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Polymer 43 (2002) 4611–4618

polymer

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A new approach to quantitatively assessing the effects of polymer additives

Peter K. Fearon[a], Tanya L. Phease[b], Norman C. Billingham[a], Stephen W. Bigger[b,*]

[a]*School of Chemistry, Physics and Environmental Science, The University of Sussex, Falmer, Brighton BN1 9QJ, UK*
[b]*School of Life Sciences and Technology, F008, Victoria University of Technology, P.O. Box 14428, Melbourne City Mail Centre, Melbourne 8001, Australia*

Received 17 October 2001; accepted 26 April 2002

Abstract

A novel approach involving stability parameter mapping and stability vector analysis is developed for assessing the effect of an additive on polymer performance. The potential usefulness of the method is illustrated by applying it to (i) DSC oxidative induction time (OIt) data for medium-density polyethylene (MDPE) formulations made using two levels of carbon black and base-stabilized with Irgafos 168™ (tris-(2,4-di-*tert*-butylphenyl)-phosphite) and Irganox 1010™ pentaerythrityl-tetrakis-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate), and (ii) chemiluminescence OIt data for low-density polyethylene (LDPE) containing 0.2% (w/w) of Chimassorb 944™ and 0.5% (w/w) or 1.0% (w/w) of dicumyl peroxide cross-linking agent and base-stabilized with 0.2% (w/w) of various commercial antioxidants. The proposed method is validated using data from a previous study on MDPE and is applied to a preliminary investigation of LDPE destabilization by dicumyl peroxide. The results suggest that a styrenated phenolic stabilizer blended with zinc dibutyldithiocarbamate and zinc stearate is an effective system for stabilizing LDPE in the presence of dicumyl peroxide. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethylene; Thermooxidative stability; Cross-linking agent

1. Introduction

In the optimization of polymeric formulations in commercial operations an approach often used involves producing a number of masterbatch samples containing various base stabilization systems from which a series of test samples containing different levels of an additive of interest is made. A particular polymer property is then measured for each formulation and a matrix of data is generated and interpreted with a view to choosing the formulation that exhibits the optimum performance. In choosing the levels of additives and base stabilizers, one may resort to using a statistical tool such as a central composite design strategy [1,2] to help minimize the number of formulations that are required to be tested. In any case, this conventional approach quite commonly leads to complex matrices of results where clear trends and the optimum formulation may not always be apparent. Furthermore, clear indications of synergistic or antagonistic interactions between the additive and the base stabilization package may become obscured in complex data matrices where, say, the effects of more than one variable are being simultaneously explored.

To overcome some of these potential difficulties we present in this paper a simplified approach to the problem of assessing the effect that an additive has on polymer performance when the additive is present in conjunction with a base-stabilizing package whose composition may be varied or whose nature may be changed in some other way. The potential usefulness of the proposed analytical method is illustrated by applying it to two separate systems. The first is a series of medium-density polyethylene (MDPE) formulations that was made using two levels of carbon black (CB) and was base-stabilized with different levels of the phosphite/phenolic co-stabilizers Irgafos 168™ (tris-(2,4-di-*tert*-butylphenyl)-phosphite) and Irganox 1010™ (pentaerythrityl-tetrakis-(3,5-di-*tert*-butyl-4-hydroxyphenyl propionate)). The second system is a series of low-density polyethylene (LDPE) formulations where the LDPE was a commercially obtained cable insulation grade. The formulations were produced using two levels of dicumyl peroxide cross-linking agent and were base-stabilized using a range of commercial packages.

The oxidative induction time (OIt) [3] was determined for each formulation at the two set levels of the additive of

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* Corresponding author. Tel.: +61-3-9688-4208; fax: +61-3-9688-4995.
E-mail address: stephen.bigger@vu.edu.au (S.W. Bigger).

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PII: S0032-3861(02)00295-1

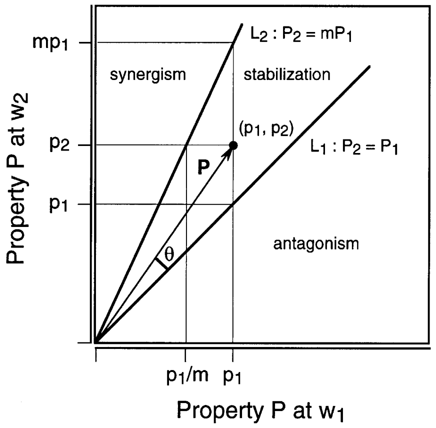

Fig. 1. Schematic diagram showing the relationship between a property, P, of a polymer formulation that is measured in the presence of two different levels of an additive, w_1 and w_2.

interest. For the systems containing CB, the OIt values were determined using a standard technique[1] based on differential scanning calorimetry (DSC) measurements. In the case of the peroxide-containing LDPE formulations, the OIt values were measured using differential scanning calorimetry (DSC) combined with chemiluminescence (CL) monitoring. The DSC–CL technique has been shown to be highly reliable for determining OIt values and is described elsewhere [4].

2. Theory

Consider the measurement of a particular polymer property, P, at two different levels, w_1 and w_2, of a given additive. If P_1 and P_2 are the values of P at additive levels w_1 and w_2, respectively, then one may compare a series of formulations by a mapping technique that involves plotting the separate coordinates (p_1, p_2) where p_1 and p_2 are pairs of values of P_1 and P_2, respectively, that have been measured for different polymer formulations. Such a plot is shown schematically in Fig. 1 for a single coordinate (p_1, p_2). With reference to this diagram it is clear that all points that lie on a line, L_1, of unit gradient represent situations where the incorporation of the additive produces no effect on the property P, i.e. $P_2 = P_1$. The regions located between the line L_1 and each of the axes define systems in which either ‘stabilization/synergism’ or ‘destabilization/antagonism’ is observed as a result of the incorporation of the additive. The assignment of these regions depends on the convention that is adopted when constructing the plot.

If one adopts as a convention the arbitrary choice to plot P_1 as the abscissa and choose w_1 as the lower of the two levels of additive (i.e. $w_1 < w_2$), then the appropriate assignment of the ‘stabilization/synergism’ and ‘destabilization/antagonism’ regions depends on whether the incorporation of the additive is expected to bring about an increase or a decrease in the property, P. For example, the incorporation of a stabilizer in the formulation will increase the oxidative stability. This could be observed, say, as either an increase in a property such as the OIt[1] or a decrease in a property such as the yellowness index (YI)[2] of the formulation. In cases where the observed property increases with an increasing level of additive, the ‘stabilization/synergism’ region will lie between line L_1 and the P_2 axis; the ‘destabilization/antagonism’ region will lie between L_1 and the P_1 axis (Fig. 1). The reverse is true in cases where the observed property decreases with an increasing level of the additive.

If m is the ratio of the two levels at which the additive has been incorporated, then a second line, L_2, can be drawn where $P_2 = mP_1$. The case where $m > 1$ is shown in Fig. 1. Clearly, the ratio m can be defined either as $m = w_1/w_2$ or $m = w_2/w_1$. The definition of m that is the more appropriate and convenient can be assigned by considering whether an increase in the level of the additive is expected to cause either an increase or a decrease in the observed property, P. If the first of these cases applies, then the line L_2 where $m > 1$ can be constructed (Fig. 1) and the region between P_2 and L_2 will be the ‘synergism’ region as it encompasses all systems where a synergistic effect is produced upon the incorporation of the additive. If the second case applies, then a line L_2 where $m < 1$ can be constructed and the region between L_2 and P_1 will represent the ‘synergism’ region.

The region between L_1 and L_2 encompasses systems that lie within the boundary conditions of ‘no effect’ and ‘directly additive’ effect. The latter can, of course, be either desirable or undesirable depending on the system under investigation. Thus the region between L_1 and L_2 can be one that pertains to the occurrence of either ‘stabilization’ or ‘destabilization’ depending on the nature of the additive under consideration. The analysis plane bound by the domain P_1 and range P_2 is completely symmetrical and analogous generalizations can be drawn if other conventions are adopted in the assignment of P_1 and P_2 and/or the definition of m.

3. Experimental section

3.1. MDPE and LDPE formulations

A commercial grade, MDPE resin having a melt flow index[3] (MFI) of 14.6 dg min^{-1} (190 °C, 2.13 kg) and density[4] of 0.953 g ml^{-1} was used to make the formulations containing CB. The phenolic antioxidant (AO) Irganox 1010™ (AO1, pentaerythrityl-tetrakis-(3,5-di-*tert*-butyl-4-hydroxyphenyl propionate) and the phosphite Irgafos 168™

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[1] ASTM test method D-3895.

[2] ASTM test method D-1925.

[3] ASTM test method D-1505.

[4] ASTM test method E-794.

Table 1
Base stabilization details for the MDPE formulations together with corresponding values of (i) the additive effectiveness parameter, k_1, (ii) the OIt at 0.726% (w/w) CB (τ_1) and at 2.33% (w/w) CB (τ_2), (iii) the OIt difference, $\Delta\tau = \tau_2 - \tau_1$, and (iv) the function $F_1(r, \theta)$

ID	Concentration (ppm)[a]		k_1[b]	τ_1 (min)	τ_2 (min)	$\Delta\tau$ (min)	F_1 (r, θ)
	AO1	AO2					
A1	0	990	0.50	1.5	2.22	0.72	3.78
A2	1980	990	1.54	56.4	59.0	2.6	84.7
A3	990	1980	1.59	53.7	56.9	3.2	82.1
A4	290	290	1.78	7.8	10.6	2.8	17.2
A5	990	0	2.75	18.8	22.7	3.9	34.6
A6	990	990	4.72	30.0	36.8	6.8	56.5
A7	290	1690	5.53	17.1	24.6	7.5	41.1
A8	1690	1690	5.75	57.6	65.6	8.0	97.3
A9	1690	290	6.22	32.3	40.0	7.7	61.6

[a] Nominal additive concentrations are given.
[b] Units of k_1 are min/%w/w CB [5].

(AO2, tris-(2,4-di-*tert*-butylphenyl)-phosphite) were obtained from Ciba Australia Limited and were used as received. Carbon black (Vulcan P™ grade) was supplied by Cabot Limited, Australia, and was used as received. Further details of the additives, the choice of their levels, the incorporation of CB in the formulations via masterbatch addition, and the gravimetric determination of the final CB levels, are given elsewhere [5]. These formulations have been designated A1–A9 and are listed in Table 1.

A commercial, cable grade of LDPE was used to make a series of 11 formulations where each formulation contained: (i) dicumyl peroxide cross-linking agent at a level of either 0.5 or 1.0% (w/w), (ii) 0.2% (w/w) of the hindered amine light stabilizer (HALS) Chimassorb 944™ (Ciba Specialty Chemicals, Basle, Switzerland) and (iii) 0.2% (w/w) of a commercial base stabilizing package belonging to one of the following classes of systems: hydrolysis-stabilized phosphite; hindered phenol/thiophenol blend; polybutylated bisphenol A; hindered phenolic; lactone; polysiloxane-bound HALS; hindered bis-thiophenol; styrenated thiophenol. These formulations have been designated B1–B11 and further details are given in Table 2. The formulations were compounded at 130 °C in a Brabender mixer where the additives were incorporated in three mixing stages: 30 rpm (2 min, primary AOs), 50 rpm (3 min, secondary AO) and a final mixing stage of 2 min during which the peroxide cross-linking agent was incorporated.

3.2. OIt analyses by DSC and DSC–CL

The DSC-OIt tests [6] were performed on MDPE samples using a Perkin–Elmer DSC-7 instrument. The instrument was temperature-calibrated at 1 °C min^{-1} using tin and indium standards. Each sample (ca. 8 mg) was placed in a clean aluminium pan and crimped with an

Table 2
Details of the base-stabilizing systems used in the LDPE formulations containing dicumyl peroxide cross-linking agent

ID	Type of stabilizer	Details of stabilizer package
B1	Phosphite	Hydrolysis-stabilized phosphite
B2	Phenolic/S-containing AO blend	Blend of phenolic and sulfur-containing AOs
B3	Sterically hindered phenol	2,2′-Methylene-bis-(4-methyl-*tert*-butylphenol)
B4	Polybutylated bisphenol A	Reaction products of 4,4′-(methylethylidene)-bis-phenol with isobutylene and styrene
B5	Sterically hindered phenol	Octadecyl-3-(3,5-di-*tert*-butyl)-4-hydroxyphenol propionate
B6	Difunctional sterically hindered phenol	Ethylene-bis-(oxyethylene)-bis-(3-(5-*tert*-butyl-4-hydroxy-*m*-tolyl)-propionate)
B7	Lactone blend	Blend of 42.5% tris-(2,4-di-*tert*-butylphenyl)-phosphite, 42.5% pentaerythrityl-tetrakis-(3,5-di-*tert*-butyl-4-hydroxyphenyl propionate) and 15% 5,7-di-*tert*-butyl-3-(3,4-dimethylphenyl)-3*H*-benzofuran-2-one
B8	Polymer-bound HALS	Polysiloxane-bound HALS
B9	Sterically hindered bis-thiophenol	2,2′-Thio-bis-(4-methyl-6-*tert*-butylphenol)
B10	Polymeric dihydroquinolene	2,2,4-Trimethyl-1,2-dihydroquinolene polymer
B11	Styrenated phenol/S-containing AO blend	Blend of styrenated pentaerythrityl-tetrakis-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate) with zinc dibutyldithiocarbamate and zinc stearate

aluminium lid that had a 3 mm diameter hole in its centre to allow adequate contact between the sample and oxygen during the test. An empty pan was used as a reference. The sample and reference pans were heated to 210 °C under nitrogen at a constant flow rate of 50 ml min^{-1}. After thermal equilibration (2 min) at the preset temperature, the pans were exposed to pure oxygen (flow rate of 50 ml min^{-1}) until the exotherm occurred.

Specimens of peroxide-containing LDPE, in the form of pellets (ca. 15 mg), were subjected to simultaneous DSC–CL analysis using a Mettler model 821^e DSC instrument onto which was fitted a photomultiplier tube (Thorn-EMI, Middlesex, UK; model 9813-QB) connected to a single-gated photon counter (Stanford Research Systems, USA; model SR400). Each sample was contained in an aluminium sample pan. Before each run the sample was brought to temperature in a nitrogen atmosphere and allowed to attain thermal equilibrium. Isothermal oxidation at 180 °C was then commenced by the admission of oxygen (1 bar) to the sample chamber at a flow rate of 100 ml min^{-1}. A temperature of 180 °C was chosen for the experiments because it is high enough to give measurable oxidation within a reasonable experimental time. The DSC instrument was temperature-calibrated in the range 95–191 °C using three calibration standards, namely benzil, indium and salophen.

In the case of both the DSC and DSC–CL methods, the OIt was taken as the time corresponding to the point at which the extrapolated exotherm or the CL signal intersects the extended baseline. It is important to realize, however, that during accelerated testing at elevated temperatures the effects of factors such as additive volatility under the conditions of the test are not usually taken into account. These effects may result in the reduced performance of a polymer during the accelerated test but may not necessarily be manifest under the conditions of use of the polymer. For example, certain types of HALS that are notoriously volatile additives may cause such complications. In the current study polymer-bound and high molecular weight HALS stabilizers were used wherever possible to minimize such effects.

4. Results and discussion

4.1. Formulations of MDPE containing carbon black

Carbon black retards the thermal oxidation of polymeric materials either by acting as a mild thermal AO or by influencing the activity of other AOs [6–11]. Thus, the addition of CB to a polymeric formulation will, in general, increase the observed OIt. Indeed, a linear relationship between the observed OIt and the level of CB has been found for systems containing low concentrations of CB in the range of 2–5.6% (w/w) CB [12] as well as for systems containing phenolic AOs [13–17] and mixtures of phenolic AOs with phosphites [18–21]. At sufficiently low levels of CB the relationship between OIt and the level of CB can be expressed as

$$\tau = k_1 w + \tau_0 \qquad (1)$$

where τ is the OIt, k_1 is a constant, w is the level of CB and τ_0 is the OIt in the absence of CB. It has been identified previously [5] that the value of τ_0 is indicative of the efficiency of the base stabilization and the gradient k_1 is indicative of the effectiveness of CB within the given formulation.

Table 1 gives the values of k_1 that were obtained in a previous study [5] by plotting the OIt against the level of CB over four different levels of CB. The OIt values obtained at the two lowest CB levels of $w_1 = 0.726\%$ (w/w) and $w_2 = 2.33\%$ (w/w) in that study (i.e. τ_1 and τ_2, respectively) are also listed in Table 1 together with the difference between these values, $\Delta\tau = \tau_2 - \tau_1$. The nine formulations appearing in Table 1 have been listed in order of increasing effectiveness of CB in the formulation as indicated by the k_1 parameter.

The following approximation can be derived from Eq. (1)

$$k_1 = \mathrm{d}\tau/\mathrm{d}w \approx \Delta\tau/\Delta w \qquad (2)$$

where Δw is the difference between the two levels of CB that were investigated. Thus, $\Delta\tau$ is proportional to k_1, since Δw is a constant. With regard to Fig. 1, $\Delta\tau$ is equal to the vertical distance between the point (p_1, p_2) and the line L_1 and is a quantitative indicator of the effectiveness of CB in a given formulation. In general, the realization that $\Delta\tau$ is indicative of the effectiveness of the additive is useful in differentiating between two formulations that exhibit, say, identical abscissa values but have different ordinate values.

Fig. 2 is a plot of τ_2 versus τ_1 for the formulations A1–A9. This plot illustrates the potential usefulness of the stability parameter mapping technique in resolving the

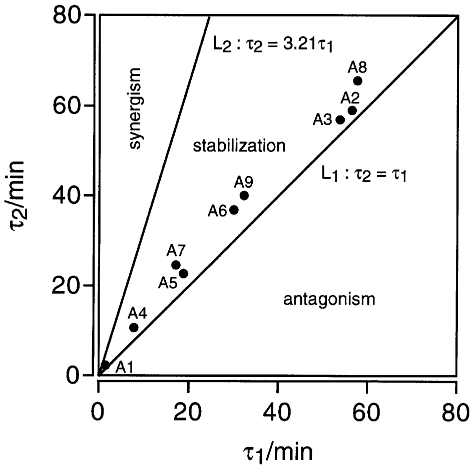

Fig. 2. Plot of τ_2 (min) versus τ_1 (min) for the formulations A1–A7 that contain carbon black where τ_1 is the OIt at CB level $w_1 = 0.726\%$ (w/w) and τ_2 is the OIt at CB level $w_2 = 2.33\%$ (w/w). The line L_2 has gradient $m = 3.21$ where $m = w_2/w_1$.

relative stabilities of the formulations by giving a clear graphical representation of the order of these stabilities. Indeed, formulation A1 has the lowest stability of the formulations considered and its low value of $\Delta\tau$ reflects the poor effectiveness of CB in this formulation. This observation is also consistent with the fact that poor stabilities are usually found in formulations that contain AO2 alone as the base stabilizer [14,22,23]. The formulation that exhibits the greatest stability is A8 and this result is consistent with the findings of a previous study [5]. Formulations A2 and A3 exhibit OIt values that are comparable to that of formulation A8. However, the effectiveness of CB in A2 and A3 is not as high as it is in A8 [5] and high levels of base stabilization are needed to achieve the OIt values exhibited by A2 and A3. Thus for these reasons, formulations A2 and A3 are considered to be inferior to formulation A8.

The line L_2 that represents cases where a 'directly additive' effect is observed upon the incorporation of CB in the formulation has been drawn in Fig. 2 for comparison. This line has a gradient of 3.21 which is the numerical value of the ratio w_2/w_1 used in the series of CB-containing formulations. Systems whose coordinates lie in the region between L_1 and L_2 are systems where the incorporation of CB results in stabilization of the polymer. Systems that lie in the region between L_2 and the τ_2 axis are ones where the incorporation of CB at the higher level of w_2 produces a greater than additive effect on stability and so this region is the one in which the coordinates of synergistic systems will be located. Using similar reasoning, the region between L_1 and the τ_1 axis is the region in which the coordinates of antagonistic systems will be located. Each of these regions has been labelled in Fig. 2.

The observation that most of the points in Fig. 2 lie close to the line L_1 and not L_2 reflects the fact that CB is a mild thermal antioxidant [6–11] and suggests that the stability imparted to a given formulation by the incorporation of CB is by no means a 'directly additive' effect. The latter may be a consequence of the uneven distribution of CB in the polymer [9,24] or other complicated effects caused by the interaction between CB and the base stabilization [5]. Nonetheless, for the polymer systems A1–A9 the addition of CB is expected to increase the OIt and so the magnitude of $\Delta\tau$ is expected to increase as the effectiveness of CB in the formulation increases. Fig. 3 is a plot of $\Delta\tau$ versus k_1 for the formulations A1–A9. The gradient of the regression line has a value that is reasonably close to the theoretical value of $\Delta w = 1.6$ used in these formulations. The linearity of this plot confirms that $\Delta\tau$ can be taken as an indicator of CB effectiveness within the formulation, as expected.

It is possible to derive from the OIt data plotted on the stability parameter map shown in Fig. 2 a single quantity for each formulation where the magnitude of that quantity reflects the degree of stability of the formulation. A set of such quantities calculated for a given series of formulations in which the base stabilization has been varied is useful for identifying the optimum formulation and/or differentiating between formulations of similar stability.

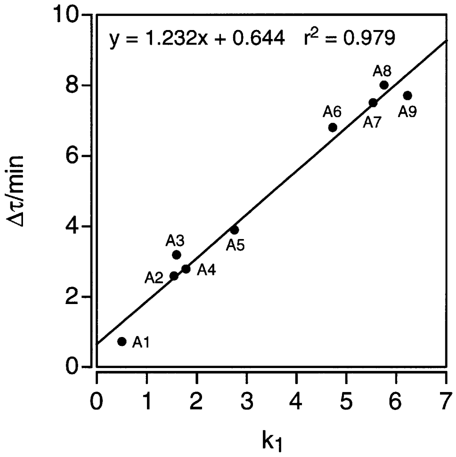

Fig. 3. Plot of the OIt difference, $\Delta\tau = \tau_2 - \tau_1$ (min) versus the additive effectiveness parameter, k_1, for the formulations A1–A7 where τ_1 (min) is the OIt at CB level w_1 (%w/w) and τ_2 (min) is the OIt at CB level w_2 (%w/w). The linearity of this plot confirms that $\Delta\tau$ can be taken as a direct indicator of additive effectiveness within the formulation. Note: units of k_1 are min/%w/w CB [5].

Consider the case of a formulation that has its OIt coordinates (τ_1, τ_2) within the 'stabilization' region of the stability parameter map, as is the case for each of the points plotted in Fig. 2. The magnitude, r, of the vector **P** drawn from the origin to $P(\tau_1, \tau_2)$ is indicative of the stability of the particular formulation (see also Fig. 1). Furthermore, if one considers two such vectors of equal magnitude drawn in this region then one may differentiate between the corresponding formulations on the basis of the angle, θ, that each vector makes with the line L_1. The formulation in which the additive exhibits greater effectiveness will be the one whose vector lies at a more obtuse angle to the line L_1. When considering a series of formulations, one may propose that the optimum formulation is the one that has the maximum value of the function $F_1(r, \theta)$

$$F_1(r, \theta) = r \times f(\theta) \tag{3}$$

where $F_1(r, \theta)$ is the product of the vector magnitude, r, and an angular function, $f(\theta)$. Clearly, in terms of τ_1 and τ_2, r is given by Eq. (4):

$$r = \left(\tau_1^2 + \tau_2^2\right)^{1/2} \tag{4}$$

Within the 'stabilization' and 'synergism' regions the angle θ between the vector **P** and the line L_1 is given by Eq. (5) where θ can vary in the range $0 \leq \theta \leq \pi/4$.

$$\theta = \tan^{-1}(\tau_2/\tau_1) - \pi/4 \tag{5}$$

The nature of the function $f(\theta)$ must be such that $f(0) = 1$ and $f(\theta) \to \infty$ as $\theta \to \pi/4$. Eq. (6) is the simplest function that exhibits this behaviour and may be used in conjunction with Eqs. (3)–(5) to calculate the value of $F_1(r, \theta)$ for a

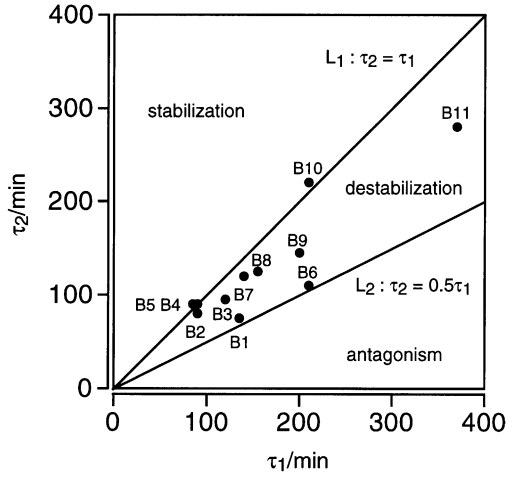

Fig. 4. Plot of τ_2 (min) versus τ_1 (min) for the formulations B1–B11 that contain dicumyl peroxide cross-linking agent where τ_1 is the CL-OIt at peroxide level $w_1 = 0.5\%$ (w/w) and τ_2 is the OIt at peroxide level $w_2 = 1.0\%$ (w/w). The line L_2 has gradient $m = 0.5$ where $m = w_2/w_1$.

given formulation

$$f(\theta) = (\pi/4 - \theta)^{-1} - 4/\pi + 1 \qquad (6)$$

Values of $F_1(r, \theta)$ were calculated for each of the formulations A1–A9 and these are listed in Table 1. The relative order of magnitudes of these values corresponds directly to the order of stability amongst the formulations as indicated by the stability parameter map (Fig. 2).

4.2. Formulations of LDPE containing peroxide

The detrimental role that polymer hydroperoxides play in the oxidative degradation of polyolefins is well established [8,23,25–29] and so it is expected that the presence of hydroperoxides, and indeed peroxides, in a LDPE formulation will destabilize the material and lead to shorter OIt values. Fig. 4 is a plot of the CL-OIt obtained for the peroxide-containing LDPE formulations at $w_2 = 1.0\%$ (w/w) cross-linking agent (τ_2/min) versus the CL-OIt at $w_1 = 0.5\%$ (w/w) of cross-linking agent (τ_1/min). It is clear from this plot that the addition of dicumyl peroxide cross-linking agent generally destabilizes the LDPE formulation since most of the points lie below the line L_1. The individual values of τ_1 and τ_2 from which Fig. 4 was constructed appear in Table 3 along with the corresponding values of $\Delta\tau$ It is important to note that the magnitude of $\Delta\tau$ is expected to decrease as the sensitivity of the base stabilization to dicumyl peroxide decreases. Thus, formulations with low values of $\Delta\tau$ are ones that are least affected by the incorporation of dicumyl peroxide.

The line L_1 in Fig. 4 has a gradient of unity and the region between L_1 and the τ_2 axis represents those systems, albeit unlikely ones in this particular case, where synergistic interactions occur between the additive and the substrate. Thus coordinates in this region correspond to unlikely systems where the addition of 1.0% (w/w) dicumyl peroxide produces an OIt that is greater than that obtained in the presence of 0.5% (w/w) dicumyl peroxide. The line L_2, where $\tau_2 = m\tau_1$ and $m = w_1/w_2$ defines systems where the incorporation of the additive produces an effect that is proportional to the level of the additive. The region between L_2 and the τ_1 axis encompasses systems where antagonistic interactions occur between the additive and the substrate. Thus systems whose coordinates lie in this region are ones in which an increase in the level of dicumyl peroxide from 0.5% (w/w) to 1.0% (w/w) produces a decrease in the OIt that is greater than a factor of two. The region between L_1 and L_2 encompasses systems that range from a situation where the incorporation of the additive has 'no effect' (i.e. along L_1) to one where it has a 'directly additive' effect (i.e. along L_2). Thus the region between lines L_1 and L_2 is the one in which 'destabilization' occurs to an extent that can be considered to be 'normal' given the nature of the additive.

The relative order of stabilities of the peroxide-containing formulations can be numerically established in an analogous manner to that used in the case of the CB-containing formulations. However, in the case of peroxide-containing formulations an increase in the level of the additive (i.e. dicumyl peroxide) is expected to bring about a decrease in the observed property (i.e. the OIt). In terms of

Table 3
Base stabilization details for the LDPE formulations together with corresponding values of (i) the OIt at 0.1% (w/w) dicumyl peroxide (τ_1) and the OIt at 0.5% (w/w) dicumyl peroxide (τ_2), (ii) the OIt difference, $\Delta\tau = \tau_2 - \tau_1$ and (iii) the function $F_2(r, \theta)$

ID	Antioxidant (AO) system	τ_1 (min)	τ_2 (min)	$\Delta\tau$ (min)	$F_2(r, \theta)$
B1	Hydrolysis-stabilized phosphite	135	75	− 60	90.9
B2	Phenolic/S-containing AO blend	90	80	− 10	109.2
B3	Sterically hindered phenol	120	95	− 25	125.4
B4	Polybutylated bis-phenol A	90	90	0	127.3
B5	Sterically hindered phenol	85	90	− 5	129.5
B6	Difunctional sterically hindered phenol	210	110	− 100	131.8
B7	Lactone blend	140	120	− 20	162.0
B8	Polysiloxane-bound HALS	155	125	− 30	165.9
B9	Sterically hindered bis-thiophenol	200	145	− 55	187.0
B10	Polymeric dihydroquinolene	210	220	10	315.7
B11	Styrenated phenol/S-containing AO blend	370	280	− 90	365.2

the angular function, $f(\theta)$, the formulation that exhibits the least susceptibility to the additive will be the one whose vector **P** lies at the most acute angle to the line L_1. Thus, in the 'destabilization' region, the optimum formulation will be the one having the maximum value of the function $F_2(r,\theta)$ where the latter is the quotient between the vector magnitude, r, and the angular function $f(\theta)$:

$$F_2(r,\theta) = r/f(\theta) \qquad (7)$$

In the 'destabilization' region, θ varies in the range $0 \le \theta \le \pi/4$ and its value is calculated using Eq. (8)

$$\theta = \pi/4 - \tan^{-1}(\tau_2/\tau_1) \qquad (8)$$

Values of the function $F_2(r,\theta)$ for the peroxide-containing formulations B1–B11 were calculated using Eqs. (4) and (6)–(8) and the values appear in Table 3.

The data in Table 3 are listed in order of increasing values of the function $F_2(r,\theta)$ and this enables the relative stabilities of the formulations to be compared. Perhaps a more distinct assessment of the relative stabilities of the formulations can be made when the values of $\Delta\tau$ are plotted against the corresponding $F_2(r,\theta)$ values as shown in Fig. 5. This plot highlights the wide range of sensitivities of the base formulations to the addition of dicumyl peroxide as evidenced by the variation in the values of $\Delta\tau$. The plot also enables the most stable formulations to be readily identified as those that have the highest values of the function $F_2(r,\theta)$ and shows groupings of stabilization systems that possess similar stability. Most notable is the case of the various phenolic stabilizers that were studied, all of which are seen to form a cluster on the basis of their $F_2(r,\theta)$ values.

Fig. 5 reveals an increasing trend in the stability of peroxide-containing polyethylene (PE) as the base stabilization package is varied from a system containing phosphite alone, through hindered phenolic systems, lactone and polymer-bound HALS systems, to the hindered bisthiophenol, the polymeric dihydroquinoline (DHQ) and the blend of a styrenated phenolic/sulfur-containing AO.

It is interesting to note that formulation B1 exhibits the lowest value of $F_2(r,\theta)$. This possibly reflects the sensitivity of phosphites to oxidation in general and again illustrates the poor stability achieved when a phosphite AO is incorporated in the absence of a phenolic AO [14,22,23] (cf. results for formulation A1). Formulations B11 and B10 exhibit high stabilities as evidenced by their values of $F_2(r,\theta)$. The $\Delta\tau$ values suggest that formulation B11 is more sensitive to dicumyl peroxide addition than B10; the latter formulation seemingly showing a slight 'synergistic' interaction with the dicumyl peroxide cross-linking agent to produce a stabilizing effect as evidenced by its positive value of $\Delta\tau$. The apparent stability of formulation B10 may be due to the polyfunctional nature of its stabilizer and this may also account for the greater stability of B10 compared with, say, formulation B9. Nonetheless, the observed OIt values for the B10 formulation are lower than those observed for the B11 formulation and so B11 is deemed to possess the highest thermooxidative stability of all the formulations tested. The sensitivity of B11 to dicumyl peroxide addition could be due to: (i) a reduced effectiveness of the phenol resulting from its styrenation and consequent reduced mobility in the polymer matrix and/or (ii) dicumyl peroxide attack of species such as zinc dibutyldithiocarbamate that form part of the commercially blended stabilizer package.

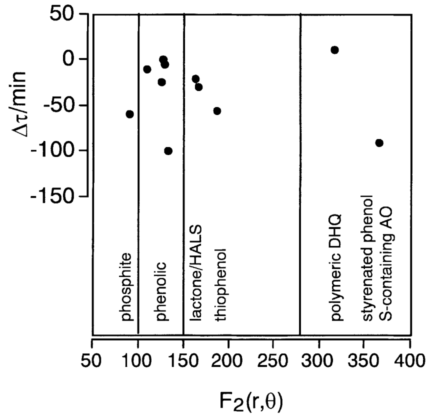

Fig. 5. Plot of the CL-OIt difference, $\Delta\tau$ (min) versus the corresponding value of the function $F_2(r,\theta)$ for formulations B1–B11.

The formulations B2–B5 inclusive contain hindered phenolic AO systems and most of these formulations have low sensitivities to dicumyl peroxide addition as evidenced by their comparatively low values of $\Delta\tau$. It is likely that these results reflect the efficiency with which phenolic AOs react with peroxyl radicals. However, the relatively low OIt values observed for these systems suggest that during processing the phenolic AO may be used primarily in a reaction with the dicumyl peroxide cross-linking agent thereby reducing the effective concentration of the AO in the processed material and ultimately the ability of the AO to protect the substrate. Formulation B6 shows a particularly high sensitivity to dicumyl peroxide addition compared with the other systems that contain hindered phenolic AOs. This may be attributable to the phenolic AO in formulation B6 being difunctional or the fact that this AO is the least hindered of the phenolic AOs studied. A high sensitivity to peroxides is also exhibited by formulation B11, which contains a tetrafunctional hindered phenolic stabilizer as part of its stabilizing package.

It is interesting to note that formulations B7 and B8, which contain the lactone blend and polymer-bound HALS systems, respectively, exhibit similar stabilities and similar sensitivities to dicumyl peroxide addition (Fig. 5). These AO systems impart an intermediate degree of stability to the polymer as indicated by their $F_2(r,\theta)$ values. One might expect the polymer-bound HALS to perform in this way due to its decreased mobility in the substrate and so the apparent equivalence of these two AO systems perhaps reflects more the suppressed performance of the lactone blend in the presence of the dicumyl peroxide cross-linking agent.

5. Conclusions

The techniques of stability parameter mapping and stability vector analysis developed in this paper show considerable potential for a more general application to: (i) other polymer properties that reflect oxidative stability and (ii) other formulations of commercial interest. The application of stability vector analysis to the now well-characterized system of MDPE containing CB produces results that are compatible with those obtained previously using a different technique of stability assessment. Stability vector analysis can also be applied successfully to the treatment of OIt data derived from experiments designed to assess the stability of LDPE in the presence of dicumyl peroxide cross-linking agent. In the case of the latter, the application of the method confirms: (i) the expectedly low oxidative stability imparted to PE by the use of a phosphite stabilizer in the absence of a phenolic co-stabilizer, and (ii) the efficiency of phenolic AOs in interacting with peroxides. It was found that a styrenated phenolic stabilizer blended with zinc dibutyldithiocarbamate and zinc stearate is an effective system for maintaining the stability of LDPE cross-linked in the presence of dicumyl peroxide.

The data presented in the latter part of the paper are part of a wider study of the effects of incorporating cross-linking peroxides on the thermooxidative stability of PE that is currently underway in our laboratory.

Acknowledgments

The authors are grateful to Pirelli Cables Limited for financial support for PKF and to Dr John Scheirs, ExcelPlas Australia Limited for his help in relation to stabilizer identities. SWB acknowledges Victoria University of Technology for supporting his sabbatical leave during which time this project was undertaken. He is also indebted to NCB and the members of the polymer research group at the University of Sussex for their helpful discussions and kind hospitality extended during his visit.

References

[1] Park SH, Lim JH, Baba Y. Annal Inst Stat Math 1993;45:655–64.
[2] Zhang L, Liang YZ, Jiang JH, Yu RQ, Fang KT. Anal Chim Acta 1998;370:65–77.
[3] Billingham NC, Bott DC, Manke AS. In: Grassie N, editor. Developments in polymer degradation—3. London: Applied Science Publishers; 1988. p. 63–100.
[4] Billingham NC, Fearon PK, Whiteman DJ, Dudler V. Proceedings of the Fifth Addcon World Conference, Prague, Czech Republic; October 1999, paper 23.
[5] Phease TL, Billingham NC, Bigger SW. Polymer 2000;41:9123–30.
[6] Foster G. In: Pospisil J, Klemchuk PP, editors. Oxidation and inhibition in organic materials, vol. 2. Boca Raton, FL: CRC Press; 1990. p. 203–85.
[7] Hawkins WL. Polym News 1977;4:132.
[8] Hawkins WL. J Polym Sci 1976;57:319–28.
[9] Hawkins WL, Matreyek W, Winslow FH. J Polym Sci 1959;41:1–11.
[10] Mwila J, Miraftab M, Horrocks AR. Polym Degrad Stab 1994;44:351–6.
[11] Kovacs E, Wolkober Z. J Polym Sci, Polym Symp Ser 1976;57:171–80.
[12] Pleshanov VP, Berlyant SM, Burukhina GA. Polym Sci USSR 1982;24:1462–8.
[13] Gugumus F. Polym Degrad Stab 1994;46:123–40.
[14] Pauquet JR, Todesco RV, Drake WO. Limitations and applications of OIt to quality control of polyolefins. Basel, Switzerland: Ciba-Geigy Ltd; 1993.
[15] Pusey BB, Chen MT, Roberts WL. Proc 20th Int Wire Cable Symp 1971;209.
[16] Howard JB. Proc 21st Int Wire Cable Symp 1972;329.
[17] Kiss K, Malawer E. Proc 26th Int Wire Cable Symp 1977;68–82.
[18] Schmutz Th, Kramer E, Zweifel H. OIt—a tool to characterize the thermooxidative degradation of a PE-MD pipe resin. Basel, Switzerland: Ciba-Geigy Ltd; 1995.
[19] Bernstein B, Lee P. Proc 24th Int Wire Cable Symp 1975;202–12.
[20] Chen Y, Ranby B. J Polym Sci, Polym Symp Ser 1990;28:1847–59.
[21] Moss S, Zweifel H. Polym Degrad Stab 1989;25:217–45.
[22] Pauquet JR. Oxygen induction time—influence of phosphite on OIt. Intermediate report, Basel, Switzerland: Ciba-Geigy Ltd; 1989.
[23] Gugumus F. In: Scott G, editor. Mechanisms of polymer degradation and stabilisation. London: Elsevier; 1990. p. 169–210.
[24] Scott G. In: Klemchuk PP, editor. Polymer stabilization and degradation, vol. 14. Missouri: American Chemical Society; 1985. p. 173–96.
[25] Pauquet J. Kunststoffe 1996;86:940–6.
[26] Bolland J, Gee G. Trans Faraday Soc 1946;42:236–44.
[27] Faucitano A, Buttafava A, Camino G, Greci L. Trends Polym Sci 1996;4:92–8.
[28] Gugumus F. Polym Degrad Stab 1995;49:29–50.
[29] Hawkins WL, Winslow FH. In: Raff RAV, Doak KW, editors. Crystalline olefin polymers—2. New York: Interscience Publishers; 1964. p. 361–98.