Efficiency of processing stabilizers using a micro-oxygen uptake technique

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The thermooxidative stability of various low density polyethylene (LDPE) film formulations was investigated using the technique of micro oxygen uptake measurement following multiple extrusions. The results show that the micro oxygen uptake technique is more sensitive than conventional test methods. High molecular weight hindered phenolic stabilizers are more effective in reducing gel formation during polymer film production than are lower molecular weight species such as butylated hydroxytoluene (BHT). The antioxidant 2,2'-ethylidene-bis-(4,6-di-tert-butylphenol) is an effective stabilizer, but it forms a highly coloured complex with transition metal impurities. The hindered phenol/organic phosphite system, comprising a combination of 0.008% (wt/wt) octadecyl-3-(3,5-di-tert-butyl)-4-hydroxy-phenol propionate and 0.032% (wt/wt) tris-(2,4-di-tert-butyl)phenyl phosphite, is effective in suppressing the formation of coloured products but does not provide adequate thermal stability.

INTRODUCTION

The current trend towards higher rates of production and greater use of reclaimed materials has meant that low density polyethylene (LDPE) is subjected to increased thermal and shear stresses. This creates the need for improved processing stability of LDPE[1]. Various high molecular weight film grades of LDPE are particularly susceptible to thermal instability during processing which can cause irregularities in the film. These irregularities are known as 'gels' or 'fisheyes' and are particles of loosely crosslinked polymer[2]. Cross-linking and subsequent gel formation are a result of oxidation during polymer processing at temperatures of the order of 200°C. In particular, gels originate from the extrusion process, where pockets of the polymer are trapped in circulating 'dead-spots' or 'hang-ups' in the flow path of the extruder. Polymer 'hang-ups', which occur near the extruder die, can cause film irregularities that are aligned in the machine direction and are termed 'arrowheads' due to their characteristic chevron shape[3]. Flow instability in the recirculating polymer melt, which can result from shear-thinning and chain-scission processes, may lead to crosslinked particles being torn away and swept back into the mainstream of flow. This causes the formation of gel 'showers' and 'haze bands' in the blown film. The oxidized gel particles may create localized film distortion and can produce film haze and reduction in gloss. Furthermore, the particles create stress concentrations which lower the tensile and impact strength of the film[4]. More effective means of thermal stabilization are currently being investigated in order to minimize gel formation in polymers.

The generally accepted scheme for the oxidative degradation of polyolefins was proposed originally by Bolland and coworkers[5]. Free radicals can be formed in a variety of initiation processes such as mechanical shear, the decomposition of hydroperoxides, homolytic cleavage of the polymer chains or direct reaction of the polymer with oxygen. The thermooxidative degradation of polymers begins slowly with an increase in concentration of the hydroperoxide species up to a critical level during the induction period[6-8]. This is followed by the auto-catalytic stage in which the hydroperoxide concentration decreases as hydroperoxyl radicals initiate other chain processes which ultimately result in a maximum rate of oxidation. A reduction in the rate of reaction occurs as the polymer begins to crosslink. During thermal oxidation in air the hydroperoxyl radicals in the polymer have a lifetime of about 10^{-2} s, compared with the much shorter lifetime of macroalkyl radicals[9] ($\approx 10^{-8}$ s). Therefore, the reaction between hydroperoxyl radicals and the polymer will proceed at a slower rate than that which occurs between oxygen and the macroalkyl radicals. This is consistent with the observed increase in the concentration of hydroperoxides during the induction period. However, due to high shear in the extruder many more macroalkyl radicals are formed and they have longer lifetimes because there is a limited amount of oxygen present. As a consequence, higher equilibrium concentrations of macroalkyl radicals can arise[10]. Similarly, lower equilibrium concentrations of hydroperoxides are expected to be formed during extrusion.

Termination reactions involving macroradical recombination are primarily responsible for crosslinking and gel formation. The extent of crosslinking as a result of these reactions is dependent on the oxygen concentration, because macroalkyl radical recombination competes with the formation of peroxyl radicals at lower oxygen concentrations. During extrusion the concentration of available oxygen is low[11] and thus the rate of reaction between macroalkyl radicals and oxygen is much lower than the rates of the radical recombination reactions[12-14].

Transition metal impurities are known to catalyse the oxidation of polyethylene in the melt during extrusion[15].

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These impurities may be residues of polymerization catalysts, such as titanium and aluminium ions, or may be species incorporated into the polymer during processing due to diffusion into the melt of iron and copper ions[16].

The amount of oxygen taken up per unit weight of polymer and the rate of autooxidation increase with the increasing number and size of chain branches. Tertiary hydrogen atoms at the branch points are more susceptible to abstraction and are more likely to take part in chain propagation reactions than methylene hydrogen atoms[17]. It is the enhanced reactivity of tertiary carbon–hydrogen bonds which makes LDPE less stable than high density polyethylene (HDPE), and leads to a higher degree of gel formation in LDPE at a given processing temperature.

Hindered phenols, such as 2,6-di-tert-butyl-4-methyl-phenol, (otherwise known as butylated hydroxy toluene or BHT), compete with the polymer substrate for peroxyl radicals and thus terminate the propagation reaction by readily transferring the labile hydrogen atom from their hydroxyl group. A phenoxyl radical is formed and it can undergo further radical scavenging[18,19].

The relatively low molecular weight of BHT results in good mobility within the polymer, but also leads to high losses during processing[20,21]. This high volatility is believed to be the cause of gel formation, because small quantities of polymer trapped in 'hang-ups' in the extruder will have their supply of BHT rapidly depleted. Other defects in films, such as bubbles and surface etch marks, can be formed by the migration of BHT to the surface where it evaporates to form small irregularities[22]. Extrusion losses of phenolic antioxidants cannot be compensated for due to the following reasons: the compatibility of low molecular weight additives with LDPE is considerably lower than with other poly-olefins[23]; high concentrations of hindered phenolics can actually promote oxidative degradation as a result of the pro-oxidant effect[24]; and excessive discoloration of the polymer substrate can occur.

The problem of high volatility may be overcome by modifying the antioxidant structure. The incorporation into the molecule of a long aliphatic chain, such as that present in octadecyl-3-(3,5-di-tert-butyl)-4-hydroxyphenol propionate[25], increases retention and solubility in the polymer matrix. The polar functional groups of the fatty acid chain are believed to cause stronger interaction between the polymer and stabilizer, leading to better compatibility and permanence[26]. On the other hand, bridging of two hindered phenolic rings with an alkylidene bond, as in the case of 2,2'-ethylidene-bis-(4,6-di-tert-butylphenol), imparts low volatility to the relatively low molecular weight antioxidant[27]. In addition, this stabilizer has twice the radical scavenging functionality of monocyclic antioxidants such as BHT.

Hindered organic phosphites decompose hydroperoxides and can preserve the colour of the polymer by interaction with the stilbene–quinone dimer or other coloured conversion products of phenolic stabilizers[28,29]. Sterically unhindered organic phosphites, such as tris-nonylphenyl phosphite, do not act as inhibitors but are mainly used to reduce discolouration[30]. A major drawback of most organic aliphatic phosphites is that they are quite susceptible to hydrolysis, which causes a gradual reduction of their effectiveness and the evolution of volatile products during extrusion. Aromatic phosphites, such as tris-(2,4-di-tert-butyl)phenyl phosphite, are inherently more resistant to hydrolysis than their

aliphatic counterparts[31]. Synergistic effects have been observed by using combinations of radical scavengers and hydroperoxide decomposers, such as organic phosphite co-stabilizers. This synergism has been explained in terms of the interruption of chain propagation and chain-branching reactions[32]. Synergist systems also have the advantage of reducing processing discolouration and are generally cheaper than systems containing phosphite stabilizers alone[33].

A variety of test methods are used to evaluate the overall performance of melt and heat stabilizers[34]. An accelerated test such as oven ageing for assessing the effectiveness of long-term heat stabilizers is unsuitable as an indicator of processing stability because it does not expose the polymer to the combined effects of temperature and shear. More suitable techniques involve the measurement of certain physical or chemical changes in the polymer as functions of the number of passes through an extruder. Examples include the change in the melt-flow index[35-37], the extent of yellowing[38], oxidative induction time (OIT)[39-42], oxygen uptake[43,44], tensile strength[45-47] and carbonyl content[48,49]. Multi-pass extrusion simulates the behaviour of commercial processing operations. However, laboratory scale extruders operate at lower shear rates than commercial extruders. Furthermore, slight differences in the extrusion conditions between passes tend to have cumulative effects which may distort the overall result.

Oxygen uptake measurements have been used previously to determine relative oxidative stabilities of polymeric formulations subjected to elevated temperatures[50,51]. These tests commonly measure only the induction time prior to the auto-oxidation stage because of the low sensitivity of mercury manometers. However, the rate of thermal oxidation during the induction period can be determined by using a sensitive differential pressure transducer (DPT) to record the decrease in the partial pressure of oxygen in the sample cell[52-55].

The oxygen uptake and OIT measurements should yield comparable results. However, identical results are not obtained and this reflects differences between the two methods. Some important advantages of oxygen uptake measurements over OIT determinations are: oxygen uptake measurements use larger samples which give more representative results; OIT measures the stability of the melt and the results cannot be extrapolated accurately to lower temperatures[56-59]; OIT results may not be reproducible[60] due to problems associated with the accumulation of volatile oxidation products on the thermocouple sensors and/or poor thermal contact which is due to warping of the sample; greater sensitivity of pressure transducers allow the detection of oxidation during the induction period; OIT measurements for different formulations are made at different test temperatures to obtain results in a reasonable time and consequently the absolute induction times cannot be compared.

This paper describes a modified version of the oxygen uptake cell which was used previously for photo-oxidation studies[61]. Effectiveness of four melt stabilizing systems for LDPE was determined using the modified cell. In particular, a comparison is made between the oxygen uptake data and other conventional test methods with a view to determining the applicability of oxygen uptake measurements as a means of assessing the effectiveness of stabilizer systems.

EXPERIMENTAL

The physical properties of the LDPE materials used in this study are listed in *Table 1*. The density values were measured in accordance with the ASTM method D792-66. The stabilizers used were: octadecyl-3-(3,5-di-tert-butyl)-4-hydroxyphenol propionate (AO-1), 2,6-di-tert-butyl-4-methylphenol (AO-2), tris-nonylphenyl phosphite (AO-3), 2,2'-ethylidene-bis-(4,6-di-tert-butylphenol) (AO-4) and tris-(2,4-di-tert-butyl)phenyl phosphite (AO-5).

Master batches of the formulations were prepared by tumble blending LDPE(1) resin with melt stabilizers for 20 min and compounding them on a Haake laboratory extruder. Each of the master batches was added to the LDPE(2) resin at a loading of 4% (wt/wt) to produce samples with final stabilizer concentrations as shown in *Table 2*.

The multi-pass extrusions were performed on a 2.5 inch Telford–Smith extruder with a screw L/D ratio of 25:1 and a screw speed of 60 rpm. The temperature profile was: 170°C in the hopper, 180 and 190°C in the extruder barrel, and 200°C in the die. The compounds were extruded through a four-lace die, quench cooled and chopped into pellets. After a single pass through the extruder a 20 kg sample of the chopped polymer was retained and the remainder of the polymer was passed again through the extruder. This process was repeated nine times and samples were retained after every second pass.

Polymer films were produced by the blown film method with a blow up ratio of 3:1. Fourier transform infrared spectra of the bulk LDPE film and gel regions were recorded using a Mattson *FT*i.r. fitted with a micro-transmittance attachment. Optical micrographs of gel particles were taken on a Heerbrugg Photomicroscope M400 at 40 × magnification.

The melt flow indices (MFI) were measured in accordance with the ASTM method D1238-7. The OIT measurements were made using a Perkin–Elmer DSC-2C differential scanning calorimeter fitted with a flow-through cover and vented sample pan lids. The size of the sample was 10 ± 1 mg and a sensitivity setting of 10 mcal s^{-1} was used. An oxygen flow rate of 20 cm^3 min^{-1} was maintained in each cavity and the samples were maintained at 30°C for 10 min whilst flushing the system with oxygen. The temperature was raised at a rate of 320°C min^{-1}.

Table 1 Physical characteristics of the polymers

Material	$M_w \times 10^{-3}$ (a.m.u.)	Dispersity (M_w/M_n)	MFI$_2$[a]	Density (g cm^{-3})
LDPE(1)	161	4.56	2.5	0.921
LDPE(2)	228	5.43	0.4	0.921

[a] Units: g/10 mins at 190°C

Table 2 LDPE formulations

Sample	% Additive (wt/wt)					
	AO-1	AO-2	AO-3	AO-4	AO-5	SiO$_2$
A	0.044	–	–	–	–	–
B	–	0.044	0.010	–	–	0.200
C	–	–	–	0.044	–	–
D	0.008	–	–	–	0.032	–

The oxidative induction time was determined by extrapolating the exotherm to the baseline of the trace.

Colour measurements were made on 3 mm thick compression moulded plaques. Yellowness index data were obtained from transmittance measurements at 10 nm intervals from 780 to 380 nm using a Varian Series 634 u.v.-visible spectrophotometer fitted with an integrating sphere. A barium sulphate background plate was used as the reference. The tristimulus values were evaluated by numerical integration in accordance with ASTM method D1925-70. Reproducibility of colour measurements was found to be within ± 0.5 units.

The oxygen uptake apparatus consists of a sample cell and a reference cell of equal free volume. The cells are separated by a differential pressure transducer (DPT) and are coupled to nitrogen and oxygen supplies. The original apparatus[61] was modified by replacing the quartz sample cell window with a stainless steel cover. The apparatus was placed in a high temperature bath maintained at 122 ± 0.2°C in order to avoid excessive sample oxidation and evolution of volatile degradation products. Each sample was equilibrated at the test temperature in a nitrogen atmosphere. At the commencement of the oxygen uptake experiment the sample cell was purged with preheated oxygen at atmospheric pressure. The samples were circular, 40 μm thick and 3.806 cm in diameter. These thin films allow unhindered diffusion of oxygen.

RESULTS AND DISCUSSION

Melt flow index

Figure 1 shows the MFI value for each of the polymer formulations as a function of the number of passes through the extruder. Samples A, B and C have relatively unchanged values of MFI during processing, showing that the stabilizer systems AO-1, the mixture of AO-2 and AO-3, as well as AO-4 effectively suppress crosslinking of the polymer during multiple extrusions. A significant decrease in the MFI value of the unstabilized control sample shows that extensive crosslinking occurs with increased processing. Sample D exhibits poor
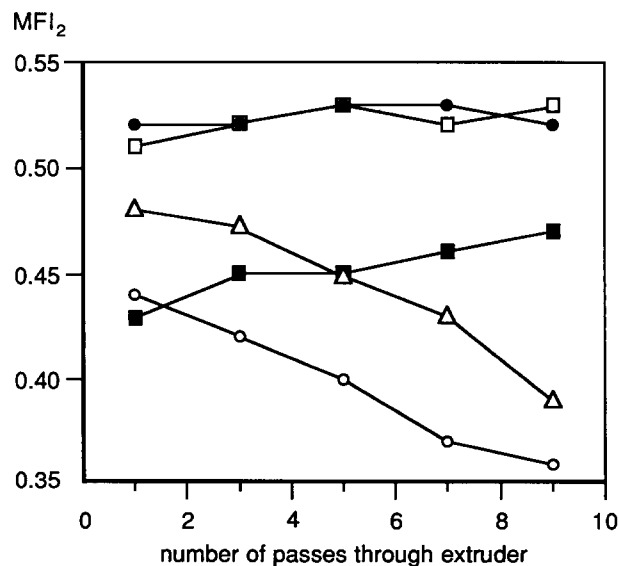

Figure 1 Melt flow indices as a function of number of extrusions for the LDPE formulations. ●, Sample (A); ■, sample (B); □, sample (C); △, sample (D); ○, control

thermal stability which is reflected by its MFI value decreasing at approximately the same rate as the unstabilized control sample.

Oxidative induction time

The results of the OIT experiments are shown in *Figure 2*. A different test temperature must be used for each antioxidant system and, therefore, the induction times for different samples cannot be directly compared. However, the percentage decrease in the OIT value for a given antioxidant system serves as a useful indication of its relative effectiveness.

Samples A and C both show reasonable oxidative stability during processing, with sample A being slightly better. Sample B exhibits the smallest percentage decrease in the induction time during processing and, as such, appears to have the highest oxidative stability. However, after multiple extrusions this formulation produces extensive gel formation resulting in film of poor optical quality. On the other hand, the largest decrease in oxidative induction time occurs in the case of sample D which indicates that this antioxidant system does not retard oxidation during processing. This result is consistent with the MFI data which show that this stabilizer system fails to prevent crosslinking.

Yellowness index

The yellowness index data are shown in *Figure 3*. The unstabilized control sample shows only minor discoloration after processing which can be attributed to the formation of conjugated bonds along the polymer backbone[62]. Sample A exhibits a very slight yellow discoloration after processing which is believed to be due to conjugated oxidation products[63]. This is in contrast to sample B which was slightly yellow prior to the multi-pass extrusion and a grey colour after processing. This significant colour change can be attributed to the formation of stilbene quinone oxidation products which are formed by the dimerization of phenoxyl radicals under extrusion conditions[64,65].

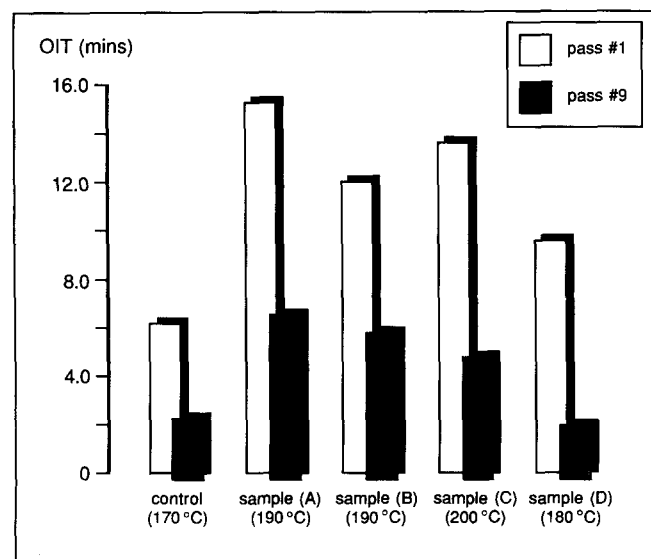Sample C displayed a pronounced brown-orange discoloration after multi-pass processing. The antioxidant
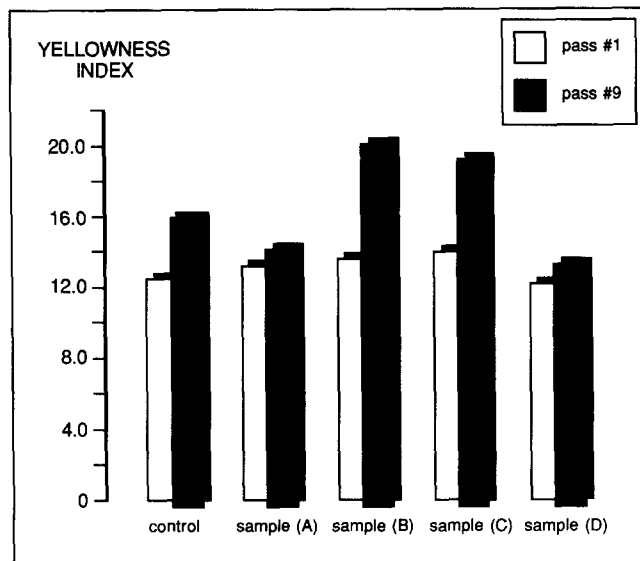
Figure 3 Yellowness index of the LDPE formulations

AO-4 has a bis-phenol structure which prevents it from forming stilbene quinone dimers. The discoloration in this case may be attributable to a phenolate complex formed between the stabilizer and transition metal impurity ions[66–71]. Sample D demonstrates the highest resistance to discoloration, indicating that the combination of a hindered phenol and a phosphite stabilizer is an effective system for decomposing stilbene compounds. However, the results of the MFI and OIT experiments indicate that this system does not provide a high degree of melt stability for LDPE.

Film quality

Figure 4a is an optical micrograph of an 'arrowhead' defect in the LDPE control film. The gel particle is aligned in the machine direction as indicated by the die-lines. *Figure 4b* is an optical micrograph of a 'fisheye' defect in the control sample which also shows a 'shower' of micro gel particles that are smeared out along the machine direction.

Samples A and C show excellent film appearance with high clarity and gloss and very few gel particles. The control sample and sample D display deteriorating film quality with increasing number of passes. The films produced from these two samples exhibit poor clarity and high haze due to a large number of very small gels. The extent of gel formation in films of sample B increases significantly with the amount of processing, despite the fact that the MFI value remains relatively constant. This may be attributed to loss of the highly volatile AO-2 stabilizer from those parts of the polymer that have increased residence time in the extruder and thus a more severe thermal history. This leads to oxidative crosslinking in the regions of the polymer from which the antioxidant had been depleted.

The infrared spectrum of the bulk LDPE film (*Figure 5a*) shows that no significant oxidation has occurred. *Figure 5b* is a microtransmittance spectrum of a gel particle. The intense $1090\,\mathrm{cm}^{-1}$ peak indicates the presence of transverse ether bonds which are largely responsible for crosslinking and gel formation in polymers such as high density polyethylene[72,73]. In addition, the increase in the $3380\,\mathrm{cm}^{-1}$ band is due to formation of

Figure 2 Oxidative induction times of the LDPE formulations (test temperatures are shown below each sample)
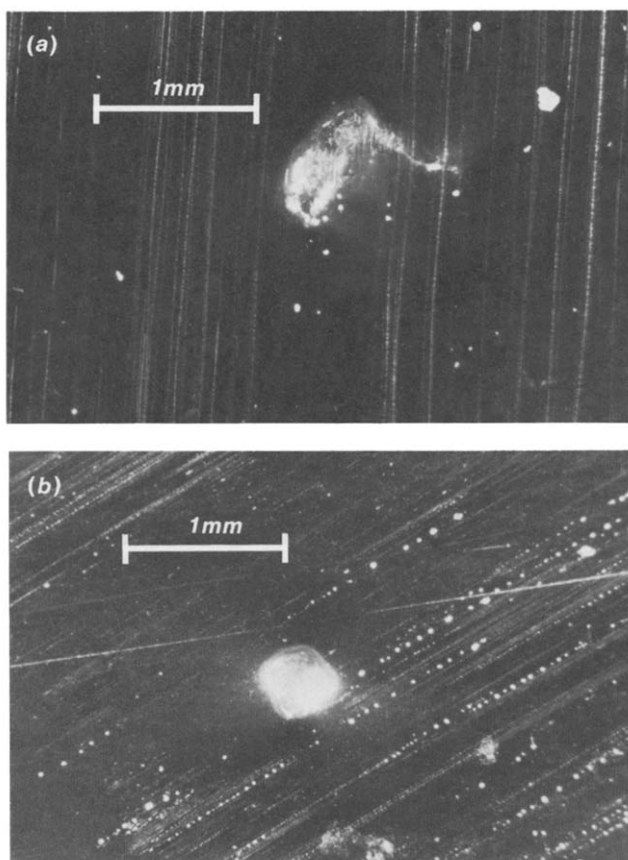
Figure 4 Optical micrographs of gel particles at 40 × magnification: (a) 'arrowhead' defect and (b) 'fisheye' defect

hydroxyl groups which occur as a result of polymer oxidation.

Oxygen uptake profiles

The oxygen uptake profiles for each of the LDPE formulations, measured after one pass and nine passes through the extruder, are shown in *Figures 6* and *7*, respectively. The control sample has the fastest rate of oxidation, as indicated by the gradient of its oxygen uptake profile. This result is consistent with its poor performance as shown by the OIT measurements, by its decrease in melt flow index after multiple extrusions and by its unacceptable film quality. In contrast to this, the rate of oxygen uptake for sample A is approximately one third that of the control sample. The higher degree of processing stability is consistent with the trends found in the melt flow index values, OIT and film quality assessments.

After one pass sample C reacts with about half as much oxygen as the unstabilized (control) sample. However, its stability is not quite as high as that of sample A. This may be attributed to the fact that the AO-1 stabilizer in sample A possesses a long aliphatic moiety which imparts to it a higher solubility in the polymer and thus a greater degree of compatibility. The AO-4 antioxidant in sample C has a greater hindered phenolic functionality, enabling it to donate two labile hydrogen atoms which interfere with the propagation steps in the degradative process. However, its bulky, bridged polycyclic structure renders it less compatible with the polymer matrix and consequently reduces its overall effectiveness.

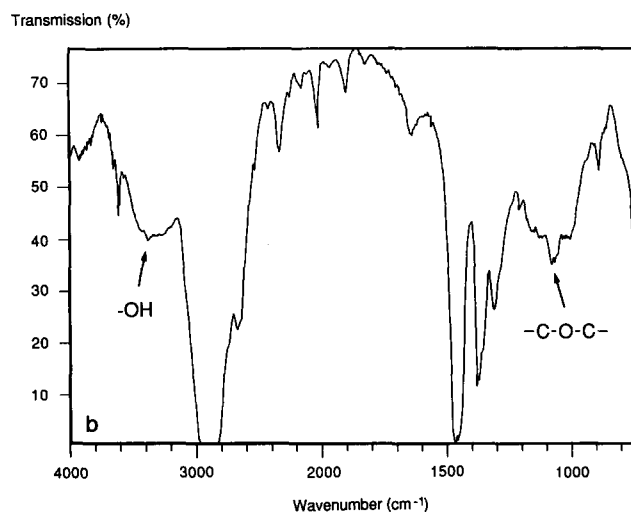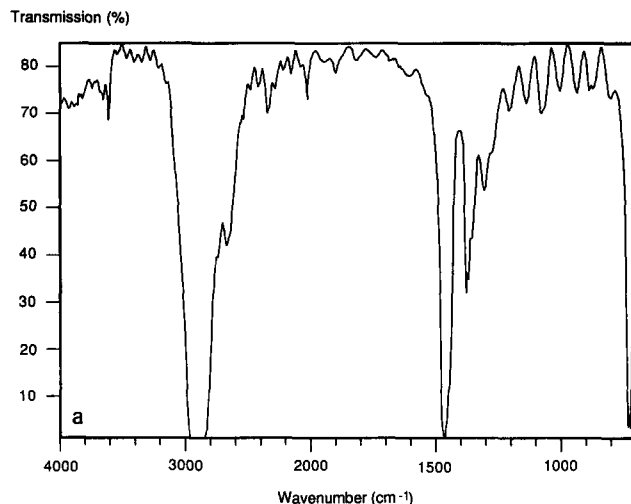Sample D shows an oxidative stability which is

Figure 5 Fourier transform infrared microtransmittance spectra of a LDPE film: (a) bulk film and (b) gel particle in LDPE film. Collection conditions: 100 μm aperture, 64 scans, 4 cm^{-1} resolution, narrowband MCT detector

consistent with its observed film quality as well as its MFI and OIT data. This may be due to the nature of the stabilizer system in sample D which consists mostly of a hydroperoxide decomposer (AO-5) together with a free radical scavenger (AO-1). Consequently, the hydroperoxide decomposer is not fully utilized because insufficient oxygen in the extruder limits the formation of appreciable quantities of hydroperoxides in LDPE[74]. The slight stabilizing action that is observed may be attributed to the presence of the AO-1 stabilizer. It appears that this system is not particularly useful for stabilizing LDPE although the phosphite antioxidant (AO-5) reduces discoloration very effectively.

Sample B which contains a BHT/phosphite antioxidant system (AO-2 and AO-3) demonstrates a poor thermal stability. The MFI and OIT data for this formulation show that little change occurs in the extent of degradation or crosslinking during processing. The relatively high rate of oxygen uptake may be attributed to the antagonism between AO-2 and the SiO$_2$ antiblocking agent in this formulation. This antagonism may be due to the acidic surface of the silica. The oxygen uptake profiles show that the rate of oxidation after one pass is high and remains high after nine passes. This suggests that the poor stability is due either to the loss of the volatile AO-2
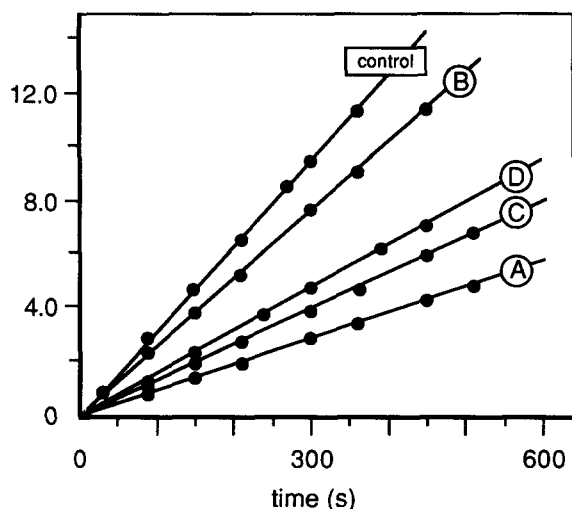
O_2 uptake (mol kg $^{-1}$) x 10^2

Figure 6 Oxygen uptake for LDPE samples after one pass through the extruder, (122°C, 1 atm pressure of O_2)
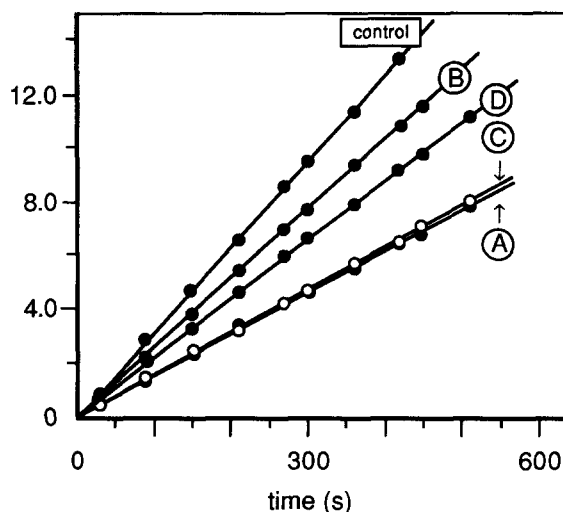
O_2 uptake (mol kg $^{-1}$) x 10^2

Figure 7 Oxygen uptake for LDPE samples after nine passes through the extruder, (122°C, 1 atm pressure of O_2)

during compounding or to the antagonism between the additives.

CONCLUSIONS

The oxygen uptake apparatus incorporating a micro-volume cell is a sensitive tool for monitoring the oxidative stability of polymeric formulations. Its performance compares favourably with other conventional methods for measuring the efficiency of processing stabilizers. The results show that higher-molecular-weight-hindered phenolic stabilizers such as AO-1 and AO-4 are more effective in suppressing gel formation in LDPE than are lower molecular weight stabilizers such as AO-2. However, the AO-2 and AO-4 stabilizers discolour the polymer during processing whereas the AO-1 antioxidant does not form appreciable amounts of highly coloured oxidation products. The combination of AO-1 and AO-5 was found to provide an unexpectedly poor thermal stability, although it is effective in suppressing the formation of highly coloured products.

ACKNOWLEDGEMENTS

REFERENCES

1   Swasey, C. C. *Proc. 34th SPE Conf.* 1976, 64
2   Mitterhofer, F. *Kunststoffe* 1977, 67, 684
3   Foster, G. N. and Metzler, R. B. US Patent 4535113 A
4   Corwin, M. A. and Foster, G. N. European Patent 68851
5   Bolland, J. L. and Gee, G. *Trans. Faraday Soc.* 1946, 42, 236
6   Hawkins, W. L. 'Polymer Degradation and Stabilization', Springer, Berlin, 1984, Ch. 8
7   Chan, M. G. and Hawkins, W. L. *Polym. Eng. Sci.* 1967, 7, 264
8   Hawkins, W. L. 'Polymer Stabilization', Wiley-Interscience, New York, 1972, Ch. 10
9   Shlyapnikov, Yu. A. *Russ. Chem. Rev.* 1981, 50, 581
10   Scott, G. *Pure Appl. Chem.* 1983, 55, 1615
11   Quackenbos, H. M. *Polym. Eng. Sci.* 1966, 6, 117
12   Holmstrom, A. and Sorvik, E. *J. Appl. Polym. Sci.* 1974, 18, 761
13   Al-Malaika, S. *Polym. Plast. Technol. Eng.* 1988, 27, 261
14   Ryshavy, D. and Balaban, L. *Polym. Sci. (USSR)* 1962, 3, 147
15   Kumar, V., Mathur, A. and Mathur, G. *Pop. Plast. Rubber* 1980, 25, 3
16   Kempermann, T. *Int. Polym. Sci. Tech.* 1982, 9, 35
17   Bickel, A. F. and Kooyman, E. C. *J. Chem. Soc.* 1953, 3211
18   Ranalli, F. *Int. Polym. Sci. Tech.* 1977, 4, 66
19   Kovarova, J. and Pospisil, J. *Eur. Polym. J.* 1977, 13, 975
20   Holcik, J., Karvas, M., Kassovicova, D. and Durmis, J. *Eur. Polym. J.* 1976, 12, 173
21   Temchin, Y., Burmistrov, Y., Medvedev, A., Kokhanov, Y., Gushchina, M. and Kiseleva, M. *Vysokomol. Soyed.* 1970, A12, 1901
22   Cogswell, F. N. 'Polymer Melt Rheology', John Wiley and Sons, New York, 1981, p. 92
23   Schwarzenbach, K. in 'Plastics Additive Handbook' (Eds R. Gachter and H. Muller), Hanser Publishers, Munich, 1984, p. 17
24   Kumar, V. and Mathur, G. *Pop. Plast.* 1978, 23, 20
25   Product data sheet, Irganox 1076, Ciba-Geigy, 1974
26   Luston, J. in 'Developments in Polymer Stabilisation—2' (Ed. G. Scott), Applied Science Publishers, London, 1980, p. 234
27   Product data sheet, Isonox 129, Schenectady Chemicals, 1980
28   Schwetlick, K. *Pure Appl. Chem.* 1983, 55, 1629
29   Mukmeneva, N., Sabirova, L., Kaadyrova, V., Zverev, V., Katyshev, A. and Kirpichnikov, P. *Zhur. Prikl. Khim.* 1977, 50, 604
30   Pobedimskii, D., Mukmeneva, N. and Kirpichnikov, P. in 'Developments in Polymer Stabilisation—2' (Ed. G. Scott), Applied Science Publishers, London, 1980, p. 167
31   Kovacs, E. and Wolkober, Z. *J. Polym. Sci., Symp. Ser.* 1973, 40, 73
32   Ray, W. C. and Isenhart, K. *Polym. Eng. Sci.* 1975, 15, 703
33   Bartz, K. *Polymer Prepr.* 1984, 25, 74
34   Gordon, D. A. *Adv. Chem. Ser.* 1968, 85, 224
35   Suh, N. P. and Sung, N. in 'Science and Technology of Polymer Processing', MIT Press, London, 1979, p. 809
36   Sadmohaghegh, C. and Scott, G. *Eur. Polym. J.* 1980, 16, 1037
37   Ridel, G. R. and Padget, J. C. *J. Polym. Sci.* 1976, 57, 1
38   Rothstein, E. C. *J. Appl. Polym. Sci.* 1968, 12, 1279
39   Kramer, E. and Koppelmann, J. *Polym. Degrad. Stab.* 1986, 16, 261
40   Kramer, E. and Koppelmann, J. *Polym. Eng. Sci.* 1987, 27, 945
41   Charsley, E. L. and Dunn, J. G. *J. Therm. Anal.* 1979, 17, 535
42   Marshall, D. I., George, E. J. and Turnipseed, J. M. *Polym. Eng. Sci.* 1973, 13, 415
43   Horng, P. and Klemchuk, P. *Polym. Prepr.* 1984, 25, 76
44   Mucha, M. *Coll. Polym. Sci.* 1986, 264, 113

45 Miltz, J. and Narkis, M. *J. Appl. Polym. Sci.* 1976, **20**, 1627
46 Sudol, M., Schneider, Z. and Nowakowska, M. *Int. Polym. Sci. Tech.* 1979, **6**, 98
47 Chirinos Padron, A., Colmenares, M., Rubinztain, Z. and Albornoz, L. *Eur. Polym. J.* 1987, **23**, 723
48 Adams, J. H. *J. Polym. Sci. A-1.* 1970, **8**, 1077
49 Amin, M. U. and Scott, G. *Eur. Polym. J.* 1974, **10**, 1019
50 Rysavy, D. *Polymer* 1967, **8**, 449
51 Frank, H. P. *J. Polym. Sci., Polym. Symp.* 1976, **57**, 311
52 Billingham, N. C. and Walker, T. J. *J. Polym. Sci., Polym. Chem. Edn.* 1975, **13**, 1209
53 Wozny, J. C. *Polym. Sci. Technol.* 1984, **26**, 111
54 Grattan, D. W., Carlsson, D. J. and Wiles, D. M. *Chem. Ind.* 1978, 228
55 Ranaweera, R. P. and Scott, G. *Eur. Polym. J.* 1976, **12**, 591
56 Howard, J. B. *Polym. Eng. Sci.* 1973, **13**, 429
57 Howard, J. B. and Gilroy, H. M. *Polym. Eng. Sci.* 1975, **15**, 268
58 Billingham, N. C., Bott, D. C. and Manke, A. S. in 'Developments in Polymer Degradation—3' (Ed. N. Grassie), Applied Science Publishers, London, 1981, p. 63
59 Still, R. H. in 'Developments in Polymer Degradation—1' (Ed. N. Grassie), Applied Science Publishers, London, 1977, p. 11
60 Kokta, E. T. *Proc. 24th Int. Wire and Cable Symp.* 1975, 220
61 Bigger, S. W. and Delatycki, O. *J. Polym. Sci., Polym. Chem. Edn.* 1987, **25**, 3311
62 Scarry, G. and Smith, P. D. *Plast. Engng.* 1982, **38**, 37
63 Bartelink, H., Beulen, J., Bielders, G., Cremers, L., Duynstee, E. and Konijnenberg, E. *Chem. Ind.* 1978, 586
64 Henman, T. in 'Developments in Polymer Stabilisation—1' (Ed. G. Scott), Applied Science Publishers, London, 1979, Ch. 2
65 Lerchova, J. and Pospisil, J. *Int. Polym. Sci. Tech.* 1977, **4**, 57
66 Lazareva, N. P. and Lukovnikov, A. *Soviet Plastics* 1967, 76
67 Mukmeneva, N., Akhmadulina, A., Kurmaeva, N. and Kirpichnikov, P. *Int. Polym. Sci. Tech.* 1976, **3**, 91
68 Holtzen, D. A. *Plast. Eng.* 1977, **33**, 43
69 Kresta, J. and Majer, J. *Int. Chem. Eng.* 1971, **11**, 430
70 Klender, G., Glass, R., Kolodchin, W. and Schell, R. *Proc. 43rd SPE Conf.* 1985, 989
71 Lazareva, N., Makarova, G., Khokhlova, L., Sotnikova, L., Zavitaeva, L., Sokolova, T. and Parfenova, D. *Int. Polym. Sci. Tech.* 1981, **8**, 60
72 Neiman, M. 'Aging and Stabilization of Polymers', Consultants Bureau, New York, 1965, Ch. 4, p. 97
73 Grafmuller, F. and Husemann, E. *Makromol. Chem.* 1960, **40**, 161
74 Al-Malaika, S. and Scott, G. in 'Degradation and Stabilization of Polyolefins' (Ed. N. Allen), 1983, p. 247