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ADVANCED FIRE SAFE MATERIALS FOR AIRCRAFT INTERIORS

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ABSTRACT

Phenomenological equations for solid material burning in combination with pyrolysis kinetics and uncoupled transient heat conduction provide relationships between material properties and the fire response of polymeric solids. The predicted scaling of ignition temperature, time to ignition, heat of gasification, mass loss rate, and heat release rate with thermodynamic, kinetic, and transport properties is in reasonable agreement with available data for polymeric solids using this simple approach.

1. INTRODUCTION

Heat release rate is considered to be the single most important fire parameter in determining the fire hazard of a material. Unfortunately, no analytic results for heat release rate in terms of chemical or physical properties of materials are available to guide chemists in their syntheses of fire resistant polymers. Current material fire models are computational loops in computer-based fire codes. Material parameters required by these computational fire models include at a minimum the chemical heat of complete combustion of the material, a combined heat transport parameter (thermal inertia), and a "decomposition temperature" at which the material becomes a gaseous fuel. In a few sophisticated fire codes two additional pyrolysis kinetic parameters may be required to complete the material model. These material fire models have no physical basis outside of the computational regime and are of little value to material scientists seeking a qualitative understanding of how thermodynamic, kinetic, mechanical, and transport properties of polymeric materials effect their fire response. In order to provide some physical insight into the phenomenology of materials combustion, simple scaling relationships between tailorable material properties and the fire response of polymeric solids are developed and verified in the following sections. It is hoped that these analytic results will help guide the development of totally fire resistant materials for next generation aircraft interiors.

2. RATE-DEPENDENT DECOMPOSITION TEMPERATURE OF POLYMERS

The peak mass loss rate (decomposition) temperature for a thermally decomposing polymer is obtained from the appropriate kinetic expression. For the first-order pyrolysis of a polymer with volatile mass, m , and non-volatile (char) mass, m_c ,

$$-\frac{dm}{dt} = k(m-m_c) \quad (1)$$

Assuming an Arrhenius rate constant,

$$k = A \exp(-E_a/RT) \quad (2)$$

and a constant heating rate, $dT/dt = \dot{T}$, the peak pyrolysis temperature is obtained by setting the time derivative of the mass loss rate in Equation 1 (second time derivative of mass) equal to zero at $T = T_p^{\max}$, i.e.,

$$-\dot{m} = k_p \dot{m} + (m - m_c) \dot{k}_p = 0 \quad @ \quad T = T_p^{\max}.$$

The resulting non-dimensionalized equation in terms of T_p^{\max} is [1]

$$\ln \left[\frac{E_a}{R T_p^{\max}} \right]^2 + \frac{E_a}{R T_p^{\max}} + \ln \left[\frac{R \dot{T}}{A E_a} \right] = 0 \quad (3)$$

Solution of Equation 3 for the dimensionless root, $[E_a/RT_p^{\max}]$ for a particular heating rate, \dot{T} , gives the temperature at maximum mass loss rate with the use of the Arrhenius parameters, A , E_a . A plot of calculated T_p^{\max} vs. \dot{T} for polymethylmethacrylate (PMMA, $A=10^{12}/s$, $E_a=160$ kJ/mol) is shown in Figure 1.

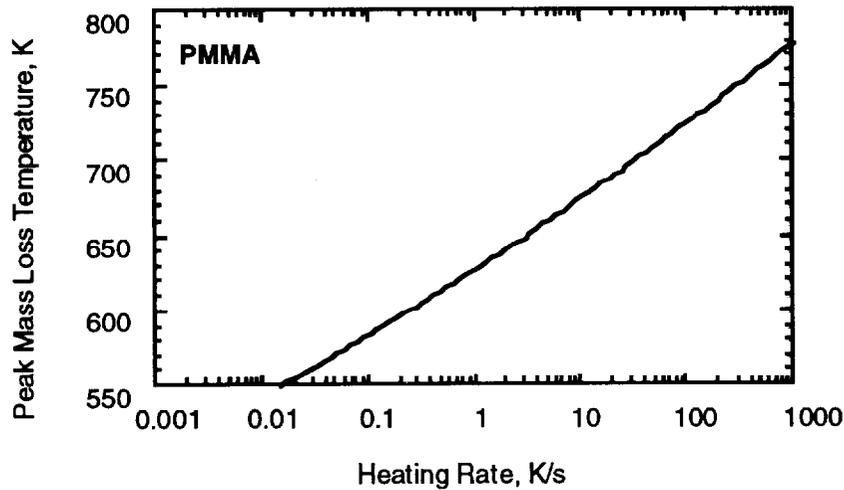


Figure 1. Temperature at peak mass loss rate versus linear heating rate for PMMA according to first-order kinetics.

3. IGNITABILITY

The thermal theory of ignition assumes that ignition occurs when the surface temperature of the material reaches its ignition temperature, i.e., $t = t_{\text{ign}}$, at $T_s = T_{\text{ign}}$, at which time and temperature sufficient fuel generation takes place to sustain flaming combustion. Consequently, this ignition temperature is on the order of a thermal decomposition temperature for the material. In the previous section it was shown that the peak decomposition temperature of a polymer has a strong dependence on heating rate in the region 1-100 K/s typically encountered in fire testing.

The surface temperature history for a semi-finite slab with a constant net heat flux to the surface, \dot{Q}_{net} , is

$$T_s(t) = T_o + 2\dot{Q}_{\text{net}} \left[\frac{t}{\pi \kappa \rho C_p} \right]^{1/2} \quad (4)$$

with T_s the surface temperature at time t , and T_o the initial (ambient) temperature of the material. Rearranging Equation 4 with the assumption that the surface temperature at ignition is the (rate dependent) peak pyrolysis temperature, $T_s = T_{ign} = T_p^{max}$, gives for the time to ignition

$$t_{ign} = \pi \kappa \rho C_p \left[\frac{T_p^{max} - T_o}{2\dot{Q}_{net}} \right]^2 \quad (5)$$

Equation 5 calculates the time to ignition of a thermally thick polymer specimen using the rate (heat flux) dependent peak pyrolysis temperature for a particular \dot{Q}_{net} . The heating rate at the surface of a thermally thick polymer specimen during radiant heating is not constant, but may be approximated by a single time-average rate of temperature rise, $\langle dT/dt \rangle$. The semi-infinite slab result valid up to time, $\tau = \rho C_p b^2 / 4\kappa$, for a net heat flux, \dot{Q}_{net} on the face of a slab of thickness, b , density, ρ , thermal conductivity, κ , and heat capacity, C_p , gives for the time-averaged heating rate [1]

$$\dot{T} = \left\langle \frac{dT}{dt} \right\rangle = \frac{1}{\tau} \int_0^{\tau} \frac{\dot{Q}_{net}}{\sqrt{\pi \kappa \rho C_p}} \frac{dt}{\sqrt{t}} = \frac{4}{\sqrt{\pi}} \frac{\dot{Q}_{net}}{\rho b C_p} \quad (6)$$

The results of Equations 6 and 3 for poly(methylmethacrylate) (PMMA) exposed to net heat flux levels from 5 to 75 kW/m² were substituted into Equation 5 and the results plotted in Figure 2. It is seen that a rate-dependent decomposition temperature correlates the measured time-to-ignition for PMMA over a range of incident heat flux levels [2] using $A = 10^{12}/s$, $E_a = 160$ kJ/mol [3] for the Arrhenius parameters, and $\kappa \rho C_p = 6 \times 10^5$ W²-s/m⁴-K² [4] for the thermal capacitance. At external heat fluxes below about 10 kW/m² the semi-infinite slab conduction solution (Equation 4) over predicts the surface temperature (under predicts time-to-temperature) so that a finite-slab calculation which takes into account heat losses from the rear surface at the longer heating times must be used to obtain an accurate surface temperature history. The finite slab calculation (not shown) indicates that below about 8 kW/m² incident heat flux the surface temperature of PMMA never reaches the peak decomposition temperature, in general agreement with a measured critical heat flux of about 10 kW/m² [5].

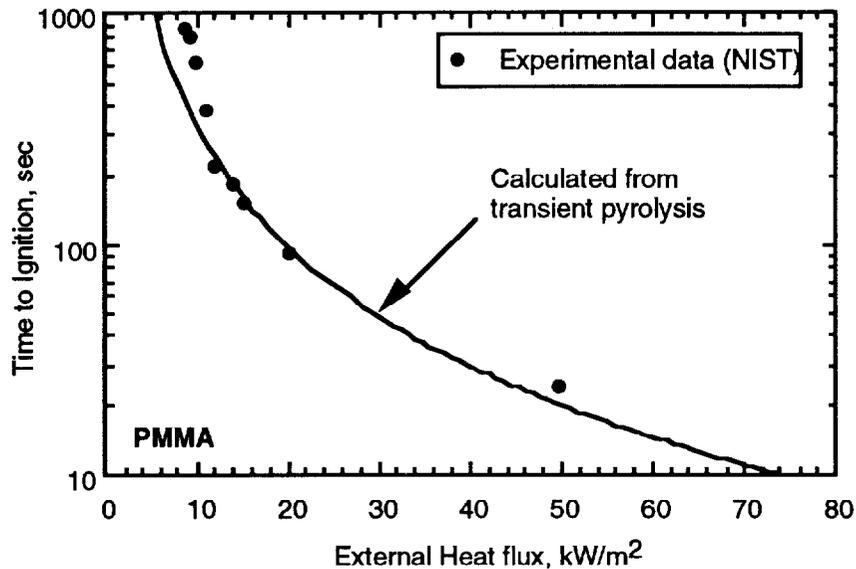


Figure 2. Calculated and measured time-to-ignition for PMMA assuming $T_{ign} = T_p^{max}$

Figure 2 demonstrates that the time to ignition of a material (PMMA) can depend strongly on the net heat flux to the surface and that this effect is reasonably well predicted by transient conduction with a heating rate effect on the peak pyrolysis temperature.

In the previous treatment it was assumed that, $T_p^{max} = T_s$, for flaming combustion. By the same reasoning if $T_p^{max} > T_s$, i.e., the pyrolysis temperature of the material is above the equilibrium surface temperature for flaming combustion at a particular incident heat flux, then the fuel volatilization rate may be insufficient to support burning of the sample. Equation 7 gives the equilibrium surface temperature of a specimen in terms of \dot{Q}_{net} , the sample emissivity, ϵ , and the surface convective heat transfer coefficient, \bar{h} [5]

$$\dot{Q}_{net} = \epsilon\sigma(T_{\infty}^4 - T_o^4) + \bar{h}(T_{\infty} - T_o) \quad (7)$$

For a horizontal specimen with, $\epsilon=0.8$, and surface convective heat transfer coefficient, $\bar{h} = 24 \text{ W/m}^2\text{-K}$ it is found that, $T_{\infty} \approx 675\text{C}$ at a net surface heat flux, $\dot{Q}_{net} = 50 \text{ kW/m}^2$. Consequently, materials tested in a cone calorimeter with a peak pyrolysis temperature greater than about 675C would not be expected to burn at a net surface heat flux of 50 kW/m^2 . Figure 3 shows the measured rate of heat release at an external heat flux of 50 kW/m^2 for a variety of polymeric materials for which reasonable values of both the 180s average heat release rate and the decomposition temperature are available. It is seen that as the pyrolysis temperature of the material approaches the equilibrium surface temperature for a particular surface heat flux the heat release rate approaches zero.

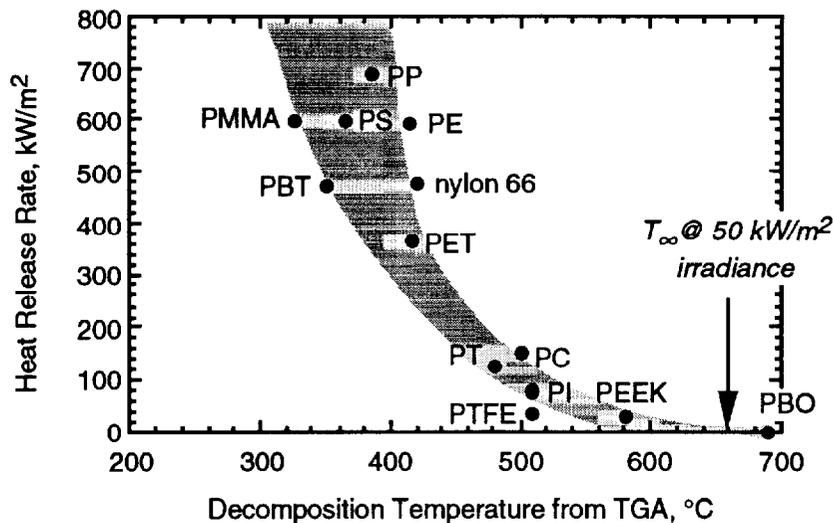


Figure 3. Average heat release rate at 50 kW/m^2 irradiance versus temperature at peak mass loss rate for a variety of polymers.

4. MASS LOSS RATE

To provide insight into the physical phenomenon governing heat release and smoke generation rates of materials in fires an analytic equation was developed for the one-dimensional, steady-state mass loss rate of a burning polymer. The approach is to propagate the isothermal layer through the material via uncoupled thermal diffusion and calculate the mass loss rate at each time and temperature from isothermal pyrolysis kinetics. The dynamic mass loss problem is formulated as a steady-state process characterized by a constant surface (pyrolysis zone) temperature, $T_s = T_p^{max}$. The simplifying assumption of a constant surface

temperature during steady-state mass loss (burning) implies dynamic equilibrium at the gas-solid interface and eliminates the need to determine the complete energy and species balance to solve the geometric problem.

From Equation 1 with initial conditions; $m = m_o$ @ $t = 0$, the isothermal mass loss history for a polymer of initial mass, m_o , is

$$\frac{m}{m_o} = Y_c + (1 - Y_c)e^{-kt} \quad (8)$$

with, $Y_c = m_c / m_o$, the char yield of the polymer. From Equation 8 the fractional mass loss rate is

$$-\frac{dm(t)}{dt} = km_o(1 - Y_c)e^{-kt} \quad (9)$$

Since the surface area (S) and volume (V) of a planar specimen are related to thickness, δ , as, $S=V/\delta$, the areal mass loss rate from Equation 9 is

$$\dot{m}_A = -\frac{1}{S} \frac{dm(t)}{dt} = k \delta \frac{m_o}{V} (1 - Y_c) e^{-kt} = k \delta \rho (1 - Y_c) e^{-kt} \quad (10)$$

where $m_o/V = \rho$ is the initial material density. We assume that pyrolysis is confined to a quasi-isothermal layer or pyrolysis zone of depth, δ , whose average temperature is within $\pm 5\%$ of the surface temperature and calculate how the mass loss rate within this layer changes with time. For a semi-infinite slab with a constant flaming surface temperature, T_s , the depth at which the temperature drop through the layer is less than 10% of the total temperature drop through the material is

$$\delta \cong \frac{\sqrt{\alpha t}}{5}$$

where $\alpha = \kappa/\rho C_p$ is the thermal diffusivity of the material, assumed to be independent of temperature and conversion. Substituting for the quasi-isothermal layer depth, δ , in Equation 10

$$\dot{m}_A = \frac{\rho\sqrt{\alpha}}{5} (1 - Y_c) [k t^{1/2} e^{-kt}] \quad (11)$$

The mass loss rate history in the isothermal layer (Equation 11) is plotted in Figure 4 for a polymer of low thermal stability (PMMA) and a high temperature polymer, poly(benzobisoxazole)(PBO), using tabulated values for Arrhenius and physical parameters and approximate surface temperature at ignition (assumed equal to the peak pyrolysis temperature) at $\dot{Q}_{net} = 50 \text{ kW/m}^2$.

PMMA; $A=10^{12}$, $E_a=160 \text{ kJ/mol}$, $T=T_s=400\text{C}$, $\alpha=1.3 \times 10^{-7} \text{ m}^2/\text{s}$, $\rho = 1000 \text{ kg/m}^3$, $Y_c = 0$
PBO; $A=10^{14}$, $E_a=290 \text{ kJ/mol}$, $T=T_s=625\text{C}$, $\alpha=1.3 \times 10^{-7} \text{ m}^2/\text{s}$, $\rho = 1200 \text{ kg/m}^3$, $Y_c = 0.7$

The maximum in Figure 4 corresponds to a balance between the rate of increase of isothermal mass by thermal diffusion and the rate of mass loss due to isothermal pyrolysis. This is the steady-state condition. Setting the derivative of Equation 11 equal to zero and solving

$$\frac{\partial \dot{m}_A}{\partial t} = k\rho\sqrt{\alpha} (1 - Y_c) e^{-kt} \left\{ \frac{1}{2t^{1/2}} - kt^{1/2} \right\} = 0 \quad (12)$$

gives the characteristic time, $t = 1/(2k)$, which when substituted back into Equation 11 yields the steady-state mass loss rate for a burning material with a surface temperature, $T_s = T_p^{\max}$,

$$\dot{m}_A = \rho(1-Y_c)\sqrt{\frac{\alpha A}{50e}} \exp\left(-\frac{E_a}{2RT_s}\right) . \quad (13)$$

Equation 13 is plotted in Figure 5 for PMMA using the above property set with $Y_c = 0$.

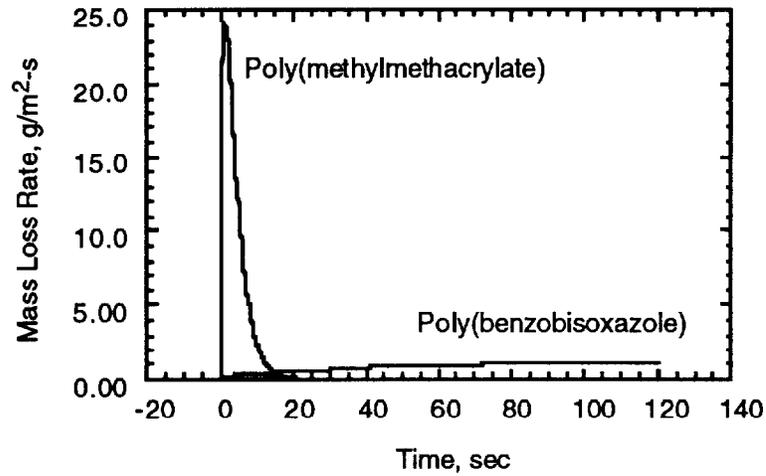


Figure 4. Mass loss rate versus time for isothermal layer in transient pyrolysis model

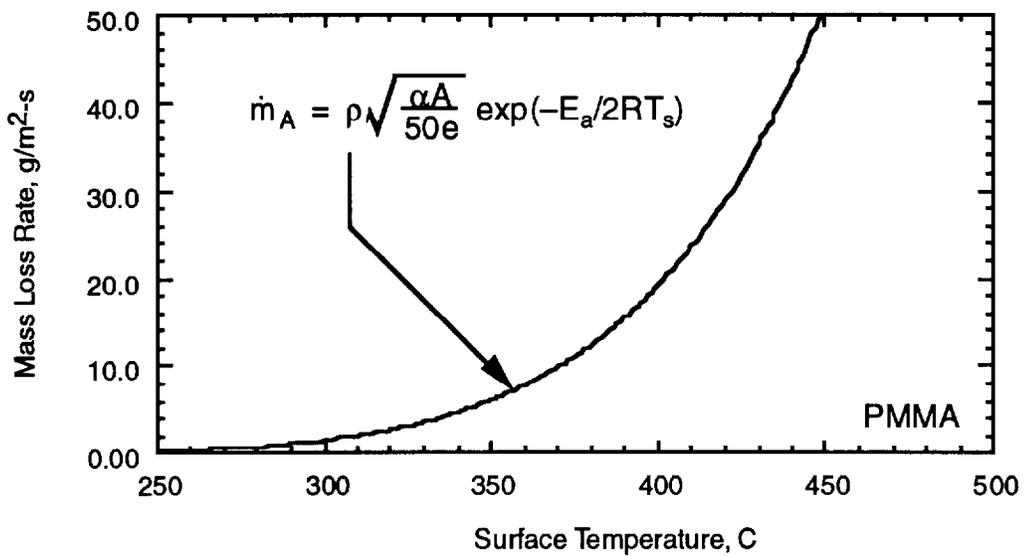


Figure 5. Mass loss rate versus surface temperature for PMMA according to Equation 13.

Since the surface recession velocity, v , is related to the areal mass loss rate as $\dot{m}_A = \rho v$, the time-independent recession velocity is

$$v = \frac{\dot{m}_A}{\rho} = (1-Y_e) \sqrt{\frac{\alpha A}{50e}} \exp\left(-\frac{E_a}{2RT_s}\right) \quad (14)$$

which has the same form as the usual result for the flame front propagation speed, S_u , of a premixed laminar flame [6], i.e.

$$S_u \propto \sqrt{\alpha} \exp\left(-\frac{E_a}{2RT}\right) \quad (15)$$

For PMMA the above property set substituted into Equation 14 for a flaming surface temperature, $T_s = 400^\circ\text{C}$, gives a surface recession velocity, $v \approx 20 \mu\text{m/s}$, from which

$$\dot{m}_A = \rho v = (1000 \text{ kg/m}^3)(1000 \text{ g/kg})(20 \times 10^{-6} \text{ m/s}) \approx 20 \text{ g/m}^2\text{-s}$$

which compares favorably with experimental measurements of $\dot{m}_A = 23\text{-}28 \text{ g/m}^2\text{-s}$ for PMMA during flaming combustion at 50 kW/m^2 irradiance where measured surface temperatures are in the 400°C range [2].

5. HEAT OF GASIFICATION

The Arrhenius relation (Equation 2) was originally derived with the assumption that the reactants are at equilibrium with a high energy state and could proceed to products with no further energy requirements. The assumption of equilibrium between the reactants and activated complex allows us to attach a thermodynamic significance to the constants in the Arrhenius equation. From the definition of the free energy at equilibrium,

$$\ln K = \ln \frac{k_p}{k_{-p}} = -\frac{\Delta G_a}{RT} = -\left[\frac{\Delta H_a}{RT} - \frac{\Delta S_a}{R}\right] \quad (16)$$

where k_p , k_{-p} , are the forward (pyrolysis) and backward (recombination) rates of the reaction and, ΔG_a , ΔH_a , and, ΔS_a , are the molar free energy, enthalpy, and entropy of activation, respectively. It follows that

$$k_p = A e^{-(E_a/RT)} = [k_{-p} e^{\Delta S_a/R}] e^{-(\Delta H_a/RT)} \quad (17)$$

where the pre-exponential factor now has the identity, $A = [k_{-p} e^{\Delta S_a/R}]$, and, $E_a = \Delta H_a$, is the molar enthalpy of pyrolysis (depolymerization). Kishore and Pai Verneker have shown that the enthalpy of pyrolysis, which they assumed to be equal but opposite in sign to the heat of polymerization, is equal to the activation energy of pyrolysis for a variety of polymers [7].

The phenomenological equation relating areal mass loss rate to net heat flux is [8],

$$\dot{m}_A = \frac{\dot{Q}_{\text{net}}}{L_g} = \frac{\dot{Q}_{\text{ext}}}{L_g} + \frac{\dot{Q}_{\text{flame}} - \dot{Q}_{\text{loss}}}{L_g} \quad (18)$$

where L_g (kJ/g) is a quantity called the heat of gasification which relates the net heat flux to the surface to the observed mass loss rate. In Equation 18, \dot{Q}_{net} is seen to be the difference between the incident heat from an external heater, \dot{Q}_{ext} , or surface flame, \dot{Q}_{flame} , and the heat lost through reradiation to the surroundings, \dot{Q}_{loss} . In practice L_g is determined experimentally as the slope of a plot of peak mass loss rate versus external radiant heat flux, \dot{Q}_{ext} .

Since it is found that the molar heat of depolymerization (gasification) is numerically equal to the molar activation energy for pyrolysis, E_a , the heat of gasification *per unit mass*, L_g , is related to the molar activation energy for pyrolysis through the molecular weight of the decomposition products, M_g ,

$$L_g = \frac{\Delta H_a}{M_g} = \frac{E_a}{M_g} \quad (19)$$

Polymers which pyrolyze to monomer (depolymerize) at near-quantitative yield such as polymethylmethacrylate, polyoxymethylene, and polystyrene, should have M_g equal to the monomer molecular weight, M_o , i.e., $M_g/M_o \approx 1$. Polymers such as polyethylene and polypropylene which decompose by random scission to multi-monomer fragments would have $M_g/M_o > 1$. In contrast, polymers with high molecular weight repeat units ($M_o \geq 200$ g/mol) such as nylon, cellulose, polycarbonate, or with good leaving groups (e.g., polyvinylchloride) are known to yield primarily low molecular weight species (water, carbon dioxide, alkanes, HCl) on pyrolysis and should have, $M_g/M_o < 1$.

The Table shows the ratio M_g/M_o predicted from the relation

$$\frac{E_a/M_o}{L_g} = \frac{M_g}{M_o} \quad (20)$$

for a variety of common polymers for which L_g has been measured [8].

Heat of Gasification [8], Thermal Activation Energy [3,9], and Calculated Molecular Weight of Decomposition Products for Common Polymers with Known Pyrolysis Modes [9].

POLYMER	M_o (g/mol)	L_g (kJ/g)	E_a (kJ/mol)	M_g / M_o	PYROLYSIS PRODUCTS
polypropylene	42	2.5	243	2.3	C ₂ - C ₉₀ saturated and unsaturated hydrocarbons
polyethylene	28	2.4	264	3.9	
polystyrene	104	2.2	230	1.0	40-60% monomer
polymethylmethacrylate	100	1.6	160	1.0	100% monomer
polyoxymethylene	30	2.7	84	1.0	100% monomer
nylon 6,6	226	2.6	160	0.3	H ₂ O, CO ₂ , C ₅ HC's
cellulose	162	3.2	200	0.4	H ₂ O, CO ₂ , CO
polyvinylchloride	62	2.5	110	0.7	HCl, benzene, toluene

The qualitative agreement between the observed modes of pyrolysis (random scission, depolymerization, solid-phase oxidation/fragmentation) and the calculated fragment molecular weight using Equation 20 is strong support for the identity, $L_g = E_a/M_g$. Consequently, L_g determined experimentally from a plot of peak mass loss rate versus external heat flux has the significance of a thermodynamic property. From Equations 18 and 19 the effective mass loss rate in terms of the net heat flux to the surface, is

$$\dot{m}_A = \frac{\dot{Q}_{net}}{L_g} = \frac{M_g}{E_a} \dot{Q}_{net} \quad (21)$$

6. HEAT RELEASE RATE

The phenomenological equation relating mass loss rate to heat release rate is,

$$\dot{Q}_c \text{ (kW/m}^2\text{)} = \chi \Delta H_c \dot{m}_A \quad (22)$$

where χ , ΔH_c , and \dot{m}_A , are the combustion efficiency, chemical heat of complete combustion, and the mass loss rate per unit area, respectively. Substituting Equation 13 for the areal mass loss rate of a char forming polymer into Equation 22 gives the heat release rate of a burning polymer in terms of its flaming surface temperature as

$$\dot{Q}_c = \Delta H_c \chi \dot{m}_A = \chi(1-Y_c) \Delta H_c \left[\frac{\kappa \rho}{C_p} \frac{A}{50e} \right]^{1/2} \exp\left(-\frac{E_a}{2RT_s}\right) \quad (23)$$

Figure 6 shows the excellent correlation ($r^2 = 0.94$) between steady-state heat release rate calculated from Equation 23 and measured values for a wide variety of polymers for which heat release rate data (10-13) and char yields (3,9,13) were available as well as reliable kinetic parameters (3,9,10) for the calculation of the flaming surface temperature, $T_s \approx T_p^{\max}$ at an external heat flux of 50 kW/m².

In terms of the net heat flux to the surface, the heat release rate from Equations 21 and 22 is

$$\dot{Q}_c = \frac{\chi \Delta H_c M_g}{E_a} \dot{Q}_{\text{net}} \quad (24)$$

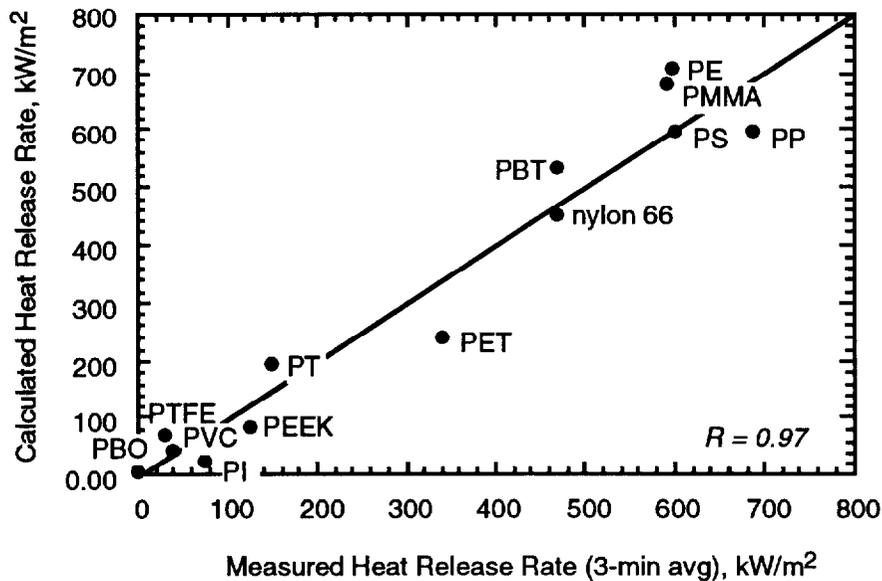


Figure 6. Calculated versus measured heat release rate for a variety of polymers

SUMMARY

The objective of this work was to find simple relationships between the fire response of polymeric materials and their thermodynamic, kinetic, and transport properties. Polymer thermal stability was assumed to be completely described by first-order Arrhenius pyrolysis kinetics modified to account for char yield. Analytic expressions for the time-to-ignition, mass loss rate, heat of gasification, and heat release rate were developed from phenomenological equations, transient heat conduction analyses, and the Arrhenius parameters and thermal properties of the material. Qualitative agreement between predicted and experimental fire response data for a wide range of polymeric materials is obtained by this simple approach.

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Discussion

Henri Mitler: Do I understand you to say the main difference in your formulation is the assumption of the existence of this charred mode?

Richard Lyon: There are a couple of subtle things, and I'm not sure that any one thing is the most important. What I have done here is assume parallel reactions. I allowed for gas and char formation. Equally important is the assumption of a transition state. That goes back to the physical chemistry theory of reactions. This is a transition state in its degradation to gas and char.

Masahiro Morita: What kind of atmosphere did you use?

Richard Lyon: It was a small 5 mg sample, no oxygen.