Evaluation of the Oxidative Stability of Multiextruded Polypropylene as Assessed by Physicomechanical Testing and Simultaneous Differential Scanning Calorimetry–Chemiluminescence

PETER K. FEARON,[1] NIALL MARSHALL,[1,*] NORMAN C. BILLINGHAM,[1] STEPHEN W. BIGGER[2]

[1] School of Chemistry, Physics and Environmental Science, The University of Sussex, Falmer, Brighton, BN1 9QJ, United Kingdom

[2] School of Life Sciences and Technology, F008, Victoria University of Technology, P.O. Box 14428, Melbourne City Mail Centre, Melbourne, 8001, Australia

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ABSTRACT: Common physicomechanical tests comprising impact strength, the melt flow index (MFI), and the yellowness index (YI) were used to study the thermooxidative stability of polypropylene (PP) following multipass extrusion. Differential scanning calorimetry (DSC) coupled with chemiluminescence (CL) monitoring was also used to assess the stability. Three PP formulations were studied: (i) PP-1 containing 0.050% w/w of the phenolic antioxidant Irganox 1010™, (ii) PP-2 containing 0.028% w/w Irganox 1010, 0.056% w/w of the phosphite costabilizer Irgafos 168™ and 0.014% w/w of the lactone processing stabilizer HP 136™, and (iii) PP-3 containing 0.050% w/w Irganox 1010 and 0.100% w/w of the phosphite Ultranox 641™. All formulations contained 0.045% w/w of the hydrotalcite acid scavenger DHT-4A™. The results suggest that physicomechanical tests cannot reliably detect the small difference in the stability between PP-2 and PP-3 but can detect the larger difference between these and the less stable PP-1. The oxidative induction time (OIT) determined by CL monitoring (i.e., CL–OIT) is consistent with the OIT determined by DSC but has better reliability. The CL–OIT data suggest that PP-3 has superior oxidative stability to PP-2 in the early stages of multipass extrusion. However, PP-2 exhibits a better resistance to yellowing. A correlation between the CL–OIT data and each of the MFI and YI data was found. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 733–741, 2001

Key words: polypropylene (PP); thermooxidation; multipass extrusion; impact testing; melt flow index (MFI); yellowness index; differential scanning calorimetry (DSC); chemiluminescence (CL); oxidative induction time (OIT)

INTRODUCTION

Due to the effectiveness of modern stabilizer systems, many of today's polymer formulations have long expected lifetimes.[1] In studying such stable systems, it is almost impossible to induce measurable and quantifiable changes in the material under ambient conditions that can be used as an assessment of its expected lifetime. Accelerated testing[2] must therefore be used in such cases. This involves exposing the polymer to environmental factors such as heat, oxygen, and/or light at levels higher than those usually encountered by it during its service life. In particular, the standard method of assessing the thermal stabil-

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Correspondence to: S. W. Bigger (Stephen.Bigger@vu.edu.au).

* *Present address:* Polifin Polypropylene Division, Polifin Ltd., P.O. Box 72, Modderfontein 1645, South Africa.

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ity of a polymeric formulation involves heating it in an oven for a long period while maintaining a continuous flow of air.[2] Samples are removed periodically and measurements of, say, the impact strength,[3] melt flow index (MFI),[4,5] yellowness index (YI),[6] carbonyl index,[7–11] tensile strength,[12] and/or extent of embrittlement[2] are made. To evaluate the stability of a polymeric formulation for processing, it is common to monitor changes in these properties as it is subjected to multiple extrusions.

The measurement of physicomechanical quantities during aging is aimed at determining the time it takes for the polymer to "fail," where the point of failure is defined by a set of predetermined criteria such as the 50% retention of a mechanical property. Thus, the results of these tests can be viewed as being a measure of the extent to which degradation has progressed toward an arbitrarily defined point of failure. As such, physicomechanical tests do not measure directly the residual stability of the formulation, but, rather, the occurrence of a failure that is usually catastrophic.[2] Furthermore, these tests often suffer from the disadvantages of: (i) being labor-intensive and time-consuming and (ii) producing results that are highly subjective, variable, and/or insensitive to the small, but often significant, differences that can exist between different formulations. In particular, mechanical testing is very dependent on the sample preparation (e.g., notch radius in impact testing[13]), sample conditioning (e.g., postinjection molding), sample dimensions, and test conditions (i.e., there exist various ISO, DIN, and ASTM standards).

The oxidative induction time (OIT) of a polymeric formulation[14] can be measured by differential scanning calorimetry (DSC) and is a quantity related directly to the stability imparted to the polymer by the stabilizing package. Unfortunately, the usefulness of DSC in measuring OITs is somewhat limited by: (i) the need to work above the melting temperature of the polymer and (ii) the inherent sensitivity of DSC to all thermal events, not just the oxidative degradation. On the other hand, the technique of monitoring the emission of chemiluminescence (CL) from a polymer during its oxidation[15,16] is an alternate means by which its OIT can be measured.

It has been known for many years[15,16] that the oxidation of polymers is accompanied by low-level light emission, and the application of CL to polymer degradation studies has been extensively reviewed.[17,18] It is generally believed that CL arises from the termination of two alkyl peroxyl radicals. When a good antioxidant is present, it will trap such radicals before they can recombine and so the CL is suppressed until the antioxidant is consumed. At this point (i.e., the OIT), light emission can be measured. With modern single-photon detectors, the end of the OIT can be detected with great sensitivity.

The CL technique exhibits excellent long-term stability and has been shown to be more reliable than is DSC over long induction times.[19] Unlike the DSC response, the CL signal is unaffected by other endothermic or exothermic processes that may occur during the experiment.[19] Furthermore, the development of CL imaging techniques that utilize sensitive charge-coupled device cameras of a wide dynamic range[20] has made possible the simultaneous monitoring of CL from multiple samples. This has already shown great potential to be a reliable and efficient method of determining OITs.[19]

The determination of the residual oxidative stability of a polymeric formulation during its multipass extrusion is of immediate relevance to the area of polymer recycling.[21] Although a number of articles[22,23] reported the effect of multipass extrusion on the thermooxidative stability of polyethylene as monitored by CL, there has been little work reported on the effect of multipass extrusion on polypropylene (PP) as assessed by this technique. Furthermore, there have been few studies devoted to exploring any correlation that may exist between the results of physicomechanical tests and CL experiments.

Reported in this article are the results of a series of experiments aimed at investigating the possible correlation between physicomechanical tests (i.e., experimental techniques that measure the extent of polymer degradation) and techniques such as DSC and CL that measure residual oxidative stability. In particular, a selection of typical physicomechanical tests, namely, impact strength, MFI, and YI, together with DSC and CL analyses were performed on PP that was subjected to multipass extrusion. Two different stabilizing systems were used in the study: The first is a standard package containing a phenolic antioxidant, a phosphite costabilizer, and an acid scavenger. The second system is based also on a phenolic antioxidant and phosphite costabilizer combination, but, in addition, contains a lactone processing stabilizer (i.e., a carbon-centered radical scavenger) as well as an acid scavenger.

The results reported herein are interpreted with a view to: (i) assessing the relative effectiveness of the two stabilizing systems during multi-

Table I Polymer Formulations Used in the Study

	Additive Concentration (% w/w)				
Formulation	Irganox 1010	Irgafos 168	Ultranox 641	DHT-4A	HP 136
PP-1	0.050	—	—	0.045	—
PP-2	0.028	0.056	—	0.045	0.014
PP-3	0.050	—	0.100	0.045	—

pass extrusion, (ii) assessing the potential usefulness of the CL technique as a means of measuring the stability of PP during multipass extrusion, (iii) identifying any correlation between the OIT obtained by CL (i.e., CL–OIT) and the physicomechanical techniques investigated, and (iv) comparing isothermal OITs obtained from conventional DSC and CL experiments for PP at temperatures below the melting point of the polymer that result in long induction times.

EXPERIMENTAL

Polymer Formulations

Unstabilized PP reactor powder was obtained from Polifin Ltd. (Modderfontein, South Africa). Portions of the powder were dry-blended with: (i) the phenolic antioxidant Irganox 1010™ (pentaerythrityl tetrakis-(3,5-di-*tert*-butyl-4-hydroxyphenyl propionate) (Ciba Specialty Chemicals, Basel, Switzerland), (ii) either the phosphite Irgafos 168™ [tris-(2,4-di-*tert*-butylphenyl)phosphite] (Ciba Specialty Chemicals) or the phosphite Ultranox 641™ (2,4,6-tri-*tert*-butyl-phenyl-2-butyl-2-ethyl-1,3-propanediol phosphate) (GE Specialty Chemicals, Bergen-op-Zoom, The Netherlands), and (iii) a hydrotalcite acid scavenger DHT 4A™ (Kyowa Chemicals Inc., Tokyo, Japan). The sample containing Irgafos 168 additionally contains a lactone HP 136™ (Ciba Specialty Chemicals) that is capable of scavenging carbon-centered radicals. All additives were used as received and at loadings recommended by the suppliers in order to produce the formulations listed in Table I.

Each of the dry blends was extruded on a 19-mm single-screw extruder (Brabender, Model PL 2000-6, 19/25 D) with a 3:1 metering screw running at 40 rpm. The temperature profile used on the extruder was 190, 200, 210, and 220°C. The extrudate was cooled in a water bath and then pelletized. Enough of the polymer was retained after each extrusion to allow for the measurement of impact strength, MFI, and YI as well as OIT using a simultaneous DSC and CL technique. The remaining polymer was reextruded.

Physicomechanical Testing

Pieces for mechanical impact strength testing were prepared by injection molding using a Ray–Ran laboratory pneumatic injection-molding machine. The barrel temperature was set at 220°C, and the mold temperature, at 30°C. Prior to testing, the specimens were conditioned at room temperature for at least 72 h. Izod impact tests were performed at 23°C in accordance with a standard method[24] on specimens with dimensions of 12 × 4 mm (width × thickness). The specimens were notched to a depth of 2 mm with a 0.25-mm radius. The reported results are an average of seven measurements.

The MFI of the samples was measured using a Ceast 6942 melt flow tester under the standard PP test conditions of 230°C and 2.13 kg.[25] Yellowness index measurements on pellets of the polymers were also performed in accordance with an appropriate standard method[6] using a Data-Colour Chroma QC Model 2000 instrument.

Simultaneous DSC–CL Experiments

Specimens of the multiextruded materials, in the form of pellets, 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, Sunnyvale, CA, USA; Model SR400). During each run, the sample (ca. 15 mg, in the form of a pellet) was contained in an aluminum sample pan and was first equilibrated for 5 min at 150°C in nitrogen at a flow rate of 100 mL min^{-1}. Isothermal oxidation at 150°C was then commenced by admitting oxygen to the sample chamber at the same flow rate. This temperature was chosen for oxidation be-

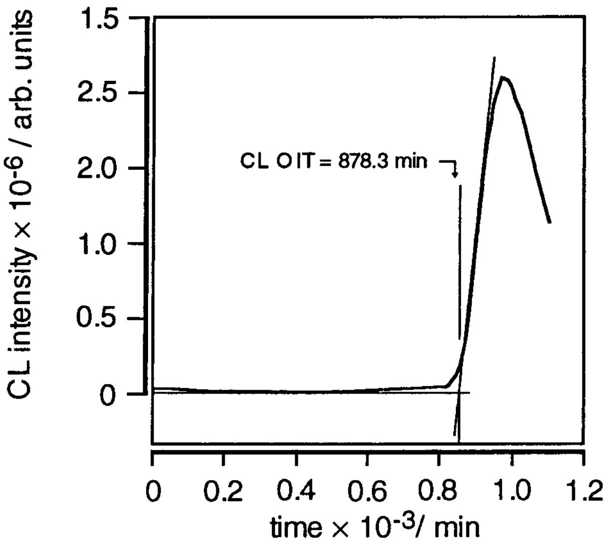

Figure 1 Typical example of a CL emission profile. The CL OIT is the time corresponding to the point of intersection between the extended baseline and the extrapolated CL emission curve. The data shown were obtained for a sample of PP-1 (control) after two extrusions.

cause it is high enough to give measurable OITs while being below the melting temperature of the polymer. The DSC instrument was temperature-calibrated in the range 95–191°C using three calibration standards: benzil, indium, and salophen. Figure 1 shows a typical CL–OIT curve illustrating the sharp ending of the induction period and the clearly defined OIT. The OIT is taken to be the time corresponding to the point of intersection between the extended baseline and the extrapolated CL emission curve.

RESULTS AND DISCUSSION

Figure 2 is a plot of the impact strength versus the number of extrusions for the control (PP-1) and the costabilized (PP-2 and PP-3) formulations. The results are, perhaps, typical of such experiments[3] in so far as any small difference between the stabilities imparted by the two costabilizing systems is undetectable due to the scatter in the experimental data. Nonetheless, there is a significant difference between both of the costabilized materials and the control. The retention of the initial impact strength with multiple extrusions in the costabilized materials is consistent with the contention that, although increased degradation is expected to have occurred in these formulations, there has been insufficient lowering

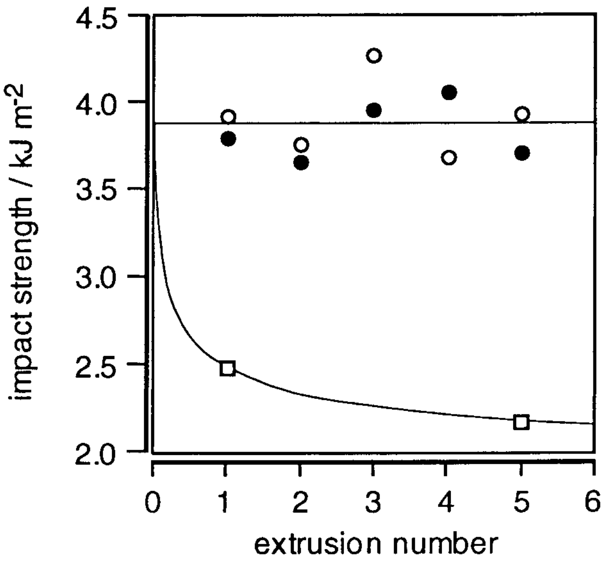

Figure 2 Plot of the impact strength (kJ m^{-2}) versus the number of extrusions for the (open squares) PP-1 control, (open circles) PP-2, and (filled circles) PP-3 formulations. The solid lines drawn through the data are intended to indicate only the trends.

of the molecular weight to dramatically affect their mechanical properties. Thus, in the case of the PP-2 and PP-3 formulations, the measurement of impact strength is insufficiently sensitive to detect the extent of degradation that has occurred.

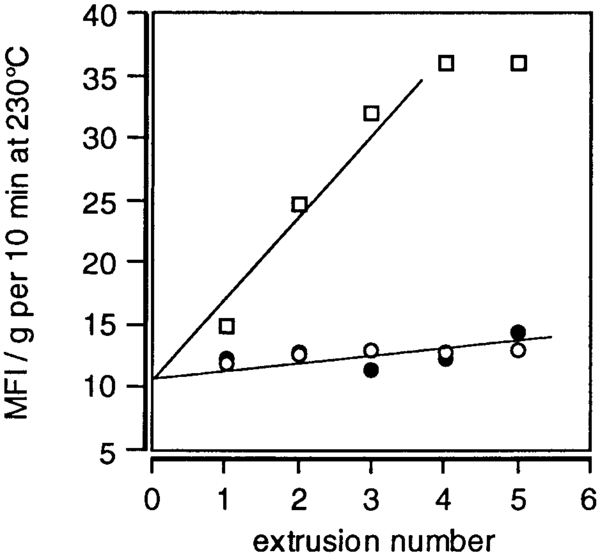

Figure 3 Plot of the MFI (g/10 min at 250°C, 2.13 kg) versus the number of extrusions for the (open squares) PP-1 control, (open circles) PP-2, and (filled circles) PP-3 formulations. The solid lines drawn through the data are intended to indicate only the trends.

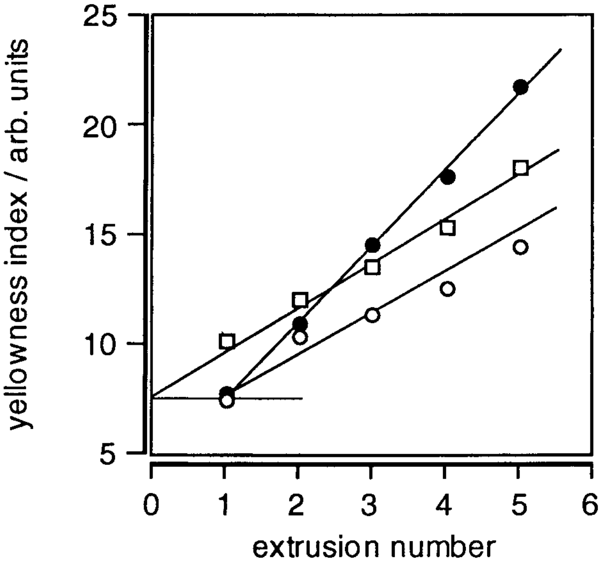

Figure 4 Plot of the YI (arbitrary units) versus the number of extrusions for the (open squares) PP-1 control, (open circles) PP-2, and (filled circles) PP-3 formulations. The solid lines drawn through the data are intended to indicate only the trends.

Shown in Figure 3 is a plot of the MFI versus the number of extrusions for the control and costabilized PP formulations. As in the case of the impact strength data (see Fig. 2), the MFI data suggest there is no significant difference between the two costabilized formulations PP-2 and PP-3, although a marked difference between the costabilized samples and the control is, once again, apparent. The observed increase in the MFI with an increasing number of extrusions is consistent with results reported elsewhere in the literature.[22,23,26]

In Figure 4, the YI values for each of the formulations are plotted against the number of extrusions. It is observed that color development increases proportionally with the number of extrusions for each of the fomulations, although the rate is different for each system of additives. It is known that certain of the transformation products of phenolic antioxidants, notably conjugated and nonconjugated quinoidal compounds, are chromophoric and thus contribute to the polymer color.[27] Less well understood is the contribution to the color made by the processing stabilizers, although both phosphites used in this work have been shown to form the 2,4-di-*tert*-butylphenoxyl radical[22] which can undergo dealkylation to form a stilbene–quinone chromophoric species.

The data in Figure 4 also show that after one extrusion the YI of each of the costabilized systems is maintained at a level consistent with that expected after zero extrusions of the unstabilized material. Furthermore, the data suggest that: (i) the PP-2 formulation is superior to the PP-3 formulation with regard to maintaining a lower YI than is the control material across the domain of multiple extrusions investigated, and (ii) the PP-2 formulation exhibits a lower propensity to increase its YI with multiple extrusions than does the PP-3 formulation.

It is interesting to note that in a previous study of multiextruded PP Scheirs et al.[23] found that after one extrusion less color is produced in PP stabilized with Ultranox 626™ [bis(2,4-di-*tert*-butylphenyl)pentaerythrityl diphosphate] than is produced in the same polymer stabilized with Irgafos 168. Neri et al.[28] found a similar trend to Scheirs et al.[23] after 10 extrusion passes in a study using the same phosphites in PP. Both Scheirs et al.[23] and Neri et al.[28] compared the phosphites at equal phosphorus loadings; hence, Irgafos 168 was used at twice the concentration of Ultranox 626, thereby invoking a threefold higher propensity of the formulation to form chromophoric compounds.

In the present work, Ultranox 641 was used rather than Ultranox 626 and it imparts lower resistance to color development than does Irgafos 168. On the basis of the number of aryl groups associated with each phosphite at the concentrations used, the higher resistance of the PP-2 formulation to yellowing cannot be attributed to it having a lower level of potential chromophoric aryl groups than has PP-3. Indeed, on a molar basis, PP-2 contains about 20% more phosphite aryl groups than does PP-3. Given also that the respective levels of phenolic and phosphite stabilizers in PP-2 are lower than are those of their counterparts in PP-3, the higher resistance to yellowing exhibited by PP-2 may be attributed to the presence of the lactone-processing stabilizer. The latter enables a similar degree of stabilization to be achieved with lower loadings of both the phenolic and phosphite antioxidants. A similar improvement in color upon the addition of a lactone-processing stabilizer was also observed by King.[29]

The OIT for each formulation was determined after each extrusion using a simultaneous DSC and CL measurement technique. The results of these experiments were used to construct Figure 5, which is a plot of the OIT obtained by DSC versus the corresponding OIT obtained by CL for a selection of OITs covering the range of OITs observed. The plot shows that there is good agree-

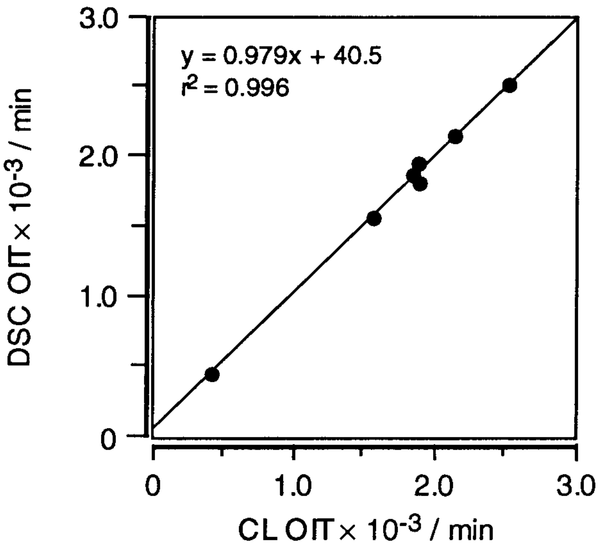

Figure 5 Plot of the OIT obtained by DSC (DSC–OIT, min) versus the corresponding OIT obtained simultaneously by CL (CL–OIT, min) for formulations where the DSC gave an unambiguous OIT.

ment between the two techniques as to the onset time and that both techniques measure the same oxidative event, albeit from different steps in the oxidative mechanism. On a few occasions during the course of these experiments, the DSC thermogram failed to exhibit an onset that was clear and unambiguous. Indeed, it has been suggested that the reliability of DSC measurements for measuring OITs may be questionable, especially for long-term isothermal experiments conducted on highly stabilized samples at temperatures below their melting temperature.[19] In view of this, it was decided to select the CL technique instead of DSC as the preferred method of detecting any significant differences that may exist between the thermooxidative stabilities imparted to the substrate by each of the costabilizer packages.

Figure 6 is a plot of the CL–OIT of each formulation versus the number of extrusions. The CL–OITs of two replicate samples of the PP-2 and PP-3 materials that were subjected to one, two, and three extrusions were measured and the mean OITs were calculated. The 95% confidence intervals for the means were calculated using the appropriate value of the Student *t*-distribution for 2 degrees of freedom.[30] A comparison of the OITs and their respective confidence intervals suggests that the observed difference between the oxidative stability of the PP-2 and PP-3 formulations up to at least three extrusions is significant at the 95% level, the stability of the PP-3 formulation being superior to that of the PP-2 formulation. It is interesting to note that this order of stability is the reverse to that suggested by the YI results. This, perhaps, supports the belief that YI measurements are unreliable indicators of thermooxidative stability due to the effect of other factors such as the formation of chromophoric species that originate from the stabilizing package itself.[22]

The data in Figure 6 also suggest that the residual stability in formulations PP-2 and PP-3 after, say, four extrusions is reduced to that comparable to the virgin control material (estimated by extrapolating the control data) which has a relatively low thermooxidative stability. Presumably, the relative stabilities of PP-2 and PP-3 after six or more extrusions become similar and follow the downward trend shown by the PP-1 control. This is an interesting observation as it raises the point that evaluating the stability of the polymer by any of the mechanical tests such as the flexural or tensile modulus always requires at least one additional thermal processing step, namely, the fabrication of the test piece. This means if mechanical testing is used no measurement can be made that represents the inherent stability of the nascent polymer. In contrast, the

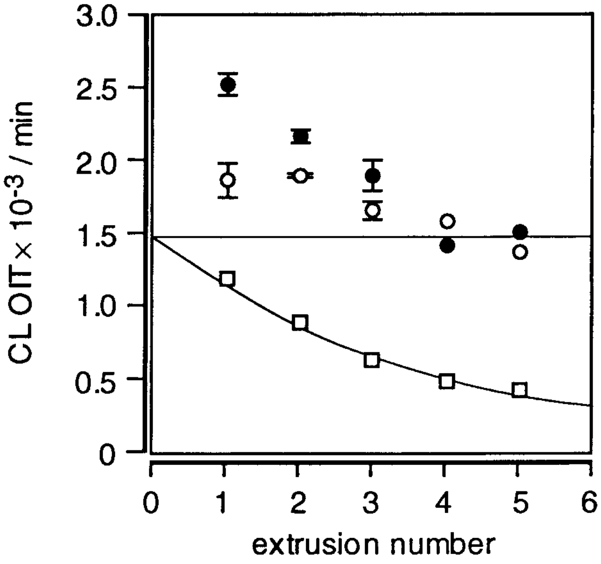

Figure 6 The OIT determined by isothermal CL (CL–OIT, min) at 150°C in oxygen (1 bar, flow rate 100 mL min^{-1}) plotted against the number of extrusions for the (open squares) PP-1 control, (open circles) PP-2, and (filled circles) PP-3 formulations. The 95% confidence intervals shown on PP-2 and PP-3 data at one, two, and three extrusions were calculated from the OITs of two replicate samples in each case. The solid line drawn through the data for PP-1 is intended to indicate only the trend.

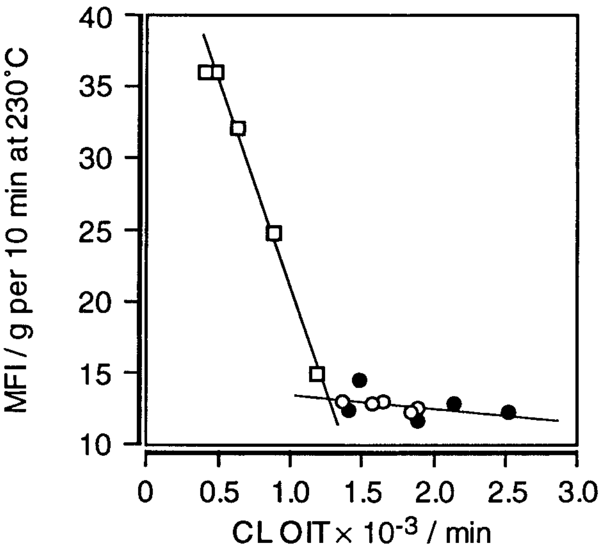

Figure 7 Plot of the MFI (g/10 min at 230°C, 2.13 kg) versus the CL–OIT (min) for the (open squares) PP-1 control, (open circles) PP-2, and (filled circles) PP-3 formulations. Lines obtained from linear regression analyses of the data are shown.

CL technique provides a direct assessment of the inherent stability and can be applied to nascent material just as easily as it can to any other, say, thermally treated material.

The possible correlation between CL–OIT and the results of the physicomechanical tests was investigated. Considering first the impact data, it is clear that these are quite scattered and do not reveal any significant difference between the two costabilized systems. This is due, in part, to the scatter in the impact strengths resulting from: (i) surface defects on test specimens, (ii) variances in notch radii, and (iii) possible ductile breaks in the specimens despite the fact that conditions are chosen for brittle breaks to occur.[3] However, the significant difference between the costabilized materials and the control (see Fig. 2) is also reflected by the CL–OIT data (see Fig. 6).

Figure 7 is a plot of the MFI versus the CL–OIT for the PP-1 (control), PP-2, and PP-3 formulations. The variation in MFI and CL–OIT for each formulation is that which has resulted from the multiple extrusions. The data pertaining to the control material, which is of lower thermooxidative stability than is either the PP-2 or PP-3 formulations, are remarkably linear with a regression coefficient, $r^2 = 0.991$. This suggests that a strong correlation between the results of the two types of test can be observed when the degradative changes are large enough to be detected by the MFI measurements. The data pertaining to the PP-2 and PP-3 materials are scattered and do not conform to a linear trend (regression coefficients of $r^2 = 0.555$ and $r^2 = 0.181$, respectively). This is presumably due to the failure of the MFI measurement to detect the changes that occur in the costabilized material during multipass extrusion as these changes are small and fall within a range of about ±10%, which is taken to be the inherent error of the method.[4] The CL–OIT data for the PP-2 and PP-3 materials, nonetheless, reveal a steady downward trend as the number of extrusions increases (see Fig. 6), whereas the corresponding MFI values are quite scattered (see Fig. 3).

The observed increase in MFI with multiple extrusions confirms that chain scission is the predominant mode of degradation for PP. The addition of a stabilizer retards the observed loss of the molecular weight, which implies that the degradative mechanism is primarily a chemical process rather than the suggested mechanical chain-breaking process[31] that results from shear. This is confirmed by the fact that the stabilizer is consumed as evidenced by the fall in the OIT with an increasing number of extrusions. The facts that: (i) the MFI levels off at a high degree of degradation, presumably due to the decreased influence of mechanical shear as the molecular weight and, hence, viscosity decreases and (ii) even in well-stabilized samples there is a small increase in the MFI during processing (see Fig. 3) suggest that some mechanochemistry is also involved.

A possible correlation between the YI data and the CL–OIT was investigated in a similar way to that depicted in Figure 7 for the MFI data. Plots of the YI versus the CL–OIT were constructed for the PP-1 (control), PP-2, and PP-3 formulations (see Fig. 8). The lines drawn through the data highlight the trends and serve to illustrate an inverse relationship between the variables but no generalization can be made due to the scatter in the data, particularly in the case of the costabilized PP-2 and PP-3 materials. The scatter is presumably a consequence of the insensitivity of the YI measurements to the small changes that are induced in the costabilized materials during their multipass extrusion.

The plot of YI versus CL–OIT illustrates clearly the inadequacy of YI as a measure of the inherent stability of a given formulation. In particular, a horizontal line drawn on the plot through an arbitrarily chosen value of YI intersects the trend lines at three significantly different values of the CL–OIT. This means that it is possible for three materials of very different in-

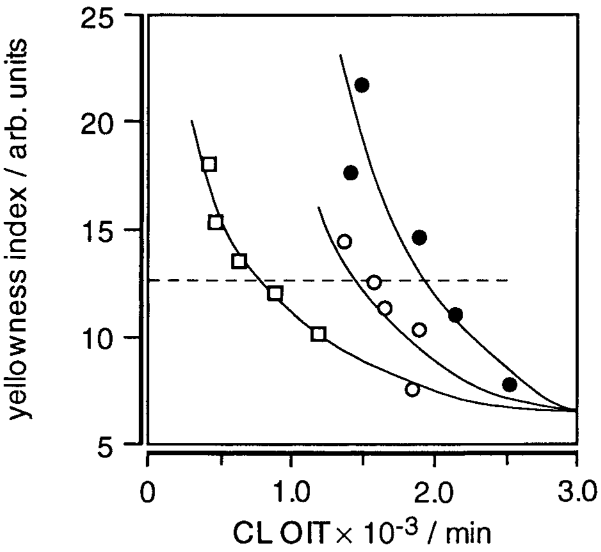

Figure 8 Plots of the YI (arbitrary units) versus the CL–OIT (min) for the (open squares) PP-1 control, (open circles) PP-2, and (filled circles) PP-3 formulations. The solid lines drawn through the data are intended to indicate only the trends.

herent stabilities to have the same YI value. The development of color in polymers is therefore a complex phenomenon and there are a number of different modes by which it can occur. For example, in the case of the PP-3 formulation, color development may result from both an additive–additive interaction[22,27] and by the inherent discoloration of the base polymer during processing. Thus, after prolonged processing, the YI of this formulation is expected to approach a relatively large value compared with the control sample (PP-1) which will approach a lower YI, reflecting the inherent discoloration that is due to the base stabilization only. The data shown in Figure 4 also support this assertion.

CONCLUSIONS

The reliable assessment of polymer stability using the physicomechanical test methods examined in this work is conditional upon there being sufficiently large, detectable changes in the test material brought about by the degradative environment. In the cases of impact testing and MFI determinations, distinctions can only be made between materials of widely different stability. The YI data, however, appear to enable a difference to be detected between formulations that have comparatively smaller differences in stability, but these data can be unreliable indicators of stability as complexities such as additive–additive interactions can often affect the observed YI.

The technique of CL monitoring produces OITs that are highly consistent with those obtained by the more commonly used method of DSC. In the present study, the CL method was found to be more reliable than is DSC at providing clear OIT onsets. Unlike the physicomechanical tests, the CL method is able to detect a significant difference between the thermooxidative stability imparted to PP by each of the costabilizer systems investigated. On the basis of the CL results, the PP-3 formulation imparts superior thermooxidative protection during the first three stages of multipass extrusion compared with the package containing the carbon-centered radical scavenger, PP-2. After four or more extrusions, both costabilizer packages are almost depleted and the stability of the substrate becomes comparable to that of the control. The replacement of some of the phosphite stabilizer by the carbon-centered radical scavenger is beneficial to the color performance of the stabilization package.

It was found that a remarkably linear correlation exists between the MFI and CL–OIT data for the control formulation, this having the lowest stability and, consequently, the largest variation in its MFI during multipass extrusion. An inverse trend between the YI and the CL–OIT data was observed, but, due to the inherent scatter in the YI data, the correlation cannot be described as being a strong one. The identification of any relationship that may exist between the CL–OIT and any one of the physicomechanical tests examined is severely hampered by the insensitivity of the latter to the small changes that occur in the more highly stabilized materials during multipass extrusion. The CL technique appears to be able to detect such changes reliably.

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