A Physical Basis for Comparing Flammability of Aircraft Cabin Materials Using a Microscale Combustion Calorimeter

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Final report
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In this study, a burning model is used to link the molecular-level processes of flaming combustion measured in thermal analysis to the fire response of a polymer at the continuum level. A flammability parameter that includes ignitability and burning rate, driven by heat release, emerging from this analysis is called the Fire Growth Capacity (FGC). The FGC was measured in a micro (10^{-6} kg) scale combustion calorimeter for 30 polymers, and successfully ranked the expected fire performance of these polymers in bench (kg) scale flame and fire tests.
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<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>ABS</td>
<td>Acrylonitrile Butadiene Styrene</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BPC-CE</td>
<td>Cyanate Ester of Bisphenol-C</td>
</tr>
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<td>BPC-PC</td>
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</tr>
<tr>
<td>CFR</td>
<td>Code of Federal Regulations</td>
</tr>
<tr>
<td>FAA</td>
<td>Federal Aviation Administration</td>
</tr>
<tr>
<td>FEP</td>
<td>Fluorinated Ethylene Propylene</td>
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<tr>
<td>FGC</td>
<td>Fire Growth Capacity</td>
</tr>
<tr>
<td>HDPE</td>
<td>High Density Polyethylene</td>
</tr>
<tr>
<td>HIPS</td>
<td>High Impact Polystyrene</td>
</tr>
<tr>
<td>MCC</td>
<td>Microscale Combustion Calorimeter</td>
</tr>
<tr>
<td>PA66</td>
<td>Polyhexamethyleneadipamide</td>
</tr>
<tr>
<td>PAI</td>
<td>Polyamideimide</td>
</tr>
<tr>
<td>PBI</td>
<td>Polybenzimidazole</td>
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<td>PC</td>
<td>Polycarbonate of Bisphenol-A</td>
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<td>PVC</td>
<td>Polyvinyl Chloride</td>
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<td>Polyvinylidene Fluoride</td>
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<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>---------</td>
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<tr>
<td>TA</td>
<td>Thermal Analysis</td>
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Executive summary

A model for the fire response of charring and non-charring combustible solids at the continuum (kg) level was used to identify the temperatures at ignition and burning at the molecular level, so that they could be conveniently measured in a micro ($10^{-6}$ kg) scale combustion calorimeter. The fire response model shows that flame spread is driven by the combustion heat of the fuel gases and follows a path of least thermal resistance (ignition or burning) in the solid. This is the physical basis for an intrinsic, molecular-level, flammability parameter called the Fire Growth Capacity ($FGC$), which can be measured in a microscale combustion calorimeter using milligram samples. The $FGC$ spans three orders of magnitude for the combustible solids examined in this study and successfully ranks 30 polymers according to their expected fire performance in bench- and full-scale fire tests.
1 Introduction

The heat produced by combustion of fuel gases generated during the burning of polymeric solids in a fire begins with thermally-induced cleavage of primary/covalent chemical bonds between constituent atoms of the molecule, and culminates with the reaction of volatile decomposition products with oxygen in a diffusion flame to produce heat. The arrangement and composition of atoms in the solid (i.e., the molecular architecture) determines whether bond recombination (charring) or bond scission (gas forming) reactions are thermodynamically favored during thermal decomposition, but it is the rate of these chemical reactions coupled with heat and mass transfer at the continuum level that largely determines the fire hazard of a material.

The influence of molecular architecture on the rates of fuel generating reactions can been decoupled from heat/mass transfer using reactive molecular dynamics simulations [1-4], molar group contributions to thermodynamic combustion properties [5-8], and direct correlation with micro (10^-6 kg) scale reaction rates and thermodynamic properties measured by thermal analysis (TA) [9-11]. Many of the thermodynamic and kinetic parameters obtained from TA are molecular-level properties that are used in finite element pyrolysis models to simulate burning at bench (kg) scale [11-20] and full (10^3 kg) scale [18].

Another approach has been to parameterize transient fire response at the continuum level, using time-averaged fire behavior in bench-scale fire calorimeters [21-25]. These bench (kg) scale fire response parameters have proven useful for qualitative ranking of material fire performance in flame and fire tests [25-30] and at full-scale [31-32]. Fire response parameters measured at the micro (10^-6 kg) scale in TA experiments have also been used to rank the fire performance of materials at the continuum level in flame and fire tests [27-29,33-37]. To date, these micro-scale heat release parameters have been moderately successful at ranking bench-scale burning/heat release rates in forced flaming combustion [36], but they do not include ignitability, or account for the effects of heat and mass transfer in the solid, or reaction kinetics in the flame, which are operative in bench scale flame and fire tests [29,33-35]. This study proposes a micro/molecular scale flammability parameter that includes ignitability, and is therefore expected to be a better predictor of pass/fail tests of flame spread than micro-scale heat release alone.

2 Approach

Figure 1 is a schematic diagram of the transient, one-dimensional temperature profiles $T(x,t)$ for ignition and burning of a non-charring and a charring polymer as they are thought to occur in a fire calorimeter exposed to a constant external heat flux (irradiance) at time $t = 0$. The
consecutive processes of ignition and burning lead to the establishment of a surface flame and the development of a pyrolysis zone of thickness $\delta$ that moves through the solid at velocity $v$, generating fuel gases that mix with oxygen and combust in the surface flame. The pyrolysis zone is bounded by the burning temperature $T_{\text{burn}}$ at the surface $x = 0$ and by onset pyrolysis/ignition temperature $T_{\text{ign}}$ at depth at $x = \delta$.

Figure 2A and 2B show idealized surface temperature $T(0,t)$ and mass flux $\dot{m}$ histories for the burning model of Figure 1 for a polymer slab subjected to a constant external heat flux, $\dot{q}_{\text{ext}}^*$ at time $t = 0$, and initial temperature $T(0,0) = T_0$. The mass flux approaches the minimum (critical) value for piloted ignition $\dot{m}_{\text{ign}}^*$ at surface temperature, $T_{\text{ign}}$, at which point ($t_{\text{ign}}$) a pre-mixed volume of fuel and air ignites. A diffusion flame is established on the surface and the incident heat flux increases to $\dot{q}_{\text{ext}}^* + \dot{q}_{\text{flame}}^*$. At this point ($t_{\text{burn}}$) the mass flux and surface temperature increase to $\dot{m}_{\text{burn}}^*$ and $T_{\text{burn}}$, respectively.

![Figure 1. Transient temperature histories for ignition and burning](image-url)
2.1 Kinetics

The volumetric mass loss rate (kg/m³-s) in the pyrolysis zone at position $x$, time $t$, is $\dot{m}(x,t) = \rho(x,t) \dot{k}(x,t) = \rho(x,t) A \exp[-E_a/RT(x,t)]$, with $A$ and $E_a$ the frequency factor and activation energy of the thermal decomposition reaction. Conservation of mass for the pyrolysis volume gives the mass/fuel flux (kg/m²-s) exiting the surface $x = 0$ at temperature $T_{burn}$ from a specimen of thickness, $b$,

\[
\dot{m}''(t) = (\rho v)_0 - \int_0^b \rho(x,t) A \exp\left[-\frac{E_a}{RT(x,t)}\right] dx \int_0^b \rho(x,t) A \exp\left[-\frac{E_a}{RT(x,t)}\right] dx
\]

Once a diffusion flame is established, and ignition is sustained, a pyrolysis zone of thickness $\delta$ moves through the solid at velocity $v$ generating gaseous fuel. Each infinitesimal particle of material in the pyrolysis zone will experience a temperature history characterized by an average rate of temperature rise, $\Delta T/\Delta t \approx v(T_{burn} - T_{ign})/\delta = \dot{m}''(T_{burn} - T_{ign})/\rho \delta \approx 1 \text{K/s}$ for a typical mass flux.
(5x10^{-3} \text{ kg/m}^2\cdot\text{s}),\text{ temperature difference } (T_{\text{burn}} - T_{\text{ign}} = 200\text{K}),\text{ density } (1100 \text{ kg/m}^3),\text{ and pyrolysis zone thickness } (10^{-3} \text{ m}).\text{ Assume that a particle in the pyrolysis zone of a burning polymer can be represented by a milligram sample in a nonisothermal analysis experiment at constant heating rate } \dot{\theta} = \Delta T/\Delta t,\text{ and that the fraction of solid fuel that has been converted to gaseous products at temperature } T \text{ is } \alpha,\text{ a dimensionless variable that ranges from 0 to 1 over the course of the pyrolysis reactions. In this case, the ignition temperature } (T_{\text{ign}}) \text{ and fuel exhaustion temperature } (T_{\text{burn}}) \text{ would correspond to a temperature } T_1 \text{ at } \alpha \approx 0 \text{ and } T_2 \text{ at } \alpha \approx 1, \text{ respectively. These temperatures are determined by the short-term thermal stability } (T_1) \text{ and thermal decomposition chemistry } (T_2) \text{ of the molecule. In a micro-scale thermal analysis experiment at constant heating rate } \dot{\theta} \text{ in which the reaction rate } d\alpha/dt \text{ is measured, } T_1 \text{ and } T_2, \text{ will be solutions to the isokinetic relationship [38],}

\begin{equation}
\frac{T}{\dot{\theta}} \frac{d\alpha}{dt} = T \frac{d\alpha}{dT} = \frac{d\alpha}{d\ln[T]} = 1
\end{equation}

Figure 3 shows hypothetical surface temperatures at ignition \((T_{\text{ign}})\) and burning \((T_{\text{burn}})\) in a fire calorimeter (3A), as well as the temperatures at incipient pyrolysis \((T_1)\) and fuel exhaustion \((T_2)\) in a constant heating rate TA experiment (3B). The equivalence of \(T_{\text{burn}}\) and \(T_2\) is based on the assumption that an infinitesimal particle in the pyrolysis zone of a fire calorimeter sample experiences a similar temperature and mass loss history as a milligram sample in a thermal analysis experiment, so the onset and endpoint temperatures of the fuel generating reaction are similar. Note that the open circles in Figure 3B indicate isokinetic temperatures.
2.2 Thermodynamics

The specific energy (J/kg) required to melt and thermally decompose the solid and vaporize the pyrolysis products is [21-24]

\[ H_g = c \Delta T_{gas} + L_g \]  

In Equation 3, \( c \) is the heat capacity of the sample (J/kg-K) and \( \Delta T_{gas} = T_{burn} - T_0 \) is the temperature increase above ambient \( T_0 \) over which the sample is heated, thermally decomposed, and gasified. If \( \phi_{ign} = c \Delta T_{gas}/H_g = c \Delta T_{gas}/(L_g+c \Delta T_{gas}) \) is the fraction of \( H_g \) stored as sensible heat at burning, and \( \phi_{burn} = L_g/(L_g+c \Delta T_{gas}) \) is the fraction of \( H_g \) that is absorbed by the thermal decomposition process during burning (latent heat), a lower bound estimate of the thermal resistance to gasification in a fire, \( \Delta T_{LB} \) using \( \phi_{ign} \) and \( \phi_{burn} \) as weighting factors for ignition and burning, respectively, would be
\[
\frac{1}{\Delta T_{LB}} = \frac{\phi_{ign}}{\Delta T_{ign}} + \frac{\phi_{burn}}{\Delta T_{burn}}
\]

In Equation 4, \(\Delta T_{ign} = T_{ign} - T_0\) is the temperature increase above ambient at ignition, and \(\Delta T_{burn} = T_{burn} - T_{ign}\) is the burning (gasification) temperature interval as per Figure 1. Since, \(\phi_{ign} + \phi_{burn} = 1\), Equation 4 becomes,

\[
\frac{1}{\Delta T_{LB}} = \frac{c \Delta T_{gas}/(c \Delta T_{gas} + L_g)}{\Delta T_{ign}} + \frac{L_g/(c \Delta T_{gas} + L_g)}{\Delta T_{burn}}
\]

It has been shown experimentally that \(c \Delta T_{gas} = L_g\) [39], so the fire compliance of a combustible material having fire resistance, \(\Delta T_{fire}\), can be written,

\[
\frac{1}{\Delta T_{fire}} \equiv \frac{1}{\Delta T_{LB}/2} = \frac{1}{\Delta T_{burn}} + \frac{1}{\Delta T_{ign}}
\]

Multiplying Equation 6 by the effective heat of combustion of the fuel gases, \(H_c\) gives an expression for the amount of heat released by combustion per degree of temperature rise through the processes of ignition and burning in a fire,

\[
\frac{H_c}{\Delta T_{fire}} = \frac{H_c}{\Delta T_{ign}} + \frac{H_c}{\Delta T_{burn}}
\]

The continuum-level fire growth parameter, Equation 7, can be evaluated at micro-scale by recognizing that the specific heat of complete combustion is, \(Q_c = (1-\mu)H_c/\chi\), where \(\mu\) is the mass fraction of char that remains after burning, \(\chi\) is the combustion efficiency of the fuel gases in a diffusion flame, and \(T_1 = T_{ign}\) and \(T_2 = T_{burn}\) are micro-scale temperatures at the onset and completion of the fuel generation process, respectively, in a nonisothermal experiment at constant heating rate,

\[
FGC \equiv \frac{Q_c}{T_1 - T_0} + \frac{Q_c}{T_2 - T_1}
\]

It has been shown by experiment that \(T_1 \approx T_{ign}\) [42], but it remains to be shown experimentally that \(T_2 \approx T_{burn}\), so that the intrinsic flammability parameter \(FGC\) can be measured at micro-scale, and that \(FGC\) is a robust predictor of the fire performance of combustible materials at bench- and full-scale.
3 Experimental

3.1 Materials

The materials tested in this study are listed in Table 1. These are natural, unfilled polymers with minimal processing aids obtained from manufacturers or distributors as extruded profiles, cast sheets, or fibers. Two research polymers [46], the cyanate ester of bisphenol-C (BPC-CE) and the polycarbonate of bisphenol-C (BPC-PC), were also included in the study. The fire and combustion properties of all of the polymers in Table 1 have been reported previously [12-16, 22, 27-30, 37, 42-50]. However, the FGC of these polymers is new to this study. Gases used for fire calorimetry and microscale combustion calorimetry were ultra-high purity grades (>99.99%) obtained from local suppliers.

Table 1. Polymers of this study

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Symbol</th>
<th>Polymer</th>
<th>Symbol</th>
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<tbody>
<tr>
<td>High Density Polyethylene</td>
<td>HDPE</td>
<td>Poly-para-aramid</td>
<td>KEVLAR</td>
</tr>
<tr>
<td>Polystyrene (crystal, food grade)</td>
<td>PS</td>
<td>Polyphenylsulfone</td>
<td>PPSU</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>PP</td>
<td>Polyvinyl chloride (rigid)</td>
<td>PVC</td>
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<tr>
<td>High Impact Polystyrene</td>
<td>HIPS</td>
<td>Polyetheretherketone</td>
<td>PEEK</td>
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<td>Acrylonitrile Butadiene Styrene</td>
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<td>Polyetherimide</td>
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<td>Polyhexamethyleneadipamide</td>
<td>PA66</td>
<td>Polyetherketoneketone</td>
<td>PEKK</td>
</tr>
<tr>
<td>Polymethylmethacrylate*</td>
<td>PMMA</td>
<td>Fluorinated ethylene propylene</td>
<td>FEP</td>
</tr>
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<td>Polycarbonate of Bisphenol-A</td>
<td>PC</td>
<td>Phenol formaldehyde thermoset</td>
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<td>Nomex</td>
</tr>
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</table>

*PMMA tested from extruded sheet of linear polymer (transparent) and cast sheet (black)*
3.2 Methods

3.2.1 Fire calorimetry

Experiments were conducted in triplicate on a non-charring polymer (black cast PMMA) and a charring polymer (PEEK) in a bench scale fire calorimeter (Cone 1, Fire Testing Technologies). Monolithic solid samples, having dimensions 10cm x 10cm x 0.3cm (PEEK) or 10cm x 10cm x 0.6 cm (black cast PMMA), were subjected to external heat fluxes above the critical values for sustained ignition, \( q_{\text{ext}}^* = 35 \text{ kW/m}^2 \) (PMMA) and \( q_{\text{ext}}^* = 50 \text{ kW/m}^2 \) (PEEK), according to a standard method [51] using an edge frame holder and electrical igniter positioned 25 mm above the sample surface. Surface temperatures at ignition and sustained burning were measured in separate experiments by manually positioning 0.8-mm diameter Type-K thermocouple beads in the pyrolysis layer at the heated surface until a stable diffusion flame appeared and burning had commenced. Duplicate measurements were performed.

3.2.2 Microscale combustion calorimetry

Microscale combustion calorimeter (MCC) experiments were conducted in accordance with the standard Method A of ASTM D7309-19[52]. Samples weighing \( \leq 5\text{mg} \) were heated at a constant rate of temperature rise, \( \beta = 1 \text{ K/s} \) under a N2 purge flow of 80 cm\(^3\)/min, and the pyrolysis gases combined with oxygen flowing at 20 cm\(^3\)/min in a combustor at 1173K (900°C) to effect complete combustion in excess oxygen. The heat release rate of the polymer at each sample temperature was computed by oxygen consumption flow calorimetry. Samples of each material were tested in triplicate.

4 Results and discussion

The phenomena illustrated in Figure 1 and Figure 2 are demonstrated in Figure 4 for a 6-mm thick sample of black cast PMMA tested in a cone calorimeter, according to the standard method [51], at an external heat flux of \( q_{\text{ext}}^* = 35 \text{ kW/m}^2 \). The surface temperatures (left ordinate) and heat release rate (right ordinate) were measured in separate experiments and are shown as average values of duplicate experiments versus time after exposure to a constant heat flux of 35 kW/m\(^2\) (abscissa). A surface temperature, \( T_{\text{ign}} = 550\pm20\text{K} \), is recorded at the time of sustained piloted ignition, \( t_{\text{ign}} = 58\pm5\text{s} \). A surface temperature, \( T_{\text{burn}} = 780\pm20\text{K} \), is recorded at the time of sustained burning, \( t_{\text{burn}} = 75\pm5\text{s} \).
Figure 5 shows the ignition and burning temperatures of PMMA in the cone calorimeter from Figure 4 on the left hand side and the specific heat release rate temperatures of PMMA on the right hand side in a MCC experiment at heating rate, $\beta = 1\, \text{K/s}$. Also shown, as white circles on the specific heat release rate history, $Q'(T)$ of PMMA on the right hand side of Figure 5, are the isokinetic temperatures, $T_1$ and $T_2$. These temperatures bracket about 90% of the combustion heat, and about 2/3 of the temperature interval between ignition and burning. Open circles on MCC data are isokinetic temperatures.

Figure 4. Surface temperature and heat release rate histories for black cast PMMA
Figure 6 shows separate cone calorimeter experiments [49] to measure the surface temperature (left ordinate) and heat release rate (right ordinate) histories of a 10cm x 10cm x 0.3cm sample of the char-forming polymer, polyetheretherketone (PEEK), after exposure to a constant irradiance, \( \dot{q}_{ext}^r = 50 \text{ kW/m}^2 \) at \( t = 0 \) in a cone calorimeter, according to the standard method [51]. The heat release rate of PEEK has a maximum value, \( \dot{q}_{max}^r = \Delta H_c m^r_{burn} \approx 400 \text{ kW/m}^2 \) at the measured burning temperature \( T_{burn} \), after which the surface forms a stable char that is 50% of the original mass and absorbs radiant energy. This causes the heat release rate to decrease significantly due to the temperature gradient through the char, \( T(0)-T(x_c)/x_c \), which lowers the effective burning temperature from \( T(0) = 1050\text{K} \) to \( T(x_c) = 950\text{K} \), as shown in the experimental data of Figure 6 and schematically on the right hand side of Figure 1.
Figure 7 shows the ignition and burning temperatures of PEEK in the cone calorimeter on the left hand side and the corresponding specific heat release rate temperatures of PEEK on the right hand side for an MCC experiment at a constant heating rate, $\beta = 1\, \text{K/s}$. Also shown as open circles on the $Q'(T)$ history of PEEK, on the right hand side of Figure 7, are the isokinetic temperatures, $T_1$ and $T_2$. As seen in Figure 5 for PMMA, these temperatures bracket only about 90% of the combustion heat, and about 2/3 of the temperature range between ignition and burning. Figure 5 and Figure 7 support the burning model concept of Figure 1 and Figure 2, and the hypothesis that a milligram sample in a micro-scale test experiences a similar temperature and mass loss history as an infinitesimal particle in the pyrolysis zone of a continuum-level cone calorimeter sample.
Figure 8 is a plot of fire resistance, $\Delta T_{\text{fire}} = (1/\Delta T_{\text{ign}} + 1/\Delta T_{\text{burn}})^{-1}$ versus thermal decomposition temperature range, $T_2 - T_0 = (T_2 - T_1) + (T_1 - T_0) = \Delta T_{\text{burn}} + \Delta T_{\text{ign}}$, of the combustible polymers in Table 1. Figure 8 shows that fire resistance ($\Delta T_{\text{fire}}$) on the ordinate is poorly correlated with thermal decomposition range ($T_2 - T_0$) on the abscissa. This is because fire resistance ($\Delta T_{\text{fire}}$), as defined by Equation 6, is a lower bound of the equally weighted ignition resistance ($\Delta T_{\text{ign}}$) and burning resistance ($\Delta T_{\text{burn}}$), i.e., fire propagation follows the path of least thermal resistance. For this reason, the overall thermal stability of the polymer is less important to fire compliance (propagation) than the relative magnitudes of $\Delta T_{\text{ign}}$ and $\Delta T_{\text{burn}}$, the smaller of which will determine the fire resistance. In particular, the fire resistance $\Delta T_{\text{fire}}$ is high when both $\Delta T_{\text{ign}}$ and $\Delta T_{\text{burn}}$ are large and of similar magnitude, while $\Delta T_{\text{fire}}$ is low when either of these components of thermal stability is small. This is the physical basis for $FGC$ as the propensity for fire growth. In particular, fire propagation of combustible materials is driven by the heat released by combustion of the fuel gases ($Q_c$) and resisted by the thermal barriers to ignition and burning.
The qualitative description of the kinetics and energetics of ignition and burning above provides a physical basis and formula for a fire growth parameter measured at milligram scale that captures the processes of fire growth for use in comparing the flammability of materials used in aircraft cabins [53, 54]. Previous studies of MCC parameters and fire performance of materials in standard bench scale flame and fire tests [29] showed that $Q_c$ and $\eta_c = Q_c/(T_2-T_1)$ were the single best predictors of fire performance. Although neither was particularly discriminating in fire tests where ignitability was a contributing factor, or where extrinsic factors associated with thick samples, flame inhibition, or char barrier formation influenced the fire test result, since none of

Figure 8. Molecular-level ignition and burning resistance
these are captured by the specific heat release rate measured in the micro (10⁻⁶ kg) scale MCC test.

Figure 5 and Figure 7 showed that the kinetic parameters $T_1$ and $T_2$ are representative of the temperature range of continuum-level ignition and burning. However, Equation 2 shows that determination of $T_1$ and $T_2$ requires an accurate value for the absolute reaction rate measured in the microscale combustion calorimeter, $d\alpha/dt = Q'/Q_c$, which depends on a good estimate of the zero-point value (baseline), $Q' = 0$ from initiation ($\alpha = 0$) to completion ($\alpha = 1$) of the fuel generation reaction. Moreover, the isokinetic temperature $T_2$ is not unique for multi-step reactions with well-resolved maxima and minima in $Q'$, an example of which is shown in Figure 10.

To avoid the baseline and uniqueness problems of determining isokinetic $T_1$ and $T_2$ directly from the differential curve, $Q'$ measured in ASTM D7309-A [52], a standardized integral procedure was adopted in which the onset pyrolysis (ignition) temperature $T_1$ is taken to be the temperature at $\alpha = Q/Q_c = 0.05$, i.e., the temperature at which 5% of the specific heat of combustion has been released in a constant heating rate microscale combustion calorimeter experiment at $\beta = 1$K/s. Likewise, the completion (burning) temperature $T_2$ is taken to be the temperature at $\alpha = Q/Q_c = 0.95$, i.e., the temperature at which 95% of the specific heat of combustion has been released in the MCC. Figure 9 is a plot of the standard integral temperatures for ignition ($T_{95\%}$) and burning ($T_{95\%}$) versus the corresponding isokinetic differential temperatures, $T_1$ and $T_2$, for the 13 polymers of Table 1 that are shown in the legend. Figure 9 shows that the standard integral burning temperatures, $T_{95\%}$, are somewhat higher than the corresponding isokinetic differential temperatures, $T_2$, for the thermally-stable, char-forming polymers, PEI, PPSU and PEEK, which undergo a two-step thermal decomposition process, producing about 50% char by weight. This is because combustion of the thermal decomposition products of the char accounts for more than 5% of $Q_c$. The standard and isokinetic temperatures of the other 10 polymers in Figure 9 are seen to agree to within the level of approximation, $T_{\text{ign}} = T_1$ and $T_{\text{burn}} = T_2$ in Figure 5, Figure 7 and [42].
Figure 10 shows ASTM D7309-19A data, \( dQ/dT = Q'/\beta \), for a 50/50 weight percent blend of polycarbonate/PC and poly(acrylonitrile-butadiene-styrene)/ABS tested in a microscale combustion calorimeter. Solid line in Figure 10 represents the specific heat release rate. Dashed line in Figure 10 represents the fractional heat release.
The $FGC$ is calculated by Equation 8 with temperatures, $T_{\text{ign}} \approx T_1 = T_{5\%}$, and $T_{\text{burn}} \approx T_2 = T_{95\%}$,

$$FGC = \frac{Q_c}{T_{5\%} - T_0} + \frac{Q_c}{T_{95\%} - T_{5\%}} = \frac{Q_c}{(T_{95\%} - T_{5\%})} \frac{(T_{95\%} - T_0)}{(T_{5\%} - T_0)} \tag{9}$$

From the data in Figure 10, $Q_c = 29.3$ kJ/g, $T_{\text{ign}} = T_1 = T_{5\%} = 695K$, $T_{\text{burn}} = T_2 = T_{95\%} = 837K$, and $T_0 = 298K$, the $FGC$ for PC/ABS according to Equation 9 is,

$$FGC = \frac{29.3 \text{ kJ/g}}{(837K - 298K)} \frac{(837K - 298K)}{(695K - 298K)} = 280 \text{ kJ/g} - K = 280 \text{ kJ/g} - ^\circ C$$

Table 2 is a listing of the Fire Growth Capacities of 30 polymers from $Q(T)$ measured in accordance with ASTM D7309-19A in the MCC and computed using Equation 9.

Table 2. Fire Growth Capacities of the polymers in Table 1

$PMMA1 = \text{Extruded polymer (clear)}, \ PMMA2 = \text{Cast polymer (black)}$
<table>
<thead>
<tr>
<th>Symbol</th>
<th>FGC (J/g-K)</th>
<th>Symbol</th>
<th>FGC (J/g-K)</th>
<th>Symbol</th>
<th>FGC (J/g-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>1031</td>
<td>PET</td>
<td>275</td>
<td>PEI</td>
<td>78</td>
</tr>
<tr>
<td>PS</td>
<td>862</td>
<td>PEN</td>
<td>265</td>
<td>PEKK</td>
<td>59</td>
</tr>
<tr>
<td>PP</td>
<td>818</td>
<td>PVDF</td>
<td>216</td>
<td>FEP</td>
<td>38</td>
</tr>
<tr>
<td>HIPS</td>
<td>607</td>
<td>POM</td>
<td>197</td>
<td>Phenolic</td>
<td>38</td>
</tr>
<tr>
<td>ABS</td>
<td>540</td>
<td>PSU</td>
<td>185</td>
<td>PBO</td>
<td>31</td>
</tr>
<tr>
<td>PA66</td>
<td>505</td>
<td>PPS</td>
<td>180</td>
<td>PAI</td>
<td>28</td>
</tr>
<tr>
<td>PMMA1</td>
<td>437</td>
<td>KEVLAR</td>
<td>130</td>
<td>PBI</td>
<td>22</td>
</tr>
<tr>
<td>PC</td>
<td>361</td>
<td>PPSU</td>
<td>100</td>
<td>PI</td>
<td>21</td>
</tr>
<tr>
<td>PMMA2</td>
<td>352</td>
<td>PVC</td>
<td>88</td>
<td>BPC-CE</td>
<td>13</td>
</tr>
<tr>
<td>PC/ABS</td>
<td>280</td>
<td>PEEK</td>
<td>85</td>
<td>BPC-PC</td>
<td>11</td>
</tr>
</tbody>
</table>
Figure 11 is a graphical ranking of the FGC in Table 2 plotted on a logarithmic scale. Note that the FGC of these polymers spans three orders of magnitude, and the FGC rank is in general agreement with the observed fire performance of these polymers in bench scale fire and flame tests [27, 28].
Figure 12 is a plot of the expected fire performance and FGC of the polymers in upward flame spread, after brief ignition of a vertical, thin prismatic bar (1.6mm x 13mm x 127mm) by a small flame [55,56]. Fire test performance in Figure 12 for the polymers of Table 1 is based on Underwriters Laboratories (UL) classifications in product data sheets, on-line databases, and in the literature for unmodified polymers.

![Figure 12. Expected UL 94V classification vs. FGC of the polymers in Table 2](image)

Figure 13 is a plot of expected fire performance and FGC of the polymers in the Code of Federal Regulations, Part 25 test for peak heat release rate of aircraft materials in a vertical orientation in a fire calorimeter exposed to a pilot flame and radiant heat at $q''_e = 35 \text{ kW/m}^2$ [57,58]. This test involves simultaneous upward spread and in-depth burning after forced localized ignition by a small premixed flame. A passing result in 14 CFR 25 was assigned to the polymers in Table 2 if they met either of the following conditions:

- The measured peak heat release rate of samples, having dimensions 150mm x 150mm and thickness 1.5mm or 3mm, was less than the FAA limit of 65 kW/m²
- The critical heat flux (CHF) for piloted ignition measured in a cone calorimeter in a horizontal orientation in accordance with ASTM E 1354 [51] exceeded the incident heat flux $q^*_{e,i} = 35 \text{ kW/m}^2$ in 14 CFR 25 [21-30, 47-49].
5 Conclusions

A conceptual model supported by experimental data for the fire response of charring and non-charring polymers was used to relate the ignition and burning temperatures at the continuum (kg) level to the temperatures over which fuel is generated at the molecular level in a micro (10^{-6} kg) scale combustion calorimeter. The assumption that fire propagation is driven by the heat released by the flame (Q_c), and follows a path of least thermal resistance (\Delta T_{\text{ign}} or \Delta T_{\text{burn}}), is the physical basis for an intrinsic, molecular-level, flammability parameter called the Fire Growth Capacity (FGC), which spans three orders of magnitude and successfully ranks 30 polymers according to their expected fire performance in bench- and full-scale fire tests.

6 References


55. Flammability of Plastic Materials, Northbrook, IL: Underwriters Laboratories Inc., 1991, UL 94 Section 2 (Horizontal: HB), and Section 3 (Vertical: V-0/1/2).

