

## Effect of soil environment on the photo-degradation of polyethylene films

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**ABSTRACT:** Outdoor weathering field trials performed with oxo-degradable polyethylene (PE) thin films were conducted across temperate, grassland, and subtropical sites around Australia. It was found that a site factor, that was apparently independent of total solar dose and temperature, significantly impacted the rate and extent of photo-oxidation. Controlled laboratory-based accelerated aging trials of both PE film with no prodegradant and oxo-degradable PE films (containing iron stearate) revealed that the rate and extent of PE photo-oxidation did not correlate with temperature under the film or UV exposure, but was soil dependent. Under accelerated photo-oxidative conditions, the time to reach embrittlement for a PE film aged over the soil from the temperate site (OM 8.4) was half (24.5 days) the time taken when aged over air (48 days). Further investigation revealed that humic acids and fulvic acids within soil organic matter may contribute to an increased rate of PE photo-oxidation, possibly through the formation of volatile reactive oxygen species that may form under photo-oxidative conditions. The presence of water also had a significant impact on the rate of photo-oxidation. Overall, the impact of soil on PE photo-oxidation was found to be complex and likely dependent at least in part on soil components that varied between different soil types, consequently influencing their photo-chemistry. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42558.

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### INTRODUCTION

Polyethylene (PE) is a thermoplastic polymer used extensively in agricultural applications such as thin films, mulch films, and crop propagation films. PE crop propagation films mimic a “mini greenhouse” as presented in Figure 1. Under the films, a sealed environment will promote crop production by increasing soil temperature and moisture retention in the headspace, while reducing the amount of fertilizer and herbicides required to produce a crop.<sup>1–3</sup>

However, PE is not readily degradable within the timeframe of a growing season and results in the accumulation of plastic waste at the end of its use, requiring collection and disposal, generally by burial in landfill or incineration. To enhance the degradability of the PE, different prodegradants can be incorporated into the polymer during processing to promote oxidation through the acceleration of hydroperoxide decomposition.<sup>4–8</sup> These prodegradant containing films are designed to degrade in

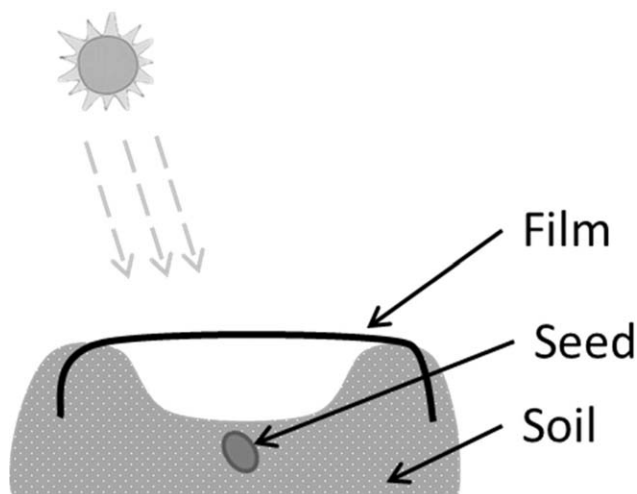
the presence of oxygen, heat, and/or ultraviolet (UV) exposure into small, low-molecular weight fragments which are believed to continue to oxidize to CO<sub>2</sub> over time.<sup>9</sup> The prodegradants used in PE films are mostly based on transition metal salts or their carboxylates, such as stearates, which are miscible in the PE matrix.

In some applications, such as crop propagation films, it is necessary to accurately control the rate of degradation of the film above-ground (to between a few weeks to several months), to allow the crop to penetrate the film at the appropriate time (Figure 2).

The rate of PE film degradation depends on several factors such as, but not limited to, the type and concentration of prodegradant, UV exposure,<sup>1,10–14</sup> temperature,<sup>1,10–14</sup> humidity conditions,<sup>1,10,13</sup> rain,<sup>13</sup> geographical location,<sup>12,13</sup> season,<sup>1,12,15</sup> pesticides and herbicides,<sup>16</sup> and other external environmental factors.<sup>12,13</sup> These factors may interact synergistically.<sup>5</sup> The fundamental parameters typically

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**Figure 1.** Cross section of a mini-greenhouse of the film in the field.

considered during accelerated laboratory aging of PE to model the environmental degradation are solar radiation dose, air temperature, and the relative humidity. Several studies undertaken using different types of polyolefin have shown that the rate of oxidation increases at higher relative humidity or air temperature.<sup>12,13,15</sup> It has been proposed that higher relative humidity enhances the formation of hydroxyl radicals.<sup>17,18</sup> It has also been shown in a study conducted by Sampers<sup>12</sup> that PE lifetime estimates from accelerated laboratory aging are much longer than those actually measured during outdoor weathering trials, even considering the combination of these fundamental parameters. This is attributed to the different weathering parameters that are not taken into account during laboratory aging, such as rain and wind.

While many studies have investigated the aging of PE buried in soil or compost,<sup>9,19–22</sup> research into the effect of soil on polymer degradability has predominantly focused on the rate of biodegradation of agricultural films based on biodegradable polymers,<sup>20,23</sup> rather than oxo-degradable PE films. More specifically, the impact of soil chemistry on the above-ground degradation of linear low-density PE (LLDPE) films has not been conclusively investigated and this study reports conditions in which the soil properties dramatically impact on the above-ground degradation of such films.

## MATERIALS AND METHODS

### Materials

The base polyethylene used in this study was a resin blend composed of LLDPE (93.5%, mix of 45% Dow Elite 5400GS and 48.5% DOWLEX 2045G; Dow Plastics), linear low density polyethylene (LDPE) (5%, H210; Qenos) and a polyisobutylene (PIB, 1.5%, Mw 2000 g/mol; Daelim Corporation).

The Ampacet masterbatch used was a commercial prodegradant (predominantly iron stearate, 2565 ppm as the metal ion Fe<sup>24</sup>) designed by Ampacet Corporation to accelerate photo-degradation in PE.

### Polymer Processing

Two different polymer production processes were used, as a larger scale of manufacturing was required for field trial testing.

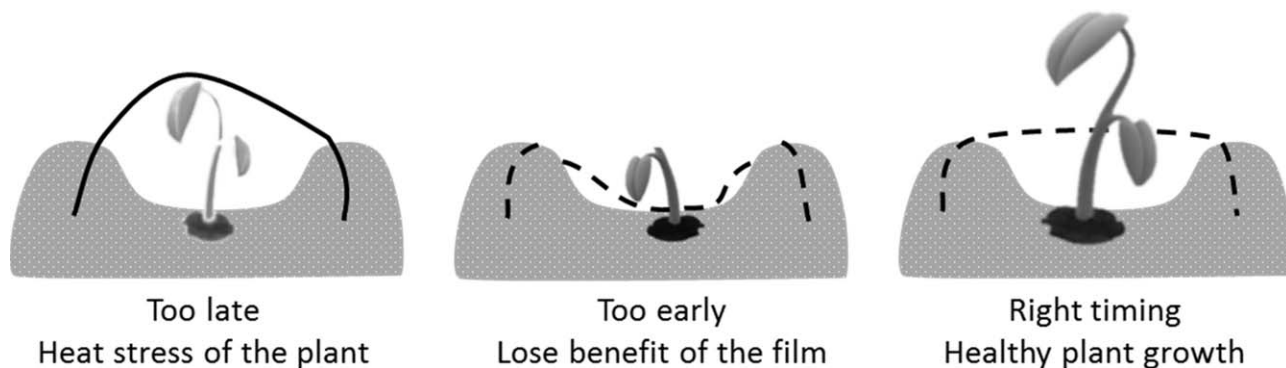
**Film for Natural Outdoor Field Trials.** A PE film containing 5 wt % of Ampacet was commercially blown and stretched by Integrated Packaging (Melbourne, Australia). Film thickness was evaluated using a Teclock upright micrometer, the average film thickness measured was  $10 \pm 1 \mu\text{m}$ .

A laboratory scale PE film without prodegradant was blown using a single screw extruder as described in Film for Accelerated Laboratory Trials section.

**Film for Accelerated Laboratory Trials.** A laboratory scale single screw extruder coupled with a film blowing tower (25 L/D Axon BX25 extruder fitted with a blowing die of 40 mm in diameter) was used to prepare thin oxo-degradable PE films. Full details of the manufacturing process are given in a previous study.<sup>8</sup> Film formulations are summarized in Table I. Film thickness was measured using a Teclock upright micrometer. Average film thicknesses were  $13 \pm 3 \mu\text{m}$ .

### Film Aging

**Natural Outdoor Field Trials.** Ampacet containing film was exposed to natural outdoor weathering conditions during the Australian mid-spring 2009 across three field trials sites in Australia. The three sites were spread across different climates. One site was located in a subtropical region of Queensland at Pinjarra Hills (27.5333°S; 152.9000°E), over a soil with organic matter (OM) content of 4.4%, designated as OM 4.4; one in a warm temperate grassland region of New South Wales at Narrabri (30.3167° S, 149.7667°E), over a soil of OM 1.2% content



**Figure 2.** The impact of variable times of film embrittlement on plant growth.

**Table I.** Concentration of Prodegradant in the Final Film Formulation

Film code	Prodegradant
PE (control)	-
FeSt	1000 ppm as Fe(II)

(designated as OM 1.2); and one in a cool temperate region in Tasmania at Forthside (41.2362°S, 146.2500°E), with soil of OM 8.6% content (designated as OM 8.6). Strips of films, 10 m long and 1.2 m wide were laid over the soil to mimic mini-greenhouse conditions.

PE film without prodegradant was exposed to outdoor weathering during the Australian Summer 2014 across two sites located only 20 km apart from each other in a subtropical region of Queensland: Pinjarra hills (27.5333°S; 152.9000°E) soil OM 4.4% (designated as OM 4.4), and Thornlands (27.5500°S, 153.2667°E) with a soil OM 3.9% (designated as OM 3.9). Strips of films 1 m long and 15 cm wide were laid.

Samples were monitored for embrittlement every 2–3 days. Weather data (solar radiation, temperature, rainfall and relative humidity) were collected from the Bureau of Meteorology Australia<sup>25</sup> for each site.

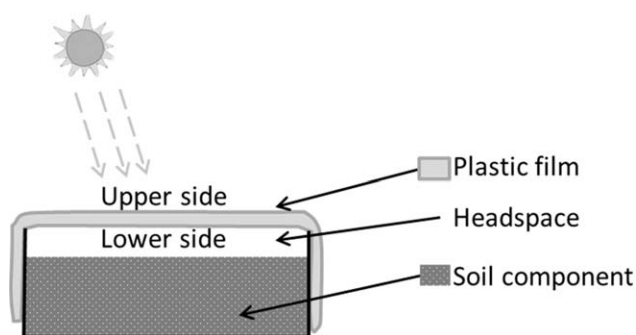
**Accelerated Laboratory Aging.** A QSun Xenon test chamber, model Xe-3-H (Q-LAB) equipped with a chiller, was used as the accelerated aging device to simulate day and night cycles, while controlling the air temperature and humidity according to ASTM D2565,<sup>26</sup> without water spray. Table II summarizes the irradiance ( $\text{W m}^{-2}$ ), air chamber temperature, black panel temperature, and relative humidity used in both the day and night cycle during the accelerated tests. At the end of each 24 h cycle, the films were analyzed. The UV irradiance and black panel temperature were calibrated every 500 h with an independently calibrated radiometer (CR-20) and thermometer (CT202) to the conditions used in the experiment.

Three different soils to be used in the accelerated aging study within the QSun were collected from different locations (OM 4.4, OM 3.9, and OM 8.4) at a depth of 10 cm. They were sieved through a 2-mm mesh screen to remove gravel and large plant materials.

Humic acid (HA) granulate and fulvic acid (FA) powder were purchased from Omnia Specialities Australia. The HA was derived from plant material that had formed natural deposits of Australian Leonardite in the Victorian Gippsland region in Australia. The FA was extracted from naturally aged humus and concen-

**Table II.** QSun Program Used to Assess Film Performance

Cycle	Time (hours)	Irradiance ( $\text{W m}^{-2}$ ) at 340nm	Air chamber temperature (°C)	Relative humidity (%)
Light	18	0.68	45	50
Dark	6	-	45	50

**Figure 3.** Cross-section of the film laid over the petri dish during accelerated aging trials. The upper side is directly facing the light and under side is directly facing the soil.

trated into a completely water soluble dry powder, with the end product containing 70% FA, with some HA and potassium.

Before accelerated aging experiments, each sample of soil, HA, and FA was prepared by mixing with Milli-Q water to reach a moisture content of 30% w/w, to be in agreement with the moisture content of the soil OM 8.4 (as received). The samples were then placed into separate glass petri dishes of 2 cm depth. Each film formulation was tested in duplicate by placing the film over the soil and acids with the edges secured by a rubber band (Figure 3).

Controls of each film formulation were included in the experimental suite, where each formulation was laid over an empty petri dish (air) as well as over a petri dish containing Milli-Q water (water), where the Milli-Q water was refreshed after each cycle.

#### Soil

The soil from each site was subjected to extensive characterization (available in Supporting Information Appendix A) by a commercial laboratory, SWEP, in South Australia. The key soil characteristics are presented in Table III.

Soil reflectance was measured using a UV-Vis-NIR Cary5000 Stheno spectrometer across the visible wavelength spectral range 400–800 nm (available in Supporting Information Appendix B). The soil reflectance was characterized by the percentage of light reflection at the beginning of the visible spectrum at 400 nm. The reported values are the average of two measurements.

#### Film Analysis

**Temperature Under the Film During the Accelerated Laboratory Aging.** The temperature under the film was measured using a thermocouple which was in direct contact with the underside of the film. The thermocouple was calibrated before use. The reported values are the average  $\pm 1$  standard deviation (SD) from a minimum of three measures, once the temperature reached a stable value (reached within 30 min of the QSun light cycle).

**Film Embrittlement.** In this study, the embrittlement point was defined as the aging time elapsed until the film fractured multidirectionally when a small stress was manually applied normal to the film plane. This equates to the point where the elongation at break was less than 5% of the original film, as stated by

**Table III.** Soil Characterization

Soil	OM 4.4	OM 3.9	OM 8.4	OM 1.2
Site	Subtropical 1	Subtropical 2	Temperate	Grassland
Type	Commercial	Chromosol	Krasnozem	
Texture	Coarse sandy clay loam	Fine sandy clay loam heavy	Medium clay	Heavy Clay
Colour	Grey	Light brownish grey	Red brown	Brownish grey
Reflectance at 400 nm	6.7 ± 0.3	11.2 ± 0.3	2.7 ± 0.1	14.1 ± 0.1
pH (water)	6.5	6.5	5.2	7.6
Total organic carbon (%)	2.2	2.0	4.4	0.6
OM (%)	4.4	3.9	8.4	1.2

Wiles and Scott.<sup>6</sup> At the embrittlement point, the film was too delicate to handle and would break into small flakes.

**FTIR-ATR Spectroscopy.** Fourier transform infrared—attenuated total reflectance (FTIR-ATR) spectroscopy was used to determine the oxidation products, as quantified by calculating the carbonyl index (CI) of each film with aging. CI production differs according to prodegradant type, environment, and which side of film was exposed to the light. Spectra were measured on both sides of the film, that is, the surface facing the soil (underside), as well as the surface directly facing the light (upper side) (Figure 3). Spectra were collected using a Nicolet 5700 Nexus FTIR spectrometer equipped with a Smart Endurance single bounce diamond-window ATR. Spectra were collected using OMNIC (Thermo-Nicolet, Madison, WI) software, in the spectral range 4000–525  $\text{cm}^{-1}$ , using 32 scans, 4  $\text{cm}^{-1}$  resolution, gain of 8, and a mirror velocity of 0.6329  $\text{cm s}^{-1}$ . The FTIR-ATR/diamond window measures approximately 2  $\mu\text{m}$  penetration depth into the film surface. Before FTIR-ATR analysis, each film was gently rinsed with deionized water and pat-dried with a lint-free tissue to remove soil particles from the film.

CI values were calculated as the ratio of the height of the carbonyl stretching band at 1713  $\text{cm}^{-1}$  to the height of the  $\text{CH}_2$  scissor band at 1463  $\text{cm}^{-1}$ . Measures were taken from baseline corrected spectra using Grams/32 software (Galactic Industries Corporation). The reported values are the average  $\pm 1$  SD from a minimum of three spectra per sample.

**Statistical Analysis.** The statistical analysis for multiple comparisons was performed using one-way analysis of variance, using Minitab software. A  $P \leq 0.05$  was regarded as a statistically significant difference at the 95% confidence level.

## RESULTS AND DISCUSSION

### Outdoor Aging at Different Locations

A commercially produced PE film containing 5 wt % of Ampacet was exposed above-ground across three sites in Australia: OM 4.4 (Subtropical, Queensland); OM 1.2 (Grassland, New South Wales); and OM 8.4 (Temperate, Tasmania).

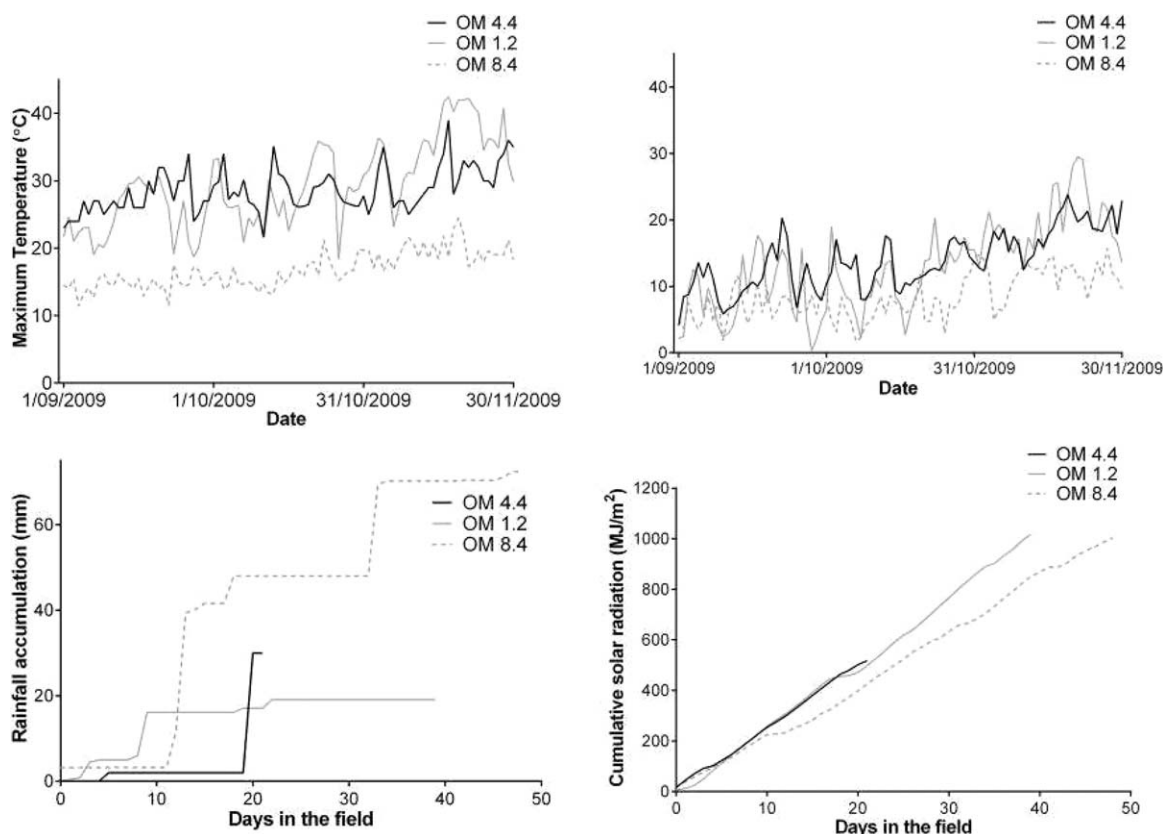
Table IV shows the time to embrittlement for the Ampacet film at each site. The total solar radiation dose for the Ampacet film to reach embrittlement was marginally higher over OM 8.4 (1004  $\text{MJ m}^{-2}$ ) compared with OM 1.2 (987  $\text{MJ m}^{-2}$ ), even though the maximum daily temperature for OM 8.4 was approximately 10°C lower compared with OM 1.2 and OM 4.4 sites during the length of the trial. In contrast, the film exposed over OM 4.4 required almost half the solar radiation dose to reach embrittlement (517  $\text{MJ m}^{-2}$ ), compared with the other two sites. This was unexpected as the OM 4.4 site and the OM 1.2 site have similar daily maximum temperatures, as presented in Figure 4. These results suggest that the embrittlement of the Ampacet film is independent of the daily maximum temperature at these sites.

To rule out the influence of prodegradant type between sites on the rate of PE photo-oxidation, a PE control film was exposed above-ground over two sites in a subtropical region: OM 4.4 and OM 3.9. Figure 5 shows that the maximum and minimum daily temperatures at both sites were almost identical during film exposure; however, the total solar radiation dose to reach embrittlement for the PE control film was more than double over OM 3.9 compared with over OM 4.4.

From the literature, it was expected that the dominating factors influencing the rate of photo-degradation of an oxo-degradable

**Table IV.** Time to Embrittlement Above-Ground for the CoSt-Com Film at Each Location

Location	OM (%)	pH	Time to embrittlement Days	Embrittlement		
				Carbonyl Index		Total solar radiation dose $\text{MJ/m}^2$
				Av.	St dev	
Subtropical 1 (QLD)	4.4	6.5	21	0.311	0.024	517
Grassland (NSW)	1.2	7.1	39	0.279	0.082	987
Temperate (TAS)	8.4	5.2	48	0.190	0.003	1004



**Figure 4.** Weather data: maximum and minimum daily temperatures, rainfall accumulation, and cumulative solar radiation at each site throughout the 2009 trial.

PE film would be the total solar radiation dose and the temperature.<sup>1,10–14</sup> However, the field aging results presented suggest that a “site dependence” factor other than UV, temperature, and rainfall was impacting on the rate of PE photo-oxidation. This effect was observed in a number of field trials with a wider range of formulations and sites. The difference observed was suspected to be related to soil type. Differences in soil properties, such as reflection, color, texture, pH, and OM content were observed between soils taken from each sites and to investigate this further soil samples were taken from key trial sites and film was exposed over these soils under controlled accelerated laboratory conditions.

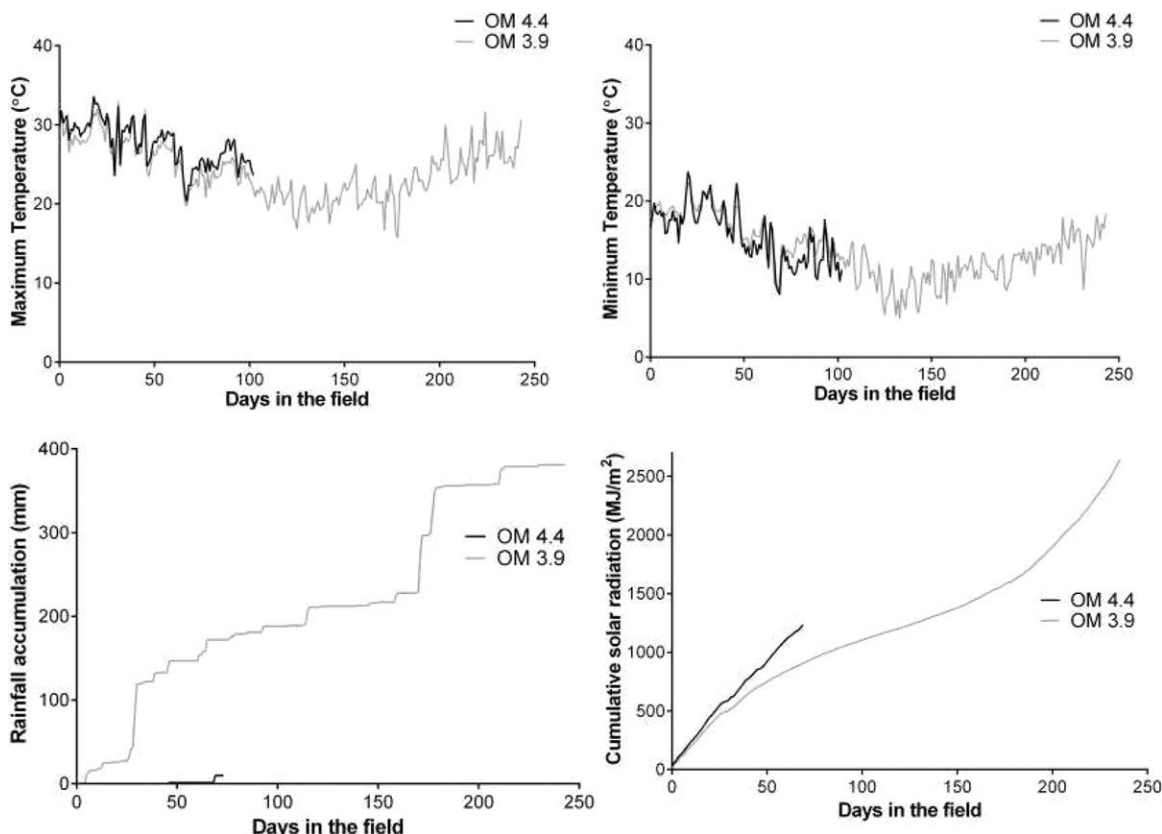
#### Accelerated Photo-Oxidation of Films versus Soil Type

**PE Film.** The time to embrittlement (Figure 6) and the measured CI (Figure 8) showed that the rate and extent of PE photo-oxidation were significantly impacted by the different soils from each site.

The results presented in Figures 6 and 7 suggest that the time to embrittlement is not directly correlated to the temperature. This is particularly noticeable when comparing the time to embrittlement data in Figure 6 with the temperature under the film, given that for example, the film over FA showed the highest temperature (60°C) but this did not result in the most rapid time to embrittlement. As temperature effects did not appear to be the sole influence on the rate of PE photo-oxidation, the impact of differences in soil properties were investigated.

The soil reflectance at 400 nm reported in Table III again did not correlate with the time to embrittlement, as the soil with the highest reflectance at 400 nm (OM 3.9, with reflectance of 11.2%) was the slowest to degrade (43 days). As soil reflectance was not one of the soil key parameters influencing the time to embrittlement, other factors were therefore investigated. Soil consists of a complex variety of materials, combined with a rich mixture of microbial consortia. The composition of a typical soil is approximately 45% mineral, 25% water, 25% air, and 5% OM (by volume).<sup>27</sup> Although the OM represents the smallest portion of the soil composition, it is believed to be the most photo-active part of the soil.<sup>27</sup> In particular, when laid over the soil OM 8.4 the PE control film degraded fastest (24.5 days) compared with the PE control over air (48 days). The time to embrittlement increased as the concentration of OM within the soil decreased to 4.4% (OM 4.4) and 3.9% (OM 3.9) (29 and 43 days, respectively).

As one of the main soil constituents is water, the impact of water on the photo-oxidation of PE was also investigated. Compared with PE aged over the different soils, PE aged over water was not significantly different (30 days) to OM 4.4 soil (29 days), suggesting that the results for PE photo-oxidation for this soil may be due to an effect of water. In contrast, for the film over OM 8.4 soil, embrittlement was approximately 7 days earlier than over water, suggesting that the soil was enhancing the photo-degradation of the film. In the case of the OM 3.9

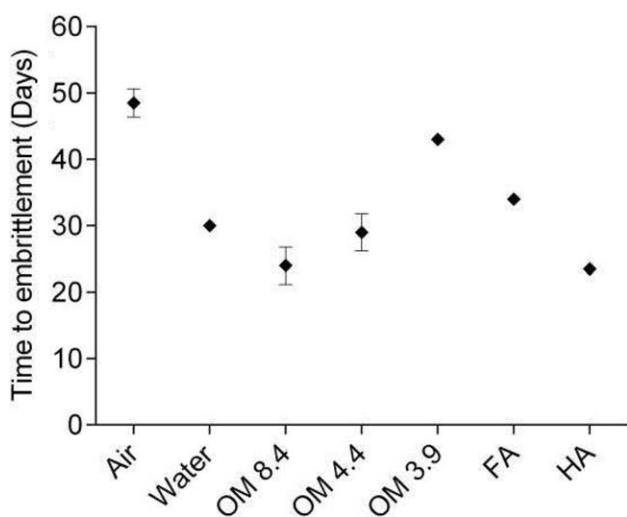


**Figure 5.** Weather data: maximum and minimum daily temperatures, rainfall accumulation, and cumulative solar radiation at each site throughout the 2014 trial.

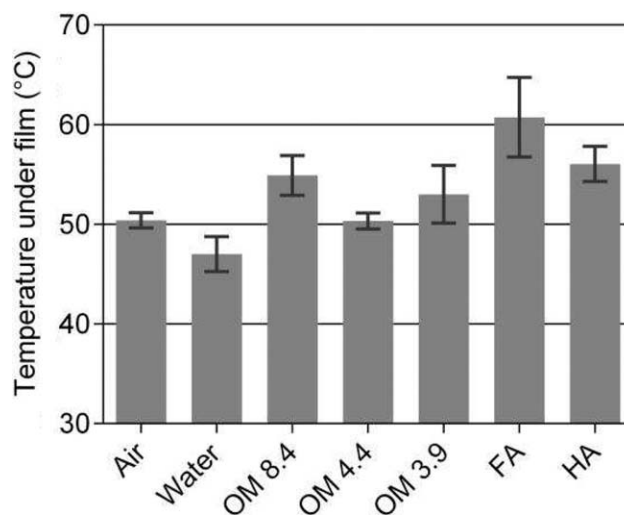
soil, the time to embrittlement was much longer (43 days) compared with water alone (30 days) suggesting constituents within the soil were in this case suppressing the photo-oxidation of PE.

The CI was determined on both sides of the PE. As illustrated in Figure 8, the CI value at embrittlement was different depending on the environmental exposure of the film. A higher CI on

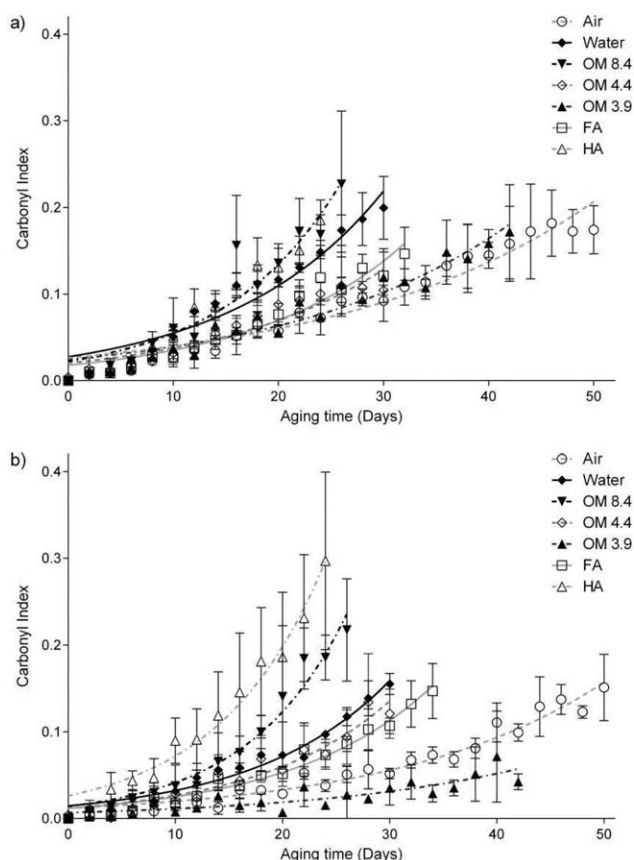
the upper side of the film would be indicative of UV induced chemistries dominating the mechanism of PE oxidation and consequently embrittlement of the film. In contrast, a higher CI on the underside of the film compared with the upper side would suggest that chemistries occurring from the water and/or soil under the film are contributing factors for the photo-oxidation of the PE.



**Figure 6.** Time to embrittlement (days) for PE film when exposed under accelerated laboratory conditions (Q-Sun) over the different substrates (SD  $n = 2$  for each formulation, SD = 0 when both replicate embrittled at the same time).

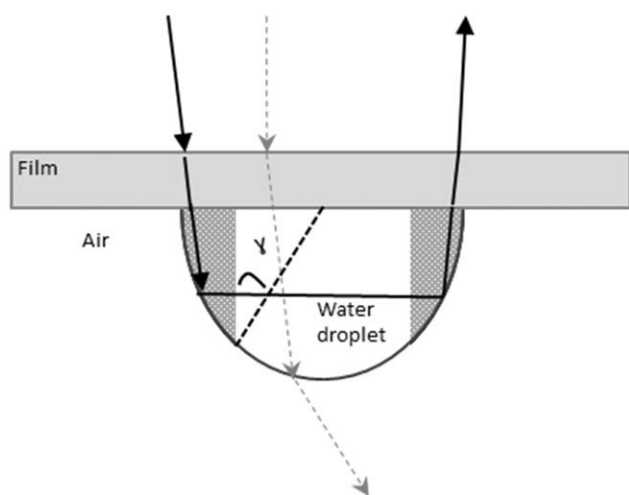


**Figure 7.** Temperature (°C) under the film when exposed to accelerated laboratory conditions (Q-Sun) over the different substrates.

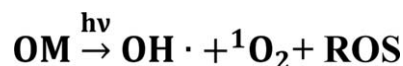


**Figure 8.** Evolution of the CI for the upper side (a) and underside (b) of PE film during accelerating aging over the different substrates, in the Q-Sun.

A comparison of the CI profiles for PE aged over the three soil types showed that OM 8.4 soil resulted in the highest degree of PE oxidation on both the upper side and underside of the film, although the CI on the upper side was highly scattered com-



**Figure 9.** Scheme of the sunlight pathway through the film and the water droplet. In solid line, the incident light hitting the droplet at an angle of incidence higher than the limit angle  $\gamma$  is shown, which leads to total reflexion of the light. In grey dashed line the pathway of the incident light hitting at an angle lower than  $\gamma$ , is given.

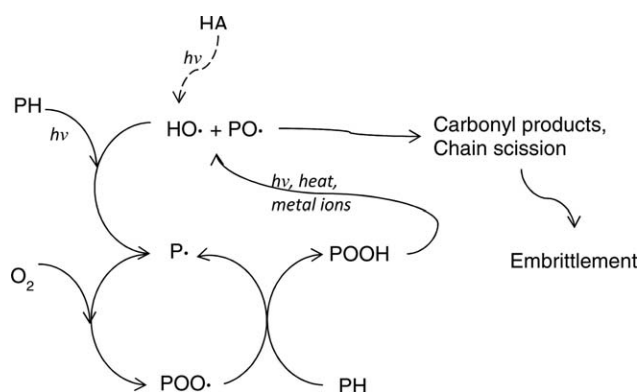


**Scheme 1.** Formation of  $\text{HO}\cdot$  and  ${}^1\text{O}_2$  from OM or HA exposed to sunlight.<sup>48</sup>

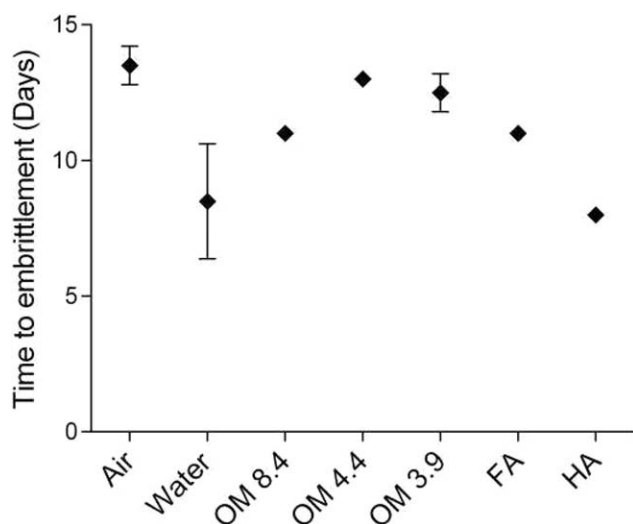
pared with the underside. The extent of oxidation on both sides of PE film aged over the OM 8.4 soil, particularly the underside, was higher than observed for the underside of PE film aged over water, suggesting that soil was impacting on PE oxidation in addition to effects from water alone. The CI profile on the underside of PE film aged over OM 4.4 soil showed a similar extent of oxidation compared with PE film aged over water. This indicates that photo-chemistries for this soil might be comparable with water alone in terms of PE photo-oxidation. The most dramatic differences in PE photo-oxidation were observed for the OM 3.9 soil, with a significantly lower CI on the underside of the film compared with the upper, which were considerably lower than over water alone. The CI evolution on the underside of the PE film aged over the OM 3.9 soil was also lower than both the upper side and underside of the PE control (air). Those CI accelerated aging results clearly demonstrated the effect of soil on the degradation of films.

One of the key components of soil is the OM. The soil OM is composed of three different humic substances (HSs)<sup>27</sup>: HA, FAs, and humin. HA contain functional groups such as phenolic and carboxylic groups, which contribute to surface charge exchange and reactivity. Their molecular weight ranges from 10 to 100 kDa and they precipitate from aqueous solution at  $\text{pH} < 2$ . FA have a much lower molecular weight ranging from 1 to 10 kDa and are soluble in water irrespective of pH,<sup>27</sup> whereas humin are much larger molecules (100–10,000 kDa) and are not soluble in water at any pH and are resistant to rapid decomposition under photo-oxidation conditions.

To isolate the more active components within the soil that may be contributing to the acceleration or inhibition of PE photo-oxidation, accelerated aging trials evaluating PE film photo-oxidation over commercial HA and FA were performed. PE film laid over HA embrittled approximately 10 days earlier (23.5 days) compared with FA (34 days), suggesting that the evaluated commercial grade of HA was more active than FA. PE aged over HA also showed a greater extent of oxidation compared with



**Scheme 2.** Cascade reactions of the PE oxidation process, where P = PE backbone (scheme adapted from N. Billingham<sup>39</sup>).



**Figure 10.** Time to embrittlement in days for PE film containing FeSt when exposed under accelerated laboratory conditions in a Q-Sun over the different substrates (SD  $n=2$  for each formulation, SD = 0 when both replicates embrittled at the same time).

FA. The underside of the HA exposed film showed a considerably greater extent of oxidation compared with the upper side. The FA experiment showed a higher extent of oxidation on the upper side of the film compared with the underside dark, but was still more oxidized on both sides compared with the PE control (air) after 30 days under the same conditions, suggesting it was also active, but to a lesser degree compared with the HA.

The differences observed in rate of degradation could be due to soil properties as well as the presence of water under the film. As soil does contain water, condensation on the surface of the film can occur due to the difference in temperature between the air and the plastic film. The presence of water condensation can influence the degradation of the film by changing light intensity due to sunlight reflection<sup>28</sup> and environmental stress cracking effects.<sup>29–32</sup> Condensation on the surface of the film reduces solar transmission by 13%, compared with dry film.<sup>28,33,34</sup> Part of the light is scattered and reflected by the presence of water droplet on the surface of the polymer film;<sup>35</sup> if the angle of the incident light hits the droplet at an angle higher than the specific angle ( $\alpha$ ) the incident light will be totally reflected Figure 9.

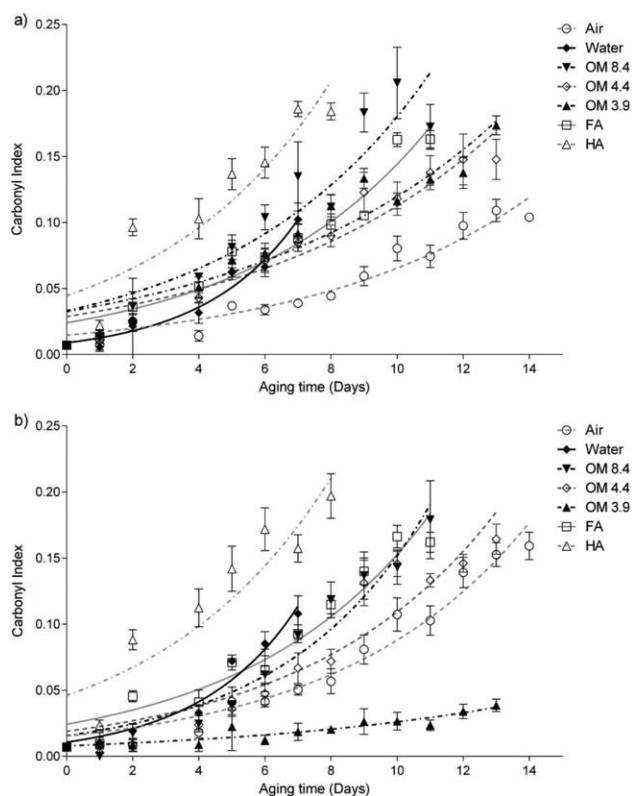
The reflected light thus increases the amount of light the film receives, which would lead to an increase in photo-degradation and a decrease in the days to embrittlement for PE film laid over water alone compared with a dry air control. Another possibility is that specific organic material may also be present in the water, which can cause environmental stress cracking.<sup>31</sup> As underlined by the results of the PE film over OM 8.4 soil and over HA, some soil effects were additional to the possible water condensation contribution.

It has been reported in the literature that FA and HA are reactive under photo-oxidative conditions<sup>36–40</sup> and have been noted to act as either photosensitizers<sup>41–43</sup> or inhibitors<sup>36,44</sup> of reactive oxygen species (ROS) production, which potentially may impact on the photo-oxidation of PE film. The quantity of photo-

chemically produced hydrogen peroxide from HA and FA has been reported previously.<sup>37,39</sup> In some cases, the production rate was significantly higher from HA compared with FA.<sup>40</sup> This may accelerate the rate of PE photo-oxidation by photolysis into hydroxyl radicals<sup>45</sup> and abstraction of a proton from the PE backbone followed by an auto-oxidation mechanism.<sup>46</sup>

It was evident from a thorough survey of the literature that the photochemistry of HSs is complex, variable, and in some cases diverse. The structure and properties of HSs can be variable and differ in polarity and aromaticity which would then result in different photo-activities.<sup>47</sup>

The photo-degradation of HSs promotes changes in the OM structure, leading to numerous reactions allowing the formation of volatile low molecular weight molecules, ROS,  $^1\text{O}_2$  and OH radicals (Scheme 1), hydrogen peroxide, formaldehyde, humic excited state ( $^3\text{HS}^*$ ) and other volatiles species<sup>48–55</sup> capable of degrading chemicals. Celina *et al.* has discussed the potential for hydroperoxides, peroxides and other reactive oxygen containing species that are formed during the polymer auto-oxidation process to initiate and accelerate polymer oxidation via the gas phase resulting in infectious spreading within and between polymers.<sup>56</sup> This suggests that when sunlight is absorbed by the OM, especially by HA and FA, photo-generated species may be produced and trapped under the polymer film. These volatile species in direct contact with the film can act as infectious species and participate in the PE cascade degradation as described in Scheme 2.



**Figure 11.** Evolution of the CI on the upper side (a) and the underside (b) for FeSt containing film during accelerating aging over the different substrates, in the Q-Sun.



The oxidation mechanism of polyolefins involves the formation of a polymer radical  $P\cdot$ , which will lead to the formation of a peroxy radical  $PO_2\cdot$  in presence of oxygen. The overall rate limiting factor of the film oxidation in Scheme 2 is the decomposition of hydroperoxide. The introduction of more ROS from photo-oxidized OM, HA, or FA could be expected to enhance the polymer oxidation.

**Iron (II) Stearate Films.** The accelerated aging of PE film containing iron (II) stearate (FeSt) as a prodegradant was also evaluated over the same soils and HSs as used in the PE film experiments.

The prodegradant film aged over the HA embrittled at a faster rate compared with the OM 8.4 soil (Figure 10). FeSt films embrittled significantly earlier over the OM 8.4 soil compared with OM 4.4 and OM 3.9 soils ( $P \leq 0.05$ ) and was faster on all soils compared with FeSt film aged over air ( $P \leq 0.05$ ). These results suggest that the rate of degradation was affected by the properties and characteristics of each soil, as well as by the presence of water. The most rapid degradation occurred when the film was over HA compared with FA ( $P \leq 0.05$ ).

The evolution of the CI for each side of the film during photo-oxidation was characterized during the experiment (Figure 11).

For the film containing prodegradant iron (II) stearate, a more rapid increase in the CI was observed when film was degraded over HA or the OM 8.4 soil compared with air. Here, again the rate of CI production was dependent on the soil type as well as the type of HS. These results confirmed the trends already noted with the PE film control film (no prodegradant), where the rate of carbonyl production varied between films and soils.

## CONCLUSION

To achieve optimum control of the lifetime of agricultural film above ground, it is necessary to understand the relationship between environmental exposure (UV, temperature, and soil type) and PE photo-oxidation. This work has presented an additional degree of complication when predicting PE photo-oxidation, indicating that temperature and UV are not the only parameters controlling the photo-degradation rate. It was demonstrated that the soil type and components within the OM may influence the rate of degradation of oxo-degradable and conventional PE films under both accelerated and outdoor weathering conditions. Furthermore, HA, one of the components within OM, had a significant impact on the rate of PE photo-oxidation, whereas a mild impact was observed for FA. The presence of water was also shown to have a significant effect on the rate of photo-oxidation. Due to the complex environment involved in the photo-oxidation of PE over soil, a photo-oxidation mechanism could not be conclusively elucidated.

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