Cracking and delamination behaviors of photovoltaic backsheet after accelerated laboratory weathering
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ABSTRACT

The channel crack and delamination phenomena that occurred during tensile tests were utilized to study surface cracking and delamination properties of a multilayered backsheet. A model sample of commercial PPE (polyethylene terephthalate (PET)/PET/ethylene vinyl acetate (EVA)) backsheet was studied. Fragmentation testing was performed after accelerated aging with and without ultraviolet (UV) irradiation in two relative humidity (RH) levels (5 % RH and 60 % RH) at elevated temperature (85 °C) conditions for 11 days and 22 days. Results suggest that the embrittled surface layer resulting from the UV photo-degradation is responsible for surface cracking when the strain applied on the sample is far below the yielding strain (2.2 %) of the PPE sample. There was no surface cracking observed on the un-aged sample and samples aged without UV irradiation. According to the fragmentation testing results, the calculated fracture toughness ($K_{IC}$) values of the embrittled surface layer are as low as 0.027 MPa-m$^{1/2}$ to 0.104 MPa-m$^{1/2}$, depending on the humidity levels and aging times. Surface analysis using attenuated total reflectance Fourier transform infrared and atomic force microscopy shows the degradation mechanism of the embrittled surface layer is a combination of the photo-degradation within a certain degradation depth and the moisture erosion effect depending on the moisture levels. Specifically, UV irradiation provides a chemical degradation effect while moisture plays a synergistic effect on surface erosion, which influences surface roughness after aging. Finally, there was no delamination observed during tensile testing in this study, suggesting the surface cracking problem is more significant than the delamination for the PPE backsheet material and conditions tested here.

Keywords: photovoltaic, backsheet, polymeric multilayer, cracking, delamination, degradation, ultra-violet, accelerated weathering/aging

1. INTRODUCTION

Photovoltaic (PV) modules rely on polymeric packaging materials including encapsulants, backsheets, and sealants to ensure performance, safety, and durability in field operation. Among these packaging materials, polymeric multilayer laminates are commonly used as backsheets on the back side of PV modules for not only protecting the back-side against all environmental aging factors but also providing the breathable construction that allows egress of deleterious substances and therefore reducing the corrosion of solar cells. Due to the nature of multilayer laminates and the constraints of the PV module and module frames, backsheets are inevitably subject to residual and external stresses caused by the manufacturing processes, installation, thermal cycling, wind, rain, snow, and some environmental mechanical loadings. As backsheet materials gradually degrade and lose their mechanical strength to sustain the residual and external stresses, backsheet cracking occurs, which accelerates PV module failure and leads to safety concerns.

Film cracking behavior in film/substrate systems depends on residual tensile or compressive stresses, the ductility of the film and substrate, and the elastic mismatch between the film and substrate. Many efforts have been made to characterize the degradation of backsheets based on property changes such as yellowing, chemical structures and microstructures, tensile strength, and adhesion strength. Some studies have addressed aging characterization of polymeric single-layer and multilayer films on mechanical property performance. However, little work has been done on polymeric backsheet or multilayer laminate cracking behavior after degradation. Embrittled surface layers

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within a certain degradation depth have been found to be responsible for surface cracking of stabilized and/or pigmented polymers after aging with ultraviolet (UV) irradiation.\textsuperscript{15,16} The degradation depth profile of aged polymers can be altered significantly by the addition of antioxidants, hydrolysis stabilizers, heat stabilizers, UV absorbers/stabilizers, curing agents, and pigments in the manufacturing processes.\textsuperscript{15,17} Nevertheless, according to the current International Electrotechnical Commission (IEC) qualification testing, there is no requirement for UV exposure on the back side of PV modules despite the estimated 12 % to 20 % of albedo for the reflected light on the backsheet during field exposure.\textsuperscript{4,5} Hence, it prompted this study to correlate UV accelerated aging and cracking behavior, as well as the accompanied delamination phenomenon, for polymeric multilayer backsheets.

The main objective of the work is to investigate the surface cracking behavior of a polymeric multilayer backsheet by fragmentation testing\textsuperscript{6,19} followed by accelerated aging with and without UV irradiation. Realistically, in field exposure, backsheet surface cracking occurs due to bi-axial stresses when mechanical loadings are applied. In this study, in order to simplify the problem and utilize an analytical model to study the cracking behavior, a uni-axial fragmentation testing was performed instead of a bi-axial fragmentation testing.\textsuperscript{18,20} Further, backsheet bulk mechanical properties were monitored by conventional tensile testing. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and atomic force microscopy (AFM) were used to study the surface degradation of the backsheet. The synergistic behaviors of the UV and moisture aging effects, degradation of backsheet material properties, and surface cracking were investigated.

2. EXPERIMENTAL*

2.1 Samples and accelerated laboratory weathering

A commercial free standing backsheet (polyethylene terephthalate/polyethylene terephthalate/ethylene vinyl acetate (PET/PET/EVA), labeled as PPE backsheet) was used as received in the present work. The sample storage closet was kept at ambient conditions and no light when not in use. The PPE backsheet was composed of seven layers, including a pigmented white PET (WPET) outer layer, a PET core layer, an EVA inner layer, a pigmented EVA layer, an EVA outer layer and two adhesive layers, and layer composition was described in our previous work.\textsuperscript{21} The cross-sectional image of the PPE sample is shown in Figure 1. The nominal thicknesses for each layer are 55 \textmu m, 126 \textmu m, 25 \textmu m, 50 \textmu m, 25 \textmu m, 6.5 \textmu m, and 8 \textmu m for WPET, PET core, EVA inner, pigmented-EVA, EVA outer, PET/PET adhesive, and PET/EVA adhesive, respectively.\textsuperscript{21} Note that the WPET layer is designed to be the weathering resistant layer and is bi-axially oriented in the manufacturing process, while the EVA layers are engineered to be adhered with module encapsulant and are oriented with respect to machining direction. Care was taken to handle the PPE samples with the same orientation in this study.

To fully understand the surface cracking behavior of the PPE backsheet after UV exposure, rectangular samples (70 mm x 104 mm) were cut from the backsheet and the WPET side was exposed to UV radiation on the NIST (National Institute of Standards and Technology) SPHERE (Simulated Photodegradation via High Energy Radiant Exposure). The NIST SPHERE has the ability to precisely control temperature and relative humidity, and produces a highly uniform UV irradiance.\textsuperscript{21,22} The accelerated weathering tests were performed with UV intensity of approximately 170 W/m\textsuperscript{2} (300 nm to 400 nm) at two different relative humidity (RH) levels (5 % RH (dry) and 60 % RH (humid)) at elevated temperature (85 °C) for 11 days (d) and 22 d. Exposure on the NIST SPHERE without UV light (referred to as dark conditions) was also performed as a control. Fragmentation testing, tensile testing, ATR-FTIR spectroscopy, AFM surface imaging, and laser scanning confocal microscopy (LSCM) imaging were further carried out to determine the effects of aging on the backsheet properties. For comparison, fresh (un-aged) samples were also characterized using the same test techniques. The details of these analyses are described below.

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*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.

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2.2 Tensile testing

Rectangular strips with a width of 5 mm ± 0.1 mm and a length of 70 mm ± 0.1 mm were cut from the 70 mm x 104 mm rectangular sample using a shear cutter (GRAVOGRAPH, USA) as described in American Society for Testing and Materials (ASTM) D6287-09. Following ASTM D882-12, tensile testing was then conducted on a mini-tensile test device (MTEST Quattro, ADMET, Inc., USA) at room temperature with a crosshead speed of 0.02 mm/s and specimen gauge length of 35.0 mm ± 0.1 mm. The displacement was controlled by a servo loop with a digital proportional integral derivative (PID) filter for precise control, and the corresponding load was recorded by a 500 lb load cell. A preload of 0.2 N ± 0.1 N was introduced to reduce slack of the strip sample when it was secured on the grips. However, such a preload was not always sufficient to remove the slack. Hence, the remaining slack was removed from the data by linearly fitting the elastic region of the stress-strain curves and shifting the curve to zero strain. The curve shift is approximately 0.3 % of the strain values. Note that strain was calculated in an engineering manner, while true stress was extracted according to the Equation (8) by Faridmehr et al. due to significant change of sample cross-sectional area observed during the mid-to-late stages of tensile testing. A minimum of five individual replicates were tested per sampling interval to ensure sufficient repeatability.

2.3 Fragmentation testing

Rectangular samples as described above were tested by fragmentation testing with a gauge length of 35.0 mm ± 0.5 mm. The fragmentation testing was conducted on a Zeiss LSM510 META (Carl Zeiss, Inc., Germany) laser scanning confocal microscope (LSCM) with a custom manual tensile apparatus (in-house) mounted on its automation x-y-z stage. The manual tensile apparatus provides displacement control by using one fixed grip end and another moving grip end controlled by high precision screw shaft. A fine scale graduated dial was attached on the screw shaft so that a minimum applied strain (ε) scale of 0.0297 % ± 0.0074 % can be achieved by manually turning the screw shaft. Because no load cell with preload setting was equipped on the manual tensile apparatus, the alignment of the WPET surface with the focal plane of a 50× objective (Zeiss, Germany) on the LSCM was taken as the starting point of applied strain.

The fragmentation testing was carried out at ambient conditions, and the strain was applied in intermittent steps. For every 5 min, a strain step of 0.0594 % ± 0.0074 % was added by manually turning the screw shaft. When crack density (ρ), which is equal to the number of cracks per unit length, was saturated, a higher strain rate of 0.1189 % ± 0.0074 % strain steps per minute was performed. LSCM in reflection mode with a laser wavelength of 543 nm under the above mentioned 50× objective was used to acquire images of the WPET surface during the step strain increment of fragmentation testing. By adjusting the focal plane in the z-direction, a series of single images (optical slices) were stacked and digitally summed over the z-direction to obtain a 3-D image. The z-direction step size was 0.4 μm, and a same-location image on sample surface was captured by adequately adjusting the x-y stage location after applying strain.

Figure 1. LSCM image of the cross-section of fresh PPE backsheet with polymer layers labeled accordingly.
on the sample. The LSCM image is 1536 pixels by 512 pixels and its corresponding image dimension is 504 µm by 168 µm, which is composed of three 512 pixels by 512 pixels (168 µm x 168 µm in dimension) images. An automatic plane fit surface tilt correlation was used to remove image tilt along with a numerical filter which averages surface roughness values for each 3 pixels x 3 pixels region.

Combining the step strain increment process and LSCM imaging, the sample surface status at each applied strain was imaged by LSCM, and the progressive cracking of the WPET surface was analyzed in terms of crack density vs. applied strain. Note that extra care was taken to take LSCM images only in the regions far away from the grip ends and sample edges based on the concern of Saint-Venant’s Principle and free edge effect of laminates.\(^{26}\)

### 2.4 ATR-FTIR

Infrared analysis on WPET surface was carried out using a Nicolet Nexus 670 FTIR (Nicolet Instrument Corporation) equipped with a mercury cadmium telluride (MCT) detector in attenuated total reflection mode. Spectra were recorded with a resolution of $4 \text{cm}^{-1}$ for 128 scans between 650 cm\(^{-1}\) and 4000 cm\(^{-1}\). Dry air was used as the purge gas. Consistent pressure on the strips was applied using the force monitor on the SensIR Durascope (Smiths Detection) attenuated total reflectance (ATR) accessory. Spectral analysis, including spectral baseline correction and normalizing, was carried out using a custom software program developed in the Polymeric Materials Group at NIST to catalogue and analyze multiple spectra.\(^{27}\) For the sake of repeatability, at least three locations for two replicates were measured for the FTIR measurements. Standard uncertainties associated with this measurement are $\pm 1 \text{cm}^{-1}$ in wavenumber and $\pm 5\%$ in absorbance.

### 2.5 AFM and LSCM imaging

AFM topographical images of WPET surfaces were acquired with a Dimension Icon\(^{\circledR}\) AFM (Bruker) operating in peak force tapping mode using an antimony doped silicon probe (TESP, Bruker). The probe spring constant is $42 \text{N/m} \pm 5 \text{N/m}$ with resonant frequency of approximately $320 \text{kHz}$. Scans with a size of $20 \mu\text{m} \times 20 \mu\text{m}$, scan speed of $0.5 \text{Hz}$, and collected points of 512 per line were performed at ambient conditions. Image analysis was performed with the Nanoscope Analysis Software (Bruker). The surface tilt and bow effects on the topography images were adjusted by a second order polynomial flattening algorithm.

LSCM imaging was performed to inspect sample cutting, degradation, and tensile fracture surfaces. Besides the $50\times$ objective mentioned previously, 10x and $150\times$ objectives with z-direction step size of $1 \mu\text{m}$ and $0.1 \mu\text{m}$ respectively were used as needed. The same experimental parameters and image processing methods were used as described above.

Surface roughness was evaluated on the flattened images by the calculation of root mean squared roughness ($R_q$) for both AFM and LSCM images according to the Equations (1) and (2) by Wang et al.\(^{28}\)

### 3. RESULTS AND DISCUSSION

It has been proven that the quality of sample cutting significantly affects the tensile testing results for polymeric film, sheet, and laminates.\(^{23}\) The cutting-surface images (local area) of fresh and UV humid condition weathered PPE backsheat samples are shown in Figure 2. They all appear relatively flat and smooth with minimal artificial flaws or delamination of the adhesive, suggesting the feasibility of using the shear cutter for sample preparation. Note that the roughness (not shown) of the cutting-surface measured by LSCM for each layer is not influenced by aging conditions or aging times.
Figure 2. LSCM images of PPE sample cutting-surface (local area) cut by shear cutter before (a) and after NIST SPHERE aging for 11 d (b) and 22 d (c) in UV humid condition.

Figure 3 shows the tensile testing results for the PPE backsheet before and after NIST SPHERE aging. The tensile strength and strain at break were found to be dependent on humidity and UV exposure. In Figure 3(c), the increase of elastic modulus after aging suggests an annealing effect occurred during the aging tests at elevated temperature. Note that the elastic modulus was extracted by fitting the linear-elastic region of the stress-strain curve. The average elastic moduli of 2.16 GPa ± 0.04 GPa for fresh sample and 2.35 GPa ± 0.04 GPa for aged samples are different from the average elastic moduli of PET layers measured in previous work using cross-sectional nano-indentation. However, by applying the rule of mixtures for the PPE multilayer with the modulus values of 4.0 GPa ± 0.3 GPa for WPET/PET layers and 20 MPa for EVA layers with respect to the layer thicknesses mentioned in Section 2.1, the derived value of 2.58 GPa ± 0.19 GPa is very close to the elastic moduli measured from our tensile testing in this study. This implies the rule of mixtures can achieve good agreement for the elastic modulus calculation for the PPE multilayer sample. It is worth mentioning that the yielding strain of about 2.2% (not shown), tensile strength of about 235 MPa, and strain at break of about 120% are not significantly influenced by aging conditions and aging times. Compared with the fresh sample, the mechanical properties of the PPE sample still hold its performance after 22 d aging regardless of aging conditions. Therefore, the PPE backsheets still possess good bulk mechanical properties after the accelerated weathering testing by the NIST SPHERE.

Figure 3. Plot of tensile strength (a), strain at break (b), and elastic modulus (c) as functions of NIST SPHERE aging time for PPE multilayer backsheet. Data were extracted from tensile tests.

Despite the robust bulk mechanical property stability, after weathering by the NIST SPHERE at different conditions and aging times, WPET surface cracking was noticed during fragmentation testing for the samples aged with UV irradiation. Note that there was no WPET surface cracking observed on fresh and dark condition aged samples. Therefore, this observed WPET surface cracking is dominated by the embrittled surface layer resulting from the UV photo-degradation. Figure 4 shows an example of surface crack evolution during fragmentation testing for the UV humid sample aged for...
In the early stage of fragmentation testing, cracking that is perpendicular to the strain direction starts to occur when the applied strain reaches critical strain ($\varepsilon_c$), and then nearly-regularly spaced cracks continue to appear as the applied strain increases (Figures 4(b) to 4(d)). After crack density reaches saturation, crack width increases with increasing applied strain as shown in Figures 4(e) to 4(f). Transverse cracks (cracks parallel to the strain direction) occur due to Poisson’s effects when the amount of applied strain is very high (Figure 4(f)). However, this study deals with surface cracking behavior only within the elastic region (i.e., $\varepsilon_c < 2.2\%$) because, in field exposure, backsheets on the PV module are only subject to a certain amount of strain due to residual stresses or external loadings, not a high-stretch deformation.

Figure 4. LSCM images showing the evolution of WPET surface cracking during fragmentation testing for UV humid 11 d aged PPE sample. The set of images was taken at the same location of WPET surface with the PPE sample tensioned to the $\varepsilon_c$ of (a) 0.0 %, (b) 0.475 %, (c) 0.654 %, (d) 1.070 %, (e) 1.783 %, and (f) 17.597 %. The application of strain is illustrated by the red schematic in Figure (a) and every other figure strain was applied in the same way. The images were post-processed to add a yellow background for better visual contrast.

Figure 5(a) shows the measured crack density as a function of applied strain for aged PPE samples by means of fragmentation testing. For all aging conditions and aging times, a similar saturated crack density is reached. The only difference for various aging conditions and aging times is the critical strain, which is determined from a linear extrapolation of the crack density vs. applied strain curve in the early fragmentation stages. To further understand how deep the cracks penetrate into the WPET surface, height information was generated from LSCM topography image as indicated in Figure 5(b). The crack depth (one standard deviation) measured by LSCM for samples aged in UV dry 11 d, UV dry 22 d, UV humid 11 d, and UV humid 22 d conditions are $4.78 \pm 0.58 \mu m$, $5.06 \pm 0.43 \mu m$, $4.89 \pm 0.65 \mu m$, and $4.74 \pm 1.07 \mu m$ respectively. Note that the total thickness of the WPET layer is around 55 $\mu m$. The result of a similar crack depth (taking 5 $\mu m$ for convenience) is reasonable because all samples have similar bulk mechanical properties and a similar saturated crack density is reached for all of the aging conditions and aging times.

Among several models to investigate the effects of aging conditions and aging times on the WPET surface cracking, a rigorous analytical model of film/substrate cracking developed by Hsueh and Yanaka (HY)$^{13,34}$ was used for further analysis with some assumptions.$^{35-37}$ First, due to aging at elevated temperature, the mismatch strain ($\Delta\varepsilon$) between layers of the multilayer was considered to be negligible because of the annealing effect. Second, crack depth (5 $\mu m$) was taken as film thickness ($t$) for HY’s model, i.e., the photo-degraded WPET layer was seen as a film, so that the rest layers of PPE, including the un-cracked WPET, were considered as a substrate for HY’s model. According to the multilayer construction, film modulus ($E_f$) measured from previous work by cross-sectional nano-indentation is 4.5 GPa,$^{30}$ and
substrate modulus \((E_s)\) can be calculated using the rule of mixtures as discussed previously. The same calculation was made for Poisson’s ratios of the film \((\nu_f)\) and substrate \((\nu_s)\) by using 0.30 (assuming a 10% embrittlement for the photo-degraded WPET layer), 0.34, and 0.49 for the photo-degraded WPET layer, WPET/PET layers, and EVA layers, respectively.\(^\text{38}\) Using the thicknesses and mechanical properties discussed, the surface cracking fracture behaviors of the photo-degraded WPET layer were analyzed as follows.

![Graph](image)

**Figure 5.** (a) Measured crack density as a function of applied strain for PPE samples after aging at 85°C in dry and humid conditions with UV irradiation for 11 d and 22 d. Error bars represent one standard deviation. (b) Illustration of crack depth measurement by LSCM image. Height information at the location of the white arrow on the micrograph is at the bottom of (b).

Based on the HY’s model and the above addressed assumptions, the fracture energy \((\Gamma)\) for the photo-degraded WPET layer is given as

\[
\Gamma = \frac{3}{4\alpha} \left[ \frac{E_f \varepsilon_f^2 (1 - 2\nu_f \nu_s + \nu_s^2)}{(1 - \nu_f^2)} \right],
\]

where

\[
\alpha = \left[ \frac{3}{2s(t + (1 - \nu_f^2)E_f)} \right]^{1/2}.
\]

In Equation (2), \(s\) denotes an effective substrate thickness rather than an actual substrate thickness. The use of an effective substrate thickness is essential for an analytical stress-transfer model in a film/substrate system, and it has been discussed.\(^\text{33,34}\) In order to solve for \(s\), the relationship between the applied strain and the crack density is used so that

\[
\frac{\varepsilon_a}{\varepsilon_c} = \sqrt{\frac{3}{2R}},
\]

with

\[
R = 4 \tanh \left( \frac{\alpha l}{2} \right) - \frac{e^{\alpha l} - e^{-\alpha l} + 2\alpha l}{e^{\alpha l} + e^{-\alpha l} + 2} - 2 \tanh(\alpha l) + \frac{1}{2} \frac{e^{2\alpha l} - e^{-2\alpha l} + 4\alpha l}{e^{2\alpha l} + e^{-2\alpha l} + 2}.
\]

where \(l\) is half of crack spacing and relates to the crack density and the average crack spacing \((\bar{l})\) through\(^\text{33,34}\)
\[
\frac{1}{\rho} \bar{l} = \frac{3}{2} \bar{l} .
\] (5)

Hence, the measured crack density as a function of applied strain as shown in Figure 5(a) can be described by HY’s model based on Equations (2) through (5) when the effective substrate thicknesses are solved (Figure 6). Using the values of \( s \) and \( \varepsilon_c \) along with Equation (1), the estimated fracture energy can be extracted as listed in Table 1. The mode I fracture toughness \( (K_{IC}) \) is determined by the relationship of

\[
\Gamma = \frac{K_{IC}^2}{E_f} .
\] (6)

And the film strength \( (\sigma_{str}) \) is given by\(^{33,34}\)

\[
\sigma_{str} = \frac{E_f}{(1-v_f)} \left[ \frac{(1-v_f v_s) \varepsilon_c}{(1+v_f)} \right] .
\] (7)

By using Equations (6) and (7), the results of \( K_{IC} \) and \( \sigma_{str} \) obtained from the analysis for the photo-degraded WPET layer are listed in Table 1.

![Normalized crack density \((t/\bar{t})\) as a function of normalized applied strain \((\varepsilon_d/\varepsilon_c)\) for PPE backsheet samples after aging at different conditions and aging times comparing predicted results obtained from HY’s analytical model (solid lines) and experimental data (symbols).](image)

Figure 6. Normalized crack density \((t/\bar{t})\) as a function of normalized applied strain \((\varepsilon_d/\varepsilon_c)\) for PPE backsheet samples after aging at different conditions and aging times comparing predicted results obtained from HY’s analytical model (solid lines) and experimental data (symbols).

The calculated fracture energy results for the photo-degraded WPET layers are in the range of 0.16 J/m\(^2\) to 2.4 J/m\(^2\). The lower fracture energy indicates the relatively brittle nature of the films. Compared with the fracture energy of an SiO\(_x\) coating, which is in the region of 8 J/m\(^2\) to 12 J/m\(^2\), extracted from a SiO\(_x\)/PET system,\(^{34}\) the obtained \( \Gamma \) values are of a reasonable order for the photo-degraded WPET layer. It is worth mentioning again that there was no WPET surface cracking observed on fresh and dark condition aged samples. Moreover, the obtained \( K_{IC} \) values of 0.027 MPa⋅m\(^{1/2}\) to 0.104 MPa⋅m\(^{1/2}\) are much smaller compared to the reported \( K_{IC} \) values of 4.5 MPa⋅m\(^{1/2}\) to 5.5 MPa⋅m\(^{1/2}\) for a typical fresh PET.\(^{39}\) The calculated film strength is far below the yielding stress of the bulk PPE sample (yielding strain is 2.2 % and Young’s modulus is 2.58 GPa), which means the photo-degraded WPET layer is prone to fail when it is subject to a...
very low amounts of residual and external stresses. It is suggested that the UV irradiation induced photo-degradation layer is responsible for the surface cracking of the PPE sample after accelerated weathering. Moisture plays a synergistic effect on the degradation process of the embrittled surface layer.

To understand the extent of surface degradation for the PPE samples, ATR-FTIR spectroscopy and AFM microscopy were performed. The intensities of ATR-FTIR spectra are typically dependent on optical effects caused by the contact between the polymer surface and the ATR detector. The band at 1410 cm⁻¹, which results from phenyl ring in-plane vibration of PET, is generally considered to be insensitive to molecular orientation and conformation, and is believed to be a suitable reference band.⁴⁰ In addition, the formation bands at 1425 cm⁻¹ and 1685 cm⁻¹ (in-plane vibration of acid groups due to degradation formed oligomeric structure), and the decreasing of the band at 1715 cm⁻¹ corresponding to chain scission of carbonyl ester group are usually used as indicators for PET degradation.⁴¹-⁴³ Using the intensities of these bands divided by the intensity of the band at 1410 cm⁻¹, the relative intensities as a function of NIST SPHERE aging time at different aging conditions are shown in Figure 7. Relative intensities of degradation formed acid groups to PET carbonyl ester C=O are shown in Figure 7(d) as well. A clear trend shows that the UV irradiation and aging time effects are more pronounced than the moisture effect for up to 22 d NIST SPHERE aging. This is consistent with the results of our previous work as WPET is stabilized with a hydrolysis-resistant end-group.¹⁷

AFM topography images provide an approach to explain the synergistic effect of moisture on the degradation process of the embrittled surface layer (Figure 8). In absence of UV irradiation, there was no significant morphological change after 22 d NIST SPHERE aging as seen in Figures 8(a) to 8(c). However, comparing aging conditions between dry (Figures 8(d) and 8(e)) and humid (Figures 8(f) and 8(g)) levels with UV irradiation, a moisture erosion effect can be readily seen. It is believed that the formation of the cyclic oligomeric structure with acid end groups take place along with the surface aggregation of pigments.⁴¹,⁴⁴,⁴⁵ The degradation mechanism is a combination of the photo-degradation with a certain degradation depth and the moisture erosion effect depending on the moisture level. The UV degradation with minimal moisture effect can provide severe deterioration to the WPET surface as illustrated by the significant decrease of fracture toughness and film strength (Table 1) compared with fresh PET and PPE sample.

It is worth mentioning near the end of the tensile test, edge-cracks were found immediately before sample breaking as seen in Figure 9. The edge-crack occurred for every aging condition and aging time, and at the moment of 96.7 % ± 1.3 % of the strain at break. However, a further inspection of the lateral view of the edge-crack shows no delamination between the WPET and PET core layers (Figures 9(d) to 9(f)). This provides a qualitative way to compare the significance of failure mode between surface cracking and delamination. The surface cracking and delamination behaviors of a multilayer or film/substrate system depend on how stresses/strain is applied and the relative elastic combination between layers.⁶,⁸ For the PPE backsheet, surface cracking appears in the early stage of tensile testing, and crack penetration rather than crack deflection takes place immediately after the appearing of edge-crack without delamination. The surface cracking could be the main failure mode compared with delamination for the PPE backsheet after aging up to 22 d on the NIST SPHERE.

Table 1. The analysis results of WPET surface cracking behavior (one standard deviation) based on HY’s analytical model.

<table>
<thead>
<tr>
<th>Aging conditions</th>
<th>Aging time (d)</th>
<th>ε_c (%)</th>
<th>s (µm)</th>
<th>Γ (J/m²)</th>
<th>K_Ic (MPa·m¹/²)</th>
<th>σ_st (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV dry</td>
<td>11</td>
<td>0.814±0.028</td>
<td>20.25±1.85</td>
<td>2.399±0.139</td>
<td>0.104±0.003</td>
<td>35.5±1.2</td>
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<td>25.25±2.00</td>
<td>2.197±0.107</td>
<td>0.099±0.002</td>
<td>31.7±0.4</td>
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<tr>
<td>UV humid</td>
<td>11</td>
<td>0.306±0.009</td>
<td>46.10±3.85</td>
<td>0.560±0.026</td>
<td>0.050±0.001</td>
<td>13.3±0.4</td>
</tr>
<tr>
<td></td>
<td>22</td>
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<td>74.40±4.00</td>
<td>0.158±0.005</td>
<td>0.027±0.0004</td>
<td>6.2±0.3</td>
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</tbody>
</table>

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Figure 7. Plot of ATR-FTIR spectra relative intensity data as a function of NIST SPHERE aging time based on the intensity ratios of (a) $1425 \text{ cm}^{-1}$ to $1410 \text{ cm}^{-1}$, (b) $1685 \text{ cm}^{-1}$ to $1410 \text{ cm}^{-1}$, (c) $1715 \text{ cm}^{-1}$ to $1410 \text{ cm}^{-1}$, and (d) $1685 \text{ cm}^{-1}$ to $1715 \text{ cm}^{-1}$. 
Figure 8. AFM topography images of WPET surface before aging (a) and, after dark conditions aging with dry (b) and humid (c) levels for 22 d; and after UV dry conditions aging for 11 d (d) and 22 d (e); and after UV humid conditions aging for 11 d (f) and 22 d (g). The corresponding $R_q$ values and height scales are marked accordingly. All images are a scan size of 20 $\mu$m x 20 $\mu$m.
4. CONCLUSIONS

The surface cracking and delamination behaviors of a commercial PPE backsheet were studied by tensile testing and fragmentation testing before and after NIST SPHERE aging with and without UV irradiation in two relative humidity levels (5 % and 60 %) at elevated temperature (85 °C) conditions for 11 days and 22 days. ATR-FTIR spectroscopy and AFM microscopy were employed to aid in the surface analyses. There was no surface cracking observed on the un-aged sample and samples aged without UV irradiation during and after the fragmentation testing and tensile testing. The UV irradiation induced embrittled surface layer with a certain photo-degradation depth is responsible for the surface cracking of the PPE sample after accelerated weathering. According to the fragmentation testing results and the analysis using HY’s analytical model, the calculated fracture toughness ($K_{IC}$) values of the embrittled surface layer are as low as 0.027 MPa·m$^{1/2}$ to 0.104 MPa·m$^{1/2}$, depending on the humidity levels and aging times. For all aging conditions with UV irradiation, the critical strain values in the range of 0.14 % to 0.81 % were found to be much lower than the yielding strain of about 2.2 % for a bulk PPE sample. ATR-FTIR and AFM results indicate that UV irradiation provides a chemical degradation effect while moisture plays a synergistic effect on surface erosion, which influences surface roughness after aging. Finally, there was no delamination observed in tensile testing in this study, suggesting the surface cracking problem is more significant than the delamination for the PPE backsheet.

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