Modelling the thermal oxidative degradation kinetics of polyethylene film containing metal pro-oxidants

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The variation of degradation, as measured by change in percentage elongation with time, was evaluated at different temperatures for low density polyethylene–starch composite films containing varying amounts of manganese and iron as pro-oxidant. An equation for change of peroxy radicals with time was derived to reflect change of percentage elongation with time. This equation was then used in curve fitting results of percentage elongation of films and estimating oxidative degradation rates in the form of half lives of starch polymer composite films. This adaptation of the model by Guryanova appears to describe remarkably well the variation in elongation of polyethylene film with degradation, and may also be instrumental in linking variation of mechanical properties to chemical kinetics. The model was applied to experimental data and the curve parameters and half-lives derived appeared to vary in an Arrhenius fashion with temperature. The variation of the curve parameters with temperature in conjunction with the model equation describing percentage elongation with time were then used to derive an equation describing degradation with temperature and time for low density and linear low density polyethylene–starch composite films containing metal pro-oxidants.

(Keywords: degradation; polyethylene; pro-oxidants)

INTRODUCTION

Polyolefins are thermodynamically unstable in the presence of oxygen in air, degrading to eventually form carbon dioxide and water[1]. The degradation process takes a long time to occur for stabilized and unstabilized polyethylene, and the initiation of the process is accompanied by loss of useful tensile properties. However, the large amounts of plastic ending up in the waste stream has resulted in a trend towards manufacture and development of plastics with accelerated degradation times. Some of the methods used to accelerate this process are the addition of transition metal pro-oxidants or carbon monoxide polymer, both of which are designed to catalyse photodegradation and thermal degradation[2–4]. However, thermal oxidative mechanisms are taking effect even when the plastics are on shelves. It is therefore necessary to be able to predict useful lifetimes of the plastic at ambient temperatures. In order to predict or extrapolate lifetimes of plastics, a scheme to curve fit or model the degradation process is required, which would thereby result in rates of degradation. However, experimental work using starch–polyethylene composites containing metal catalysts in laboratory oven ageing studies has not yet developed a scheme to evaluate rates of degradation[1,5,6].

The objective of this study is to develop a model for describing the degradation of starch–polyethylene composite films containing metal pro-oxidants, using percentage elongation as the indicator of degradation. Mechanical properties were examined because they are the most sensitive to changes occurring during degradation, with percentage elongation being the most sensitive; percentage elongation is itself more sensitive in the direction transverse to machine extrusion of the polymer film[7,8]. The model should facilitate quantitative representation of degradation rates and extrapolation of these rates.

An equation from a kinetic model for the change of peroxy radicals with degradation, developed by Guryanova *et al.*[9] was adapted to describe the variation of percentage elongation with time. This adapted equation was then used to fit curves through the results of the percentage elongation *versus* time of the films oven-aged at a particular temperature. Curve parameters describing the shape of the curve were then used to estimate polymer lifetime in the form of calculated half-lives. Half-lives were defined as the time taken for percentage elongation to decrease by half of the percentage elongation after manufacture or initial testing. The variation of the curve parameters with temperature for samples oven-aged at different temperatures were evaluated for an Arrhenius relationship. The variation of the curve parameters with temperature in conjunction with the equation describing percentage elongation with time were then used to derive an equation for the variation of half-life with temperature and time.

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Table 1 Description of films A, F and K

				Metal content	
Sample	Polymer	Additive	Thickness (cm)	Fe	Mn
A	LDPE	none	0.0028±0.0001	b.d.[a]	b.d.[a]
F	LDPE	16% Polyclean-C	0.0043±0.0001	76±3	152±3
K	LLDPE	16% Polyclean-C	0.0059±0.0001	80±2	182±1

[a] b.d., below detection limit of method; detection limits were Mn<3 ppm and Fe<12 ppm

EXPERIMENTAL

Low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) controls, and films containing modified starch and pro-oxidant transition metal additives, were provided by the Archer Daniels Midland Company (ADM), Decatur, IL, USA. All films were manufactured by the Griffin[10] process as modified by ADM. The films had been stored at ambient temperature until received at the laboratory. Upon arrival at the laboratory the films were then stored in the dark at ambient temperature (23±3°C).

Five measurements of film thickness by micrometer averaged 0.0028, 0.0043 and 0.0059±0.0001 cm, respectively, for the control LDPE film A, and the LDPE and LLDPE starch composites F and K containing pro-oxidants (*Table 1*). The metal pro-oxidants, manganese (Mn) and iron (Fe), and stearates and stabilized starch in the form of 16% Polyclean-C (404) (a proprietary mixture from ADM) were added. The reported starch content was 8% for the composite films F and K.

Films were cut into sections, approximately 79.5 cm by 8.2 cm, and were oven-aged at 80, 70, 60 and 40°C for 215, 323, 433 and 1110 h, respectively, in a Fisher Isotemp 500 series oven. The oven was preheated to the required temperature within an accuracy of ±1°C. A container of calcium chloride was used to keep the oven at minimum humidity. Films were placed with the fold positioned over a bar of the oven rack. Once removed, films were tested for their load at break, extension, and energy to break. Films stored in the dark, at room temperature (20±3°C) were also tested for their tensile properties at 7728 and 13 344 h after initial testing.

Tensile testing was carried out on three strips, 1.27 cm × 6 cm, from each side of an individual test film, transverse to the original machine extrusion direction, to give six replicates. Tensile properties of the films were determined using an Instron model 1011 Universal Testing Machine using ASTM test method D882[11]. Crosshead speed was 50.8 cm min^{-1} with a gauge length of 5.08 cm. The load at break, extension at break, and energy to break were recorded for each film sample.

Metal analysis of film samples was also carried out on three replicate samples of approximately 1 g, weighed to an accuracy of 10^{-4} g. The film was then placed in a covered porcelain crucible and heated in a muffle furnace for 3 h at a temperature of 500±25°C. Once the ash of the film had cooled, a 1:1 (by volume) solution of nitric acid and deionized distilled water was added. The ash and nitric acid solution were heated on a hot plate for 2 h at 70°C. The solutions were then filtered through a 0.4 μm Nucleopore filter and made up to a fixed volume with deionized distilled water for metal analysis. Metals were analysed using flame atomic absorption spectrophotometry on a Perkin–Elmer Zeeman 5000 atomic absorption spectrophotometer.

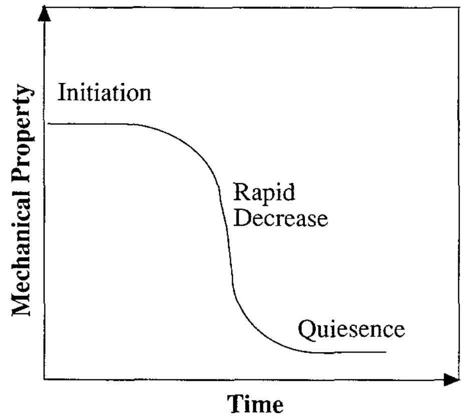

Figure 1 Variation of mechanical properties of polyethylene with degradation

THE MODEL

The classic sigmoidal shape (*Figure 1*) of mechanical property variation with degradation has been depicted frequently[12–14]. A model that is capable of describing the variation in elongation with oxidative degradation should have this type of curve. The stages of the curve can be described by the terms initiation, rapid decrease and quiescence (*Figure 1*).

A chemical kinetic model by Guryanova *et al.*[9] for change of peroxy radical concentration with time was examined. By rotating the curve given by Guryanova's model[9] around a line parallel to the x axis, a curve comparable to that of the variation of mechanical property with time can be obtained. The mathematical description for the rotated curve requires only a change in the sign of the equation. Further, the cumulative values generated by this curve describe a similar inverse curve with different proportions, the significance of which will be addressed later.

Using the nomenclature of Reich and Stivala[15], the chemical equations necessary to describe the kinetic model of Guryanova *et al.*[9] are given below. The model examined the oxidation of polyformaldehyde in the presence of inhibitors and free radical initiators using a chemoluminescence technique. The proposed mechanism was:

$$\mathrm{Y} \xrightarrow{k_1} \mathrm{R}\cdot \tag{1*}$$

$$\mathrm{R}\cdot + \mathrm{O}_2 \xrightarrow{k_2} \mathrm{RO}_2\cdot \tag{2*}$$

$$\mathrm{RO}_2\cdot + \mathrm{RH} \xrightarrow{k_3} \mathrm{RO}_2\mathrm{H} + \mathrm{R}\cdot \tag{3*}$$

$$2\mathrm{RO}_2\cdot \xrightarrow{k_6} \text{Products} \tag{6*}$$

$$n\mathrm{RO}_2\cdot + \mathrm{In\,H} \xrightarrow{k_{87}} \text{Products} \tag{87*}$$

where n is a stoichiometric factor, Y is a free radical initiator and $RO_2\cdot$ represents peroxy radicals.

Using the above equations, Guryanova *et al.*[9] carried out mathematical manipulations to arrive at the following equation, where the subscript 0 denotes absence of metal pro-oxidants, t is time and Z an integration constant:

$$-\frac{[RO_2\cdot]_0}{[RO_2\cdot]}+\ln\frac{[RO_2\cdot]_0+[RO_2\cdot]}{[RO_2\cdot]_0-[RO_2\cdot]}=k_{87}[RO_2\cdot]_0t+Z \qquad (153^*)$$

This equation was used as the starting point to develop an equation to describe the variation of percentage elongation ($\%E$) with time during thermal oxidative degradation. Initially, the quantity $[RO_2\cdot]/[RO_2\cdot]_0$ was hypothesized to be proportional to $\%E/\%E_{T=0}$. Initial curve fits to the data using this type of equation appeared good. The equation was generalized to include changes of sign and variable parameters (equation (1)). A hypothesis that describes the validity of assumption $[RO_2\cdot]/[RO_2\cdot]_0$ being proportional to $\%E/\%E_{T=0}$ is discussed later.

$$\frac{B}{\%E/\%E_{T=0}}-C\ln\frac{(1+\%E/\%E_{T=0})}{(1-\%E/\%E_{T=0})}+D=t \qquad (1)$$

where B, C and D are constants having dimensions of time. Equation (1) was applied only to percentage elongation *versus* time data during thermal oxidative degradation where the percentage elongation of a polymer at a given temperature decreased by over 50%. A simple technique using a spreadsheet, described elsewhere[16], was used to force the curve through all the data points.

Substituting $\%E/\%E_{t=0}$ in equation (1) will result in the half lifetime of the polymer $t_{1/2}$, which is called half-life in this paper:

$$2B-C\ln(3)+D=t_{1/2} \qquad (2)$$

To express lifetime for some fraction x of the percentage elongation, equation (1) can be represented as:

$$\frac{B}{x}-C\ln\left(\frac{x}{1-x}\right)+D=t \qquad (3)$$

Information as to the variation of the curve parameters with temperature would result in equations that describe the temperature–time variation of percentage elongation during oxidative degradation.

RESULTS

Variation of tensile properties with temperature

At all temperatures, the order of decrease in percentage elongation with time was film F > film K > film A. For each respective film, increasing temperature decreased the time required for comparable changes in percentage elongation.

Comparatively little variation in percentage elongation of control film A was seen with increase in time of oven ageing. Percentage elongation of control film A after 168 h at 80°C exhibited a decrease of only 42% (*Figure 2*). At 70°C, even after 672 h of oven ageing control film A showed an increase of 15% in percentage elongation.

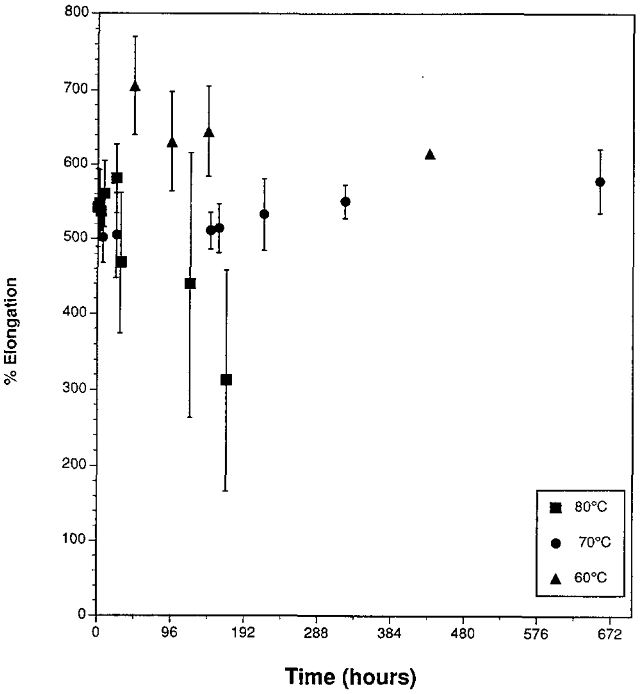

Figure 2 Percentage elongation *versus* time for control film A at 80°C, 70°C and 60°C

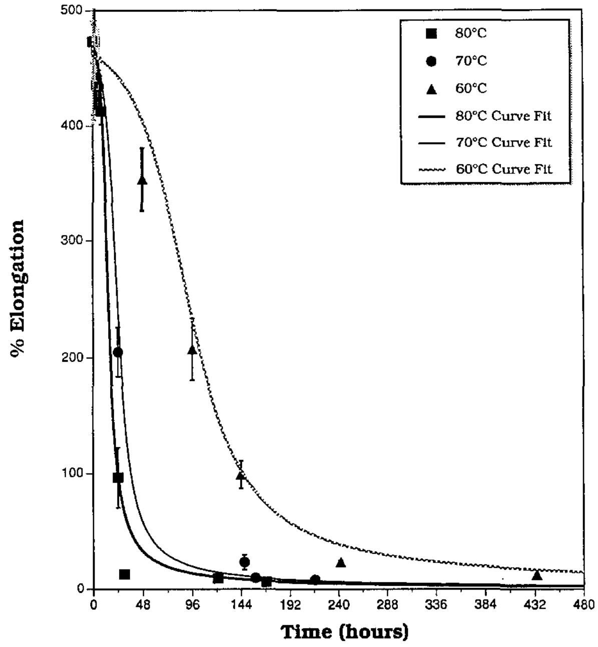

Figure 3 Percentage elongation *versus* time for film F at 80°C, 70°C and 60°C

Films F and K exhibited a somewhat exponential decrease in percentage elongation (*Figures 3* and *4*). An increase in temperature decreased the time required for comparable changes in percentage elongation. A slight increase (13%) in percentage elongation of K films retrieved within 6 h of oven ageing at 80, 70 and 60°C were seen (*Figure 4*). However, subsequent samples showed decreases in percentage elongations. At 80°C, film K decreased by 98% within 24 h, whereas for a comparable decrease at 70°C, 157 h were needed. At 40°C film K needed 451 h, before catastrophic decrease in percentage elongation occurred. After being stored at 20°C for 13 344 h (1.5 yr), percentage elongation of film F had decreased from 498.0 to 245.7% (*Figure 5*). Film K, however, exhibited a decrease of less than 15% under similar conditions (*Figure 5*).

Percentage elongation of the oven-aged films A, F and

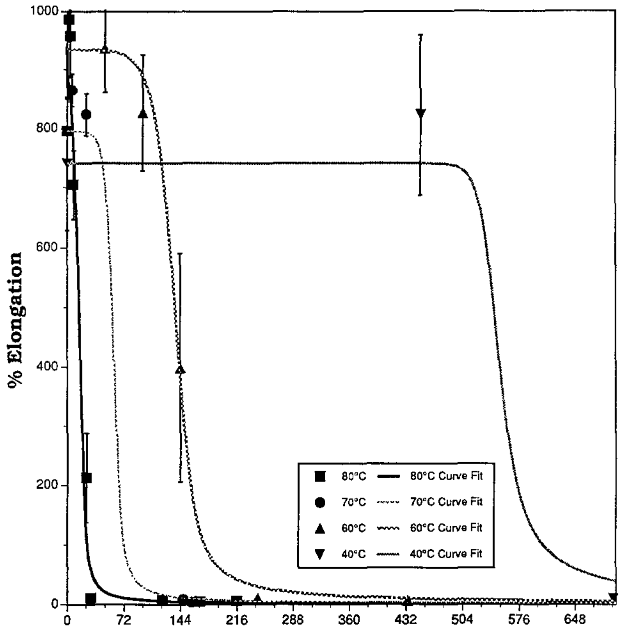

Figure 4 Percentage elongation *versus* time for film K at 80°C, 70°C, 60°C and 40°C

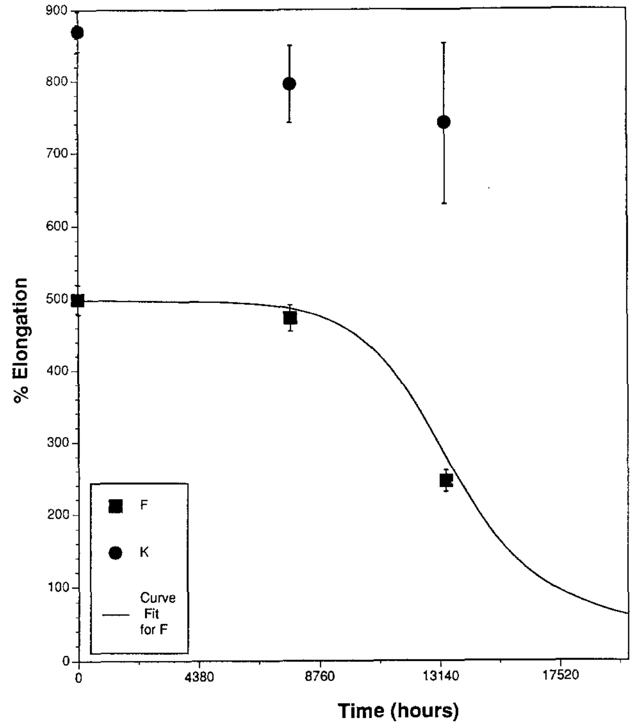

Figure 5 Percentage elongation *versus* time for films F and K at 20°C

K were fitted to equation (1) and the curve parameters *B*, *C* and *D* evaluated, where percentage elongation at time = 0 values for A, F and K were 546.7, 498.4 and 869.9, respectively, excepting at 40°C for K where percentage elongation was 764.9 (*Table 2*, *Figures 3*, *4* and *5*). The films at 20°C (room temperature) were similarly treated. A curve fit for film K at 20°C was not done as a decrease of over 50% in percentage elongation was not observed and hence a curve fit would be meaningless (*Figure 5*). Experimental half-lives were then calculated using the parameters *B*, *C* and *D* in equation (2) (*Table 2*).

Experimental half-lives varied from a low of 15.5 h for F at 80°C, to a high of greater than 13 344 h for K at 20°C. Half-lives were observed to increase with decreasing temperature and were always greater for K at a given temperature.

Variation of curve parameters and experimental half-lives with temperature

The Arrhenius relationship is described by equation (4), in which the parameter m is equivalent to E_a/R, where E_a is activation energy and R is the universal gas constant. A is the pre-exponential factor in the Arrhenius relationship:

$$\text{parameter (h)} = Ae^{m/T(\mathrm{K})} \qquad (4)$$

Linear regressions of the natural log of the parameters *B*, *C* and *D* and half-lives *versus* the inverse of temperature (in K) resulted in significant fits for all parameters and half-lives of F and K, other than parameter *C* of film K (*Figures 6* and *7*, *Table 3*). The slope = m and $\exp^{\text{intercept}} = A$ from *Table 3*.

Equation (3) can be written, taking into account the variation of the constants with temperature, by substituting in the equation for variations of each parameter with temperature in the form of an Arrhenius relationship. This results in an equation describing the temperature–time variation of elongation with degradation. Using the values for variation of curve parameters *B*, *C* and *D* in *Table 3*, the equations for 95% confidence limits for any fraction x of initial percentage elongation of F and K can be evaluated for any temperature K (in kelvin).

For F:

$$\frac{e^{\frac{9679}{K}-27}}{x} - e^{\frac{10313}{K}-28}\ln\left(\frac{x}{1-x}\right) + e^{\frac{11681}{K}-31} = t \qquad (5)$$

and:

$$\frac{e^{\frac{11168}{K}-31}}{x} - e^{\frac{11489}{K}-32}\ln\left(\frac{x}{1-x}\right) + e^{\frac{12678}{K}-33} = t \qquad (6)$$

For K:

$$\frac{e^{\frac{6306}{K}-18}}{x} - e^{\frac{331}{K}+1}\ln\left(\frac{x}{1-x}\right) + e^{\frac{7720}{K}-18} = t \qquad (7)$$

Table 2 Parameters and half-lives for untreated films F and K at various temperatures

Film	Temperature (°C)	B^a (h)	C^a (h)	D^a (h)	Experimental half-life^b (h)
F	80	2.4	3	14	15.5
	70	3	6	25	24
	60	12	26	100	95.4
	40	n.d.^{c}	n.d.^{c}	n.d.^{c}	n.d.^{c}
	20	800	1600	13 950	13 972
K	80	0.6	6	21	15.6
	70	1.2	6.2	64	59.6
	60	3	15.5	150	139.0
	40	8	11	550	553.9
	20	n.d.^{c}	n.d.^{c}	n.d.^{c}	> 13 344

[a] Parameters *B*, *C* and *D* from equation (1)
[b] Half-life from equation (2)
[c] n.d., not determined

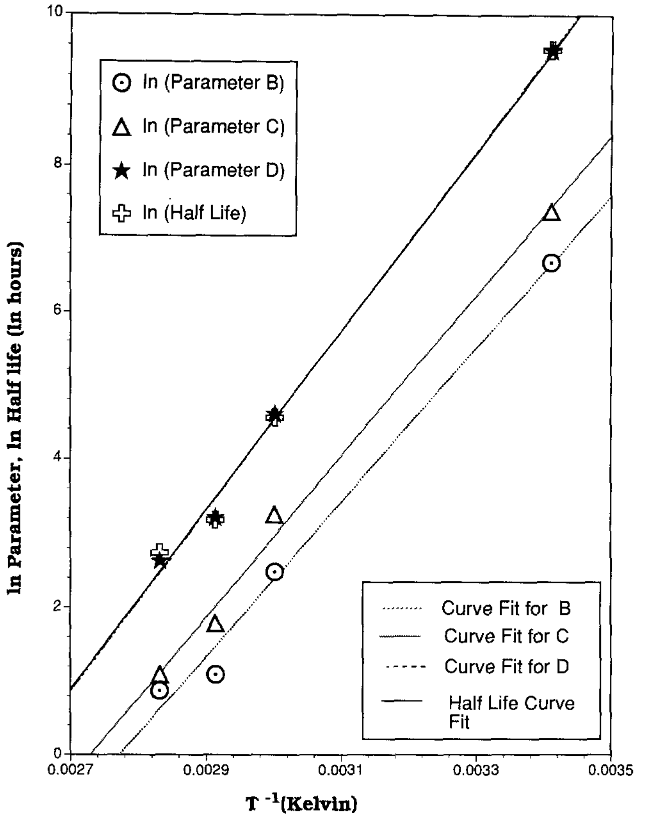

Figure 6 Natural logarithm of parameters *B*, *C*, *D* and half-lives *versus* inverse of temperature for film F

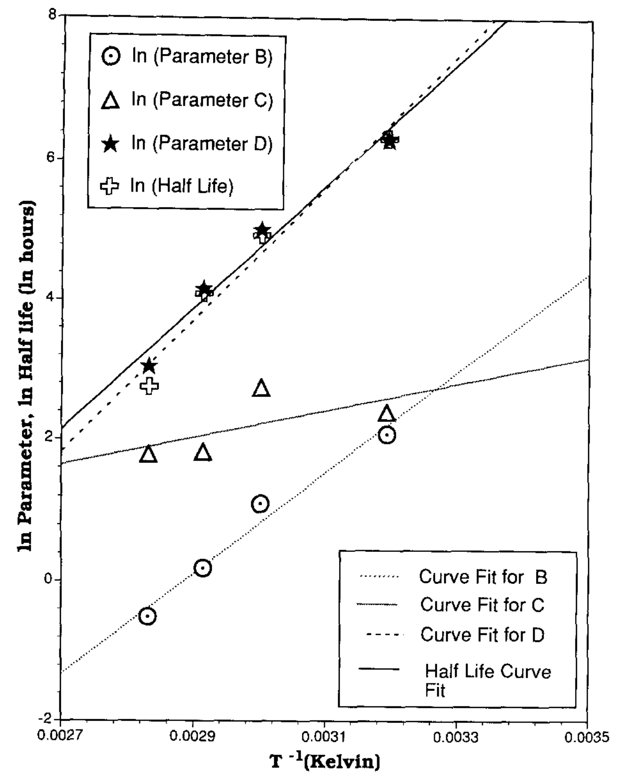

Figure 7 Natural logarithm of parameters *B*, *C*, *D* and half-lives *versus* inverse of temperature for film K

Table 3 Regression statistics of the natural log of each curve parameter *B*, *C* and *D* and half-life with inverse of temperature (in K)

Film		*B*	*C*	*D*	Half-life
F	Slope[a]	10423±744	10901±587	12179±498	12112±637
	Intercept[b]	−28±2	−30±2	−32±2	−31±2
	R^2	0.989	0.994	0.996	0.994
	F-statistic	196 (s)	344 (s)	597 (s)	361 (s)
K	Slope	7150±844	1930±1599	8763±1043	9468±1332
	Intercept	−20±3	−3.5±5	−21±3	−21±3
	R^2	0.97	0.982	0.985	0.961
	F-statistic[c]	71 (s)	1.4 (n.s.)	71 (s)	50 (s)

[a] Slope has units of K^{-1} and is equivalent to E_a/R, where E_a = activation energy and R = universal gas constant
[b] Intercept has units of natural log (h) and is equivalent to the log of the pre-exponential factor A in the Arrhenius relationship
[c] F-statistic value to be evaluated at two degrees of freedom for significance of slope being different from zero
n.s., not significant at 0.05 level of probability; s, significant 0.05 level of probability

and:

$$\frac{e^{\frac{7995}{K}-23}}{x}-e^{\frac{3530}{K}-8}\ln\left(\frac{x}{1-x}\right)+e^{\frac{9806}{K}-25}=t \qquad (8)$$

Substituting $x=0.5$ in equations (5)–(8) gives the 95% confidence limits of predicted half-lives of films F and K at various temperatures. The experimental half-lives with a 10% error for films F and K were within the predicted half-life curves (*Figures 8* and *9*).

DISCUSSION

The model and curve fitting

The adaption of Guryanova *et al.*'s[9] equations for percentage elongation is useful in evaluating the oxidative degradation curves of polyethylene films. This equation further facilitates description of degradation rates by the use of half-lives. However, the transition from an equation describing the variation of peroxy radicals to an equation describing percentage elongation should be examined to make the equations physically meaningful. Given below is a hypothesis that links peroxy radicals with percentage elongation.

Free radical initiation in the presence of pro-oxidant has long been considered to be given by[17]:

$$\text{Initiation} = \phi = k_i[\text{RH}][\text{OH}_2][\text{M}] \qquad (9)$$

where k_i = rate constant, [RH] = polymer concentration, $[O_2]$ is oxygen concentration, and [M] is the pro-oxidant concentration.

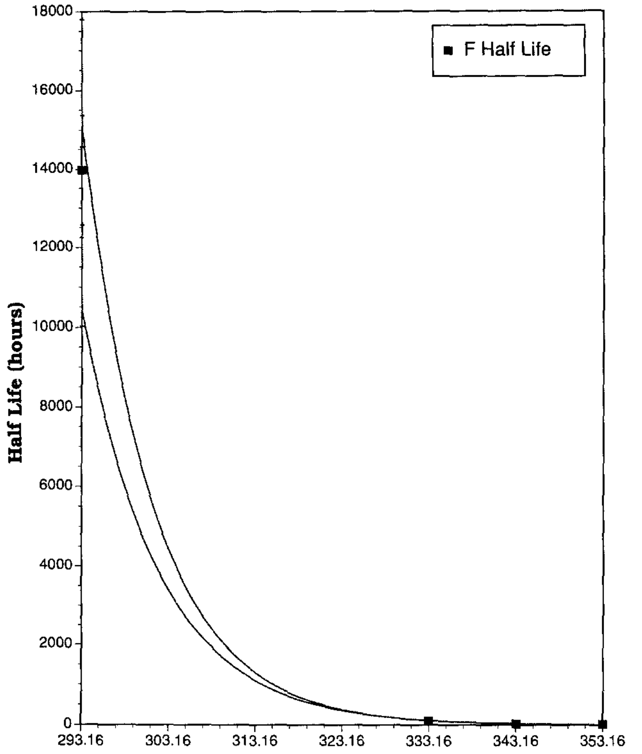

Figure 8 Half-lives and half-life prediction curves from equations (5) and (6) for film F; 10% error bars have been added to the experimental half-lives

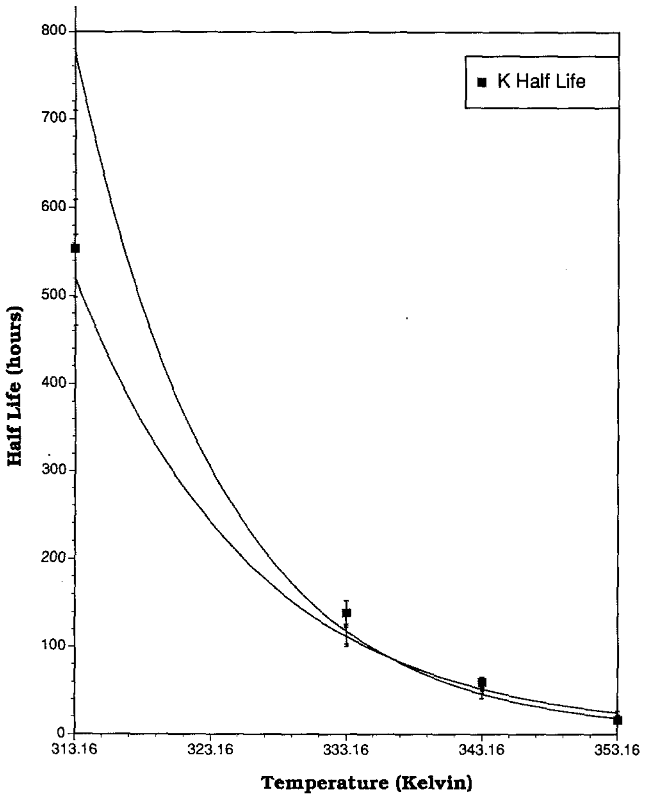

Figure 9 Half-lives and half-life prediction curves from equations (7) and (8) for film K; 10% error bars have been added to the experimental half-lives

However, in the case of thin films where diffusion effects are negligible and where oxygen pressure is the atmospheric pressure or ambient oxygen pressure, the factor $[O_2]$ can be considered to be constant. If the plastic film is not in contact with aqueous solutions it is unlikely that leaching of metal pro-oxidant would occur and hence keep [M] constant. Therefore it could be said for a thin film where diffusion effects are minimal that:

$$\text{Initiation}=[R\cdot]\propto[RH] \qquad (10)$$

In a well oxygenated environment it could be argued that for a thin film the initiation free radicals $[R\cdot]$ are all converted to mainly the peroxy radicals $[RO_2\cdot]$ and therefore the initiation step is given by:

$$[RO_2\cdot]\propto[RH] \qquad (11)$$

The molecular average has been shown to be proportional to tensile properties[18]. Tensile strength of polyethylene film has also been shown to decrease with decreasing molecular weight (MW)[13], i.e.

$$MW\propto\%E \qquad (12)$$

Equation (12) can also be written as:

$$[RH]\propto\%E \qquad (13)$$

Combining equations (11) and (13) the following can be inferred:

$$[RO_2\cdot]\propto\%E \qquad (14)$$

This implies that the behaviour of percentage elongation with time (*Figure 1*) mimics the peroxy radical concentrations with time. Using equation (14) for percentage elongation and a proportionality constant (P) with dimensions of concentration:

$$[RO_2\cdot]=P\,\%E \qquad (15)$$

where no impurities or metal catalysts are present:

$$[RO_2\cdot]=P\,\%E_0 \qquad (16)$$

It has been observed that polyolefin degradation is initiated by impurities present in polymers, and that the absence of metal impurities results in low thermal oxidative degradation rates[15]. So it could be said that negligible changes occur in percentage elongation for polymers having no impurities, in comparison to changes in percentage elongation for polymers having metal pro-oxidants.

Therefore the following transition can be made for a film that has had no previous thermal exposure or when thermal exposure has been at temperatures where thermal oxidation is very slow:

$$\%E_0=\%E_{T=0} \qquad (17)$$

Substituting equations (15), (16) and (17) into (153*) we get:

$$-\frac{\%E_{T=0}}{\%E}+\ln\frac{[(1/\%E_{T=0})+(1/\%E)]}{[(1/\%E_{T=0})-(1/\%E)]}=k_{87}t\,\%E_{T=0}+C \qquad (18)$$

which can be rearranged and generalized to give equation (1):

$$\frac{B}{\%E/\%E_{T=0}}-C\ln\frac{(1+\%E/\%E_{T=0})}{(1-\%E/\%E_{T=0})}+D=t \qquad (1)$$

Though the generalized equation (1) has allowed for differing values for the curve parameters B and C, the derivation from the model for peroxy radicals requires that they be equal (equation (18))[9]. The slightly different values seen are possibly artifacts arising from curve fitting to the sparse sampling intervals in the experimental data.

However, it also possible that these differing values indicate different pathways or different stoichiometric relationships in the chemical reactions from those given in the original model for peroxy radicals.

The assumption that $[RO_2\cdot] \propto \%E$ is most likely true only for thin films. In thick polymer films the reaction of the polymer free radicals $[RH\cdot]$ with O_2 to give $[RO_2\cdot]$ will be controlled by diffusive processes (equation (2*)). As such, this model would be limited to thin films or else should be modified to contain a term taking into account diffusive processes that would affect equation (9). Films with varying pro-oxidant concentration can also be modelled if equation (10) contains the pro-oxidant concentration term when derived from equation (9).

The curve parameters B, C and D are related to the reaction rate (k_{87}) of the peroxy radical with the polymer. As reaction rates are expected to follow an Arrhenius relationship, it can be inferred that the curve parameters B, C and D, in whole or parts thereof, should follow this relationship too.

The parameters B, C and D also describe the stages of the degradation curve. The most important parameter is D, which determines the initiation time before a rapid decrease is observed. It should be noted that a very short initiation period causes the degradation curve to approximate an exponential curve. The parameter B describes the rate of change from the initiation period to a rapid decrease. The parameter C describes the rate of change from rapid decrease to quiescence.

It has been shown that the peroxy radicals decompose into carbonyl groups[19]. It follows that the cumulative values of the peroxy radicals with time should depict carbonyl bond concentrations with time. However, it was shown that peroxy radical concentrations were proportional to percentage elongation. Hence cumulative values of percentage elongation should mimic a curve similar to that of carbonyl concentrations. A plot of the cumulative percentage elongation curve appeared similar to carbonyl concentrations with time (*Figure 10*)[20–22].

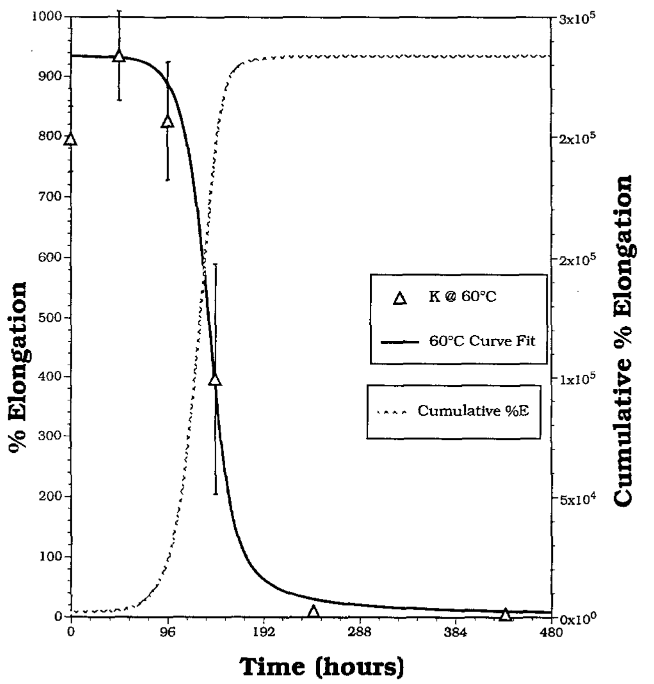

Figure 10 Percentage elongation and cumulative percentage elongation curves

This relationship between carbonyl content and tensile strength appears consistent with the observed decrease in the tensile properties and increased carbonyl content of weathered polyethylene films[13,20,21].

Temperature–time relationship for films F and K

Half-lives for films F and K were evaluated at many temperatures. This enabled examination of trends of half-lives. Half-lives increased exponentially with decrease in temperature for films F and K (*Figures 3*, *4* and *5*). Linear regression of the log of parameters and half-lives *versus* the inverse of temperature (in K) appear to indicate an Arrhenius relationship for parameters B, C and D of films F and K (*Table 3* and *Figures 6* and *7*). The failure of parameter C for film K to demonstrate the Arrhenius relationship could possibly be attributed once again to erroneous curve fitting due to sparseness of the experimental data (*Figures 4* and *7*). Similar curves for oxygen uptake with time during isothermal oxidation of LDPE were modelled in two segments and each segment was also shown to have an Arrhenius-type relation with temperature[23].

The initiation of the degradation process was longer for film K than for film F at any given temperature (*Figures 3*, *4* and *5*). The linearly oriented molecules of LLDPE would be less permeable[24]. This would impede oxygen diffusion and hence delay the increase of peroxy radical concentrations to a level where autocatalysis could take place. At lower temperatures, longer initiation periods are seen for both films F and K. This could be ascribed to the lower thermal energy associated with lower temperatures causing slower formation of peroxy radicals.

It should be noted that the temperature–time equation for percentage elongation does not account for variation of pro-oxidant type and concentrations, nor for variation in film thickness. As such, the equations for films F and K are most likely valid only for films having similar pro-oxidant concentrations and thickness. Equations (5)–(8) also fail to predict physically meaningful times for retained percentage elongations higher than 70%. This is due to the nature of the degradation curve, which can have long initiation times during which negligible changes in percentage elongation are seen. Sampling of the degradation process at very small time intervals and deriving curve parameters may result in more accurate prediction of degradation time for higher values of retained elongation.

The temperature–time equations for percentage elongation during oxidative degradation were used in comparison with results from other investigations. Many investigations have focused on the degradation of LDPE films[5,6]. Equations (5) and (6), for predicting degradation curves of the LDPE composite, film F, were used to compare with data from the other investigations. Comparable estimates were predicted when data from other investigations were compared to the time needed for film F to degrade to a similar extent, using equations (5) and (6) (*Table 4*). Iannotti *et al.*[6] reported that approximately 24 weeks (168 days) were required for LDPE film with 5.5% starch and pro-oxidant of unknown quantities to degrade to a 60% retained elongation at 35°C. The calculated life for a 60% retained elongation for film F at 35°C would be 35–42 days.

Fair *et al.*[5] showed that a compost bag with extra pro-oxidant required approximately 2 weeks to degrade

Table 4 Comparison between model results and results of previous investigations

Sample type	Temp. (°C)	Retained elongation	Time (day)	Reference	Calculated Calculated for film F[a]
LDPE starch 5.5% and pro-oxidant	35	~0.6	168	6	35–42
Compost bag	50	~0.5	14	5	12
Compost bag	70	~0.2	~4	5	1.3
Trash bag	50	~0.5	10	5	12
Trash bag	70	~0.1	7	5	3

[a] Degradation time calculated using equations (5) and (6) for film F

to 50% retained elongation at 50°C. The calculated value for film F would be 12 days. Fair *et al.*[5] also showed a change of retained elongation with time, at 90, 70 and 50°C for a trash bag of ADM formulation. The time taken to reduce to approximately 50% retained elongation at 50°C was approximately 10 days. The corresponding value calculated for film F was 12 days. In addition, approximately 7 days were required to degrade the ADM trash bag to 10% retained elongation at 70°C compared to a calculated value of 3 days for film F.

Prior thermal exposure could also affect the thermal degradation process[12]. Thermal exposure could initiate degradation and hence give shorter degradation times under experimental conditions or in the field. For film K oven-aged at 40°C, the percentage elongation at $T=0$ is 764.9, compared to 869.9 for film K oven-aged at 80, 70 and 60°C. After 80, 70 and 60°C testing, film K was kept at room temperature for over 6 months before samples could be tested at 40°C. This thermal history affected film K's percentage elongation at $T=0$ and hence the curve fit and half-life estimation.

Film type/thickness effects on half-life

Studies have shown that film thickness may influence the rate of oxidative degradation[23]. Lower oxidation rates are observed when thicker samples are used, possibly because of less diffusion of oxygen into the sample and less diffusion of oxidative products out of the sample[23]. However, little difference has been shown for degradation rates for film thicknesses ranging from 0.0025 to 0.025 cm[23]. This may be due to the overlap of degradation gradients from both sides of a thin film. As all films used in this study are between 0.0028 and 0.0059 cm thick, it is doubtful that film thickness influenced half-lives (*Table 1*).

Half-lives at all temperatures for film F were shorter than for film K. The metal additive contents were comparable for films F and K, hence the variation in half-lives may be attributed to variation of the type of base polymer. The base polymer for K was LLDPE and LDPE for F. The more crystalline LLDPE has more oriented polymers and longer chains, which are slower to react to the thermal oxidative process, resulting in longer half-lives for film K[24].

CONCLUSIONS

The adaptation of the model by Guryanova *et al.*[9] appears to describe remarkably well the variation in elongation of polyethylene film with degradation, and may describe the variation in carbonyl concentrations as well. The model appears capable of describing physical and chemical properties of thin polyethylene film during the thermal oxidative degradation process. The model may be further enhanced by taking into account varying pro-oxidant concentrations. Taking into account diffusion of oxygen the model may be extended to describe the thermal degradation of thicker films. Half-lives calculated using this model facilitate description of the degradation properties of polyethylene film.

The log of half-lives was seen to vary linearly with the inverse of temperature (in K), indicating an Arrhenius-type relationship. Half-lives for polyethylene starch composites containing metal pro-oxidants were in the order of hours at 80°C, months at 40°C, and years at 20°C.

A study evaluating the degradation process using elongation and carbonyl concentrations would further support the ability of the model to link chemical and physical properties during thermal oxidative degradation of polyethylene. Further investigations into the variations of the model with polymer type, thickness, starch and metal content also need to be done.

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