Depth profiling of degradation of multilayer photovoltaic
backsheets after accelerated laboratory weathering:
Cross-sectional Raman imaging

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Abstract

Understanding of the durability of each individual layer and their interfaces in a multilayered photovoltaic (PV) backsheet is critical to the design and selection of materials for making reliable and high performance PV modules. In this study, Raman imaging was used to depth profile the chemical degradation of a multilayer commercial backsheet film exposed to ultra-violet (UV) radiation at 85°C, 5% relative humidity (RH, dry) and 85°C, 60% RH (humid) on the NIST (National Institute of Standards and Technology) SPHERE (*Simulated Photodegradation via High Energy Radiant Exposure*). The backsheet film was a multi-part laminate comprising of a pigmented polyethylene terephthalate (PET)-based outer layer, PET core layer and three ethylene vinyl acetate (EVA) layers having different vinyl acetate (VA) contents, along with two inner adhesive layers between PET outer and PET core layers, and PET core and EVA layers. Cross-sectional samples were prepared by cryo-microtomy for various characterizations. The multilayer structures were examined by laser scanning confocal and atomic force microscopies, while their chemical degradation profiles were obtained by Raman spectroscopic imaging. Non-uniform degradation was observed in the aged backsheet film, and both UV and moisture appeared to significantly affect the degradation profiles of the multilayers. Severe degradation, indicated by high fluorescence, occurred in the outermost region of the pigmented PET outer layer, and the degradation gradient extended to approximately 20 μm to the bulk. It was also found that the inner adhesive layers were severely deteriorated under moist condition, indicating that the long-term adhesion between the layers could be a major area of concern for multilayer backsheets used in a humid environment. The relationship between the sharp

(non-uniform) degradation profile, resultant internal stress, and ultimate failures (cracking and delamination) was discussed as well.

Keywords: multilayered backsheet, photovoltaic module, cross-section, degradation profile, Raman imaging, accelerated laboratory weathering

1. Introduction

Polymeric packaging materials are important to the safety, performance, durability, and reliability of photovoltaic (PV) modules during field operation. The backsheet, the outermost packaging material on the back side of a PV module that directly adheres to encapsulant, is the first line of back side defense against environmental aging in the field [1,2]. In general, the backsheet is a polymeric multilayer laminate system engineered so that each layer can address multiple purposes such as weatherability, insulation, adhesion promotion, and light reflection. Fluoropolymers are commonly used as the outermost weathering resistant layer of backsheets due to their chemical and thermal stability. Polyethylene terephthalate (PET) is often used as an insulation layer (usually core layer of the backsheet) because of its low cost, low electrical conductivity and high mechanical strength [1-3]. Moreover, to block ultra-violet (UV) from the back side and redirect reflected sunlight from the front side of a PV module, white inorganic pigments, such as titanium dioxide (TiO_2) and barium sulfate (BaSO_4), are widely used in backsheet layers to modify opacity and reflectivity of polymeric layers [2].

To improve long-term stability and prolong service life of backsheets, complex additives such as antioxidants, hydrolysis stabilizers, heat stabilizers, UV absorbers/stabilizers, silane coupling agents, curing agents, and flame retardants are commonly added in the polymeric matrix of each layer for various purposes. The existence of additives results in the polymer degradation processes having multiple variable mechanisms. Usually, the amounts of each additive are as small as 0.1% to 2.0% mass fraction [4-8]. Consequently, it is difficult to detect the additives using conventional vibrational spectroscopy. However, the formation of conjugated double bonds such as α , β -unsaturated carbonyl groups during weathering may contribute significantly to the

enhanced fluorescence and/or luminescence emission when degraded samples are illuminated with UV or visible light [4]. Therefore, besides conventional vibrational spectroscopies, fluorescence and luminescence-based analytical techniques can be employed as a synergistic approach to monitor the extent of degradation [9-11].

The current requirement of greater than 25-year service life for PV module is a big challenge to module and backsheet manufacturers. Practical in-field testing results showed that significant backsheet failures such as cracking, yellowing and delamination occurred within a 5-year service [2]. Previous research efforts have investigated backsheet degradation and failure by studying either individual material components or mini-modules [2,3,12-18]. Some studies focused on characterization of backsheet film as a whole as well as its top/bottom surfaces [2,14-16], while others addressed the adhesion behaviors between layers by peeling tests [3,12,13]. However, there are limited data showing a degradation profile across backsheet layers and how different aging stresses impact individual layers [17,18]. For this reason, an in-depth investigation on the degradation profile of polymeric multilayer backsheet is needed for a better understanding of backsheet failure mechanisms.

Cross-sectional analysis can provide robust information for depth profiling of multilayer systems [19,20]. Raman spectroscopy is known to be non-destructive for samples, and can reveal polymer degradation by means of not only the fingerprint of vibrational spectrum but also fluorescence emission [10]. Furthermore, instead of single-point or one-dimensional spectroscopic characterization, two-dimensional spatial spectroscopy such as Raman imaging has been shown to accurately describe complex polymeric components [21,22]. For these reasons, we have employed the combination of

cryo-microtomy cross-sectioning

and
5

Raman

microscopic

imaging to investigate degradation profile in multilayer backsheet system.

In this study, a commercially available backsheet consisting of PET/PET/ethylene vinyl acetate (EVA), commonly named as PPE, was selected as a model sample due to its low cost compared to fluoropolymer-based backsheets. Unless stated otherwise, the accelerated laboratory weathering of multilayer PPE backsheet was performed for 1600 hours (h) at 85 °C/5% RH (dry) and 85 °C/60% RH (humid) conditions on the NIST (National Institute of Standards and Technology) SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) weathering chamber. The accumulated UV irradiance on each specimen is approximately 170 W/m² between 300 nm and 400 nm after 1600 h exposure on the SPHERE. Assuming 10 % albedo for the reflected light on the backsheet during field exposure [2,23], the UV dose for the 1600 h exposure (~980 MJ/m² between 300 nm and 400 nm) is approximately equivalent to that of a 25-year field exposure on the back side of a non-rack PV module in Phoenix, Arizona.

To analyze the depth profile after degradation, cryo-microtomy was used to obtain cross-sectional PPE specimens with a flat surface parallel to the film thickness. The evolution of the multilayer structure and chemical degradation profiles were examined before and after accelerated laboratory weathering by laser scanning confocal microscopy (LSCM), atomic force microscopy (AFM), and Raman imaging.

2. Experimental^{*}

2.1. Backsheet specimens and accelerated laboratory weathering

A commercial, free-standing, multilayer PPE backsheets film was used as received for

^{*} Certain commercial equipment, instruments or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for this purpose.

this study. Circular specimens with 19 mm in diameter were punched from the PPE backsheet film and then placed on a sample holder for accelerated laboratory weathering on the NIST 2-meter diameter integrating sphere-based high intensity UV weathering facility, referred to as SPHERE [24] at $85^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ under $5\% \pm 3\% \text{RH}$ (dry) and $60\% \pm 3\% \text{RH}$ (humid) for 1600 h. A few specimens were exposed up to 3280 h to investigate ultimate failure modes including cracking or delamination. The UV irradiance on the PET outer layer side of the samples was approximately 170 W/m^2 between 300 nm and 400 nm.

To prepare cross-sectional specimens, 3 mm x 4 mm pieces cut from the center of the 19 mm circular sample were embedded in an epoxy molding. Cryo-microtoming was carried out on a Leica EM FC7 (Leica Mikrosysteme GmbH) with glass blade for coarse surfacing and then followed with diamond blade for fine surfacing. *The liquid N₂ was used to cool the sample, ensuring a brittle fracture resulted from the microtoming to minimize the surface roughness for microscopic and spectroscopic imaging [25].* The cross-section is parallel to the film thickness. Care was taken to make sure that the microtoming direction did not cross the layers of PPE to avoid smearing between layers as the blue arrow shown in Figure 1.

2.2. Laser scanning confocal microscopy and atomic force microscopy characterizations

Images of the cross-section and exposed (weathered) surfaces were acquired using a Zeiss LSM510 META (Carl Zeiss, Inc., Oberkochen, Germany) laser scanning confocal microscope in reflection mode with a laser wavelength of 543 nm. A series of single images (optical slices) each having a z-direction step size of 100 nm were obtained by adjusting the focal plane in the z-direction. Objectives of 10x and 50x (Zeiss, Germany)

were used to observe two or more samples per sampling interval with sufficient observation locations to check uniformity of sample. The pixel size of the LSCM images is 512 pixels by 512 pixels. The optical slices of each specimen were carefully analyzed and representative images located at proper z-position are presented.

AFM topographical images were acquired by using a Dimension Icon[®] AFM (Bruker) with PeakForce QNM[®] (Quantitative Nanomechanical Property Mapping) based on peak force tapping mode. An antimony doped silicon probe with reflective aluminum back side coating (RTESPA, Bruker) was used. The probe spring constant is 40 N/m $\pm$ 5 N/m with resonant frequency of approximately 300 kHz. Scan size of 25 μ m x 25 μ m with scan speed of 0.5 Hz was performed at ambient conditions.

2.3. Raman imaging

Raman imaging was performed on a Senterra Raman microscope with a high-precision motorized XYZ stage controlled by OPUS 7 software (Bruker). The optical configuration of the Raman microscope is dispersive and 180° back scattering coupled with a charge-coupled device (CCD) camera for bright field imaging. An excitation wavelength of 785 nm was provided by a diode laser. The laser power, number of scans and integration time used were in the ranges of (25 to 50) mW, (1 to 5) scans, and (10 to 20) sec, respectively. A 50x metallurgical objective (N.A.=0.75, MPlan, Olympus) was used for mapping, and the spatial resolution and laser spot size were estimated to be 0.5 μ m and 2 μ m, respectively [22]. A high throughput slit aperture of 50 μ m x 1000 μ m was utilized to shorten the time of mapping. Raman spectra were collected in the wavelength range of 70 cm⁻¹ to 3200 cm⁻¹. Raman mapping images were constructed in user-defined desired areas (170 μ m x 50 μ m to 100 μ m x 50 μ m) on the

sample cross-section with a step size of $2\text{ }\mu\text{m}\pm0.01\text{ }\mu\text{m}$, so that each Raman image contains *thousands* of Raman spectra. Individual Raman images were taken from different regions centered at the PET outer layer, PET core layer and EVA layers. All mapping was performed under room temperature. Note that care was taken to make sure microscopic optical axis was normal to sample cross-section, and laser parameters and focus on sample cross-section were kept the same for each mapping layer/material in order to compare spectrum intensity between samples [26]. The standard uncertainty is $\pm 3\text{ cm}^{-1}$ in wavenumber, and the relative standard uncertainty is $\pm 5\%$ in intensity.

OPUS 7 software was used for further processing of Raman spectra and images. Firstly, Raman spectra were inspected to determine the location of the interface between layers, and then Raman images were trimmed for each layer and/or each material. The layer/material thickness presented in each trimmed Raman image is smaller than the actual thickness by $6\text{ }\mu\text{m}\pm 2\text{ }\mu\text{m}$ due to the laser spot size of Raman microscope. Two types of Raman images were acquired: one is based on spatial intensity distribution of fluorescence emission and the other on characteristic Raman peaks. To analyze the evolution of certain characteristic bands for chemical information, the fluorescence emission was subtracted using a method of endpoint constrained polynomial fitting provided in the OPUS 7 software. All fluorescence emission-subtracted spectra were carefully inspected to ensure no significant artifacts caused from the operation of subtraction. **Note that the scaling of Raman images is shown as “0 to 1”, which is the normalized scale based on the maximum intensity in the same image. However, the intensity shown in line profiles is the raw intensity, not the normalized value [27].** Raman spectra and images were then analyzed for chemical degradation profiling. It was found that the relative standard uncertainty of intensity

associated with spatial measurement strongly depends on aging conditions. Instead of standard deviation, all of the measurement data are presented at each depth location for line profile results unless stated otherwise.

3. Results and discussion

3.1. Structure of the PPE backsheets film

ALSCM image of the cryo-microtomed cross-section of fresh PPE backsheets is shown in Figure 1. Combined with the chemical information provided by Raman spectra of each individual layer (Figure 2), it is suggested that the PPE backsheets are comprised of five main layers, a PET outer layer, a PET core layer, an EVA inner layer, a pigmented-EVA layer and an EVA outer layer, along with two visible adhesive layers between PET outer and PET core layers (designated as PET/PET adhesive), and PET core and EVA inner layers (designated as PET/EVA adhesive). The thicknesses measured from the LSCM image for each layer are approximately 55 μm , 126 μm , 25 μm , 50 μm , 25 μm , 6.5 μm , and 8 μm for PET outer, PET core, EVA inner, pigmented-EVA, EVA outer, PET/PET adhesive, and PET/EVA adhesive, respectively. Similar thickness values for each layer can be obtained from Raman images. However, due to pixel size, the thickness values obtained by Raman imaging are slightly smaller, at least 4 μm , than those obtained by LSCM. It is worth mentioning that the PET outer layer is heavily pigmented, while the PET core layer is lightly pigmented, as shown in the LSCM image and the Raman spectra discussed later. The randomly distributed dark spots on PET core layer in Figure 1 are probably due to the aggregation of pigments.

Figure 2 shows the raw (as collected) Raman spectra for each layer of fresh PPE backsheets. As seen in Figure 2(a), the Raman spectra of both PET outer and core layers

are quite similar. Table 1 gives the assignments of typical bands of PET Raman spectra [18,28-30]. The main characteristic bands of PET that are utilized for the study of degradation are the carbonyl (C=O) stretching at 1726 cm^{-1} , and a group of bands at 1115 cm^{-1} , 1094 cm^{-1} , and 998 cm^{-1} , which are commonly attributed to mixed modes of ring CH in-plane bending, glycol C-O stretching, COC and CCO bending, and C-C stretching of PET. The bands at 454 cm^{-1} and 990 cm^{-1} shown in the inset of Figure 2(a) for the PET outer layer are attributed to barium sulfate [31,32]. The presence of these bands suggests that the PET outer layer is filled with barium sulfate pigments. Bands in the region of 950 cm^{-1} to 1200 cm^{-1} of a PET material (see inset of Figure 2(a)) have been reported to be associated with its conformation and crystallinity [30]. Later in this paper, we will use the intensity ratio of the bands at 1094 cm^{-1} and 1115 cm^{-1} to evaluate the changes in PET crystallinity after UV exposure.

Raman spectra of the PET/PET and PET/EVA adhesive layers are displayed in Figure 2(b). These Raman spectra suggest that the adhesives are based on polyurethane, as evidenced by the strong band at 1445 cm^{-1} and the shoulder at 1242 cm^{-1} for isocyanate, N-H, and urethane amide III [33,34]. Based on the characteristic C=O and ring C=C bands at 1726 cm^{-1} and 1614 cm^{-1} , respectively, we suggest that the main composition of the polymer matrix of the adhesives is an aromatic polyester-based polyurethane. The characteristic bands at 941 cm^{-1} , 765 cm^{-1} , and 656 cm^{-1} are the proof of silane coupling agents such as γ -glycidoxypyrpyl-trimethoxysilane (GPTS) and γ -aminopropyl-triethoxysilane (APTS) [35], which are commonly used as adhesion promoters in adhesives. In addition, the small but distinctive P-O band at 1180 cm^{-1} indicates the presence of phosphorus-oxyacid-based antioxidants in the formulation [5,36]. Comparing the CH ranges from 2850 cm^{-1} to 3200 cm^{-1} between the two spectra, it is

believed that there are some formulation differences between the PET/PET and PET/EVA adhesives. However, due to the proprietary information of the backsheet, the details of these differences are not known.

Raman spectra of the EVA layers of the PPE backsheet are shown in Figure 2(c), and the assignments of the bands are given in Table 2. The C=O stretching around 1727 cm^{-1} is solely from vinyl acetate (VA) of the EVA copolymer [37,38]. The relative intensity of this band with respect to that of 1461 cm^{-1} (due to ethylene CH_2 rocking) provides information about the relative content of VA in the EVA copolymer. The EVA outer layer had a lower VA content than the EVA inner layer and pigmented-EVA layer. Generally, a lower VA content in EVA tends to bring about a higher value of melting point or modulus, but a lower adhesion strength [41,42]. Different VA components used in various EVA layers may be due to the need of processing, cost and performance. The pigmented-EVA shows two characteristic bands at 609 cm^{-1} and 446 cm^{-1} , assigned to the Ti-O bonds [43,44], indicating that rutile titanium dioxide was used for enhancing the UV reflectivity (albedo) of the film. Additionally, the defined C=C stretching band at 1614 cm^{-1} is probably due to aromatic additives in the formulated EVA, while the detailed proprietary information is not known.

3.2. Degradation profiles and interfacial microscopies

3.2.1. Raman spectra and mapping

Examples of one-dimensional Raman mapping spectra, which are the constructing elements of the Raman images, are displayed in Figure 3. Figure 3(a) shows a set of raw Raman spectra as a function of depth of the PET outer layer after 1600 h aging under UV/85°C/5% RH. Each spectrum has its spatial location corresponding to the

position of the PET outer layer cross-section, where the top spectrum L was taken from a site close to the exposed surface while the bottom spectrum A was from a site close to the adhesive layer between PET outer layer and core layer (see inset in Figure 3(a)). The spectrum of the fresh PET outer layer before exposure is also shown as a reference. The intensity of the fluorescent emission background sequentially changes as a function of the sample depth, specifically, the closer to the UV-exposed surface, the higher the background emission intensity. Figure 3(b) presents the same set of spectra but after the baseline correction to eliminate the fluorescence emission.

As stated in the experimental section, there are two types of Raman images presented in this study. One is based on the intensity of the background fluorescence emission from the raw Raman spectra (i.e. Figure 3(a)), the other is based on the intensity of the specific Raman band after subtracting the background fluorescence emission (i.e. Figure 3(b)). The former, namely as fluorescence emission image, is generally related to the amount of chromophores (additives, discoloration products, etc.) due to the nature of the conjugated structures of most fluorescent materials. The latter, namely as Raman image, provides information about chemical or physical structural changes during UV exposure, because the selected bands are those representing the intrinsic structures of the materials and are sensitive to aging.

3.2.2. PET outer layer

Two types of Raman images of the PET outer layer after 1600 h aging in UV/85°C at two humidity levels and their corresponding Raman intensity line profile are displayed in Figures 4(a) to 4(d) and Figures 4(e) to 4(f), respectively. The intensity at 1660 cm^{-1} was chosen as an index of the fluorescence emission for the fluorescence imaging because no visible Raman absorption was observed at 1660 cm^{-1} and therefore, the intensity of this

band could be assigned to the fluorescence emission solely. The red region of the fluorescence images in Figures 4(a) and 4(c) indicates that the UV exposed outermost region of the PET outer layer has a higher fluorescence emission than the blue central region. This is consistent with our observation of yellowing on the surface of the UV-exposed PPE (yellowing data not shown in this article). The sample aged in dry conditions shows a gradual decrease in fluorescence emission from the surface to the bulk (Figures 4(a) and 4(e)), while that aged in humid conditions presents a much higher but a sharper decrease in fluorescence intensity near the exposed surface (Figures 4(c) and 4(e)). This result indicates that moisture diffusion affects the profile of the fluorescence emission in the PET outer layer, and damage by moisture seems to be confined mainly near the surface region. Moreover, this implies that the PET outer layer of this multilayer PPE backsheet might be hydrolysis-resistant by end-group capper, as designed for most PET-based backsheets. Note that fluorescence is generated not only by the degradation of PET polymer matrix but also by the deterioration of additives/pigments such as UV stabilizers, absorbers, and inorganic BaSO₄ pigments during the exposure.

Photo-degradation of PET generally involves the ether bond cleavage of the ester groups to yield carboxylic acid, aldehyde and other volatile small molecules such as CO₂ [7,8,18]. Raman images of the PET outer layer constructed using the ester C=O Raman band to map the degradation of PET are illustrated in Figures 4(b) and 4(d). The blue region near the surface indicates that the amount of ester groups in the surface region is much lower than that in the central region for the aged PET outer layer, and the quantitative change in the intensity can be seen from a line profile of C=O across the thickness of PET outer layer shown in Figure 4(f). These results suggest that severe degradation has occurred near the UV exposed surface of the PET outer layer, and the

region of decreased ester groups was extended up to approximately 20 μm from the surface in both dry and humid exposure conditions, with the most severe changes occurring in the top 10 μm from the exposed surface (Figure 4(f)). Figure 4(f) also reveals that the loss of the ester C=O band for samples aged at dry and humid conditions are similar. This result implies that UV radiation is the main factor responsible for the degradation process of the PET outer layer, compared to the effects of moisture, especially for the hydrolysis-resistant PPE. However, the low sensitivity of Raman signal to the carbonyl groups due to the large dipole moment of the groups also gives challenges to identify the degradation products such as acid, aldehyde from ester based on C=O stretching vibration. A supplemental test, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), on the same sample showed that the moisture affected the photodegradation of the PET outer layer (data not shown). However, the UV irradiation is still the dominant factor.

Furthermore, a thickness reduction was observed for the aged PET outer layer. The thickness of fresh PET outer layer is about 55 μm (see Figure 1), while the thicknesses of both dry and humid conditions aged PET outer layers are about 42 μm plus $6\mu\text{m} \pm 2\mu\text{m}$ if considering the laser spot size of Raman microscope. The thickness decrease in both dry and humid conditions as observed by LSCM is also consistent with Raman intensity line profile results shown in Figures 4(e) and 4(f). Such thickness reduction is common for the polymers during degradation[45] due to loss of volatile materials resulting from chemical degradation, and physical erosion of degraded products and pigments.

Figure 5 shows the depth-dependent evolution of Raman spectra of PET outer layer in the range of 950 cm^{-1} to 1230 cm^{-1} . It has been reported that during hydrolytic and

photolytic degradation, changes in the crystallinity of PET could take place along with chemical degradation [8,46]. According to Figure 5(c), using the intensity ratio between the bands at 1094 cm^{-1} and 1115 cm^{-1} (I_{1094}/I_{1115}), which is representative of relative concentration of *trans*-glycol conformers[29,47], we have investigated the crystallinity change of PET after UV exposure in dry and humid conditions. A lower intensity ratio of I_{1094}/I_{1115} generally corresponds to a lower crystallinity. The value of I_{1094}/I_{1115} decreases from bulk to the exposed surface in the PET outer layer, suggesting that the crystallinity of PET near the surface region becomes lower after aging. A similar trend is observed for samples exposed in dry or humid conditions. However, the appearance of a sharp Raman shift of BaSO_4 pigments (990 cm^{-1}) near the humid exposed surface in Figure 5(b) suggests that the surface aged in humid conditions is enriched with BaSO_4 pigments. The appearance of the new bands at 1040 cm^{-1} and 1050 cm^{-1} indicates that a secondary reaction of degraded products with moisture might have occurred, however, the origin of those products is not certain.

3.2.3. PET core layer

Figures 6(a) to 6(c) present the Raman images of the ester C=O intensity of the unaged, and aged PET core layer exposed in dry and humid conditions. The profiles of the ester C=O for both aged samples are similar to that of the unaged sample, which has an overall uniform contrast with some random heterogeneity across the whole PET core layer. This result suggests that the PET outer layer has effectively blocked the UV irradiation, and the degradation of PET core layer was mostly dominated by relatively uniform thermal degradation in the multilayer system. Note that the thermal degradation effect was further confirmed by Raman spectra as shown in Figure 7. Random low C=O intensity (blue) spots in these Raman images are probably caused by aggregation of

pigments as mentioned above in Figure 1.

However, a careful examination of Figure 6(c) reveals that there is a narrow but distinct low C=O intensity region near the EVA side exposed in humid conditions (left in Figure 6(c)). The fluorescence emission image in Figure 6(d) provides additional evidence of changes in this vicinity. The strong red contrast implies that the species with high fluorescence emission are formed in the PET core layer near the EVA side. The results are probably related to the moisture effect on PET degradation or/and the possible additive migration between the interfacial region between PET core layer and EVA inner layer. Additional information about the effect of moisture on the PET core layer can also be seen from the Raman spectra taken along the thickness of this layer (Figure 7). Compared to the fresh sample, the fluorescence emission of the samples aged in dry conditions was slightly and evenly enhanced, but a more progressive, increased fluorescence was seen for those aged in humid conditions, especially when the location is closer to the EVA side. The Raman image shown in Figure 6(d) clearly presents such evolution of the fluorescence emission with the depth.

3.2.4. AFM images and Raman spectra of interfaces of PET Outer/PET Core layers and PET Core/EVA layers

To better understand why the PET core layer experienced different aging effects on its opposing sides, AFM topographical images were acquired in two interfacial regions for both aged and unaged samples: between PET outer and PET core layers (Figures 8(a), 8(c), and 8(e)), and between PET core and EVA inner layers (Figures 8(b), 8(d), and 8(f)). The dark and bright color regions in Figure 8 correspond to areas below and above the surface, respectively. Before exposure, each region exhibits an adhesive layer featured with many small nodules, similar to latex structures from emulsion polymerization.

However, after aging, the nodular structure was substantially diminished, and thickness reduction of the adhesive layers took place, particularly for samples aged in humid conditions. A groove-like structure of aged samples indicates a substantial loss of materials. For the PET/PET adhesive, such loss is further confirmed by its Raman spectra (Figure 9), showing intensity loss of the polyurethane bands at 1445 cm^{-1} and 1242 cm^{-1} , as well as the loss of some additives such as silane (656 cm^{-1}) [48-50] after aging in humid conditions. It was also found that the adhesive layers were soft and easily smeared during microtoming after aging in humid conditions, and the narrowing of the PET/PET adhesive layer after aging in humid conditions (Figure 8(e)) made it difficult to acquire Raman spectra of the adhesive-only layers without interference from the PET sides. Chemical and morphological changes near or in the PET/PET interfacial region (Figures 8 and 9) may be attributed to several phenomena, including thermal and hydrolytic degradation of the adhesive layers, further coalescence of the latex-like microstructures, and diffusion of water-soluble molecules and degradation products from the adhesive to the PET layer near the interface. It should be mentioned that polar molecules and hydrophilic surfactants and additives have a strong affinity for water. During exposure to water or high humidity, these materials tend to migrate to the hydrophilic interface, which attracts multiple monolayers of water and causes loss of adhesion [51]. Hence, the changes of the PET/PET and PET/EVA interfacial regions are probably resulting from the susceptibility of the adhesive layers to moisture at elevated temperature. That may also influence the non-uniform degradation of PET core layer near the EVA side in humid conditions.

3.2.5. EVA layers

EVA layers were on the back side of PPE samples during the UV exposure, and the

EVA outer layer was directly exposed to moisture. Because of the low intensity of C=O band in the EVA, integration of aliphatic CH band region from 2800 cm^{-1} to 3000 cm^{-1} of the Raman spectra was chosen for the study of EVA degradation [10]. Figures 10(a) through 10(c) show Raman images of the EVA layers based on the aliphatic CH band intensity (fluorescence emission-subtracted) before aging and after aging in dry and humid conditions. Figures 10(e) and 10(f) are intensity line profiles for the aliphatic CH band and fluorescence emission. From the results of Figure 10, the following observations are made: (1) the lower aliphatic CH intensity (blue regions in Figures 10(a) to 10(c)) of the pigmented-EVA layer in comparison to other EVA layers is due to reduced aliphatic CH concentration in the presence of TiO_2 pigments; (2) the distribution profile of aliphatic CH intensity across three EVA layers for the sample aged in dry conditions is similar to that of the fresh sample; only a slight difference in the EVA inner layer or outer layers, probably due to thermal aging; (3) in humid conditions, the thickness of the pigmented-EVA layer is dramatically decreased, and the aliphatic CH intensity in this layer is much lower than the fresh and the dry aged samples; these changes may be due to water-assisted degradation of pigmented-EVA, a detailed mechanism is not yet clear due to proprietary information; (4) the strong contrast in Raman image (Figure 10(d)) and the markedly high intensity of the fluorescence emission (Figure 10(f)) observed in the TiO_2 -pigmented-EVA layer suggests the formation of higher emission species in this layer during exposure in humid conditions. The reaction to form these higher emission species may involve the pigments, moisture, or EVA and/or their combination. Pigments may accelerate the EVA degradation in the presence of moisture. One postulation could be related to the acid-base reaction between acetic acid resulting from EVA degradation [4-6,8] and the basic nature of TiO_2 surface with high moisture. In summary, degradation

in the three-layered EVA structures is localized due to different compositions of each layer.

3.3. Backsheet failure assessment

When combining the degradation profiles of the entire PPE multilayers, it is found that the most damaged regions are the PET outer layer, pigmented-EVA layer, and the two adhesive layers. Severe degradation of pigmented-EVA layer is responsible for visible yellowing observed (yellowing data not shown in this article) on the EVA side of PPE backsheet. To assess the failure mode of the PPE backsheet, weathering tests with prolonged exposure time up to 3280 h were performed under similar weathering conditions [2]. As seen in Figure 11, the exposure surface of PET outer layer has experienced significant crack development during aging; visible holes/cracks were observed after 1600 h in humid conditions, while there were no significant changes even after 2500 h in dry conditions. After 3280 h exposure, the propagation of the cracks in humid conditions was more severe as well (Figures 11(c) vs. 11(e)). Furthermore, a spontaneous delamination between PET outer and PET core layers was observed during exposure in humid conditions (Figure 11(f)). Note that there was no delamination observed in dry conditions, nor for EVA layers due to the nature of its self-priming. This indicates that the adhesive layer between PET outer and PET core layers become the weakest region in the multilayers during aging with humidity. This is consistent with the results of AFM imaging and Raman spectra of the region (Figures 8 and 9), showing dramatic degradation occurring between PET outer layer and PET core layer.

In addition, as shown in Figure 11(f), it should be noted that the delaminated PET outer layer presents high internal residual stress according to its upward curled shape with

a significant curvature [52]. The curling direction indicates that the internal stress distribution in the PET outer layer is in tension near the exposure surface side. Based on the degradation profile shown in Figures 4(a) and 4(c), and the radius of curvature of PET outer layer, the average internal stress of the PET layer can be relatively estimated by a modified Stoney's equation describing the internal stress of the sharp degraded region [53]. Using this approach, the mode I stress intensity factor for PET exposed in humid conditions is approximately an order magnitude greater than that aged in dry conditions. As a result, the exposed surface of PET outer layer is more prone to form cracks after aging in humid conditions. The details of this study will be published in the future.

4. Conclusions

We have applied Raman spectroscopic imaging to investigate the degradation profile in each layer of a commercial multilayer PPE backsheet after aging in 300 nm to 400 nm UV at 85 °C and two RH levels, 5% and 60%, for 1600 h. Cryo-micromed cross-sections of the aged multilayer backsheet were used for degradation depth profiling. Both Raman and fluorescence emission signals obtained in a Raman spectrum were utilized for imaging, and laser scanning confocal and atomic force microscopies were employed to aid in the analyses. It was found that non-uniform degradation took place in the aged backsheet films, and both UV and moisture significantly affected degradation of the multilayers. Severe degradation occurred on the outmost region of the pigmented PET outer layer and the degradation gradient extended to approximately 20 μm to the bulk. The most susceptible regions in the PPE multilayer were the PET outer layer, pigmented-EVA layer, and the two adhesive layers. Severe degradation of

pigmented-EVA layer was responsible for visible yellowing on the EVA side of PPE backsheet. Furthermore, cracking was also observed on the exposure surface of the PET outer layer, and this cracking behavior was strongly dependent on the humidity of the aging condition. Complete delamination between the PET/PET layers after prolonged exposure (3280 h) in humid conditions was also observed. This is consistent with the marked degradation observed in AFM and Raman imaging. The upward curling direction of the delamination suggested a residual internal stress distribution in the PET outer layer, and the magnitude of this internal stress can be relatively quantified. In summary, degradation depth profile results indicated that Raman imaging can provide useful data on the chemical degradation along the thickness of a multilayer PPE backsheet. Degradation depth-profiling presented in this study should provide insights to failure mechanisms of multilayer backsheet used in photovoltaic modules during weathering.

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Table 1. Raman band assignment for PET [28-30].

Band (cm ⁻¹)	Assignment	Intensity
1726	C=O stretch	vs
1614	Ring C=C stretch	vs
1460	Glycol C-H deformation	w
1416	Ring C-C stretch	w
1373	Glycol CH ₂ wagging	vw
1288	Mixed mode of ring-carbonyl stretch, O-C stretch, and ring CH in-plane bend	s
1184	Ring CH in-plane bend	w
1115	Mixed mode of ring CH in-plane bend, and glycol C-O stretch	m
1094	Mixed mode of ring CH in-plane bend, glycol C-O stretch, COC and CCO bending, and C-C stretch	m
998	Mixed mode of glycol C-C stretch, O-CH ₂ stretch, and ring torsion	w
893	Glycol CH ₂ rocking	w
858	Ring C-C breathing	s
795	Ring CH out-of-plane	w
703	Ring C-C-C out-of-plane bend	w
632	Ring C-C-C in-plane bend	m
279	Mixed mode of ring C-C-C in-plane, and ring C-C out-of-plane	m

Table 2. Raman band assignment for EVA [37-40].

Band (cm ⁻¹)	Assignment	Intensity
2930	Ethylene and acetate CH ₂ asymmetric stretch	s
2881	Ethylene and acetate CH ₂ and CH ₃ stretch	vs
2848	Ethylene and acetate CH ₂ stretch	vs
2722	Aliphatic CH stretch	m
1727, 1740	Acetate C=O stretch	w-m
1461	Ethylene CH ₂ rocking due to <i>all-trans</i> -(CH ₂) _n -	vs
1440	Ethylene and acetate CH ₂ bend	vs
1416	Ethylene and acetate CH ₂ bend	s
1369	Ethylene and acetate CH ₂ wagging	w
1296	Ethylene CH ₂ twisting due to <i>all-trans</i> -(CH ₂) _n -	vs
1170	CH ₂ rocking	m
1128	Ethylene C-C symmetric stretch due to <i>all-trans</i> -(CH ₂) _n -	vs
1082	Ethylene C-C asymmetric stretch of <i>trans</i> and <i>gauche</i>	s
1062	Ethylene C-C asymmetric stretch due to <i>all-trans</i> -(CH ₂) _n -	vs
1003	Vinyl C-C of >CH-CH ₂ stretch	vw
631	Acetate O-C=O deformation	w

Figure captions

Figure 1. LSCM image of the cross-section of fresh PPE backsheet with various polymer layers and their corresponding thicknesses.

Figure 2. Representative raw Raman spectra (stacked) for each layer of fresh PPE backsheet: (a) PET outer and PET core layers, (b) PET/PET and PET/EVA adhesive layers, and (c) three EVA layers.

Figure 3. The depth-dependent Raman spectra of PET outer layer after 1600 h aging in UV/85 °C at 5% RH: (a) raw Raman spectra with Raman signals reside on baseline of fluorescence emission. The inset of bright field photomicrograph shows the corresponding measurement locations on the cross-section (epoxy is the molding compound), (b) fluorescence emission-subtracted Raman spectra (stacked) corresponding to the spectra in (a). The marked band (*) is the C=O of PET.

Figure 4. PET outer layer Raman images based on the fluorescence emission intensity at 1660 cm^{-1} after 1600 h aging in UV/85 °C at 5% RH (a), and at 60% RH (c). Figures 4(b) and 4(d) are corresponding Raman images based on the C=O band intensity (fluorescence emission-subtracted) with 5% RH and 60% RH aging, respectively. All images are normalized to the same intensity from 0 to 1, representing minimum to maximum intensity, with the UV exposed surface on the right side. Figures 4(e) and 4(f) are the intensity line profiles of the fluorescence emission intensity at 1660 cm^{-1} and C=O Raman band intensity at 1727 cm^{-1} , showing quantitative changes of these bands across the thickness of the PET outer layer. Note that the gray region in Figure 4(f) represents one

standard deviation for the fresh specimen.

Figure 5. The depth-dependent evolution of Raman spectra of PET outer layer after 1600 h aging in UV/85 °C at 5% RH (a), and at 60% RH (b). Two (2) μm , 4 μm ...24 μm are the depth from the UV exposed surface. All spectra here are fluorescence emission-subtracted. Figure 5(c) shows the intensity ratio between the bands at 1094 cm^{-1} and 1115 cm^{-1} as a function of depth.

Figure 6. PET core layer Raman images based on the C=O band intensity (fluorescence emission-subtracted) before aging (a), and after 1600 h aging in UV/85 °C at 5% RH (b), and at 60% RH (c). Figure 6(d) is the corresponding Raman image based on fluorescence emission intensity at 1660 cm^{-1} at 60% RH aging. All images are normalized to the same intensity from 0 to 1, representing minimum to maximum intensity, with PET outer layer on the right side.

Figure 7. The depth-dependent evolution of raw Raman spectra of PET core layer after 1600 h aging in UV/85 °C at 5% RH (a), and at 60% RH (b). The schematic insets show the corresponding measurement locations on the cross-section. Layer thicknesses in the insets are not drawn to scale.

Figure 8. AFM topographic images of two adhesive layers. Top row: PET/PET adhesive, bottom row: PET/EVA adhesive; before aging (a), (b); after 1600 h aging in UV/85 °C at 5% RH (c), (d), and at 60% RH (e), (f). The size of each image is 25 μm x 25 μm .

Figure 9. Fluorescence emission-subtracted Raman spectra (stacked) of PET/PET adhesive layers before aging, and after 1600 h aging in UV/85 °C at 5% RH and at 60% RH.

Figure 10. EVA layers Raman images based on the aliphatic CH band intensity (fluorescence emission-subtracted) before aging (a), and after 1600 h aging in UV/85°C at 5% RH (b), and at 60% RH (c). Figure 10(d) is the corresponding Raman image of the fluorescence emission intensity at 1660 cm^{-1} with 60% RH aging. All images are normalized to the same intensity from 0 to 1, representing minimum to maximum intensity. Figures 10(e) and 10(f) are Raman intensity line profiles based on the aliphatic CH band intensity and fluorescence emission intensity, respectively. The dashed lines represent the interfaces between layers.

Figure 11. LSCM images of the exposed surface of PET outer layer before aging (a), and after aging in UV/85°C at 60% RH for 1600 h (b), and for 3280 h (c); Figures 11(d) and 11(e) are after aging in UV/85°C at 5% RH for 1600 h and 3280 h, respectively. Figure 11(f) shows delamination between PET outer and PET core layers after 3280 h aging in UV/85°C at 60% RH. The scale of the ruler is in millimeter. Note that the actual color is not reflected in the photograph.

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Degradation profiles by Raman imaging: