Thermochemical Flammability Model for Thin Materials

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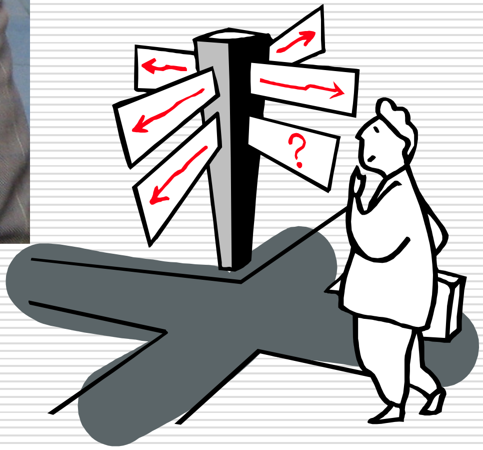
Outline

- Objective
- Background
- TGA Analysis
- DSC Analysis
- Modeling
- Results of Modeling
- Conclusions



Objective

- The goal of this research is to predict the burning of thermally thin materials by modeling.

- To provide the needed data for the model, TGA and DSC analysis have been performed

- The materials and the data of Liu with pure nylon and nylon with 5% clay additive, conducted in the Cone Calorimeter will be used for comparison

Background-1

- Burning behavior differs according to thickness & heat flux.
  - ✓ Thermally thick burning
  - ✓ Thermally thin burning
- Material flammability of nano-clay loading
  - ✓ Ignition time increased
  - ✓ The burning rate greatly reduced

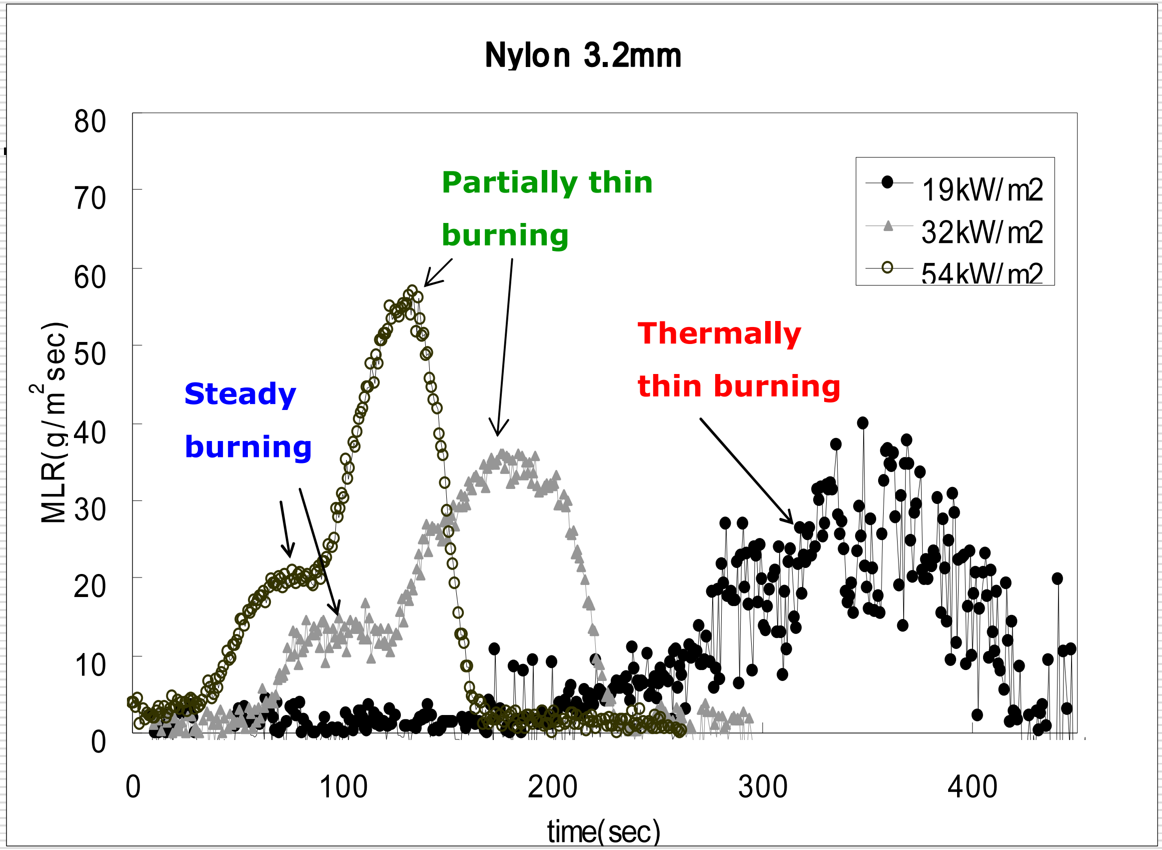


Fig.1 Thermally thick & thin burning

Background-2

- For modeling
  - It's very important to understand the decomposition effects in the burning of thermally thin material

- Is it possible to use TGA/DSC for predicting the burning behavior?

  - The heating rate(β) of TGA & DSC : 0.1~30 K/min
    The heating rate of fires :100 K/min or greater

  - E_a & a_p derived from TGA change with heating rate.
    TGA's relevance to fires has been questioned. Hence, this study will attempt to examine the use of TGA and DSC data in the thermally thin model for fire application

Definition and TGA data

- A technique in which the mass of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature program

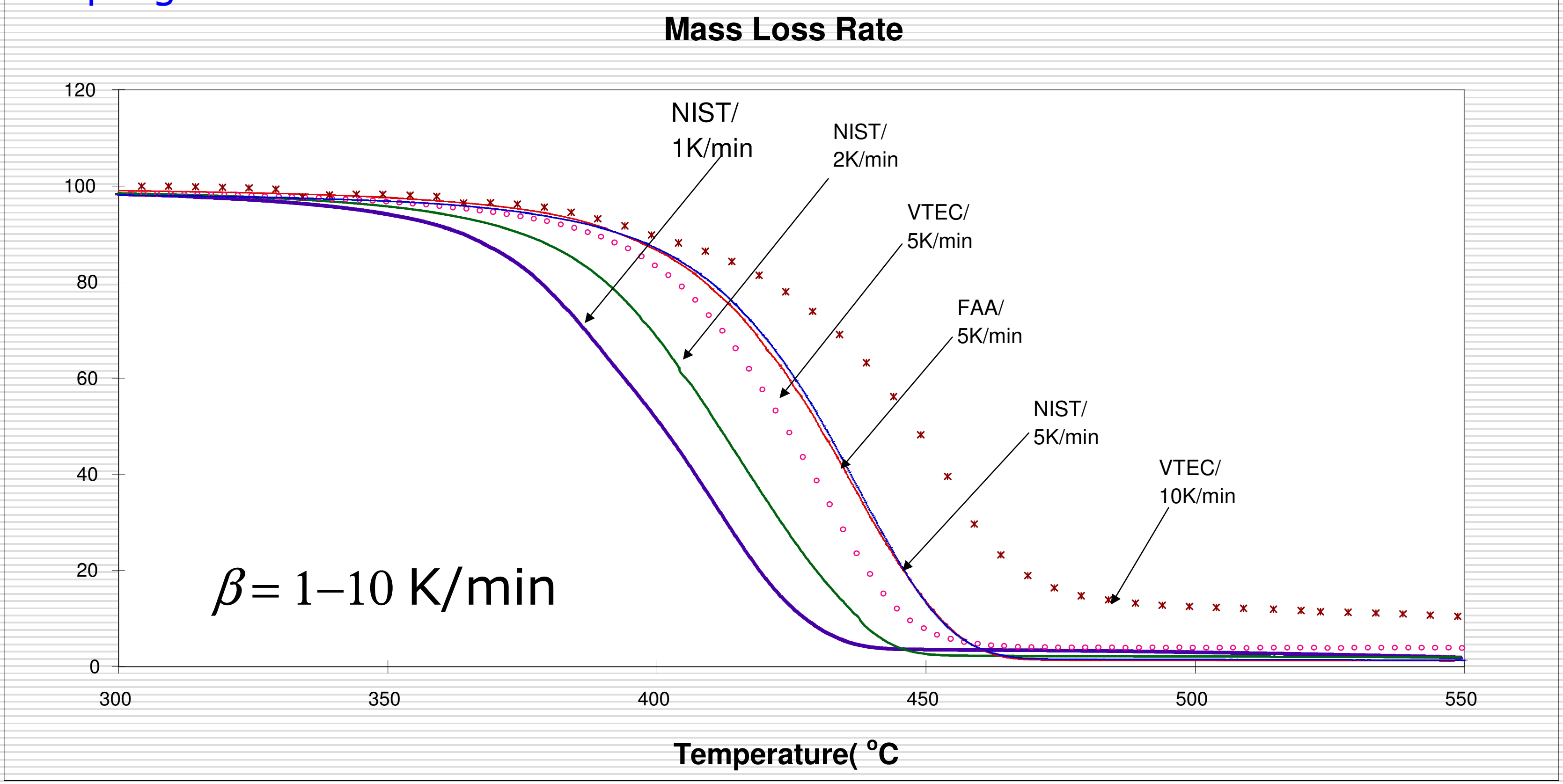


Figure 2. TGA curves of Nylon obtained from experiment

The Kinetics

- The thermal decomposition of the solid is assumed to follow first-order Arrhenius reaction

$$\frac{d\alpha}{dt} = \frac{(1-\alpha)}{(1-X_c)} a_p e^{-E_a/RT}$$

This is the basic equation needed in our TGA analysis to determine the kinetic parameters, E_a and a_p

✓ Conversion factor, $\alpha = \dfrac{m - m_i}{m_f - m_i} = \dfrac{m/m_i - 1}{X_c - 1}$

✓ Char fraction, $X_c = \dfrac{m_f}{m_i}$

TGA analysis method

- Eqn (2.19)

$$ln\left(\frac{d\alpha}{dt}\right)=ln\left\{\frac{(1-\alpha)}{(1-X_c)}\times a_p\right\}-\frac{E_a}{R}\left(\frac{1}{T}\right)$$

- ✓ E_a changes with heating rate and α

  The trend: as α ↑, E_a ↑
- ✓ Slope=- E_a /R,
- ✓ Intercept= $ln\left[\frac{(1-\alpha)}{(1-X_c)}a_p\right]$
- ✓ Kinetic parameter determined

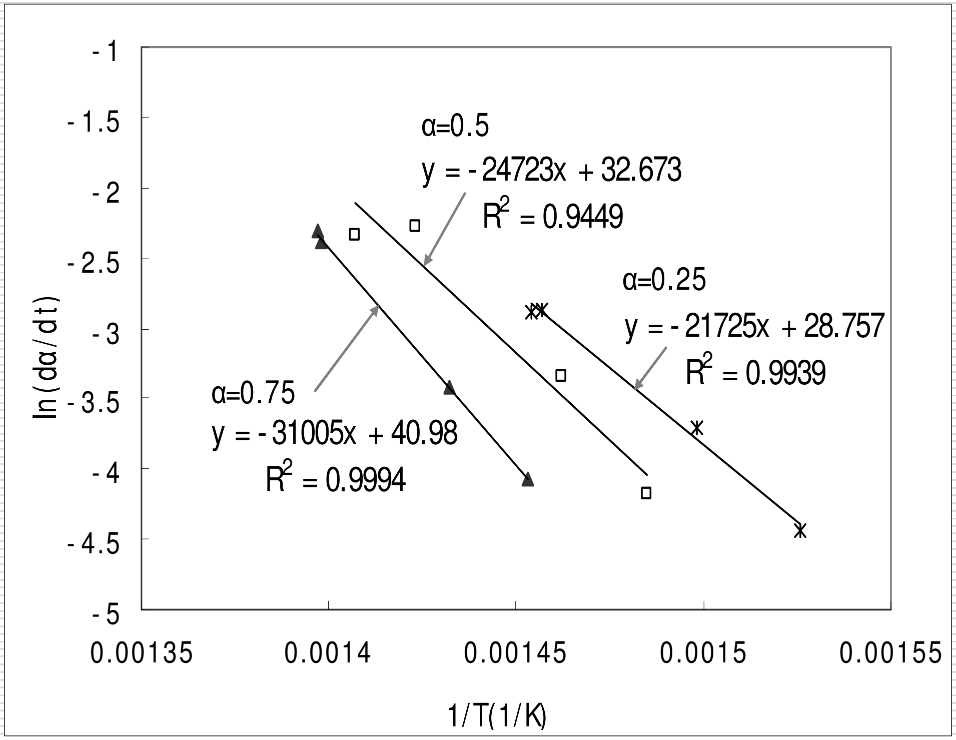


Figure 3. Determining Ea and a_p of Nylon

Results of TGA modeling

Table 2-4. Kinetic parameters

Material	Activation energy (E_a)	Pre-Exponential factor (a_p)
Nylon	223 kJ/mol	1.5×10^{14} s^{-1}
Nylon+5%	223 kJ/mol	2.1×10^{14} s^{-1}

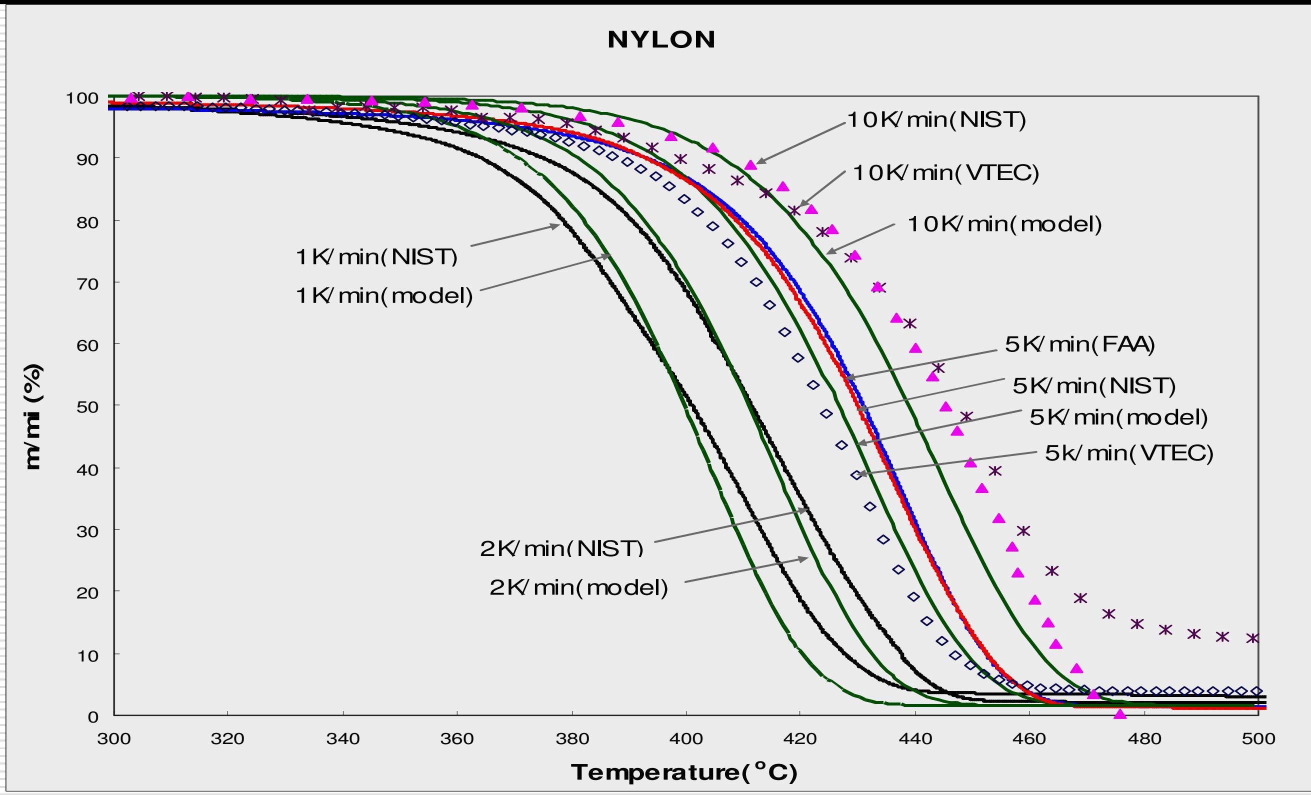


Figure 4. Comparing the model to the experiment

Definition and use of DSC

- DSC measures the difference in energy inputs into substance and reference material as a function of temperature while these are subjected to a controlled temperature program

✓The difference of power supplies between two cups shows that C_p, Q_m, and Q_p

✓The interpretation ultimately relies on a careful procedure involving the establishment of a "baseline" signal for no sample,

✓and a special procedure to evaluate the heat loss between the heater-cup system and flowing gas

✓Big help from FAA

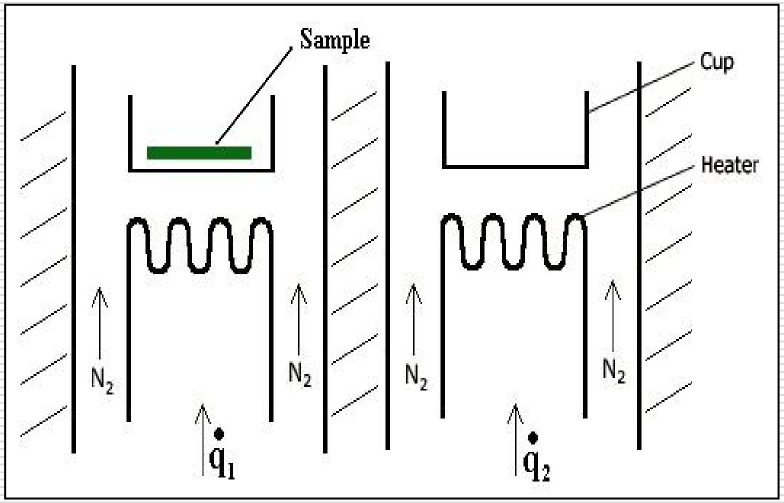


Figure5. Schematic of heat transfer in DSC

DSC data

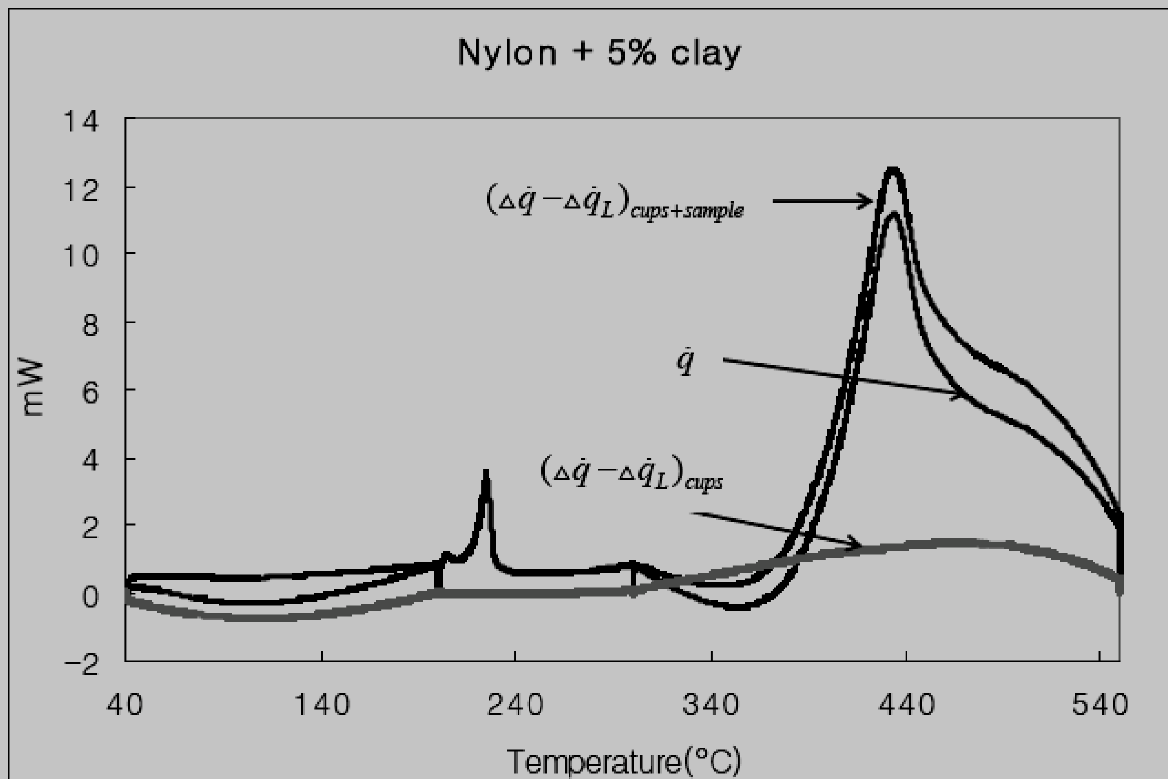


Figure 3-7. Power supplies to the sample

Figure 6. Power supplies to the sample

Results of DSC analysis-1

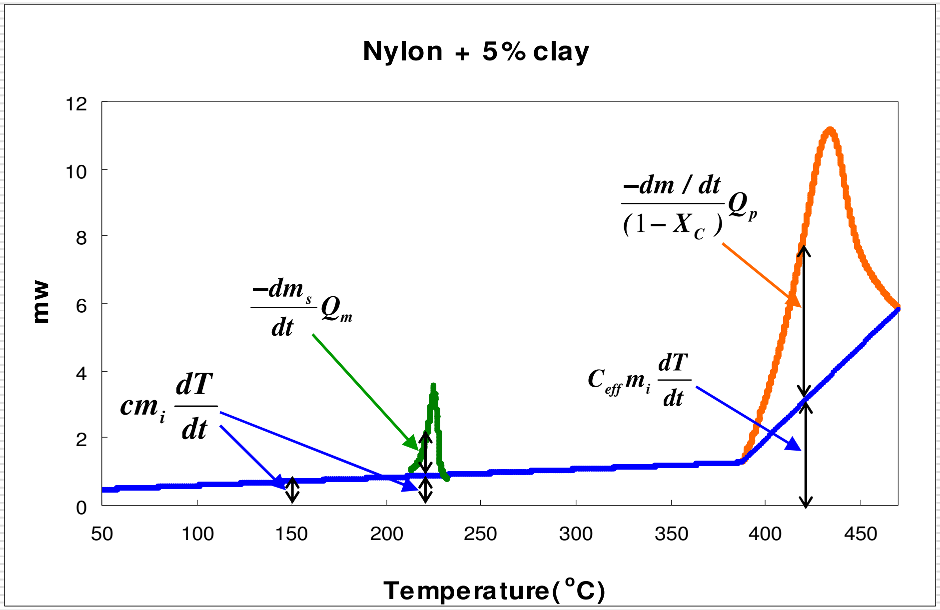


Figure 7. Sample signal of Nylon+5% clay

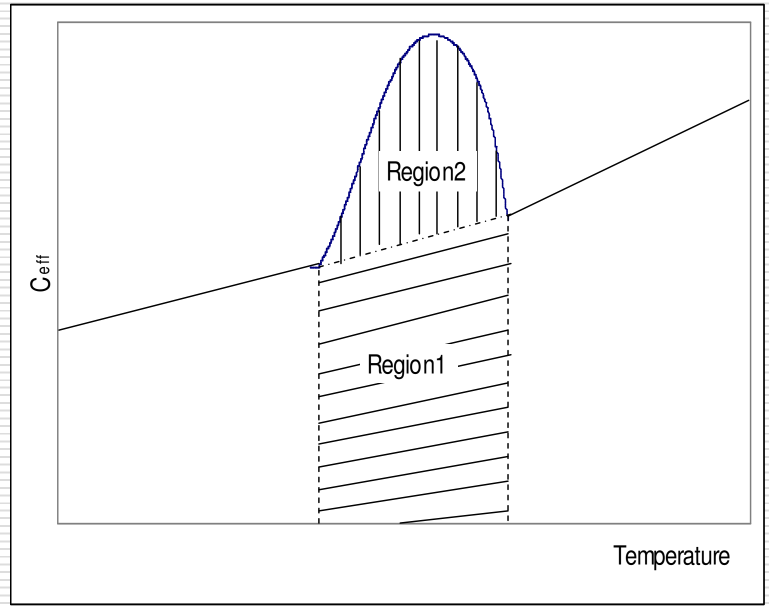


Figure 8. The effective c_p

$$c_{eff} = \frac{\dot{q}}{m_i \beta}$$

$$\int c_{eff}\, dT$$

$$= \frac{1}{m_i}\int_{m_i}^{m_f} \frac{(-dm)}{(1-X_C)} Q_p + \int c\, dT$$

$$= Q_p + \int c\, dT$$

Results of DSC analysis-2

	Values measured		Values selected in modeling	
	Nylon	Nylon +5 % Clay	Nylon	Nylon +5 % Clay
Heat of Melting, kJ/g	32, 35	35, 73	35	73
Heat of Decomposition, kJ/g active	388, 549	522, 557, 618, 671	550	670
Specific Heat of Solid, J/g-K 50 – 220 ºC	1.6 – 2.5	1.5 – 2.5	1.12 + 0.0075(T-T_∞)	1.21 + 0.0073(T-T_∞)
Specific Heat of Melt, J/g-K 220 – 400 ºC (decomposition 400 – 450 ºC)	2.5 - 4	2.5 - 4	-82 + 0.22(T-T_∞)	-79 + 0.21(T-T_∞)

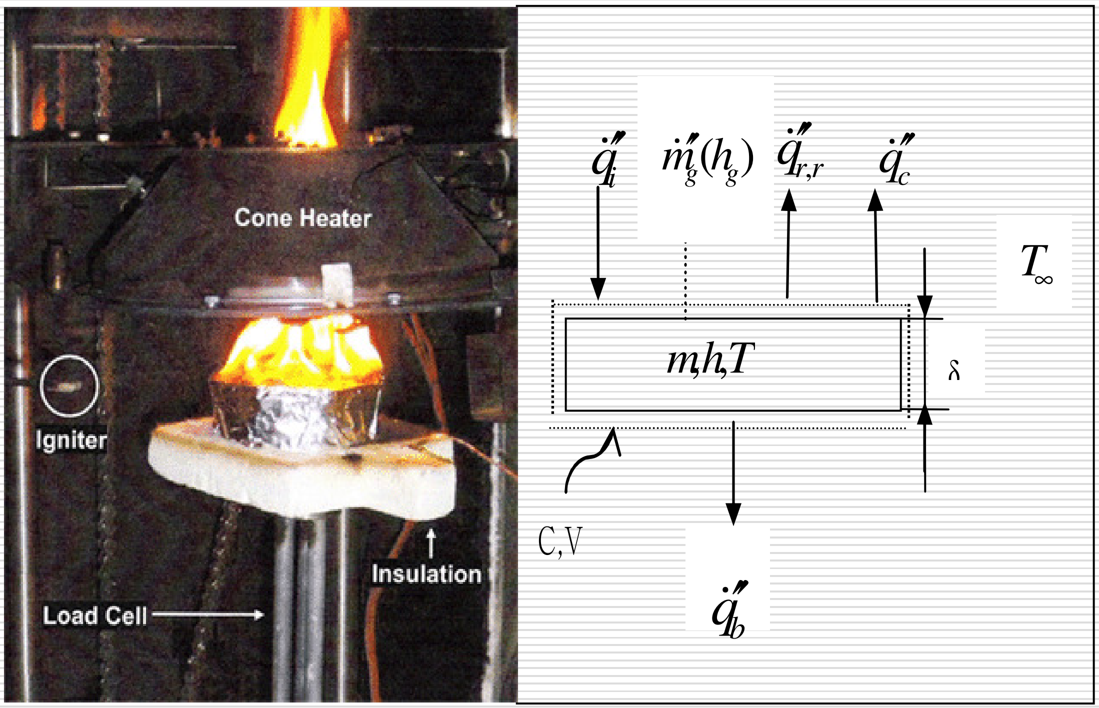
Theory of the modeling

- With kinetic and thermodynamic properties from TGA/DSC, the burning rate of thin polymers under radiant heat can be formulated.

  The model results will be compared with the data from Cone Calorimeter experiments carried out by Xiu Liu

- The transient exposure and response of the thin material is divided into 4 phases
  - ✓Pre-heating to melt
  - ✓Melting phase
  - ✓Decomposing to ignition
  - ✓Flaming phase

Formulation of the model-1



δ **: Thickness of a material**

$\dot{q}''_i$ **: Incident heat flux from the cone heater**

$\dot{q}''_f$ **: Flame heat flux after flaming**

$\dot{q}''_c$ **: Convective heating flux when no flame**

$\dot{q}''_{r,r}$ **: Re-radiative heat flux to surroundings** T_∞

$\dot{q}''_b$ **: Conductive heating flux to the insulator on the bottom**

Cone calorimeter assembly & heating of material in C.V

✓ The general equation is

$$\rho c_p \delta \frac{dT}{dt} = \dot{q}'' + Q_m \frac{\rho \delta}{\Delta t_m} + Q_p \frac{d\rho}{dt} \delta$$

Formulation of the Model-2

- The model is formulated from the conservation laws
  - Energy, mass, species(kinetics) conservation

1. Pre-heating

$$\rho c_P \delta \frac{dT}{dt} = \alpha \dot{q}_i'' - \varepsilon\sigma(T^4 - T_\infty^4) - h_c(T - T_\infty) - \sqrt{\frac{\pi k' \rho' c_p'}{4t}}(T - T_\infty)$$

2. Melting : T_m is constant

$$\rho c_p \delta \frac{dT}{dt} = \alpha \dot{q}_i'' - \varepsilon\sigma(T^4 - T_\infty^4) - h_c(T - T_\infty) - \sqrt{\frac{\pi k' \rho' c_p'}{4t}} - Q_m \frac{d\rho}{dt}\delta$$

3. Decomposing

✓ Energy conservation

$$\rho c_P \delta \frac{dT}{dt} = \alpha \dot{q}_i'' - \varepsilon\sigma(T^4 - T_\infty^4) - h_c(T - T_\infty) - \sqrt{\frac{\pi k' \rho' c_p'}{4t}}(T - T_\infty) + Q_p \frac{d\rho}{dt}\delta$$

Formulation of the Model-3

- ✓ Kinetics of decomposition

$$\frac{d\rho}{dt} = -\rho_a a_p \exp(-E_a / R \cdot T)$$

- ✓ Mass conservation

$$\frac{d\rho}{dt} = (1 - X_C)\frac{d\rho_a}{dt}$$

4. Flaming burning

- ✓ Energy conservation

$$\rho c_P \delta \frac{dT}{dt} = \alpha \dot{q}_i'' + \dot{q}_f'' - \varepsilon\sigma(T^4 - T_\infty^4) - \sqrt{\frac{\pi k' \rho' c_p'}{4t}}(T - T_\infty) + Q_p \frac{d\rho}{dt}\delta$$

- ✓ Decomposition Kinetics
- ✓ Mass conservation

- ❖ These equations were solved by Mathematica.

Modeling: ignition and burning

- Flash-point using the criteria, 13 kW/m^2

  $\dot{m}''_g$ =0.46 g/m^{2}s, at T_{flash}
- Fire-point using the criteria, 50 kW/m^2

  $\dot{m}''_g$ =1.79 g/m^{2}s, at T_{fire}

- Flame heat fluxes coming from Cone Calorimeter data

	Nylon	Nylon+5%clay
1.6mm	20 kW/m^2	20kW/m^2
3.2mm	30 kW/m^2	18kW/m^2

Heating Rates

- The heating rates employed by TGA were 1, 2, 5, 10°C/min whereas the heating rates in the Cone Calorimeter experiments are relatively high. It is relevant to real fire

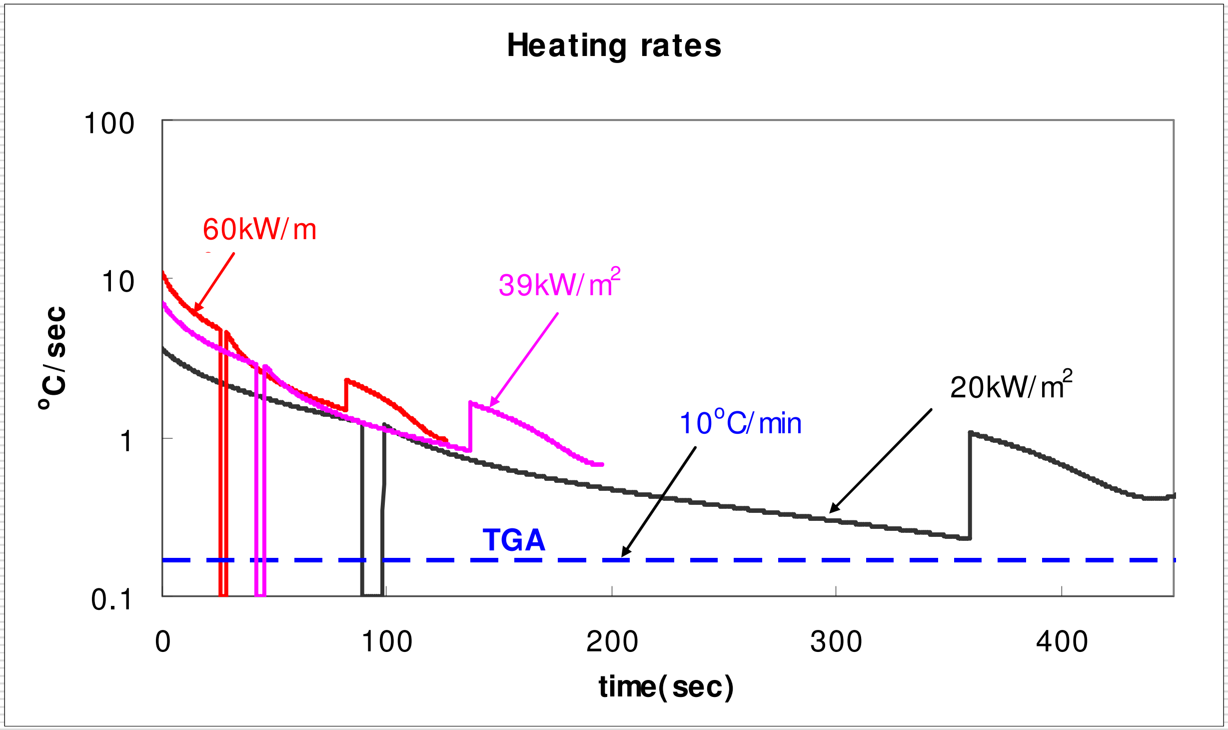
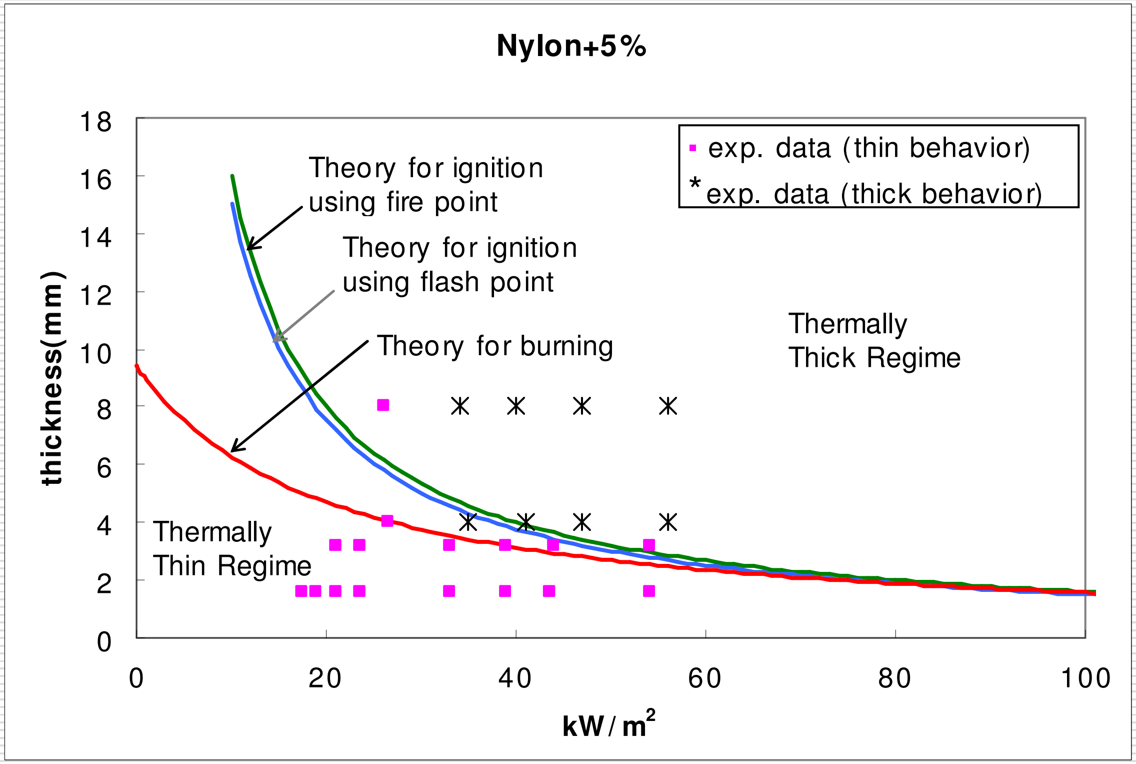


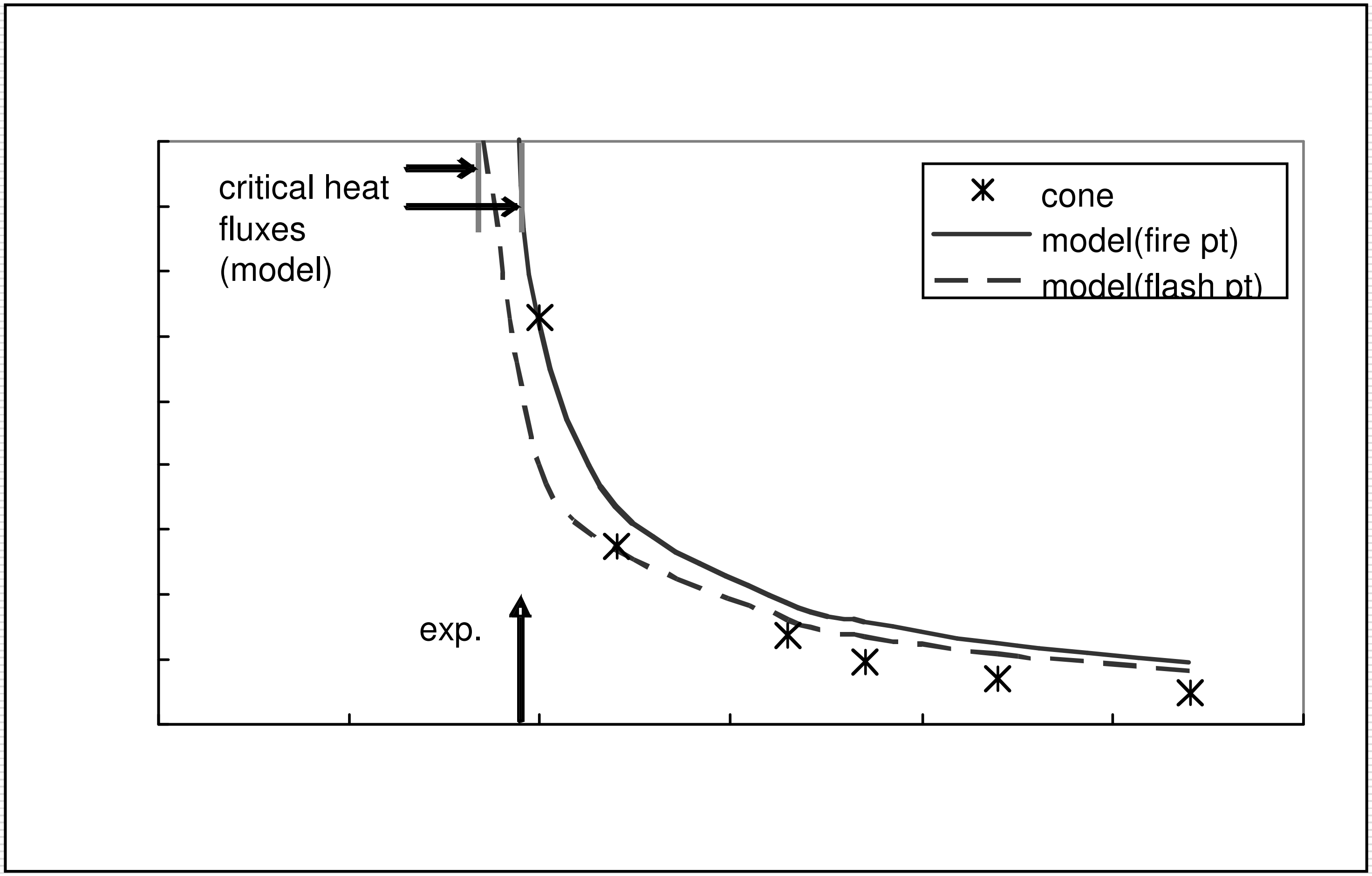
Figure 9. The heating rates in the TGA, and Cone Calorimeter

The criteria of thermally thin

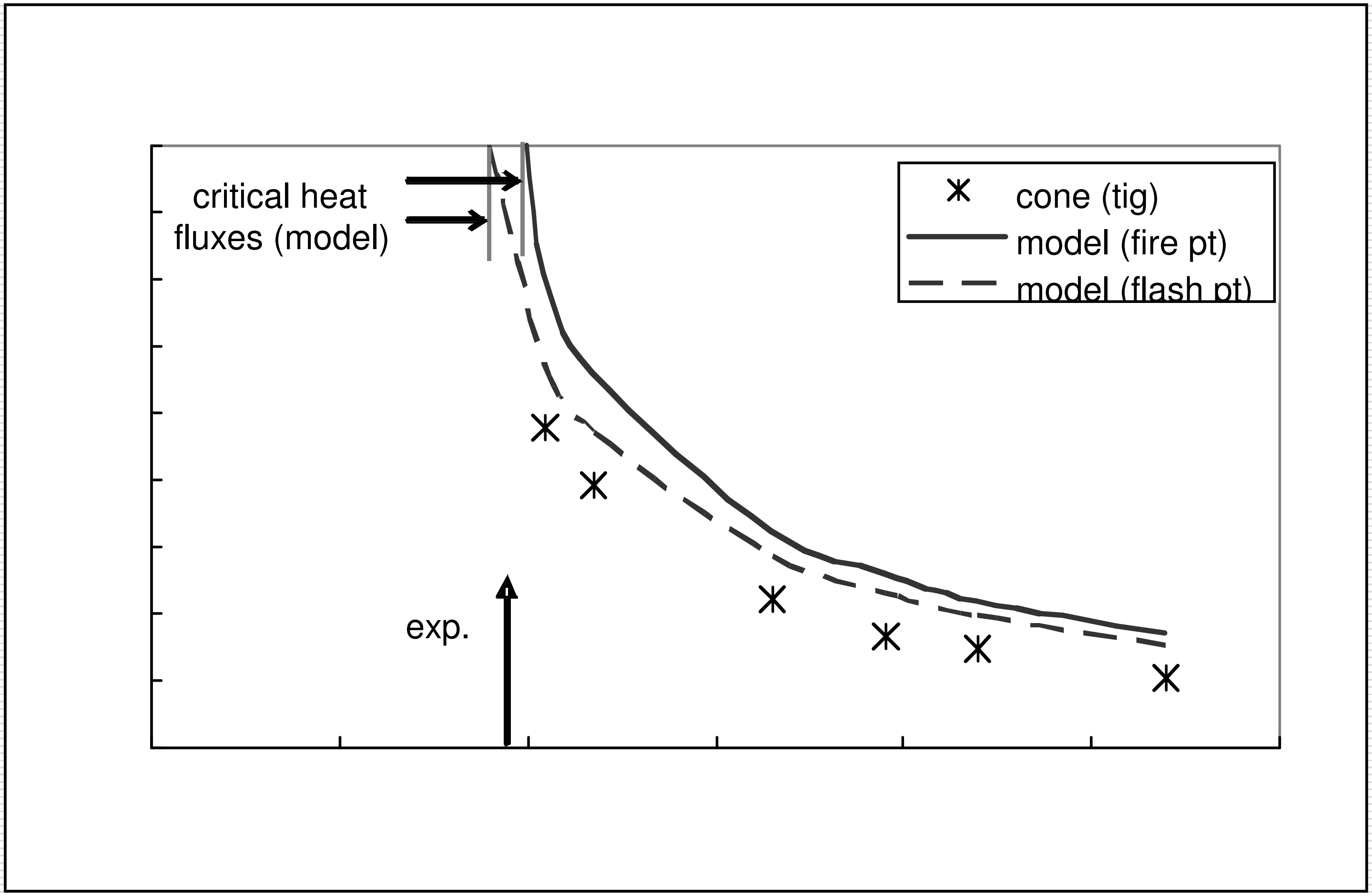
- What is the criteria of thermally thin burning?
  - ✓ A criteria for thermally thin ignition : $l_{thin} = 2\frac{k(T_{ig} - T_o)}{\dot{q}_i''}$
  - ✓ A criteria for thermally thin Burning : $\delta_s = \frac{2k(T_p - T_\infty)}{\dot{q}_{net}''}$



Prediction of Ignition

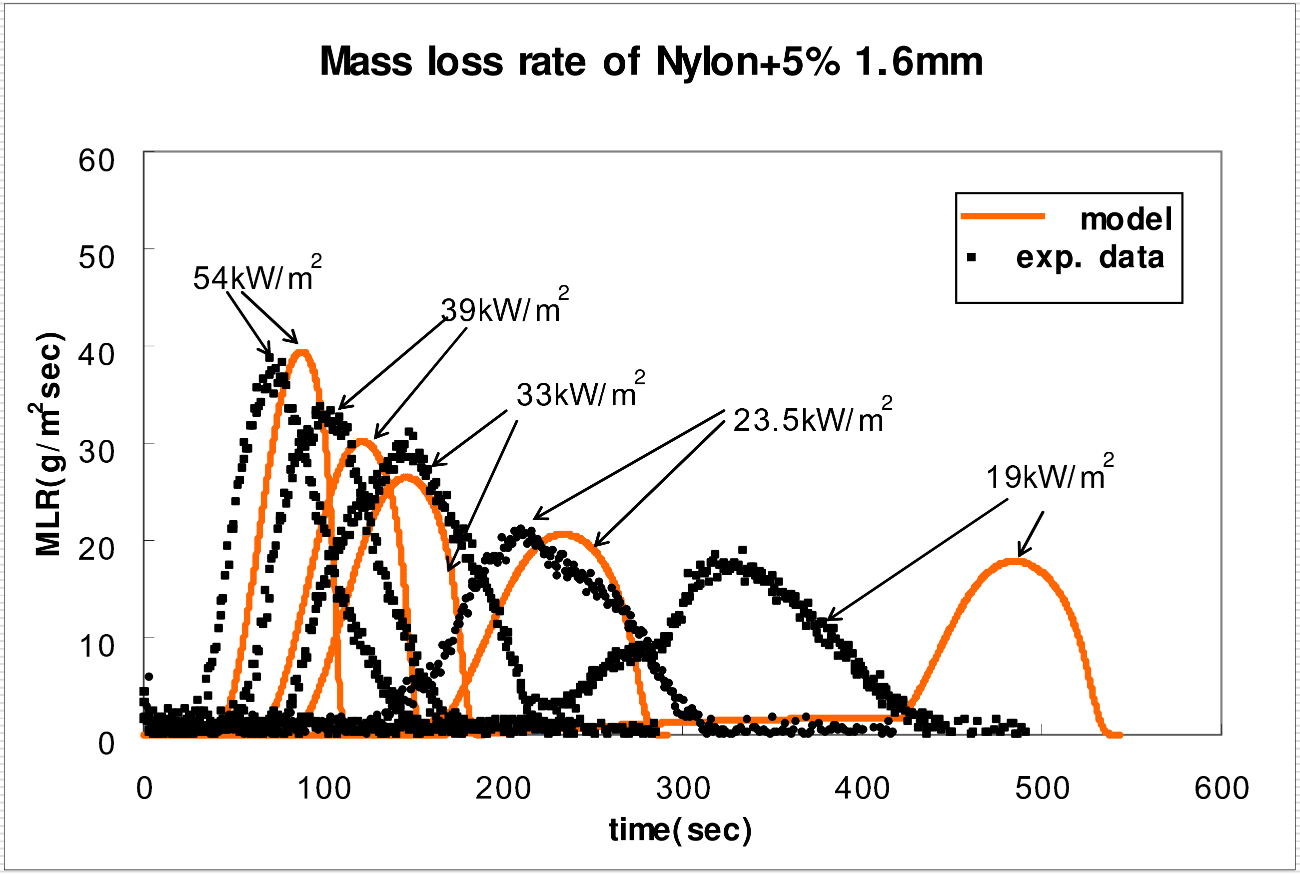


Ignition-2


critical heat
fluxes (model)
exp.
cone (tig)
model (fire pt)
model (flash pt)

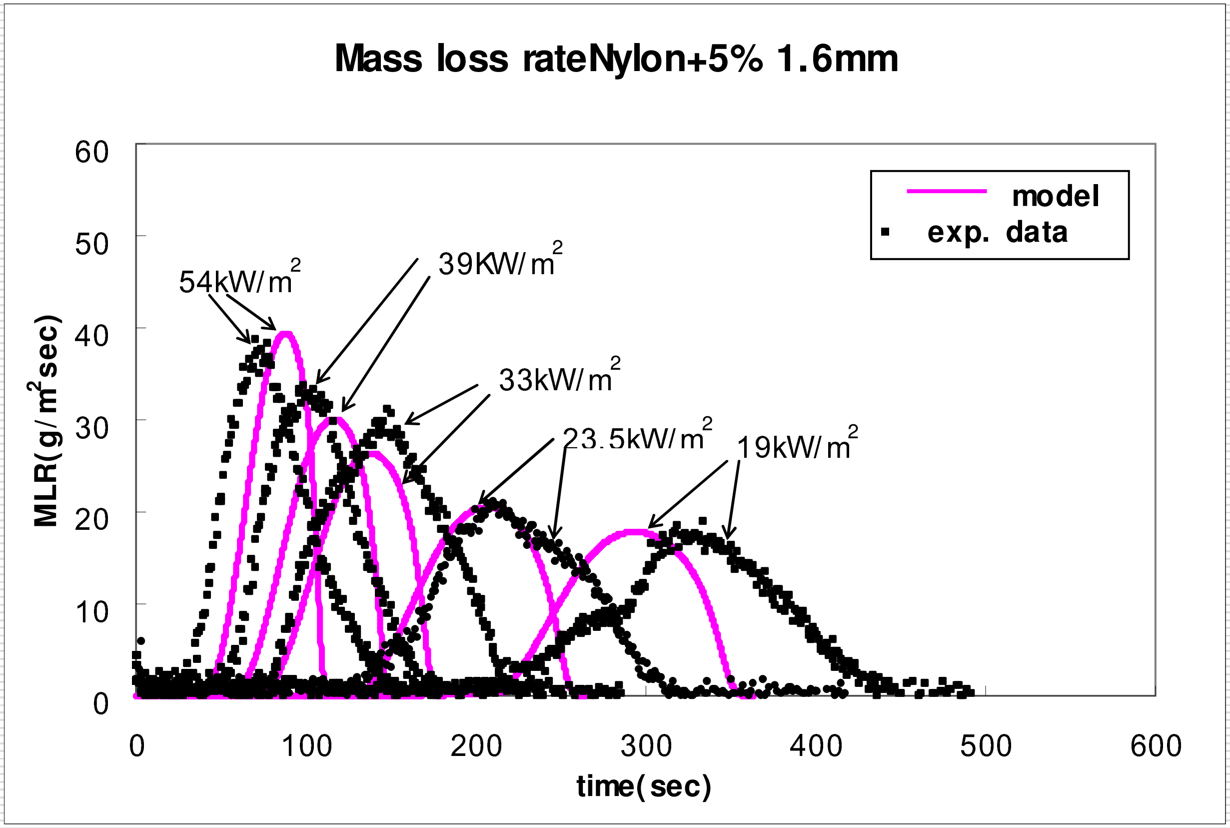
Comparing the model to the cone calorimeter data

Flaming initiated at the fire point

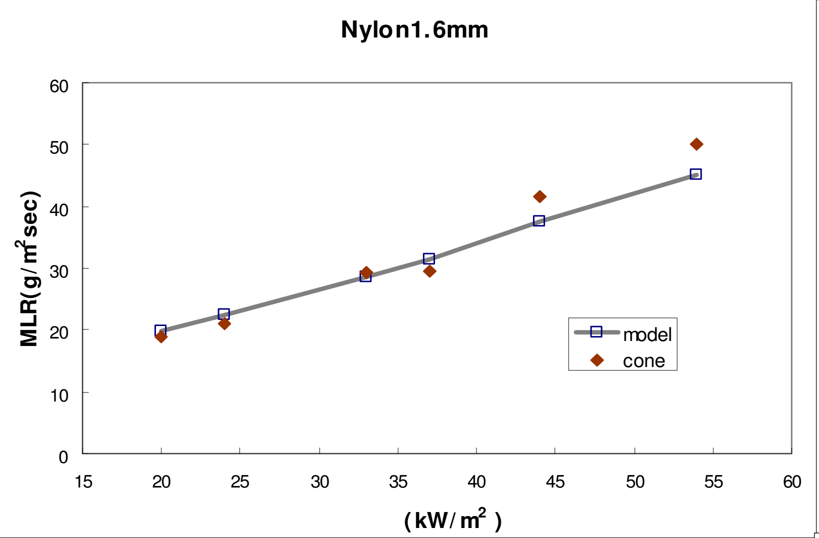


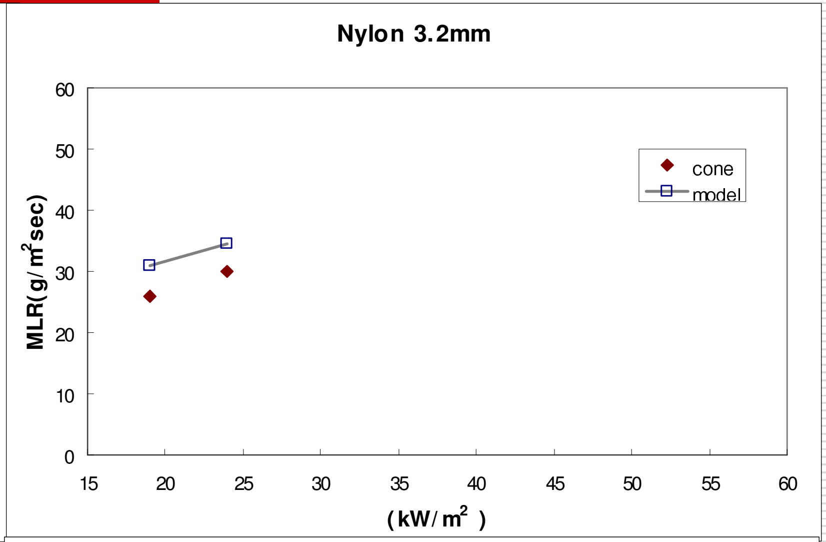
Comparing the model to the cone calorimeter data

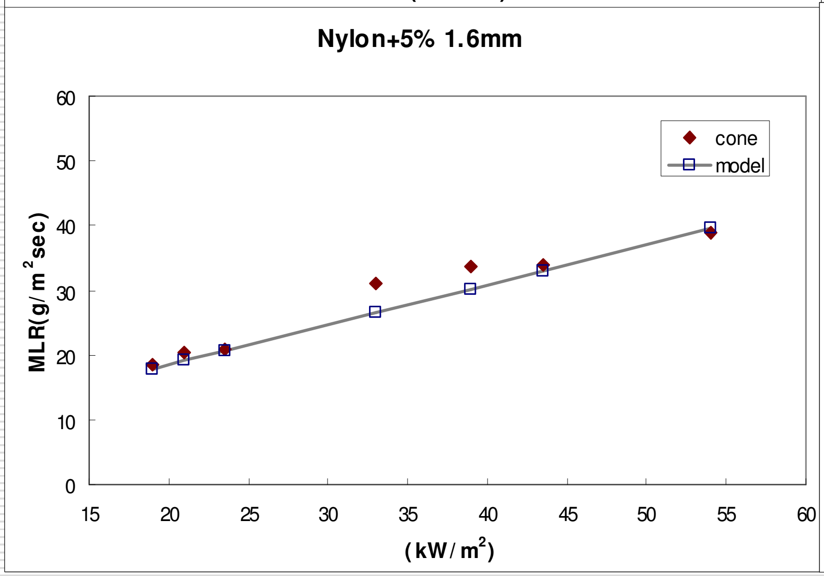
Flaming initiated at the flash point

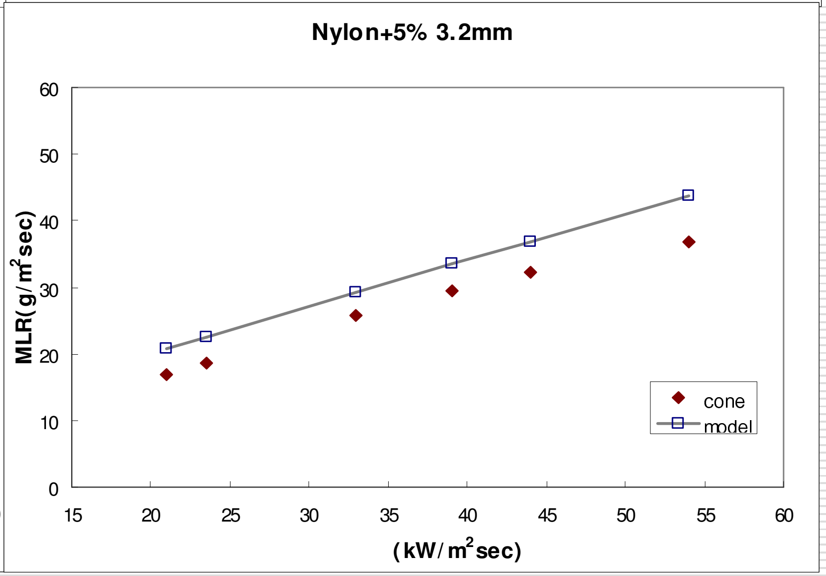


Modeling Result: Peak Average Burning Rate









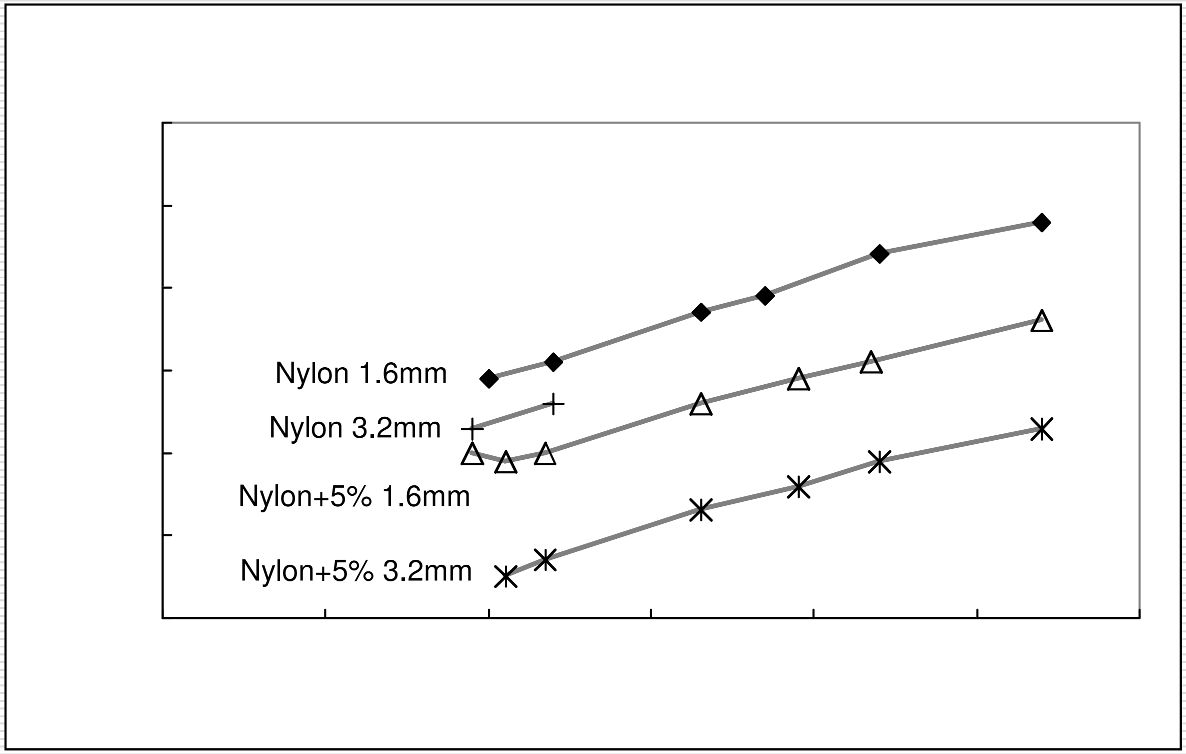
T_{flash} & T_{fire}

- The flash point and fire point calculated by the model are found to be nearly constant over the heat flux range: 19 kW/m² to 54 kW/m².

	Nylon 1.6 mm	Nylon 3.2 mm	Nylon+5% clay 1.6 mm	Nylon+5% clay 3.2 mm
Flash-point	383 ℃	372 ℃	378 ℃	367 ℃
Fire-point	406 ℃	394 ℃	403 ℃	388 ℃

Decomposition temperature

- In contrast, the temperature(T_p) on the peak burning rate increases with the radiation heat flux.



Conclusions

- ✓ The theoretical results for thermally thin ignition and burning yield good agreement with data for 1.6 mm samples of Nylon and Nylon with 5 % nano-clay.
- ✓ TGA and DSC data provide a good basis for the theory, but reveal no distinct differences between the pure Nylon and the nano-clay Nylon within the accuracy of the data.
- ✓ Hence, the inhibiting nature of the nano-clay appears to be solely that of the insulating char layer that is more significant for thick samples.
- ✓ The Nylon sample is thermally thin up to about 3.2 mm.

END