVA/PPE laminates aged under 100 % UV light intensity. If such a correlation can be established, the fluorescence imaging can be developed as an alternative tool for rapid, non-contact monitoring of polymer degradation in the PV laminates.

Discoloration of the EVA encapsulant is observed in the field and during indoor accelerated tests, and is partly responsible for the well-documented decrease in maximum current of a module with time, because some visible light is absorbed by the encapsulant instead of the solar cell. Figures 6 (a) and 6 (b) show the depth-dependent UV-Vis absorbance spectra of the EVA encapsulant exposed to 100 % UV light, along with the yellowness index at different depths. The results were obtained based on the UV-Vis-NIR microspectrophotometry using 2 μm thick cryo-mictomed slices from different depths of the encapsulant EVA. Two characteristic UV absorbance peaks at (260 to 310) nm and (310 to 370) nm were observed for the fresh sample. After degradation, the absorbance peaks became broader and extended to longer wavelengths in the visible region. The yellowness index of the EVA encapsulant decreases significantly from the exposed side to the backsheet side, then it reaches a lower limit at the same level as the fresh EVA at about (100-200) μm depth. The yellowness index and the fluorescence emission follow similar trends.

**FIGURE 6** Depth dependent (a) UV-Vis spectra from UV-Vis-NIR microspectrophotometry, (b) yellowness index and (c) relative concentration of UV absorber of fresh and aged (100 % UV) EVA encapsulant. Error bars represent standard deviations from the results obtained at 3 replicated locations on the cross-section of sample. [Colour figure can be viewed at wileyonlinelibrary.com]
An important origin for the discoloration and fluorescence of EVA encapsulant is the interactions among stabilizing additives, peroxides and polymers. Specifically, the interaction between the peroxides, phosphite thermal stabilizer or radicals from degradation of polymers with the benzophenone based UV absorbers could lead to chromophore formation. A recent interlaboratory study by Miller et al. shows that the UV absorber is mostly responsible for the discoloration of EVA, as no obvious discoloration is found for EVA encapsulant without UV absorbers. As shown in Figure 6 (c), the concentration of the UV absorber (UVA) near the exposed surface of the aged EVA encapsulant drops significantly, compared to the fresh encapsulant, and the concentration reaches a plateau at about 200 μm depth, similar to the depth-profile of yellowing and fluorescence. The similarity between the yellowing or fluorescence and UVA loss is another confirmation of the linkage between UVA and discoloration of EVA encapsulants.

ATR-FTIR spectra of fresh and exposed EVA on the surface (glass-side) are shown in Figure 7 (a). The main peak of interest for degradation of EVA is at 1740 cm⁻¹, which is assigned to ester or aldehyde groups. There is no obvious change in intensity for this band, which could be due to the competition between destruction of esters and formation of aldehydes. Nonetheless, a broadening of this band is observed and absorption shoulders around 1715 cm⁻¹ and 1780 cm⁻¹ appear, indicating the formation of other carbonyl groups such as ketones and lactones, respectively. Ketones are formed either by Norrish III reaction or by decomposition of hydroperoxides, while formation of lactones is related to the back-biting process in the vinyl acetate groups.

There is a strong depth dependence for carbonyl groups formation (as represented by the absorbance at 1715 cm⁻¹) in the aged EVA encapsulant, shown in Figure 7 (b). The carbonyl products decrease rapidly further from exposed surface, and the degradation depth is consistent with the evolution in the fluorescence and discoloration, showing that the kinetics of EVA degradation and chromophore formation are similar. Carbonyl products from the degradation of EVA can be conjugated with double bonds, and the resultant α,β unsaturated ketone contributes to the discoloration and fluorescence, which has been discussed widely in the literature. By comparing with model compounds, Rodríguez-Vázquez et al. proposed that the discoloration of EVA is not due to polyene formation, while it is linked to α,β-unsaturated carbonyl species. The relative concentration of carbonyl products reaches a stable level at a depth of about 200 μm.

The Derjaguin-Muller-Toporov (DMT) modulus of the EVA encapsulant before and after aging across the thickness is measured by QNM-AFM (Figure 8 (a)). The modulus of the EVA encapsulant is an important degradation indicator, because a reduction in the modulus after aging would increase the risk of creep, while an increase in the modulus could induce higher internal stress and possibly lead to cracking of the more brittle PV materials (e.g. solar cell, metallization). For the fresh sample, the DMT modulus of the EVA encapsulant is constant with small variations. After aging, a substantial drop in the modulus is observed near the glass/EVA interface, which increases toward the backsheet side, though still lower than the value at the same location of the fresh EVA. The depth-profile for modulus does not appear to follow that of the fluorescence, discoloration, UVA, or chemical changes (carbonyl formation), thus it is likely linked to other material changes such as lower molecular mass induced by chain scission and crystal structure, and so forth. The decrease in modulus near the exposed side is consistent with the investigation of Röder et al., in which they found that the storage modulus of EVA encapsulant at 40°C in a UV aged module is lower compared with the unaged sample. A similar reduction in storage modulus in the temperature range from 0°C to 50°C was also observed based on the dynamic mechanical analysis (DMA) results by King et al. for EVA encapsulants in a module after aging for 7 years and by Shiota et al. for module with outdoor exposure for 20 years.

DSC was used to determine the melting enthalpy and crystallinity of the EVA encapsulant, because these properties may be better correlated to the mechanical properties than the measured optical and chemical changes. The aged EVA encapsulant samples were cut into two halves: from top to middle (top part) and from middle to backsheet (bottom part). DSC curves for the fresh EVA encapsulant, top part, and bottom part of aged EVA are shown in Figure 8 (b). A broad melting peak ranges from 41°C to 89°C for different samples.
originating from different crystalline phases. The higher temperature part is a result of the larger and regularly formed crystallites, while the lower temperature part is attributed to the melting of smaller, imperfect crystallites.7,24,48 Significant decrease in crystallinity of bulk EVA encapsulant in the fielded modules has also been reported recently.57 In this study, the aging temperature at 85°C exceeds the melting temperature of EVA. After aging, the ordered crystallites (i.e. higher temperature part) could be degraded, and the recrystallization of the lower-molecular degradation products resulting from chain scission could facilitate the formation of imperfect, smaller crystallites, accompanying with a drop in the melting enthalpy. This could be the main reason for the substantial reduction of modulus near the exposed side of the aged EVA encapsulant.

The correlation of various material properties to each other indicates related mechanisms of degradation (Figure 9). The fluorescence intensity rapidly decays to a level seen in the fresh specimens at about 200 μm depth, which closely matches the profiles for increase in yellowness and ketone content, and decrease in UVA concentration. Thus, the degradation products responsible for each of these characteristics are distributed near the exposed side of the sample and their concentration decreases from the exposed surface to the internal part of the sample, indicating non-uniform degradation as a function of depth. The modulus and melting enthalpy do not closely match the fluorescence profiles, but follow a similar trend between themselves, suggesting a relationship between the thermal/structural and mechanical properties across the depth of the EVA encapsulant. The fluorescence imaging is much faster in sampling and measurement than the other techniques (yellow index, FTIR, UVA concentration), therefore, it is an ideal alternative to quantify degradation related changes.

FIGURE 8 (a) DMT modulus of fresh and aged (100 % UV) EVA encapsulant. Modulus of each data point was averaged from three replicate locations with an area of (1 μm × 1 μm). (b) DSC curves for the fresh EVA encapsulant as well as aged EVA from the top part (near the exposed side) and bottom part (near the backsheet side) and (c) corresponding melting enthalpy of each sample. The error bars represent the standard deviations of three replicate samples. [Colour figure can be viewed at wileyonlinelibrary.com]

FIGURE 9 Depth-profile of fluorescence, optical (yellowness index), oxidation, UVA concentration, mechanical (Derjaguin-Muller-Toporov (DMT) modulus), and thermal (melting enthalpy) properties of the EVA encapsulant aged under 100 % UV. Error bars represent standard deviations from the results obtained at 3 locations on the cross-section of sample. [Colour figure can be viewed at wileyonlinelibrary.com]

3.2 Depth-dependent degradation of PPE backsheet layers in the glass/EVA/backsheet laminate

The capability and sensitivity of fluorescence imaging in depth-dependent degradation characterization of PV laminates can be further demonstrated by the study of the PPE backsheet in the UV exposed glass/EVA/PPE laminate. Figure 10 shows the fluorescence images and corresponding line profiles of the cross-section of the PPE backsheet before and after glass-side exposure to UV/85 C/0 % RH. Strong fluorescence emission is observed on the unexposed PET outer layer, probably resulting from the fluorescent whitening agent added to this layer designed to brighten the white color. After exposure, the fluorescence of the PET outer layer decreases with increased UV light intensity. In contrast, the EVA middle layer shows a non-symmetrical distribution of the fluorescence emission, which increases with increasing UV intensity. Additionally, a clear fluorescence emission is observed from the two adhesive layers after exposure. The fluorescence intensity of the two adhesive layers appears to be independent of light intensity except for those under 40 % ND filters, indicating that the degradation of adhesive layers is mainly thermal-
FIGURE 10  Fluorescence emission images of the PPE backsheet in (a) fresh glass/EVA/PPE and samples exposed to UV/85°C/0 % RH under (b) 40 %, (c) 60 % and (d) 100 % ND filters, and (e) the corresponding line profiles. [Colour figure can be viewed at wileyonlinelibrary.com]

FIGURE 11  QNM-AFM height and adhesion images of (a) EVA/PET adhesive layer, and (b) PET/PET adhesive layer in glass/EVA/PPE samples before and after exposure to UV/85 °C/0 % RH under 100% UV. [Colour figure can be viewed at wileyonlinelibrary.com]
induced. This hypothesis is further supported by the similar fluorescence intensity observed from the adhesive layers in backsheet aged under different wavelengths (as shown in Figure S7). There are no obvious changes in the PET core layer. These results provide the direct evidence on the degradation of the EVA middle layer and two adhesive layers, indicating that the instability of those layers, and potential inner layer failure within the backsheet, which could raise safety concerns for electrical insulation, and ultimate reliability issues of the PV modules.

The degradation of the adhesive layers has been further confirmed by AFM-QNM of the PPE film in the glass/EVA/PPE samples exposed at UV/85 °C/0 % RH under 100 % UV (Figure 11). For the fresh sample, small nodule structures in each adhesive layer are found, which are dispersed uniformly in the matrix and the adhesion of nodule structures is relatively lower than the matrix material. The interfaces between the adhesive and the adjacent layers are sharp and clear. After exposure to 100 % UV, for the EVA/PET adhesive layer (Figure 11 (a)), the size of the small nodules basically remains unchanged, while the interfaces with the EVA and PET layers is less defined. For the PET/PET adhesive layer (Figure 11 (b)), the small nodule structures observed in the fresh sample become larger, probably due to the coalescence of the small latex particles under heat, and a groove-like structure appears after aging, indicating the loss of some material. These results indicate the degradation of both adhesive layers has taken place, leading to microstructural and mechanical changes during exposure, which was previously evidenced by their high fluorescence emission. These results also suggest a potential risk of inner layer failures within the backsheet, which could raise safety concerns for electrical insulation, and ultimate reliability issues of the PV modules.

4 | CONCLUSIONS

This study has demonstrated that fluorescence imaging is an effective and spatially sensitive technique to monitor depth dependent degradation, which is important for failure mechanism analysis for PV modules. The degradation depth-profiles of UV aged glass/EVA/PPE PV laminates were investigated by fluorescence imaging in combination with micro-UV-Vis spectroscopy, micro-FTIR-ATR, GC-MS, QNM-AFM, and DSC. Laminates were exposed under different UV light intensities and wavelengths at 85 °C/0 % RH for 3840 h. Based on the results, a few conclusions can be drawn:

1. Non-uniform, depth-dependent degradation has occurred in the EVA encapsulant. The decrease in the fluorescence intensity as a function of depth follows the attenuation of the UV light, and can be described by the Lambert-Beer law.

2. The depth profile of the fluorescence is consistent with the change of yellowness index, ketone formation, and UV absorber concentration, indicating that the mechanisms of degradation of these properties are probably related.

3. The modulus and melting enthalpy do not closely match the fluorescence profiles, but follow a similar trend between themselves, suggesting a relationship between the thermal/structural and mechanical properties across the depth of the EVA encapsulant.

4. Fluorescence imaging has also showed the obvious degradation of the EVA middle layer and two adhesive layers in the PPE backsheet, suggesting a potential risk of inner layer failures within the backsheet, which could raise potential safety concerns and ultimate reliability issues of the PV modules.

In summary, fluorescence imaging has enhanced our ability to visualize heterogeneous degradation in-depth and opened a new route for the understanding of the gradient degradation of each layer in multi-layer PV packaging materials, which would unlock new opportunities in rapid failure assessment for whole PV systems.

ACKNOWLEDGEMENTS

We greatly acknowledge the support from a NIST/Industry consortium on Characterization and Modeling of Polymers for Photovoltaic Systems. Companies involved in this consortium include 3M, AGC, Arkema, DuPont, Dakin America, First Solar, and Underwriter Laboratory.

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