Photo-oxidation of poly(ethylene terephthalate) films intended for photo-voltaic backsheet

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Abstract

The photodegradation of 36 μm thick poly(ethylene terephthalate) film under artificial weathering conditions has been investigated. A weatherometer was used to expose samples to a broad wavelength range of light in an oxidative environment, replicating outdoor exposure. Irradiations were also performed using UV lamps of wavelengths 302 nm and 365 nm light, in an oxidative environment. After exposure, the extent of degradation was determined using attenuated total reflectance Fourier transform infrared spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy, UV-visible spectroscopy, fluorescence spectroscopy, differential scanning calorimetry, contact angle measurements, and scanning electron microscopy. Results show the production of a series of degradation products, including carboxylic acid end groups, anhydrides, aldehydes, quinones and monohydroxy terephthalate groups.

Keywords: poly(ethylene terephthalate); photodegradation; UV irradiation; weathering; FTIR

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1. Introduction

Photovoltaics is the technology that generates electrical power by converting sunlight directly into electricity. Within a typical solar panel, there are several different layers, shown in the illustration in *Figure 1*. A layer of glass is generally used as the top layer to protect the solar panel, allowing the transmission of light and providing mechanical strength. The solar cells are the most important part of the device as they are the functional elements that convert sunlight to electrical current. They are protected directly by the encapsulant. A commonly used encapsulant is ethylene-vinyl acetate copolymer (EVA), which provides long-term protection of the solar cells whilst allowing the transmission of sunlight. In turn, the purpose of the backsheet is to protect the active layer and encapsulant against environmental degradation, while also acting as an electrical insulator. Therefore, it is important that the backsheet does not degrade when exposed outdoors. In addition to resistance to heat (the panels can reach temperatures of 80°C) and humidity (both the subject of other studies in our laboratories) the backsheet must be resistant to UV. A backsheet will typically see 10% of the UV falling on the top surface.

Figure 1: Cross-section of a typical solar panel showing the three-layer backsheet.

Polymeric backsheets are typically made up of a three-layer laminate. An illustration of the structure of a typical backsheet is given in *Figure 1*. The core layer is commonly made of

poly(ethylene terephthalate) (PET), providing high mechanical strength and electrical insulation. PET is a semi-crystalline, synthetic polymer commonly synthesised from the polyesterification reaction between terephthalic acid and ethylene glycol. The repeat unit of PET is given in *Figure 2*. This core layer is sandwiched between the inner and outer layers. The inner layer is often EVA or low-density polyethylene, while the outer layer is a fluorine-containing polymeric material, typically poly(vinylidene fluoride). The backsheets are essential for long-term durability of the cell. Increasingly, there are commercial drivers to the use of a single-layer, PET-only, backsheets and the photostability of PET becomes critical to the performance and life-time of the entire photovoltaic device.

Figure 2: Structure of repeat unit of PET.

PET has been reported to have a much longer lifetime than polyolefins but on exposure to UV light PET films still tend to degrade, which often leads to brittleness and loss of transparency.¹ During the photodegradation of PET, a number of chemical changes occur, including the formation of hydroperoxides, aldehydes, ketones and carboxylic acids. However, the degree of chemical degradation is not the only factor that should be evaluated when considering the durability of polymer products; the depth profile of degradation and surface deterioration are also important parameters.² Studying the photodegradation process of PET involves analysing both the purely photolytic chemistry and photo-oxidative reactions taking place during exposure.³

From UV-visible spectroscopy, a thin sample of PET film was found to absorb light of wavelength near 310 nm, transmit light >320 nm and was opaque to wavelengths <302.5 nm. It was noted that PET has an absorption edge at 310 nm and degrades most significantly when irradiated under light of this wavelength or lower. Using a thinner cast film in experiments exposed a strong absorption maximum near 240 nm and a weaker absorption

near 290 nm. Similar absorption maxima were found in several solutions of phthalate esters and therefore it was concluded that, in the range of 240-320 nm, the main chromophore was the terephthalate ester moiety.⁴

The atmospheric UV cut-off is ca. 300 nm and, in typical photovoltaic use, the 240 and 290 nm absorptions are therefore unimportant. In practice, too, whilst PET can be thought of as undergoing both photolytic and photo-oxidative degradation, the absorption edge means that the bulk of the photochemistry will occur at the film surface and will be oxidative in nature.

Photo-oxidation reactions take place in the presence of air, and polymers tend to degrade faster in these conditions than in an inert environment. The differences in environment, with oxygen present, have been reported to show several significant differences. Irradiations of PET performed in non-oxidative conditions showed discoloration and crosslinking to the extent that the material was insoluble in *o*-chlorophenol. Performing irradiations in an oxidative atmosphere showed chain scissions and fluorescent species build-up, but there was no crosslinking and only minor discoloration.^{5,6}

The photodegradation of PET has been studied by different groups under a range of artificial light sources.^{4,7-11} Day and Wiles reported the production of carbon monoxide, carbon dioxide, carboxylic acid end groups and monohydroxy terephthalate groups during exposure. They noted that the production of carbon dioxide was considerably higher, in an oxidative atmosphere compared to a non-oxidative environment, suggesting that oxygen was participating in the reaction. Based on their results the authors proposed a photo-oxidative pathway, shown in *Figure 3*.¹²

Figure 3: Photo-oxidation mechanism proposed by Day and Wiles.¹²

The authors also found that the production of carboxylic acid end groups under oxidative conditions was very similar to experiments undertaken in a non-oxidative environment. Therefore, they proposed their formation was independent of irradiation wavelength and environment and were produced in the same way as those under non-oxidative conditions.

Figure 4: Fechine *et al.* proposed photo-oxidation reaction undergone by PET when exposed to UV light. Radicals R can be produced either by a Norrish Type-I reaction or in this reaction cycle.¹¹

Fechine *et al.* questioned this, reporting that this would not explain the differences seen between the bulk and surface of the film, as there would be lesser amounts of oxygen present in deeper positions of the films. Therefore, a reaction was proposed for the production of carboxylic acid end groups under oxidative conditions, shown in *Figure 4*.¹¹ The authors also proposed a mechanistic pathway for the production of quinone groups during the photo-oxidation of PET.¹ More recently, Lee *et al.* characterised the changes in PET irradiated at

room temperature in air under UV of the spectral range 290 - 380 nm. 2D correlation Fourier transform infrared spectroscopy showed that the irradiation induced changes in both the methylene and ester groups with the formation of esters, peresters and benzoic acids. The methylene groups were considered to be more readily oxidised than the terephthalate units.^{13,14}

Our research was concerned with understanding the effects of exposing PET films to simulated solar radiation (290 - 800 nm) and narrower bands of UV light centred on 302 and 365 nm. The simulated solar irradiation provided information on the overall weathering at an acceleration factor of ca. x3 whilst the narrow wavelength ranges provide more specific information on the most damaging wavelengths. A combination of Attenuated Total Reflection Fourier Transform Infra-red spectroscopy, ATR FT-IR, (surface sensitive) and Diffuse Reflectance Fourier Transform Infra-red spectroscopy (bulk sensitive) allowed differentiation of the chemistry occurring at the PET surface and within the bulk.

2. Materials and Methods

2.1 Materials

The PET film investigated in this study was 36 μm Melinex type S, supplied by DuPont Teijin Films[®]. The films contained 0.2 wt% china clay and no UV stabilisers. The films were characterised using attenuated total reflectance Fourier transform infrared spectroscopy (ATR FT-IR), diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), UV-visible spectroscopy and differential scanning calorimetry (DSC) (*see Section 3.1*).

2.2 Irradiation chamber

Irradiations were performed in an Atlas Suntest XLS+ weatherometer using a daylight filter with a cut-off at 290 nm. The films were exposed to an irradiation intensity of $365 \pm 35 \text{ W m}^{-2}$, measured between 290 - 800 nm, and a black standard temperature, BST, of 37.5 ± 2.5 °C. Samples were irradiated for 10 weeks and analysed every week. One week of irradiation in the weatherometer is equivalent to approximately 3.5 weeks outdoor exposure at the UK average.¹⁵

Exposures were carried out according to ASTM D5071-06 *Exposure of Photodegradable Plastics in a Xenon Arc Apparatus*. A SunCal calibration sensor was used to calibrate the weatherometer before starting a new programme. The sensor allows simultaneous calibration of both irradiance and BST. This weatherometer model follows ISO 4892-1 for measuring and controlling the maximum surface temperature of a black sample. Samples were placed in the weatherometer for 10 weeks and analysed every week (equivalent to a dosage of approximately $61 \times 10^4 \text{ W hr m}^{-2}$) using ATR FT-IR, DRIFT, UV-visible spectroscopy, fluorescence spectroscopy, DSC, contact angle measurements and SEM.

Irradiations, under narrower wavelength ranges, were performed using UVP XX-series bench lamps of wavelengths 302 nm and 365 nm. The lamps used, produce wavelength bands centred on 302 nm and 365 nm but are referred to as the 302 nm and 365 nm lamps throughout this study.

Irradiations were carried out at room temperature under air. The films were exposed to an average intensity of $31.7 \pm 4.0 \text{ W m}^{-2}$ for 1 week and analysed every 24 hours using ATR FT-IR, DRIFT, UV-visible spectroscopy, DSC, and SEM.

Irradiations were also performed using a high intensity Hönle LED Cube 100 lamp of wavelength 365 nm. The samples were exposed to an average intensity of $825.5 \pm 20 \text{ W m}^{-2}$ and a temperature of $43 \pm 2.5 \text{ }^\circ\text{C}$. Samples were exposed for 1 week and analysed every 24 hours.

2.3 Infrared Spectroscopy

An Agilent ATR FT-IR spectrometer was used in the range of $4700\text{-}650 \text{ cm}^{-1}$, with a resolution of 2 cm^{-1} and number of scans set to 64. An Agilent Exo-Scan 4100 was used to collect DRIFT spectra in the range of $5200\text{-}650 \text{ cm}^{-1}$, with a resolution of 4 cm^{-1} and number of scans set to 128. Four spectra were taken each time the sample was analysed.

ATR is a surface technique with a penetration depth of approximately 2 to 5 μm whereas DRIFT is a technique which allows the bulk of the sample to be analysed with a penetration depth of approximately 400 μm . Analysis of the spectra included baseline correction and normalisation to the peak at 1410 cm^{-1} assigned to aromatic skeletal stretching.

2.4 UV-visible Spectroscopy

UV-visible spectroscopy was conducted using a UV-1800 UV-visible Spectrophotometer with a scan range of 190-600 nm.

2.5 Fluorescence Spectroscopy

A Horiba Scientific FluoroMax-4 Spectrofluorimeter was used to collect fluorescence spectra. An excitation wavelength of 340 nm was used, with the emission spectrum collected between 350 to 550 nm.

2.6 Differential Scanning Calorimetry

A TA Instruments Q1000 DSC with an RC90 refrigerated cooling system was used to analyse the polymer films. All samples were prepared in aluminium DSC pans. A heat-cool-heat method was implemented, heating the samples from 40°C to 320°C and cooling from 320°C to 40°C at a rate of 10°C min⁻¹ under a flow of nitrogen (40 mL min⁻¹). All data collected was processed using TA software and all temperature values are quoted to the nearest integer.

2.7 Contact Angle

A Kruss Drop Shape Analyser DSA25 was used to conduct contact angle measurements. Measurements were carried out in triplicate. The Sessile Drop Technique was used for contact angle measurements with a probe liquid of water and a resolution of 0.1°.

2.8. Scanning Electron Microscopy (SEM)

SEM was carried out on a Cambridge Scanning Electron Microscopy Stereo scan 90. The film samples were covered with a thin layer of conductive material, in this case, silver, using a sputter coater. The sample size was 10 by 10 mm.

3. Results and Discussion

3.1 Characterisation of PET

The PET films were characterised using ATR FT-IR, DRIFT, DSC and UV-visible spectroscopy. The band assignments for the peaks in the ATR FT-IR and DRIFT spectra are given in *Table 1*.

A control sample of 36 μm PET film showed a melt endotherm with a maximum at 255°C and a crystallisation peak with a maximum of 209°C. During the second heat cycle two melting endotherms occur at 247°C and 254°C, corresponding to two distributions of lamellar thickness.¹⁶

The UV-visible spectrum of the PET film shows that longer wavelengths (315-400 nm) are absorbed weakly whereas shorter wavelengths (300 – 315 nm) are absorbed strongly. This absorbance is due to the $n - \pi^*$ transitions of the ester carbonyl chromophoric groups, present in polyesters.¹⁷

Table 1: Band assignments for the ATR FT-IR and DRIFT spectra of 36 μm PET control film.

Wavenumber (cm^{-1})		Assignment
ATR FT-IR	DRIFT	
3630	3625	Aqueous O-H stretching vibration ⁷
3550	3540	Alcoholic O-H stretching vibration ⁷
3430	3430	First overtone of the carbonyl peak ⁷
3100-3060	3100, 3078, 3067, 3054	Aromatic C-H stretching ⁷
3016, 2970, 2909	3015, 2970, 2908	Crystalline aliphatic CH_2 stretching ¹⁸
2965, 2855	2963, 2855	Amorphous aliphatic CH_2 stretching ¹⁸
1722, 1714	1743, 1731	Amorphous and crystalline carbonyl stretching ¹⁸
1652	1654	Interaction between the hydroxy and the unsaturated ester carbonyl ¹⁹
1578, 1506	1577, 1505	Amorphous and crystalline ring stretching ¹⁸
1472, 1454	1470, 1453	Crystalline and amorphous glycol CH_2 bending ¹⁸
1409	1411	Aromatic skeletal stretching ¹⁸
1370, 1341	1370, 1345	Amorphous and crystalline glycol CH_2 wagging ¹⁸
1244	1225	Ester group stretching ¹⁸
1175, 1120	1173, 1115	Indicative of aromatic 1, 4-substitution pattern ¹⁸
1097	1090	C-O stretching vibration from saturated aliphatic esters ¹⁸
1044	1042	Amorphous CH_2 deformation ¹⁸
1023, 1017	1025, 1017	Crystalline and amorphous in plane stretching of C-H bond ¹⁸
989	988	O- CH_2 stretching of ethylene glycol segment ¹⁸
970	970	Stretching of C-H bond of the trans isomer of the ethylene glycol unit. ¹⁸
898	897	Stretching of C-H bond of the cis isomer of the ethylene glycol unit. ¹⁸
848	849	C-H deformation of two adjacent hydrogens on the terephthalic ring ²⁰
870	873	Isolated hydrogen on aromatic ring ²⁰

3.2 Weatherometer Irradiation

3.2.1 ATR FT-IR

Samples of PET film were irradiated in the weatherometer for 10 weeks and analysed every week.

Figure 5 shows part of the ATR spectra of samples irradiated in the weatherometer for 10 weeks in 2 week increments. *Figure 5(a)* shows the region between 3800-2100 cm^{-1} , where changes in the hydroxy region are present, while *Figure 5(b)* shows the changes in the carbonyl region. Peak assignments are given in *Table 2 and 3*, respectively. The rear surface of the samples showed no notable change with exposure time.

It is clear from *Figure 5(a)* that there is a marked increase in the absorbance across the region between 3800-2100 cm^{-1} of the spectrum upon weathering, consistent with the generation of carboxylic acid end group and hydroxyl moieties. Carboxylic acid groups have been proposed to be formed photolytically by homolytic scission followed by H-abstraction or by a Norrish Type-II process^{12,21}. Alternatively, they can be formed by a photo-oxidative pathway that also sees the generation of mono- and di- hydroxy terephthalate species.¹¹ Individual assignments are shown in *Table 2*.

Table 2: Band assignments for the region between 3800-2100 cm^{-1} of the ATR FT-IR spectrum of PET.

Peak (cm^{-1})	Assignment
3630	Aqueous O-H stretching vibration ⁷
3550	Alcoholic O-H stretching vibration ⁷
3430	First overtone of the carbonyl peak ⁷
3290	Carboxylic acid end groups ⁷
3100-3060	Aromatic C-H stretching ¹⁸
3016, 2970, 2909	Crystalline aliphatic CH_2 stretching ¹⁸
2928	C-H symmetric stretching vibration associated with the Ar-CH_3 group.
2965, 2855	Amorphous aliphatic CH_2 stretching ¹⁸
2640, 2540	Characteristic of the carboxylic acid dimer ²²

Figure 5: ATR FT-IR spectra of 36 μm PET films irradiated in the weatherometer for up to 10 weeks in the region between (a) 3800-2100 cm^{-1} and (b) 1850-1550 cm^{-1} (carbonyl region).

Of note are there are two peaks that have evolved at 2665 and 2550 cm^{-1} and which are representative of carboxylic acid dimers and the peak at 2928 cm^{-1} that has been assigned to the C-H stretching vibration associated with the Ar-CH₃. A suggested pathway for the photolysis of PET shows the production of phenyl and methyl radicals.⁸ It is thought that these radicals could combine together to produce an Ar-CH₃ group, confirmed by the production of the peak at 2928 cm^{-1} during exposure.

The broadening of the carbonyl peak at longer wavenumbers, shown in *Figure 5(b)*, is thought to be due to the formation of anhydride groups (*Table 3*). These groups have been reported previously during the degradation of PEN but not PET, due to the differences in segmental mobility between the two polymers at the particular irradiation temperature.²³ It is proposed that anhydrides could be produced during our exposure of PET, as irradiations were performed at temperatures below its T_g , which would inhibit the radicals from diffusing apart. This provides the environment for the pathway for anhydride production to occur. At longer wavenumbers, there is also the development of another peak at 1738 cm^{-1} which has been assigned to the carbonyl stretch from an aliphatic aldehyde.

Peaks at 1722 and 1714 cm^{-1} assigned to the amorphous and crystalline carbonyl stretch from the ester group have shown a decrease in absorbance after exposure. This was expected as chain scission occurs at the ester group during exposure and so the decrease in absorbance of these peaks indicates the breakdown of the ester.

Table 3: Band assignments for the carbonyl region of the ATR FT-IR spectrum of PET.

Peak (cm^{-1})	Assignment
1785	Carbonyl stretch from anhydride carbonyl ^{23,24}
1738	Carbonyl stretch from aliphatic aldehyde ²⁵
1722	Amorphous carbonyl stretch from ester ¹⁸
1714	Crystalline carbonyl stretch from ester ¹⁸
1705	Carbonyl stretch from carboxylic acid dimer ^{24–26}
1700	Carbonyl stretch from carboxylic acid end groups ²⁶
1695	Carbonyl stretch from quinone groups ²⁷
1685	Carbonyl stretch from terephthalic acid

Analysis of the carbonyl region also shows the development of additional peaks at 1705, 1700, 1695 and 1685 cm^{-1} attributed to the carboxylic acid dimer, end groups, quinone species and the terephthalic acid monomer. The increase in concentration of these groups after exposure has caused the broadening of the carbonyl at lower wavenumbers.

Quinone groups have been identified using UV-visible¹ and IR spectroscopy,²⁷ in degradation studies, and mechanistic pathways for their production have already been proposed.

A spectrum of terephthalic acid and irradiated PET were overlaid to confirm the peak at 1685 cm^{-1} as the carbonyl stretch from terephthalic acid; the development of this peak indicates the breakdown of the polymer into its monomer units.

Figure 6 shows the fingerprint region of samples irradiated in the weatherometer for 10 weeks in 2 week increments. Peaks that have changed or developed in the spectra after exposure have been assigned in Table 4.

Figure 6: ATR FT-IR spectra of 36 μm PET films irradiated in the weatherometer for up to 10 weeks in the fingerprint region between 1500-700 cm^{-1} .

Peaks at 1430 and 1220 cm^{-1} are associated with the carboxylic acid dimer and have developed upon exposure. As far as is known these peaks have not yet been reported in the literature for photodegraded PET.

After irradiation a reduction in size of the peaks at 970 and 898 cm^{-1} , assigned to the trans and cis isomer of the C-H stretching of the ethylene glycol unit, was identified. The reductions are related to the scission of ester links in the polymer chain during photodegradation of PET.

A peak at 940 cm^{-1} has developed during exposure and has been assigned to the C-H vibration associated with vinyl groups. Its appearance in the spectra is consistent with the Norrish Type-II Scission route to carboxylic acid end groups.

Table 4: Band assignments for the fingerprint region of the ATR FT-IR spectrum of PET.

Peak (cm^{-1})	Assignment
1430	Combination band due to C-O stretching and O-H deformation vibration, associated with carboxylic acid dimer. ²⁵
1220	C-O stretching vibration, associated with carboxylic acid dimer. ²⁵
970	Stretching of C-H bond of the trans isomer of the ethylene glycol unit. ¹⁸
940	C-H vibration associated with vinyl groups. ²¹
898	Stretching of C-H bond of the cis isomer of the ethylene glycol unit. ¹⁸
848	C-H deformation of two adjacent hydrogens on the terephthalic ring ²⁰
778	Out-of-plane deformation vibrations of mono-substituted rings ²⁵
769	Out-of-plane deformation vibrations of 1, 2, 3-substituted rings ²⁵
758	Out of plane deformation vibrations of 1, 2, 4-substituted rings ²⁵

The region between 850-750 cm^{-1} is sensitive to changes in the substitution pattern of the terephthalic ring. After exposure, there has been a change in the peak at 848 cm^{-1} and the development of peaks at 778, 769 and 758 cm^{-1} .

There is a minor reduction in the size of the peak at 848 cm^{-1} assigned to the C-H deformation of two adjacent hydrogens on the terephthalic ring, suggesting that substitution has occurred on the ring. The development of peaks at 769 and 758 cm^{-1} assigned to the 1, 2, 3-substituted and 1, 2, 4-substituted rings further supports the suggestion that substitution has occurred on the terephthalic ring.

The evolution of the peak at 778 cm^{-1} has not previously been observed in the literature, during the photodegradation of PET, but is thought to be due to mono-substituted aromatic rings. Day and Wiles propose (*Figure 3*) that the phenyl radical produced upon the loss of CO_2 during photo-oxidation will abstract a hydrogen atom from the backbone of the polymer chain to form phenyl end groups.

3.2.2 DRIFT

Figure 7 shows part of the DRIFT spectra of samples irradiated in the weatherometer for 10 weeks in 2 week increments. *Figure 7(a)* shows the region between 3800-2100 cm^{-1} , where changes in the hydroxy region are present, while *Figure 7(b)* shows the changes in the carbonyl region. Peak assignments are given in *Table 5*, respectively.

The DRIFT spectra show the same trends as the ATR spectra, but the changes are less pronounced (compare, for example, *Figure 5(a)* and *Figure 7(a)*). This is indicative of the photochemistry occurring predominantly at the surface. DRIFT, as a probe of the entire film, will be less sensitive to the surface changes than ATR.

Table 5: Band assignments for the region between 3800-2100 cm⁻¹ and the carbonyl region of the DRIFT spectrum of PET.

Peak (cm⁻¹)	Assignment
3620	Aqueous O-H stretching vibration ⁷
3550	Alcoholic O-H stretching vibration ⁷
3430	First overtone of the carbonyl group in ester ⁷
3335	First overtone of carbonyl group in carboxylic acid end group ²⁸
3290	Carboxylic acid end groups ⁷
3100, 3078, 3067, 3054	Aromatic C-H stretching ¹⁸
3015, 2970, 2908	Crystalline aliphatic CH ₂ stretching ¹⁸
2963, 2855	Amorphous aliphatic CH ₂ stretching ¹⁸
1785	Carbonyl stretch from anhydride carbonyl ²³
1743	Carbonyl stretching vibration of an ester ²⁸
1683	Carbonyl stretch from terminal acid end groups ²⁸

Figure 7: DRIFT spectra of 36 μm PET films irradiated in the weatherometer for up to 10 weeks in the region between (a) 3800-2100 cm^{-1} and (b) 1850-1550 cm^{-1} (carbonyl region).

3.2.3 UV-visible Spectroscopy

The UV-visible spectra of samples irradiated in the weatherometer for 10 weeks in 2 week increments are shown in *Figure 8*.

The UV-visible spectra show an increase in absorbance at 340 nm and a minor increase at 400 nm upon exposure. The increase at longer wavelengths, after exposure, has been reported by Fechine *et al.*¹ and is indicative of the production of new chromophores.

Figure 8: UV-visible spectra of 36 µm PET control film and samples irradiated in the weatherometer for up to 10 weeks.

Specifically, the increase at 340 nm has been attributed to monohydroxy terephthalate groups. These species were first identified by Pacifici and Straley,²⁹ and a mechanism was proposed for their formation by Day and Wiles.¹²

Figure 8 also shows a small increase in absorbance at 400 nm. This is mainly due to the formation of quinone and diquinone groups during the photodegradation of PET. Possible reactions leading to the formation of quinone and diquinone groups, during exposure to UV light, have been proposed.¹

The change in absorbance at 340 nm over time is shown in *Figure 9*. The degree of change become less pronounced at longer times, presumably as the new chromophoric species undergo secondary reactions.

Figure 9: Change in absorbance at 340 nm for 36 μm PET films irradiated in the weatherometer for up to 10 weeks. The error in each point is estimated to be ± 0.03 units.

3.2.4 Fluorescence

Figure 10 shows the initial natural fluorescence spectrum of PET and samples irradiated in the weatherometer for 10 weeks in 2 week increments.

Various groups have studied the emission band at 370 nm, but at present, this is known as the excimer band.^{11,30,31} Currently, Chen *et al.*, Fukazawa *et al.* and Fehine *et al.* have all attributed the peak at 370 nm to an excimer.^{11,30,31}

Figure 10: Fluorescence spectra of 36 μm PET control film and samples irradiated in the weatherometer for up to 10 weeks

There have also been considerable amounts of research into the assignments for the peak at 385 nm. It has been suggested that the emissions at 385 and 410 nm are related to the carbonyl groups in the main chain of PET.³⁰ At present, emission at 385 and 410 nm are known to be associated with a ground state dimer.¹¹

After exposure, the intensity of the initial emission peaks decreases. This has been reported as being due to a loss of interaction between chromophores, caused by chain scission.¹¹ It has been suggested that production of the emission at 475 nm is an exciplex from the interaction between the excited carbonyl group and the phenylene π -electrons.³⁰ Therefore the evolution of the emission at 475 nm has been assigned to the production of monohydroxy terephthalate groups.¹¹

More obviously than the UV data, the fluorescence data shows that there is not a monotonic increase in monohydroxy terephthalate concentration. *Figure 11* clearly shows the levelling off as the monohydroxy terephthalate group undergoes secondary reactions.

Figure 11: Change in intensity at 475 nm, with time, for 36 µm PET irradiated in the weatherometer for up to 10 weeks. The error in each point is estimated to be $\pm 0.17 \times 10^4$ units.

3.2.5 DSC

The cooling cycle of the control film and samples irradiated in the weatherometer for 10 weeks in 2 week increments are shown in *Figure 12*.

It is clear that there was an initial increase in T_c after 2 weeks of exposure, consistent with the evidence from the IR data that chain scission has occurred. By producing shorter, more mobile, chain fragments, chain scission can increase the rate of crystallisation, leading to the increase in T_c .

After this initial increase, the T_c starts to decrease with exposure time, and the exotherm broadens, indicating that branching and cross-linking reactions could be occurring. By limiting chain mobility and restricting close-packing, such processes will inhibit crystallisation.

Figure 12: Cooling cycle of DSC thermogram for 36 µm PET irradiated in the weatherometer for up to 10 weeks

3.2.6 Contact Angle

The average contact angle values for 36 µm PET film irradiated in the weatherometer are given in *Figure 13*.

This shows that there is an initial decrease in contact angle with time, suggesting that the surface of the films have become more hydrophilic upon irradiation. This agrees with the production of carboxylic acid end groups, which are known to be produced during photodegradation.

This decrease is then followed by an increase in contact angle, which could be explained by contact angle hysteresis. In literature, the general conclusion seems to be that contact angle hysteresis arises from surface roughness and/or heterogeneity.³² This increase could

therefore be due to the heterogeneity of the surface or surface roughness. Contact angles measured on heterogeneous or rough surfaces would not solely reflect surface energies as surface topography now needs to be considered.

Figure 13: Contact angles of front side of 36 μm PET irradiated in the weatherometer for up to 10 weeks.

3.2.7 SEM

SEM images of 36 μm PET films irradiated in the weatherometer in 1 week increments for 10 weeks are shown in *Figure 14*.

The images show that there are no obvious changes to the surface morphology up to six weeks, despite the considerable changes detectable spectroscopically. However, after 7 weeks surface cracks are visible and by 9 weeks of exposure fractures are now apparent.

Figure 14: SEM images of 36 μm PET irradiated in the weatherometer for up to 10 weeks, in 1 week increments. To give scale, each image represents 100 μm in the vertical direction.

3.3 302 nm vs. 365 nm exposures

3.3.1 ATR FT-IR

Figure 15(a) and (b) shows the region between 3800-2100 cm^{-1} for the control and samples exposed to 302 nm and 365 nm light for 1 week in 24 hour increments, respectively. A summary and discussion of the assigned peaks in this region are given in *Table 2, Section 3.2.1*.

Figure 16(a) and (b) shows the carbonyl peak region for samples exposed for 1 week, in 24 hour increments, under 302 nm and 365 nm light, respectively. The various peaks contained within the carbonyl in the ATR spectra have been assigned and are given in *Table 3, Section 3.2.1*.

The fingerprint region of the control film and films exposed to 302 nm and 365 nm light for 1 week in 24 hour increments are shown in *Figure 17(a) and (b)*, respectively. Assignments for peaks that have changed or developed in this region, after exposure to 302 nm light, are given in *Table 4, Section 3.2.1*.

Figure 15: ATR FT-IR spectra of 36 μm PET films in the region between 3800-2100 cm^{-1} for samples exposed for up to 1 week to (a) 302 nm light and (b) 365 nm light.

Figure 16: ATR FT-IR spectra of 36 μm PET in the carbonyl region between 1850–1550 cm^{-1} for samples exposed for up to 1 week to (a) 302 nm light and (b) 365 nm light.

It is clear that samples of PET exposed to 302 nm light showed change in the ATR spectra in the region between 3800-2100 cm^{-1} , as well as the carbonyl and fingerprint regions. These changes are akin to those observed in PET subjected to weatherometer irradiation. However, samples exposed to 365 nm light showed only minor changes in the spectra. This is consistent with the observation that PET absorbs strongly in the region below 310 nm but only weakly at 365 nm. As photochemistry can only occur subsequent to the absorption of a photon 302 nm UV is much more damaging than 365 nm UV of the same intensity. The rear surface of the samples showed no notable change with exposure time in either case.

Interestingly, there has been no development of a peak at 778 cm^{-1} when samples were exposed to 302 nm or 365 nm light. This is in contrast to the results for samples irradiated in the weatherometer, shown in *Figure 6*. The peak at 778 cm^{-1} is believed to be associated with the production of mono-substituted rings. These results indicate that for this peak to evolve a broad wavelength range must be used during exposure instead of narrow wavelength ranges. In other words, it may be the result of sequential photochemistry at different wavelengths.

From the ATR spectra, it can be concluded that PET is more susceptible to 302 nm light than 365 nm light, of the same intensity, at the surface of the film. This is entirely in keeping with the absence of significant absorption bands in the region of 365 nm in contrast to the high absorption at 302 nm.

Figure 17: ATR FT-IR spectra of 36 μm PET in the fingerprint region between 1500-650 cm^{-1} for samples exposed for up to 1 week to (a) 302 nm light and (b) 365 nm light.

3.3.2 DRIFT

The DRIFT spectra of samples, in the region between 3800-2100 cm^{-1} , exposed to 302 nm and 365 nm light for 1 week, in 24 hour increments, are shown in *Figure 18(a) and (b)*, respectively. The band assignments for this region are given in *Table 5, Section 3.2.2*.

The carbonyl region of the DRIFT spectra of samples exposed to 302 nm and 365 nm light, are given in *Figure 19(a) and (b)*. The band assignments for this region are given in *Table 5, Section 3.2.2*.

It is clear from the DRIFT spectra that samples exposed to 302 nm and 365 nm light show changes with exposure time but from comparing the ATR and DRIFT spectra, it is clear that 302 nm light acts predominantly at the surface, with the ATR spectrum showing more obvious changes with exposure time. On the other hand, whilst 365 nm light has much less effect overall, and produces little change at the surface, the deeper penetrating DRIFT spectroscopy shows minor changes within the bulk of the film upon exposure.

Figure 18: DRIFT spectra of 36 μm PET films in the region between 3800-2100 cm^{-1} for samples exposed for up to 1 week to (a) 302 nm light and (b) 365 nm light.

Figure 19: DRIFT spectra of 36 μm PET in the carbonyl region between 1900-1550 cm^{-1} for samples exposed for up to 1 week to (a) 302 nm light and (b) 365 nm light.

3.3.3 UV-visible spectroscopy

Similar to the observations in 3.3.1, samples exposed to 302 nm light show a much greater spectral changes than those exposed to 365 nm light.

Figure 20(a) shows the UV-visible spectra for PET exposed to 302 nm light for 1 week in 24 hour increments. From the UV-visible spectra, it is apparent that there has been an increase in absorbance at 340 nm and a minor increase at 400 nm, with exposure time. This indicates that new chromophores have been produced during exposure. This has been discussed in further detail in *Section 3.2.3*.

On the other hand, PET exposed to 365 nm light (*Figure 20(b)*) shows a minor increase in absorbance at 340 nm and 400 nm with exposure time, indicating that new chromophores are produced, but to a lesser extent.

Figure 20: UV-visible spectra of 36 μm PET exposed to (a) 302 nm and (b) 365 nm light for up to 1 week.

3.3.4 DSC

Figure 21(a) shows the cooling cycle of the control film and samples exposed to 302 nm light for 1 week in 24 hour increments. The thermograms show that T_c has increased with exposure time, indicating that chain scission has occurred.

After the increase in crystallisation temperature there is no subsequent decrease, as seen with samples irradiated in the weatherometer (*Figure 12*). Again, this indicates that a broad spectrum of light is required for all of chain scission, branching and crosslinking to occur.

The cooling cycles for the samples exposed to 365 nm light, in 24 hour increments, for 1 week are shown in *Figure 21(b)*. The crystallisation temperature does not change significantly with exposure time. However, the cooling cycle for the sample exposed for 120 hours, depicted by the dark yellow line on the graph in *Figure 21(b)*, shows a small decrease in T_c . This is thought to be an outlier as each DSC scan was carried out on a separate piece of PET film each time.

Figure 21: Cooling cycle of DSC thermograms for 36 μm PET exposed to (a) 302 nm light and (b) 365 nm light for up to one week.

3.3.6 SEM

SEM images of 36 μm PET films exposed to 302 nm light for 1 week in 24 hour increments are shown in *Figure 22*.

The images show significant changes on the surface after only 72 hours of exposure. At 72 hours surface cracking is visible, which appears to get progressively worse with exposure. Surface cracks can lead to fractures, which will affect the physical properties of the polymer.

Samples exposed to 365 nm light showed no significant changes.

Figure 22: SEM images of 36 μm PET film exposed to 302 nm light for 1 week, in 24 hour increments. To give scale, each image represents 100 μm in the vertical direction

3.4 High intensity 365 nm exposures

As minor changes were identified, in the DRIFT spectra, when PET films were exposed to 365 nm light a more intense source with an average intensity of $825.5 \pm 20 \text{ W m}^{-2}$ was used to better accentuate the degradative changes occurring.

3.4.1 FT-IR spectroscopy

Figure 23(a) shows the ATR spectra for samples of PET exposed to high intensity 365 nm light for 6 weeks in 2 week increments. Peak assignments for the ATR spectra of PET have already been discussed in detail in *Section 3.2.1*. Only minor changes in the region between $3800\text{-}2100 \text{ cm}^{-1}$ and the carbonyl region are observed. However, the DRIFT spectra, shown in *Figure 23(b)*, shows that changes have occurred in the bulk of the film, in the region between $3800\text{-}2100 \text{ cm}^{-1}$ and in the carbonyl peak region upon exposure. Clearly, at sufficiently high dosages, 365 nm light does induce degradation. Unlike 302 nm light, which is strongly absorbed and causes most degradation within only a few μm of the surface, 365 nm penetrates further with a significant degradative effect on the bulk of the film. Peak assignments for the DRIFT spectra of PET have been discussed in detail in *Section 3.2.2*.

Figure 23: (a) ATR FT-IR and (b) DRIFT spectra of 36 μm PET film exposed to high intensity 365 nm light for up to 6 weeks.

3.4.2 UV-visible spectroscopy

The UV-visible spectra of samples exposed to high intensity 365 nm light for 6 weeks, in 2 week increments, are shown in *Figure 24*. As anticipated, the spectrum post-exposure shows more pronounced changes than the low intensity exposure with a marked increase in absorbance at 340 nm and a smaller but still significant increase at 400 nm. The origin of this increase in absorbance has been discussed in *Section 3.2.3*: the increase at 340 nm has been attributed to monohydroxy terephthalate groups, whilst that at 400 nm is due to the formation of quinone species.

UV-visible spectroscopy analyses the whole thickness of the film, and as changes were already identified in the DRIFT spectra, changes were expected in the UV-visible spectra. This, again, indicates that 365 nm light is affecting the bulk of the film.

Figure 24: UV-visible spectra of 36 µm PET film exposed to high intensity 365 nm light for up to 6 weeks

4. Conclusions

The photodegradation reactions occurring in PET, during exposure to conditions simulating outdoors, were investigated. Results show the production of various degradation products, including carboxylic acid end groups, dimers, anhydrides, aldehydes, quinones and monohydroxy terephthalate groups. In addition, there was evidence of substitution, chain scission, branching and crosslinking reactions. A more hydrophilic surface, as well as surface cracks, were also reported after exposure. After only 1 week of exposure, this is approximately equal to 3.5 weeks outdoors, the PET films were already showing signs of degradation.

It is thought that PET degrades under the broad wavelength range of the weatherometer due to its high absorbance at shorter wavelengths, initially. The primary degradation products can absorb light of longer wavelengths, which subsequently causes another reaction sequence to occur. This being said, it is near impossible to determine the role of each individual wavelength in the degradation when exposing PET to a broad wavelength range of light. For this reason, narrower wavelength ranges of light were used to study the role of different wavelengths in the photodegradation of PET.

The effect of wavelength on the photodegradation reactions taking place in PET during exposure was studied, using 302 nm and 365 nm light. PET films were shown to degrade more when exposed to 302 nm light compared to 365 nm light of the same intensity. Films exposed to 302 nm light showed production of carboxylic acid end groups, dimers, anhydrides, aldehydes, quinones and monohydroxy terephthalate groups. These latter compounds absorb at longer wavelengths than PET allowing for the possibility of secondary photochemistry. Furthermore, results indicated substitution and chain scission reactions, as well as surface cracks, occurring in the samples exposed to 302 nm light, while samples at 365 nm light showed only minor changes. Comparing results to those from irradiation in the weatherometer, it is thought that some degradation products, such as phenyl end groups, are the result of secondary photochemistry.

Some degradation is initiated directly by 365 nm light despite some reports to the contrary. Here, with high intensity 365 nm light we have been able to show that photochemistry occurs with the production of monohydroxy terephthalate groups and quinone species. Whereas 302 nm light is strongly absorbed, limiting much of the chemistry to the surface, the deeper penetrating 365 nm light allows photochemistry to occur throughout the bulk of the film.

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Data availability

The data required to reproduce these findings are available to download from <https://doi.org/10.15129/38e49515-9d74-416e-a043-4637f08f0b15>

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