Effects of temperature and the partial pressure of oxygen on the rate of photooxidation of polyethylene

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Using a novel apparatus, the uptake of oxygen by high density polyethylene (HDPE) and low density polyethylene (LDPE) when exposed to ultraviolet (u.v.) irradiation, was measured in a series of experiments that are intended to test the effects of u.v. stabilizer, temperature and the partial pressure of oxygen on the rate of polymer photooxidation. It is shown that the rate of photooxidation approximately doubles for every 10°C increase in temperature. The kinetics analyses of the oxygen uptake curves, at different initial partial pressures of oxygen, indicate that at low oxygen pressures the photooxidative process is controlled by the available oxygen. As the partial pressure of oxygen is increased, a critical value is reached above which the incipient stage of photooxidation is limited by the initial number of reactive (or oxidizable) centres in the polymer. This behaviour is formally quantified and related to the currently accepted mechanism of polymer photooxidation.

(Keywords: photooxidation; uptake of oxygen; partial pressure; temperature dependence)

INTRODUCTION

The reaction kinetics of polymer oxidation have been extensively studied and reported in the literature [1–9]. The accepted mechanisms for photo- and thermal oxidation of polymers are similar in many respects. Expressions that describe the rate of oxygen uptake during photooxidation can be derived by considering the mechanistic steps of initiation, propagation and termination[4] which are shown by equations (1)–(5).

Initiation	$PH + h\nu \rightarrow P^{\bullet} + H^{\bullet}$	k_1	(1)
Propagation	$P^{\bullet} + O_2 \rightarrow POO^{\bullet}$	k_2	(2)
	$POO^{\bullet} + PH \rightarrow POOH + P^{\bullet}$	k_3	(3)
Termination	$2P^{\bullet} \rightarrow$ inactive products	k_4	(4)
	$2POO^{\bullet} \rightarrow$ inactive products	k_5	(5)

If v_i, v_p and v_t are the rates of initiation, propagation and termination, respectively, and I_a is the intensity of light that is absorbed by the polymer during photooxidation then equations (6)–(8) hold under steady-state conditions.

$$v_i = k_1 I_a \tag{6}$$

$$v_p = k_2[P^{\bullet}][O_2] - k_3[POO^{\bullet}][PH] \tag{7}$$

$$v_t = v_p = v_i \tag{8}$$

In the case where photooxidation is carried out under conditions of low oxygen concentration, termination occurs almost exclusively by the recombination of macroradicals as indicated by equation (4). Under these conditions, the concentration of polymer radicals ($P^{\bullet}$), particularly in the terminating stages of the reaction, is far in excess of the polymer peroxyl radicals ($POO^{\bullet}$). It follows from equation (4) that $[P^{\bullet}] = (v_t/k_4)^{1/2}$ from which equation (9) is derived.

$$-d[O_2]/dt = k_2(k_1 I_a/k_4)^{1/2}[O_2] \tag{9}$$

Equation (9) indicates that, under conditions of constant light intensity and low oxygen concentration, the rate of oxygen uptake is proportional to the concentration of available oxygen that is present at any given time. In this case oxygen is the limiting reagent and thus controls the extent of the reaction.

If polymer photooxidation is carried out in the presence of surplus oxygen then termination occurs almost exclusively by the recombination of polymer peroxyl radicals ($POO^{\bullet}$) as shown by equation (5). It is also true that, under these conditions, the rate of combination of polymer radicals ($P^{\bullet}$) with oxygen (equation (2)) is relatively fast and so $[P^{\bullet}] \ll [POO^{\bullet}]$. It follows from equation (5) that under the conditions of surplus oxygen $[POO^{\bullet}] = (v_t/k_5)^{1/2}$. An expression for the rate of oxygen uptake by the polymer in the presence of surplus oxygen (equation (10)) is obtained by combining equations (6)–(8).

$$-d[O_2]/dt = k_3(k_1 I_a/k_5)^{1/2}[PH] \tag{10}$$

Hence, under conditions of constant light intensity and surplus oxygen, the rate of oxygen uptake is proportional to the concentration of polymeric species that are available for the initiation process. In more general terms this result suggests that the rate of oxygen uptake is proportional to the number of reactive centres at any given time that are available for the chemical combination of oxygen with the polymer.

Equations (9) and (10) show that oxygen uptake under steady-state conditions is a first order process. This

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process undergoes a transition as the oxygen concentration of the system changes. The rate of photooxidation of the polymer depends on the ratio of available oxygen to the number of reactive centres, which is determined by the partial pressure of oxygen in the gas phase.

The effects of the partial pressure of oxygen and the temperature on the rate of photooxidation are of considerable importance in relation to the study of polymer degradation[10-13]. Grassie and Weir[10] have shown that a typical Arrhenius plot of the logarithm of photooxidation rate *versus* the reciprocal of the absolute temperature can be used to determine the activation energy that is associated with the photolysis of polystyrene. Furthermore, Heacock and co-workers[14] have measured the total percentage of oxygen that is incorporated in low density polyethylene upon exposure to ultraviolet (u.v.) irradiation and found that it is possible to calculate an activation energy of this process by means of an Arrhenius plot of the experimental data.

We have developed an apparatus to study the photooxidation of polymeric samples[15]. The apparatus provides rapidly a measure of the rate of photooxidation by monitoring the oxygen uptake of the sample upon its exposure to u.v. light. The early stage of the photooxidative process is of first order with respect to the partial pressure of oxygen and is described by the expression: $n(t)=x_i(1-e^{-kt})$. In this expression $n(t)$ is the number of moles of oxygen that have reacted with the polymer at any given time t. (All such expressions appearing in this paper are based on 1 kg of polymer.) The number of moles of reactive centres in the polymer that are produced by the initiation and propagation steps (and which are sites for the reaction with oxygen) is x_i, and k is a first order rate constant.

The initial quantum yield for oxygen uptake upon u.v. exposure, ϕ_i, is a measure of the inherent photostability of a polymeric formulation[15] and can be calculated readily from the parameters x_i and k. In particular, $\phi_i(\lambda) \propto m x_i k / A_s \lambda$, where m is the mass of the polymer sample (kg) and A_s is the surface area (m^2) of the sample exposed to the incident u.v. irradiation of wavelength λ (nm). An expression for the initial rate of photooxidation, v_0, can be obtained by differentiating the function $n(t)$ and evaluating it at time $t=0$, in which case $v_0 = x_i k$.

The effect of an u.v. absorber on the photostability of low density polyethylene (LDPE) and high density polyethylene (HDPE) over a range of temperatures and partial pressures of oxygen was measured and analysed using the mathematical model for oxygen uptake, outlined above, which pertains to the early stages of photooxidation. The results are presented and discussed in this paper.

EXPERIMENTAL

The oxygen uptake characteristics of samples of LDPE and HDPE were determined by their exposure to u.v. irradiation in an apparatus which consists of two equivolume cells (reference and sample cells), which are separated by a differential pressure transducer. The samples were irradiated by a 2.5 kW xenon arc lamp and the resulting decrease in pressure in the sample cell was monitored as a function of time in order to determine the oxygen uptake profile. Further details of the apparatus are presented elsewhere[15].

Table 1 gives the physical characteristics of the LDPE and HDPE materials that were examined: 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$_s$ (g/10 min at 190°C). All MFI$_s$ values and sample densities were measured in accordance with the appropriate ASTM standards[16,17]. All formulations were stabilized with 0.01% (w/w) calcium stearate and 0.05% (w/w) of the antioxidant octadecyl-3-(3,5-ditertiarybutyl-4-hydroxyphenyl)propionate and were compounded for 5 min in a Brabender Torque Rheometer heated to 180°C (all zones) at a mixing rate of 40 rev min^{-1}. The mixed, molten polymers were moulded into thin films in a pneumatic press which was pre-heated to 180°C. The films were quench-cooled to approximately 20°C in 30 min and samples were cut from the films using a circular cutter (3.806×10^{-2} m diameter).

Some of the samples were u.v. stabilized using the u.v. absorber 2-hydroxy-4-octyloxybenzophenone. Ultraviolet absorber levels of 0.25% (w/w) and 0.40% (w/w) were used for the LDPE and HDPE samples, respectively.

LDPE containing 0.25% (w/w) of u.v. absorber and HDPE containing only the base stabilizers were used in a series of photooxidation experiments that were performed over the temperature range 25–70°C. The gas used in these experiments was air at 1.0 atm and samples were irradiated with u.v. light of intensity of 0.27 W m^{-2} (measured at 340 nm). The temperature during the photooxidation process was maintained constant to within ±0.1°C for runs that were carried out close to ambient conditions and to within ±1.5°C at the higher temperatures examined. Temperatures in the experiments were limited to a maximum of 70°C due to complications caused by significant thermal oxidation occurring simultaneously with photooxidation at higher temperatures. Under such conditions the interpretation of results is difficult.

The effect of the partial pressure of oxygen on the rate of photooxidation was determined by using gas mixtures of various oxygen/nitrogen ratios. Polymer samples of the mass of 0.1662 ± 0.0007 g were degassed by pumping out the sample cell. The system was then purged with the gas mixture and the pressure in the sample and reference cells was adjusted to the initial value of 1.0 atm. Samples were equilibrated in the gas mixture for a period of 10 h prior to photooxidation. Photooxidations were carried out at 25.0±0.1°C under conditions of constant light intensity, I_a, of either 0.27 or 0.47 W m^{-2} (measured at 340 nm).

RESULTS AND DISCUSSION

Effect of temperature on photooxidation rate

Table 2 gives the results that were obtained from a series of experiments that were carried out on samples of

Table 1 Physical characteristics of the polymers

Material	$M_w \times 10^{-3}$ (a.m.u.)	Dispersity (M_w/M_n)	Density (g cm^{-3})	MFI$_s$ (g/10 min at 190°C)
LDPE	39	6.7	0.921	1.3
HDPE	120	8.0	0.954	1.5

Table 2 Effect of temperature on the photooxidation kinetics of LDPE and HDPE formulations

	LDPE (0.25% (w/w) of u.v. absorber) $I_a = 0.27\ \mathrm{W\,m^{-2}}$				HDPE (no u.v. absorber) $I_a = 0.27\ \mathrm{W\,m^{-2}}$			
T (K)	298.0	322.9	337.7	340.6	298.0	322.9	336.4	342.0
$x_i \times 10^3$ (mol kg^{-1})	8.776	9.149	9.389	9.484	10.49	10.83	11.06	11.18
$k \times 10^5$ (s^{-1})	1.34	3.23	5.11	5.57	1.87	2.83	3.22	3.73
$v_0 \times 10^7$ (mol kg^{-1} s^{-1})	1.17	3.00	4.80	5.28	1.96	3.06	3.56	4.17

Maximum error in $x_i = \pm 1.5\%$ and maximum error in $k = \pm 3.0\%$

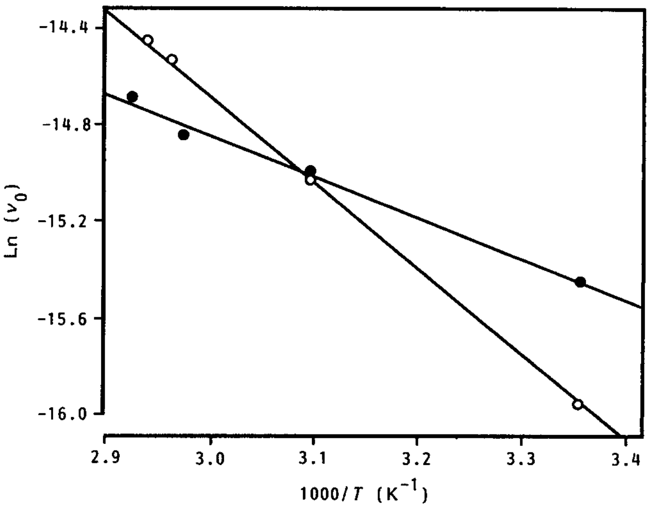

Figure 1 Arrhenius plots of $\ln(v_0)$ *versus* $1/T$ (K^{-1}) for (○) LDPE (stabilized with 0.25% (w/w) of the u.v. absorber octadecyl-3-(3,5-ditertiarybutyl-4-hydroxyphenyl)-propionate) and (●) unstabilized HDPE. Photooxidations were carried out using air at 1.0 atm as the test gas and an incident light intensity of 0.27 W m^{-2} (measured at 340 nm)

stabilized LDPE [0.25% (w/w) of u.v. absorber] and unstabilized HDPE. The effect of temperature on the rate of photooxidation was determined.

The results indicate that the value of the first order rate constant, k, significantly increases as the temperature is increased. The larger increase in the value of k at higher temperatures suggests that photooxidation occurs more readily under these conditions. This may be due, in part, to the increased oxygen mobility within the polymer matrix. On the other hand, the value of x_i does not appear to be as sensitive to temperature changes as k. The slight increase in the observed value of x_i is due possibly to increased thermal oxidation of the polymer at elevated temperatures.

The Arrhenius equation $k = A\exp(-E_a/RT)$, where A is a constant, E_a is the activation energy (kJ mol^{-1}) and T is the absolute temperature (K), can be applied to the results in *Table 2*. The Arrhenius equation can be rewritten in terms of the initial rate of photooxidation, v_0, by substituting $v_0 = x_i k$ in the equation, which gives the expression $\ln(v_0) = \ln(x_i A) - E_a/RT$.

Plots of $\ln(v_0)$ *versus* the reciprocal of the absolute temperature are shown in *Figure 1*. Activation energy values from *Figure 1* are 29.7 kJ mol^{-1} for the LDPE formulation and 14.3 kJ mol^{-1} for the HDPE formulation. The significantly higher E_a for the LDPE is attributable to the presence of the u.v. absorber in this formulation. The results show that the rate of photooxidation approximately doubles for every 10°C rise in temperature[11–13].

It should be pointed out, however, that these values of E_a were obtained by plotting the logarithm of the initial reaction rate against the reciprocal of the absolute temperature and are, therefore, based on the assumption that the value of x_i is independent of temperature. According to the results listed in *Table 2* this assumption is not strictly correct since the value of x_i varies slightly with temperature. However, plots of $\ln(k)$ *versus* $1/T$ using the data in *Table 2* show that the values of E_a based on this parameter differ by only 5% from the original values. This suggests it is reasonable to assume that, to within the experimental accuracy, x_i does not vary significantly with temperature over the range of temperatures investigated.

Effect of partial pressure of oxygen on photooxidation rate

Table 3 gives the results for the photooxidation of HDPE formulations for a range of partial pressures of oxygen. These results show that, under conditions of constant light intensity, the value of the initial quantum yield for oxygen uptake, ϕ_i, increases markedly when the photooxidation of HDPE is carried out in pure oxygen at 1.0 atm as compared with air at 1.0 atm. The increase in the value of ϕ_i is due to the increase in the values of both x_i and k. The increase in the value of k is more significant than that of x_i. This is due to the fact that an increase in the oxygen partial pressure in the gas phase results in a higher oxygen concentration in the polymer substrate. This suggests that, as its concentration increases, oxygen is able to react with sites that are located much deeper under the polymer surface and in substantially less time.

At low partial pressures of oxygen the value of x_i varies linearly with oxygen pressure and is linearly related to the number of moles of oxygen introduced initially into the sample cell. Under these conditions all of the available oxygen is used in the photooxidative process since the number of moles of reactive centres is greater than the number of moles of oxygen available for photooxidation. The rate of reaction is, therefore, controlled by the concentration of oxygen, as indicated by equation (9).

If n_0 is the initial number of moles of oxygen present in the system and $n'(t)$ is the number of moles of oxygen remaining in the gas phase at any time t, then, under conditions of low oxygen pressure, $x_i = n_0$. Since $n'(t)$ is equal to the difference between n_0 and $n(t)$, equation (9) can be integrated between the limits of n_0 and $n'(t)$ which gives $n(t) = n_0(1 - e^{-kt})$, the expression for the uptake of oxygen as a function of time under conditions of low partial pressure of oxygen. Under these conditions, the oxygen uptake curve asymptotically approaches the value n_0. As the partial pressure of oxygen is increased, the value of x_i increases proportionally and remains equal

Table 3 Kinetics of HDPE photooxidation as a function of oxygen partial pressure

O_2 pressure (Torr)	1.0	2.0	4.0	6.0	10	80	159.2	300	450	600	760
HDPE (no u.v. absorber, $I_a = 0.27\ \mathrm{W\,m^{-1}}$)											
$x_i \times 10^3$ (mol kg^{-1})	1.4	2.8	5.6	8.2	9.3	9.9	10.5	11.8	12.8	14.1	15.7
$k \times 10^5$ (s^{-1})	0.09	0.09	0.09	0.09	0.14	1.00	1.87	3.13	4.30	4.88	5.98
$\phi_i(P) \times 10^2$ (±4%)	0.06	0.11	0.23	0.34	0.56	4.47	8.86	16.7	24.8	31.0	42.5

O_2 pressure (Torr)	10	15	20	25	30	80	159.2	300	450	600	760
HDPE (no u.v. absorber, $I_a = 0.47\ \mathrm{W\,m^{-2}}$)											
$x_i \times 10^3$ (mol kg^{-1})	14.1	20.6	28.1	34.2	35.8	38.0	40.0	43.9	47.9	52.9	58.2
$k \times 10^5$ (s^{-1})	0.15	0.16	0.15	0.16	0.18	0.45	0.85	1.47	1.99	2.44	2.81
$\phi_i(P) \times 10^2$ (±4%)	0.57	0.85	1.13	1.42	1.70	4.50	8.97	17.0	25.0	33.8	42.9

O_2 pressure (Torr)	0.2	0.5	1.0	1.5	5.0	8.0	159.2	300	450	600	760
HDPE (0.40% (w/w) of u.v. absorber, $I_a = 0.47\ \mathrm{W\,m^{-2}}$)											
$x_i \times 10^3$ (mol kg^{-1})	0.28	0.69	1.37	2.10	2.40	2.94	3.42	4.30	5.45	6.29	7.39
$k \times 10^5$ (s^{-1})	0.05	0.05	0.05	0.05	1.43	1.89	3.20	4.80	5.72	6.50	7.04
$\phi_i(P) \times 10^2$ (±4%)	0.01	0.02	0.03	0.05	1.54	2.49	4.94	9.34	14.1	18.5	23.4

to the number of moles of oxygen. This can be calculated from the ideal gas law.

As the partial pressure of oxygen is increased, a critical pressure P_c is reached above which there is more oxygen than available reactive centres. The value of the first order rate constant k remains unchanged up to the point where the critical pressure is reached. This suggests that the rate of photooxidation is controlled by the amount of available oxygen for partial pressures of oxygen less than P_c.

In the case where the initial partial pressure of oxygen is such that the number of moles of oxygen is equal to x_i, termination by either of the reactions described by equations (4) and (5) is equally likely. Furthermore, under these conditions the concentration of reactive centres in the polymer, $[PH]_t$, and the oxygen concentration, $[O_2]_t$, at any time t will be equal. The assumption that $[P^\bullet] \approx [POO^\bullet]$ can be used to derive an expression for oxygen uptake in terms of the parameters x_{ic} and k_c, which are the values of x_i and k at the critical pressure P_c.

If $[P^\bullet] \approx [POO^\bullet]$ then $v_t = k_4[P^\bullet]^2 + k_5[POO^\bullet]^2 \approx (k_4 + k_5)[POO^\bullet]^2$ and under steady-state conditions $v_t = k_1 I_a$. These results can be substituted into equation (7) and upon the elimination of the terms involving radical species, equation (11) is obtained.

$$-\mathrm{d}[O_2]/\mathrm{d}t = [k_1]_a/(k_4 + k_5)]^{1/2}(k_2 - k_3)[O_2] = k_c[O_2] \tag{11}$$

When $t = 0$, $[O_2] \equiv x_{ic}$ and at time t, $[O_2] \equiv x_{ic} - n(t)$. Equation (11) can be integrated between these limits and the expression $n(t) = x_{ic}(1 - \exp(-k_c t))$ is obtained. This describes the asymptotic approach of the oxygen uptake curve to the value x_{ic}, which is observed experimentally, in the case where photooxidation is carried out using a partial pressure of oxygen equal to P_c.

For partial pressures of oxygen above P_c, the value of x_i was observed to increase linearly with pressure over the pressure range studied. The oxygen uptake curve is described by the function $n(t) = x_i(1 - e^{-kt})$ and the observed increase in the value of x_i with increasing pressure may be attributed to the corresponding increase in the availability of oxygen to the reactive centres within the polymer. The gradient, a_0, of the line of x_i *versus* the partial pressure of oxygen, P, in the region where $P > P_c$ is found to be less than the gradient of the plot for pressures lower than P_c. In the region $P < P_c$, the value of $x_i m$ is equivalent to the initial partial pressure of oxygen in the system, n_0RT/V, where m is the mass of polymer (in kg) and V is the free volume of the sample cell (in m^3).

The values of the parameters $a_0 = \mathrm{d}x_i/\mathrm{d}P$ (for $P > P_c$), x_{ic} and P_c are influenced by factors such as the light intensity, the type and amount of stabilizer in the polymer substrate and the permeability of the material to oxygen. In particular, the parameter a_0 may be interpreted as being a measure of the sensitivity of a formulation to photooxidation as the partial pressure of oxygen changes. The values of a_0 and P_c increase as the intensity of light increases. More reactive centres are produced with the increasing light intensity so that more oxygen is required for the equilibrium between $[PH]_t$ and $[O_2]_t$. At a sufficiently high light intensity the value of a_0 is expected to reach a limiting value equal to the slope of the x_i *versus* P line for the region where $P < P_c$.

Figure 2 shows plots of the initial rate of photooxidation v_0 (mol kg^{-1} s^{-1}) *versus* the partial pressure of oxygen (Torr) for various HDPE and LDPE formulations that were studied. The results suggest that the parameter $a_1 = \mathrm{d}v_0/\mathrm{d}P$ (for $P \geqslant 0$) gives an indication of the photooxidative sensitivity of a given formulation to changes in the partial pressure of oxygen (as does the parameter a_0). The results show that the initial rate of photooxidation varies in direct proportion to the partial pressure of oxygen[10]. It is interesting to note also that the linear dependence of oxidation rate on the pressure of oxygen has been observed for the solid-state thermal oxidation of polyolefins[18,19].

Since the initial quantum yield for oxygen uptake, ϕ_i, is directly proportional to the product of x_i and k, the linearity between v_0 and P suggests that under conditions of constant light intensity the value of ϕ_i is also directly proportional to the partial pressure of oxygen.

Although specific photooxidation results have been listed in *Table 3* for HDPE formulations, it should be noted that the LDPE formulations tested were found to behave in a similar manner. *Table 4* summarizes the

Table 4 Values of the parameters a_0, a_1, x_{ic} and P_c for HDPE and LDPE

Material	I_a (W m^{-2})	$a_0 \times 10^6$ (mol kg^{-1} Torr^{-1})	$a_2 \times 10^9$ (mol kg^{-1} s^{-1} Torr^{-1})	$x_{ic} \times 10^3$ (mol kg^{-1})	P_c (Torr)
HDPE (no u.v. absorber)	0.27	8.376	1.207	9.26	6.66
	0.47	29.76	2.145	35.9	25.8
HDPE (0.40% u.v. absorber (w/w))	0.27	6.301	0.684	2.55	1.84
LDPE (0.25% u.v. absorber (w/w))	0.27	32.97	0.738	3.55	2.56
	0.47	86.33	1.262	13.3	9.59

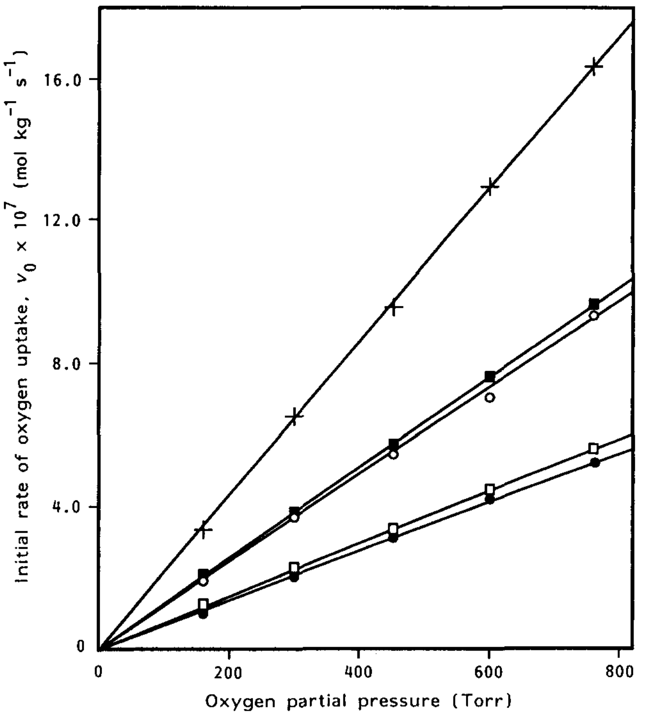

Figure 2 Plots of the initial rate of oxygen uptake, v_0 (mol kg^{-1} s^{-1}), *versus* oxygen partial pressure (Torr) for LDPE (0.25% (w/w) u.v. absorber), HDPE (0.40% (w/w) u.v. absorber) and unstabilized HDPE. Results are shown for incident light intensities, I_a, of 0.27 and 0.47 W m^{-2} (measured at 340 nm). All photooxidations were carried out at 25.0±0.1°C. I_a=0.47 W m^{-2}: +, HDPE (unstabilized); ■, LDPE (0.25% (w/w) u.v. absorber). I_a=0.27 W m^{-2}: ○, HDPE (unstabilized); □, LDPE (0.25% (w/w) u.v. absorber); ●, HDPE (0.40% (w/w) u.v. absorber)

results that were obtained for the HDPE and LDPE formulations by listing the parameters a_0, a_1, x_{ic} and P_c.

CONCLUSIONS

The effect of the temperature and the partial pressure of oxygen on u.v. stabilized and unstabilized samples of LDPE and HDPE were measured using a new oxygen uptake apparatus. The activation energy of the photooxidative process was calculated from a plot of the initial rate of oxygen uptake *versus* the reciprocal of the absolute temperature. The results suggest that the initial rate of photooxidation of the polymers approximately doubles for every 10°C increase in the temperature.

The results of the experiments using a range of partial pressures of oxygen show a transition in the photooxidative mechanism which is attributed to the change from a process controlled by the availability of reactive sites at high partial pressures to a process controlled by the supply of oxygen at low partial pressures. Using an oxygen uptake model it is shown that the initial rate of oxygen uptake and the partial pressure of oxygen are related linearly.

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