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ABSTRACT
The total chemiluminescence from polypropylene (PP) films heated in an inert atmosphere is a sensitive measurement of the hydroperoxide content in the induction period of photo-oxidation. The PP films show a very rapid increase in the hydroperoxide content in the early stages of photo-oxidation which could not be detected by ATR-IR or XPS analysis. This appears as a peak in all of the films which increases in area with film thickness, indicating it is a bulk property. These are believed to form by the rapid oxidation of the PP in localized zones of high photoinstability.

The integrated chemiluminescence is affected by a number of common stabilisers, particularly free radical scavengers. It was found that only the thiodipropionate ester and a 2-hydroxy benzophenone UV absorber affected the kinetics of hydroperoxide formation and decomposition and increased the induction period as measured by carbonyl index. A hindered triphenyl phosphite produced an immediate increase in integrated chemiluminescence and was a prodegradant unless a hindered phenol was incorporated to inhibit peroxy radical attack on the stabiliser. A commercial hindered piperidine caused a lowering of the chemiluminescence which is consistent with a weak radical scavenging and hydroperoxide decomposing activity of the amine.

INTRODUCTION
The photo-oxidation of PP has been recognised to involve the initiation of a free radical chain reaction by the photolysis of hydroperoxide groups and other adventitious impurities in the polymer [1]. Although some success has been achieved in applying liquid phase kinetic models to this oxidation chain reaction, it is not possible to attach significance to the resultant rate parameters because of the non-homogeneous nature of the solid state reaction [2, 3]. It has been suggested from a study of the termination rate of polypropylene alkyl peroxy radicals by electron spin resonance (esr) that the oxidative degradation of PP occurs to a very great extent in small zones in the polymer [2, 4].

The polymer hydroperoxide plays a major role in photo-oxidative degradation. In addition to being implicated in the initiation process, it is a product of the oxidation chain reaction. From many studies of the reactions of PP hydroperoxide [5, 6] it has been shown that intramolecular propagation in the oxidation produces extended sequences of adjacent hydroperoxides. Measurements of mechanical properties and polymer molecular weight [7] have shown that extensive degradation occurs in the induction period and the useful life extends little beyond this point [8]. It has therefore been the focus of much current research to develop techniques which measure the extent and rate of oxidation at the early stages of oxidation at the early stages of oxidation in the induction period. Attenuated total reflectance infrared spectroscopy (ATR-IR) [9], particularly with the use of FTIR instruments has been the most generally useful method. By using selective derivatization reactions, identification of
primary, secondary and tertiary hydroperoxides as well as specific aldehydes, ketones, esters and acids is possible [10]. In this way it has been shown that the surface of photo-oxidised PP is highly degraded to a depth of 0.5 m during the induction period, leading to microcracks and loss of mechanical properties.

Chemiluminescence has also been researched as a technique for measuring polymer oxidation in the induction period [11]. While the mechanism for emission of radiation is still widely studied [13], the exothermic termination reaction of alkyl peroxy radicals has been considered consistent with much experimental data. While this method has been used to study the auto-oxidation of PP, it must be modified for the study of the early stages of photo-oxidation. One method which may be used is to heat the previously photo-oxidised sample in an inert atmosphere to a sufficiently high temperature to decompose all of the hydroperoxides in the sample while measuring the chemiluminescence. Since at any temperature the instantaneous emission intensity is proportional to the rate of hydroperoxide decomposition, the integrated emission intensity is a measure of the hydroperoxide concentration [12]. For oxidised PP in the induction period, a direct proportionality between integrated chemiluminescence intensity and hydroperoxide concentration, as measured by iodometry, was found [13].

One successful photostabilisation strategy for this polymer involves the inhibition of the photochemistry and secondary free radical reactions of these impurities. This has been achieved by using photo-stable hydroperoxide decomposers such as certain sulphur compounds [14] or free radical scavengers, particularly the hindered amines [15, 16]. An over-riding consideration in the photo-oxidation and stabilisation of PP is the non-homogeneous nature of the oxidation reactions and also the solubility and migration of the stabilisers in the polymer [3, 17]. A particular problem in studies of the fundamental chemistry of stabilised polymers is the change in the nature and distribution of polymer oxidation products that occur when the stabiliser is present [11]. A more recent study of chemiluminescence from stabilised, photo-irradiated films was limited by the photochemical reactions of the stabiliser which occurred at short wavelength (220 nm) being used for irradiation [18].

We present a chemiluminescence study of PP in the very early stages of photo-oxidation and also PP containing a range of stabilisers with a known mechanism of action. From a comparison with the photo-oxidation of stabilised PP it is suggested that evidence has been found for zones of high reactivity in the polymer which are rapidly photodegraded in the induction period of the photo-oxidation.

**EXPERIMENTAL**

**Materials**
The polymer used in the present study were: Hostalen unstabilised PP in powder form (Hoechst: PPK 0160, MFI at 230°C/2.16 Kg, 0.9 Kg/10 min.), Hostalen commercial stabilised PP (Hoechst; PPN 1060F, MFI=1.7 ASTM D1238) in pellets form (HOPP), and a commercial stabilised extruded PP film (film A) of thickness 0.07 mm. The stabilisers used were: An ultra-violet light absorber (UV 531) (I); radical scavengers: (Irganox 1010) (II) and (Tinuvin 770) (III) from Ciba Geigy; Hydroperoxide decomposers: (Irgafos 168) (IV) from Ciba Geigy and (Hostalen SE2) (V) from Hoechst.

![Chemical structures](https://example.com/structures.png)

C₁₈H₃₇ - CO₂(CH₂)₇ S - (CH₂)₂ - O₂C - C₁₈H₃₇
Procedure
Mixing: PP powder was mixed with the stabiliser in cold hexane. The stabiliser was dissolved in hexane and mixed with PP powder thoroughly under vacuum using a rotary evaporator, while raising the temperature gradually to 60°C. The powder was dried in a vacuum oven at 50°C for 24 hours before melt pressing into films as described above (0.12 mm).

Film preparation: The films were pressed from unstabilised and stabilised PP powder and pellets (3 g), using glazing plates at 220°C. After 1 minute with the platens at constant pressure, a 15 x 10³ Kg (15 tonne) pressure was applied for one minute and then the platens quenched with water to room temperature. Strips of constant thickness were cut and used for the UV irradiation. The thickness of the films were: unstabilised PP = 0.12 mm; commercially stabilised melt pressed film B (HOPP) = 0.2 mm.

Irradiation: The polymer films were subjected to the exposure of UVA-340 lamps inside a cabinet with a controlled temperature of 50°C. The UVA-340 lamp simulates sunlight at the short wavelength band edge. Cumulative UV dose was measured by monitoring the changes in the UV spectrum of PP film [19]. This was linear with time of exposure and the dose rate was 0.72 J/cm² per hour.

Analysis of hydroperoxide by chemiluminescence: The formation of hydroperoxide during UV exposure was measured by a chemiluminescence technique. The apparatus used in this study is similar to that used in the most recent studies of polymer chemiluminescence, and is described elsewhere [20]. The chemiluminescence intensity from a polymer film was measured while heating at 10°C/min from 50°C under an atmosphere of nitrogen. This is shown in Figure 1 (curve 1). The resultant curve was integrated to give a measure of the total hydroperoxide concentration in the sample [12, 13]. In this way the change in hydroperoxide concentration with time of UV exposure could be determined. As the analysis resulted in melting of the film, each data point represents a new film sample. Some of the samples, after measuring the total chemiluminescence intensity, were cooled under nitrogen atmosphere to room temperature and the sample reheated. The peak due to decomposition of hydroperoxide was then absent (curve 2, Figure 1).

![Figure 1: Curve 1: Chemiluminescence intensity from an unstabilised polypropylene film which was photo-irradiated for 12 mins prior to heating from 50° to 180° under nitrogen. Curve 2: Chemiluminescence intensity after cooling the sample from curve 1 under nitrogen.](image)

Oxidation products: Infrared absorption spectra were run on a Perkin-Elmer FTIR 1600 spectrometer. The band at 1710 cm⁻¹ (carbonyl groups) was chosen for the determination of changes caused by the photo-oxidation. The carbonyl index is defined as the ratio of absorbance at 1710 cm⁻¹ to that at 2722 cm⁻¹. Attenuated total reflectance (ATR) spectra were obtained on a Mattson Sirius FTIR spectrometer using a KRS-5 crystal.

Surface analysis: X-ray photoelectron spectroscopy (XRS) with a PH1 560 apparatus (Mg anode, 1254 eV) was used to study the surface oxidation of polymer films. Multiplex spectra (100 eV bandpass) were collected in the carbon 1S (280-295 eV) and oxygen 1S (530-542 eV) regions and atomic concentration obtained using band areas and sensitivity factors in the PH1 software.

Extraction: Commercial stabilised polymer films
were extracted with analytical grade cold hexane for the time required to remove the additives.

Electron spin resonance: ESR spectra of irradiated films were run on a Bruker 200D X-band spectrometer fitted with a variable temperature unit operable from 100°K to 550°K.

RESULTS AND DISCUSSION

Figure 2 shows the changes in the integrated intensity of chemiluminescence and carbonyl index from unstabilised PP films as a function of UV irradiation time. The carbonyl index is constant up to around 20 hours of UV irradiation after which it rapidly increases, consistent with autoacceleration following the end of the oxidation induction period. In contrast, the integrated chemiluminescence intensity shows a rapid increase after only 14 hours UV irradiation. This reflects the sensitivity of chemiluminescence in measuring the hydroperoxide content of a PP film [13]. There is little information which may be obtained from the carbonyl index in the induction period, whereas the integrated chemiluminescence shows that the hydroperoxide concentration increases steadily in the induction period. In addition there appears to be complex behaviour at very short times of UV irradiation (Figure 3), where there is an increase in emission intensity immediately after UV irradiation commences. After reaching a maximum around 15 minutes irradiation, the integrated intensity decreases over several hours before increasing through the later stages of the induction period. Alternative explanations for the luminescence other than from hydroperoxide decomposition have been considered. For example, recombination luminescence may be observed from polyolefins when heated following high energy irradiation at low temperature [11]. This results from the thermal detrapping of electrons and their recombination with positive ions. When the PP films studied by ESR spectrometer following 15 and 30 minutes UV irradiation no signal attributed to either trapped electrons, free radicals or ions was observed at 120°K, 295°K or when subsequently heated to 453°K (the maximum temperature when measuring the integrated chemiluminescence). The sample, following irradiation, was also stable on storage as shown in Figure 4. This shows the chemiluminescence from a PP film immediately after 6 minutes irradiation (curve 1) and another identical film stored for four days in the dark prior to the measurement (curve 2). Curve 3 is that obtained on heating an unirradiated film. There is very little reduction in integrated emission intensity on storage following irradiation, and on the basis
of this and the ESR experiments, it is concluded that the chemiluminescence does not arise from a short lived radical or ionic species. The reproducibility of the observation from a number of different film suggest that it is not an artifact. If the chemiluminescence peak is due to the appearance of hydroperoxide as suggested above, then the following questions must be addressed: (i) can the hydroperoxide be detected by other analytical techniques; (ii) why is a peak observed in the hydroperoxide curve and does it have any significance in the overall photochemical stability of the polymer.

One possible explanation is that the peak results from surface oxidation. In view of the importance of the polymer surface in photo-oxidation, the results of sensitive surface analytical techniques such as FTR-ATR and X-ray photoelectron spectroscopy (XPS or ESCA) are shown in Figure 5. While both XPS and ATR-IR show the build-up of oxidation products in the later stages of the induction period, neither technique shows a growth in oxidation products over the first two hours of UV irradiation which is the period in which the maximum in integrated chemiluminescence intensity occurs. It therefore appears that the peak is not linked to a surface specific phenomenon. This is also supported by the observation that the total area under the chemiluminescence curves from the films in which the stabiliser was removed (Figure 7) increases in order of film thickness.

![Figure 4: Chemiluminescence curves from unstabilised polypropylene film.](image)

**Curve 1:** UV irradiated for 6 mins and heated under nitrogen immediately. **Curve 2:** As for 1 but stored for 4 days in the dark before heating under nitrogen. **Curve 3:** Unirradiated film heated under nitrogen.

**Figure 5: Increase in surface photo-oxidation products on UV irradiation of unstabilised polypropylene film:**
- $n_1^o$, atomic concentration of oxygen per 100 carbon atom from XPS;
- $n_2^o$, carbonyl absorbance at 1720 cm$^{-1}$ by ATR-FTIR.

It is significant that the magnitude of the peak in the chemiluminescence is apparently independent of the processing history or presence of processing stabilisers. It would be expected that the trace oxidation during processing would be very different for each of these films, leading to a different rate of photo-oxidation if hydroperoxides alone were the species responsible for photo-initiation [14].

If the photochemical instability of PP is linked to the sites of high reactivity then similar behaviour should also be observed from unstabilised, unprocessed PP powder during photooxidation. Figure 6 shows the integrated
Figure 6: Integrated chemiluminescence intensity from unstabilised polypropylene powder during photo-oxidation.

Chemiluminescence from the same powder used to press the unstabilised film which had the oxidation behaviour shown in Figure 3. It is seen that the growth in chemiluminescence is around 30 times faster from the powder than the film in the induction period. In addition as shown in Figure 7, the powder shows a more rapid increase in integrated intensity in the very early stages of photo-oxidation without the pronounced maximum that was seen from the film. The major difference between the powder and film is the surface area. Diffusion control of the oxidation of the polymer during the secondary stage of photolysis of hydroperoxides to ketones and their subsequent photo-oxidation would be less likely than from the melt pressed film. This secondary oxidation is therefore much faster from the powder and a continuous increase in hydroperoxide concentration is observed but at a slower rate than the initial photolysis.

In order to understand the origin of the above behaviour, the photo-oxidation of commercial stabilised extruded PP film (A) and a melt pressed film from stabilised PP pellets (B) has been studied before and after extraction to remove the stabilisers. Again the integrated chemiluminescence increases before the carbonyl index shows any change, (Figure 8). Film B obviously contains a more efficient stabilisation package than film A and both show a similar relation between the carbonyl index and integrated chemiluminescence. The most significant difference compared to unstabilised film is in the chemiluminescence intensity at short times where the characteristic maximum is totally absent from
stabilised films A and B. It appears that the stabiliser has either suppressed the formation of the hydroperoxide species responsible for the early peak, or interfered with the chemiluminescence analysis. To examine this, films A and B were extracted in hexane before UV irradiation. The chemiluminescence curves are very similar and the peak at short times is not observed, (Figures 9 and 10). The difference between the curves is believed to reflect the difference in thickness of the films. To determine if the stabilisers are affecting the chemiluminescence analysis a stabilised film was exposed to the UV radiation and then extracted with hexane and dried prior to the chemiluminescence analysis. As shown in Figure 11, the early peak in integrated chemiluminescence is now observed after heating in nitrogen. It therefore appears that the stabilisers are quenching the chemiluminescence, and the hydroperoxides are formed at short times of UV irradiation even in the presence of stabilisers.

Further understanding of the photo-initiation process may be achieved by examining the nature of the curves shown in Figures 10 and 11 within a kinetic framework for hydroperoxide formation and decomposition on UV irradiation [21]. It has been clearly demonstrated that the oxidation of PP films is non-uniform and from UV microscopy it has been shown that around 5% of the film oxidises at a very high rate compared to the remainder of the film [3]. This has been linked to the non-uniform distribution of catalyst residues in the polymer particles. Atactic material segregated at spherulite boundaries has also been shown to undergo a higher rate of oxidation.

Figure 9: Photo-oxidation of stabilised polypropylene film after hexane extraction to remove stabilisers: *, carbonyl index, film A; □, carbonyl index, film B; +, integrated chemiluminescence, film A; •, integrated chemiluminescence, film B.

Figure 10: The early stages of the integrated chemiluminescence curves during photo-oxidation: *, extracted film A (thickness 0.07mm); □, unstabilised meltpressed film (thickness 0.12mm); +, extracted film B (thickness 0.2mm).

In this investigation, photo-oxidation behaviour of all samples of PP has been consistent with a model of rapid hydroperoxide formation and photolysis in the induction period followed by slower secondary oxidation. The sites of this rapid hydroperoxide formation could be regions containing catalyst residues as have been implicated in the non-uniform thermo-oxidative behaviour of PP [3]. The observation that stabilisers present in two commercial films do not affect the early growth of hydroperoxide may be of significance to the ultimate improvement in the photostability of PP. These stabilisers are able to
also inhibited by the addition of the hindered phenol antioxidant (II). The induction period for this combination was greater than for the hindered phenol (II) alone; (iv) the thiopropionate ester (V) showed a greater photostability than all stabilisers other than the UV absorber and the hindered amine (III).

The results for the inhibition of carbonyl group formation may be compared to those for the formation of hydroperoxide groups as measured by integrated chemiluminescence. These are shown in Figures 12 and 14 and it is apparent that, while this technique is able to rank the stabilisers in the same order as the carbonyl index shown, there is a great increase in sensitivity by using the chemiluminescence analysis of hydroperoxide. Figure 13 shows the change in UV absorbance of several of the stabilised films during photo-oxidation. The most marked effect is the immediate decrease in absorbance at 245 nm in the film containing the hindered triphenyl phosphite.

Figure 11: The early stages of the integrated chemiluminescence from stabilised polypropylene film B:□, exposed to UV and then extracted prior to analysis; *, extracted prior to UV exposure.

Inhibit the secondary oxidation as given by the increased induction period for carbonyl growth and the lower rate of appearance of hydroperoxide.

The examination of the wide range of PP photostabilisers (radical scavengers, metal chelators, UV absorbers and peroxide decomposers) and their effect on the early formation of hydroperoxides from integrated chemiluminescence may lead to a better understanding of the photoprocesses involved and optimum photostabilisation. The following points are noted when different types of stabilisers are used: (i) the UV absorber (I) is the most efficient photostabiliser at the concentration used; (ii) all stabilisers studied except the hindered triphenyl phosphite (IV) increased the induction period for photo-oxidation. When the phosphite stabilised film was stored for three months prior to irradiation there was now a slight increase in photostability compared to the control film; (iii) the photosensitising effect of the phosphite (IV) was

Figure 12: The changes in the integrated chemiluminescence intensity from stabilised polypropylene films during UV exposure; *, control; +, 0.5% (IV); □, 0.5% (II); △, 0.5% (II+IV); ◆, 0.5% (V); ◊, 0.5% (III); *, 1% (I).
Figure 13: The UV absorbance at 275nm of stabilised polypropylene films against time of exposure; +, control; *, 0.5% (IV) (at 245nm), ○, polymer films containing 0.5% (IV) stored in the dark at room temperature for 3 months; x, 0.5% (II); φ, 0.5% (II+IV); Δ, 0.5% (V).

This wavelength corresponds to the absorption maximum of (IV) and indicates that it is photolysed immediately as UV exposure commences. Following the minimum absorbance there is a steady increase which corresponds to the increase in carbonyl index as shown in Figure 14. Addition of the free radical scavenging hindered phenol (II) to the sample along with (IV) prevents the rapid pro-oxidant effect of the triphenyl phosphite. Also when the sample containing (IV) was stored for three months prior to photolysis there was no decrease in the stabiliser concentration due to photolysis. The only other stabiliser which showed a decrease in UV absorbance was the hindered phenol (II). The decrease in absorbance from the sample containing both (II) and (IV) was very similar to that containing (II) alone, suggesting that only the consumption of (II) is responsible for the decrease in absorbance. Hindered phenols are known to be unstable to UV radiation [22] and may lead to peroxy dienones and thus increased photoinitiation.

The poor performance of the hindered triphenyl phosphite appears to be linked to its photoysis to yield a photoactivating species. This must be a free radical which can rapidly initiate oxidation of the PP since it can be very effectively inhibited by the hindered phenol (II). Scott [23] has suggested that the lack of photostabilisation of high density polyethylene by phosphites such as tris (nonyl phenyl) phosphite may be due to their inherent UV instability. The fact that the degradant behaviour of (IV) disappears after the material is stored for several months may be linked to this ability to reduce hydroperoxides to the corresponding alcohol. Figure 15 shows the chemiluminescence intensity at short times of irradiation from the unstabilised film, films containing the radical scavenging stabiliser (II) and
extracted films after UV exposure but prior to analysis. This result suggests that the free radical scavenger is preventing the termination reaction of alkyl peroxy radicals which leads to the chemiluminescence. A similar result was obtained by Billingham et al. in which Topanol CA (a hindered phenol free radical scavenger) was found to suppress the chemiluminescence from preoxidised natural rubber when it was heated in nitrogen [13]. Indeed this result, and the observation that a peroxide decomposing antioxidant (nickel diethyl dithiocarbamate) also suppressed chemiluminescence, have been used to support the mechanism of chemiluminescence involving termination of alkyl peroxy radicals which are produced by thermolysis of polymer hydroperoxides [24, 13]. It may be demonstrated that the free radical scavenger is interfering with the chemiluminescence analysis and not suppressing hydroperoxide formation during UV irradiation by simply extracting the film after UV irradiation but prior to analysis. This is also shown in Figure 15 and it is seen that there is a total recovery of the chemiluminescence intensity.

The sulphur based peroxide-decomposing antioxidant (V) would also be expected to suppress the chemiluminescence by decomposing hydroperoxides by a non-radical route [25]. Figure 16 shows that the integrated chemiluminescence following irradiation is not totally suppressed but is reduced to a steady value of around 20% of that from the unstabilised film. Of even greater interest is the observation that the emission is not totally recovered after the stabiliser is completely extracted prior to analysis. This suggests that this additive is suppressing hydroperoxide formation during UV irradiation. This was the only stabiliser studied which produced a decrease in the integrated chemiluminescence after the photolysed sample was extracted.

 Hindered amines based on piperidine such as Tinuvin 770 (III), are among the most efficient photostabilisers in PP and have been considered to function as photostable hydroperoxide decomposer and free radical scavengers, principally through their oxidation products such as the hindered nitroxyl radical and substituted hydroxylamine [15, 17]. Figure 16 shows that Tinuvin 770 itself is only a weak free radical scavenger and hydroperoxide decomposer since the chemiluminescence peak from the unextracted film is only reduced by about 40% compared to the total removal of chemiluminescence by the thiodipropionate ester (V). The data for the extracted films in Figure 17 clearly show that it has had no effect on the early formation of hydroperoxides during photo-oxidation. It is therefore concluded that additives such as (III) are not effective in preventing the initial rapid photo-oxidation which is believed to be occurring in the highly reactive centers, possibly associated with residual catalyst, in the PP films [21]. This is in contrast to the hypothesis that the hindered amines were of highly photoprotective efficiency because of their preferred association with hydroperoxides in these zones of high oxidisability [26]. They are, however, very efficient at preventing the propagation of the photo-oxidation following the photolysis of the initially
formed hydroperoxide, as evidenced by the very long induction period for the formation of both hydroperoxide (Figure 12) and carbonyl groups (Figure 14).

The results obtained from the photo-oxidation of PP containing the UV absorber Cyasorb 531 (I) are of particular interest. As shown in Figure 18 this additive had a marked effect on the photolysis of the hydroperoxide, but had little effect on the kinetics of formation [27].

It was noted that the only additive which lowered the concentration of hydroperoxide groups in the early stages of photo-oxidation was the thiodipropionate ester (V). The decomposition of the hydroperoxide groups cannot be initiating a free radical chain reaction since the induction period was increased. This is consistent with the reported mechanism for stabilisation of polyolefins by (V) in which the hydroperoxides are reduced to alcohols in the first step of a catalytic process [25].

The photostabilising efficiency of (V) is limited by the photo-dissociation of the resultant sulphoxide which will produce free radicals and thus a shorter induction period than expected. For this reason the thiol esters are frequently used in combination with a UV absorber [25]. As shown in Figures 12 and 14 it is less efficient than either the hindered amine (III) or UV absorber (I) in extending the induction period of the polymer film.

**CONCLUSION**

The observation of a peak in the integrated total chemiluminescence from PP film after photo-oxidation for short times indicates rapid formation and photolysis of hydroperoxides which cannot be detected by other analytical techniques such as
Figure 18: The early stages of the integrated chemiluminescence curves during photo-oxidation: , control; +1% (I).

FTIR-ATR or XPS. It was found that stabilisers in two commercial films did not prevent the rapid formation and photolysis of hydroperoxides in the induction period. From a kinetic analysis it is concluded that the very rapid rate of formation of hydroperoxides is consistent with a model of localised zones of high reactivity in the polymer. These may be linked to residual catalyst particles but no definite evidence was available to confirm this.

The photo-oxidation of unstabilised powder occurs at a much higher rate than from film since diffusion control of the oxidation is less likely. The rapid initial photolysis to form hydroperoxides and the secondary oxidation at a lower rate result in a shoulder in the total integrated chemiluminescence rather than the well defined peak observed from the thicker film.

The effect of different classes of stabilisers on the formation and photolysis of hydroperoxide in the very early stages of PP photo-oxidation has been studied by chemiluminescence. Several stabilisers interfered with the chemiluminescence analysis experiment. Hindered phenols efficiently scavenged the alkyl peroxy free radicals formed when the photo-oxidised sample was heated in nitrogen so that no chemiluminescence was observed. When the sample was extracted to remove the stabiliser following photo-oxidation, but prior to analysis, the full emission intensity was recovered, indicating that the hindered phenol could not inhibit the formation of hydroperoxides or their photolysis. Hindered piperidine additives were found to quench the emission only weakly and had no effect on the early stages of photo-oxidation. Their efficiency in photo-stabilising PP (as given by a low carbonyl index and hydroperoxide formation at long exposure times) had most probably resulted from their efficiency at inhibiting the propagation reaction of free radicals escaping the small highly-oxidised initiation zones. The 2-hydroxy benzophenone UV-absorber also successfully inhibited photo-oxidation. The integrated chemiluminescence at short UV exposure times showed that the additive greatly reduced the photolysis of the hydroperoxide in the early stages of the induction period but did not reduce the peak hydroperoxide concentration. The only additive which greatly reduced the peak in hydroperoxide concentration at short exposure times was a thiodipropionate ester. This also greatly reduced the chemiluminescence emission prior to extraction of the additive, consistent with the known mechanism of hydroperoxide decomposition by this stabiliser. In contrast to the photostabilisation by the thiodipropionate ester, another hydroperoxide decomposer, a hindered triphenyl phosphite, was found to be a prodegradant. This caused an immediate increase in hydroperoxide concentration in the film and a negligible induction period. This effect was removed by the addition of a hindered phenol to prevent peroxy radical attack on the stabiliser. It was also removed when the stabilised film was stored for three months prior to exposure, although the protective efficiency was much less than from the thiodipropionate ester.
From the diverse behaviour of the stabilised films it is apparent that the study of the formation of hydroperoxides in the very early stages of photodegradation can provide new information on the behaviour of stabilisers. While the effect of stabilisers on the peak in hydroperoxide concentration is consistent with a simple kinetic scheme for hydroperoxide formation and photolysis, the full quantitative interpretation of the data is limited by the non-homogeneous nature of photo-oxidation of the solid polymer.

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