

The effect of carbon black on the oxidative induction time of medium-density polyethylene

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Abstract

An extensive series of: (i) oxidative induction time (OIT) measurements derived from differential scanning calorimetry experiments, and (ii) stabilizer analyses by high performance liquid chromatography were conducted on medium-density polyethylene (MDPE) stabilized with various levels of Irganox 1010 (penta-erythrityl-tetrakis-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate), Irgafos 168 (tris-(2,4-di-*tert*-butyl-phenyl)-phosphite), and carbon black (CB). The OIT data were analyzed using a novel interpretation method, which is described and applied. It was found that: (i) addition of CB to base-stabilized MDPE increases stability and reduces OIT variability; (ii) the optimum effective concentrations of Irganox 1010, Irgafos 168 and CB are 1690 ppm, 1580 ppm and 2.5% w/w, respectively; and (iii) interactions between CB and the base co-stabilizers may occur at high loadings of the latter but CB does not affect the extraction of the base co-stabilizers which are extracted with efficiencies of ca. 80% and 100% for Irganox 1010 and Irgafos 168, respectively. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The thermooxidative stability of a polymeric formulation may be assessed by using a differential scanning calorimeter to measure its oxidative induction time (OIT) which is the time when the onset of thermal oxidation occurs in the melt [1]. The measurement of OIT is one of the most practical and commonly used methods for obtaining information on polymer stability, antioxidant effectiveness, and the degree of degradation incurred during polymer processing. However, OIT data that are derived from differential scanning calorimetry (DSC) experiments need to be interpreted cautiously as these data are obtained at temperatures above the melting point of the polymer [2].

The addition of an antioxidant to a polymer inhibits its oxidative degradation. If the concentration of antioxidant is increased, the onset of oxidation is delayed and an increase in the OIT is observed. In the case of sterically hindered phenolic antioxidants, a linear relationship exists between the concentration of the stabilizer and the observed OIT [3–7]. Thus, the measurement of the OIT could be used as an analytical method for estimating the level of a known

phenolic antioxidant. It is important to note, however, that the stabilizing efficiency of a particular additive depends on its chemical structure and so the OIT response depends on the type of antioxidant that is used [8].

A linear relationship between the concentration of the antioxidant and the OIT has also been found for combinations of phenolic and phosphite stabilizers [9–12], where the slope of the calibration curve established using different levels of phenolic antioxidant increases with increasing phosphite concentration. It has been reported [13], however, that phosphite stabilizers alone do not increase the OIT of polyethylene (PE) in the temperature range of 180–210°C. Nonetheless, it is reasonable to suggest that OIT measurements can be used for the purposes of quality control provided the nature of the stabilizing system is known [9,14–16]. However, no conclusions can be drawn about the concentrations of individual components in blended stabilizing systems if OIT data are the only data that are available. As is the case for most accelerated degradation tests involving PE, caution should be exercised when using OIT data for the prediction of long-term thermal stability of polymeric formulations [9,15,16].

It is generally agreed that the efficiency of a given stabilizing package depends on the solubility, diffusion and

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migration within the polymer of its individual additives [17,18]. In this regard, one study [19] has suggested that the synergy observed between a thermal antioxidant and an ultraviolet stabilizer is a result of the migration of the antioxidant molecules from the inner regions of the material to the surface. The interior of the material may thus act as a reservoir that supplies antioxidant to the surface where it is utilized more efficiently than in the bulk. This reasoning may explain the increase in synergy that occurs upon increasing the thickness of the sample [19]. Moreover, the migration and loss of antioxidants in a certain grade of medium-density polyethylene (MDPE) used for hot water pipes has been extensively reviewed and modelled by Gedde et al. [20–25].

The addition of an additive such as carbon black (CB) to a polymer containing a stabilizing system might be expected to interfere with the migration of the antioxidant and decrease, or even eliminate, any synergy that would otherwise occur. Nonetheless, it has been established that CB plays a significant role in retarding the thermal oxidation of polymeric materials, either by acting as a mild thermal antioxidant or by influencing the activity of other antioxidants [26–31]. It is therefore expected that the incremental addition of CB to a polymeric formulation will, in general, increase the observed OIT.

Carbon black has a particle size that is comparable to the size of the crystallites in PE and so the mixing of CB with PE is usually performed above the melting point of the polymer to optimize the dispersion of the CB. In the liquid state, the polymer is completely amorphous and so molecular species such as antioxidants can become almost uniformly dispersed. On the other hand, the migration of CB particles may be inhibited by their large size [26,28,29] and so CB particles may not be as uniformly dispersed in the polymer melt as are molecular stabilizers. In the solid state, the inherently heterogeneous nature of PE ensures that CB [28] and other additives [17,18,32,33] are concentrated in the amorphous regions of the polymer, resulting in an overall uneven distribution [28,34]. Presumably, the addition of CB changes the morphology and crystallinity of the solid polymer, as the growing crystals have to accommodate the CB particles.

Kovacs and Wolkober [31] suggest that an interaction takes place between various stabilizers and the active sites of CB in which CB particles absorb antioxidant molecules on their surface thereby reducing the mobility of the antioxidant. However, the extent of such an effect depends very much on the chemical nature of the CB. In contrast to this, Hawkins and Winslow [35] suggest the presence of CB has a positive effect on the performance of an antioxidant. Furthermore, the contention that CB particles interact in some way with antioxidant molecules is supported to some extent by Moisan [17] who suggests that losses of phenolic antioxidant by migration in low-density polyethylene (LDPE) are considerably reduced in the presence of CB. This effect could be either due to binding between the

antioxidant and CB or an increase in the tortuosity experienced by the antioxidant in the presence of CB.

Although the individual and synergistic effects of antioxidants and CB on the oxidative stability of PE have been well documented, it appears that few studies have examined the effect of CB on the variability of OIT measurements derived from DSC measurements. This paper reports the results of an extensive series of OIT measurements and stabilizer analyses that were made on a medium-density, pipe-grade PE containing various base stabilizing packages in order to: (i) assess the extent of variability in OIT measurements in the presence and absence of CB; (ii) explore a novel approach to results interpretation that is aimed at determining the optimum level of each additive in the stabilizing package; and (iii) explore the question of whether interactions occur between CB and the base stabilizing package.

2. Experimental

2.1. Materials

A commercial grade, MDPE resin having a melt flow index (MFI) of 14.6 dg min⁻¹ (190°C, 2.13 kg) and density of 0.953 g ml⁻¹ was used to make all formulations for the study. The MFI and density were determined in accordance with appropriate standard methods [36,37]. The unstabilized resin and all formulations made from the resin were stored in a refrigerator under nitrogen to avoid oxidation.

The primary antioxidant Irganox 1010 (AO1, pentaerythrityl-tetrakis-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate) and the secondary antioxidant Irgafos 168 (AO2, tris-(2,4-di-*tert*-butylphenyl)-phosphite) were obtained from Ciba Australia Limited and were used as received. Carbon black (Vulcan P, supplied by Cabot Limited, Australia) was found to impart a pH of 7.4 to water when measured using the standard method [38]. It had a volatile content less than 2% w/w, particle size range of 10–25 nm and specific gravity of 1.75. These characteristics were determined using appropriate standard methods [39–41].

2.2. Polymer formulations

Formulations for analysis were selected on the basis of a central composite design (CCD) strategy to reduce the number of formulations necessary [42,43]. The CCD was manipulated so as to take into consideration the specification range for the antioxidants when used in commercial applications. A zero point and levels well below and above the specification range were also included. As a result, nominal antioxidant levels of zero, 290, 990, 1690 and 1980 ppm were used at ratios specified by the CCD strategy. Nine formulations containing AO1 and/or AO2 were prepared using four levels of CB, i.e. nominally zero, 1.0, 2.5 and 4.0% w/w, making a total of 36

Table 1

Details of base stabilization of MDPE formulations together with results of linear least-squares regression analyses performed on OIT data obtained at different loadings of CB

| Sample set | Concentration (ppm) ^a | | Ratio AO1/AO2 | τ_0 (min) | k_1 ^b | r^{2c} |
|------------|----------------------------------|------|------------------|-----------------------|------------------------|----------|
| | AO1 | AO2 | | | | |
| S1 | 0 | 990 | 0 | 1.3 [^] 0.3 | 0.50 [^] 0.12 | 0.942 |
| S2 | 990 | 0 | – | 14.5 [^] 3.2 | 2.75 [^] 1.41 | 0.785 |
| S3 | 290 | 290 | 1:1 | 6.5 [^] 0.1 | 1.78 [^] 0.04 | 0.999 |
| S4 | 290 | 1690 | 1:6 | 13.1 [^] 1.2 | 5.53 [^] 1.44 | 0.743 |
| S5 | 1690 | 290 | 6:1 | 27.8 [^] 3.5 | 6.22 [^] 1.55 | 0.939 |
| S6 | 990 | 990 | 1:1 | 26.6 [^] 2.4 | 4.72 [^] 1.23 | 0.862 |
| S7 | 1690 | 1690 | 1:1 | 52.5 [^] 1.8 | 5.75 [^] 1.25 | 0.986 |
| S8 | 990 | 1980 | 1:2 | 53.1 [^] 0.9 | 1.59 [^] 0.41 | 0.981 |
| S9 | 1980 | 990 | 2:1 | 55.4 [^] 0.6 | 1.54 [^] 0.49 | 0.905 |

^a Nominal additive concentrations are given.

^b Units of k_1 are min/% w/w CB.

^c Linear least-squares regression coefficient, r^2 .

formulations. Details of the base stabilizing packages are listed in the first four columns of Table 1.

2.3. Masterbatch preparation and compounding

To achieve homogeneity, all additives were incorporated in the MDPE via appropriate masterbatches. The masterbatches for AO1 and AO2 were prepared using a Brabender plasticorder. Batches (40 g) of unstabilized MDPE fluff and antioxidant were plasticized and homogenized for 5 min at 170°C and 60 rpm to achieve a masterbatch of 10% w/w antioxidant. The CB masterbatch containing 20% w/w of CB was prepared by physically blending unstabilized MDPE fluff and free CB [44]. This was followed by twin-screw extrusion using a ZDSK extruder operated at 190°C and 120 rpm.

The final formulations were produced in the plasticorder. Batches (40 g) of unstabilized MDPE fluff and additives in the form of a masterbatch were plasticized and homogenized for 5 min at 170°C and 60 rpm in the plasticorder. The homogenized mixture was removed from the plasticorder, cooled to room temperature and finely ground in a Wiley mill. The ground material was compression-moulded [45] for 1 min at 180°C into a 0.5 mm thick plaque using a Specac 10-tonne press. The plaque was immediately quenched in cold water (10°C).

2.4. Oxidative induction time analyses

The OIT tests [30] were conducted using a Perkin–Elmer DSC-7 instrument equipped with a robotic autosampler. The instrument was temperature-calibrated at 1°C min⁻¹ using tin and indium standards. Samples, in the form of discs, were punched from the compression-moulded plaques. Each sample had a diameter of ca. 5 mm and weighed ca. 8 mg. The sample was placed in a clean aluminium pan and crimped with an aluminium lid to facilitate its reliable handling by the robotics system of the instrument. The aluminium lids had a 3 mm diameter hole in the 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. The OIT was taken as the time corresponding to the point at which the extrapolated exotherm intersects the extended baseline. A minimum of six replicates were taken from a plaque made for each formulation and tested (see first four columns of Table 1 for details of base stabilization).

2.5. Thermogravimetric analyses

The level of CB introduced into each formulation through masterbatch addition was measured by thermogravimetric analysis using a Perkin–Elmer TGA-7 instrument. The instrument was temperature-calibrated at 50°C min⁻¹ using a perk alloy standard. For thermogravimetric analysis of the polymer samples, the procedure involved taking a small cutting (ca. 8–12 mg) from each of the compression-moulded plaques and heating it from 50 to 200°C at 100°C min⁻¹ under nitrogen (flow rate of 20 ml min⁻¹) followed by heating from 200 to 850°C at 50°C min⁻¹ under pure oxygen (flow rate of 20 ml min⁻¹).

2.6. Stabilizer extraction and HPLC analysis

The levels of AO1 and AO2 in the PE formulations after the compounding stage were determined by an extraction procedure that preceded analysis by high performance liquid chromatography (HPLC). The extraction procedure involved taking an accurately known mass of ca. 1 g of the finely ground PE formulation, placing it in 20 ml of AR chloroform and heating it in an oven at 60°C for at least 8 h. Extracts were cooled and filtered into 2 ml vials ready for analysis.

The HPLC analysis of the sample extracts was performed

using a Hewlett-Packard 1050C instrument equipped with a LiChrospher 60 RP-Select B, 5 μm (250 \times 4 mm²) column. The mobile phase was pure acetonitrile (flow rate 2.0 ml min⁻¹), the detector wavelength was 280 nm and the injection volume was 5.0 μl .

2.7. Relative error calculations

All relative errors in this work were calculated at the 95% confidence level in accordance with Eq. (1) and using the appropriate value of the Student *t*-distribution [46]:

$$\text{relative error} = t \frac{\sigma}{(\bar{x}\sqrt{n})} \quad (1)$$

where *t* is the critical value of the Student *t*-distribution at the set level of confidence, σ the standard deviation, *n* the number of samples, and \bar{x} the sample mean.

3. Results and discussion

3.1. The variability in OIT measurements

Fig. 1 is a plot of the percentage error in the OIT (%) against the level of CB (% w/w) calculated across all of the 36 formulations prepared for this study. Six replicates were run for each formulation and so the data shown in Fig. 1 are derived from the results of 216 separate OIT experiments. Thermogravimetric analyses were performed on each of the formulations to establish the analytical concentration of CB. The small variations in the CB levels observed within the data plotted in Fig. 1 are due to variances arising from CB masterbatch addition.

The data suggest that the variability in the observed OIT decreases from ca. 13 to 7% as the level of CB is increased above ca. 1% w/w. The spread in the error in OIT is high at each of the CB levels as evidenced by the magnitude of the confidence intervals. The decrease in the variability of the OIT as the CB level is increased may be attributed to the assertion that CB remains uniformly dispersed in PE in both the melt and solid phases [26,28,29] and its presence may facilitate the uniform distribution of antioxidant molecules. Thus at higher loadings of CB the distribution of the antioxidant is expected to be more uniform than it is at lower loadings. Consequently, lower variability in the OIT is observed, as the samples become more homogeneous. This explanation is also consistent with the suggestion that CB absorbs to some extent antioxidants on its surface [17,31,35].

Fig. 2 shows plots of the OIT versus the level of CB for two formulations of similar base stabilization efficiencies as revealed by the similar value of the intercept of each plot (τ_0) with the vertical axis. The 95% confidence intervals for the OITs support the observation that the variability of the OIT decreases as the level of CB increases. Furthermore, the data suggest that, to a good approximation, there is a linear relationship between the OIT and the level of CB. This is

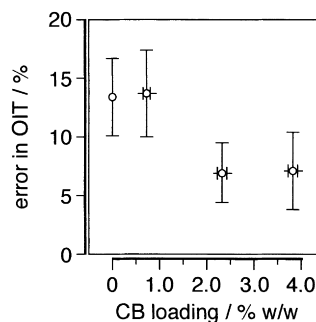


Fig. 1. Plot of the error in OIT (%) versus the CB level (% w/w) calculated across all of the 36 formulations prepared for this study. For each formulation, six replicates were run. The error was calculated at the 95% confidence level using the appropriate value of the Student *t*-statistic.

particularly so at low levels of CB and is consistent with the work of Pleshanov et al. [47] who report that, in the case of PE oxidation, there is a linear increase in the induction period with an increase in CB concentration over the range of 2–5.6% w/w CB. At CB levels greater than 9% w/w, it was found that CB no longer imparts a proportional antioxidant effect on PE and, in some cases, a decreased antioxidant effect is even observed [47]. Thus, at high levels of CB a deviation from linearity may occur and this is apparent in Fig. 2(a). At sufficiently low levels of CB the relationship between OIT and the level of CB can be represented by the simple linear Eq. (2):

$$\text{OIT} = k_1 \times [\text{CB}] + \tau_0 \quad (2)$$

where k_1 is a constant, [CB] the level of CB and τ_0 the OIT in the absence of CB.

Clearly, the value of τ_0 is indicative of the efficiency of

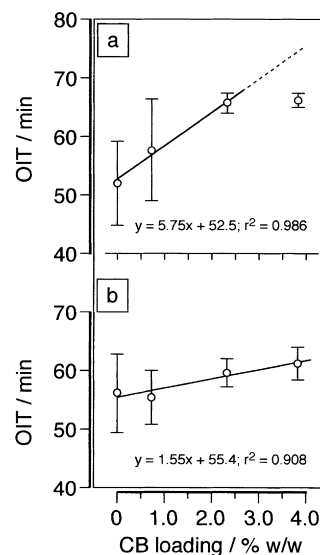


Fig. 2. Plots of OIT (min) versus the level of CB (% w/w) for: (a) sample set S7 and (b) sample set S9 which have similar base stabilization efficiencies. The values of τ_0 and k_1 are, respectively, indicative of the efficiency of the base stabilization and the effectiveness of CB within the formulation.

the base stabilization and the gradient k_1 is indicative of the effectiveness of CB within the given formulation. In particular, for a given increment in the level of CB, the corresponding increase in OIT will be greater, as the value of k_1 becomes greater. From the data plotted in Fig. 2 it is clear that for levels of CB less than 3% w/w the effectiveness of CB in sample set S7 (Fig. 2(a)) is greater than its effectiveness in sample set S9 (Fig. 2(b)).

3.2. Identifying the optimum base stabilization

Plots of the OIT versus the level of CB were constructed for all sample sets and the results of linear least-squares regression analyses of these plots are listed in Table 1 along with the corresponding base stabilization details for comparison. The level of CB at which the relationship between OIT and the level of CB begins to deviate from linearity varies amongst the formulations depending on the concentration of AO1 and AO2 used in the base stabilization. Thus, in some cases, the linear regression analyses (Table 1) were performed using only the data corresponding to the three lowest levels of CB.

The linear regression data listed in Table 1 can be used to determine the optimum levels of AO1, AO2 and CB within the sample sets that were studied. Clearly, the formulation that simultaneously exhibits a high inherent stability (reflected in its value of τ_0) as well as a high effectiveness of CB within the formulation (reflected in its value of k_1) will be the one that has the optimum stability. In order to easily identify any such formulation, the linear regression data in Table 1 were displayed in the form of a “map” where the constants k_1 and τ_0 are plotted as the abscissa and ordinate, respectively. Fig. 3 shows the “map” constructed from the regression data listed in Table 1. Although the interactions amongst the additives in each of the formulations are expected to be complex, a detailed analysis of the data listed in Table 1 in conjunction with the “map” shown in Fig. 3 reveals a number of interesting features:

1. Sample set S1 exhibits the poorest stability which is expected as it is known [4,13,48] that AO2 used alone in a formulation does not produce a significant OIT. Indeed, a certain threshold concentration of AO1 is necessary to enable AO2 to extend the OIT.
2. A comparison of sample sets S2 and S4 supports the notion [4,12] that the OIT is not a function of the concentration of AO1 alone. Sample set S2 contains AO1 alone at ca. 990 ppm and this produces an OIT of ca. 14.5 min. Sample set S4 contains both AO1, at a level of ca. 290 ppm which is significantly lower than the level of AO1 in S2, and AO2 at a level of ca. 1690 ppm. Despite its lower level of AO1, the latter formulation has a similar OIT to that of the S2 formulation. Similar behaviour is revealed by comparing sample set S5 with S6, S7 with S8 and S9 with S8.
3. The data for sample sets S3 and S5 suggest that, at a low

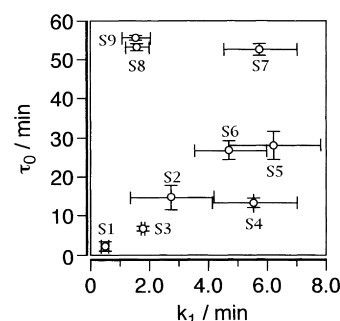


Fig. 3. Plot of τ_0 (min) versus k_1 (min/% w/w CB) parameters which constitutes a “map” enabling the optimum base stabilization to be readily determined. Sample set S7 is the optimum formulation since its parameters are located furthest from the origin.

and constant loading of AO2, both the effectiveness of CB and the stability of the formulation increases as the level of AO1 is increased. Similarly, the data for sample sets S3 and S4 suggest that, at a low and constant loading of AO1, the effectiveness of CB and the resultant stability of the formulation increases as the level of AO2 is increased.

4. The data for sample sets S3, S6 and S7 show that the inherent stability of the formulation, as reflected in its value of τ_0 , increases as the level of base stabilization is increased which is, of course, expected. The data also suggest that the effectiveness of CB, as reflected in the value of k_1 , increases as the level of base stabilization increases. However, the effectiveness of CB “levels off” at the highest level of base stabilization, which suggests that complex additive–additive interactions at such levels may disrupt any synergy that occurs at the lower levels. If the synergy results from a surface adsorption phenomenon, then presumably there will be a certain level of base stabilization at which all of the antioxidants will be adsorbed on the surface of the CB. If more antioxidant is added it will not interact with the CB and so no further enhancement of stability occurs.

Indeed, the possibility of there being an antagonistic interaction between the base stabilization and CB at high levels of the former is supported by the following observations:

1. A comparison of the data for sample sets S1, S6 and S9 (see Table 1) shows that, at a medium loading of AO2, the effectiveness of CB initially increases with the level of AO1 but then decreases markedly at the highest loading of this additive. On the other hand, the inherent stability of the formulation, as reflected in its value of τ_0 , increases with the level of AO1 for all loadings of AO1.
2. Similarly to the previous observation, a comparison of the k_1 data for sample sets S2, S6 and S8 (see Table 1) suggests that a situation analogous to the case of high-level loadings of AO1 exists also in the case of AO2. However, the overlap of the 95% confidence intervals for the k_1 data of AO2 means that a similar interpretation

cannot be made, as the differences between the data are not statistically significant. Nonetheless, the observed increase in the stability of these formulations with increased levels of AO2 is significant across all loadings of AO2.

3. The data plotted in Fig. 3 show that, with the exception of sample sets S8 and S9, there is a broad, upward trend between the inherent thermal stability of the formulation (i.e. the τ_0 value) and the effectiveness of CB within it (i.e. the k_1 value). The failure of sample sets S8 and S9 to conform to this trend may be attributed to antagonism between CB and the base stabilizers AO1 and/or AO2, when the level of either of these is increased above a certain level, say, ca. 1690 ppm.

It is clear from the “map” shown in Fig. 3 that sample set S7 contains the optimum base stabilization since its τ_0 and k_1 parameters lie furthest from the origin (i.e. at the top right-hand corner of the “map”). To determine the optimum level of CB in sample set S7 it is necessary to re-examine the plot of the OIT versus the level of CB for this formulation (see Fig. 2(a)). From this plot, the maximum antioxidant effect is reached at a CB loading of ca. 2.5% w/w. At levels of CB higher than this a departure from the ideal, linear behaviour is observed and a concomitant enhancement of the stability with an increasing level of CB no longer occurs.

3.3. HPLC analyses of the base co-stabilizers

The concentration of AO1 and AO2 in each sample set was determined analytically and plotted against the respective levels of these additives that were nominally added at the formulation stage in order to determine: (i) the extent to which each of the base stabilizers is consumed during processing; (ii) the efficiency by which each of these additives may be extracted from the polymer substrate under the extraction conditions used; and (iii) the extent to which CB interacts with the additives in the extraction process. Furthermore, the information gained from such an analysis enables the effective antioxidant level to be determined by correcting the nominal level for any loss during processing.

Fig. 4 shows plots of the concentrations of AO1 and AO2 determined analytically versus the nominal levels of these stabilizers that were added at the point of compounding. The plots were constructed using experimental data obtained across all of the four levels of CB used in this study. Hence, the linearity of these plots indicates from the outset that: (i) the presence of CB has little effect on the extraction of AO1 or AO2; and (ii) if the antioxidants are absorbed on the surface of the CB as has been suggested elsewhere [19,35,49] then this is easily reversed. To test the former assertion further, a series of linear least-squares regression analyses were performed on the extraction data that pertain to sample sets having the same level of CB. The results of these analyses are summarized in Table 2. It is clear that the gradient, k_2 , at each level of CB is not, at the 95% confi-

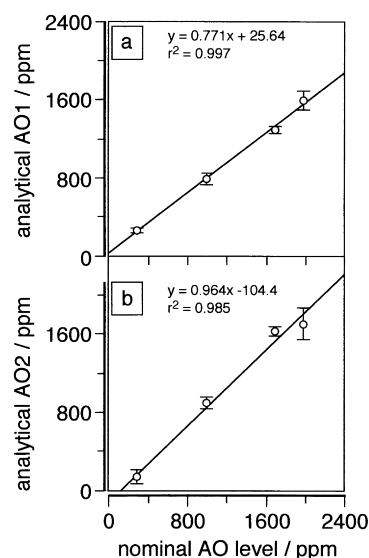


Fig. 4. Plot of the concentration of stabilizer (ppm) that was determined analytically following extraction versus the nominal level of the stabilizer (ppm) that was added during compounding for the co-stabilizers: (a) AO1; and (b) AO2. Each point is an average of the data obtained across all levels of CB used in this study.

dence level, significantly different to the average gradient taken across all levels of CB. This more detailed analysis supports further the assertion that the presence of CB does not significantly affect the efficiency by which either of the antioxidants AO1 or AO2 is extracted from the MDPE.

The point at which each of the regression lines in Fig. 4 intersects the horizontal axis is indicative of the amount of the antioxidant that is “consumed” during the processing of the formulation. For AO1, the regression line passes close to the origin. Within experimental error, the line can be considered to pass through the origin, as its intercept on the vertical axis is a small, positive value. Assuming the line passes through the origin, then this suggests that an undetectable amount of AO1 is consumed during processing. In contrast, the regression line for AO2 has a comparatively larger,

Table 2

Linear least-squares regression analyses of extraction experiments performed on AO1 and AO2

| Stabilizer | CB content (% w/w) | k_2 | c (ppm) | r^2 ^a |
|------------|--------------------|--------------------|-----------|--------------------|
| AO1 | 0 | 0.80 \wedge 0.06 | 21.4 | 0.994 |
| | 1.0 | 0.75 \wedge 0.02 | 27.4 | 0.999 |
| | 2.5 | 0.78 \wedge 0.07 | 67.0 | 0.993 |
| | 4.0 | 0.76 \wedge 0.05 | 48.7 | 0.996 |
| | Average | 0.77 \wedge 0.04 | 38.7 | 0.997 |
| AO2 | 0 | 0.97 \wedge 0.18 | -102.5 | 0.967 |
| | 1.0 | 0.99 \wedge 0.06 | -96.7 | 0.996 |
| | 2.5 | 0.89 \wedge 0.19 | -44.5 | 0.956 |
| | 4.0 | 1.02 \wedge 0.06 | -174.2 | 0.996 |
| | Average | 0.96 \wedge 0.12 | -104.4 | 0.985 |

^a Linear least-squares regression coefficient, r^2 .

negative intercept with the vertical axis which results in an intercept on the abscissa axis at 108 ppm. This suggests that ca. 108 ppm of AO2 is consumed during processing. Thus, the effective concentration of AO2 in the processed polymer can be calculated by subtracting 108 ppm from the nominal level of AO2 that was initially added.

The observed behaviour is consistent with the fact that in commercial applications, AO2 is added as a processing aid [9] that is sacrificed to ensure that AO1 is maintained through the elevated temperatures endured during processing. It is also known [13,50] that, in addition to protecting the polymer, AO2 preserves AO1. The preservation of AO1 by AO2 is achieved either by AO2 decreasing the yield of specific radicals that would otherwise be treated by AO1, or by AO2 regenerating phenolic moieties in AO1. The observed loss of AO2 may also occur as a result of the analytical procedure itself, as it is known [51] that AO2 is very readily oxidized by peroxides and/or hydroperoxides that may be present even in HPLC-grade solvents that are used in its analysis.

The slope of each line in Fig. 4 is indicative of the efficiency with which the particular antioxidant is extracted from the polymer. For AO1, a slope of ca. 0.8 suggests that about 20% of this additive is retained the MDPE matrix under the conditions used in the extraction procedure. However, a similar retention does not occur in the case of AO2 where the gradient being close to unity indicates that this additive is extracted very efficiently.

Pauquet et al. [4] and Moss and Zweifel [12] have considered a case where the level of AO1 analysed by HPLC differs significantly from the nominal level that was added prior to it being compounded with PE. Since AO1 is a tetrafunctional molecule, it was proposed that one of its four phenolic groups may react with the polymer during processing which, in turn, may cause some of the AO1 to be entrained in the polymer. Moreover, the fact that AO1 remains effective as a stabilizer despite such a reaction may be explained by the availability of its three remaining phenolic moieties to participate in stabilization reactions in the usual way. However, the lower extraction efficiency of AO1 compared with AO2 that is observed in the present study cannot be explained by the supposition that AO1 is entrained due to its reaction with the polymer. If AO1 is partially consumed during processing, then one would expect to observe a non-zero intercept on the abscissa axis of the plot in Fig. 4(a). The experimental data do not indicate this. Indeed, the experimental data suggest that a fixed proportion of AO2 is partitioned between the substrate and the extract across all levels of AO2.

The difference between the extraction efficiencies of AO1 and AO2 may be due to the considerable difference in the molecular weight (MW) of the two antioxidants. Generally, an increase in the MW of a stabilizer results in a decrease in its mobility within the polymer matrix [12,35]. Since AO1 is a much larger molecule than AO2, its lower mobility may prevent its complete extraction under the experimental

conditions used in this study. In addition, the higher MW of AO1 may render this compound more compatible with the substrate than AO2. This may explain the difference in the partitioning of these compounds during the extraction procedure.

4. Conclusions

The addition of CB to MDPE containing a phenolic and phosphite base co-stabilizing package enhances the OIT performance of the formulation. Furthermore, an increase in the level of CB results in a general decrease in the variability associated with the OIT results. The precise mechanism by which CB achieves this is unclear although it is likely that the presence of CB creates a more uniform distribution of the base stabilizers resulting in a more homogeneous material. Indeed, the additive–additive interactions that occur in the systems investigated are complex and there is an obvious need for further systematic experiments to be performed before a more definitive explanation of this observation can be proposed.

A plot of τ_0 , the inherent stability of a formulation that is produced by the base stabilizing package versus k_1 , the CB effectiveness indicator, is a novel and effective way of identifying formulations that possess desirable levels of stability. This method was successfully applied to the data generated during the present study. The optimum package of AO1, AO2 and CB that imparts maximum thermooxidative stability to the MDPE substrate is one in which the effective concentrations of AO1, AO2 and CB are ca. 1690 ppm, 1580 ppm (corrected for AO2 consumed during processing) and 2.5% w/w, respectively.

Some evidence of interactions between CB and the base co-stabilizers was obtained at high loadings of the latter. However, there is no evidence in the present study to suggest that CB affects the extraction efficiency of either of the base co-stabilizers. Indeed, AO1 can be extracted with an efficiency of ca. 80% and AO2 is extracted with almost 100% efficiency across all concentrations studied. The results indicate that ca. 108 ppm of AO2 is consumed during the processing operation and that a negligible amount of AO1 is consumed in this operation.

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