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Rapid measurement of Polymer Photo-Degradation by FTIR Spectrometry of evolved Carbon Dioxide.

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ABSTRACT

A novel method, allowing simultaneous UV exposure of a polymer sample and IR interrogation of the vapour in a specially constructed cell, has been applied to polyethylene (PE) samples containing TiO₂ pigments with different photo-activities. Measurements of the CO₂ generated by films exposed to ultraviolet irradiation (UV) were completed in 5 hours – very much less than conventional accelerated tests. The TiO₂ pigments used included anatase and rutiles with different surface treatments. Anatase-pigmented material gave significantly higher CO₂ emission than unpigmented PE whilst rutile-pigmented PEs either gave reduced CO₂ emission or enhanced emission, according to the surface treatment. The ranking of the pigments as protectants or pro-degradants correlated well with the carbonyl index measured after more than 300 hours exposure to UVA fluorescent tubes in a QUV machine.

The method was then used to probe mechanistic aspects of the photo-oxidation of pigmented polyethylene (PE) film. For unpigmented polymer the photo-degradation was sensitive to changes in the small fraction of incident UV below 300 nm, but for pigmented films this was much less important. This is because unpigmented film degrades by direct photochemical attack whereas, for pigmented film, photocatalysis by TiO₂, which absorbs in the 300-400 nm region, is important. For films whose photo-oxidation was dominated by photocatalysis by the TiO₂ the rate of oxidation was shown to vary as the square root of the UV intensity. By contrast, for unpigmented films the rate of direct photochemical oxidation was linearly proportional to UV intensity. The difference is a consequence of the controlling role of electron-hole recombination in photocatalytic processes. For both unpigmented and pigmented films the rate of oxidation was shown to increase with increasing humidity and oxygen content of the atmosphere.

1. Introduction

Most polymers degrade under solar ultraviolet (UV) irradiation and various stabilizers are used to improve their UV resistance [1-3]. Both carbon black and TiO₂ are effective UV absorbers and confer significant protection from UV because of rapid attenuation produced by absorption and scattering. Despite this, some forms of TiO₂ increase degradation of polymers [4-6] because UV absorption leads to heterogeneous initiation of photocatalytic oxidation at the surface of the TiO₂ particles. In this paper, direct UV initiated degradation of the polymer will be referred to as *photochemical* degradation, whereas breakdown initiated by UV generation of active intermediates at the surface of the TiO₂ will be designated *photocatalytic* oxidation. Because of the complexity of these processes *ab initio* prediction of polymer stability is not possible. Rapid test methods are required to accelerate development of improved stabilizers, to assess the effect of pigments and fillers in polymer composites, and to assist prediction of the service lifetime of polymers.

We have recently developed an early measure of paint photo-degradation [5-7] by using a specially designed FTIR cell to measure photo-generation of CO₂. A related infrared (IR) assay of evolved CO₂ has been developed by Worsley, Searles and co-workers and applied to PVC plastisols [8, 9]. This paper describes the extension of our *in situ* method to measure photo degradation of unpigmented and pigmented polyethylene films. A primary focus of the work was to determine whether the FTIR method could be used to discriminate between the activities of different TiO₂ pigments and for this purpose the CO₂ measurements have been compared with the results of a conventional test of polymer stability – carbonyl group development.

As well as differentiating between pigments, the earlier work on paint photoactivity made it possible to probe details of the photo-degradation mechanism by allowing measurement of the effect of oxygen partial pressure, humidity, and of UV intensity (I) and wavelength on breakdown of both acrylic and alkyd films. It was, for example, possible to demonstrate that the breakdown depends on $I^{1/2}$ [6,11], as predicted from model experiments over 20 years ago [10] but never previously demonstrated for real paints. Therefore a further aim of the work reported in this paper was to measure the effects of changes in atmosphere and irradiation on polymer-degradation, and thus demonstrate the usefulness of the FTIR/CO₂ method for mechanistic studies.

2. Experimental

2.1 Materials

Low density polyethylene samples made from LDPE Riblène MR10 (Polimeri Europa) were provided by Huntsman Tioxide, (Billingham, Cleveland, UK and Calais, France) Pigmented films were pigmented with a selected range of either commercially available or experimental TiO₂ pigment (Table 1) at a loading of 5 parts per hundred parts of resin (phr).

2.2 Reaction Cell and UV Exposure Conditions

An IR cell in which the sample was mounted and exposed to UV from a xenon lamp via a flexible light guide and a calcium fluoride window was central to these experiments (Fig. 1). The evolution of carbon dioxide, generated by UV irradiation of the sample, was monitored by an interrogating IR beam that passes through the cell parallel to the sample surface (and perpendicular to the UV illumination) via calcium fluoride windows. The 8 mm i.d. samples (typical weight 11 mg.) were held against a magnetic disc by a shaped metal

ring and fixed to it by magnetizable wires ~ 0.5mm in diameter and 1 mm long. Within the cell, the sample could be located either at the rear, position A, or – as shown in Fig. 1- at the front. In the latter case the sample-holder was mounted on two microscope slides positioned with the plane of the slides at right angles to the infrared windows. In this way the forward extension of the sample holder did not block the infrared beam. The cell had ports to admit gas and before measurements began it was flushed, for at least an hour, with the gas in which the reaction was to take place. At the start of the run the taps were closed and the cell contents isolated. Measurements were made with the cell placed in a Bio-Rad FTS-60 spectrometer fitted with a liquid nitrogen cooled narrow-band MCT detector.

The broad band, ~280 -800 nm, output from a 150 W high-pressure Xenon arc lamp (Oriel) was filtered by a 100 mm water filter, to reduce IR heating, and selected solar filters (AM0 & AM1.5 either singly or in combination) were used to remove short wavelength radiation. The spectral distribution shown in Fig. 3 was measured by using a UV-Visible Radiometer (Optronic Laboratories Model 730A) and demonstrates that, by itself, the AM1.5 filter reduces the UV much more than does the AM0. The main effect of the AM0 is, in combination with the AM 1.5, to remove wavelengths below 300 nm. The UV light was projected onto the sample in the FTIR compartment *via* a 1 m flexible light guide (Oriel, Model 77556), which was connected to the light source *via* a beam turning assembly fitted with a dichroic mirror. During these studies the UV intensity incident on the cell window was monitored daily. All the results relating to a specific investigation, e.g. of the effects of changes in humidity, were made as part of a concerted programme conducted over a short period of time. Drift in the lamp output over long periods prevented absolute comparison of results separated by long time intervals and UV intensities are reported in arbitrary units.

2.3 *Reaction Atmosphere and Measurement Procedure.*

Cylinder oxygen humidified by bubbling through de-ionised water at room temperature was adopted as a 'standard' atmosphere. The cell was flushed with this 'wet oxygen' for one hour, the outlet ports were then closed and the cell placed in the FTIR spectrometer. The sample compartment of the spectrometer was then purged with nitrogen until the spectrum showed that the levels of both water and carbon dioxide were constant. Prior to UV irradiation, spectra were then recorded, in 'the dark' for one hour. During irradiation, the build up of carbon dioxide within the cell was followed, using the IR band centred at 2360 cm^{-1} , for three hours. Then the UV illumination was turned off and spectra were recorded for a further hour. This final phase was adopted initially to ensure that there was no leakage into or out of the cell. It was retained as part of the standard procedure because some samples continued to emit carbon dioxide after the UV source was switched off, possibly the result of continuing oxidation promoted by the radicals that had accumulated during photo degradation.

In other experiments the cell was purged with either nitrogen or a 20:80 v/v % $\text{O}_2:\text{N}_2$ mixture instead of (wet) oxygen, again using the water bubbler. Alternatively, to vary the humidity, which was monitored by measuring the IR water band at 1557 cm^{-1} , the bubbler was omitted and the oxygen was either fed directly into the cell or was first passed through a 600 mm column of silica gel.

3. Results

3.1 *Carbon Dioxide generation and the ranking of different samples.*

The growth in the carbon dioxide absorbance when an anatase pigmented film (A2), in the back sample position, A, was irradiated by an AM 1.5 filtered xenon lamp is shown in Fig. 4. During the initial dark period, CO_2 generation was negligible, but on UV exposure, a

CO₂ signal immediately developed and increased at a constant rate. When radiation ceased so did CO₂ generation. When, following an hour in the dark, the sample was reirradiated, CO₂ increased as before.

FIGURE 4 NEAR HERE

The CO₂ was generated significantly faster from A2 pigmented film than from unpigmented PE, $\sim 31 \times 10^{-4}$ and 22×10^{-4} absorbance units (a.u.) h⁻¹ respectively. Although both evolved less carbon dioxide than typical paint films [5, 7] the reproducibility of duplicate runs was excellent. The linearity of the CO₂ growth suggests that even for anatase pigmented PE, which is more photoactive than both unpigmented and rutile pigmented PE, the effects of changes in oxygen and water concentration caused by reaction during a typical experiment are negligible. (The effects of deliberately introducing large changes in atmosphere prior to commencement of the test are reported in section 3.2.3).

If the same experiment was carried out in the absence of a PE film a small and increasing level ($3 - 4 \times 10^{-4}$ a.u. h⁻¹) of carbon dioxide, which depended on the type of vacuum grease used on the demountable joints and on the 'age' of the cell, was detected. This CO₂ source was attributed to photochemical degradation of traces of organic vapour in the cell. The background level was sufficiently low to be ignored in most experiments, but was significant for very photo-stable films. For those, the forward sample position was used. This reduced the stray UV light in the cell and the background CO₂ signal fell to $\sim 1 \times 10^{-4}$ a.u. h⁻¹. Correspondingly the amount of UV incident on the sample was increased and hence the amount of CO₂ originating from polymer degradation increased by $\sim 20\%$.

Figure 5 NEAR HERE

Figure 5 shows corresponding results for duplicate experiments on three different PE films pigmented with a surface-coated rutile pigment. Although the rates of CO₂ evolution, ($10 - 20 \times 10^{-4}$ a.u. h⁻¹) are again much lower than for paint films ($\sim 250 \times 10^{-4}$ a.u. h⁻¹ for

anatase-pigmented acrylic paint [5] and up to 25×10^{-4} a.u. h^{-1} for 14 day old alkyd films *in the dark* [7]), the reproducibility allows photoactivity ranking of four different pigments in the order $A2 > R3 > R4 > R5$. These rankings compare well with those obtained from a conventional accelerated method of measuring photoactivity, the development of carbonyl groups as monitored by the C=O stretching absorption near 1710 cm^{-1} in the infrared spectrum [12]. Typical spectra are shown in fig. 6a and in Figure 6b FTIR absorbances, of separate discs obtained from the same film, are plotted as a function of exposure time at 30°C to UVA-340 QUV fluorescent tubes. They, too, follow the order $A2 > R3 > R4 > R5$ derived from rates of CO_2 generation. More details of UV induced carbonyl development in these materials are given in reference 13 in which the effects of applying mechanical load during exposure is also reported.

FIGURE 6A AND 6B NEAR HERE

The correspondence between the two measures of photoactivity is demonstrated for a much wider range of samples in Fig. 7. Since the samples included pigments which are current market leaders with respect to photostability, the reaction rate was fairly low and the carbon dioxide experiment was extended to 10 hours. For these measurements, the films, exposed to an AM0 filtered Xenon arc lamp, were located in the forward position in the IR cell to minimize the build-up of background carbon dioxide. Fig. 7 demonstrates the excellent correlation between carbonyl absorption measured after ~ 330 h. exposure in a QUV accelerated weathering apparatus [14], with UVA-340 tubes and operated at $42 \pm 1.5^\circ\text{C}$, and the carbon dioxide generation. The correlation coefficient, R^2 , has a value of 0.92 for the set of 10 films derived from the same polymer -one unpigmented and 9 containing rutile pigments ranging from a lightly coated to a heavily coated 'super-durable' pigment

FIGURE 7 NEAR HERE; This is the key figure please print it larger than others

3.2 *The Sensitivity of CO₂ Evolution to Experimental Variables*

The demonstrated correlation between CO₂ evolution rates and carbonyl development suggests that the CO₂ method, just like the carbonyl method, can be used to determine the relative photosensitivities of polymer compounds. The simple and compact cell coupled with the relatively short test time required make it appropriate for the investigation of the dependence of the rates of CO₂ generation on light intensity, wavelength distribution and gas-phase composition. This study relates directly to the robustness of the CO₂ method as a practical measurement technique and also explores its usefulness for investigating oxidation mechanism – using conventional tests for such investigations is, at best, experimentally tedious.

3.2.1 *The effect of UV Intensity.*

In any weathering study, light intensity is a key parameter, and in commercial accelerated weathering equipment care must be taken to ensure the UV output stays within specified limits. In our experiments light intensity was controlled by interposing combinations of neutral density filters between the head of the light pipe and the cell window. For maximum sensitivity these experiments were made without AM filters for unpigmented PE but for the anatase pigmented film the filter combination (AM0 + AM 1.5) was used. As shown in Fig. 8a, the CO₂ generated on irradiation of an unpigmented film varied linearly with the UV intensity. By contrast, for an anatase pigmented film, CO₂ generation varied as the square root of the filter transmission, i.e. as the square root of the UV intensity. As will be considered further in the discussion section, this difference is attributed to degradation of the unpigmented polymer film being due to direct photochemical reaction whereas degradation of the anatase pigmented film is dominated by heterogeneous photocatalytic oxidation by the TiO₂. This implies that day-to-day variations in the lamp output will have a disproportionate

FIGURE 8a and 8b NEAR HERE

effect on the oxidation of films, such as unpigmented films, which are degraded primarily by direct photochemical effects. This implication was investigated by deliberately changing the optics to obtain a ~25% reduction of (AM0 + AM1.5) filtered UV intensity. The relative oxidation rates of unpigmented and pigmented (anatase, R3 and R4) films were then measured (Fig. 9a & 9b). As expected the rate of CO₂ evolution decreased with decreasing UV intensity and, more particularly, the activity of the unpigmented and R4-pigmented films fell from ~0.75 to ~0.65 relative to the anatase-pigmented film. Despite this, the ranking of the different films is unaltered.

FIGURE 9 NEAR HERE**3.2.2 *The effect of Wavelength Distribution.***

The effect of different filter combinations on the amounts of CO₂ generated in 3 hours by unpigmented and anatase pigmented films are shown in Table 2. Although it has not been possible to change the UV wavelength without changing intensity, the results of 3.2.1 suggest that the small effects of intensity on the relative performance of pigmented samples can be estimated to a satisfactory degree of precision.

TABLE 2 NEAR HERE

As shown in Table 2, for the anatase pigmented film, the rates of CO₂ generated when using either an AM0 or AM0 + AM1.5 filter combination agree well with the rates estimated assuming a dependence of rate on the square root UV intensity (measured at 350 nm) – and less well with those estimated on the basis of an I¹ dependence. This suggests that, for TiO₂-pigmented films, the main effect on oxidation rate of interposing UV filters is to reduce the UV *intensity* (which is why only an AM0 filter was used for the comparison shown in Fig. 7 with QUV measurements). By contrast, for the unpigmented film the experimental results are

much closer to those estimated on the basis of an I^1 dependence. However, although the estimation assuming a linear dependence of oxidation rate on UV intensity gave reasonable agreement for the AM0 filter, it gave very poor agreement for the combination of the AM0 + AM 1.5 filter. This suggests that for unpigmented film, the major effect of using the AM0 + AM1.5 filter is caused, not by the change of UV intensity but by the change of UV distribution – and in particular the near total elimination of wavelengths between 280 and 300 nm.

Figure 10 Near Here

The main consequence of omitting the AM0 filter is to increase transmission of 280-300 nm radiation. A comparison of the results in Fig 9b (AM0 + AM1.5) with those in Fig. 10 (only AM 1.5) demonstrates that whereas omission of the AM0 filter increased the CO₂ generation rate for all films, the oxidation of the unpigmented PE film was increased to such an extent that it oxidized more rapidly than all of the rutile pigmented films. However, the ranking of pigmented films remained unaltered – a demonstration of the robustness of the general procedure.

3.2.3 The effect of the oxidation atmosphere.

3.2.3.1 Oxygen content

All of the above measurements were made in an atmosphere of 100% moist oxygen, since it is impractical to measure the formation of carbon dioxide in CO₂-containing air. Using a humidified oxygen (20%)/nitrogen (80%) mixture had relatively little effect on the rate of CO₂ generation. In one series of experiments, as shown in Fig. 11, the relative rates of CO₂ generation in 100% oxygen and 20% oxygen were 75, 68 (unpigmented PE) 107, 89 (for anatase pigmented film) and 78, 49 for film pigmented with R4. Surprisingly, oxidation did not completely cease when oxygen was replaced by humidified nitrogen – measured rates

were ~30% of those in pure oxygen. At present it is unclear whether the source of oxygen is reduction of the TiO₂ – as evidenced by the development of a grey colour – or residual oxygen dissolved in the film, and investigations are continuing.

Figures 11 and 12 near here.

3.2.3.2 Effect of humidity on CO₂ evolution.

To elucidate the effect of humidity on CO₂ evolution under UV irradiation, unpigmented film and films pigmented with anatase (A2)) and rutile (R4), samples were irradiated by (AM0 +AM1.5) filtered UV. In these experiments the background signal was $\sim 12 \times 10^{-4}$ a.u. in 3 hr. Dry, moderate and moist oxygen (~30, ~45 and ~60% relative humidities estimated from the intensities of the 1557 cm⁻¹ IR band of water vapour) were obtained by (i) using oxygen from a fresh cylinder (BOC white spot) (ii) passing cylinder oxygen through a 600 mm tall 50 mm i.d. fresh silica gel column or (iii) through a water bubbler to get moist gas. For an anatase pigmented film the oxidation rate increases with increasing humidity (Fig. 12a). Similar trends were found (Figure 12b) for the other films investigated demonstrating the need to control humidity when comparing the rates of oxidation of different films.

4 Discussion

4.1 Carbon Dioxide Generation

Carbon dioxide generation during photo-degradation of PE [15], PP [16] and PE-PP [17] copolymers has been previously reported. Although the emphasis of this paper is on the development and application of a method for conveniently measuring this CO₂, it is appropriate to consider how this CO₂ may be formed. Hydroperoxides are usually considered to be the key intermediates in both the thermal and photochemical oxidation of

polyolefins [e.g. 12, 17-19]. In PE these are often, but not always [15] formed in the α position to vinylidene groups whereas in polypropylene (PP) they are formed predominantly at the tertiary carbon. [17, 18]. The hydroperoxides can react to form alkoxy radicals which then undergo scission to give end (aldehyde) or chain (ketone) carbonyl groups and end alkyl radicals. Subsequent reaction of these end alkyl radicals leads to formation of carbon dioxide [17]. Lacoste and Carlsson report that during PP oxidation [20] hydroperoxide groups clearly dominate over carbonyl species whilst in PE oxidation [21], carboxylic acid and ketone groups predominate. The detection of photogenerated CO_2 within 30 minutes UV irradiation of our PE samples is consistent with the reported presence of carboxylic acid and carbonyl groups. However, Philippart et al. detected CO_2 , by mass spectrometry, early in the photodegradation of PP [16] and Delprat et al. report [17] formation of significant concentrations of CO_2 as soon as thermo-oxidative degradation of PE-PP copolymers starts. Thus, even for PP, for which formation of esters and acids is a long way down the chain [17], carbon dioxide appears early in the degradation. We speculate that the early detection of carbon dioxide in all of these studies may be due to a high concentration of UV absorbing chromophores in the outer 7nm layer of the polymer. The presence of such chromophores was inferred by Lacoste, Deslandes, Black and Carlsson [22], on the basis of XPS measurements of comparable rates of photo-oxidation $\{\text{O/C} \approx 2.2\%$ after 8 kJ m^{-2} irradiation $\}$ when PE and PP were degraded by 313 nm radiation. In order to further elucidate the mechanism of CO_2 generation, comparative studies of CO_2 generation by PE and PP films, exposed in a QUV for increasing times, are currently in progress.

We note that on the basis of separate calibration experiments a typical absorbance increase of 60×10^{-4} a.u. in 3 hours corresponds to 2.9×10^{-5} g CO_2 [23]. If each CO_2 is formed from one CH_2 group, this would correspond to 0.92×10^{-5} g of CH_2 units. The initial 100 μm thick film weighed $\sim 11 \times 10^{-3}$ g and if we make the gross assumptions that no other

products are formed nor oxygen incorporated in the film, a weight loss of 0.92×10^{-5} g would correspond to a decrease in film thickness of $\sim 0.08 \mu\text{m}$ during the course of the experiment. This is much less than the film thickness, and less than the diameter of a single pigment particle, $\sim 0.3 \mu\text{m}$ [4]. Therefore, as suggested by the linear plots measured during the exploratory measurements, the samples were effectively unchanged by the measurements.

The general pattern of results, particularly the comparison, shown in Fig. 7, of CO_2 evolution rates with development of carbonyl groups, demonstrates that CO_2 evolution is a rapid and useful measure of photo-degradation. This confirms earlier conclusions from studies of acrylic [5] and alkyd [11] paints and extends them to thermoplastic polymers for which photo-generation of carbon dioxide is much less and for which the effects of pigment are expected to be less dominant because the pigment loadings are much smaller ($\sim 1\%$ instead of $\sim 10\%$ by volume). Despite the lower TiO_2 loading, the pigmented films were essentially opaque to UV radiation. For rutile pigment the CO_2 generated from two layers of $100 \mu\text{m}$ film (one behind the other) was, within error, the same as that generated from a single film, and the carbonyl development in the second film was only 25% of that in the front film [13]. By contrast, CO_2 generation from 100 and $250 \mu\text{m}$ unpigmented films scaled with sample thickness [23] and the carbonyl absorptions of all three films in a 3-layer sandwich were similar [13]. The interpretation of carbonyl development in multi-layer samples has been discussed more fully in ref. 13. In comparing carbon dioxide generation and carbonyl absorption, we have assumed similar action spectra for the two phenomena and that therefore any correlation is unaffected by the known variation of UV attenuation between the various films.

4.2 *The effect of radiation wavelength and intensity.*

When considering these results with the immediate focus on method sensitivity, in the wider context of polymer degradation, it is convenient to consider the separate photochemical and photocatalytic contributions to degradation of pigmented films. For the unpigmented film only photochemical degradation contributes. The UV transmission spectrum of unpigmented PE (fig. 13) shows very small UV absorption above ~300 nm and strong absorption only below ~225 nm. However, anatase and rutile absorb strongly at wavelengths below ~385 nm and 405 nm, respectively [24]. Since the absence of an AM0 filter disproportionately increases the short wavelengths (280 -300 nm), which alone are absorbed by the unpigmented PE, the oxidation rate of unpigmented film increases by an amount that is disproportionate to the overall intensity increase. Consequently, the oxidation-rate of the unpigmented PE increases relative to pigmented films, as shown by comparison of figs. 9b and 10. The effect is magnified because oxidation of unpigmented PE increases linearly with intensity (Fig. 8a) whereas for anatase-pigmented films the increase is only by $I^{0.5}$.

Anatase is generally considered to be intrinsically more photo-catalytically active than rutile [23], possibly for reasons that are discussed later. Even when a combination of AM0 + AM1.5 filters essentially eliminates wavelengths below 300 nm, the rate of carbon dioxide generation by the anatase film remains high and this measured photoactivity is considered to result almost exclusively from photocatalytic oxidation by the anatase.

Photocatalytic oxidation [10] by TiO_2 is initiated by UV absorption. UV excites electrons from the initially filled valence band to the empty conduction band, and creates an equal number of positive holes in the valence band [24]. The holes migrate to the particle surface where, most probably, they interact with water or surface hydroxyl groups to form catalytically active hydroxyl radicals. However, before reaching the surface, charge carriers may recombine at, e.g., defect centres. A simple model assumes that

$$\text{The rate of charge carrier generation} = KI \quad (\text{i})$$

$$\text{the rate of hole disappearance} = k_R[e][h] + k_{sO}[h] [\text{OH}^-] \quad (\text{ii})$$

$$\text{and the rate of electron disappearance} = k_R[e][h] + k_{sR}[e] [\text{O}_2] \quad (\text{iii})$$

where K is the absorption coefficient of the UV radiation of intensity I , and $[e]$ and $[h]$ are the concentration of UV generated conduction band electrons and valence band holes respectively. k_{sO} is the rate constant for surface formation of hydroxyl radicals, k_{sR} is the rate constant for the surface formation of adsorbed O_2^- , and k_R is the rate constant for recombination of electrons and holes. In aqueous conditions it is probable that the transfer of electrons to oxygen to form adsorbed O_2^- is the rate determining step [25]. However, during polymer oxidation the availability of hydroxyl precursors is much less and it is not possible to decide, *a priori*, which of these reactions is faster. Under steady state conditions at common experimental, and (hot climate) natural UV intensities the electron hole recombination rate dominates [10] and, as the rates of charge carrier generation and removal must be in balance, this leads to the relationship

$$\text{Rate of formation of hydroxyl radicals} = k_{sO} \sqrt{KI / k_R} \quad (\text{iv})$$

As predicted by this treatment, our investigation of the dependence of oxidation rate on UV intensity demonstrated that the rate of CO_2 formation by anatase-pigmented PE (Fig. 8b) varies as the square root of the UV intensity, in contrast to the I^1 dependence for unpigmented PE (Fig. 8a). This supports the view that photo-generation of CO_2 from the anatase pigmented PE film is primarily caused by photocatalytic oxidation of the polymer and not by direct photochemical oxidation of the polymer. The $I^{1/2}$ dependence of oxidation

rate was first demonstrated, for isopropanol oxidation [10], and has been confirmed, in the context of water treatment, for the photocatalytic oxidation of dilute solutions of other organic molecules [e.g. 26]. Its applicability has been demonstrated for both acrylic and alkyd paints [6, 11] but – to the best of our knowledge – this is the first time it has been demonstrated for photo-degradation of polyethylene films.

4.2 *The effect of oxygen content and humidity.*

The ability to make measurements in only 3 hours facilitated the studies which showed that the polymer oxidation decreased with both lessened oxygen content and lowered humidity. Decreasing the oxygen content from 100% to 80% resulted in the CO₂ formation rate being decreased by 9 %, 17% and 37% for unpigmented, anatase-pigmented and rutile-pigmented polyethylene, respectively (Fig. 11). Gijsman and Sampers reported (15) similar small effects. They found replacing oxygen by air had negligible effect of the conversion of oxygen into CO and CO₂ when unpigmented PE was exposed in an Atlas ES25 artificial-weathering chamber but an increase in conversion occurred if the exposure was in a Suntest®. As the effect of pigment on the diffusion of oxygen within the film is not known, it is not possible to comment on the small difference between the unpigmented and anatase-pigmented films. A possible explanation of the larger difference between the anatase-pigmented and rutile-pigmented films is that because the conduction band in anatase has a higher energy than the corresponding band in rutile, electron transfer to O₂ from the conduction band is energetically easier at the anatase surface and is therefore less sensitive to the oxygen concentration. The formation of carbon dioxide by the anatase and rutile films in a nitrogen atmosphere is puzzling. As shown in Fig. 11b the rate for anatase pigmented PE is comparable with the growth of the background carbon dioxide (itself associated with oxidation of grease and/or adhesive). One possibility is that the CO₂ in the cell is produced

either by previously formed CO₂ diffusing from the film or by reaction of oxygen dissolved in the polymer film. Attempts to decrease such effects, by prolonged flushing with nitrogen, gave ambiguous results as they reduced but did not eliminate CO₂ formation. A second possibility - that small amounts of carbon dioxide were formed by reduction of the TiO₂ - was suggested by the grey colour that developed when films were irradiated in a nitrogen atmosphere. The results merit further investigation.

The effects of water vapour on CO₂ formation are shown in Fig. 12b. We speculate that, for anatase, oxygen transfer to adsorbed oxygen may be relatively easy, as described above. Consequently it would be more likely for anatase than for rutile that surface reaction to form hydroxyls is rate determining; this would explain the greater sensitivity of the anatase films to variation of humidity. However, as for the study of oxygen content a less speculative analysis must await more detailed experiments.

5. Conclusions

From this study we conclude that the FTIR analysis of photo-generated carbon dioxide measures polymer photo-oxidation conveniently and rapidly, and correlates well with the widely used FTIR spectrometric analysis of carbonyl development. It merits a place as one more weapon in the arsenal of rapid tests of polymer degradation.

Significantly, the method's rapidity - hours not weeks - enables experiments focused on degradation mechanism to be made much more conveniently than previously possible. For example it could be extended to the study of polyesters - whose degradation cannot be followed conveniently by carbonyl absorption - and UV stabilizers. Exploratory measurements have shown that incorporation of a UV stabilizer into a polyethylene terephthalate (PET) film significantly reduces CO₂ evolution [23]. Hence the method opens

the way to a wide range of mechanistic studies on real polymer films without recourse to model systems. It is more than twenty years since one of us proposed on the basis of model systems that the rate of photocatalytic oxidation of paint films depends not on the intensity of the UV but on the square root of the intensity [10]. The new method has allowed that proposal to be verified for real polymer films. The significance of this verification is that it impinges on any attempt to study the effect of changing wavelength by 'normalizing' for the consequences of different UV intensities. Our preliminary results also demonstrate the use of the method to study degradation in different atmospheres.

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LIST OF FIGURES AND FIGURE CAPTIONS

1. The IR cell in which the polymer film is exposed to UV. The film can be placed close to the UV window (as shown here) or directly on the ground glass cone at A, at the side of the cell far from the UV window and behind the interrogating IR beam.
2. The arrangement of the UV source and FTIR cell for the in-situ studies. A 150 W high-pressure Xe lamp (Oriel), fitted with water and solar filters, was connected, by a 1 m flexible optical guide via a beam turning assembly, to a cell in a Bio-Rad FTS-60 spectrometer.
3. Spectral output from the 150 W Xenon lamp after being filtered by 100mm path-length water filter and AM0, AM1.5 or AM0+AM1.5 solar filters.
4. The infrared absorbance of gaseous CO₂ before, during and after UV irradiation of replicate anatase, A2, pigmented PE films placed in the back position within the cell. The Xenon lamp output was filtered by a 100 mm water filter and an AM1.5 filter.
5. The infrared absorbance of gaseous CO₂ from replicate measurements of three PE films pigmented with different rutile pigments R3 ▲ and Δ; R4 ◆ and ◇; R5 ▼ and ∇ where the fully and empty symbols are used for duplicate experiments.
Experimental conditions were as used for the results shown in fig. 4.
6.
 - a. FTIR transmission spectra of carbonyl groups for samples pigmented with anatase (A2) or rutile (R3, R4, R5) exposed to UVA-340 tubes in a QUV machine for ~1100 hr.

- b. The carbonyl absorbance of separate discs of polymer film pigmented with anatase (A2) or rutile (R3, R4, R5) exposed to irradiation from a pair of UVA-340 fluorescent tubes, at 30°C.
7. The relationship between the rate of photogeneration of carbon dioxide, from previously unexposed films, irradiated for 10 hours by an AM0 filtered xenon lamp, and the carbonyl index measured after 328 hours exposure in a QUV apparatus. The result for unpigmented film overlaps that for one of the pigmented films (at a carbonyl index of ~0.22).
8.
 - a. Dependence of CO₂ evolution from unpigmented PE film on UV intensity. The CO₂ evolution was measured after 240 minutes irradiation without an AM filter.
 - b. Dependence of CO₂ evolution from anatase pigmented PE film plotted as a function of the square root of the transmission of the neutral density filters.
9. CO₂ evolution during the photo-oxidation of different PE films at (a) high and (b) low intensities of (AM0 + AM 1.5) filtered UV. The high intensity was 25% greater than the low intensity .
10. CO₂ evolution during photo-oxidation of different PE films under the same conditions as Fig 9 b except that only an AM 1.5 filter was used.
11. The effect of the oxygen content of the cell atmosphere on the rate of oxidation of (a) rutile, R4, and (b) anatase, A2, pigmented film.
- 12.

- a. Photogeneration of carbon dioxide from anatase pigmented films exposed to an oxygen atmosphere of increasing (30, 45 or 60%) relative humidity.
 - b. Dependence of carbon dioxide absorbance on humidity for unpigmented (U1), anatase pigmented (A2), and rutile pigmented (R4), films exposed to UV for 3 hours.

13. The UV transmission of a 100 μm film of the unpigmented polymer film used in this study.

Figure 1

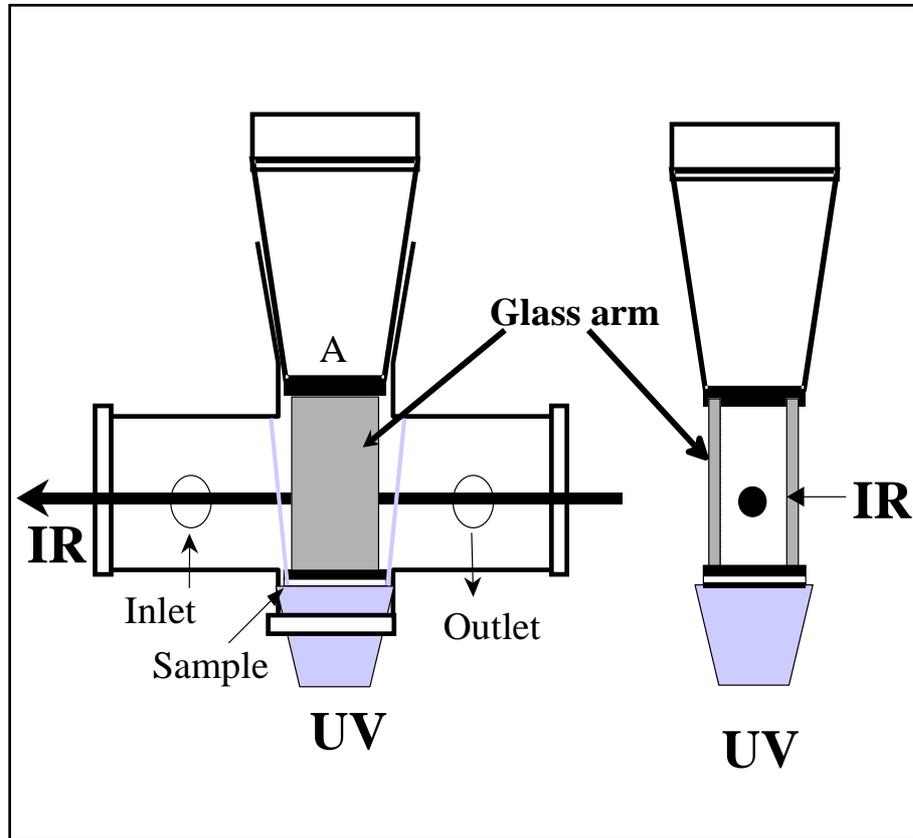
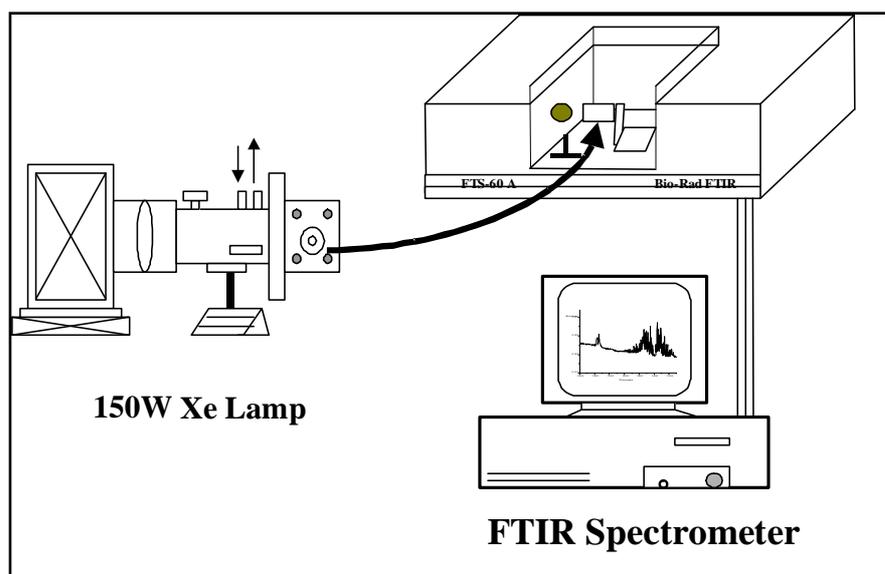


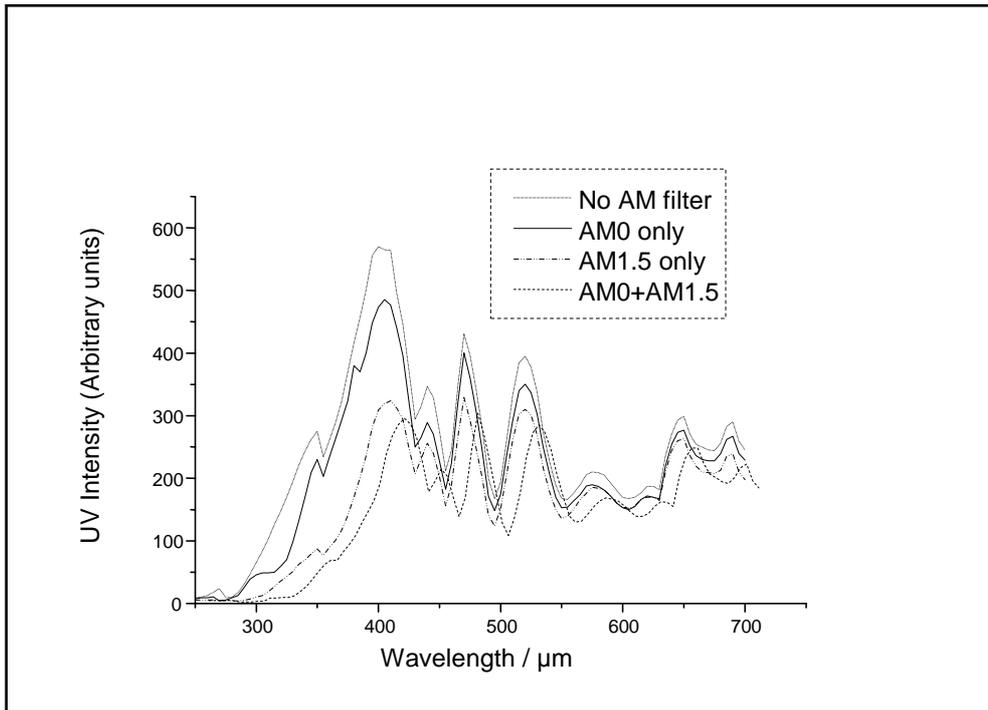
Figure1

Changqing Jin, P. A. Christensen, T. A. Egerton*, E.J. Lawson and J. R. White
Figure 2



Changqing Jin, P. A. Christensen, T. A. Egerton*, E.J. Lawson and J. R. White

FIGURE 2



Changqing Jin, P. A. Christensen, T. A. Egerton*, E.J. Lawson and J. R. White Fig 3

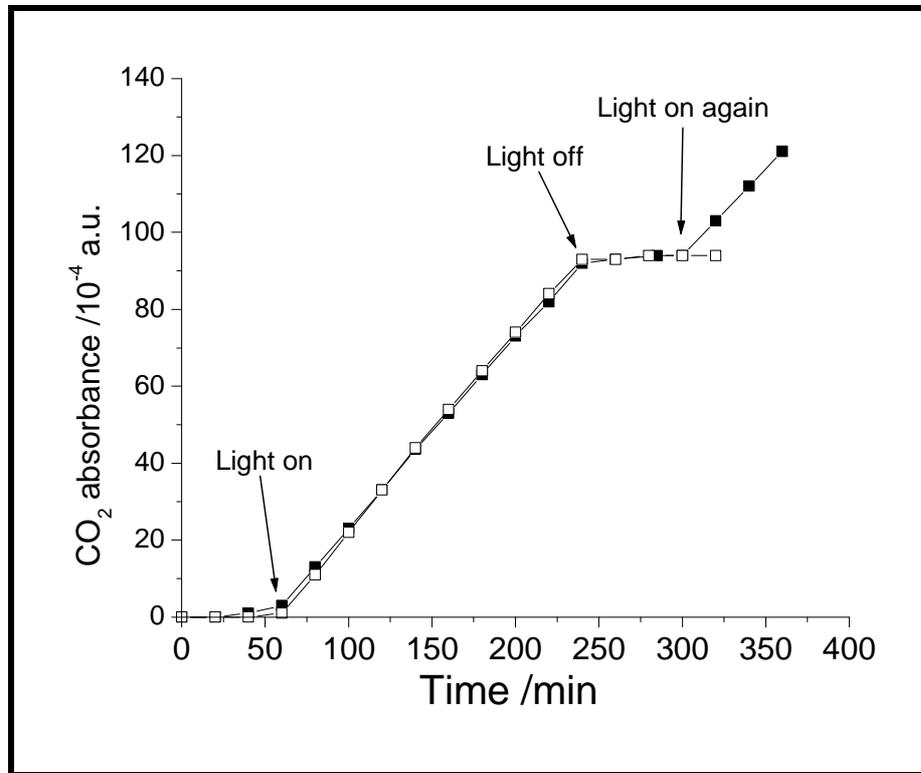
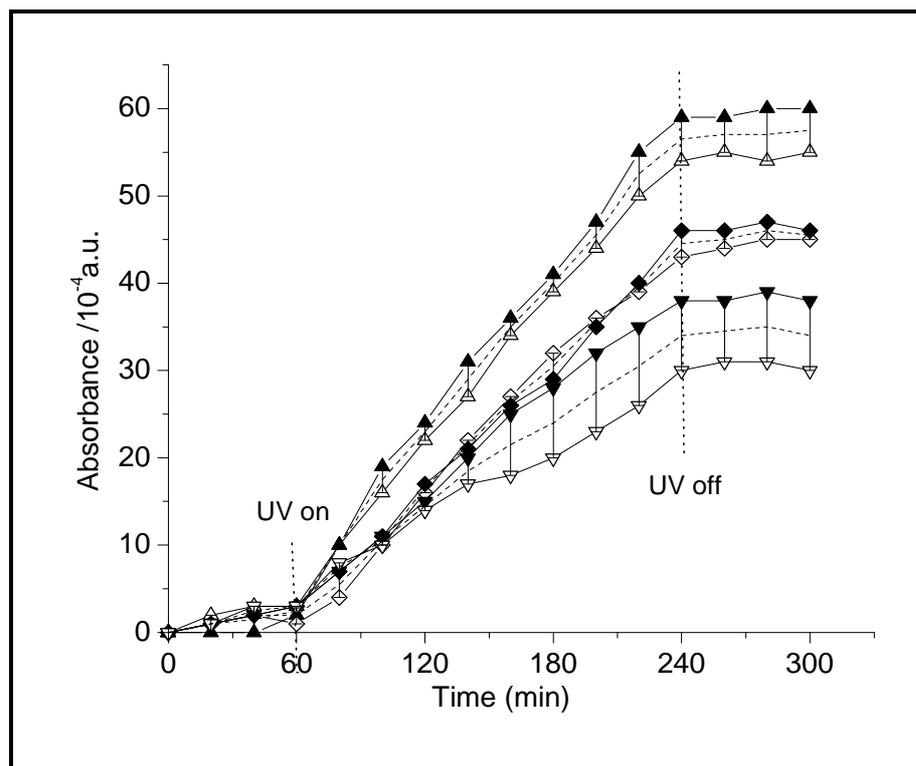
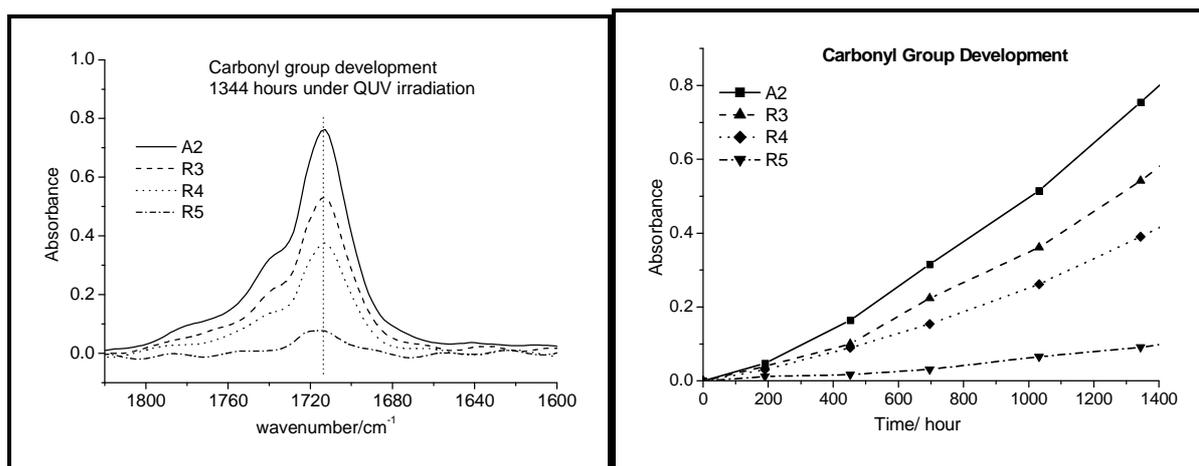


Figure 4.



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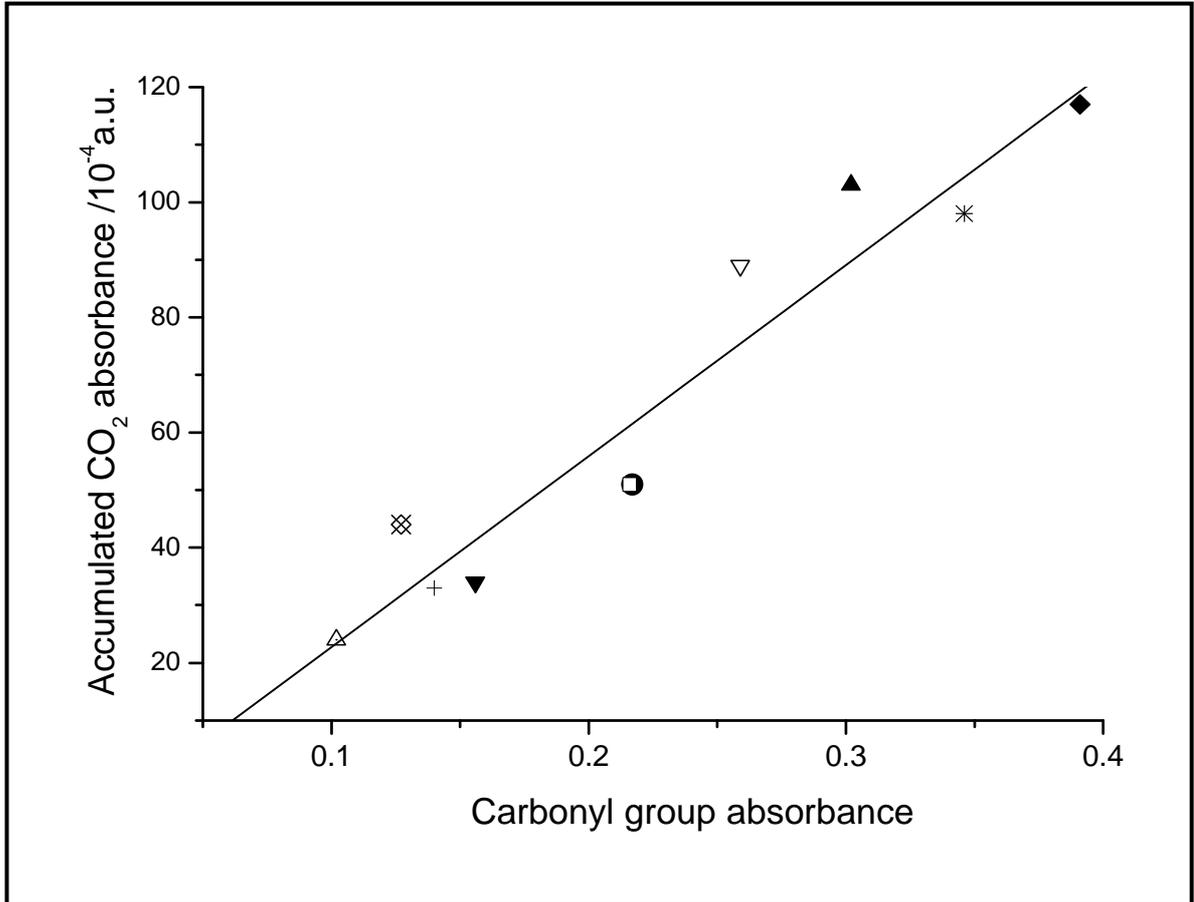
Fig 5



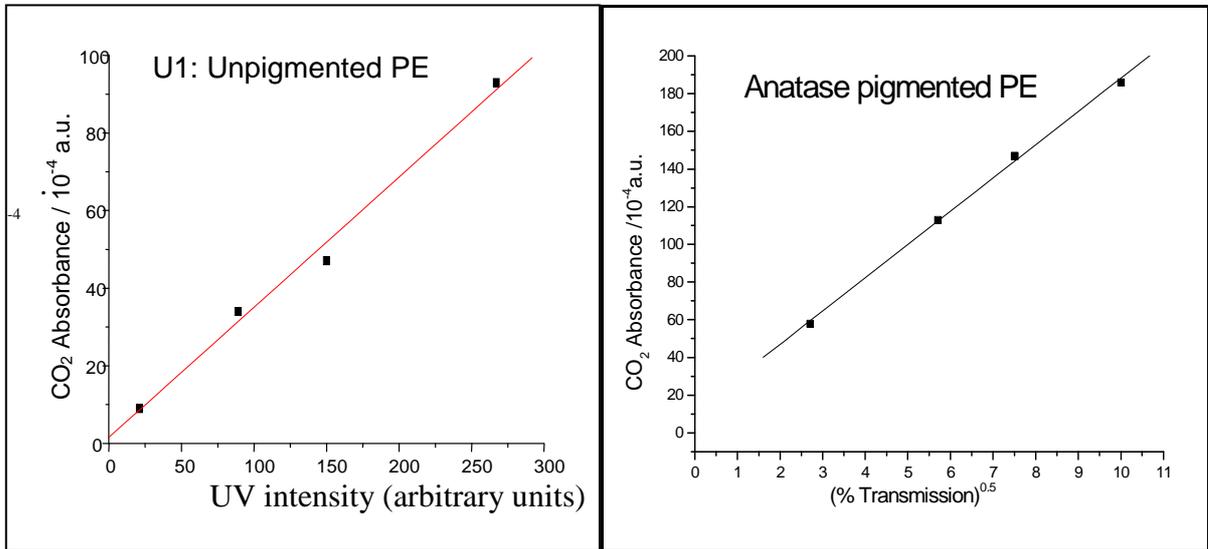
(a)

(b)

Egerton et al Figure 6a and 6b



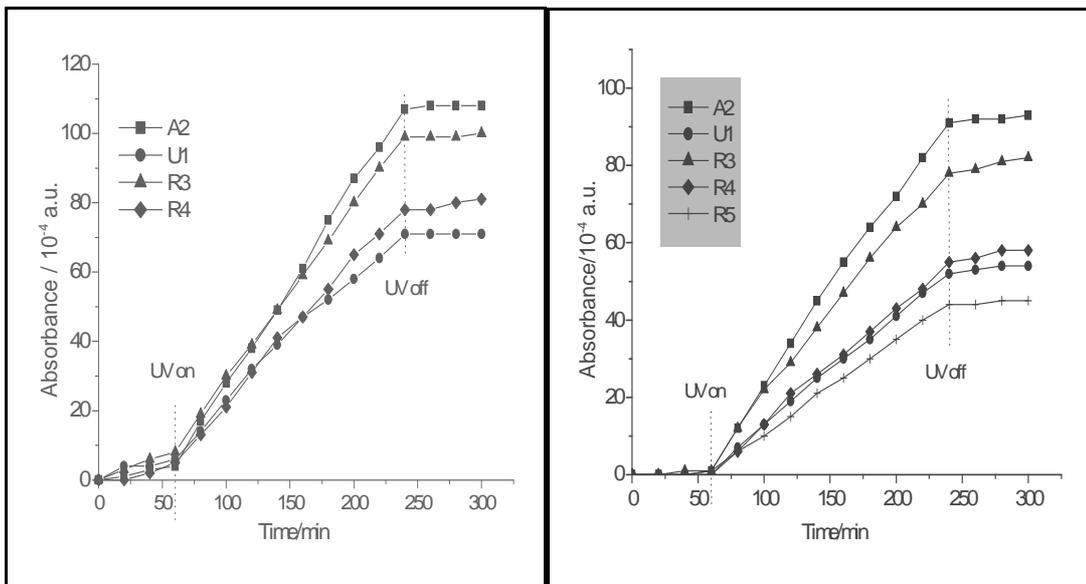
Changqing Jin, P. A. Christensen, T. A. Egerton*, E.J. Lawson and J. R. White
Fig 7



(a)

(b)

Egerton et al Figure 8a and 8b



(a)

(b)

Egerton et al Fig. 9

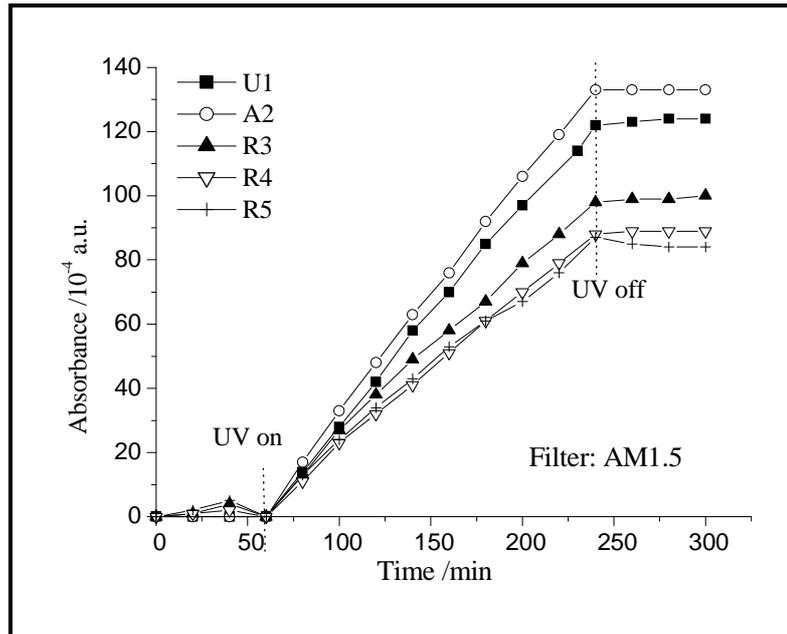
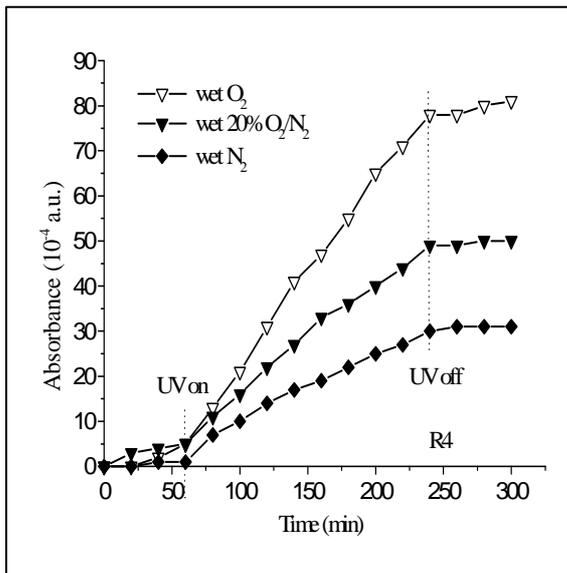
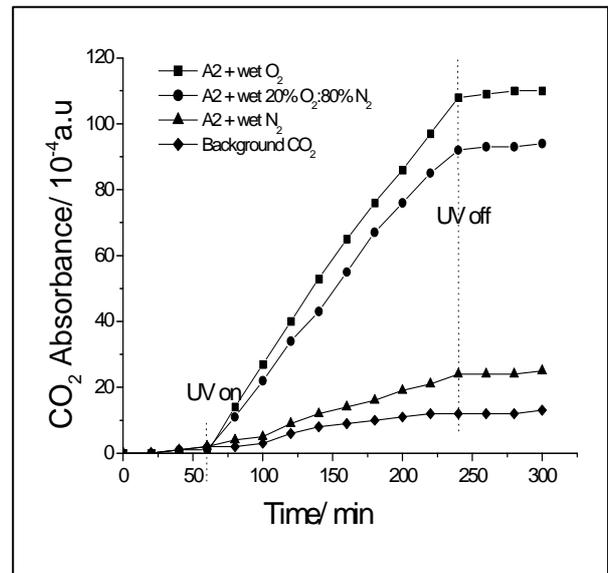


Figure 10

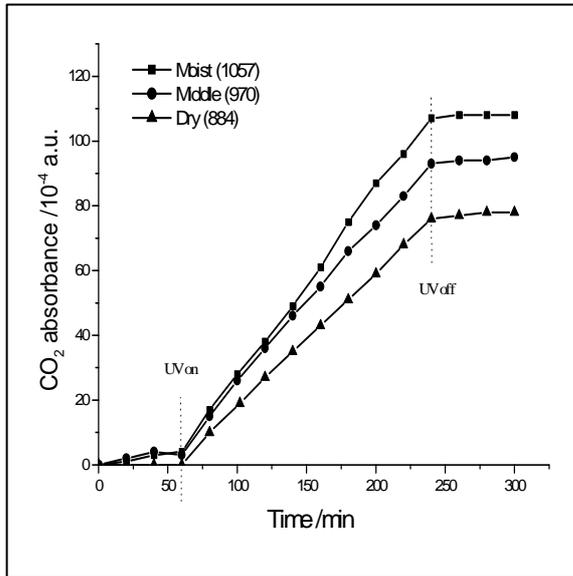


(a)

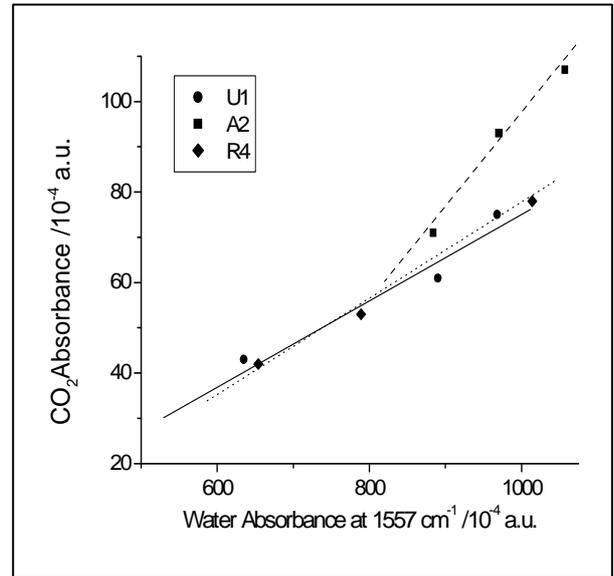


(b)

Egerton et al Fig. 11

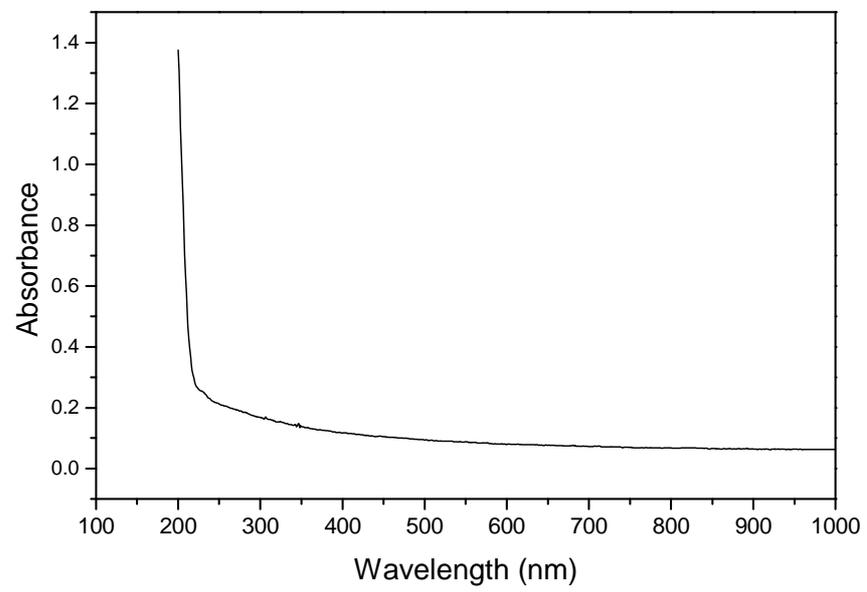


(a)



(b)

Egerton et al Figure 12



Egerton et al Fig 13

Egerton et al

TABLES

Table 1 Description of the polyethylene film samples used in this study

Sample	Crystal	Production process	uncoated or coated	Coating Level
U1	Unpigmented	Not applicable		Not relevant
A2	Anatase	Sulphate process	Coated	Low
R3	Rutile	Sulphate process	Coated: Al ₂ O ₃	Low
R4	Rutile	Sulphate process	Coated: Al ₂ O ₃	Low
R5	Rutile	Chloride process	Coated: Al ₂ O ₃ /SiO ₂	Medium
R6	Rutile	Chloride process	Coated: Al ₂ O ₃ /SiO ₂	Medium

Table 2 The amounts of CO₂ generated in 3 hours by PE films under different irradiation conditions.

	Heat Filter Only	Heat Filter & AM0	Heat Filter & AM0 +AM1.5
Relative intensities at 350 nm	100	79	26
CO ₂ measured for anatase film.	254	244	130
CO ₂ calculated for anatase film assuming an I ^{0.5} dependence.		226	127
Figures for I ¹ dependence in parentheses.		(201)	(76)
CO ₂ measured for unpigmented film	74	53	9
CO ₂ calculated for unpigmented film assuming an I ¹ dependence.		59	20
Figures for I ^{1/2} in parentheses		(68)	(38)

