

Surface photooxidation of polypropylene-based photovoltaic backsheets: A comprehensive spectroscopic investigation

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1 **ABSTRACT**

2 The prospect of cost reduction, enhanced performance, and improved sustainability has been driving
3 innovation in the development of new backsheet materials for photovoltaic (PV) modules. Among the
4 materials of interest, polypropylene (PP) has emerged as a promising alternative to fluoropolymer
5 backsheets. As backsheets serve as a barrier providing electrical insulation and protection for the sensitive
6 electrical components of PV modules, comprehensive understanding of the durability of PP-based
7 backsheets is essential to ensure module reliability in the field.

8 In this study, free-standing coextruded PP backsheets were subjected to artificial weathering to elucidate
9 the degradation behavior. The UV exposure was performed on the NIST Simulated Photodegradation via
10 High Energy Radiant Exposure (SPHERE) under three environmental conditions: 75 °C and 50 % relative
11 humidity (RH), 75 °C and 20 % RH, and 65 °C and 20 % RH. The total UV dose (295 nm to 400 nm) for
12 each film was $\approx 1710 \text{ MJ/m}^2$, or ≈ 50 years in Arizona, assuming 10 % albedo. Chemical, optical, and
13 physical changes were monitored throughout exposure. Peak-resolving analysis was applied to attenuated
14 total reflectance-Fourier transform infrared (ATR-FTIR) spectra to obtain functional group concentrations
15 with respect to exposure. The greatest chemical and physical changes are seen after initial exposure (100
16 MJ/m^2 to 220 MJ/m^2), followed by a saturation point. Spectroscopic results indicate minor accumulation
17 of oxidation products and additive migration. Raman spectroscopy showed a slight increase in
18 crystallinity of the surface layers of the backsheets. Mechanical testing revealed low cracking propensity,
19 with shallow cracks occurring under high strains.

20 Keywords: FTIR spectroscopy, backsheets, photovoltaics, polypropylene, reliability, polyolefin,
21 photooxidation

22 **1. Introduction**

23 Backsheets are typically thin polymer films found on the back surface of a photovoltaic module, and they
24 serve a critical function as a primary barrier protecting sensitive internal electrical components of the
25 module. This makes them a key element in efforts to lower levelized cost of electricity (LCOE) produced
26 by prolonging installation lifetime [1]. Most importantly, the backsheet also ensures safe operations by
27 providing essential electrical insulation [2]. However, polymers in outdoor installations are susceptible to
28 degradation resulting from a variety of environmental factors, creating potential for photooxidation,
29 thermal oxidation, hydrolysis, and mechanically or electrically induced degradation [1, 3-5]. In PV
30 installations, these degradation processes can lead to discoloration, cracking, delamination, and
31 ultimately, loss of insulation and module failure.

32 In recent years, a number of factors have been driving the development of backsheets based on polymers
33 such as polypropylene (PP), polyamide (PA), polyethylene terephthalate (PET), and derivatives.
34 Fluoropolymers such as polyvinyl fluoride (PVF) and polyvinylidene fluoride (PVDF) have long been
35 materials of choice for polymeric backsheets, due to their overall resistance to environmental degradation
36 owed to strong carbon-fluorine bonds [1, 2, 6], even though cracking or delamination has also been
37 reported on some PVDF-based backsheets [7, 8]. However, as pressure mounts to lower costs of PV
38 materials, the high price of fluoropolymers has been inciting interest in fluoropolymer-free alternatives.
39 Backsheets produced via coextrusion, such as those based on PA, PP, and PET, enable one-step
40 manufacturing and lower the LCOE compared to laminated, multi-layer, fluoropolymer backsheets.
41 Coextruded backsheets also require no adhesive, which reduces the risk of delamination in the field [9].
42 Notably, improvement of coextruded backsheets also allows for performance optimization through the
43 tuning of material properties, such as reflectivity, permeability, and thermal conductivity [10-13]. Finally,

44 fluoropolymers cannot be recycled via conventional methods and generate harmful byproducts on
45 incineration [12, 14]. These end-of-life challenges are at odds with the guiding principles at the heart of
46 renewable energy generation [15]. Eliminating the fluoropolymer layer reduces environmental harm by
47 enhancing recyclability of these emerging backsheets [16].

48 Despite the growing demand in the PV industry for more economical alternatives, there is a collective
49 apprehension surrounding coextruded backsheets in the wake of the disastrous failure of widely deployed
50 polyamide backsheets. The emergence of polyamide backsheet cracking after only 4-7 years in the field,
51 which was not detected by reliability testing, stirred alarm within the PV industry and led to extensive
52 scrutiny of both the material itself and the existing standard test methods [17-21]. However, this ordeal
53 has been accompanied by a great deal of new knowledge. Importantly, the lessons learned from the
54 polyamide failure underscore the necessity for detailed investigation of the degradation mechanisms of all
55 components of new proposed PV packaging. Furthermore, insight into the failure of these backsheets has
56 improved understanding of what may make a viable coextruded backsheet, as well as how to better detect
57 insufficiencies. This progress is demonstrated in the research and development of combined accelerated
58 stress testing (C-AST) in recent years, as well as sequential testing and solder bump testing, which have
59 each been successful in identifying failure modes in polyamide backsheets that conventional accelerated
60 stress tests had failed to predict [19, 22-26]. This wealth of new research serves as a great asset in the
61 continued effort towards innovation in fluoropolymer alternatives.

62 Recently, backsheets based on polypropylene (PP) have emerged as a novel and appealing candidate for
63 replacement of more expensive PET- and fluoropolymer-based backsheets [11, 12, 26, 27]. As PP is a
64 well-established and widely used commercial and consumer polymer, there is a variety of existing
65 literature on the degradation of PP [28-35], which serves as an excellent foundation for further
66 investigation.

67 Research on PP as a material of interest for PV backsheets, however, is still emerging. Modified PP-based
68 backsheets have been found to show low cracking propensity, with degradation confined to the surface
69 layer, using solder bump coupons subjected to sequential accelerated stress testing [26]. Recent work
70 shows selective permeability of PP backsheets, allowing escape of acetic acid, an undesirable and
71 damaging degradation product of the common encapsulant ethyl vinyl acetate (EVA), while maintaining
72 protection against atmospheric water vapor [12]. The oxygen transmission rates (OTR) for PP-based
73 backsheets is also higher than for standard PET-core backsheets [12]. Moreover, the functionalized
74 properties of PP, such as the selective permeability, as well as higher reflectance, have been shown to
75 increase performance and stability of tested PV modules [11]. These results, in addition to the lower cost
76 of production and improved recyclability of PP, create considerable interest in the continued development
77 of PP as a functional, reliable, sustainable, and affordable backsheet material.

78 However, some studies have shown PP to have relatively poor UV durability [31]. There also remains
79 limited published material investigating the photo-oxidative degradation of PP backsheets in depth,
80 specifically in service conditions expected for PV backsheets. Therefore, there remains a significant need
81 for research on the UV stability of PP backsheets under service conditions. In particular, a research gap
82 persists for the study of PP materials specifically prepared for PV service. These preparations are
83 expected to contain UV stabilizers, which will, of course, have a significant influence on the UV
84 performance of the materials.

85 Oxidation in PP has been previously shown to be most severe in surface layers [12, 26]. Results from
86 Carlsson and Wiles have also shown ATR spectroscopy to be a useful test for identifying the onset of
87 photooxidation in unstabilized PP [36]. Previous spatially resolved studies on UV degradation on PV

88 polymeric backsheets have shown depth-dependent degradation consistent with UV attenuation and
89 limited oxygen diffusion [37-39]. Furthermore, bulk damage in backsheets has generally been considered
90 to be facilitated by surface degradation [27]. Surface investigation therefore offers an excellent
91 environment for reliable quantification of oxidation and serves as an early indicator for continued
92 degradation, while allowing utilization of non-destructive methods of analysis. For this reason, the current
93 study is focused on presenting a comprehensive investigation of the surface degradation of PP-based PV
94 backsheets exposed to UV weathering. Please note that a concurrent study on this system, presenting a
95 spatially resolved evaluation of the backsheet degradation utilizing Raman spectroscopy, is forthcoming
96 [40].

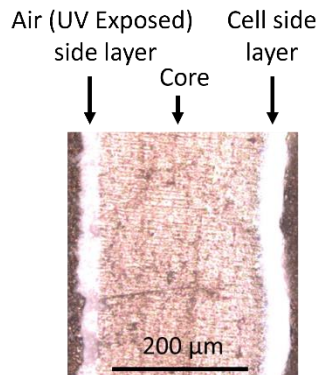
97 Free-standing coextruded PP backsheets were subjected to artificial weathering under different conditions
98 to further elucidate the degradation behavior of this material in various environmental conditions: 65
99 °C/20 % relatively humidity (RH), 75 °C/20 % RH, and 75 °C/50 % RH. These backsheets were
100 examined using a variety of spectroscopic, optical, and mechanical test methods. Different oxidative
101 degradation products were distinguished using FTIR peak-resolving technique, allowing for a quantitative
102 examination of the evolution of degradation products. Additionally, the fragmentation testing presented
103 here allows for the simulation of stress in a controlled, quantitative manner [41], enabling connection of
104 spectroscopic results to mechanical consequences. By bridging the quantitative analysis of the chemical,
105 optical, and mechanical effects of oxidative degradation, this study provides an improved understanding
106 of the long-term UV durability of PP backsheets.

107 **2. Experimental**

108 *2.1. Materials*

109 This study examined pristine, free-standing, coextruded backsheets based on a PP block copolymer
110 modified with a low amount of polyethylene (PE) [11, 12]. Based on cross-sectional measurement by
111 laser scanning confocal microscopy, the backsheets comprise three coextruded layers (Fig. 1): a $27.7 \mu\text{m}$
112 $\pm 0.4 \mu\text{m}$ PP air side (outer) layer, a $224 \mu\text{m} \pm 8.8 \mu\text{m}$ PP core, and a $26.5 \mu\text{m} \pm 2.8 \mu\text{m}$ PP cell side
113 (inner) layer, in agreement with previous published dimensions of this material [11]. The air and cell
114 layers are pigmented with TiO_2 , and Raman microscopy and XPS analysis indicates possible additional
115 mineral fillers, such as calcium carbonate (CaCO_3). More discussion of the XPS results may be found in
116 Section 3.3. No adhesives were found in the backsheets.

117 The findings presented in this paper are representative of the specific investigated backsheets described.
118 The exact UV stabilizers and fillers used are proprietary and details are not available at this time;
119 however, the UV aging of backsheets is strongly influenced by this system of additives. This should be
120 considered when evaluating the results of any weathering experiment on emerging materials.



121
 122 **Fig. 1.** Optical microscope image of cross section of PP-based backsheet. Dark regions on edges are potting material (epoxy).
 123 The cell side layer is visibly rough compared to the air side layer. In this image, roughness of the air side layer is exaggerated by
 124 the roughness of the diamond saw used to cut the sample.

125 *2.2. Accelerated laboratory weathering*

126 Three PP backsheet samples were subjected to accelerated weathering using the NIST SPHERE
 127 (Simulated Photodegradation via High Energy Radiant Exposure) [42] under an averaged ultraviolet (UV)
 128 irradiance of approximately 135 W/m² (295 nm to 400 nm). Bearing in mind the Department of Energy
 129 (DOE) target of 50-year modules, the total UV dose (295 nm to 400 nm) for each film was approximately
 130 1710 MJ/m², equivalent to approximately 50 years in Arizona, assuming 10 % albedo [43]. Samples were
 131 weathered at 65 °C and 20 % RH, 75 °C and 20 % RH, and 75 °C and 50 % RH, with one backsheet at
 132 each set of conditions. Conditions were selected according to condition A3 of IEC 62788-2 [44], and
 133 temperature and humidity were varied independently to investigate the effect of each on the degradation.
 134 Each sample was mounted on a black anodized sample holder with an anodized aluminum backing plate,
 135 with the air side of the backsheet exposed to UV (see Fig. S1). Backsheets were removed at planned
 136 intervals for nondestructive chemical, optical, and morphological testing. Additionally, a piece of each
 137 sample was cut and removed for mechanical testing, XPS measurement, and Raman measurement at 3
 138 different doses, spread out over the course of the experiment (approximately 340 MJ/m², 1110 MJ/m², and
 139 1710 MJ/m²).

140 *2.3. Attenuated total reflectance Fourier-transform spectroscopy (ATR-FTIR)*

141 In this study, a Nicolet iS50 FT-IR (Thermo Fisher Scientific, Madison, WI) with a diamond ATR
 142 accessory was used to characterize the chemical degradation of the backsheets on the air side (exposed to
 143 UV) and the cell side (not exposed to UV). The instrument is equipped with a deuterated, L-alanine doped
 144 triglyceride sulfate (DLaTGS) detector at room temperature and a potassium bromide (KBr) beamsplitter.
 145 Spectra were collected in the range of 4000 cm⁻¹ to 350 cm⁻¹, averaging 128 scans collected at a resolution
 146 of 4 cm⁻¹ with dry air as a purge gas. When necessary, FTIR spectra were corrected for atmospheric water
 147 vapor using an existing Python 3 program utilizing a least squares approach, modified to allow minor
 148 adjustments [45]. All ATR-FTIR spectra were processed and analyzed using OriginPro 2020 [46],
 149 including baseline correction and peak deconvolution, normalizing to 2722 cm⁻¹, which has been
 150 suggested to be associated with CH₃ vibrations of PP [31, 35].

151 *2.4. Yellow index (YI) measurement*

152 Colorimetry was used to characterize the optical changes of the backsheets with degradation. Yellow
 153 index measurements were obtained using a BYK Spectro-Guide Sphere Gloss handheld color meter
 154 (product number 6834) (BYK-Gardner GmbH, Geretsried, Germany), with d8 geometry and 60° gloss

155 measurement. Five measurements were taken on each side of each backsheet sample, and an average was
156 computed. Delta YI (ΔYI) is used to report the change in YI from initial measurement.

157 2.5. Laser scanning confocal microscopy (LSCM)

158 A Zeiss model LSM800 (Carl Zeiss Microscopy, White Plains, NY) LSCM was used to image the surface
159 of the backsheets over the course of exposure. Objectives of $5\times$ (z-step of $10.00\ \mu\text{m}$) and $50\times$ (z-step of
160 $1.00\ \mu\text{m}$) were used to capture images in reflection mode with a laser wavelength of 405 nm. Two-
161 dimensional images presented in this study are orthogonal projections of 3-dimensional z-stacks in the X-
162 Y plane generated by ZEN (Lite) [47] software using a maximum intensity projection method. Images
163 acquired using the $5\times$ objective are $2.56\ \text{mm}$ square, and images acquired using $50\times$ are $255.56\ \mu\text{m}$
164 square. All images consist of 1024×1024 pixels unless otherwise noted.

165 To obtain roughness data, topology data was exported to ConfoMap ST [48]. Confomap was used to
166 remove the macro-scale form variation using a degree 3 polynomial form. A standard, robust Gaussian
167 filter was applied to the data with a cut-off of $200\ \mu\text{m}$. The root-mean-square height of the surface was
168 calculated, as a quantifier of surface roughness.

169 2.6. Fragmentation testing

170 To evaluate crack propensity, samples were cut into 5 mm wide strips for fragmentation testing, mounted
171 on a mini tensile tester under a LSCM (a Zeiss model LSCM 800, described above), and imaged using a
172 $50\times$ objective (see Fig. S2 for experimental setup). Uniaxial strain was applied to each sample in planned
173 increments, increasing from 0.1 % to 20 %, and images were obtained at each interval. The images were
174 collected as three $238\ \mu\text{m}$ squares and combined to form a composite image having the dimensions 715
175 μm wide \times $238\ \mu\text{m}$ high. ConfoMap ST was used to remove the larger surface form using a degree 5
176 polynomial form, and a line profile was extracted from the sample images to examine cracking depth.
177 This fragmentation method is described in detail by Mitterhofer, *et al.*, and was shown to be capable of
178 recreating backsheet cracking in a coextruded PA backsheet and a 7-layer laminated backsheet comprising
179 PET outer and core layers, adhesive, and EVA inner layer (PPE) in controlled conditions [41].

180 2.7. X-ray photoelectron spectroscopy (XPS)

181 Surface elemental analysis of the backsheets was conducted by XPS (AXIS Ultra DLD Spectrometer,
182 Kratos Analytical). XPS measurements were performed using a monochromatic Al K_{α} source ($1486.6\ \text{eV}$)
183 operating at 140 W. The base pressure of the sample analysis chamber was $\approx 1.33 \times 10^7\ \text{Pa}$ (or 1.0×10^9
184 Torr), and spectra were collected from a nominal spot size of $300\ \mu\text{m} \times 700\ \mu\text{m}$. Measurements were
185 performed in hybrid mode using electrostatic and magnetic lenses, and the pass energy of the analyzer
186 was set at 160 eV for survey scans and 20 eV for high resolutions scans, with energy resolutions of 0.5 eV
187 and 0.1 eV, respectively. Charge neutralization was achieved using a low energy electron flood gun, and
188 all spectra were shifted with respect to the C-C peak in the C 1s envelop to be 285 eV. Three
189 measurements were taken for each sample. All XPS data analysis was completed using CasaXPS software
190 package.

191 2.8. Raman spectroscopy

192 Raman spectroscopy measurements were performed using a Senterra II confocal Raman microscope
193 (Bruker, Ettlingen, Germany) with a 785 nm excitation wavelength at 25 mW focused through a $10\times$
194 objective using a $50\ \mu\text{m} \times 1000\ \mu\text{m}$ aperture into the sample. Four 15 s exposures were averaged together
195 to generate the spectrum. Five spots were measured for each sample side. Background subtraction was
196 completed using Opus software package.

197 2.9. Nanoindentation

198 Nano-indentation was conducted to investigate the changes of Young's modulus (E) of the sample surface
 199 using a G200 nano-indenter (KLA, Milpitas, CA). A 2 μm , 90° sphero-conical diamond indenter tip was
 200 indented to a depth of 3 μm using the continuous stiffness method [49]. E was extracted from the flat
 201 areas of the depth-modulus curves of 50 indents in each sample using a custom filtering algorithm [50].

202 **3. Results**

203 3.1. FTIR spectra indicate moderate degradation of polypropylene

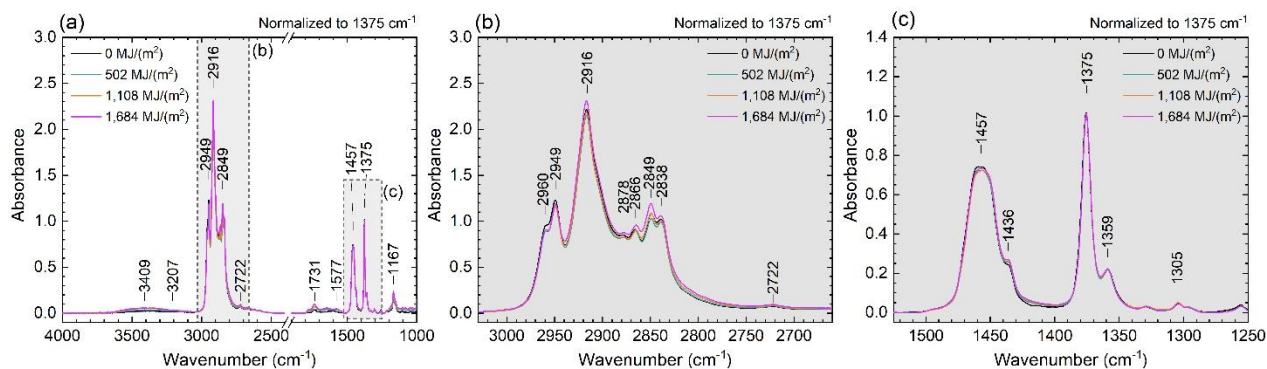
204 ATR-FTIR serves as a nondestructive means for evaluating chemical degradation of polymeric backsheets
 205 during accelerated laboratory weathering. In the case of PP, the FTIR spectrum is well documented. Peak
 206 assignments for PP from the literature are reported in Table 1. The peak at 1375 cm^{-1} (associated with
 207 symmetric in-plane bending of CH_3 in PP) was used for normalization of FTIR data [51-53]. ATIR-FTIR
 208 results show extremely minor changes in intensity of characteristic polypropylene peaks over the course
 209 of exposure, suggesting very little degradation of the polymer (Fig. 2).

210 **Table 1** FTIR and Raman peak assignments for PP backsheets.

Frequency (cm^{-1})		Polymer	Assignment	Ref.
FTIR	Raman			
2960, 2949	2955	PP	Asymmetric stretching ($\nu_{\text{as}}-\text{CH}_3$)	[51, 53-55]
2916	n/a	PP and PE	Asymmetric stretching ($\nu_{\text{as}}-\text{CH}_2$)	[51-54, 56]
2878, 2866	n/a	PP	Symmetric stretching ($\nu_{\text{s}}-\text{CH}_3$)	[51, 53, 54, 57, 58]
2849	2885, 2844	PP and PE	Symmetric stretching ($\nu_{\text{s}}-\text{CH}_2$)	[51, 52, 57-59]
2838	n/a	PP	Symmetric stretching ($\nu_{\text{s}}-\text{CH}_2$)	[51, 53, 56]
2722	n/a	PP	νCH_3^*	[31, 35]
1471, 1462		PE	Asymmetric in-plane bending ($\delta_{\text{as, in-plane}}-\text{CH}_2$)	[51, 52, 57]
1457	1460, 1439	PP	Asymmetric in-plane bending ($\delta_{\text{as, in-plane}}-\text{CH}_2$)	[51, 55, 59]
1436	n/a	PP	Asymmetric in-plane bending ($\delta_{\text{as, in-plane}}-\text{CH}_3$)	[51, 55]
1375	n/a	PP and PE	Symmetric in-plane bending ($\delta_{\text{s, in-plane}}-\text{CH}_3$)	[51-53]
	1361	PP	Wagging ($\omega-\text{CH}_3$)	[60]
1359	1359	PP	Symmetric in-plane bending ($\delta_{\text{s, in-plane}}-\text{CH}_2$)	[51, 57]
1305	1331	PP	Wagging ($\omega-\text{CH}_2$) + twisting (τCH_2)	[54, 58]
n/a	1299	PE	Wagging ($\omega-\text{CH}_2$) + bending ($\delta-\text{CH}$)	[58]
n/a	1221	PP	Twisting ($\tau-\text{CH}_2$) + wagging ($\omega-\text{CH}$) + stretching ($\nu \text{C-C}$ polymer backbone)	[55]
1167	1169	PP	Rocking ($\rho-\text{CH}_3$) + stretching ($\nu \text{C-C}$)	[51, 54, 55]
n/a	1154	PP	Stretching ($\nu \text{C-C}$ polymer backbone) + bending ($\delta-\text{CH}$)	[55]
998	n/a	PP	Rocking ($\rho-\text{CH}_3$) + wagging ($\omega-\text{CH}_2$) + bending ($\delta-\text{CH}$)	[32, 51, 54, 55]
974	975	PP	Stretching ($\nu \text{C-C}$ polymer backbone) + Rocking ($\rho-\text{CH}_3$)	[32, 51, 54, 55, 61]

898	n/a	PP	Rocking (ρ -CH ₂)	[51]
841	842	PP	Rocking (ρ -CH ₂)	[35, 51, 55]
809	810	PP	Stretching (ν C-C polymer backbone)	[51, 54, 55]
n/a	611	n/a	Rutile TiO ₂ (A _{1g})	[62, 63]
n/a	450	n/a	Rutile TiO ₂ (E _g)	[62, 63]

211 *There is some literature disagreement on the exact nature of the vibrations contributing to the peak at
 212 2722 cm⁻¹; however, there is general consensus they arise from the CH₃ group.



213

214 **Fig. 2.** (a) Full FTIR spectra (4000 cm⁻¹ to 1000 cm⁻¹) of UV-exposed side (air side) of PP-based backsheets weathered at 75 °C
 215 and 20 % RH, over the course of exposure; (b) expansion of spectra from 3030 cm⁻¹ to 2660 cm⁻¹ and (c) 1525 cm⁻¹ to 1250 cm⁻¹
 216 showing gradual decrease in characteristic PP peaks as total UV dose increases. Refer to Fig. S3 and Fig. S4 for corresponding
 217 FTIR spectra of samples exposed at 65 °C/20 % RH and 75 °C/50 % RH, as well as Fig. S5, Fig. S6, and Fig. S7 for FTIR
 218 spectra of cell side surface.

219 Oxidative degradation of PP is understood to result in the formation of various carbonyl products, which
 220 appear in the FTIR spectral region of approximately 1800 cm⁻¹ to 1700 cm⁻¹ [31-33], as well as hydroxyl
 221 products (3600 cm⁻¹ to 3200 cm⁻¹), vinyl (1660 cm⁻¹ to 1630 cm⁻¹ and 909 cm⁻¹) [32, 64], and vinylidene
 222 (1660 cm⁻¹ to 1630 cm⁻¹ and 888 cm⁻¹) [32, 64]. Numerous peaks in agreement with these previous results
 223 are present in the spectra of the aged backsheets (see Table 2). Due to the copolymer nature of the
 224 backsheets, some oxidative product peaks typically associated with the photooxidation of PE are present,
 225 as well [65, 66]. Finally, a pair of sharp peaks at 1577 cm⁻¹ and 1543 cm⁻¹ are visible in the aged samples,
 226 attributable to the additive calcium stearate (CaSt₂) [67].

227 The intensity of the oxidation product peaks remains relatively low throughout the course of the exposure,
 228 with the highest intensity peak in the carbonyl region (1737 cm⁻¹, assigned to ester products) reaching a
 229 maximum normalized intensity of 0.1, less than 5 % the normalized intensity of the strongest
 230 characteristic polypropylene peak present, 2.31 (2916 cm⁻¹) (Fig. 2). These results, together with the
 231 moderate decrease of characteristic polypropylene peaks, suggest relatively minor oxidative degradation
 232 of the PP with weathering. Please be aware these results are specific to the emerging PP-based backsheet
 233 investigated in this study.

234 3.2. Oxidation product formation

235 3.2.1. FTIR peak resolving analysis of oxidative product regions

236 Oxidative degradation of PP is known to proceed via a free radical chain oxidation mechanism resulting
 237 in hydroperoxides and ketones. Ketones generated may further degrade through Norrish type I and II
 238 reactions resulting in various oxidative products, including lactones, esters, ketones, carboxylic acids,
 239 vinyl, and vinylidenes (see discussion in Section 3.2.6) [31-33, 64]. This process is known to take place
 240 preferentially on the surface of PP, and ATR has previously been identified as a useful tool for identifying

241 the onset of PP oxidation [36]. In an effort to monitor the evolution of the oxidative degradation products
 242 of the backsheets, peak deconvolution was undertaken in the region of 1820 cm⁻¹ to 1520 cm⁻¹. A
 243 complete description of the peak identification and deconvolution process may be found in Section S2.2.
 244 The results are consistent with previous studies on outdoor-exposed PP [31-33]. To eliminate the need for
 245 C=C peaks differentiation, a similar peak-finding and deconvolution procedure was applied in the region
 246 of 920 cm⁻¹ to 860 cm⁻¹ to examine bands associated with C-H wags of vinyl and vinylidene groups. All
 247 degradation product peak assignments were made based on existing PP and PE degradation literature [31-
 248 33, 65, 66], as well as FTIR spectral analysis [53, 64], and are summarized in Table 2. An example
 249 deconvolution is shown in Fig. 3.

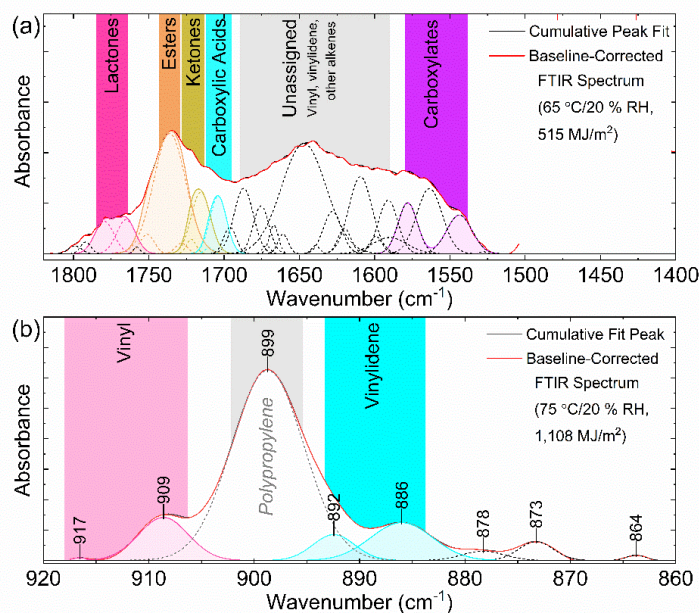
250 **Table 2** FTIR absorbance regions for oxidative degradation products of PP and PE; Ref. [31-33, 64]

Absorbance Region (cm ⁻¹)	Band Frequency (cm ⁻¹)	Degradation Products Group	Vibration
1785 to 1763	1783, 1773, 1764	Lactones	C=O stretch
1750 to 1726	1749, 1742, 1735, 1727	Esters	C=O stretch
1724 to 1714	1721, 1715	Ketones	C=O stretch
1713 to 1705	1711, 1705	Carboxylic Acids	C=O stretch
917 to 905	917, 909	Vinyl	C-H wag
895 to 885	892, 886	Vinylidene	C-H wag

251
 252 The indices of the different carbonyl products were obtained by dividing the areas of peaks associated
 253 with particular products by the area of the peak at 1375 cm⁻¹, then summing the resulting values for peaks
 254 of the same product functional group. This was repeated for each product functional group, for each
 255 measurement. Very small peaks are present in the oxidative product region on the unexposed backsheets.
 256 This may be due to a small amount of thermal oxidation occurring during manufacture [36, 68]. To
 257 examine product trends over the course of exposure, the calculated product indices are subtracted from
 258 the initial values to account for this and isolate new degradation.

259
$$Product\ Group\ Index = \sum_{n=1}^k \frac{A_{product\ peak\ n}}{A_{1375\ cm^{-1}}};$$

260 $k = \text{number of product group peaks}$



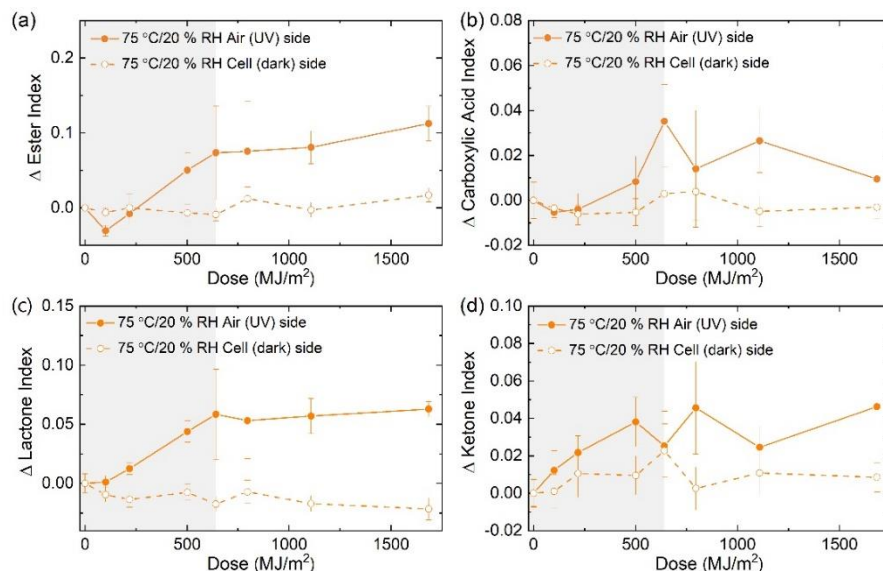
261
 262 **Fig. 3.** FTIR spectrum expansions showing (a) example deconvolution results of product peaks associated with oxidative
 263 degradation, as well as carboxylate peaks (associated with polymer manufacturing lubricant), in the region of 1850 cm⁻¹ to 1400
 264 cm⁻¹, and (b) example deconvolution results of product peaks associated with vinyl and vinylidene degradation products, in the
 265 region of 920 cm⁻¹ to 860 cm⁻¹. Shaded areas with solid lines represent the regions of product peaks of the same type for which
 266 peak areas were summed; dotted, colored lines are the component fit peaks of those regions; and black dotted lines are those
 267 peaks which were fit but excluded from the analysis (not a peak of interest for this study).

268 3.2.2. UV irradiation effect on oxidation product formation

269 Peak-resolving analysis of the oxidation product region revealed a distinct shift in oxidative degradation
 270 product trends after an initial period of exposure. Nearly all oxidative product groups show an initial
 271 sharp increase, followed by a leveling-off behavior, indicating a saturation point of these degradation
 272 products after an initial exposure period. This observation agrees with previous PP aging studies
 273 observing a saturation point of oxidation degradation products [28, 29, 69]. For carbonyl, this change in
 274 slope is seen at or around the measurements conducted after 640 MJ/m² exposure (shaded in Fig. 4, Fig.
 275 5, and Fig. 6). For some products, the quantity is seen to gradually decrease after reaching a maximum,
 276 rather than completely stagnate.

277 The present study shows significantly greater accumulation of carbonyl products on the side of the
 278 backsheet receiving UV exposure (air side). On the UV-exposed side, esters, lactones, carboxylic acids,
 279 and ketones are observed, showing a steep increase in concentration followed by a plateau, as discussed.
 280 The slight loss of carboxylic acids over time may be attributed to loss of volatile, low-molecular weight
 281 acids (such as acetic acid) [12, 69].

282 Carbonyl product formation on the cell (dark) side of the backsheets is dominated by carboxylic acid and
 283 ketones formation. These products follow a similar, though not identical, trend to the UV-exposed side,
 284 though the total amounts are considerably lower, and the differentiation is not as clear as for lactones and
 285 esters. However, esters and lactones show little change on the side not exposed to UV, seen in Fig. 4 (a)
 286 and (c), indicating the formation of lactones and esters depends more heavily on the presence of UV light.



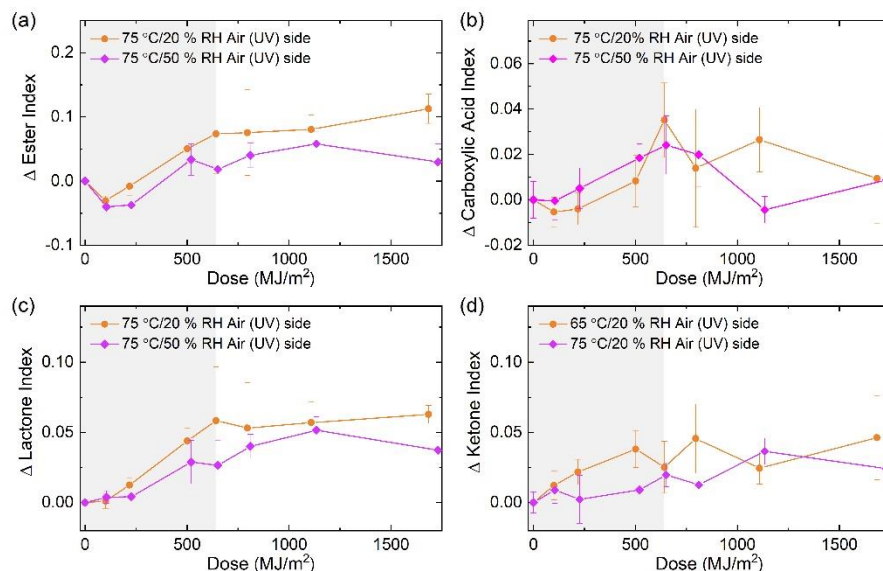
287

288 **Fig. 4.** (a) Ester index, (b) carboxylic acid index, (c) lactone index, and (d) ketone index of the air (UV) and cell (dark) side
 289 surfaces of PP-based backsheets over the course of artificial weathering at 75 °C/20 % RH, showing greater accumulation of
 290 carbonyl products on the air (UV) exposed side of the backsheets. Each data point represents an average of 3 measurements.
 291 Error bars show standard deviation. Graphs are shaded from 0 MJ/m² to 640 MJ/m². Points are connected to guide the eye.

292 **3.2.3. Effect of environmental exposure conditions on carbonyl product formation**

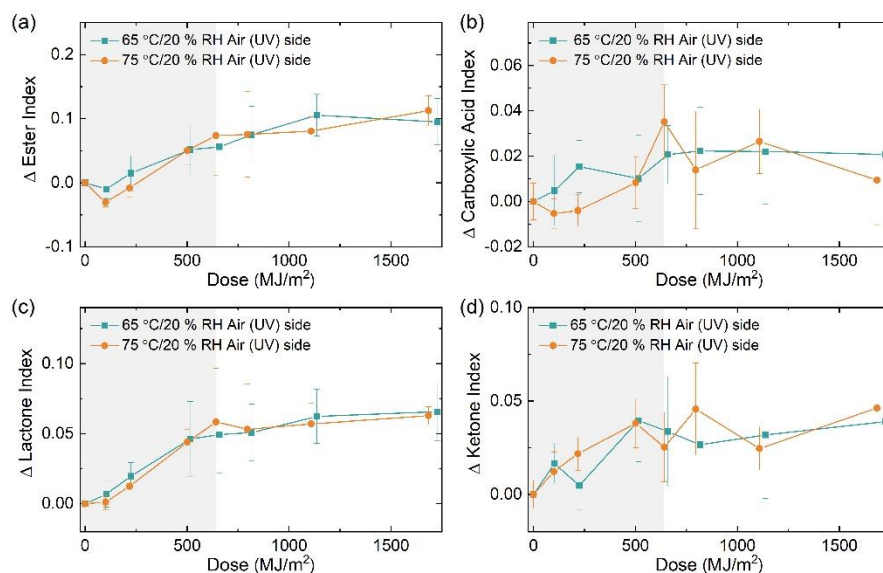
293 While some polymers are susceptible to accelerated degradation at higher humidities due to hydrolysis,
 294 PP is hydrophobic, and previous work has shown that PP is not prone to hydrolytic degradation in damp
 295 heat conditions for up to 3000 h exposure time [12]. A potential effect of humidity in PP degradation is
 296 slightly suppressed oxidation. Higher humidity in air results in slightly decreased partial pressure of
 297 oxygen (pO₂), resulting from the increased partial pressure of water vapor (pH₂O). Oxygen pressure is
 298 known to affect PP oxidation [70]. Additionally, chromophores are likely to be present on the films as a
 299 result of manufacture, even before exposure [36, 68]. Water molecules may form hydrogen bonds with
 300 these more polar species on the surface, hindering photo-oxidation.

301 The results of this experiment show the mean indices fall lower for higher humidity conditions than lower
 302 humidity conditions for nearly all points of comparison for esters and lactones, which is not observed for
 303 accumulation of carboxylic acids and ketones (Fig. 5). Of note is the apparent continuation of this trend
 304 after the saturation point has been reached. However, a significant effect cannot be concluded definitively
 305 based on the statistical analysis, due to the limited sample size and heterogeneous degradation. This
 306 remains an area for future inquiry.



307
 308 **Fig. 5.** (a) Ester index, (b) carboxylic acid index, (c) lactone index, and (d) ketone index of the air (UV) side surfaces of PP-based
 309 backsheets over the course of artificial weathering at 75 °C/20 % RH and 75 °C/50 % RH, showing a slight suppressive effect of
 310 higher humidity on ester and lactone accumulation. Indices are presented as change from initial value measured on unexposed
 311 backsheet. Each data point represents an average of 3 measurements. Error bars show standard deviation. Graphs are shaded from
 312 0 MJ/m² to 640 MJ/m². Points are connected to guide the eye.

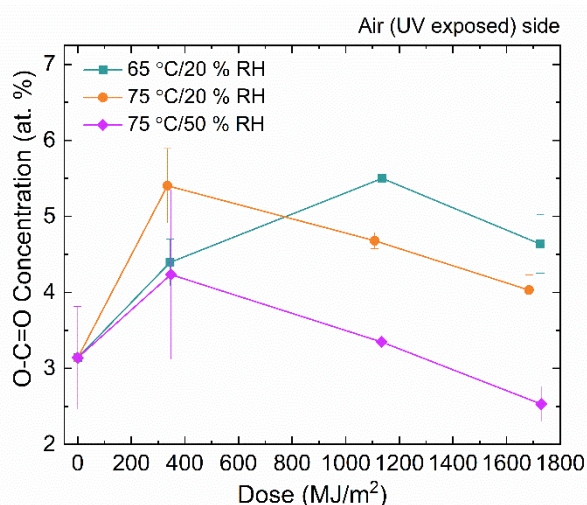
313 The results showed no significant effect of temperature on the product formation rates or quantities (Fig.
 314 6), with the possible exception of vinyl and vinylidene, which showed increased average accumulation of
 315 both vinyl and vinylidene after the carbonyl products have reached stationary states in some measurement
 316 locations. The absence of a quantifiable temperature effect is likely due to the relatively small difference
 317 in temperature chosen for this experiment.



318
 319 **Fig. 6.** (a) Ester index, (b) carboxylic acid index, (c) lactone index, and (d) ketone index of the air (UV) side surfaces of PP-based
 320 backsheets over the course of artificial weathering at 65 °C/20 % RH and 75 °C/20 % RH, showing no appreciable effect of
 321 temperature on oxidative product accumulation. Indices are presented as change from initial value measured on unexposed

322 backsheet. Each data point represents an average of 3 measurements. Error bars show standard deviation. Graphs are shaded from
323 0 MJ/m² to 640 MJ/m². Points are connected to guide the eye.

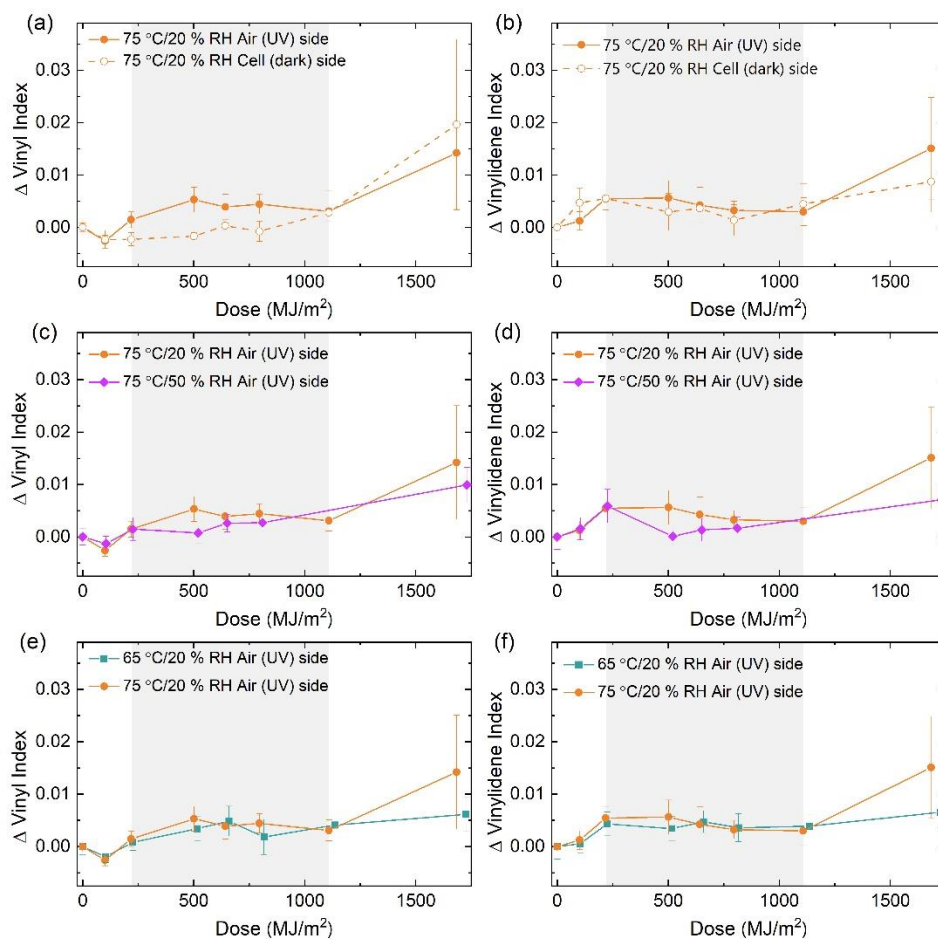
324 XPS analysis was employed to substantiate and elaborate upon observations of evolving surface
325 characteristics of the PP backsheet samples over the course of exposure by examining the changing
326 elemental composition. This analysis exposed the same general trends observed in FTIR quantification of
327 carbonyl products. The C 1s spectrum of the PP surface was subjected to peak fitting to resolve separate
328 peaks at approximately 285.5 eV, 286.8 eV, and 288.8 eV, which were attributed to C-C, C-O-C, and O-
329 C=O, respectively. The 288.8 eV peak is of particular interest in this investigation, as it provides insight
330 into carbonyl functional groups resulting from oxidative degradation. Over the course of exposure, the
331 exposed side of the PP shows a relatively steep increase in the area of this peak in the early phase of the
332 exposure, followed by a slow decrease (Fig. 7), which is mirrored in the behavior of the trends resulting
333 from peak-resolving analysis of the FTIR results above for functional groups containing O-C=O bonds,
334 such as esters, lactones, and acids (Fig. 4, Fig. 5, and Fig. 6).



335
336 **Fig. 7.** Atomic percent (at. %) of C with bond configuration O-C=O measured on the air (UV-exposed) side of PP backsheets
337 weathered at 65 °C/20 % RH, 75 °C/20 % RH, and 75 °C/50 % RH. Each data point represents an average of 3 measurements.
338 Error bars show standard deviation. Points are connected to guide the eye.

339 3.2.4. Effect of environmental exposure conditions on vinyl and vinylidene formation

340 Vinyl and vinylidene products depend on the competition between formation and consumption of vinyl
341 groups [31]. In the present study, these groups generally reach a relatively stable position early in the
342 exposure, around 220 MJ/m², and show mostly small, fluctuating changes in value until approximately
343 1110 MJ/m² exposure, after the carbonyl products have reached a plateau (Fig. 8). Vinyl and vinylidene
344 concentrations begin to rise again around 1110 MJ/m², though this behavior varies widely among the four
345 sampling locations on each film, leading to greater uncertainty. The greatest influence on vinyl and
346 vinylidene formation appears to be humidity, with higher humidity leading to lower concentrations over a
347 portion of the exposure, likely due to decreased pO₂ as proposed above. Vinyl and vinylidene groups may
348 enable crosslinking [32, 71], which may contribute to the slight embrittlement observed during
349 fragmentation testing (Section 3.4.2).



350

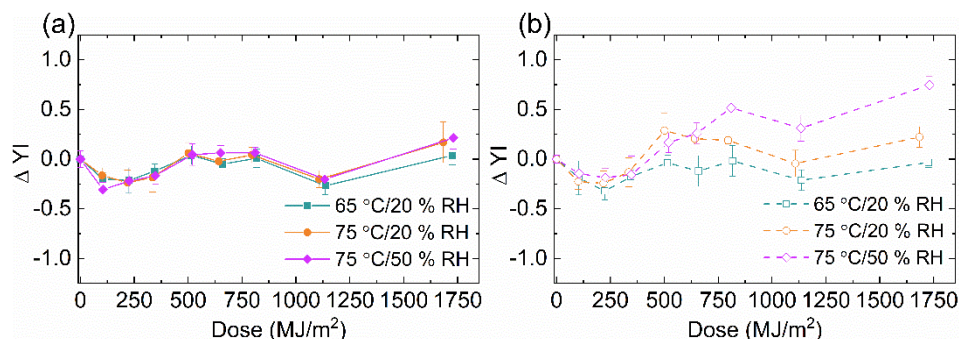
351 **Fig. 8.** Vinyl index and vinylidene index of the surfaces of PP-based backsheets over the course of artificial weathering: (a, b) Air
 352 (UV) and cell (dark) side of backsheets exposed at 75 °C/20 % RH; (c, d) Air (UV) side surfaces of PP-based backsheets exposed
 353 at 75 °C/20 % RH and 75 °C/50 % RH; (e, f) Air (UV) side surfaces of PP-based backsheets exposed at 65 °C/20 % RH and 75
 354 °C/20 % RH. Each data point represents an average of 3 measurements. Error bars show standard deviation. Graphs are shaded
 355 from 220 MJ/m² to 1110 MJ/m². Points are connected to guide the eye.

356 3.2.5. Change in yellow index with exposure

357 Yellow index measurements typically serve as an indicator of chemical changes in the polymer structure.
 358 They are often a result of the accumulation of chromophores, which may arise from photo-oxidative
 359 degradation, which give a yellow appearance [1, 72]. In this investigation, all of the samples show
 360 extremely minor changes in yellowing over exposure of both the air and cell sides, with the exposed (air)
 361 side showing very closely grouped results for all three exposure conditions (Fig. 9). Towards the end of
 362 the exposure, a slight temperature effect is suggested, which is most prominent on the back (cell) side.
 363 Overall, the YI for all three samples deviate very little from the original values for unexposed films.

364 The back (cell) side results show more differentiation between the exposure conditions, with higher
 365 temperatures and higher humidities both leading to increased yellowing. These results suggest that
 366 bleaching could be contributing to the lack of yellowing observed on the exposed side; however, even on
 367 the back side, $\Delta YI \approx 0$ for films exposed at 65 °C/20 % RH and 75 °C/20 % RH, with only the backsheet
 368 exposed at 75 °C/50 % RH showing a quantifiable increase. Additionally, even this backsheet shows a
 369 change of only $\Delta YI < 1$. This result is in agreement with previous results on this material reporting

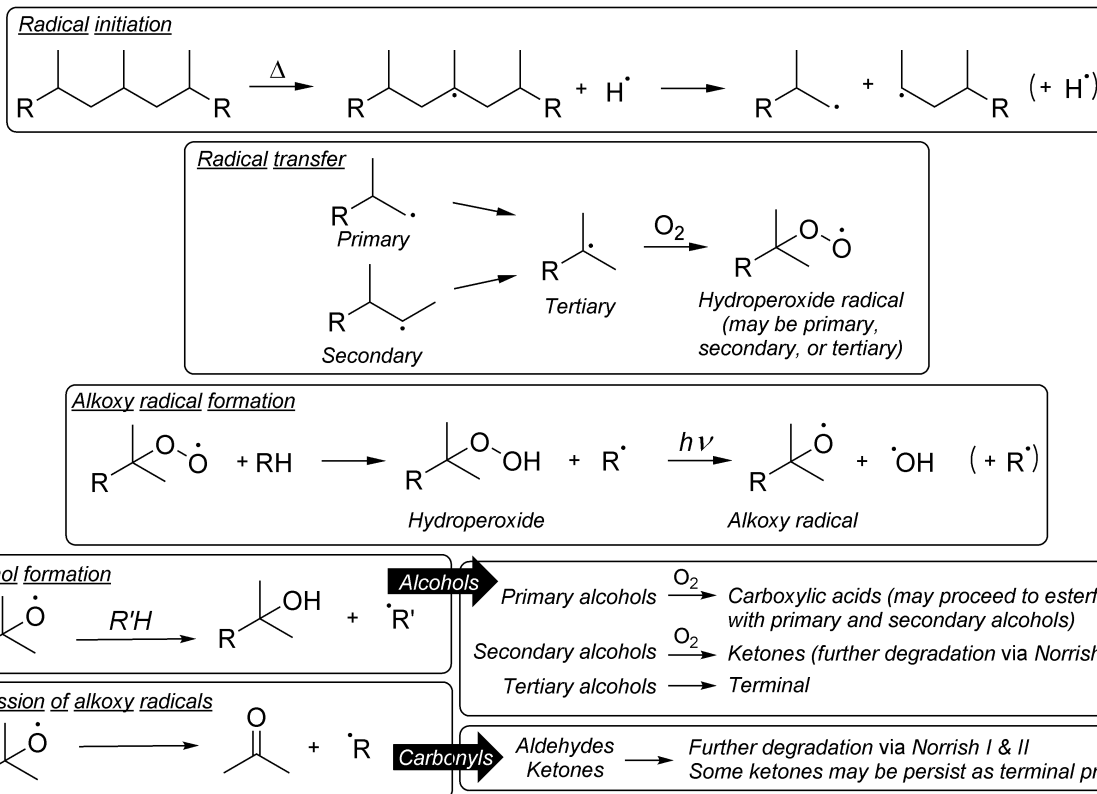
370 competition of very minor yellowing and photobleaching, resulting in nearly no net change in YI [26].
371 The dark (cell) side of the backsheets does show slightly higher concentrations of alkenes, which may
372 contribute to the yellow color, and agrees with the YI results. However, the overall ΔYI remains very
373 small, and the effect of exposure conditions on ΔYI is consequently very small as well.



374
375 **Fig. 9.** Change in yellow index (ΔYI) of the (a) air (UV) and (b) cell (dark) side surfaces of PP-based backsheets over the course
376 of artificial weathering at 65 °C/20 % RH, 75 °C/20 % RH, and 75 °C/50 % RH, showing greater yellowing on the cell side, as
377 well as a significant effect of exposure conditions on yellow index on the back side. Each data point represents an average of 5
378 measurements. Error bars show standard deviation. Points are connected to guide the eye.

379 3.2.6. Implications for oxidative degradation pathways

380 Much of the photooxidation mechanism of PP is generally considered to be well-established [31-33, 69].
381 Degradation is considered to begin via radical initiation followed by propagation, generating a peroxide
382 radical species [73-75]. These radicals may be primary, secondary, or tertiary radicals, which may in turn
383 form primary, secondary, or tertiary peroxide radicals [74]. It should be noted that radical initiation is
384 thought to be precipitated by initial impurities in the PP, likely initial thermal oxidation products from
385 manufacture [31, 36]. This phenomenon may contribute to the preferential surface oxidation observed.
386 The reactive peroxide radical can then abstract a labile hydrogen from another polymer molecule,
387 generating hydroperoxide, the tertiary form of which is generally understood to be the main product
388 resulting from radical initiation, and a key reactant in the subsequent steps of PP degradation. [69, 75].
389 Hydroperoxides may react to form alkoxy radicals, which may be primary, secondary, or tertiary [74].
390 These alkoxy radicals can abstract a hydrogen from the polymer chain and form corresponding alcohol
391 species, which may undergo further oxidation, leading to alkenes, ketones, acids, and esters [74, 75].
392 Degradation of polypropylene is understood to primarily occur through β -scission of these alkoxy
393 radicals (Scheme 1) [32, 33, 75].



394

395

Scheme 1. Radical initiation and propagation and formation of hydroperoxides and alkoxy radicals.

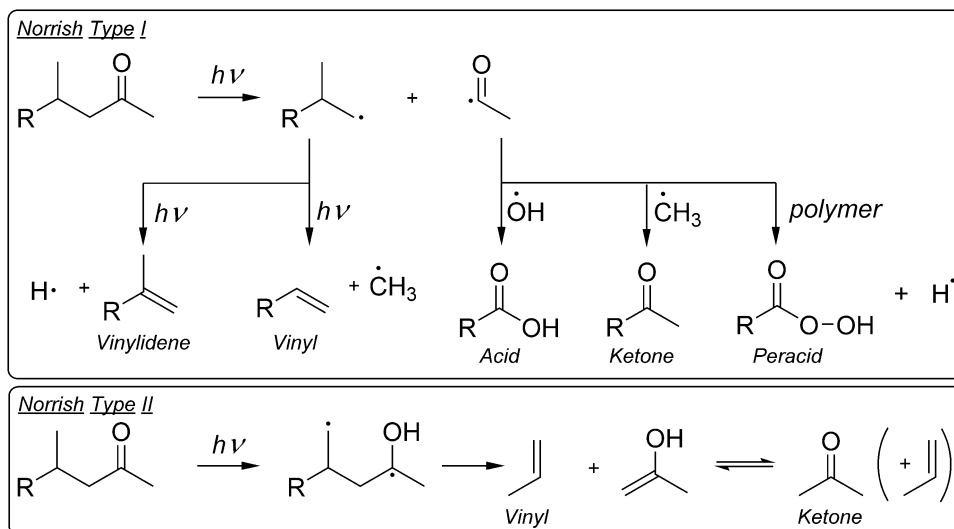
396

397

398

399

Ketones formed by this mechanism may further decompose through the photochemical Norrish I and II reactions, (Scheme 2) producing a number of products, including alkenes such as vinyl and vinylidene, as well as carboxylic acids and ketones, which may go on to further react and form esters and other oxidation products [31].



400

401

Scheme 2. Formation of oxidative degradation products of PP via Norrish Type I and II reactions.

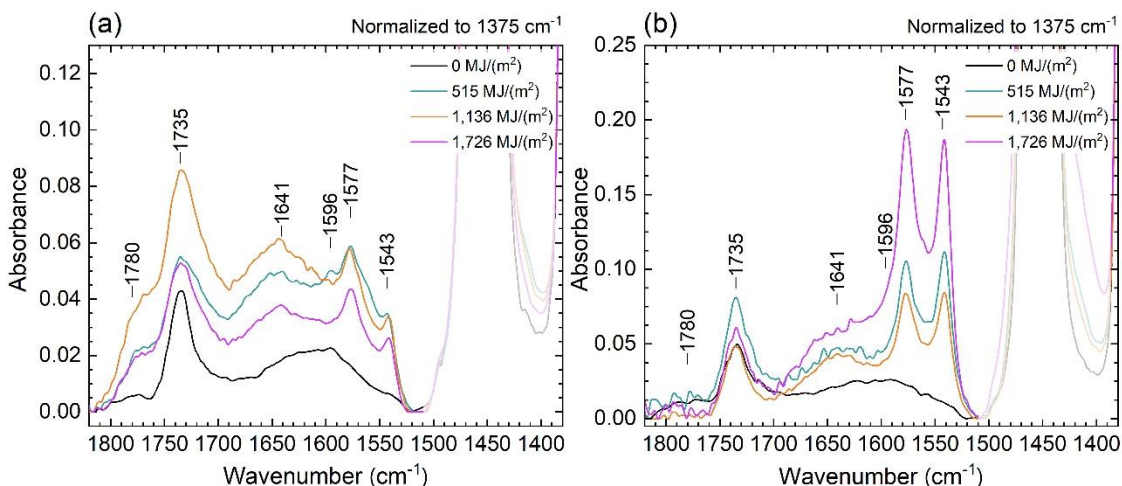
402 In the present work, ester and lactone formation appears to have the most pronounced apparent
403 dependence on weathering conditions, with the formation of lactones and esters only occurring under
404 photo-oxidation (as opposed to acids and ketones, which still formed in small quantities on the unexposed
405 surface, via thermally-driven oxidation) (Fig. 4). While several studies have asserted the presence of
406 esters and lactones in photo-oxidized PP [28, 31, 32, 69], there are few which proposed or investigated a
407 mechanism for such formation. One potential explanation for the disparity observed in this study is the
408 possibility that the formation of these products is driven almost exclusively by the photolytic Norrish
409 Type I reaction, which produces peracids, potential precursors to the formation of both lactones and esters
410 (Scheme 2) [32]. Another proposes carboxylic acids and alcohol species formed via photooxidation
411 undergo esterification with one another, a process which may be catalyzed by mineral fillers [74, 76]. It
412 should be noted that the observed lactones in this study may form by way of intramolecular esterification
413 in this manner, as well.

414 Geuskens and Kabamba proposed a mechanism for ester formation involving a photolysis of
415 hydroperoxides and ketones [77]. This mechanism was supported in work by Philippart, *et al.*, who in
416 turn observed an effect of light intensity on the distribution between acids and esters in photooxidized PP,
417 showing that higher light intensity drives the decomposition of hydroperoxides towards esters [69].
418 Philippart *et al.* concluded that high ratios of light intensity and temperature affect the decomposition of
419 hydroperoxides, with higher light intensity favoring esters and low molecular weight acids, and lower
420 light intensity favoring “chain-end” acids formation [69]. The results presented here show a strong
421 dependence on presence of UV irradiance for ester formation, but it should be emphasized that the present
422 work does not examine variations of light intensity, and the observed ester and lactone disparity may be
423 influenced by any of the factors discussed here.

424 Degradation pathways are of particular interest for the field of service life prediction for photovoltaics, as
425 reciprocity is crucial to the reliability of accelerated weathering. For this reason, additional research may
426 be necessary to elucidate the mechanism of acid and ester formation.

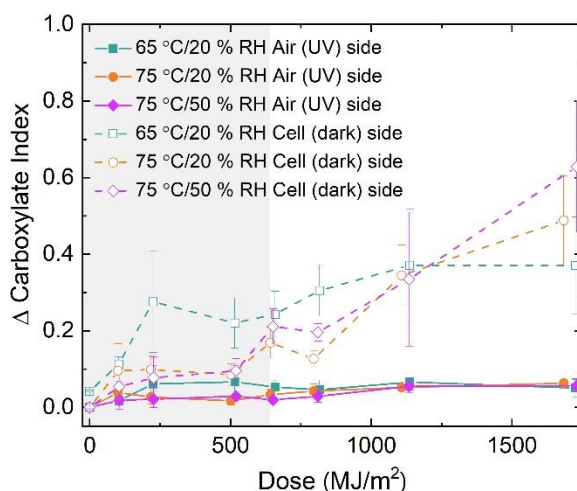
427 3.3. Observation of additive migration

428 Results for both sides of all backsheets show the emergence of a pair of sharp peaks 1577 cm^{-1} and 1543
429 cm^{-1} that are not associated with typical carbonyl degradation products (Fig. 10). The wavenumbers and
430 shapes of the peaks suggest a carboxylate functional group. Calcium stearate (CaSt_2) is a carboxylate salt
431 and known lubricant additive in PP manufacturing [34], with carboxylate bands occurring at 1577 cm^{-1}
432 and 1543 cm^{-1} . The bands are associated with the antisymmetric stretching for unidentate and bidentate
433 association with calcium ions [67]. Furthermore, XPS measurements of the cell side surfaces show
434 surface accumulation of calcium over exposure which increases in a similar fashion to the FTIR
435 carboxylate peaks (Fig. 12a). The identification of CaSt_2 is further supported by previous observations by
436 Bak, *et al.* of migration behavior of CaSt_2 in PP composites under accelerated aging [34]. Therefore, this
437 pair of peaks is concluded to be attributable to CaSt_2 migration in the backsheets.



438

439 **Fig. 10.** Expansions (1820 cm^{-1} to 1380 cm^{-1}) of FTIR spectra of PP backsheets weathered at 65 °C/20 % RH, measured on the
 440 (a) air (UV) side and (b) cell (dark) side, showing a pair of peaks at 1577 cm^{-1} and 1542 cm^{-1} attributed to CaSt_2 migration. Refer
 441 to Figs. S8 and S9 for corresponding FTIR spectra of samples exposed at 75 °C/20 % RH and 75 °C/50 % RH.



442

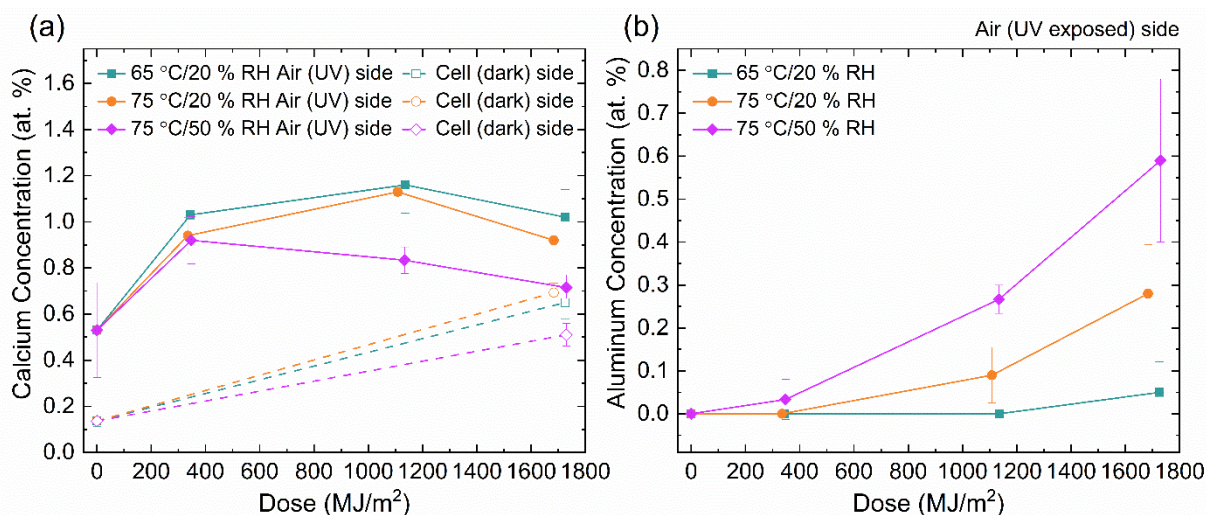
443 **Fig. 11.** Carboxylate index of the air (UV) and cell (dark) side surfaces of PP-based backsheets over the course of artificial
 444 weathering at 65 °C/20 % RH, 75 °C/20 % RH, and 75 °C/50 % RH, showing increasing CaSt_2 migration to the cell (dark)
 445 surface of the backsheets. Graph is shaded from 0 MJ/m^2 to 640 MJ/m^2 . Each data point represents an average of 3
 446 measurements. Error bars show standard deviation. Points are connected to guide the eye.

447 The CaSt_2 carboxylate peaks appear after initial exposure on both sides but show much greater
 448 persistence on the cell side (dark side) (Fig. 11). On the cell side, these peaks continue to grow in
 449 intensity throughout the exposure, even after the oxidative degradation products reach a saturation point.
 450 However, FTIR peak behavior on the air side (UV-exposed side) suggests either unfavorable conditions
 451 for migration of CaSt_2 , or consistent removal of the substance through degradation or evaporation. The
 452 carboxylate peaks reach a maximum intensity early in the exposure and remain much smaller than their
 453 corresponding peaks on the cell side.

454 XPS results show calcium on both the exposed (air) side and dark (cell) side of the backsheets, with
 455 calcium on the cell side increasing in concentration over exposure (Fig. 12a). Calcium on the air side

456 exceeds quantities found on the dark side, despite low prevalence of carboxylate peaks. This is likely due
 457 to multiple calcium sources, including both CaSt_2 and mineral fillers. Results of XPS quantification also
 458 showed continuous migration aluminum to the exposed surface (air side) (Fig. 12b). The calcium and
 459 aluminum observed on the air side of the backsheets are both attributable to mineral fillers commonly
 460 used in PP, such as talc and CaCO_3 [78]. Another possible contributor of aluminum is a Ziegler Natta
 461 catalyst, a polymerization catalyst used in PP production [79]. Of note is the observation that there is
 462 continuously increasing aluminum present on the air side, but no aluminum is observed on the cell side,
 463 suggesting a UV-driven migration mechanism.

464 Surface Raman measurements show an increase in intensity of TiO_2 peaks (450 cm^{-1} and 611 cm^{-1}) with
 465 exposure (Fig. S10 and Fig. S11) [62]. Figure S11 shows the increase in TiO_2 peak area over the course of
 466 exposure, with the greatest increase in peak area occurring in the first portion of exposure. This effect
 467 mirrors the trends of mineral additive accumulation on the backsheet seen in the XPS results, and it is
 468 further underscored by LSCM surface imaging showing surface residue accumulation in a similar pattern
 469 (see Section 3.4). This increased TiO_2 may be due to gradual loss of surface polymer, in addition to
 470 migration phenomena.



471
 472 **Fig. 12.** Atomic percent (at. %) of calcium (a) and aluminum (b) measured on PP backsheets weathered at 65 °C/20 % RH, 75
 473 °C/20 % RH, and 75 °C/50 % RH. Each data point represents an average of 3 measurements. Error bars show standard deviation.
 474 Points are connected to guide the eye.

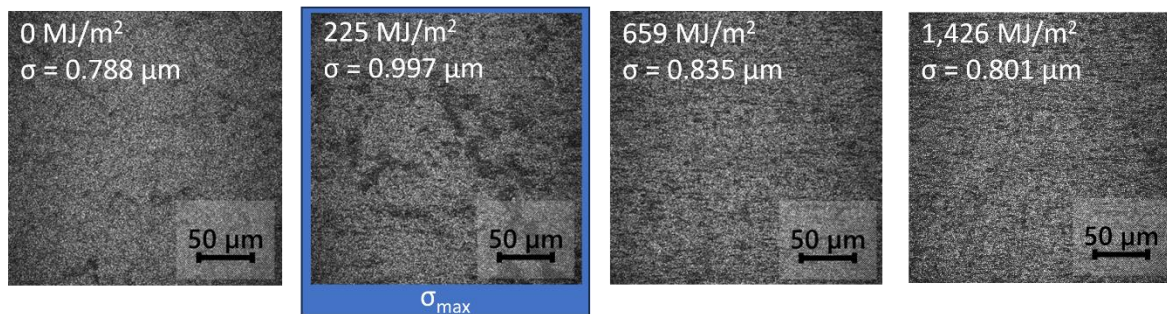
475 3.4. Consequences of observed oxidation on material properties

476 The spectroscopic results presented have physical consequences on the durability of the films; notably,
 477 surface oxidation may correlate to eventual backsheet failure [18, 27]. Additionally, the formation of vinyl
 478 and vinylidenes may lead to crosslinking [32, 71], which is a potential contributor to embrittlement.

479 3.4.1. Surface morphology

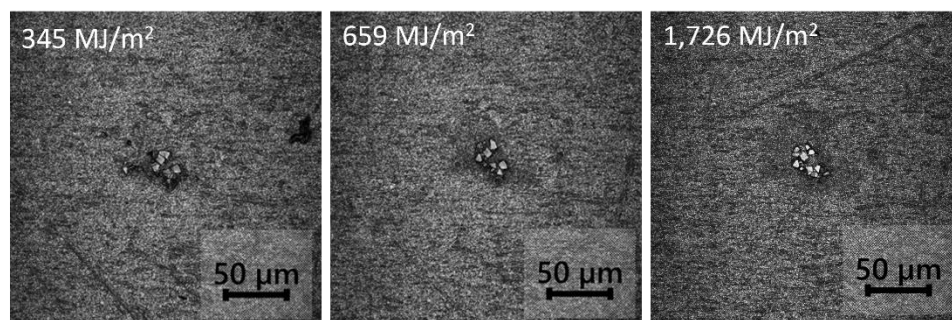
480 LSCM measurement of the air (UV-exposed) side of the backsheets shows visible (Fig. 13) and
 481 quantifiable (Fig. S12) increases in surface roughness (measured as standard deviation of height, σ) after
 482 initial period of UV exposure, followed by surface erosion (Fig. S13). The UV dose at which the spike in
 483 roughness occurs varies across the films, but it consistently appears before 640 MJ/m^2 , which is
 484 congruous with the observed change in oxidative product accumulation. Following this initial increase

485 and decrease in roughness, trends are more divergent, but generally show a much more gradual increase
486 in surface roughness with increased exposure.



487
488 **Fig. 13.** 50x LSCM images of PP backsheet exposed to UV at 65 °C and 20 % RH after 0 MJ/m², 225 MJ/m², 659 MJ/m², and
489 1426 MJ/m² irradiance. Image size is 255 μm square, with 0.25 μm per pixel (xy).

490 Surface features appearing in the initial phase of exposure, such as minor pitting and small scratches, are
491 observed in the LSCM images as gradually becoming less pronounced over the course of exposure,
492 suggesting surface erosion over time (Fig. S13 and Fig. S14). However, a visible buildup is also detected
493 in 5x LSCM images, tending to appear gradually in the latter half of exposure (Fig. S14). These are
494 potentially the result of gradual PP loss with degradation, as seen in the FTIR results, leaving behind TiO₂
495 visible as chalking. Under greater magnification (50×), fragments of crystalline material are visible in
496 small clusters on the surface of the sample (Fig. 14). This residue may be attributable to lingering salts
497 associated with a polymerization catalyst from production (such as a Ziegler Natta catalyst) [79], to
498 derivatives of such a catalyst, or to migration of mineral additives such as TiO₂ or CaCO₃. Any such
499 identification would be supported by the surface presence of titanium and calcium observed in the XPS
500 results. A combination of heterogeneous residue buildup and gradual surface erosion would account for
501 the visible loss of topographic features in the polymer alongside the measured gradual increase in
502 standard deviation of the surface height.

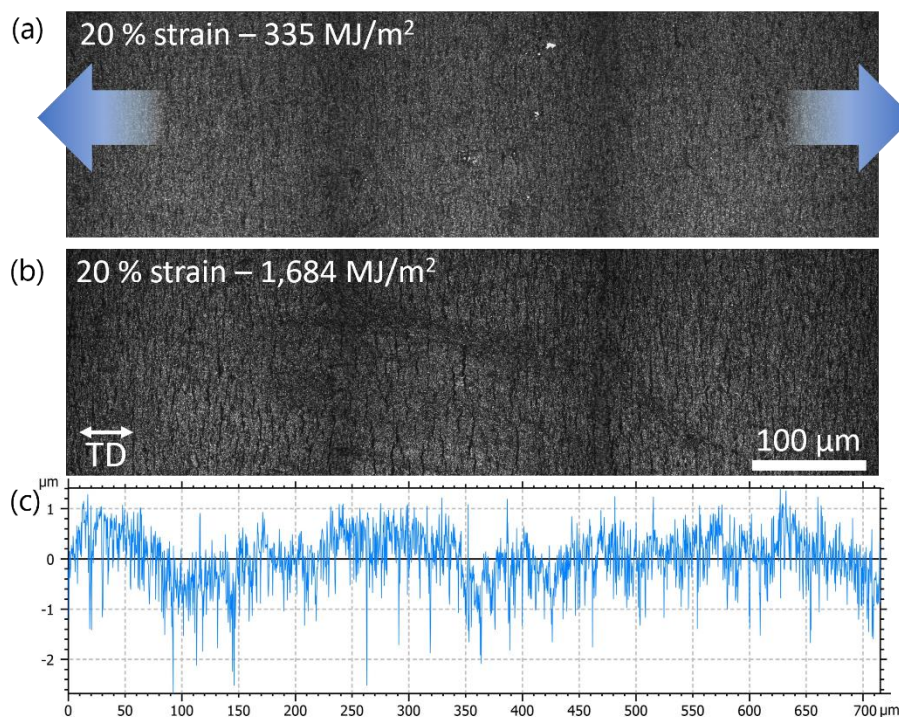


503
504 **Fig. 14.** 50x LSCM images of the same location on PP backsheet exposed to UV at 65 °C and 20 % RH after 345 MJ/m², 659
505 MJ/m², and 1726 MJ/m² irradiance. Image size is 255 μm square, with 0.25 μm per pixel (xy).

506 3.4.2. Fragmentation, crystallinity, and Young's modulus

507 To examine the degradation effect on crack propensity, samples were mounted on a mini tensile tester
508 under a LSCM, and uniaxial strain was applied in increments. This method was previously shown to be
509 capable of reproducing cracking in coextruded PA backsheets and laminated PPE backsheets, and allows
510 for controlled, quantitative characterization of crack propensity [41]. Fig. 15 shows LSCM images of the
511 aged PP backsheets after fragmentation testing, with fine, short, surface cracks visible at 20 % strain and
512 above. This cracking may be attributed to embrittlement caused by the minor oxidative degradation

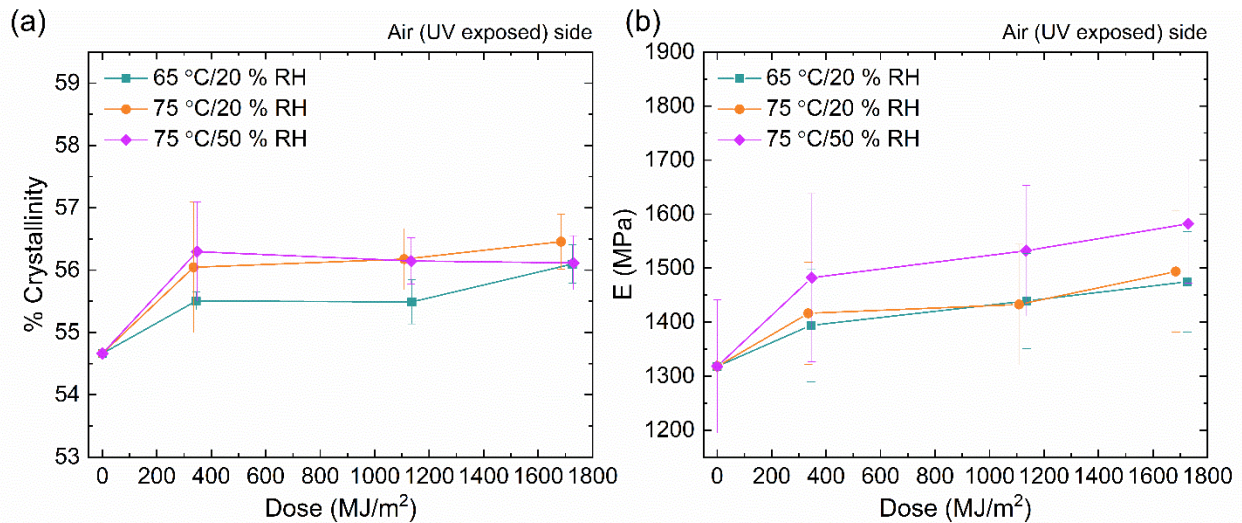
513 discussed above. The cracks observed do not show propagation across the sample, even at strains of 20 %.
514 The line profile shown in Fig. 15c shows that these fine cracks are also confined fully to the outer layer of
515 the backsheet, and generally do not exceed 3 μm in depth.



516

517 **Fig. 15.** LSCM images of fragmentation testing of PP backsheet after exposure to a) 335 MJ/m^2 and b) 1684 MJ/m^2 UV
518 irradiance at 75 °C and 20 % RH. The sample was pulled in the transverse direction at a strain of 20 %. A line profile of a
519 location on the same sample at 20 % strain, showing the cracks are < 3 μm deep.

520 Raman spectroscopy and nanoindentation were utilized to evaluate surface crystallinity and modulus of
521 the PP backsheet air (UV-exposed) side. Crystallinity was calculated as the integrated area of the
522 crystalline peak (810 cm^{-1}) [51, 54, 55] divided by the sum of the integrated areas of the crystalline peak,
523 the isomeric defect phase peak (842 cm^{-1}), and the amorphous phase peak (830 cm^{-1}) [35, 51, 55]. The
524 Raman spectra for these peaks can be seen in Fig. S15. The Raman results show a slight increase in
525 crystallinity on the backsheets surface for all exposure conditions, with the greatest increase appearing in
526 the first $\approx 340\text{ MJ}/\text{m}^2$ of exposure, which is similar to the trends seen in other indicators of degradation
527 (Fig. 16). Note that traditional differential scanning calorimetry (DSC), which measures the whole film,
528 did not detect this superficial crystallinity change; utilizing Raman spectroscopy allows for greater
529 sensitivity and enables surface-specific and depth-dependent crystallinity investigation [40]. Similarly,
530 nanoindentation results show small increase in surface modulus following a similar trend. The results
531 show little effect of exposure conditions on crystallinity and modulus change, suggesting the physical
532 changes to be primarily due to UV oxidation. These changes of modulus and crystallinity account for the
533 minor embrittlement of the PP backsheets that is apparent from the crack formation in the outer layer.
534 However, the effect reaches a plateau after initial exposure and is relatively stable over the remainder of the
535 exposure. As a result, the backsheets do not show signs of deep or propagating cracks even after high UV
536 doses. The trend observed in these physical changes, including cracking, crystallinity, and modulus, all
537 mirror the photooxidation trends observed in the chemical measurements described above.



538

539 **Fig. 16.** (a) Change in crystallinity of PP backsheets as $A_{810}/(A_{830} + A_{842})$, obtained *via* surface Raman measurements, plotted vs.
 540 UV dose. (b) Change in surface modulus obtained *via* nanoindentation, plotted vs. UV dose. Trends show slight increase in
 541 crystallinity, with greatest increase in first ≈ 340 MJ/m² exposed. Each data point represents an average of 5 measurements. Error
 542 bars show standard deviation. Points are connected to guide the eye.

543 Previously, Oreski *et al.* performed aging utilizing sequential stress testing (UV exposure and thermo-
 544 mechanical load) on solder bump coupons with PP-based backsheets, finding that PP did not show crack
 545 initiation and propagation under these conditions [26]. While the present work did produce small cracks,
 546 it should be noted that these superficial cracks appeared under much greater strains than would be
 547 experienced in the field (10 % to 20 % experimental strains vs. < 5% field strain). Conversely, polyamide-
 548 based backsheets exposed to 735 MJ/m² UV at 65 °C/20 % RH, a much lower dose than achieved in the
 549 present study, showed deep crack formation extending through the outer layer and into the core layer
 550 ($46.6 \mu\text{m} \pm 2.0 \mu\text{m}$) at only 4.5 % strain [41]. This highlights the potential of PP as a cracking-resistant
 551 backsheet alternative. Given the extreme conditions needed to produce even small cracks, and the failure
 552 of those cracks to propagate catastrophically, it's not likely the investigated backsheets would show
 553 cracking due to photo-oxidation in field modules.

554 4. Summary

555 Recently, research into fluoropolymer alternatives for PV backsheets has been driven by price pressure,
 556 the promise of improved performance, and concerns around sustainability and environmental
 557 responsibility. PP has emerged as a promising material for this application due to its low cost of
 558 production, availability, recyclability, and permeability, though work investigating the degradation of PP
 559 in PV backsheets remains limited. The aim of this work was to carefully examine the photooxidation of
 560 PP backsheets, formulated for use in PV installations and using test conditions informed by service
 561 conditions, providing a strong foundation for the continued expansion of the use of PP-based backsheets
 562 in the photovoltaic industry.

563 The backsheets showed minor decrease in intensity of characteristic PP peaks in the FTIR spectra for all
 564 exposure conditions, as well as minor accumulation of oxidation products. A thorough peak
 565 deconvolution process was applied to the FTIR region corresponding to oxidative products to obtain clear
 566 trends of oxidative products by functional group vs. exposure time under various conditions. All
 567 degradation products showed greater accumulation on the UV-exposed side, and the FTIR peak-resolving
 568 analysis of functional groups revealed a particular discrepancy in ester and lactone formation on the UV-

569 exposed (air) side vs. the dark (cell) side. Additionally, previously unassigned FTIR peaks corresponding
570 to a known PP additive were identified and attributed to calcium stearate migration to the surface, with
571 back (dark) side migration significantly exceeding that for the exposed (air) side.

572 To study the mechanical consequences of the oxidative degradation, crack propensity and crystallinity
573 were examined, using fragmentation testing and Raman spectroscopy. Overall, all major markers of
574 degradation, including oxidation product concentration, yellowing, fragmentation, and crystallinity,
575 showed the greatest changes occurring in the initial phases of exposure. Over the full experiment, no
576 properties examined showed signs of catastrophic degradation or failure, and fragmentation testing
577 showed minor cracking extending only within the outer layer of the backsheet.

578 The present work elaborates on previous studies revealing the excellent stability of these emerging PP-
579 based backsheets, including general resistance to oxidative degradation as well as mechanical failure.
580 These results, together with existing work showing the desirable functional properties of this material,
581 highlight the promise of PP-based backsheets as an inexpensive, recyclable, and durable alternative to
582 fluoropolymer-based backsheets in PV modules.

583 **Disclaimer**

584 Certain commercial products or equipment are described in this article to adequately specify the
585 procedure. In no case does such identification imply recommendation or endorsement by the National
586 Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the
587 purpose.

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