EFFECTS OF THE PMMA MOLECULAR WEIGTH ON THE THERMAL AND THERMO-OXIDATIVE DECOMPOSITION AS THE FIRST CHEMICAL STAGE OF FLAMING IGNITION

A. Galgano*, C. Di Blasi

Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli "Federico II", P.le V. Tecchio, 80125 Napoli, Italy.

* Corresponding author Tel:39-081-7682232; e-mail: agalgano@unina.it

Mathematical model

The conservation equations, the boundary conditions and the relations for the physical properties are listed in Table S1, S2 and S3. The spark is described as a finite-difference cell at the position x_i that, over an assigned period f, is instantaneously brought at the temperature T_{spark} for a time duration d. However the spark temperature only intervenes for the computation of the MMA combustion rate (eqn.49), while the temperature is still computed by means of eqn. 20a.

- Transport equations - Solid phase ($-L_s$,0)

$$\frac{d\rho_i}{dt} = -A_{di}\exp\left(-\frac{E_{di}}{RT_s}\right)\rho_i^{n_i}, \rho_i(t=0) = \nu_{i0}\rho_s \ \ for\ i = 1,2,3,4 \qquad (1a\text{-}4a,\ 1b\text{-}4b)$$

$$\omega_d = \sum_1^4 \frac{d\rho_i}{dt} \qquad (5)$$

$$\rho_s\frac{dL_s}{dt} = \int_{-L_s}^{0}\omega_d\,dx,\ L_s(t=0) = L_{s0}, V = \frac{1}{\rho_s}\int_{-L_s}^{0}\omega_d\,dx \qquad (6a\text{-}6c)$$

$$\frac{d(u\rho_g)}{dx} = \omega_d \qquad (7)$$

$$\rho_g = \frac{p_0 M_{MMA}}{RT_s} \qquad (8)$$

$$\rho_s c_s\frac{\partial}{\partial t}T_s = -uc_{MMA}\rho_g\frac{\partial}{\partial x}T_s + \frac{\partial}{\partial x}\left(k_s\frac{\partial T_s}{\partial x}\right) + \Delta h_d\omega_d + \frac{\partial}{\partial x}I_s,\ T_s(t=0) = T_0 \qquad (9a,9b)$$

$$\frac{d}{dx}I_s = I_s\big|_{x=0}\beta_s e^{\beta_s x_s} \qquad (10)$$

- Transport equations - Gaseous phase (0, L_g)

$$\omega_c = -A_c T_g^{-2}\exp\left(-\frac{E_c}{RT_g}\right)Y_{MMA}Y_{O_2}$$

(11)

$$\frac{\partial\rho_g}{\partial t} = -\frac{\partial u\rho_g}{\partial x},\ \rho_g(t=0) = \rho_{g0} \qquad (12a,12b)$$

$$\rho_g = \frac{p_0 \overline{M}}{RT_g}, \ \rho_g = \rho_{MMA} + \rho_P + \rho_{O_2} + \rho_{N_2}, \ \overline{M} = \frac{\sum_i \rho_i M_i}{\rho_g} \quad i = MMA, P, O_2, N_2 \tag{13-15}$$

$$\frac{\partial \rho_g Y_{MMA}}{\partial t} = -\frac{\partial u \rho_g Y_{MMA}}{\partial x} + \frac{\partial}{\partial x} D_{MMA} \rho_g \frac{\partial Y_{MMA}}{\partial x} - \omega_c, \ Y_{MMA}(t=0) = Y_{MMA0} \tag{16a,16b}$$

$$\frac{\partial \rho_g Y_{O_2}}{\partial t} = -\frac{\partial u \rho_g Y_{O_2}}{\partial x} + \frac{\partial}{\partial x} D_{O_2} \rho_g \frac{\partial Y_{O_2}}{\partial x} - \nu_c \omega_c, \ Y_{O_2}(t=0) = Y_{O_2 0} \tag{17a,17b}$$

$$\frac{\partial \rho_g Y_P}{\partial t} = -\frac{\partial u \rho_g Y_P}{\partial x} + \frac{\partial}{\partial x} D_P \rho_g \frac{\partial Y_P}{\partial x} + (1+\nu_c)\,\omega_c, \ Y_P(t=0) = Y_{P0} \tag{18a-18b}$$

$$Y_{N_2} = 1 - Y_{MMA} - Y_{O_2} - Y_P \tag{19}$$

$$\rho_g c_g \frac{\partial}{\partial t} T_g = -u \rho_g c_g \frac{\partial}{\partial x} T_g + \frac{\partial}{\partial x} k_g \frac{\partial T_g}{\partial x} - \omega_c \Delta h_c + \frac{dI_g}{dx} - \frac{dJ_g}{dx}, \ T_g(t=0) = T_0 \tag{20a,20b}$$

$$\frac{dI_g}{dx} = aI_g - \frac{1}{2} a \sigma T_g^4, \ \frac{dJ_g}{dx} = -aJ_g + \frac{1}{2} a \sigma T_g^4 \tag{21-22}$$

- Boundary conditions

$$u \rho_g \big|_{x=-L_s} = 0 \tag{23}$$

$$\left. \frac{\partial T_s}{\partial x} \right|_{x=-L_s} = 0, \ T_s \big|_{x=0^-} = T_g \big|_{x=0^+} \tag{24-25}$$

$$I_s \big|_{x=0} = I_g \big|_{x=0} (1 - e_s) \tag{26}$$

$$u\rho_g \big|_{x=0^+} = u\rho_g \big|_{x=0^-} \tag{27}$$

$$u\rho_g Y_{MMA} \big|_{x=0^+} - D_{MMA} \rho_g \left. \frac{\partial Y_{MMA}}{\partial x} \right|_{x=0^+} = u\rho_g \big|_{x=0^-}, \ Y_{MMA} \big|_{x=L_g} = 0 \tag{28a,28b}$$

$$u\rho_g Y_{O_2} \big|_{x=0^+} - D_{O_2} \rho_g \left. \frac{\partial Y_{O_2}}{\partial x} \right|_{x=0^+} = 0, \ Y_{O_2} \big|_{x=L_g} = Y_{O_2 0} \tag{29a,29b}$$

$$u\rho_g Y_P \big|_{x=0^+} - D_P \rho_g \left. \frac{\partial Y_P}{\partial x} \right|_{x=0^+} = 0, \ Y_P \big|_{x=L_g} = 0 \tag{30a,30b}$$

$$-k_g \left. \frac{\partial T_g}{\partial x} \right|_{x=0^+} + e_p \sigma T_s^4 \big|_{x=0^+} = -k_s \left. \frac{\partial T_s}{\partial x} \right|_{x=0^-}, \ T_g \big|_{x=L_g} = T_0 \tag{31a,31b}$$

$$I_g \big|_{x=L_g} = Q \tag{32}$$

$$J_g \big|_{x=0^+} = e_s \sigma T_s^4 \big|_{x=0^+} + e_s I_g \big|_{x=0^+} \tag{33}$$

Table S1. Model equations for the solid and the gas phase with initial and boundary conditions.

$$c_s = \begin{cases} -1330 + 8.6 T_s & if \quad T_s < T_{trans} \\ 1120 + 2.4 T_s & if \quad T_s \geq T_{trans} \end{cases} \quad [J/kgK] \tag{34}$$

$$k_s = \begin{cases} -0.01 + 4.7 \times 10^{-4} T_s & if \quad T_s < T_{trans} \\ 0.01 + 4 \times 10^{-4} T_s & if \quad T_s \geq T_{trans} \end{cases} \quad [W/mK] \tag{35}$$

$$c_g = Y_{MMA} c_{MMA} + Y_{O_2} c_{O_2} + Y_{N_2} c_{N_2} + Y_P c_P \tag{36}$$

$$c_P = 0.25 c_{H_2O} + 0.75 c_{CO_2} \quad (37)$$

$$c_{MMA} = -206 + 4.03T - 1.786\times10^{-3}T^2 + 1.04\times10^{-7}T^3 \quad [J/kgK] \quad (38)$$

$$c_{O_2} = 1081 + 0.034T_g - 2.4542\times10^7/T_g^2 \quad [J/kgK] \quad (39)$$

$$c_{N_2} = 972 + 0.15T_g \quad [J/kgK] \quad (40)$$

$$c_{CO_2} = 984 + 0.26T_g - 1.86\times10^7/T_g^2 \quad [J/kgK] \quad (41)$$

$$c_{H_2O} = 1911.6 + 0.035T_g + 3.116\times10^{-4}T_g^2 \quad [J/kgK] \quad (42)$$

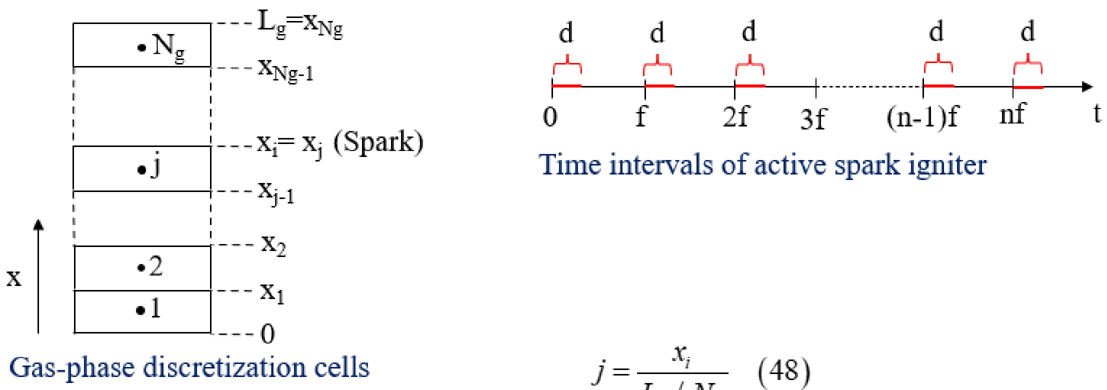
$$D_i = D_{i0}\left(\frac{T_g}{T_0}\right)^{1.75} \quad i = MMA, O_2, P \quad (43\text{-}45)$$

$$a = \beta_g Y_{MMA} \quad (46)$$

$$k_g = 0.33 + 7.63\text{x}10^{-3}\left(T_g - T_0\right) \quad [W/mK] \quad (47)$$

Table S2. Equations for the solid and gas properties.

Schematization of the electric spark



$$j = \frac{x_i}{L_g / N_g} \quad (48)$$

Spark igniter cell number

$$\omega_c(j) = -A_c \mathrm{T}_{spark}^{-2} \exp\left(-\frac{E_c}{RT_{spark}}\right) Y_{MMA} Y_{O_2} \quad if \quad f(n-1) \le t \le f(n-1) + d \qquad (n \in N) \quad (49)$$

Piloted ignition model

Table S3. Model equations and schematization of the spark.

Nomenclature

A Pre-exponential factor of MMA combustion reaction [kgK^2/m^3s] or PMMA decomposition reaction [s-1]
a Radiation absorption [m^{-1}]
c Specific heat [J/kgK]
D Molecular diffusivity [m^2/s]
d time interval where the spark temperature is equal to Tspark [s]
E Activation energy [kJ/mol]
e Emissivity
f Period of spark activation [s]
I Radiative heat flux (towards the polymer surface) [W/m^2]
J Radiative heat flux (from the polymer surface) [W/m^2]
k Thermal conductivity [W/mK]
L Length of the solid- or gas-phase domain [mm]
M Molecular weight [kg/kmol]
m Mass flux [kg/m^2s]
N Number of discretization cells
n Reaction order
p Pressure [Pa]
Q External irradiance intensity [kW/m^2]
R Universal gas constant [J/kmolK]
r Monomer to oxygen mass fraction ratio at the ignition position
T Temperature [K]
t Time [s]
u Gas velocity [m/s]
V Regression rate [m/s]
w Width of the gas-phase reaction zone (combustion rate higher than $0.5 kg/m^3s$) [mm]
x Spatial coordinate/position [mm]
x_i Spark ignitor position [mm]
Y Mass fraction
β Radiation absorption coefficient [m^{-1}]
δ Thermal depth [mm]
Δh Reaction enthalpy [J/kg]
ρ Density [kg/m^3]
ν Stoichiometric coefficient of the PMMA decomposition steps
ν_0 Stoichiometric coefficient of the MMA combustion reaction
σ Stefan-Boltzmann constant [W/m^2K^4]
ω Reaction rate [kg/m^3s]

Subscripts

0 Initial or reference
1,2,3,4 Steps of the decomposition process
c Combustion
CO2 Carbon dioxide
d Decomposition
g Gas
H2O Water
ig Ignition
max Maximum
MMA Methyl methacrylate (monomer)
N2 Nitrogen

O2 Oxygen
P Combustion products
s Solid/surface
spark Spark ignitor
trans Glass transition