Outline

✓ Background
  - Flammability Testing & Fire Processes
  - PCFC Instrument Description

✓ Theory
  - PCFC
  - Heat Release Capacity
  - Fire Test Theory & Correlations
  - Molar Group Contributions

✓ Conclusions
Flammability Testing

- Extrinsic quantities resulting from the reaction of a macroscopic polymer sample to a severe thermal exposure
  - Burning Rate
  - Ignitability
  - Flammability
  - Fire Performance

- Fire test results are dependent on
  - Orientation
  - Geometry
  - Sample Size
  - Color
  - Ambient Conditions
  - Operator

- Thermal and mass diffusion effects dominate the fire behavior in large sample tests

- An intrinsic material property is needed to correlate fire performance
Fuel Generation Process

**Pyrolysis**
- Polymer
- Endothermic
- Solid Charred Residue
- Thermal feedback from flame

**Combustion**
- Combustible & Non-Combustible Gases
- Liquid Products & Tar
- + O$_2$
- Flame
- Exothermic
Charring in fires is an **anaerobic** process.
Pyrolysis-Combustion Flow Calorimeter

Forced Non-Flaming Combustion Test

Small Sample Size: ~1mg

Rapid Screening of Materials

Measured Values:
- Heat Release Rate
- Total Heat Release
- Char Yield

Calculated Values:
- Heat Release Capacity
- Global $E_a$
Measured Heat Release Rates

- Polyethylene
- Polypropylene
- Polystyrene
- ABS
- PMMA
- PET
- PEEK
- PBI
Microcalorimeter Theory

Heat release rate by oxygen consumption normalized to initial sample mass

\[ \dot{Q}_c(t) = \frac{E \Delta O_2}{m_o} = h_{c,v}^o(t) \left[ \frac{-1}{m_o} \frac{dm(t)}{dt} \right] \]

Peak rate of heat release

\[ Q_{c}^{\text{max}} = \left[ \frac{E \Delta O_2}{m_o} \right]_{\text{max}} = h_{c,v}^o \left[ \frac{-1}{m_o} \frac{dm}{dt} \right]_{\text{max}} = h_{c,v}^o \frac{\beta (1 - \mu) E_a}{e R T_p^2} \]

Heat Release Capacity

\[ \eta_c = \frac{Q_{c}^{\text{max}}(\beta)}{\beta} = \frac{h_{c,v}^o(1 - \mu) E_a}{e R T_p^2} \]

... dependent only on material properties
Material Property

Must satisfy the following conditions:

1. Independent of sample mass
2. Independent of heating rate
3. Measurable by different methods
Heat Release Capacity by TGA-GC/MS

Heat Release Capacity (PCFC), J/g-K

β = 260 K/min

Heat Release Capacity (TGA-GC/MS), J/g-K

β = 10 K/min

1:1 Line

poly(α-methyl)styrene

PP

PS

PET

POM

PC

PPO

Nylon 66

PPS

PEEK

PI

KEVLAR

**Flammability Character - UL-94V vs. LOI**

**UL-94** - Vertical Bunsen Burner test based on operator observation where materials are classified by their burning behavior

**Oxygen Index** - Minimum amount of oxygen needed to sustain a candle-like flame for 3 minutes based on operator observation

<table>
<thead>
<tr>
<th></th>
<th>UL-94</th>
<th>LOI</th>
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<tr>
<td>Vertical Test</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Preheating of sample</td>
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<tr>
<td>Radiant component</td>
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<tr>
<td>Convective component</td>
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<tr>
<td>Conductive component</td>
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</table>

*Upward versus Downward flame spread*
Transition Region from self-extinguishing to readily burning: 200-400 J/g-K

Transition Region corresponds to 21-33 %O₂ in LOI
Cone Calorimeter

Bench Scale Flaming Combustion Test

Sample Dimensions:
10cm x 10 cm x 0.3cm

0-100 kW/m² incident heat flux

Measured Values:
- heat release rate - O₂ consumption
- mass loss rate
- time to ignition
- CO & CO₂
- smoke generation

Calculated Values:
- critical heat flux
- heat of gasification
- ignition temperature
- thermal inertia (κρc)
Fire Test Correlations - Cone Calorimeter

Cone Calorimetry - Bench scale flaming combustion test measuring heat release by oxygen consumption
Fire Test Summary

✓ Fire Tests
  - Flaming combustion tests where physical attributes influence the flammability
  - Samples can be designed to give false passes in the tests
  - Tests are hard to run and do not give quantitative results
  - Multiple tests and rigorous calculations needed to obtain material properties

✓ PCFC
  - Provides a material property directly
  - Quantitative results that represent the total fuel value of a sample
  - Quick & easy to run
Group Contribution Background

- Methods for predicting thermochemical data from molecular structure (Bensen 1968)

- Interactions of several atoms summed and approximated by structural groups (VanKrevelen 1972)

- Atomic-level bond topology used to predict molecular properties using connectivity indices (Bicerano, 1996)

- Structural group contribution method for flammability (Walters 2000)

- Group Contribution calculations can predict thermodynamic quantities such as:
  - Heat of Combustion
  - Char Yield
  - Heat Capacity
  - Thermal Decomposition Temperature
  - Glass Transition Temperature

- Theories of group contributions based on empirical correlations
Molar Group Contributions to $\eta_c$

**Heat Release Capacity**

\[
\eta_c = \frac{Q_c}{\beta} = \frac{h_c^0(1 - \mu)E_a}{eR T_p^2}
\]

**Approach:** Write the heat release capacity terms as additive molar quantities

\[
\Psi = \frac{HV E}{eR T^2} = \frac{\left(\sum_i n_i H_i\right) \left(\sum_i n_i V_i\right) \left(\sum_i n_i E_i\right)}{eR \left(\sum_i n_i T_i\right)^2}
\]

Expand summations over chemical groups, i, j, k… and neglect terms with mixed indices

\[
\Psi = \sum_i n_i \frac{H_i V_i E_i}{eR T_i^2} = \sum_i n_i \Psi_i
\]

Obtain $\eta_c$ in correct units from molar mass of component groups

\[
\eta_c = \frac{\Psi}{M_o} = \frac{\sum_i n_i \Psi_i}{\sum_i n_i M_i} = \frac{\sum_i N_i \Psi_i}{\sum_i N_i M_i}
\]
Calculating Heat Release Capacity

If $\eta_c$ is a material property it should be calculable from additive molar group contributions like other polymer properties (e.g., heat capacity, refractive index, solubility parameter, etc.)

Example: Bisphenol A Epoxy has 6 distinct chemical groups comprising the polymer repeat unit.
Calculating Heat Release Capacity

\[ \eta_c = \frac{\Psi}{M} = \frac{\sum n_i \Psi_i}{\sum n_i M_i} = \frac{\sum N_i \Psi_i}{\sum N_i M_i} = \frac{204.5 \text{ kJ/mole-K}}{340 \text{ g/mole}} = 601 \text{ J/g-K} \]
Molar Group Contributions to $\eta_c$

\[
\eta_c = \frac{\Psi}{M_o} = \frac{\sum n_i \Psi_i}{\sum n_i M_i} = \frac{\sum N_i \Psi_i}{\sum N_i M_i}
\]

<table>
<thead>
<tr>
<th>Group</th>
<th>Contribution (kJ/mol-K)</th>
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<td>Backbone=1 3.7</td>
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Calculated Heat Release Capacity (J/g-K) vs Measured Heat Release Capacity (J/g-K)

1:1 Line
Conclusions

✅ Heat Release Capacity is:

- A rate independent flammability parameter
- An intensive quantity (independent of sample mass)
- Measurable by different laboratory techniques
- A good predictor of fire and flammability behavior
- Calculable from chemical structure
- A material property: dynamic combustion potential
Acknowledgements

✓ FAA

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