

# The Second Time Derivative Analysis of Chemiluminescence Emission Profiles and Its Application to the Accurate Determination of Oxidative Induction Times

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**ABSTRACT:** The technique of second time derivative (STD) analysis is developed and applied to the chemiluminescence (CL) profiles of two polypropylene (PP) formulations and a 5% w/w blend of polybutadiene (PBD) in PP to assess this novel method of analysis as a means of reliably determining the oxidative induction time (OIT) of polymers. It is proposed that the STD technique, when used in conjunction with the integrated CL profile, can enable evaluations of the OIT to be made that are less subjective than those made using the conventional extrapolation method. This is particularly so in systems that exhibit a gradual onset towards autoacceleration and/or convoluted CL profiles. Chemiluminescence profiles of the PBD–PP blend that were obtained at different temperatures were subjected to STD analysis, and Arrhenius plots of the data were made. The results are consistent with the notion that the PBD and PP phases oxidize almost independently. The activation energies for the oxidation of the PBD and PP phases were calculated to be  $200 \pm 31 \text{ kJ mol}^{-1}$  and  $146 \pm 9 \text{ kJ mol}^{-1}$ , respectively. The higher activation energy for the PBD phase is partly attributed to the greater partitioning of thermal stabilizer in this phase. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1986–1993, 2001

**Key words:** polypropylene (PP); chemiluminescence (CL); oxidative induction time (OIT); second time derivative analysis; polybutadiene; polymer blends

## INTRODUCTION

The oxidative induction time (OIT) is one of the most commonly used indicators of polymer stability and experimental techniques that measure the extent of polymer degradation such as oxygen uptake,<sup>1,2</sup> carbonyl index,<sup>3,4</sup> differential scanning

calorimetry (DSC),<sup>5</sup> and more recently, chemiluminescence (CL),<sup>6,7</sup> can all be used to generate OIT information. A simple OIT test that measures the thermooxidative stability of a polymer was originally developed at the Bell Telephone Laboratories in 1964 for the study of the stability of polyolefin insulation materials. This test was adopted by the ASTM as a standard test method<sup>8</sup> in 1968. Due to its simplicity, this OIT test is both the preferred test and often the only test used by industry to assess the oxidative stability of a polymer. In the standard test, the OIT is obtained using a differential scanning calorimeter in which

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the sample is purged with nitrogen while temperature equilibrium is established. The temperature is rapidly ramped to a preset isothermal testing temperature, usually between 180 and 220°C.<sup>9</sup> The purge gas is then switched to air or oxygen at the same flow rate until the onset of thermal oxidation occurs, which is indicated by the appearance of an exotherm. The point at which the purge gas is changed from nitrogen to air or oxygen is taken as the zero time of the experiment, and the OIT is taken to be the time corresponding to the point of intersection of the extended baseline with the extrapolated slope of the exotherm.<sup>5,10,11</sup>

Chemiluminescence, which is believed to originate from excited-state carbonyl groups formed during the termination step in the autooxidative process,<sup>12-15</sup> can also be used to determine the OIT of many polymers. This particular technique is quite useful for measuring the OIT, as it is highly sensitive and gives greater baseline stability over long induction times than DSC.<sup>16</sup> In either case, the determination of the OIT by the linear extrapolation of the autoaccelerating region of the oxidative profile to the baseline is quite straightforward, provided the sample is "well behaved" and exhibits a linear autoaccelerating region. In cases where the autoaccelerating region is not as well defined or consists of the convolution of two or more heterogeneous processes, the determination of a reliable OIT value by the conventional extrapolation method may be much more subjective or even impossible.

Recently, it has been suggested that the width of a plot of the second time derivative (STD) of the carbonyl buildup in a polyolefin can be used as a criterion of the homogeneity of the oxidative process.<sup>17</sup> Furthermore, it has been inferred that the peak in the STD curve is related to the induction period.<sup>17</sup> In the present article we report the results of a series of CL experiments that were performed to explore the applicability of STD analysis as a reliable means of accurately determining the OIT in such experiments. The technique of STD analysis is applied to the CL profiles of: (a) an oxidatively stable sample of PP that exhibits a sharp onset of the autoaccelerating period after a long induction time, (b) an oxidatively unstable sample of polypropylene (PP) that exhibits a gradual onset of the autoaccelerating period after a short induction time, and (c) a blend of 5% w/w of polybutadiene (PBD) in PP that exhibits a complex CL profile resulting from two induction periods that originate from the separate phases in the blend.

## EXPERIMENTAL

### Materials

The three formulations studied are ones that were used in our laboratory for previous research programs. These were selected principally for the purpose of providing examples of materials with widely different thermooxidative behavior.

### *Oxidatively Stable Polypropylene*

Unstabilized PP (density of 0.903 g mL<sup>-1</sup>, melt flow index (MFI) of 9.5 g per 10 min at 230°C, 2.16 kg) was supplied in the form of a reactor powder by Polifin, South Africa. Pellets of this material were produced by dry blending the powder with 0.050% w/w of the phenolic antioxidant Irganox 1010™ (penta-erythrityl-tetrakis-(3,5-di-tert-butyl-4-hydroxyphenyl propionate), Ciba Specialty Chemicals, Basle, Switzerland) and passing it five times through 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. The density of this material was measured in accordance with an appropriate standard.<sup>18</sup> The MFI was measured using a Ceast 6942 melt flow tester, operated under standard test conditions.<sup>19</sup> Although this formulation had been subjected to multipass extrusion, its higher loading of stabilizer made it more stable than the oxidatively unstable PP formulation described below.

### *Oxidatively Unstable Polypropylene*

A sample of PP (Profax 6501, density of 0.897 g mL<sup>-1</sup>, MFI of 4.2 g per 10 min at 230°C, 2.16 kg) containing 0.005% w/w of Irganox 1010 and 0.025% w/w calcium stearate was obtained in the form of pellets from Ciba Specialty Chemicals. This material was used as received. The density and MFI values were measured in accordance with the appropriate standards.<sup>18,20</sup>

### *Polypropylene/Polybutadiene Blend*

Polypropylene (density of 0.898 g mL<sup>-1</sup>, MFI of 4.6 g per 10 min at 260°C, 2.16 kg) was supplied as a "Statoil™" product by Ciba Specialty Chemicals. Polybutadiene (PBD, Bruna, density 0.893 g mL<sup>-1</sup>) from the same source was supplied as an amorphous material originating from a melt. A blend of 5% w/w PBD in PP containing 0.10% w/w

of Irganox 1076™ (octadecyl-3-(3,5-ditert-butyl-4-hydroxyphenyl)-propionate, Ciba Specialty Chemicals) was produced by dry mixing the appropriate mass of each polymer and the stabilizer to make a 38-g charge. The charge was blended under nitrogen in a twin-screw, high-shear, cam-blade Brabender mixer. Blending was conducted at 180°C for 10 min at a speed of 40 rpm. A 10-g portion of the blended material was then placed in a rectangular stainless steel template, layered between two thick aluminium foil sheets, and pressed using a Moore hot press. The sample was pressed at 180°C and was initially held at a pressure of 10 kPa for 3 min before the pressure was increased to 150 kPa for a further 3 min. At this point the sample was removed and transferred to a water-cooled cold press where it was maintained under a pressure of 100 kPa for 3 min before being removed. The density and MFI values were measured in accordance with appropriate standard methods.<sup>18,19</sup>

### Chemiluminescence Measurements

Chemiluminescence from the isothermal oxidation of the PP samples was recorded by a single photon counting technique using a photomultiplier tube (Thorn-EMI, Ruislip, Middlesex, UK; model 9813-QB) connected to a single-gated photon counter (Stanford Research Systems, Stanford, USA; model SR400). Each sample (ca. 15 mg, in the form of a pellet) was contained in an aluminium DSC pan and oxidized in the sample compartment of an adapted DSC instrument (Mettler-Toledo, model 821<sup>e</sup>). The samples of PP were oxidized at a temperature of 150°C in oxygen (1 bar, flow rate of 100 mL min<sup>-1</sup>). Samples of the PP/PBD blend were oxidized at four different temperatures in the range of 140 to 155°C in oxygen (1 bar, flow rate 100 mL min<sup>-1</sup>). Before oxidation was commenced, each polymer blend was heated in nitrogen for 5 min, during which time thermal equilibrium was established.

## RESULTS AND DISCUSSION

### Data Treatment

The raw experimental CL data is a set of  $n$  intensities, each separated by a constant time interval,  $\delta t$ . Typically, these data may contain spikes and/or noise due to various instrumental factors and cosmic ray events. To obtain useable STD curves, it is first necessary to perform a smooth-

ing operation on the raw experimental data. A computer program was written to: (a) smooth the raw data, (b) calculate the STD curve corresponding to these data, and (c) identify all maxima in the STD curve and list the time at which each maximum occurs. In the program, the set of  $n$  raw intensity data is stored in an ordered array,  $y_1$ . The smoothing algorithm is an iterative loop in which the average of five consecutive intensities in the interval  $y_1(i)$  to  $y_1(i+4)$  is calculated and placed in position  $i+2$  in an ordered array  $y_2$  in accordance with eq. (1):

$$y_2(i+2) = \sum_{j=i}^{j=i+4} y_1(j)/5, \text{ for } 1 \leq i \leq n-4 \quad (1)$$

An "average" value for  $y_2(1)$ ,  $y_2(2)$ ,  $y_2(n-1)$ , and  $y_2(n)$  in the  $y_2$  array is calculated by eqs. (2) and (3):

$$y_2(i) = \sum_{j=1}^{j=i+1} [y_1(j)]/(i+1), \text{ for } i = 1, 2 \quad (2)$$

$$y_2(i) = \sum_{j=i-1}^{j=n} [y_1(j)]/(n-i+2), \text{ for } i = n-1, n \quad (3)$$

The  $n$  average intensities stored in the  $y_2$  array are then transferred back to the  $y_1$  array. The completion of all steps up to and including this one constitutes a single smoothing operation. The entire process may be repeated  $z$  times to give  $z$  separate smoothings. Clearly, the number of smoothings required to produce a useable STD curve depends on the signal-to-noise ratio of the raw data. In the current work, the data were given the least number of smoothings required to produce a smooth and continuous STD curve for comparison with the integrated CL intensity data. For maximum integrated CL intensities of up to, say,  $6 \times 10^5$  arbitrary units, between 10 and 50 smoothings of the raw data was found to be necessary, depending upon the extent of fine structure that was considered acceptable in the final STD curve.

The array  $D_2y$  containing  $n-2$  values of the STD of the smoothed data array  $y_1$  is obtained by first producing the array of first time derivatives,  $D_1y$ , in accordance with eq. (4), and then differentiating this array with respect to time in accordance with eq. (5):

$$D_{1y}(i+1) = [y_1(i) + y_1(i+2)] / (2 \times \delta t) \quad (4)$$

$$D_{2y}(i+1) = [D_{1y}(i) + D_{1y}(i+2)] / (2 \times \delta t) \quad (5)$$

where  $i = 1$  to  $n - 2$  and  $\delta t$  is the time interval between consecutive intensities in the array.

Values of  $D_{1y}(1)$ ,  $D_{1y}(n)$ ,  $D_{2y}(1)$ , and  $D_{2y}(n)$  were estimated from the arrays  $y_1$  and  $D_{1y}$  using eqs. (6) to (9):

$$D_{1y}(1) = [y_1(2) - y_1(1)] / \delta t \quad (6)$$

$$D_{1y}(n) = [y_1(n) - y_1(n-1)] / \delta t \quad (7)$$

$$D_{2y}(1) = [D_{1y}(2) - D_{1y}(1)] / \delta t \quad (8)$$

$$D_{2y}(n) = [D_{1y}(n) - D_{1y}(n-1)] / \delta t \quad (9)$$

Although these estimates of the extreme elements in the array were included in the program, they are not essential as the time window for the STD analysis should, in practice, be chosen such that the OIT lies well within it and not at either of its extremes.

An ordered array  $y_0$ , which contains the raw experimental data, is created initially, and is used to ensure that the smoothing algorithm does not introduce any aberrations or spurious peaks into the calculated STD curve. Each element in the  $y_1$  array after  $z$  smoothings is compared to its corresponding element in the  $y_0$  array, and an ordered array of smoothing factors  $\alpha$  calculated in accordance with eq. (10):

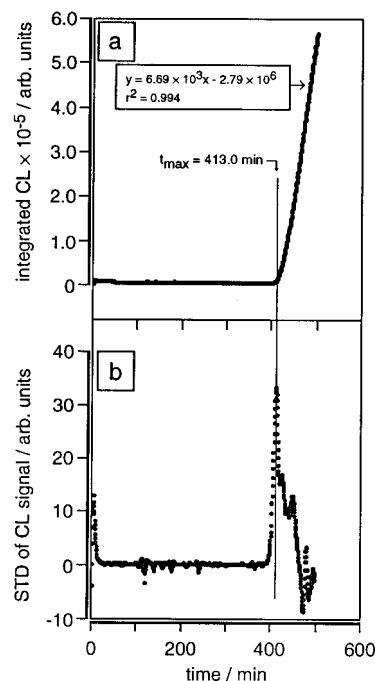
$$\alpha(i) = y_0(i) / y_1(i) \quad (10)$$

The array of STD values is thus corrected for any aberrations caused during the smoothing algorithm by multiplying each of the  $D_{2y}$  elements by its corresponding smoothing factor:

$$D_{2y}(i)_{\text{corrected}} = D_{2y}(i) \times \alpha(i) \quad (11)$$

Clearly, the closer the value of  $\alpha(i)$  is to unity, then the less effect the smoothing algorithm has had on the raw experimental data.

Although for flexibility we chose to carry out STD analysis using our own software, second derivative facilities are provided as standard in most DSC software packages, and can be applied equally to DSC as to CL data. Nonetheless, the precise algorithm by which commercial software packages smooth the raw data and calculate the



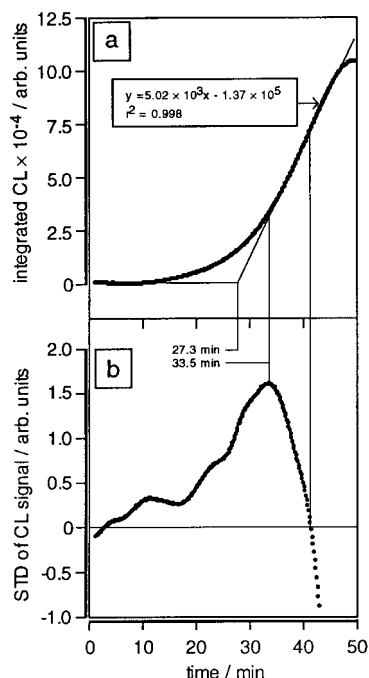
**Figure 1** Plot of: (a) the typical integrated CL emission intensity (arbitrary units) versus time (min) recorded from oxidatively stable PP which was oxidized in  $O_2$  at  $150^\circ C$ , 1 bar, flow rate  $100 \text{ mL min}^{-1}$ ; and (b) the STD versus time (min) of the data plotted in (a) after 20 smoothings of the raw CL data. The sampling interval was  $\delta t = 30 \text{ s}$ .

STD may not be made known to the user, and this may slightly affect the value of the subsequent OIT obtained from the analysis. For this reason the algorithm that was used to process the raw CL data collected in the current work is given herein.

### Oxidatively Stable Polypropylene

Figure 1(a) is a plot of the integrated CL intensity obtained from the oxidatively stable PP sample versus time. The sample behaves in an almost ideal manner in that its integrated emission exhibits a sharp, almost linear, increase after a long, flat induction period. Shown in Figure 1(b) is the corresponding STD curve that has been corrected in accordance with eq. (11) for any effects of the data smoothing procedure. The STD curve is quite sensitive to small changes in the integrated CL curve, as evidenced by the peak at the beginning of the experimental run. This peak is produced by a slight instability in the CL signal when oxygen is first admitted to the sample chamber at the start of the run.

The equation of the line of best fit through the data in the autoaccelerating region [see inset, Fig.



**Figure 2** Plot of: (a) the typical integrated CL emission intensity (arbitrary units) versus time (min) recorded from oxidatively unstable PP which was oxidized in air at 150°C, 1 bar, flow rate 100 mL min<sup>-1</sup>; and (b) the STD versus time (min) of the data plotted in (a) after 50 smoothings of the raw CL data. The sampling interval was  $\delta t = 10$  s.

1(a)] was obtained from a linear least-squares regression analysis of these data. This line was extrapolated to intersect the “baseline,” which in this case is the time axis. The resulting OIT was calculated from the equation of the line to be 417.5 min. This calculated OIT is almost equal to 413.0 min, the time at which the maximum in the STD curve occurs. Thus, for a sample such as this one where the OIT is long and the onset behaves ideally, the maximum of the STD plot may be considered as being equal to the OIT. In the case of the present sample such an assumption incurs a discrepancy of ca. 1.1%.

### Oxidatively Unstable Polypropylene

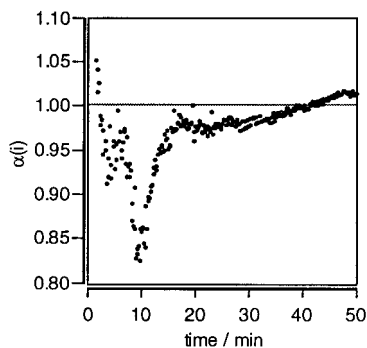
Figure 2(a) shows the typical integrated CL emission of a sample of unstabilized PP that was oxidized in air at 150°C and 1 bar. Before oxidation, the sample was heated to 200°C (i.e., above its melting temperature) in nitrogen for 5 min to reduce the likelihood of any changes to its shape occurring during the oxidation that could, in turn, result in aberrations in the observed CL profile. The resultant CL profile is one that exhibits a

gradual onset of the autoaccelerating region, and has an expectedly short induction period.

The corresponding STD curve shown in Figure 2(b) exhibits a maximum that corresponds to the point where the autoaccelerating region in the integrated CL profile becomes more linear. The STD peak in this region is quite broad, indicating that the corresponding integrated CL data are nonlinear. This brings into question the validity of adopting the conventional method of drawing a straight line through the data in the autoaccelerating region and extrapolating this line to the baseline to obtain an OIT. Nonetheless, if such an extrapolation is deemed to be acceptable, then a suitable criterion for those data that are considered to lie in the “linear” region must be set. It is in relation to setting such a criterion that the STD curve is of considerable use. In particular, the time at which the STD is zero corresponds to the point of inflexion in the autoaccelerating region of the integrated CL curve. This point can be taken as the first of two points that lie on a line to be constructed through the “linear” region. The second point on this line can be taken as the point where the integrated CL curve begins to deviate from “linearity.” The latter point can be located from the maximum in the STD curve [see Fig. 2(b)].

The line of best fit through the “linear” data in the autoaccelerating region was established by performing a linear regression analysis on the data within the time range of 33.5 min to 41.1 min. The equation of this line is given as the inset to Figure 2(a), and the line has been drawn in the figure. The point of intersection of this line with the time axis occurs at 27.3 min, and can be taken to be the OIT. Thus, it is proposed that the adoption of a suitable criterion for appropriate data selection that is derived from STD analysis enables the conventional extrapolation method for OIT determination to be applied with much less subjectivity to systems that exhibit nonideal behavior.

It has been suggested that the maximum of the STD curve corresponds to the end of the induction period.<sup>17</sup> Presumably, any nonzero value of the STD can be physically interpreted as being the result of a change in the rate of any autoaccelerating process that is taking place in the polymer. It can be argued that the point at which there is a maximum change in the rate of autoacceleration must, therefore, herald the beginning of the main autoacceleratory event. This raises the question of whether the point in time where the STD is a maximum can alone be taken as a suitable crite-



**Figure 3** Plot of the smoothing factor,  $\alpha(i)$ , versus time (min) in the range  $0 \leq t \leq 50$  min that pertains to the data plotted in Figure 2. The smoothing factor was calculated after 50 smoothings of the raw CL data.

tion for an OIT. Certainly for “well-behaved” systems such as the one shown in Figure 1, the error invoked in adopting this criterion is quite small indeed. However, for systems such as that shown in Figure 2, the difference between the OIT derived in the conventional way and that obtained by taking the STD maximum can be large (ca. 23% in the case of the system shown in Fig. 2). Of course, the percentage deviation between these two estimates of the OIT will decrease with longer OITs and sharper onsets.

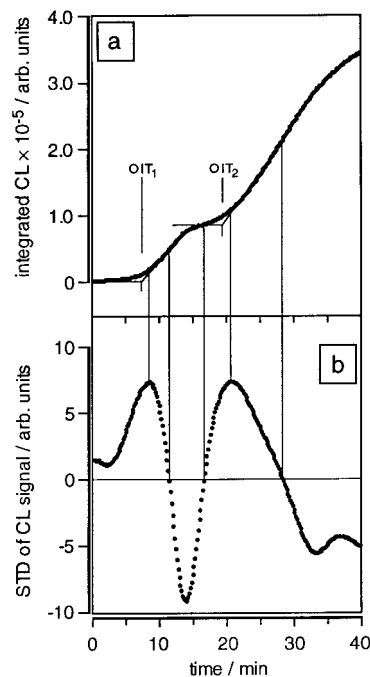
The presence of minor peaks in Figure 2(b) that occur during the approach to the autoaccelerating region may indicate the existence of secondary processes that are precursors to the autoaccelerating stage, or may simply reflect the heterogeneous nature of the oxidative process.<sup>21</sup> The origin of these peaks, however, is only speculative at this stage, and is clearly beyond the scope of this article. Nonetheless, the presence of minor peaks in the region prior to the onset reflects once again the sensitivity of the STD to small changes in the acceleration of the reactions that occur during oxidation. These changes are not immediately apparent upon the direct inspection of the integrated CL curve [Fig. 2(a)] or a plot of the raw CL data.

Figure 3 shows a plot of the smoothing factor,  $\alpha(i)$ , versus time that applies to the data shown in Figure 2. For purposes of comparison the data in Figure 3 are plotted over the same time window as that used in Figure 2. Figure 3 demonstrates numerically that the smoothing process has had only a minimal effect on the data, as the smoothing factor is close to unity in most cases, and has a maximum deviation from unity of ca. 17%. In any case, the smoothing algorithm has had little effect on the data in the range of ca. 20–50 min

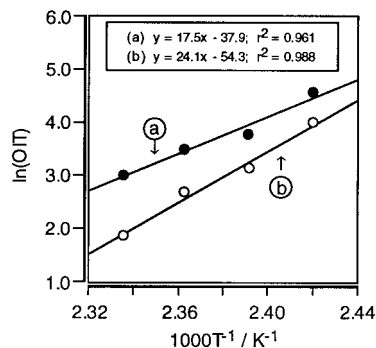
where the OIT occurs, and so one may confidently assume that the peaks in the STD occurring within this time interval are indeed real.

### Polypropylene–Polybutadiene Blend

The CL profile in Figure 4(a) was obtained from the PP/PBD blend, and demonstrates behavior typical of a blend in which the oxidation of the separate components occurs almost independently. The two-step degradation of blends has been reported previously, for example, in the case of the pyrolysis of partially miscible blends of poly(vinyl chloride) (PVC) with poly( $\alpha$ -methylstyrene–acrylonitrile–methylmethacrylate) terpolymer.<sup>22</sup> Indeed, a more complex three-step degradation process has been reported for the pyrolysis of PVC blended with acrylonitrile–butadiene–styrene terpolymer.<sup>23</sup> The first onset of an autoaccelerating region [Fig. 4(a)] is attributed to the oxidation of the PBD phase, which is inherently less stable than the PP phase,<sup>24</sup> whose oxidation is revealed in the later part of the CL profile. The susceptibility of PBD to oxidation may be attributed to the presence of unsaturated sites in its



**Figure 4** Plot of: (a) the typical integrated CL emission intensity (arbitrary units) versus time (min) recorded from a 5% w/w blend of PBD in PP, which was oxidized in  $O_2$  at  $155^\circ C$ , 1 bar, flow rate  $100 \text{ mL min}^{-1}$ ; and (b) the STD versus time (min) of the data plotted in (a) after 50 smoothings of the raw CL data. The sampling interval was  $\delta t = 10$  s.



**Figure 5** Arrhenius plots of the OITs obtained for: (a) the PP component, and (b) the PBD component of a 5% w/w blend of PBD in PP. The OITs were obtained from the CL profiles using STD analysis.

structure. Such sites have also been implicated as the cause of the oxidative susceptibility of poly(ethylidene-2-norbornene) (EPDM).<sup>25</sup>

The application of STD analysis to a convoluted CL profile such as the one shown in Figure 4(a) can enable the OITs of the component phases in the blend to be determined satisfactorily. It is clear from the constructs in Figure 4 that the times at which the STD is zero can be used to locate the points of inflexion on the integrated CL curve, and the maxima in the STD curve can be used to locate the points where the integrated CL profile enters the "linear" region.

To illustrate the usefulness of STD analysis as a reliable tool for the determination of short OITs, samples of the PP/PBD blend were oxidized at different temperatures and the OITs of the separate phases were derived using the analytical method depicted in Figure 4. In particular, the maxima of the STD curve were taken as the starting points of the two "linear" autoaccelerating regions, and the respective points of inflexion were taken to be the ends of these regions for the purposes of selecting appropriate data for linear regression analyses. The baseline associated with the second onset was taken to be a line drawn parallel to the time axis, and that passes through the appropriate point of inflexion identified from the STD curve (see Fig. 4). The OITs were calculated by solving the simple linear equations that were obtained from these analyses.

Figure 5 shows an Arrhenius plot of the OIT data obtained for each phase. The linearity of the data: (a) confirms that the system is Arrhenian over the temperature range studied, (b) is consistent with the notion that the two phases oxidize almost independently of each other, and (c) suggests that STD analysis can be successfully im-

plemented to extract OIT information from convoluted CL profiles. The activation energies for the oxidation of the two phases were calculated from the gradients of the Arrhenius plots and were found to be  $200 \pm 31 \text{ kJ mol}^{-1}$  for the PBD component and  $146 \pm 9 \text{ kJ mol}^{-1}$  for the PP component. These values are consistent in magnitude with activation energies reported in the literature for the oxidation of: (a) butyl rubber as determined by oxygen uptake measurements where the activation energy is found to be quite high and varies with temperature,<sup>26</sup> (b) unstabilized PP as determined by CL induction time measurements,<sup>21,27</sup> and (c) atactic PP stabilized with 0.10% w/w Irganox 1010 or 0.10% w/w Irganox 1076 as determined by isothermal DSC measurements.<sup>5</sup> It is also interesting to note that that values of the activation energies of 180 and 141  $\text{kJ mol}^{-1}$  are respectively obtained from the phases if one uses the maxima in the STD curves as the criterion that defines the OIT. These values lie well within the error limits of the activation energies derived from OITs that were obtained using the more conventional definition.

In the present study, the higher activation energy observed for the PBD phase compared with the PP phase may be attributed to there being a higher concentration of thermal stabilizer in the PBD phase. It has been shown, for example, that in blends of 25% w/w of EPR in PP the partitioning of Irganox 1076 in the EPR phase at elevated temperatures can be as high as 75% of the total amount of this antioxidant present.<sup>28</sup> Furthermore, it has been established that as much as 70% of Irganox 1076 is partitioned into the PBD phase in PBD/PP blends at the temperatures used in OIT studies.<sup>29</sup>

## CONCLUSIONS

The technique of STD analysis, when used in conjunction with the integrated CL profile, shows considerable potential as a means by which the OIT of polymers can be determined with less subjectivity than the conventional method. The technique is of particular merit as a tool for the analysis of: (a) systems that exhibit sharp onsets of the autoacceleration where the maximum in the STD curve corresponds closely with the OIT obtained by extrapolation, and (b) system such as polymer blends that may exhibit complex and/or convoluted CL profiles.

For systems that exhibit a gradual onset towards autoacceleration, the application of the

conventional extrapolation method is, at the very least, questionable, because the selection of the "linear" data for the extrapolation procedure is usually quite subjective. In these cases there is clearly a need for suitable criteria that can be used to either: (a) unambiguously select a set of data that is deemed to be linear if it is decided that the conventional extrapolation method is to be used; or (b) define an OIT in some other way that is unambiguous, reliable, and nonsubjective. In relation to the latter, it is proposed that the time at which the maximum in the STD curve occurs at the onset of the main autoacceleration event can be taken as an unambiguous OIT. This criterion has been applied in the study of the temperature dependence of CL originating from PBD-PP blends, and it appears to give quite satisfactory results. These results indicate that the PBD-PP system conforms to Arrhenius behavior over the temperature range studied, and are consistent with the notion that the PBD and PP phases oxidize almost independently.

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