The effects of pigments on the photostability of polyethylene

STEPHEN W. BIGGER, OSKAR DELATYCKI
Department of Industrial Science, The University of Melbourne, Parkville, 3052, Australia

The affect of carbon black and various colourizing pigments on the ultraviolet (UV) stability of high and low density polyethylene (HDPE and LDPE) was determined using a novel method for the analysis of oxygen uptake profiles. Samples were exposed to $0.27 \, W \, m^{-2}$ (measured at 340 nm) UV irradiation at $25.0 \pm 0.1° \, C$ in air at 1.0 atm. The usefulness of this method of assessment of UV stability is demonstrated. The method also enables the rapid collection of data that enable the comparison of the relative photostabilities of experimental and commercial formulations containing pigments and stabilizing additives. The results show that carbon black is an effective UV screening agent for HDPE when added at levels as low as 0.05% (wt/wt) and that increased photoprotection is achieved with increasing concentration of carbon black, up to 5% (wt/wt), above which there is no further significant increase in photostability. LDPE containing ultramarine blue pigment ($Na_7Al_6Si_6O_{24}S_3$) exhibits relatively poor photostability, whereas ferric oxide (Fe_2O_3) and chrome orange ($PbCrO_4 \cdot PbO$) pigments are better photo-stabilizers for this material. Cadmium sulphide (CdS) was found to photosensitize LDPE. A compound containing 0.10% (wt/wt) carbon black, 0.12% (wt/wt) titanium dioxide (TiO_2) and 1.78% (wt/wt) phthalocyanine green ($C_{33}H_2N_8Cl_{14}Cu$) is an effective formulation for the stabilization of LDPE. Formulations of LDPE containing ultramarine blue–TiO_2 or ferric oxide–carbon black combinations absorb heat on exposure and this may affect their photostability.

1. Introduction

Carbon black, opaque pigments and surface coatings all photoprotect polymers by reducing or eliminating the absorption of light by a chromophore [1]. Opaque pigments act as ultraviolet (UV) light screens by reflecting and/or absorbing potentially damaging radiation and thus limiting its penetration into the bulk of the polymer [2]. In general, the darker the pigment the greater is the protection that it imparts to the polymer. The absorption spectrum, dispersion, loading and the physical–chemical properties of the pigment are other important factors which affect its ability to protect the substrate [3].

Powdered metals (e.g. aluminium) enhance photo-stability of polymers, such as acrylonitrile–butadiene–styrene terpolymer, by the efficient reflection of UV light. However, metal powders may, depending on their size and distribution within the polymer matrix, cause detrimental effects by behaving as randomly placed mirrors which cause multiple light reflections throughout the bulk of the material. Many inorganic pigments such as oxides of iron (Fe_2O_3 and Fe_3O_4), chromic oxide (Cr_2O_3), zinc oxide (ZnO), titanium dioxide (TiO_2), titanium sulphides and ferrocyanides can be used to colour polymeric materials. Of these materials, iron and chromic oxides provide good UV stabilization for polyolefins [3]. In general, inorganic pigments impart adequate UV protection to materials of relatively thick cross-section [2, 4]. However, photodegradative effects, resulting from the addition of certain pigments, have been observed in thin films

containing a low concentration of pigment [5–8]. In practice, a reflecting pigment used in a protective surface coating is more effective than a dispersion of that pigment within the polymer [3].

The surface activity of a pigment may be influenced by its thermal history, the presence of organic anions and trace metal impurities, and the presence of water [3, 6]. Furthermore, some pigments may be affected by the presence of antioxidants in the polymer substrate [9]. Many organic pigments, such as azo- and thio-indigo compounds, anthraquinones, quinoacridones, isoindolinones, perylenes, dioxazines and phthalo-cyanines are widely used to colour polymers [3]. Phthalocyanine blue and green compounds show good UV absorption properties and are good photo-stabilizers under most conditions [10–12]. Other pig-ments, such as cadmium yellow (CdS/ZnO), possess light screening properties. These also promote photo-oxidative processes in polyethylene films, since an increase in carbonyl concentration and a dramatic reduction in elongation to break occurs upon UV irradiation in the presence of these materials [12].

The behaviour of many pigments in the course of polymer photooxidation is not fully understood due to the complexity of the reactions involved. The exception is TiO_2 in polyolefins. This combination has been studied extensively because of its wide use [2]. Formu-lations containing TiO_2 demonstrate relatively good photostability when compounded with an ultraviolet absorber (UVA stabilizer). Synergism is believed to occur in low density polyethylene (LDPE) films which

contain coated and refined rutile in the presence of primary and secondary antioxidants [9].

The two crystalline forms of TiO_2, anatase and rutile, have different reflectances at wavelengths above 340 nm. The rutile form is relatively inactive in polyethylene whilst the anatase form is very active and causes photodegradation [2, 9, 13, 14]. The formation of the oxygen radical anion and, possibly, other excited-state species, can occur via the electron transfer from excited-state TiO_2 to molecular oxygen. These species can react with water to form perhydroxyl or hydroxyl radicals which may subsequently abstract a proton from the polymer and initiate degradation [2, 3, 9, 15]. It has been suggested further that singlet oxygen may be produced in the presence of TiO_2 and this can react with water to produce hydrogen peroxide or, alternatively, it may attack unsaturated centres in the polymer to produce hydroperoxide species [16].

Titanium dioxide is not as effective a light screening agent as carbon black. Apart from its photosensitizing behaviour it has a tendency to scatter light throughout the polymer substrate and thus increase the likelihood of photochemical reaction. Carbon black, on the other hand, is found to be inert, light resistant and quite immobile in the polymer [17].

Carbon black operates by a number of mechanisms including free radical scavenging [18], deactivation of excited chromophores [19], peroxide decomposition [20] and the promotion of antioxidant effects [21]. Although carbon black functions primarily as a UV light screen, it is also an effective antioxidant protecting the polymer against thermal oxidation [22]. The mechanism by which it achieves this is believed to be related to its surface structure. In particular, labile hydrogen atoms, which originate from phenolic and other acidic groups that are present on the surface of carbon black, are capable of reacting with radicals which propagate oxidative degradation. In this sense carbon black functions as a chain terminating agent [23]. The free-radical properties of carbon black can be attributed to its irregular structure. Small scale structures, similar to graphite, exist but there appears to be no long-range order. This results in many free edges in the fused ring systems which constitute free radical active centres or radical traps [24].

The effectiveness of carbon black as a UV stabilizer is directly proportional to its concentration and uniformity of dispersion [25] and is inversely proportional to its average particle size [17, 18, 26]. Hawkins [20] has noted that carbon black may inhibit crystallization in its immediate vicinity. This results in a concentration of amorphous polymer about the carbon black particles and is equivalent to increasing the amount of stabilizer in the amorphous regions which are more susceptible to oxidation. It has been shown [18] that the lower the degree of surface structure, the lower is the reflectance of the carbon black. High structure furnace carbon blacks are less effective UV stabilizers due to their less desirable particle size distributions. This suggests that the high reflectivity that is associated with high structure carbon blacks is not as effective as the protection imparted by low structure

TABLE I Physical characteristics of the polymers used in the tests

	Material	
	HDPE	LDPE
MFI_5*	1.5	1.3
Density ($g\,cm^{-3}$)	0.954	0.921
$M_w \times 10^{-3}$ (a.m.u.)	120	39
Dispersity (M_w/M_n)	8.0	6.7

*units: g per 10 min at 190°C.

carbon blacks, which fill better the voids in the polymer structure.

It is believed that carbon black modifies the oxidative mechanism by increasing the kinetic chain length in the propagation stage [21, 27]. This hypothesis is supported by the observation that phenolic antioxidants are effective in the presence of low concentrations of furnace carbon black [22]. The activation of carbon black by reaction with oxygen or sulphur produces a very effective thermal stabilizer. This material is retained by the polymer under conditions which may lead to the loss of conventional antioxidants by evaporation or dissolution [22]. It has been established that (i) inactive (low oxygen content) carbon blacks can be blended successfully with amine type antioxidants; (ii) medium or highly oxidized (acidic) carbon blacks show an antagonistic effect when used in conjunction with an amine type stabilizer; (iii) acidic carbon blacks are usually antagonistic with phenolic antioxidants and (iv) basic carbon blacks when used in conjunction with either thioether or phenolic antioxidants show antagonism [23].

This paper presents the results of photooxidation experiments that were performed on samples of high and low density polyethylene (HDPE and LDPE) containing various colourizing and stabilizing additives. In particular, the stabilizing properties of carbon black as a function of its concentration is examined in order to determine an optimum level of this additive. The additives and concentrations that were chosen for the coloured samples are intended to represent those found in typical commercial formulations in an attempt to resolve some of the discrepancies that currently exist in published photostability data.

2. Experimental section

The weight average molecular weight M_w (a.m.u.), polydispersity (M_w/M_n), density ϱ ($g\,cm^{-3}$) and melt flow index MFI_5 (g per 10 min at 190° C) of the HDPE and LDPE samples that were used in these experiments are listed in Table I. Sample densities, MFI_5 values and oxygen gas transmission rates (GTR) through films made from the polymers were measured in accordance with the appropriate ASTM standards [28–30].

The film additives were titanium dioxide (organic coated rutile of 98% purity; average particle diameter 3.5×10^{-7} m), carbon black (medium to high structure furnace black), calcium stearate, an ultraviolet absorber 2-hydroxy-4-octyloxybenzophenone (UVA), and an antioxidant octadecyl-3-(3,5-ditertiarybutyl-4-hydroxyphenyl)propionate (AO). The

colourizing pigments used were phthalocyanine green ($C_{33}H_2N_8Cl_{14}Cu$), ultramarine blue ($Na_7Al_6Si_6O_{24}S_3$), ferric oxide (Fe_2O_3), chrome orange ($PbCrO_4 \cdot PbO$) and cadmium sulphide (CdS). The quantities of additives used are shown in the tables.

Formulations were compounded for 5 min on a Brabender Torque Rheometer heated to 180° C (all zones) at a mixing rate of 40 r.p.m. The mixed, molten materials were moulded at 180° C into thin films of average thickness $39.5 \pm 0.5 \mu m$, using a heated pneumatic press. The films were quench-cooled to approximately 20° C in 30 min and circular samples (3.806×10^{-2} m diameter) were cut.

3. Results and discussion

The oxygen uptake characteristics of the samples were determined by exposing them to UV irradiation in an apparatus consisting of two equivolume cells (reference and sample cells) which are separated by a differential pressure transducer. Details of the photo-oxidation apparatus are presented elsewhere [31]. In each experiment the sample was irradiated in air at atmospheric pressure by a 2.5 kW xenon arc lamp whose light intensity was measured at the wavelength of 340 nm and found to be $0.27 \, W \, m^{-2}$. The decrease in pressure in the sample cell, as oxygen was consumed, was monitored as a function of time in order to determine the oxygen uptake profile.

The incipient stage of the photooxidative process is of first order with respect to the partial pressure of oxygen [31, 32] and is described by the expression $n(t) = x_i(1 - e^{-kt})$. All results presented in this paper are based on 1 kg of polymer and, on this basis, $n(t)$ is the number of moles of oxygen that have reacted with the polymer at any given time t. The number of moles of reactive centres in the polymer that are sites for the reaction with oxygen and which are produced by the initiation and propagation steps is x_i, and k is a first-order rate constant.

The initial quantum yield for oxygen uptake, ϕ_i, is a measure of the inherent photostability of a polymeric formulation to UV irradiation [31, 32] and can be calculated from the parameters x_i and k. In particular, $\phi_i(\lambda) \propto mx_ik/A_s\lambda$ where m is the mass of the polymer sample (kg) and A_s is its surface area (m^2) exposed to the UV irradiation of wavelength λ (nm). Values of ϕ_i reported in this paper have been evaluated at the wavelength of 340 nm.

3.1. HDPE/carbon black formulations

Samples of HDPE stabilized with carbon black using a range of concentrations (see Table II) were photooxidized at $25.0 \pm 0.1°$ C. Table II lists the values of x_i, k, and ϕ_i obtained from the analyses of the oxygen uptake profiles of these samples together with values of the optical transmittance, $T\%$ (measured at 340 nm) [33], the gas transmission rate (GTR ($cm^3 mm/m^2$ 24 h atm)) of oxygen through the material [30], and the density of the samples, ϱ ($g \, cm^{-3}$) [28].

Shown in Fig. 1 are plots of x_i, k and ϕ_i against the decadic logarithm of the weight percent of carbon black in each formulation. As the concentration of carbon black increases there is a dramatic decrease in

the values of both x_i and ϕ_i. The upper asymptotic limits of x_i and ϕ_i are equal to those measured for unstabilized HDPE [31]. The value of the first-order rate constant k increase towards an upper asymptotic limit of approximately $1.3 \times 10^4 sec^{-1}$ which suggests that photooxidation is restricted to the surface sites [31].

The optical transmittance of HDPE decreases rapidly as the carbon black concentration increases and, in the case of the formulations studied, is reduced to zero at approximately 0.5% (wt/wt) loading of carbon black. This demonstrates the ability of carbon black to screen effectively the inner regions of the polymer. Furthermore, the results confirm that there is an inverse relationship between the film density and the gas transmission rate of oxygen [34]. The addition of as little as 0.001% (wt/wt) of carbon black to HDPE significantly reduces the film density and there is a corresponding decrease in the value of the GTR which suggests that carbon black particles reside preferentially in the amorphous regions of the polymer and inhibit the transport of oxygen. The transmission rate of oxygen can be related directly to the rate of oxygen consumption during photooxidation [35]. Recently, it was shown [36] that the rate of photo- and γ-induced oxidation of HDPE is reduced substantially by increasing the extent of drawing of the sample. This was attributed to the increase in the highly oriented fibrillar structure which occurs upon drawing and consequently reduces the diffusion rate and solubility of oxygen in the material. These observations, therefore, suggest a further mechanism by which carbon black can protect the material, as the transport of oxygen through a polymer is restricted mostly to the amorphous regions [37].

It has been reported [25, 38] that increased UV stability of polyethylene can be achieved by increasing the loading of carbon black in the material up to a level of approximately 5% (wt/wt). At concentrations greater than this there appears to be no further improvement in UV stability. Furthermore, it has been pointed out that the assessment of the photostability of samples containing levels of carbon black greater than 5% (wt/wt) cannot be made reliably using conventional tests, such as brittle point measurement, due to the large reduction in physical properties of the material containing higher levels of carbon black [38]. The value of the initial quantum yield for oxygen uptake approaches asymptotically a lower limit of approximately 1.8×10^{-2} as the concentration of carbon black increases (see Fig. 1 and Table II) and no significant increase in stabilization is achieved for concentrations of carbon black greater than approximately 5% (wt/wt).

3.2. Coloured LDPE formulations

The results of the analyses of oxygen uptake profiles for a number of coloured LDPE formulations are given in Table III. The formulations are listed in the order of decreasing photostability, as determined by the initial quantum yield for oxygen uptake. Each formulation contained 2.4% (wt/wt) of pigment and a base stabilization system consisting of 0.05% (wt/wt)

TABLE II Values of x_i, k, ϕ_i, density, ϱ (g cm^{-3}), optical transmittance (%) at 340 nm and gas transmission rate, GTR, of oxygen $(\text{cm}^3 \text{mm/m}^2 24 \text{h atm})$ for HDPE stabilized with carbon black

% carbon black (wt/wt)	0	0.001	0.01	0.02	0.05	0.10	0.20	0.50	1.0	2.0	5.0	10.0	20.0	30.0
Density (g cm^{-3})	0.954	0.916	0.919	0.920	0.921	0.922	0.923	0.928	0.930	0.931	0.950	0.978	1.016	1.082
$x_i \times 10^3$ (mol kg^{-1})	10.5	6.94	4.98	4.36	3.40	2.77	2.05	1.48	1.08	0.84	0.64	0.52	0.48	0.44
$k \times 10^5$ (s^{-1})	1.87	2.08	2.43	2.58	2.97	3.42	4.14	5.52	9.23	11.7	12.5	13.0	13.2	13.2
$\phi_i \times 10^2$	8.86	6.08	3.53	3.09	2.53	2.26	2.04	1.93	1.92	1.91	1.91	1.89	1.88	1.87
Transmittance (%)*	57.0	55.8	52.3	41.3	20.6	6.9	1.4	–	–	–	–	–	–	–
GTR (oxygen)	35.8	30.1	29.4	28.8	28.7	28.4	28.2	27.5	27.1	26.9	25.3	23.8	23.2	23.1

*Transmittance of samples measured at 340 nm.

Maximum errors: $\varepsilon(\varrho) = \pm 1\%$, $\varepsilon(x_i) = \pm 1\%$, $\varepsilon(k) = \pm 2\%$, $\varepsilon(\phi_i) = \pm 4\%$ and $\varepsilon(\text{GTR}) = \pm 3\%$. All photooxidation experiments were carried out in air at 1.0 atm and 25.0 $\pm$ 0.1° C. Light intensity in all tests: 0.27 W m^{-2}. Base stabilization of samples: 0.05% (wt/wt) AO and 0.01% (wt/wt) calcium stearate.
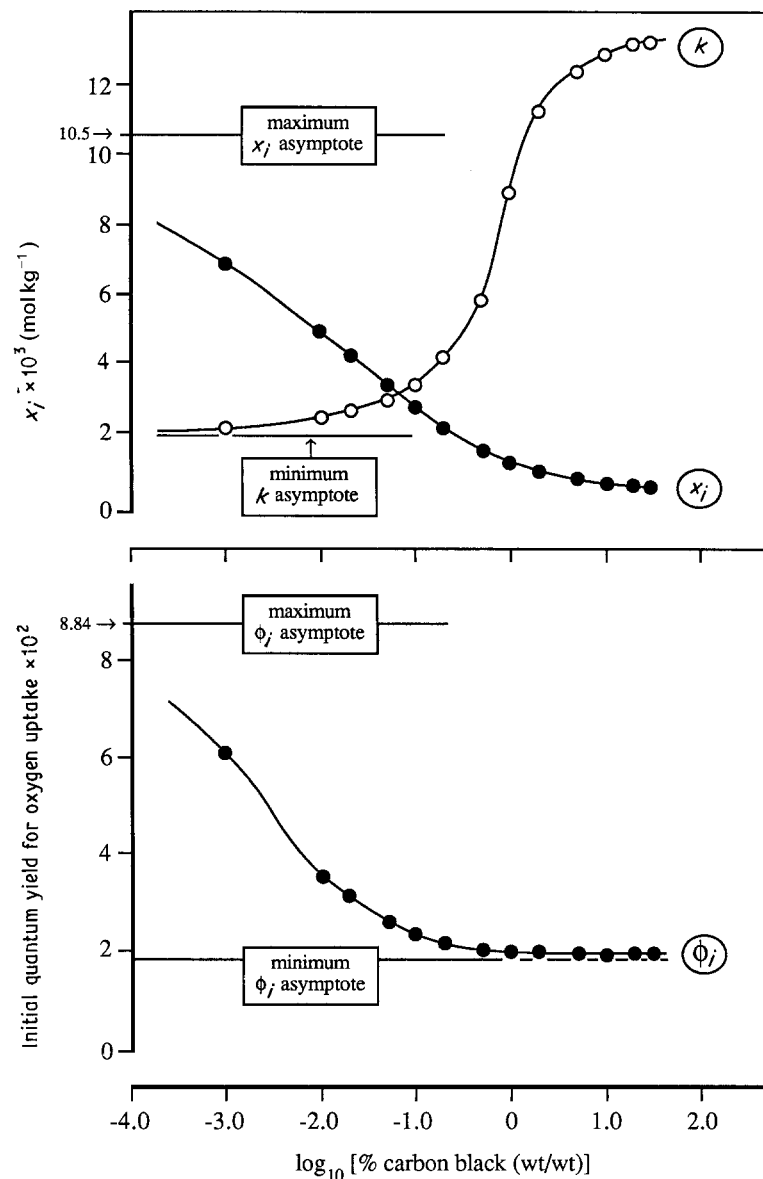

Figure 1 The parameters x_i, k and ϕ_i plotted against the decadic logarithm of the percentage of carbon black in HDPE.

AO, 0.10% (wt/wt) calcium stearate and 0.25% (wt/wt) UVA.

Several of the darker formulations that were examined showed a significant temperature increase when initially exposed to the UV source. This is attributed to the absorption of heat by these samples which increases the temperature of gas in the cell and causes an initial rise in the sample cell pressure [31]. The initial increase in the sample temperature, ΔT (° C), was calculated from the observed pressure increment by assuming the ideal gas law. The value of ΔT for each formulation tested is listed in Table III.

The results shown in Table III, indicate that, with the exception of cadmium sulphide, all of the examined pigments increase the photostability of the substrate compared with the unpigmented (control) sample. This is attributed mainly to the screening abilities of the pigments [2, 3, 39]. The decreasing order of stability established in this study is consistent with results reported in the literature [12] for accelerated weathering tests performed on coloured LDPE films of similar formulation. Furthermore, the antagonism between cadmium sulphide and a substituted benzotriazole (UVA) stabilizer has been reported [12] and the results

TABLE III Coloured LDPE formulations

Colour	Pigment	% pigment (wt/wt)	% TiO$_2$ (wt/wt)	% carbon black (wt/wt)	density (g cm^{-3})	ΔT (°C)	$x_i \times 10^3$ (mol kg^{-1})	$k \times 10^5$ (sec^{-1})	$\phi_i \times 10^2$
Green(I)	phthalocyanine green C$_{33}$H$_2$N$_8$Cl$_{14}$Cu	1.78	0.12	0.10	0.945	0.526	4.40	2.51	2.07
White	titanium dioxide TiO$_2$	–	2.00	–	0.930	0.010	5.94	2.38	2.18
Brown	ferric oxide Fe$_2$O$_3$	1.99	–	0.01	0.916	0.329	6.28	1.56	3.89
Orange	chrome orange PbCrO$_4$. PbO	2.00	–	–	0.910	0.074	7.10	1.97	4.57
Green(II)	phthalocyanine green C$_{33}$H$_2$N$_8$Cl$_{14}$Cu	1.88	0.12	–	0.919	0.024	8.65	1.44	5.14
Blue	ultramarine blue Na$_7$Al$_6$Si$_6$O$_{24}$S$_3$	1.88	0.12	–	0.922	0.281	4.04	6.82	5.84
Clear	nil pigment	–	–	–	0.921	0.033	8.78	1.38	14.1
Yellow	cadmium sulphide CdS	1.88	0.12	–	0.925	0.047	13.7	3.34	19.6

All photooxidations carried out in air at 1.0 atm and 25.0 ± 0.1° C. Light intensity 0.27 W m^{-2} (measured at 340 nm). Maximum errors: $\varepsilon(x_i) = \pm 1\%$; $\varepsilon(k) = \pm 2\%$; $\varepsilon(\phi_i) = \pm 3\%$. Base stabilization: 0.10% (wt/wt) calcium stearate, 0.05% (wt/wt) AO and 0.25% (wt/wt) UVA.

of the present study suggest that a similar antagonistic effect is obtained between cadmium sulphide and the ultraviolet absorber 2-hydroxy-4-octyloxybenzophenone. It is believed also that antagonism can arise as a result of additive–additive interactions between CdS and the antioxidant which forms part of the base stabilization [40]. It is interesting to note, however, that CdS, under certain circumstances, may behave as a mild photostabilizer in polyethylene and it has been reported [41] that CdS inhibits the formation of hydroperoxides and carbonyl groups during irradiation. The anomalous behaviour of CdS is attributable to its commercial formula. These observations emphasize the importance of considering all components of the system and their likely actions and interactions when assessing the photostability of a given formulation [15].

A value of ϕ_i equal to 0.434 was obtained for a commercially extruded HDPE coating containing 2.0% (wt/wt) CdS, 0.3% (wt/wt) of the hindered amine light stabilizer bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate and 0.3% (wt/wt) of the chelate nickel bis[o-ethyl-(3,5-ditertiarybutyl-4-hydroxybenzyl)]phosphonate. The value of ϕ_i found for this formulation is significantly higher than the values for both the unstabilized HDPE that contained only base stabilization ($\phi_i = 8.86 \times 10^{-2}$) and the LDPE yellow (see Table III). Possible explanations for this behaviour are: (i) cadmium sulphide is more antagonistic with the hindered amine–nickel chelate stabilizer system than with the UVA stabilizer; (ii) the commercial formulation may have been slightly more thermally degraded as a result of the extrusion process or (iii) TiO$_2$ which is present in the LDPE formulation provides additional protection of the material by screening the lower surface regions. The last explanation is supported by the fact that the value of k is relatively large which suggests that reaction occurs at sites that are close to the polymer surface [31].

Reported results of outdoor weathering tests that were performed on HDPE samples suggest that phthalocyanine green-pigmented samples have superior photostability to formulations containing a similar concentration (1% (wt/wt)) of cadmium red or cadmium yellow [42]. There is an approximate twofold difference in outdoor lifetimes and this is contrary to the results of another investigation [43] which suggests that there is no appreciable difference between cadmium- and phthalocyanine green-pigmented formulations [35]. The results shown in Table III suggest that the addition of 1.88% (wt/wt) of CdS to LDPE leads to an approximate four-fold increase in the value of ϕ_i.

Outdoor weathering tests, performed on bent strips of pigmented HDPE indicate decreasing relative stabilities in the order of brown, green and blue colourations [44] and this trend is also apparent in Table III. It is important to note that the results, which are reported in the literature for these formulations, must be interpreted cautiously since the levels of pigmentation are not comparable in all cases. This may account for the reported [44] superior photostability of the orange formulation over that of the brown which is contrary to the results listed in Table III.

The results reported for outdoor weathering experiments on HDPE rank the photoprotective capabilities of TiO$_2$ (both anatase and rutile) below that of phthalocyanine green [42]. It is, therefore, likely that this is the result of the decreased compatibility of TiO$_2$ with the more crystalline substrate or the destruction of crystallinity close to the TiO$_2$ particles. This may explain the observed inferior stability of HDPE containing 0.3% (wt/wt) carbon black and 7.0% (wt/wt) TiO$_2$ ($\phi_i = 3.03 \times 10^{-2}$) compared with HDPE containing 0.3%(wt/wt) carbon black only ($\phi_i = 2.00 \times 10^{-2}$). It is apparent that TiO$_2$ is less compatible with HDPE than it is with LDPE in which it imparts significant stability at a level of about 2% (wt/wt). The lower crystallinity of LDPE compared with HDPE implies that, on addition of TiO$_2$, the LDPE will have a lower loss of crystallinity compared with the HDPE and this may explain the greater compatibility of TiO$_2$ with LDPE.

The addition of 0.1% (wt/wt) of carbon black to

a LDPE formulation containing phthalocyanine green significantly increases its photostability. The enhanced photostability is almost an additive effect since the value of ϕ_i decreases by 3.06×10^{-2} which is comparable to the value of ϕ_i obtained for an HDPE sample containing the same concentration of carbon black ($\phi_i = 2.26 \times 10^{-2}$). The slight difference may be attributed to (i) the assumption that the value of ϕ_i for a carbon black concentration of 0.1% (wt/wt) is equal for both the HDPE and LDPE or (ii) the higher phthalocyanine green concentration in the formulation containing no carbon black. Under certain circumstances phthalocyanine green is believed to be a photosensitizing agent in polyethylene [45]. The results in Table III show a decrease in the value of the initial quantum yield for oxygen uptake upon the addition of phthalocyanine green to an unpigmented formulation containing the same base stabilization system. It can be concluded that the presence of the UVA-type stabilizer significantly reduces any photosensitizing effect of the phthalocyanine green.

Examination of Table III shows that the blue and brown formulations have values of ΔT that are significantly higher than the rest. During photo-oxidation these materials attain higher temperatures due to their ability to absorb greater quantities of heat from the source of irradiation. It is expected that during the accelerated and outdoor weathering of these materials, degradative effects due to heating of the material are of greater significance. The relative UV stabilities of these formulations, as determined by accelerated testing [12] or outdoor weathering studies [44], would need to be interpreted accordingly.

A dramatic heating effect is observed in the case of the green(I) formulation which is derived from the green(II) formulation by the addition of 0.1% (wt/wt) of carbon black (see Table III). The green(I) formulation attains a higher temperature during its exposure and it is reasonable to assume that it will undergo more rapid photooxidation due to the increased rate of oxygen transport through the polymer and the increased extent of thermal degradation. However, the green(I) formulation shows superior photostability which may be attributed to the combination of the multifunctional stabilizing ability of carbon black as well as the UV screening properties of TiO_2.

4. Conclusions

The oxygen uptake apparatus used in this work provides a quick, sensitive and effective method for obtaining numerical information about the relative UV stabilities of polyethylene compounds containing numerous combinations of pigments and stabilizing additives. The photochemistry of formulations such as these, is often complex and this causes considerable difficulty in interpreting the experimental results.

The results show that the addition of carbon black to a polymer formulation causes an increase in its density and a corresponding decrease in its transmission rate of oxygen. The low values of ϕ_i coupled with the relatively high values of the first-order rate constant, k, for films containing carbon black are consistent with the proposed stabilization mechanism

whereby carbon black restricts photooxidation to the immediate surface sites by preventing both oxygen and light from penetrating into the deeper regions of the polymer. Increased photoprotection is observed with increasing concentration of carbon black up to a 5% (wt/wt) loading, above which there is no further significant increase in photostability. The method of assessment used in the present work allows the determination of the photostabilities of samples containing relatively high concentrations of additives. The physical–mechanical properties of such samples may be severely reduced by high concentrations of additives and cannot serve as a measure of their expected outdoor performance.

Most of the pigments studied in the present work impart considerable photoprotection to polyethylene and this is attributable to their ability to screen UV light. A notable exception is CdS which behaves antagonistically in the presence of the UVA stabilizer, 2-hydroxy-4-octyloxybenzophenone and the antioxidant octadecyl-3-(3,5-ditertiarybutyl-4-hydroxyphenyl)propionate. On the other hand, the addition of this UVA to a formulation containing phthalocyanine green appears to offset dramatically the photosensitizing propensity of this pigment. Under the conditions used in this study, the phthalocyanine green formulation has a value of ϕ_i which is approximately four times less than that calculated for the formulation containing CdS.

The results also suggest that the photostability of polyethylene containing TiO_2 is influenced markedly by the morphology of the substrate. Furthermore, formulations that contain carbon black or certain pigments absorb a considerable quantity of heat during their exposure. This would need to be taken into account when interpreting their relative photostabilities.

References

1. D. J. CARLSSON and D. M. WILES, *J. Radiation Curing* October, 1975, p. 2.
2. A. KING, *Plast. Polym.* **36** (1968) 195.
3. B. RANBY and J. F. RABEK, "Photodegradation, Photooxidation and Photostabilization of Polymers' (Wiley-Interscience, London, 1975).
4. R. D. DEANIN, S. A. ORROTH, R. W. ELIASEN and T. N. GREER, *Polym. Eng. Sci.* **10** (1970) 228.
5. F. J. GOLEMBA and J. E. GUILLET, *J. Paint Technol.* **41** (1969) 315.
6. G. IRICK, *J. Appl. Polym. Sci.* **16** (1972) 2387.
7. F. H. McTIGUE and M. BLUMBERG, *Appl. Polym. Symp. No. 4* (1967) 175.
8. H. A. TAYLOR, W. C. TINCHER and W. F. HAMNER, *J. Appl. Polym. Sci.* **14** (1970) 141.
9. N. S. ALLEN, D. J. BULLEN and J. F. McKELLAR, *J. Mater. Sci.* **12** (1974) 1320.
10. K. P. S. KWEI, *J. Appl. Polym. Sci.* **12** (1968) 1543.
11. K. P. S. KWEI and J. K. KWEI, *J. Appl. Polym. Sci.* **12** (1968) 1551.
12. M. MLINAC, J. ROLICH and M. BRAVAR, *J. Polym. Sci. Symp. No. 57* (1976) 161.
13. N. S. ALLEN, J. F. McKELLER, G. O. PHILLIPS and D. G. M. WOOD, *J. Polym. Sci. B* **12** (1974) 241.
14. N. S. ALLEN, J. F. McKELLER and D. G. M. WOOD, *J. Polym. Sci. A1* **13** (1975) 2319.
15. N. S. ALLEN, in "Degradation and Stabilization of Polyolefins", Chapter 8, edited by N. S. Allen (Applied Science Publishers Ltd., London, 1983).

16. S. P. PAPPAS and R. M. FISCHER, *J. Paint Technol.* **46** (1974) 65.
17. F. H. WINSLOW, W. MATREYEK and A. M. TROZZOLO, *SPE Tech. Pap.* **18** (1972) 766.
18. F. R. WILLIAMS, M. E. JORDON and E. M. DANNENBERG, *J. Appl. Polym. Sci.* **9** (1965) 861.
19. M. HESKINS and J. E. GUILLET, *Macromolecules* **1** (1968) 97.
20. W. L. HAWKINS, *Polym. News* **4** (1977) 132.
21. W. MATREYEK and F. H. WINSLOW, *ACS Div. Polym. Chem., Polym. Prep.* **16** (1975) 606.
22. W. L. HAWKINS, *J. Polym. Sci., Symp.* **57** (1976) 319.
23. E. KOVACS and Z. WOLKOBER, *ibid.* **57** (1976) 171.
24. M. SZWARC, *J. Polym. Sci.* **19** (1956) 589.
25. V. T. WALLDER, W. J. CLARKE, J. B. DeCOSTE and J. B. HOWARD, *Ind. Eng. Sci.* **42** (1950) 2320.
26. J. F. AMBROSE, *Brit. Plast.* **30** (1957) 446.
27. J. MITCHELL Jr. and L. R. PERKINS, *Appl. Polym. Symp. No. 4.* (1967) 167.
28. Test Method D792-86, *ASTM Standards* **8** (1987) 488.
29. Test Method D1238-86, *ASTM Standards* **8** (1987) 552.
30. Test Method D1434-82, *ASTM Standards* **8** (1987) 611.
31. S. W. BIGGER and O. DELATYCKI, *J. Polym. Sci., Polym. Chem. Edn* **25** (1987) 3311.
32. S. W. BIGGER and O. DELATYCKI, *Polymer* **29** (1988) 1277.
33. Test Method D3349-86, *ASTM Standards* **8** (1987) 70.
34. H. ALTER, *J. Polym. Sci.* **57** (1962) 925.
35. G. R. COTTEN and W. SACKS, *J. Polym. Sci. A1* **1** (1963) 1345.
36. T. TINCER, I. CIMEN and G. AKAY, *Polym. Eng. Sci.* **26** (1986) 479.
37. A. S. MICHAELS and H. J. BIXLER, *J. Polym. Sci.* **50** (1961) 393.
38. J. B. HOWARD and H. M. GILROY, *Polym. Eng. Sci.* **9** (1969) 286.
39. N. S. ALLEN and J. F. McKELLAR, *Chem. Soc. Revs.* **4** (1975) 533.
40. N. S. ALLEN, J. L. KOTECHA, A. PARKINSON, F. F. LOFFELMAN, M. M. RAUHUT and P. V. SUSI, *Polym. Degrad. Stab.* **10** (1985) 1.
41. G. PENOT, R. ARNAUD and J. LEMAIRE, *Polym. Photochem.* **2** (1982) 55.
42. H. M. QUACKENBOS and H. SAMUELS, *Appl. Polym. Symp. No. 4.* (1967) 155.
43. R. J. MARTINOVICH, *SPE Prep.* **9** (1963) 1.
44. F. S. KAUFMAN Jr., *Appl. Polym. Symp. No. 4* (1967) 131.
45. Yu. A. ERSHOV, *Kinet. Katal.* **11** (1970) 609.