INTRODUCTION

The limiting oxygen index (LOI) is widely used as a measure of flammability because, in its standardized form \(^1\), the test is precise and produces quantitative results as opposed to the qualitative (pass/fail) results obtained in other small flame tests \(^2\). The LOI is the minimum oxygen concentration in a flowing atmosphere that will sustain downward burning of a plastic strip or fabric \(^3\). As such, the LOI involves the coupling of condensed and gas phase processes of flaming combustion at or near extinction, and for this reason, has defied simple description \(^4,5,6,7\) because the combustion characteristics that are associated with low flammability in flame and fire tests are associated with high LOI values \(^8,9\). In this paper we investigate how material and fire properties contribute to the outcome of the LOI test by measuring the heat release rate in the test and applying steady burning and flame spread criteria to explain the results.

APPROACH

The burning process in the LOI test can be a combination of one-dimensional (1-D) surface regression and flame spread, each of which is governed by different phenomena \(^10\). For 1-D surface regression by unforced flaming combustion, the heat release rate \(q''\) as occurs in the LOI test after the igniter flame is removed and the sample flame drives the burning process is \(^10,11\)

\[
q'' = \chi \frac{H_c^0}{L_g} \cdot q_{\text{net}} = \frac{H_c}{L_g} \left( q_{\text{flame}} - q_{\text{rerad}} \right)
\]

In Equation 1, \(\chi = H_c / H_c^0\) is the combustion efficiency of the fuel gases in the flame, \(H_c\) is the effective (incomplete) heat of flaming combustion of the gases, \(H_c^0\) is the heat of complete combustion of the fuel gases, \(L_g\) is the heat of polymer decomposition, \(q_{\text{flame}}''\) is the heat flux incident on the burning surface from the flame, \(q_{\text{rerad}}''\) is the heat that is reradiated per unit area of burning surface at temperature \(T_b\) to the environment at \(T_0\), \(\sigma\) is the Boltzmann radiation constant, and \(q_{\text{net}}'' = q_{\text{flame}}'' - q_{\text{rerad}}''\) is the net heat flux available to sustain flaming combustion. It has been shown that an increase in the oxygen concentration in the environment \([O_2]\) increases the heat release (burning) rate of plastics \(^11\). According to Equation 1, an increase in heat release rate must be due to an increase in \(q_{\text{flame}}''\) or \(\chi\) because
$H^c$, $L_g$ and $q''_{rerad}$ are properties of the solid. In fact, $q''_{flame}$ has been shown to be roughly proportional to the oxygen concentration as a consequence of an increase in flame temperature as the inert nitrogen is replaced by reactive oxygen and an increase in soot production that makes the flame more luminous or radiating. It follows from Equation 1 that if $L_g$ and $H_c$ can be measured in separate tests and $q''$ can be measured during the LOI test, the flame heat flux can be calculated

$$q''_{flame} = \frac{L_g}{H_c} q'' + q''_{rerad} \tag{2}$$

Furthermore, if $[O_2]$ is the oxygen concentration in the environment, the flame heat flux can be written

$$q''_{flame} = C\{[O_2] - [O_2]_{min}\} \tag{3}$$

where $[O_2]_{min} = 0.11$ is the minimum mole/volume fraction of oxygen in nitrogen that will support burning of typical hydrocarbons. If $q'' = q^*$ is the critical heat release rate for burning at the specified velocity in ASTM D 2863 and $L_g = H_g(1 - \mu)$ with $H_g$ the heat of gasification per unit mass of solid and $\mu$ the char mass fraction, then $[O_2] = \text{LOI at } q'' = q^*$ and from Equations 1 and 3

$$\text{LOI} = \frac{q^* H_g}{H_c(1 - \mu)C} + \frac{\alpha T_b^4}{C} + [O_2]_{min} \tag{4}$$

Equation 4 gives the oxygen concentration at the critical energy (heat release) release rate in terms of parameters that are obtained in this study. On the other hand, if flame spread is the governing phenomenon in the LOI test, the flame spread rate (burning velocity) in steady downward burning of a thermally-thin specimen having thickness $b$, heated length $\lambda$, ignition time $t_{ign}$, density $\rho$ and heat capacity $c$, can be written

$$v_b = \frac{\lambda}{t_{ign}} = \frac{\lambda}{\rho c b(T_b - T_0) / q''_n} = \frac{\lambda q''_{flame} - \alpha T_b^4}{\rho c b(T_b - T_0)} \tag{5}$$

A constant burning velocity, $v_b = v^* = 50$-mm/180-s = 0.28 mm/s is specified in the standard test at the LOI. Since $[O_2]$ is the independent variable in the test, the dependent variable is $q''_{flame}$ because the other parameters in Equation 5 are geometric quantities or material properties. Substituting Equation 3 for $q''_{flame}$ in Equation 5 and solving for $[O_2] = \text{LOI},$

$$\text{LOI} = \frac{v^* \rho c b(T_b - T_0)}{\lambda C} + \frac{\alpha T_b^4}{C} + [O_2]_{min} \tag{6}$$

Equations 1-6 completely characterize the burning process in the LOI test from the perspective of the condensed phase and for the purposes of this investigation.

**EXPERIMENTAL**

**Materials**

Polyoxymethylene (POM), polymethylmethacrylate (PMMA), polycarbonate of bisphenol-A (PC), poly(hexamethylene adipamide) (PA66), polyphenylsulfone (PPSU), rigid polyvinylchloride (PVC), and
polyetherimide (PEI) were obtained as commercial, natural-grade, unfilled extruded plastic sheet in 3-mm and 6-mm thickness containing no processing aids or flame retardant additives. Methane, oxygen, and nitrogen gases used for calibration and testing were dry, >99.99% purity grades obtained from Matheson Gas Products and Welco.

**Methods**

Experiments were conducted using the standard procedure but the apparatus was modified to enable the measurement of heat release rate of the burning specimen by means of oxygen consumption as shown in Figure 1. A system of baffles was attached to the top of the optional column cap on the LOI chimney to mix the combustion gases before drawing a sample for analysis of oxygen depletion. Heat release rate \( Q(W) \) was calculated from the measured oxygen depletion and total flow rate of the combustion gas stream (16.1 L/min) producing a linear velocity of 40 ± 2 mm/s at 23 ± 2°C in the nitrogen/oxygen mixture of the 92-mm diameter x 500-mm tall Pyrex glass chimney. Tests were conducted using standard LOI specimens cut from 3-mm thick sheet materials. Standard specimens had nominal length 150 mm, width 7.9 ± 0.9 mm and thickness 3.1 ± 0.1 mm. Burning velocity \( v_b \) (mm/s) and heat release rate \( Q(W) \) of standard specimens were measured over the duration of the test and time-averaged values are reported in Table 1. Heat release rate measurements were made on circular disks having diameters \( D = 10, 13, 16 \) and 19-mm that were punched from the 6-mm thick polymer sheets to determine the effect of sample area on heat release rate in the ASTM D2863 apparatus. The bottom and side of the 6-mm thick disk specimens were wrapped in aluminum foil and the specimen was supported on brass pins with negligible thermal contact. Time-averaged values of \( q'' = Q / (\pi D^2/4) \) are reported in Table 2.

**RESULTS AND DISCUSSION**

Table 1 lists the LOI, the average burning velocities \( v_b \) (mm/s) and average heat release rate \( Q(W) \) at the LOI as per the ASTM D 2863 protocol, and the heat release rate prior to significant char formation \( Q_0 \). Also listed in Table 1 are the heats of flaming combustion \( H_c \), heats of decomposition \( L_g \), char mass fractions \( \mu \) and thermal decomposition/surface burning temperatures \( T_b \) for the polymers determined in separate experiments. The effective burning area computed for one-dimensional downward burning, \( S_{eff} = Q / (\pi v_b H_c) \), is also listed in Table 1 and is, on average, approximately equal to the nominal 3 x 8 mm = 24 mm² cross-sectional area.

Figure 2 shows the data of Table 1 for the burning velocities \( v_b \) and heat release rates \( Q \) at the LOI of the 3 x 8 x 150-mm (standard) specimens. Table 2 contains the data for the heat release rate per unit area \( q'' \) of the PP, PMMA and POM disk specimens at different oxygen concentrations above the LOI of each polymer. Flame heat fluxes were computed from the data in Table 2 using the polymer data in Table 1. The oxygen coefficient of the flame heat flux \( C \) was computed using Equation 3 from the slopes in Figure 3 and the data in Table 2. These \( C \) values are reported in Table 2 for each polymer tested as disks and they are higher than \( C \approx 2\ kW/m^2-\%O_2 \) obtained for large (100 cm²) specimens of these polymers tested in a fire calorimeter.

Figure 3 is a plot of the flame heat flux \( q''_{flame} \) versus the reciprocal disk diameter (Fig. 3A) and the oxygen concentration (Fig. 3B). Flame heat flux \( q''_{flame} \) was calculated using Equation 2 from the data in Table 2 and the polymer properties in Table 1. Figure 3 shows that the flame heat flux increases as the specimen cross-section decreases and as the oxygen concentration increases.
Figure 1. The Oxygen Index Test Apparatus (ASTM D 2863-06) Modified for Oxygen Consumption Measurements.

Table 1. Burning Velocities and Heat Release Rates of 3 x 8 x 150 mm Specimens at LOI in ASTM D2863 as well as Combustion Properties and Effective Burning Area of Polymers.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>LOI (% O₂)</th>
<th>Vₙ (mm/s)</th>
<th>Q(W)</th>
<th>Qₘ(W)</th>
<th>Char Mass Fraction μ</th>
<th>Hₑ (kJ/g)</th>
<th>Hₛ (kJ/g)</th>
<th>Tₑ (K)</th>
<th>Sₑff mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>POM</td>
<td>15.0</td>
<td>0.12</td>
<td>49</td>
<td>49</td>
<td>0</td>
<td>14.7</td>
<td>3.4</td>
<td>642</td>
<td>23</td>
</tr>
<tr>
<td>PMMA</td>
<td>17.0</td>
<td>0.05</td>
<td>28</td>
<td>28</td>
<td>0</td>
<td>25.0</td>
<td>1.6</td>
<td>593</td>
<td>19</td>
</tr>
<tr>
<td>PP</td>
<td>17.5</td>
<td>0.12</td>
<td>25</td>
<td>25</td>
<td>0</td>
<td>39.3</td>
<td>2.5</td>
<td>720</td>
<td>5</td>
</tr>
<tr>
<td>ABS</td>
<td>17.6</td>
<td>0.10</td>
<td>64</td>
<td>64</td>
<td>0</td>
<td>39.4</td>
<td>2.0</td>
<td>727</td>
<td>14</td>
</tr>
<tr>
<td>PC</td>
<td>25.3</td>
<td>0.20</td>
<td>68</td>
<td>27</td>
<td>0.23</td>
<td>21.5</td>
<td>2.3</td>
<td>772</td>
<td>13</td>
</tr>
<tr>
<td>PA66</td>
<td>28.0</td>
<td>0.26</td>
<td>40</td>
<td>40</td>
<td>0.01</td>
<td>22.6</td>
<td>2.6</td>
<td>711</td>
<td>6</td>
</tr>
<tr>
<td>PPSU</td>
<td>40.5</td>
<td>0.21</td>
<td>101</td>
<td>53</td>
<td>0.44</td>
<td>17.5</td>
<td>4.4</td>
<td>830</td>
<td>23</td>
</tr>
<tr>
<td>PVC</td>
<td>41.9</td>
<td>0.18</td>
<td>83</td>
<td>66</td>
<td>0.19</td>
<td>9.0</td>
<td>1.8</td>
<td>641</td>
<td>34</td>
</tr>
<tr>
<td>PEI</td>
<td>42.2</td>
<td>0.40</td>
<td>135</td>
<td>69</td>
<td>0.51</td>
<td>19.8</td>
<td>3.5</td>
<td>800</td>
<td>14</td>
</tr>
</tbody>
</table>
Table 2. Heat Release Rates $q''$ (kW/m$^2$) for PP, PMMA and POM Disks at Indicated Oxygen Concentration and Disk Diameter in ASTM D 2863-06 Apparatus.

<table>
<thead>
<tr>
<th>Oxygen Concentration (Volume %)</th>
<th>Disk Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10-mm</td>
</tr>
<tr>
<td><strong>Polypropylene (PP), $C = 4.8 \pm 0.7$ kW/m$^2\cdot$-%O$\textsubscript{2}$</strong></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>1576 ±328</td>
</tr>
<tr>
<td>30</td>
<td>1928 ±216</td>
</tr>
<tr>
<td>35</td>
<td>2440 ±128</td>
</tr>
<tr>
<td><strong>Polymethylmethacrylate (PMMA), $C = 4.5 \pm 1.1$ kW/m$^2\cdot$-%O$\textsubscript{2}$</strong></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>1204 ±76</td>
</tr>
<tr>
<td>30</td>
<td>1508 ±92</td>
</tr>
<tr>
<td>35</td>
<td>1904 ±120</td>
</tr>
<tr>
<td><strong>Polyoxymethylene (POM), $C = 7.7 \pm 1.9$ kW/m$^2\cdot$-%O$\textsubscript{2}$</strong></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>940 ±80</td>
</tr>
<tr>
<td>35</td>
<td>932 ±24</td>
</tr>
<tr>
<td>40</td>
<td>1124 ±52</td>
</tr>
</tbody>
</table>

Figure 2. Measured Burning Velocity and Heat Release Rate (W) for the 9 Polymers in This Study.
Figure 3. Flame Heat Flux versus Reciprocal Diameter of Disk Specimens (A) and versus Oxygen Concentration (B).

Figures 4, 5 and 6 are plots of $q''$ from Table 2 for PMMA, POM and PP disks of diameter $D = 10, 13, 16$ and 19-mm at three oxygen concentrations above the LOI in order to assure sustained burning. Extrapolating $q''$ versus oxygen concentration to the LOI of PMMA, POM and PP gives $q''(LOI)$ as the Y-axis intercepts in Figures 4, 5 and 6. Figure 7 is a plot of $q''(LOI)$ so obtained versus the reciprocal surface area of the disks. The linear least-squares regression curve plotted in Figure 7 suggests that $q''(LOI)$ is inversely proportional to surface burning area, i.e., $Q$ is relatively constant as indicated in Table 1 and Figure 2. Extrapolation of $q''(LOI)$ to the reciprocal cross-sectional area of the nominal 8-x 3-mm LOI specimen (0.042 mm$^2$) gives an average value of $q''(LOI) = 2000 \pm 200$ kW/m$^2$ for the heat release per unit surface area at the LOI based on the nominal cross-section. Another estimate of the effective surface burning area $S_{eff}$ of the LOI specimens is obtained from the $q''(LOI)$ and the average $Q$ of PMMA, POM, PA66 and PP in Table 1, $S_{eff} = Q/q''(LOI) = (36 \pm 11 \text{ W})/2000 \pm 200$ kW/m$^2 = 1.8 \pm 0.6 \times 10^{-2}$ m$^2 = 18 \pm 6$ mm$^2$. This is approximately the cross-sectional area $S_0 = 24$ mm$^2$ of the 8 x 3 mm LOI specimens and is consistent with the visual observation that the flame is constrained to the tip of the specimen of non-charring polymers at the LOI.
Figure 4. Heat Release Rate $q''$ versus Oxygen Concentration [$O_2$] in the ASTM D 2863-06 Apparatus for PMMA Disks of 10, 13 and 16-mm Diameter and 6-mm Thickness.

Figure 5. Heat Release Rate $q''$ versus Oxygen Concentration [$O_2$] in the ASTM D 2863-06 Apparatus for POM Disks of 10, 13 and 16-mm Diameter and 6-mm Thickness.
Figure 6. Heat Release Rate $q''$ versus Oxygen Concentration [O$_2$] in the ASTM D 2863-06 Apparatus for PP Disks of 10, 13, 16 and 19-mm Diameter and 6-mm Thickness.

Figure 7. Plot of $q''$ at the LOI of PMMA, POM, PA66 and PP versus Reciprocal Surface Area of Disk Specimens.

Figure 8 is a plot of the empirically normalized heat release rate $q''_{LOI}$ (i.e., $Q$ divided by the nominal cross-sectional area of the individual test specimen) versus the LOI of the polymer. Normalizing for burning area in this way does not account for the porous, high surface area, voluminous char whose
burning is the cause of the high $q_{\text{LOI}}^n$ for PC, PPSU, PVC and PEI in Figure 8. An average value, $q_{\text{LOI}}^n = 1880 \pm 640 \text{ kW/m}^2$ for the heat release rate in steady downward burning at the LOI is obtained from the data in Figure 8.

![Figure 8. Heat Release Rates of Polymers at the LOI in ASTM D 2863.](image)

Figure 8 shows data for the flame heat flux $q_{\text{flame}}^n$ versus the oxygen concentration at the LOI for the 3 x 8 x 150 mm (standard) polymer LOI specimens before the voluminous char is generated, calculated using Equation 2, the $q_{\text{LOI}}^n$ in Figure 7, and the polymer properties in Table 1. The fact that $q_{\text{flame}}^n$ is much higher for thermally stable and char forming polymers at the LOI reflects the higher energy deposition rate that these polymers require to maintain the specified $v_b$.

Figure 10 is a plot of measured and calculated burning velocities versus flame heat flux at the LOI. The burning velocity was calculated from Equation 6 for the polymers using $q_{\text{flame}}^n$ from Figure 9, $T_b$ from Table 1 and typical polymer density $\rho = 1200 \text{ kg/m}^3$ and heat capacity $c = 2500 \text{ J/kg-K}$. The heated length is assumed to be, $\lambda = 10 \text{ mm}$, which is on the order of the LOI specimen perimeter. Figure 10 indicates that $v_b$ is relatively insensitive to $q_{\text{flame}}^n$ as it should be, since a constant average value ($v^* = 2.8 \text{ mm/s}$) is specified in the test procedure.
Figure 9. Calculated Flame Heat Flux at the LOI for Polymers Tested According to ASTM D-2863.

Figure 10. Measured and Calculated Burning Velocities versus Flame Heat Flux at the LOI.

Figure 11 compares measured LOI to those calculated with Equation 4 (energy criterion) and Equation 6 (flame spread criterion). The parameters used in Equation 4 are $q^* = 300$ kW/m$^2$ the critical heat release rate for flame spread$^{17}$, $C = 6$ kW/m$^2$-%O$_2$, the average flame heat flux coefficient of oxygen reported in Table 2, and the polymer properties in Table 1. In Equation 6, the heated length is $\lambda = 10$ mm as previously, with $\rho = 1200$ kg/m$^3$ and $c = 2500$ J/kg-K as previously. Qualitative agreement between measured and calculated LOI is observed with both criteria using only $\lambda$ and $q^*$ as adjustable parameters.
CONCLUSIONS

A critical heat release rate or a critical flame spread rate can account for the LOI of polymers in a qualitative sense. It is observed that oxygen increases the flame heat flux to the specimen, and it is the flame heat flux that drives the burning process. Thus, the oxygen concentration at the LOI in ASTM D 2863 corresponds to a flame heat flux that will sustain downward burning at the specified velocity either by surface regression or flame spread, or both. Equations 1 and 4 show that there is an inverse-additive relationship between $q''$ and LOI with regard to the combustion properties $\mu$, $H_g$, $H_c$ and $T_b^4$. In other words, the same properties that lead to low $q''$ and good performance in flame and fire tests produce high LOI values. This inverse-additive relationship between combustion properties and test performance explains the poor correlation between flame/fire tests and the LOI \(^{8,9}\). It remains to determine the mechanism(s) by which energy transfers from the flame to the specimen in the LOI test and to ascertain how oxygen increases the flame heat flux, whether through an increase in the flame temperature or soot production, or both.

REFERENCES


