PYROLYSIS PARAMETERIZATION AND VALIDATION FOR POLYMERIC MATERIAL

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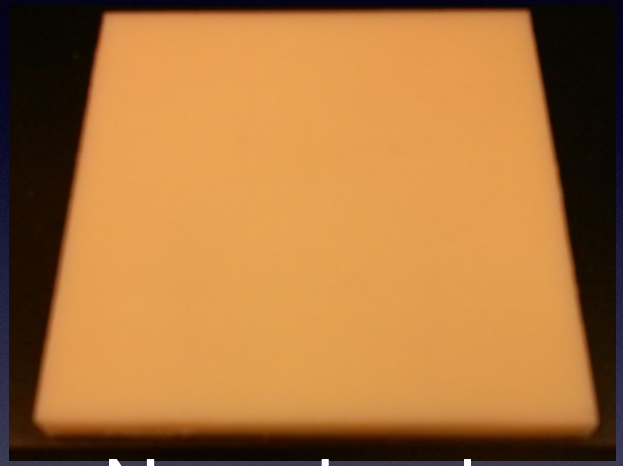
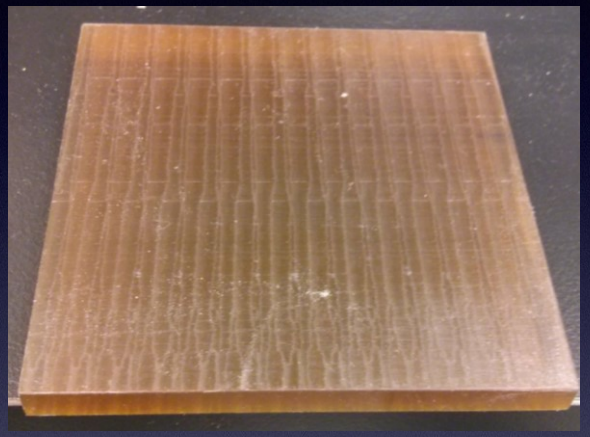
Outline

- Introduction
- Milligram-scale (Part I)
- Bench-scale (Part II)
- Conclusion

Non-charring and Charring Polymer

Before

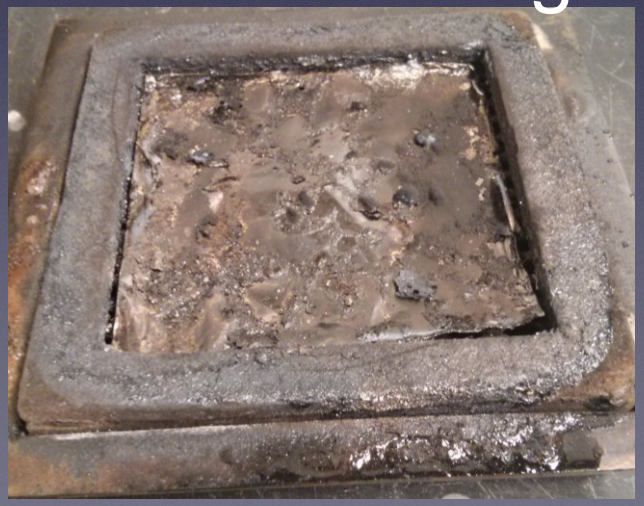




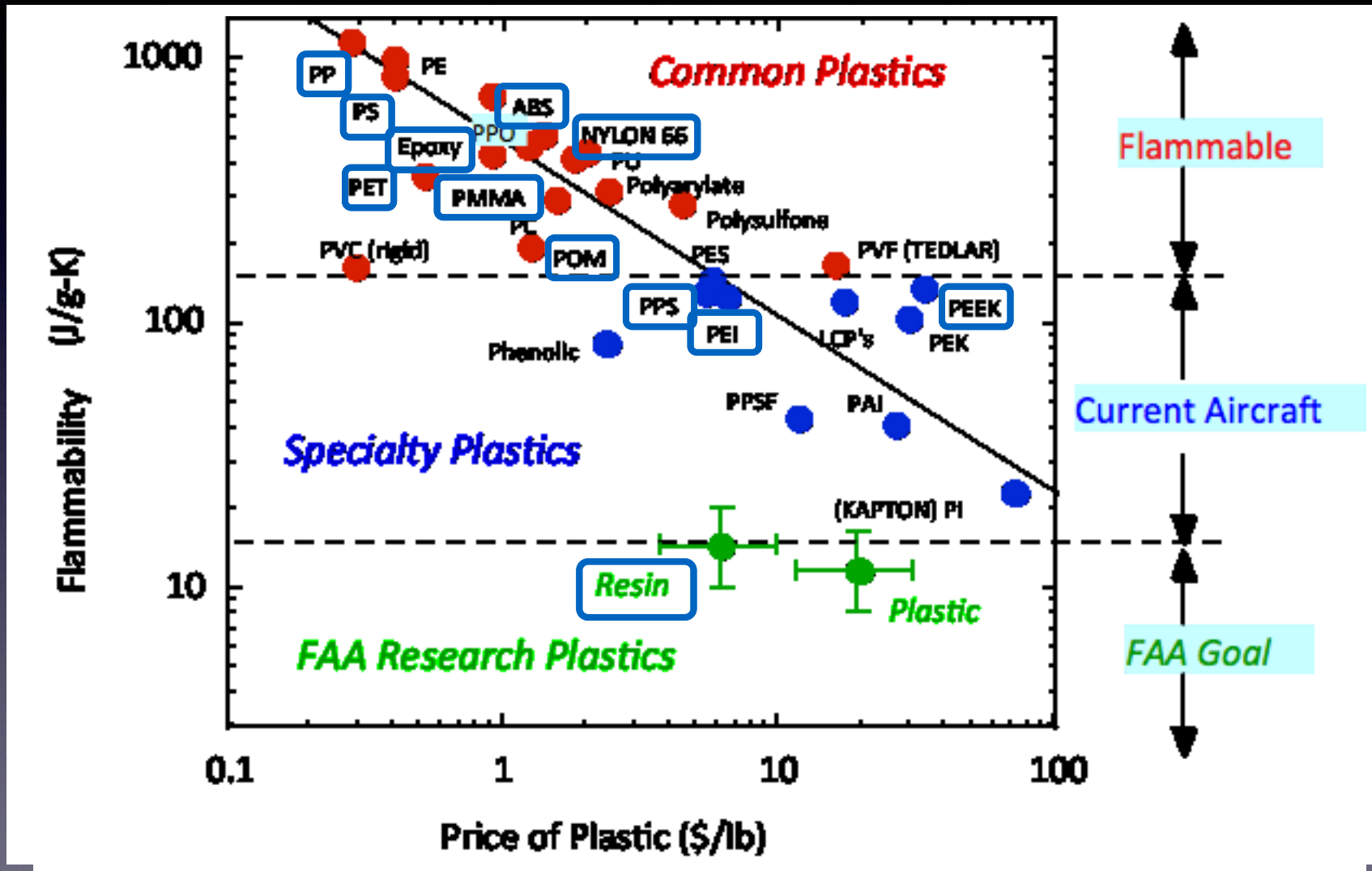
Non-charring

Charring

After



Flammability (Heat Release Capacity) Ranking by Cost

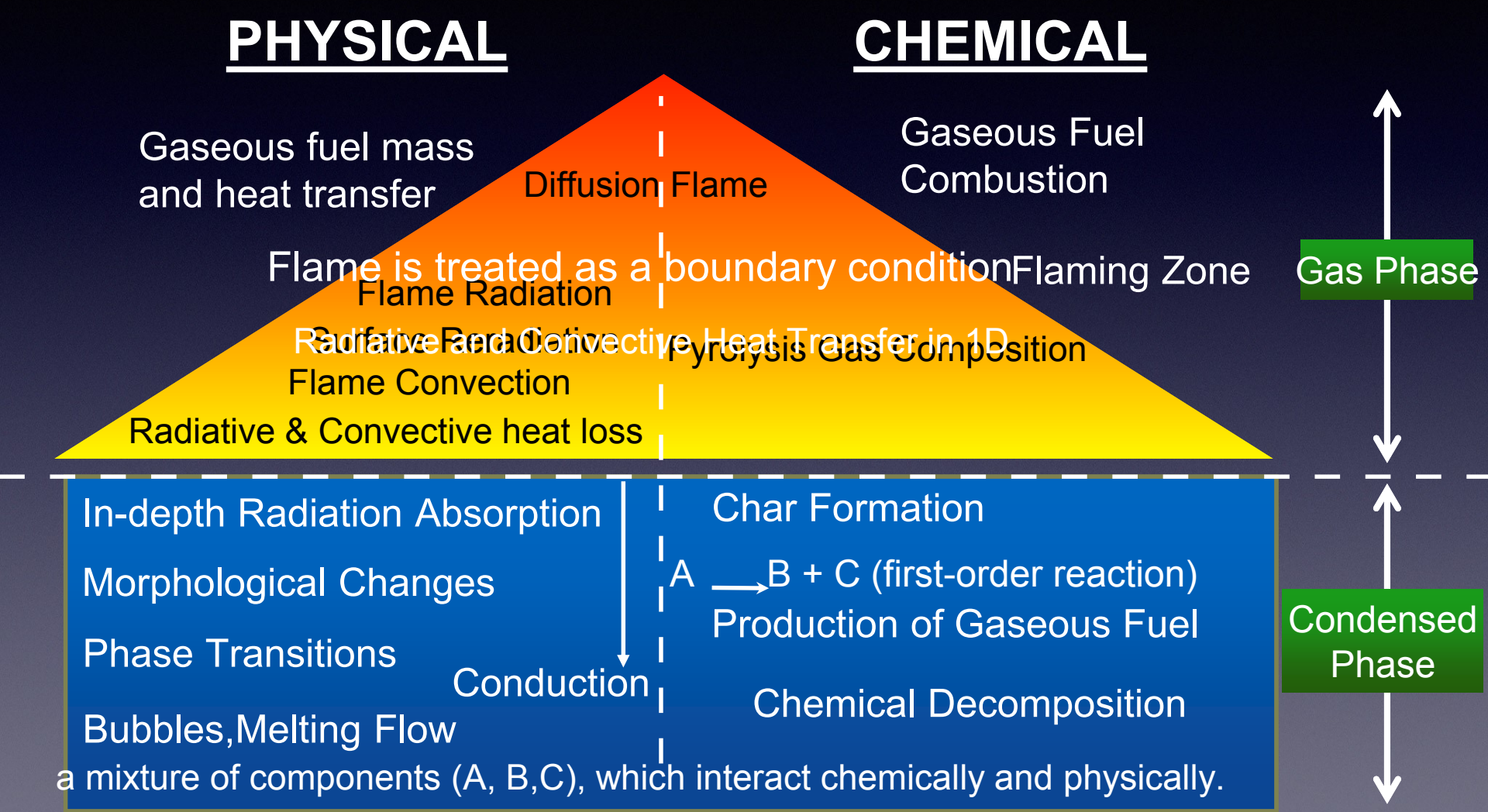


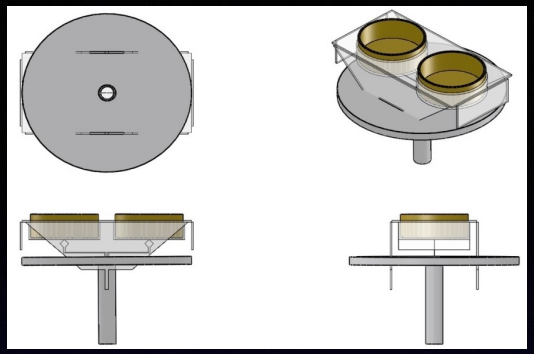
R. Lyon and R. Walter Ranking Flammability of Aircraft Materials using Microscale Combustion Calorimetry (2005)

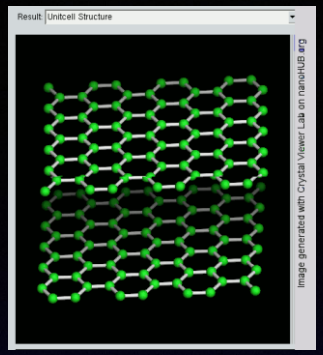
Motivation

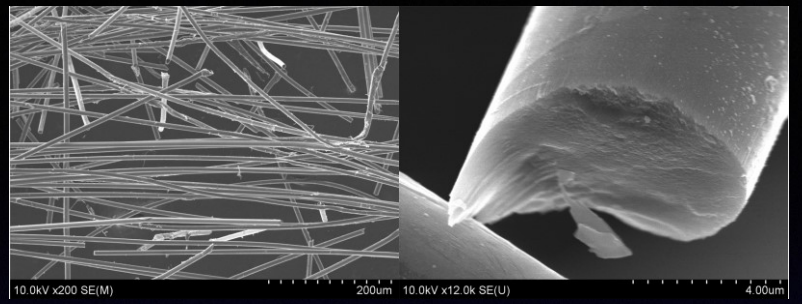
- Comprehensive numerical models that predict the rate of fuel generation by a pyrolyzing solid have been developed. (i.e. FDS, ThermaKin, Gpyro)
- Models are based on fundamental physical and chemical properties.
- Develop a systematic experimental procedure for measurement and validation of the core properties.

Mechanism of Polymer Combustion









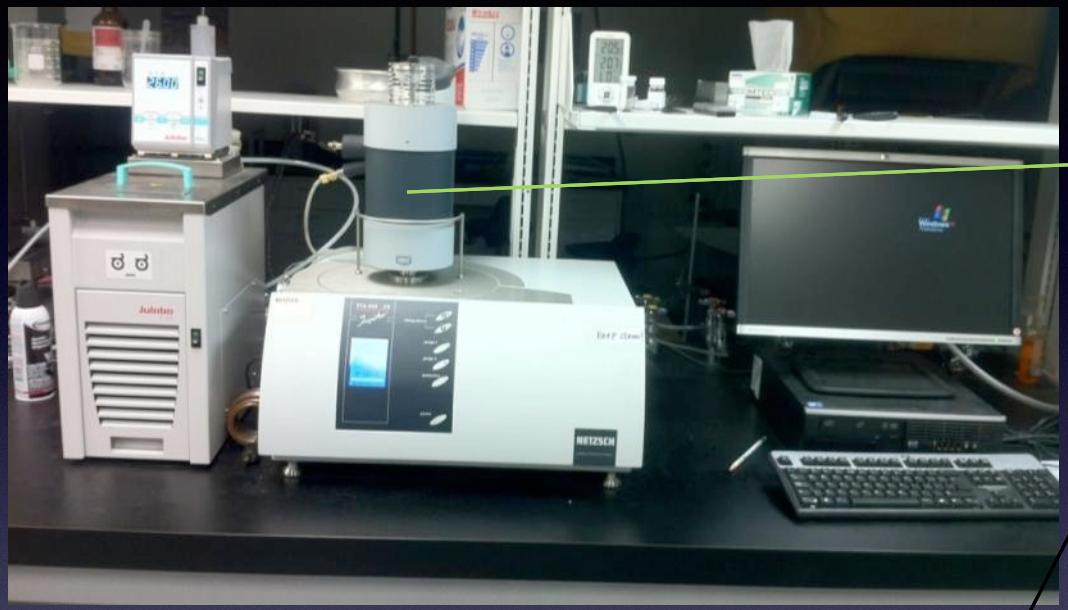
- Part 1

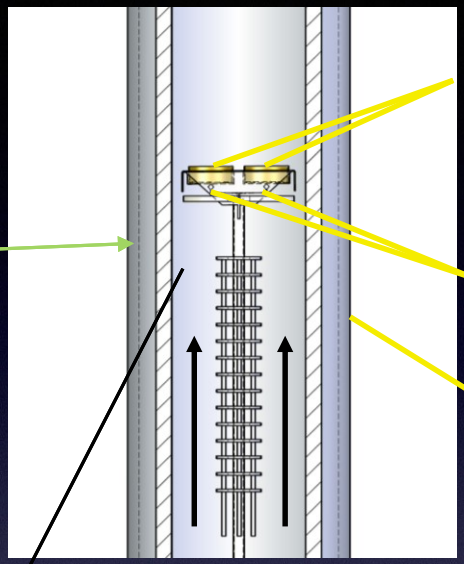
Milligram-scale Parameterization

Milligram Approach

Material Properties

Simultaneous Thermal Analysis(STA)

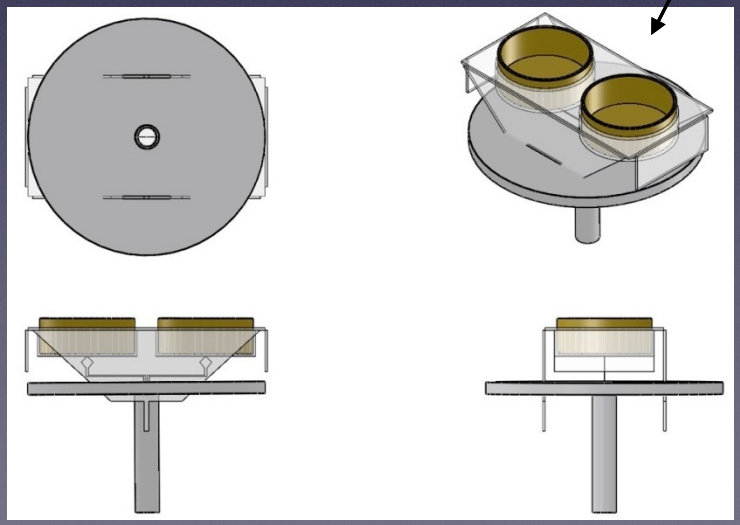




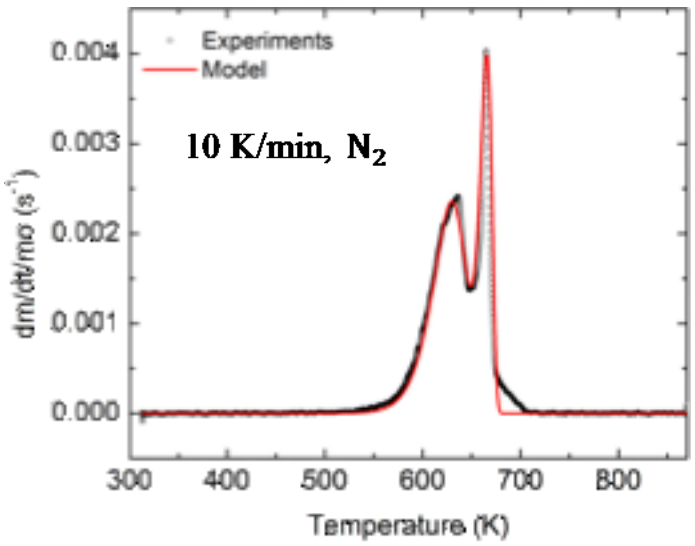
Sample and reference pans

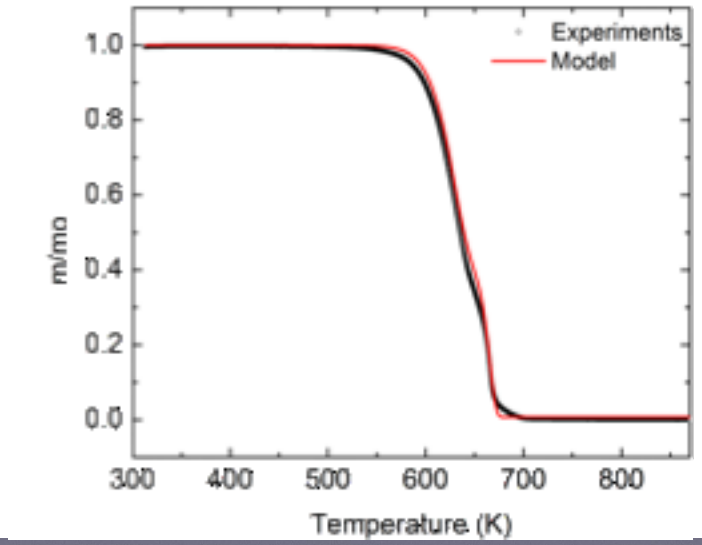
Heat flow sensing thermocouples

Electric heating element



Kinetics of Degradation of Poly(oxymethylene) (POM)

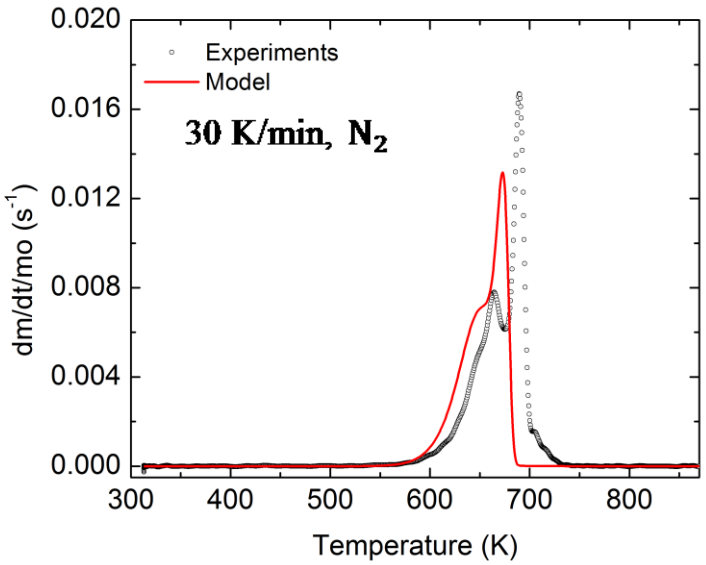


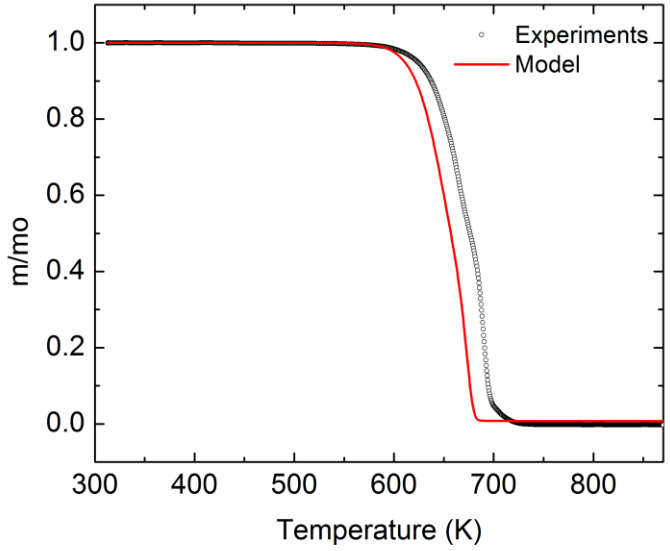


	REACTION STOICHIOMETRY
REACTION1	POM -> 0.4 POM_Res1 +0.6 POM_g1
REACTION2	POM_Res1 -> 0.02 POM_Res2 + 0.98 POM_g2

ARRHENIUS	A (s^{-1})	E (kJ mol^{-1})
REACTION1	$3.8\times 10^{14} \pm 50\ \%$	$200 \pm 5\ \%$
REACTION2	$4.8\times 10^{44} \pm 20\ \%$	$590 \pm 2\ \%$

Kinetics of Degradation of POM





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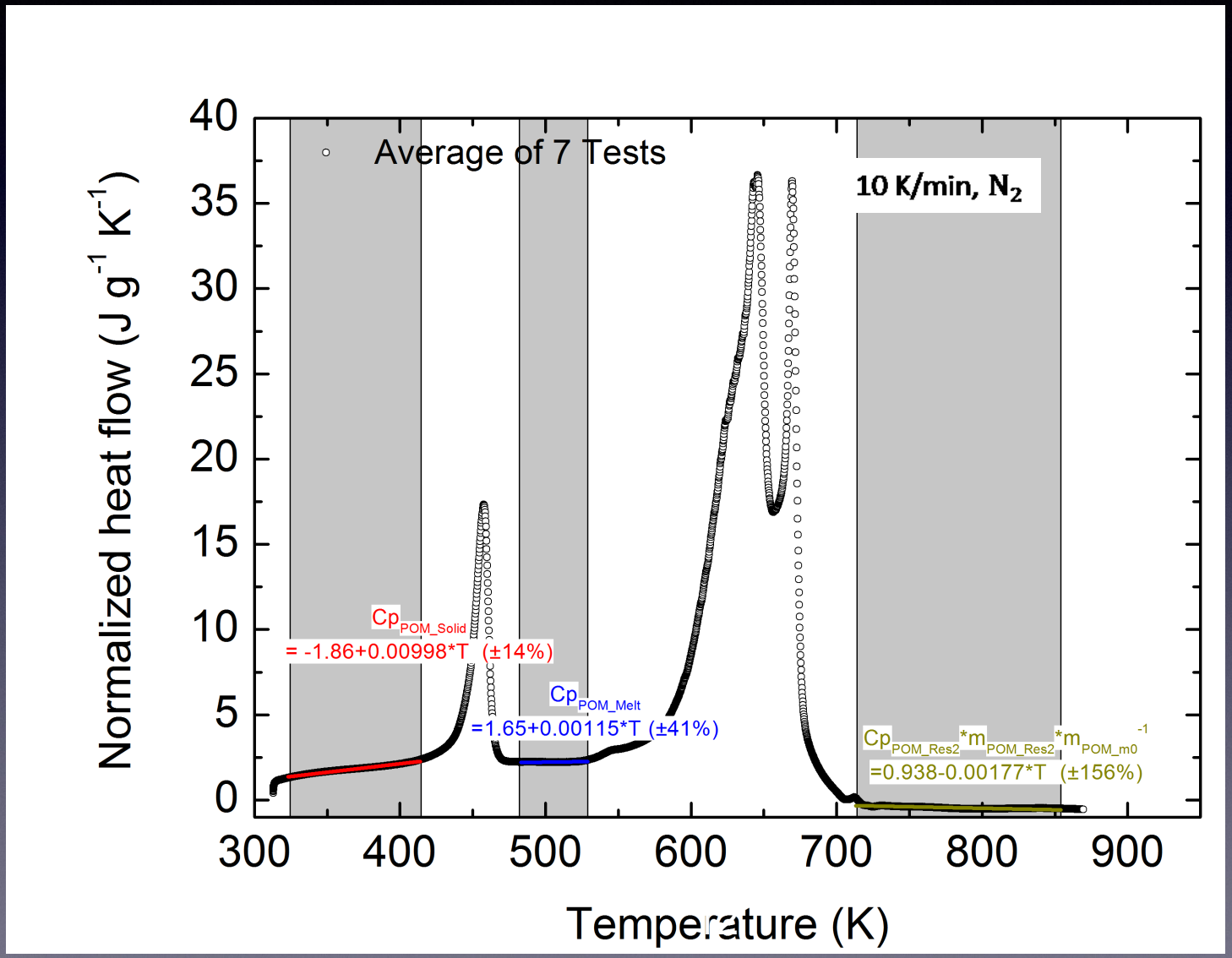
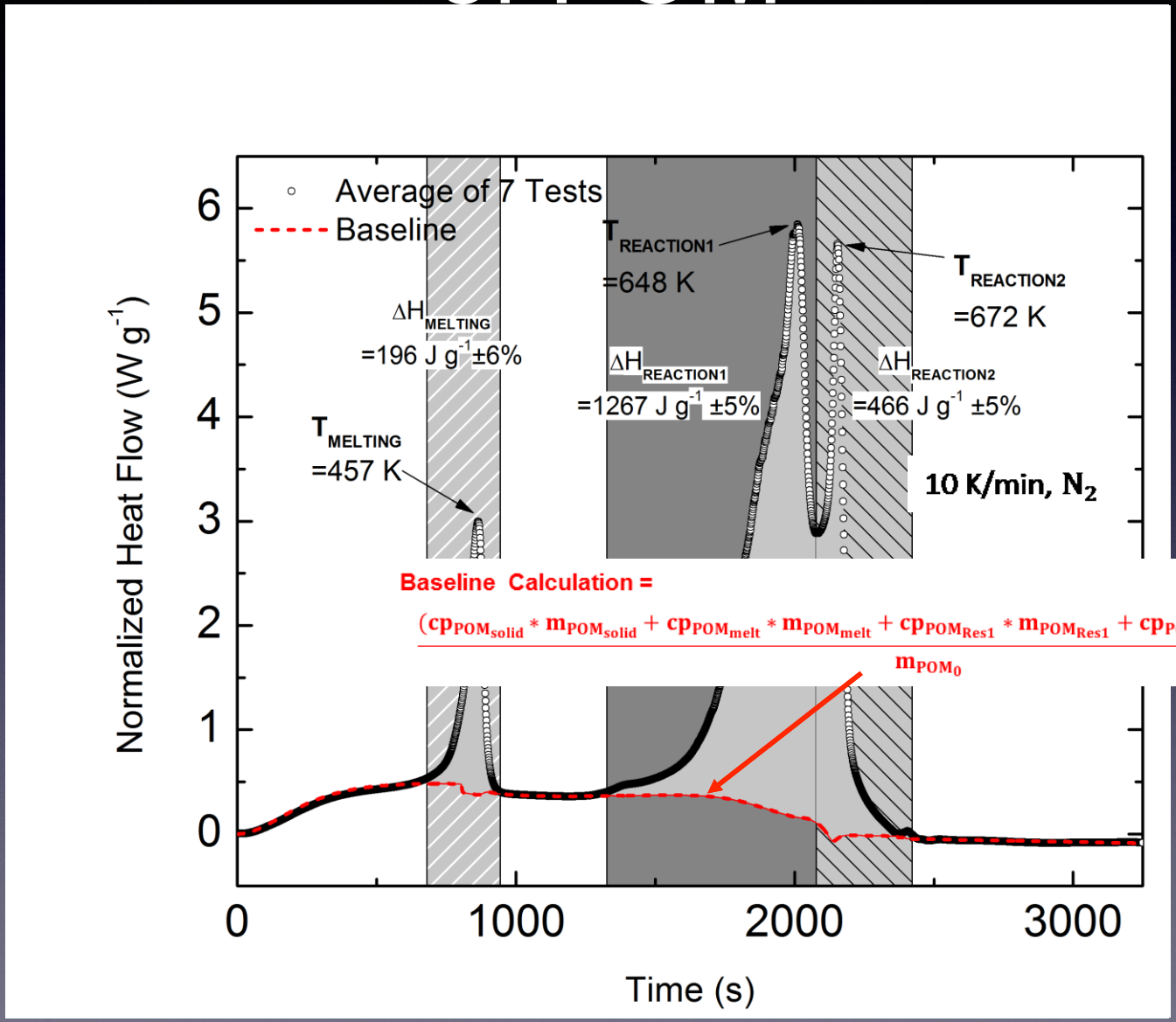
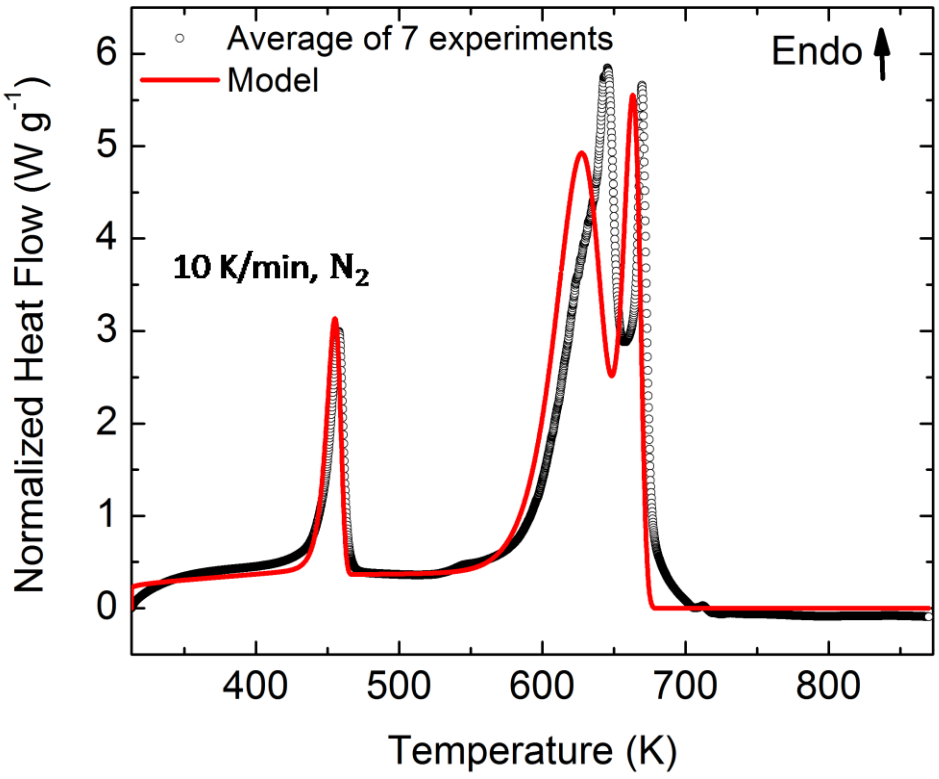
Thermodynamics of Degradation of POM



Thermodynamics of Degradation of POM



Thermodynamics of Degradation of POM

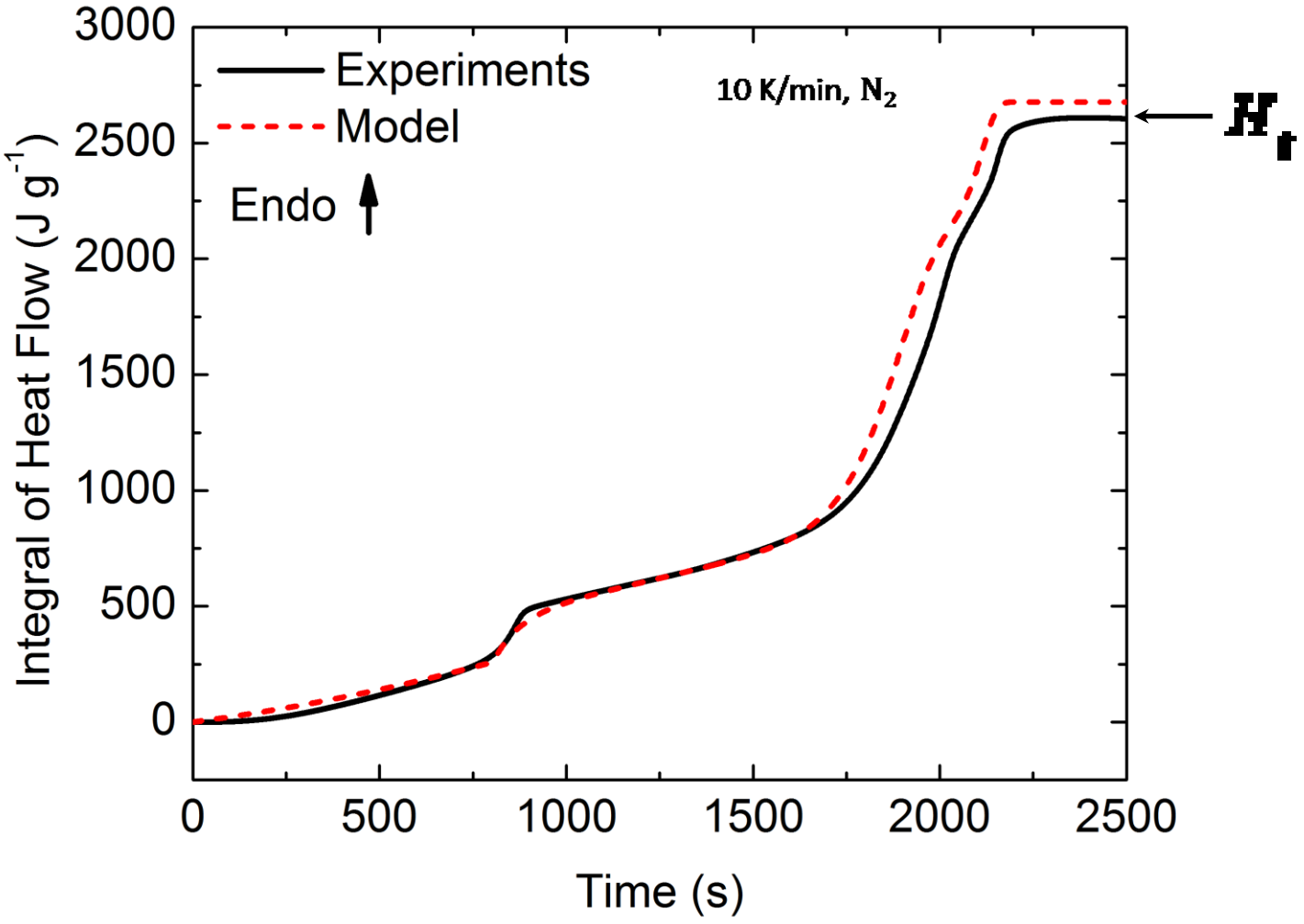


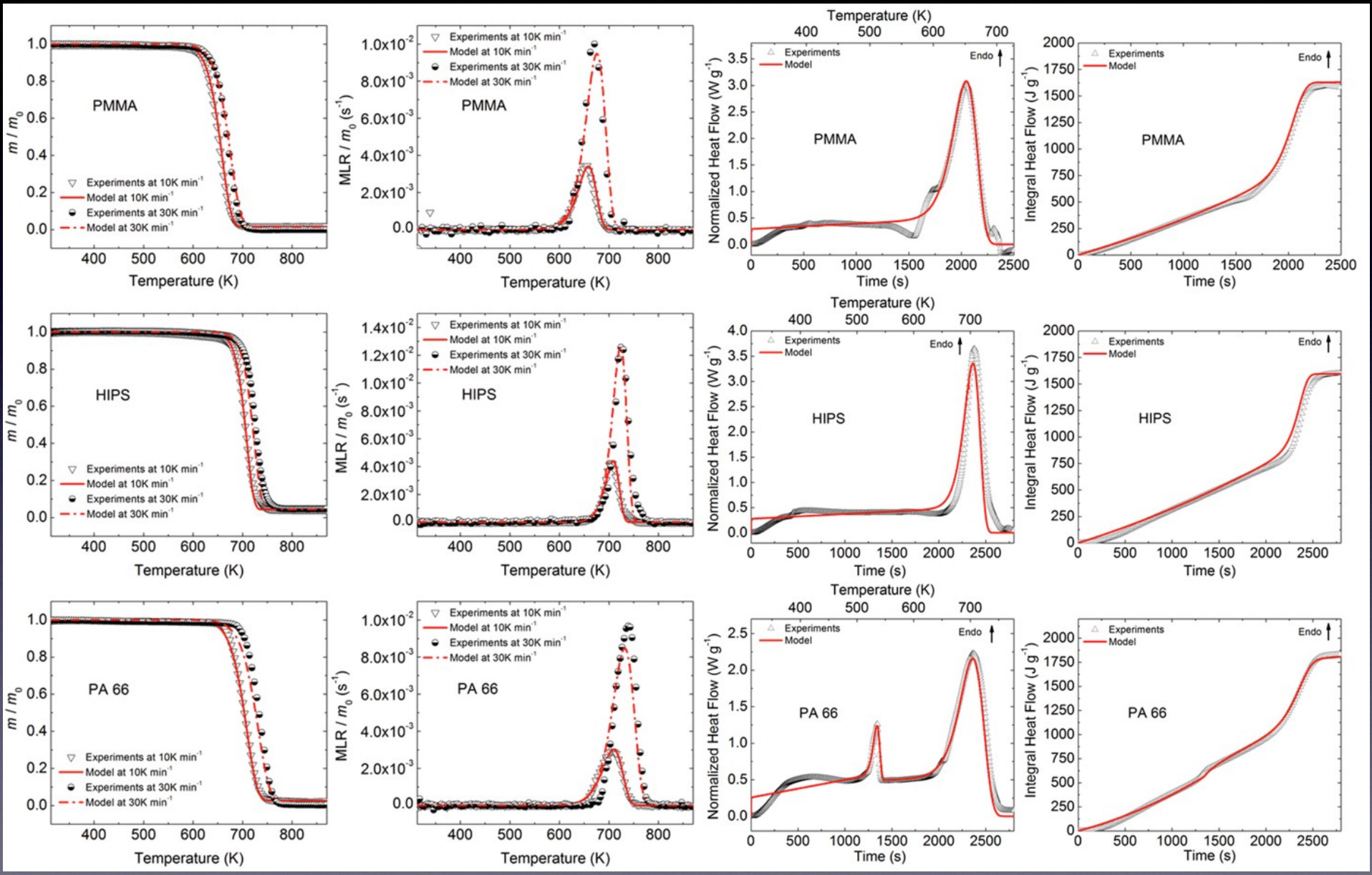
REACTION0: POM_Soild -> POM_Melt
STOICHIOMETRY: 1 1
ARRHENIUS: 2.7×10^{42} s^{-1} 382 k J mol^{-1}
HEAT: -197 J g^{-1} $\pm$ 6 %
TEMP LIMIT: L 457 K

REACTION1: POM_Melt -> POM_Res1 + POM_g1
STOICHIOMETRY: 1 0.4 0.6
ARRHENIUS: 3.8×10^{14} s^{-1} $\pm$ 50 % 200 kJ mol^{-1} $\pm$ 5 %
HEAT: -1190 J g^{-1} $\pm$ 5 %

REACTION2: POM_Res1 -> POM_Res2 + POM_g2
STOICHIOMETRY: 1 0.02 0.98
ARRHENIUS: 4.8×10^{44} s^{-1} $\pm$ 20% 590 kJ mol^{-1} $\pm$ 2 %
HEAT: -1350 J g^{-1} $\pm$ 5 %

Heat of Gasification of POM




PMMA
HIPS
PA 66
m / m0
MLR / m0 (s-1)
Normalized Heat Flow (W g-1)
Integral Heat Flow (J g-1)
Temperature (K)
Time (s)
Experiments at 10K min-1
Model at 10K min-1
Experiments at 30K min-1
Model at 30K min-1
Experiments
Model
Endo

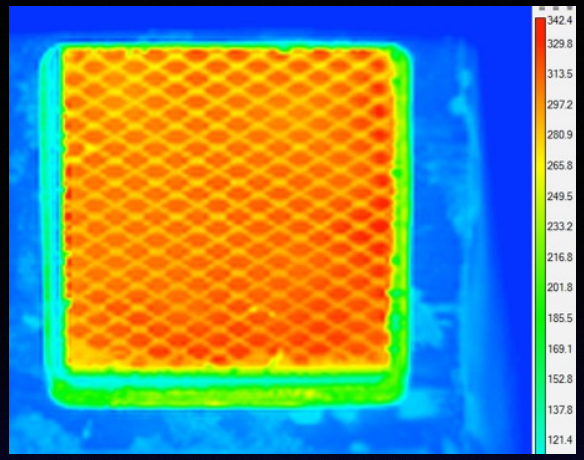
Non-charring and Charring Polymers

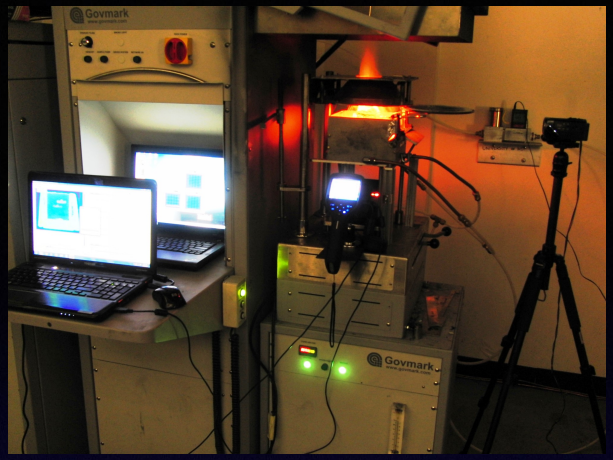
Polymer	A_1 (s^{-1})	E_1 (kJ mol^{-1})	θ_1	A_2 (s^{-1})	E_2 (kJ mol^{-1})	θ_2	A_m (s^{-1})	E_m (kJ mol^{-1})
PA 66	$3.86 \times 10^{12} \pm 50\%$	$200 \pm 2\%$	0.026	N/A	N/A	N/A	2.0×10^{39}	420
PP	$9.60 \times 10^{22} \pm 50\%$	$350 \pm 2\%$	0.018	N/A	N/A	N/A	2.5×10^{35}	308
PLA	$1.68 \times 10^{18} \pm 50\%$	$245 \pm 3\%$	0.100	$4.58 \times 10^{6} \pm 30\%$	$126 \pm 5\%$	0.400	6.0×10^{40}	355

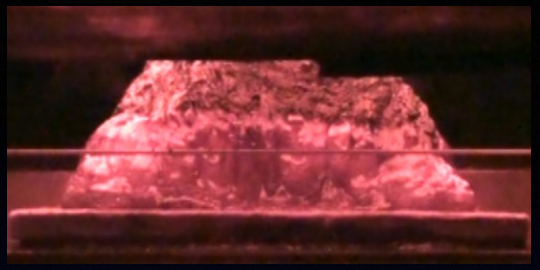
charring

J. Li; S. I. Stoliarov, *Combust Flame* 160 (7) (2013) pp. 1287-1297

J. Li; S. I. Stoliarov, *Polymer Degradation and Stability* 106 (2014) pp. 2-15

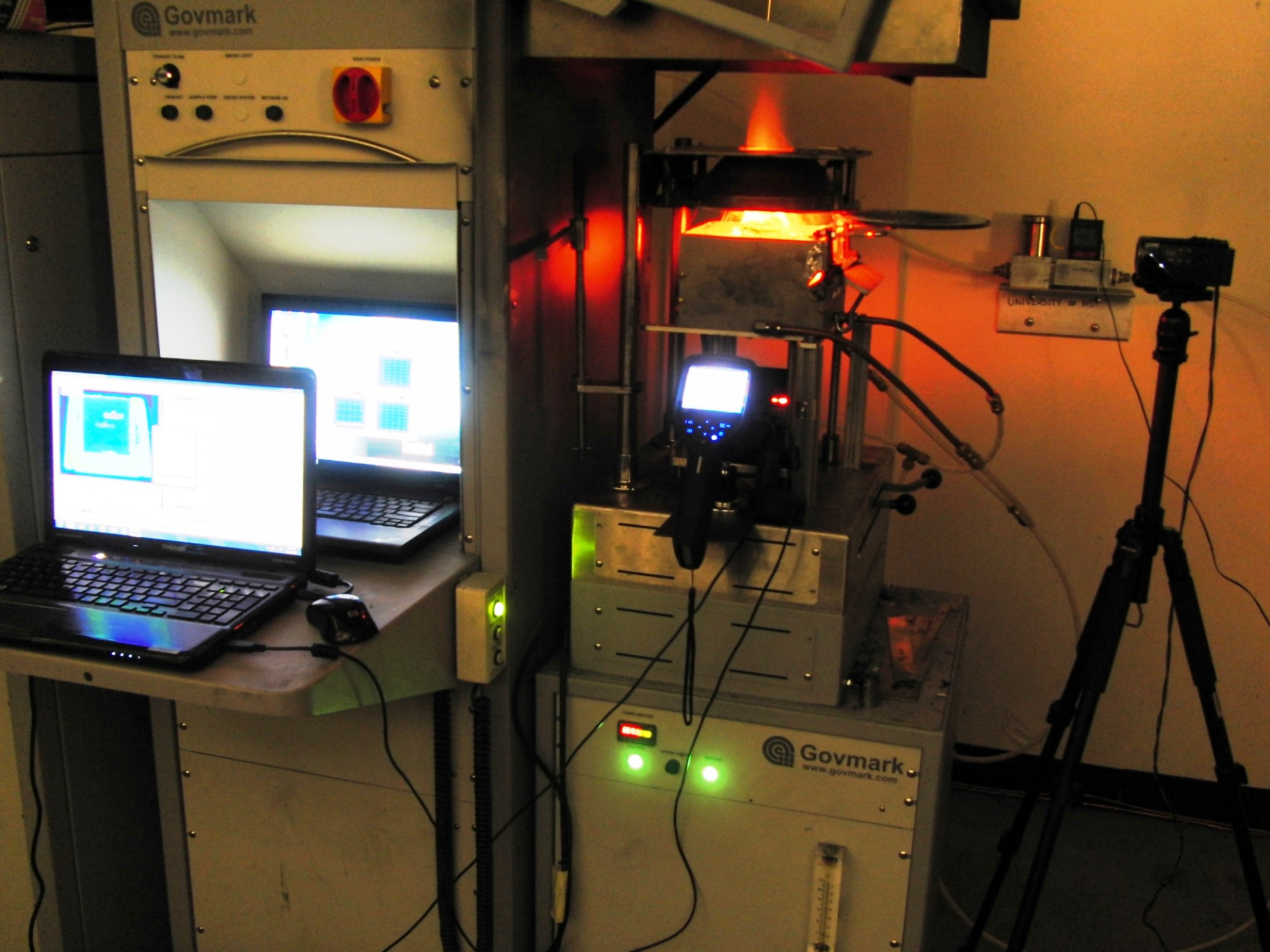




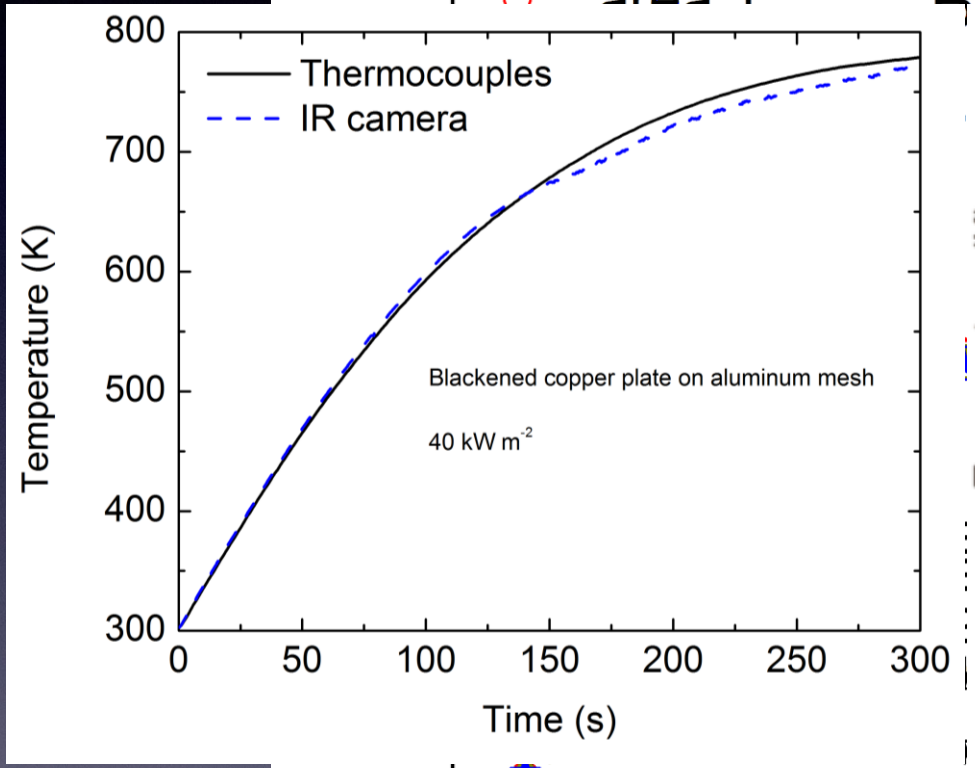


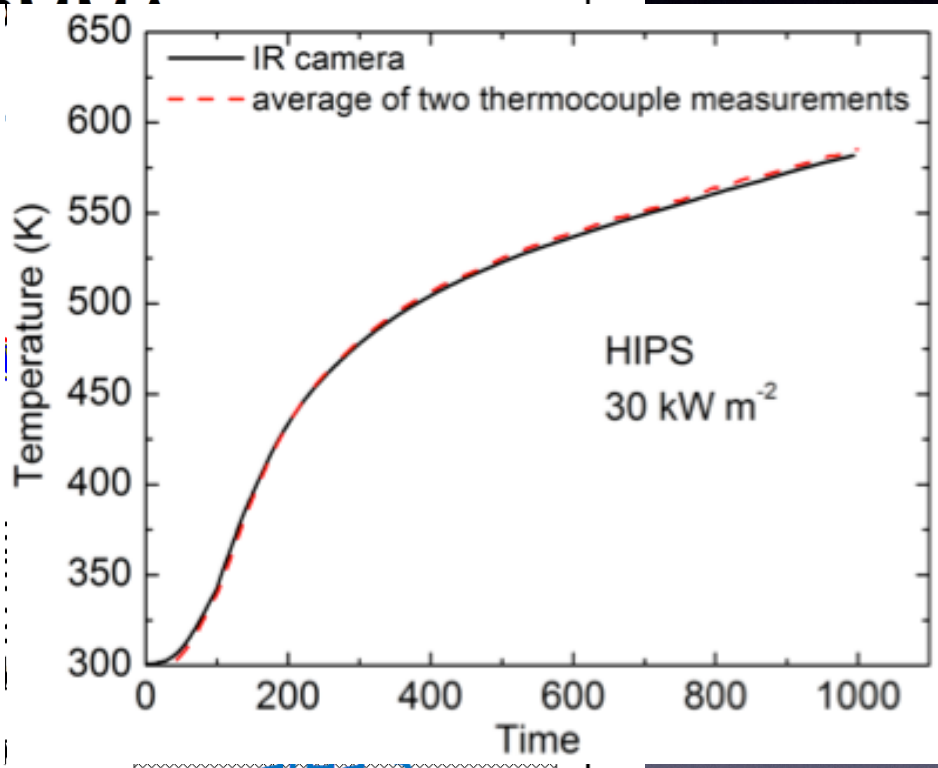
- Part II

Bench-scale Parameterization & Validation


Govmark
www.govmark.com
Govmark
www.govmark.com

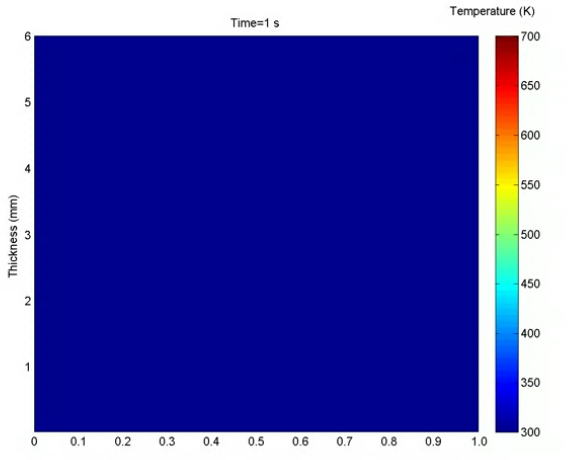
Validation of Temperature Measurement on CAPA+RTS

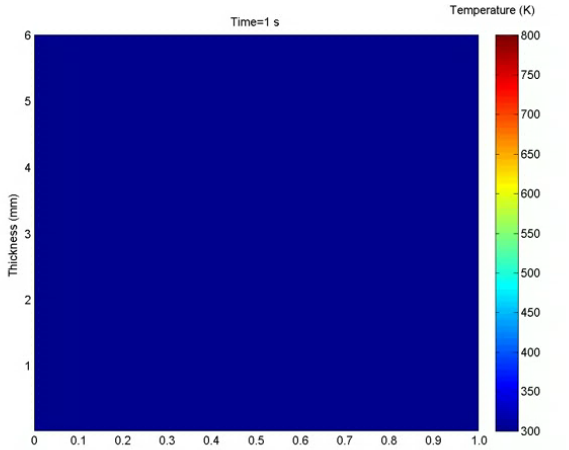


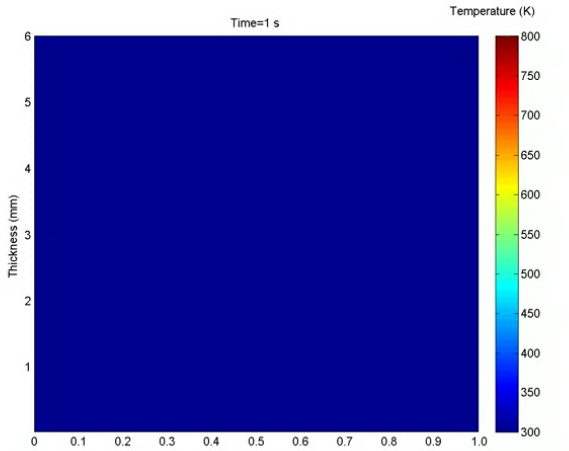


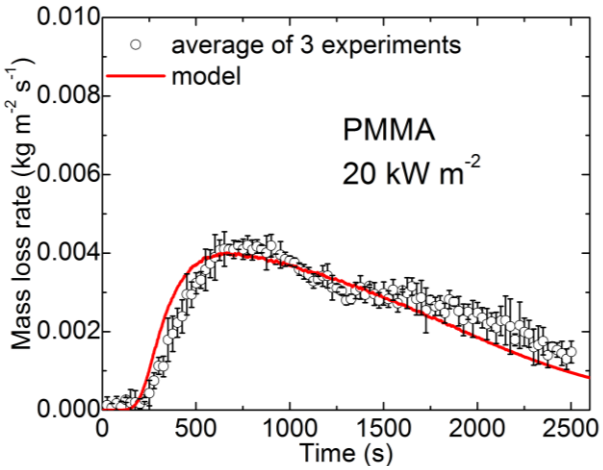
J. Li, J. Gong, S.I. Stoliarov, *Int J Heat Mass Tran*, 77 (2014) 738-744.

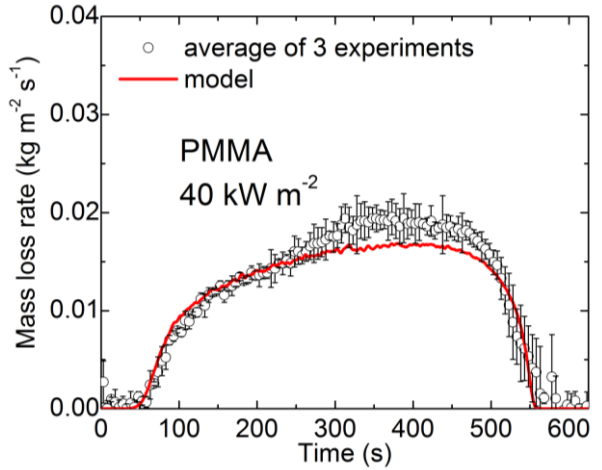
PMMA

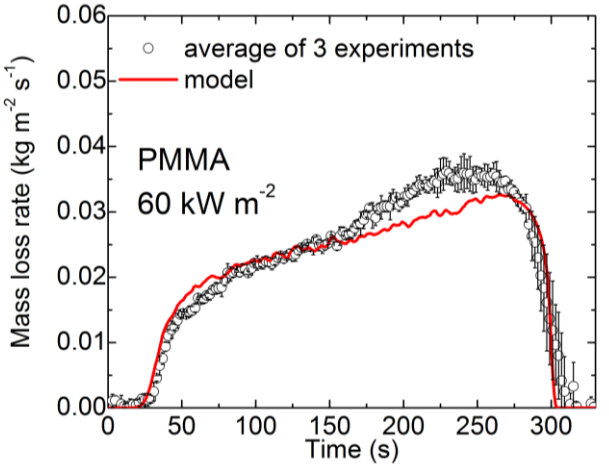

Time=1 s
Temperature (K)
Thickness (mm)


Time=1 s
Temperature (K)
Thickness (mm)

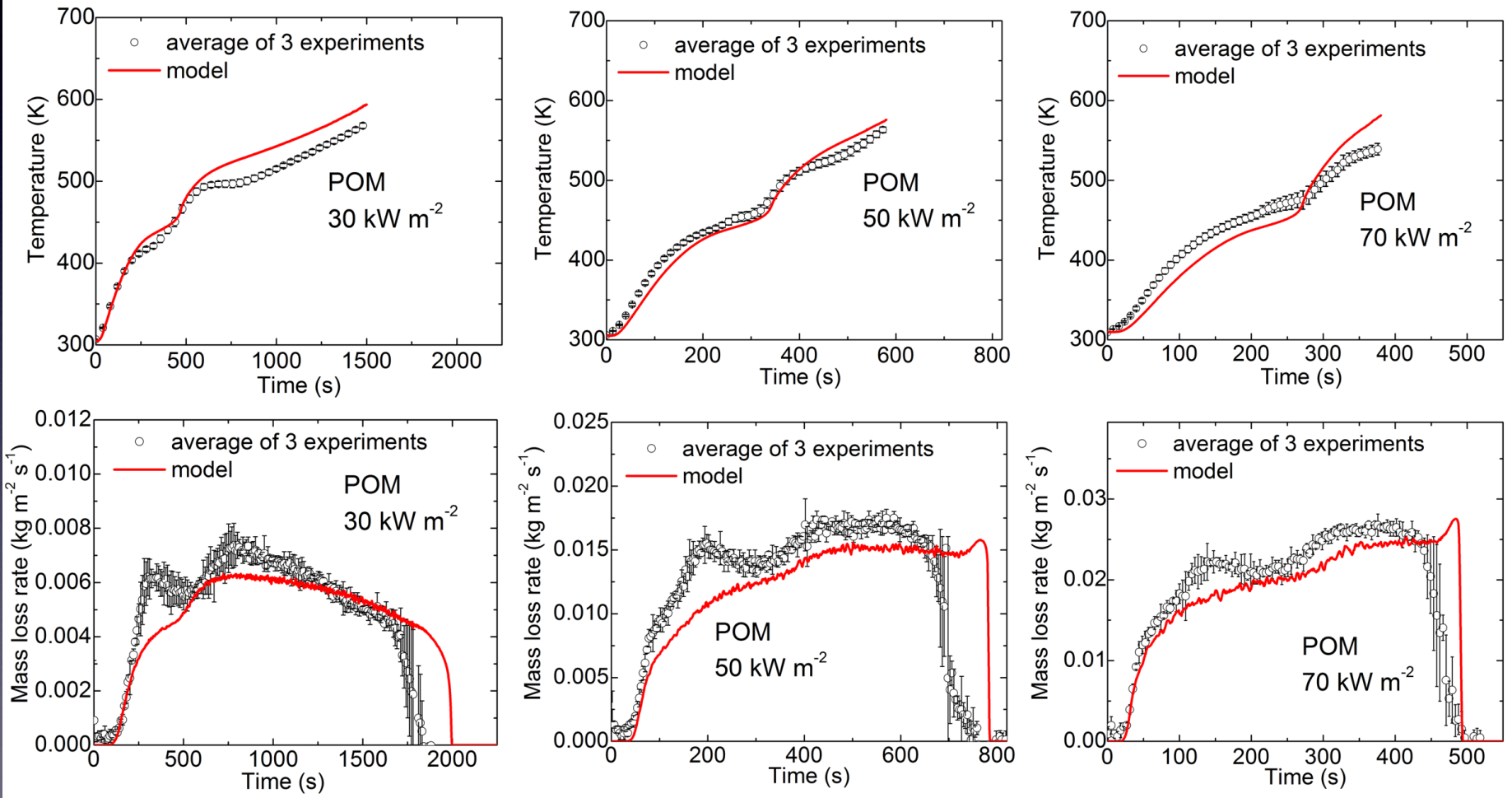

Time=1 s
Temperature (K)
Thickness (mm)


average of 3 experiments
model
PMMA
20 kW m-2
Mass loss rate (kg m-2 s-1)
Time (s)


average of 3 experiments
model
PMMA
40 kW m-2
Mass loss rate (kg m-2 s-1)
Time (s)

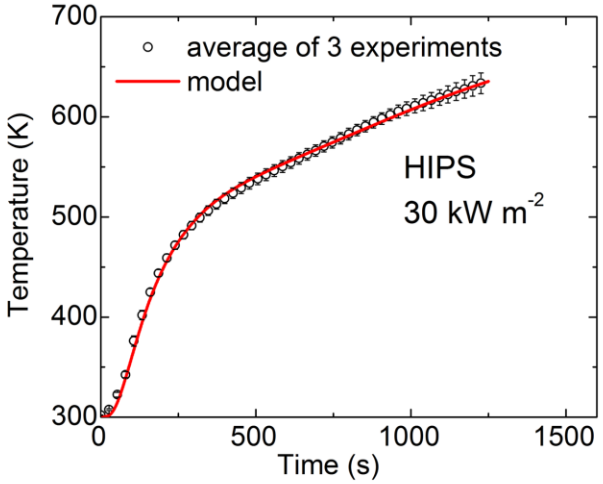

average of 3 experiments
model
PMMA
60 kW m-2
Mass loss rate (kg m-2 s-1)
Time (s)

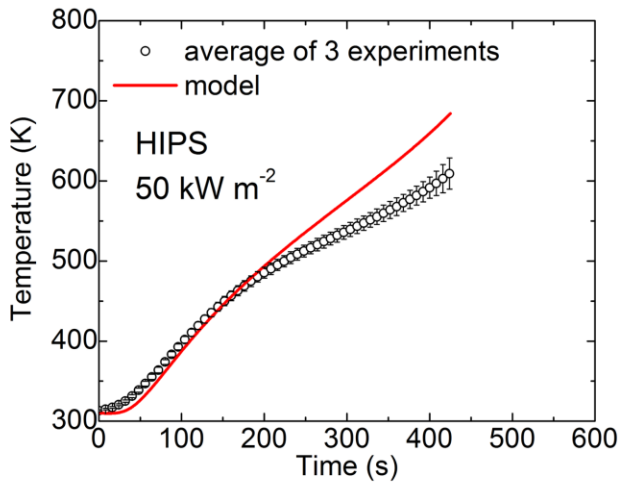
Non-charring Polymers

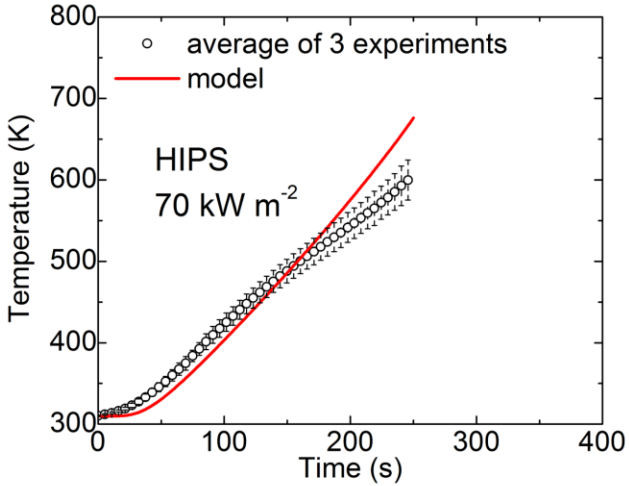


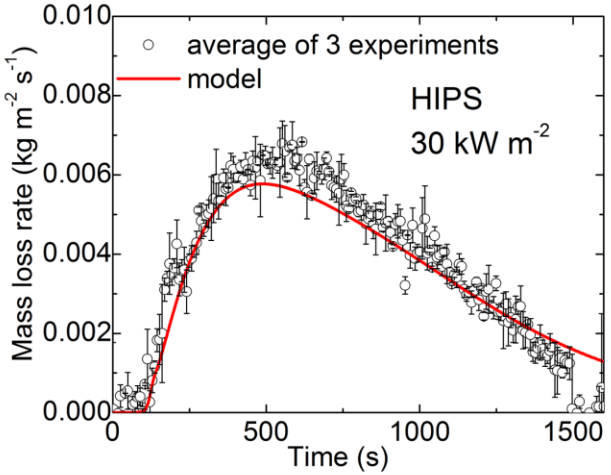
J. Li, J. Gong, S.I. Stoliarov, *Int J Heat Mass Tran*, 77 (2014) 738-744.

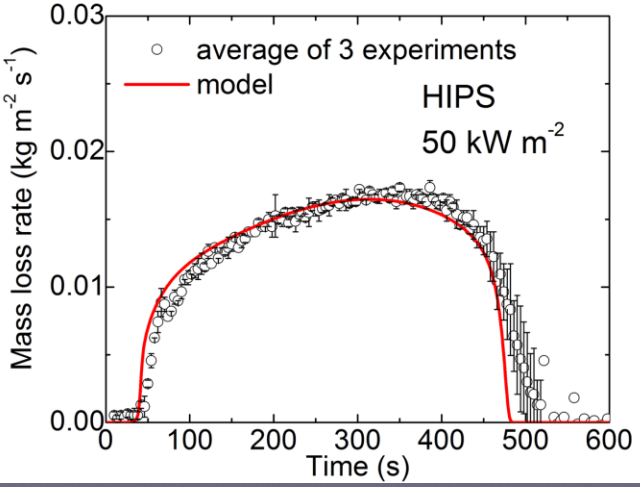
Non-charring Polymers

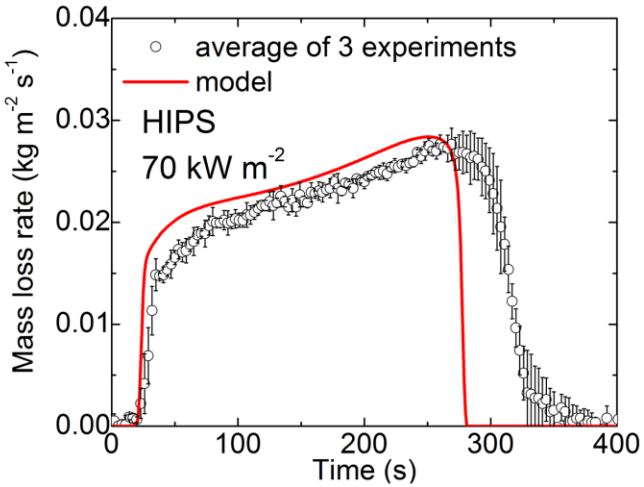












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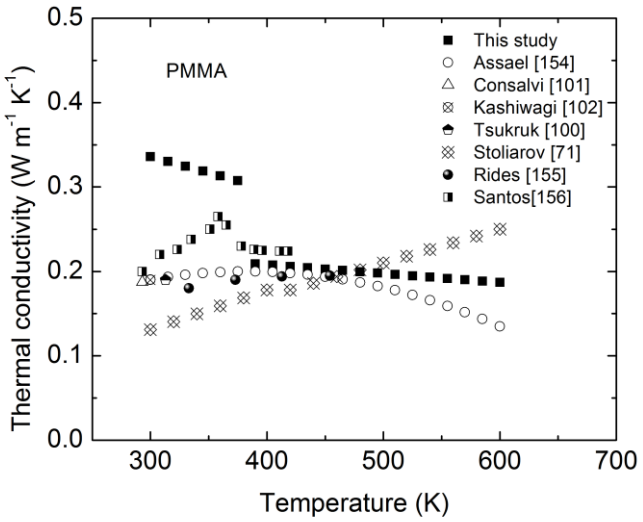
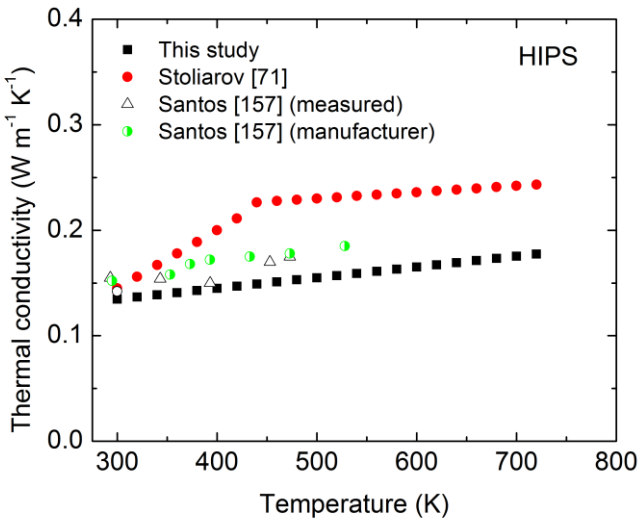
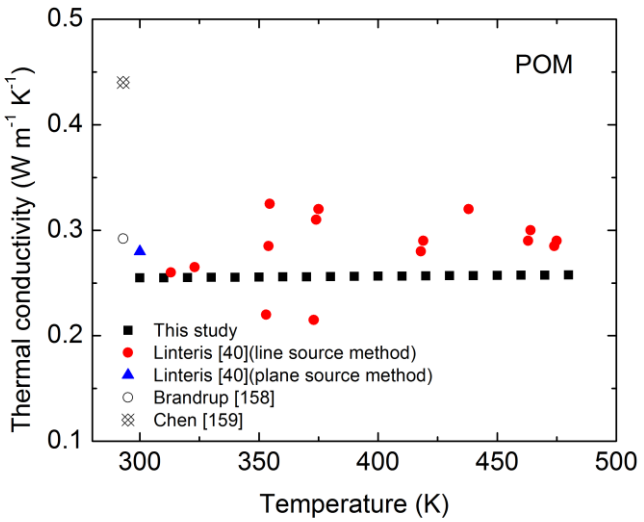
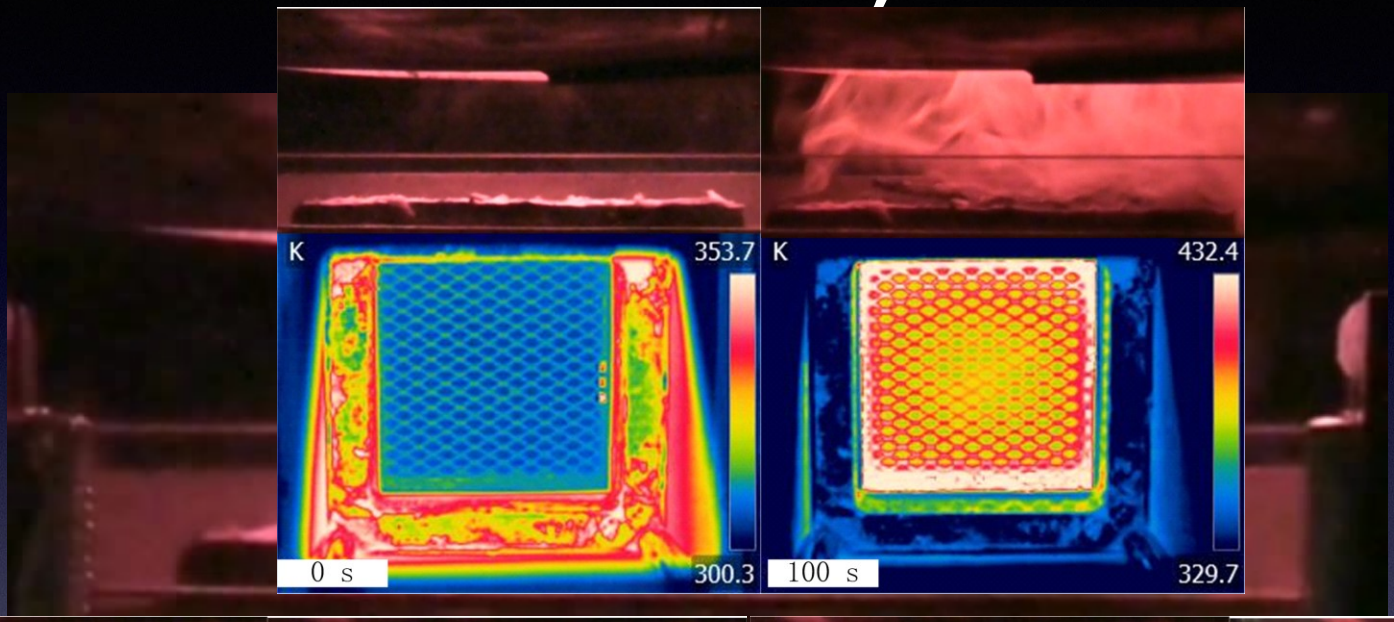
Thermal Conductivity

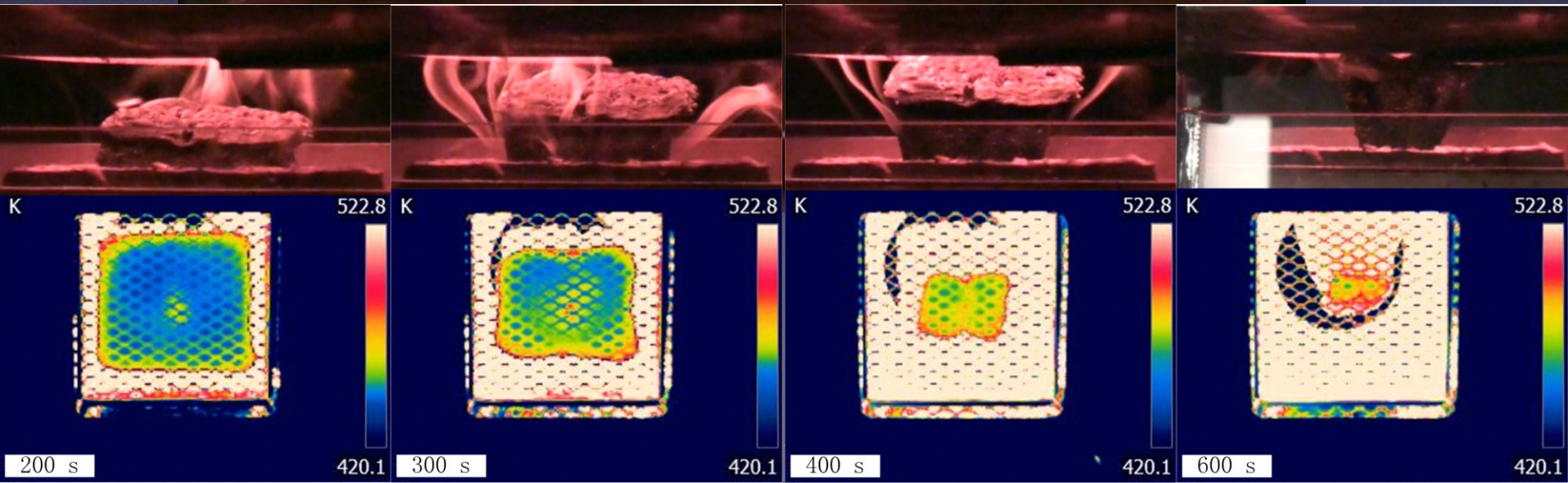




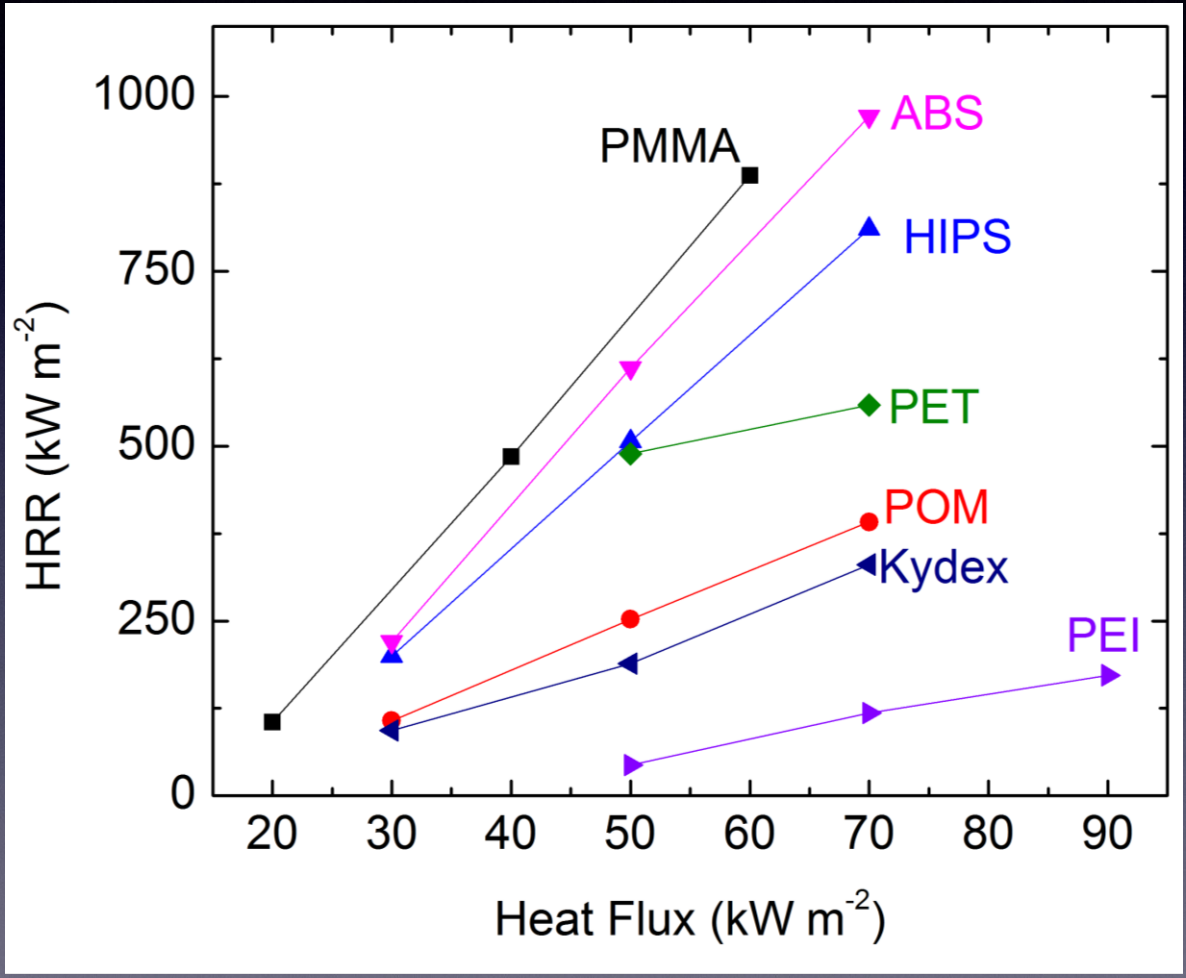


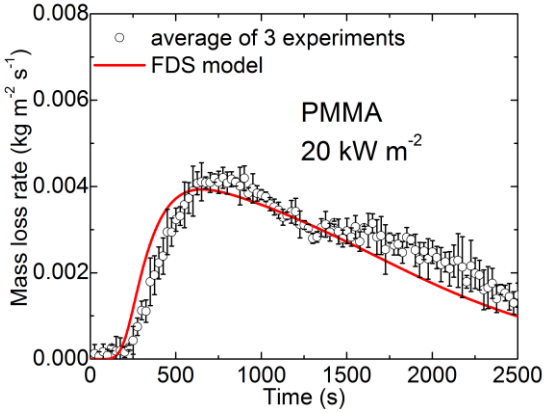
Kydex (alloy of PMMA and PVC)

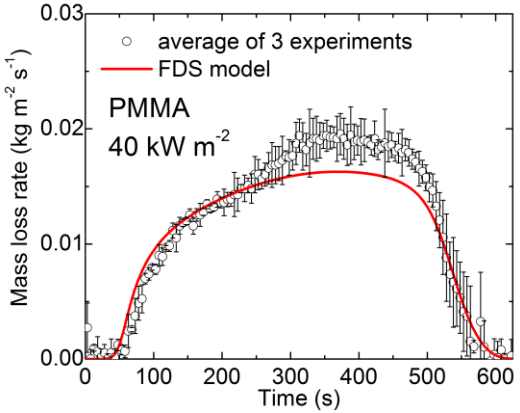


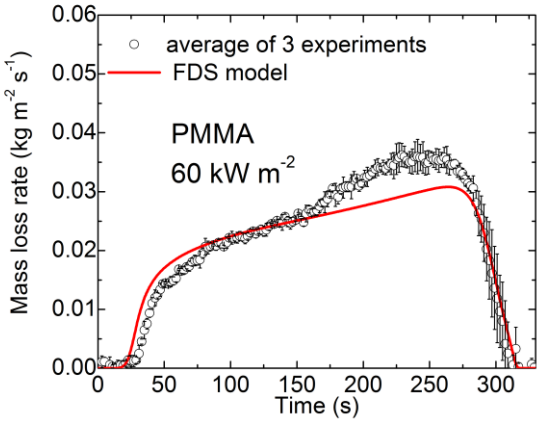


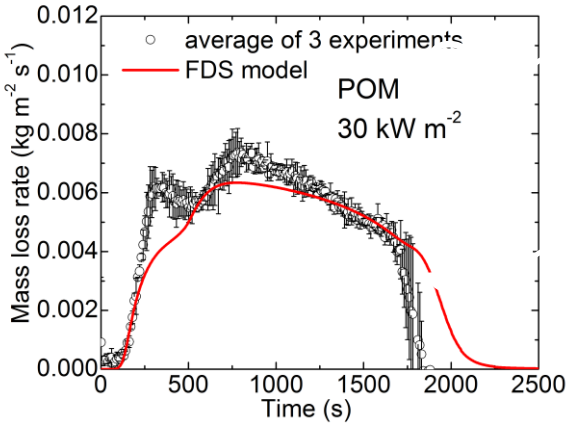
HRR vs HF

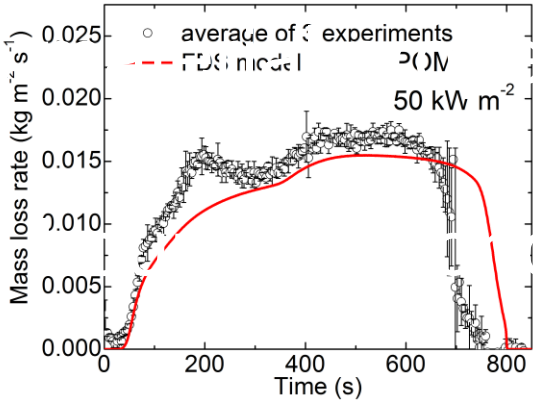

1000
750
500
250
0
HRR (kW m-2)
20
30
40
50
60
70
80
90
Heat Flux (kW m-2)
PMMA
ABS
HIPS
PET
POM
Kydex
PEI

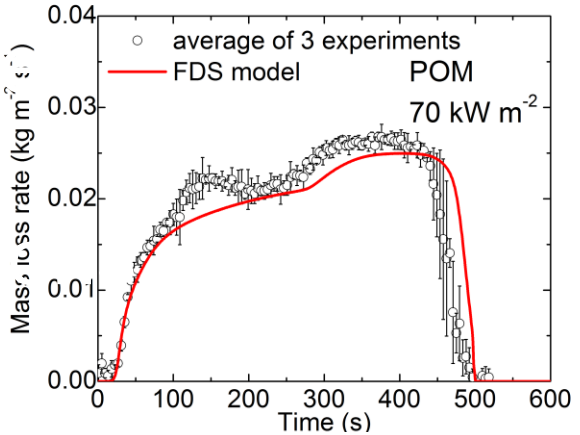

average of 3 experiments
FDS model
PMMA
20 kW m-2
Mass loss rate (kg m-2 s-1)
Time (s)

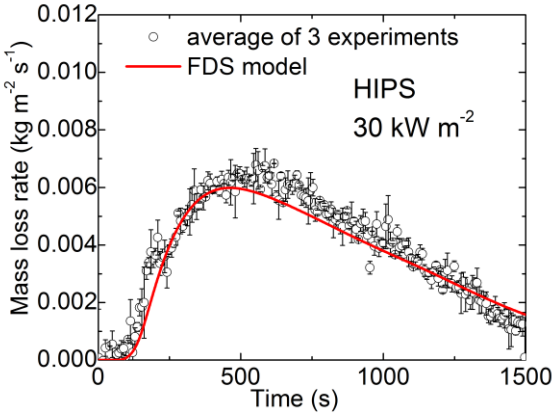

average of 3 experiments
FDS model
PMMA
40 kW m-2
Mass loss rate (kg m-2 s-1)
Time (s)

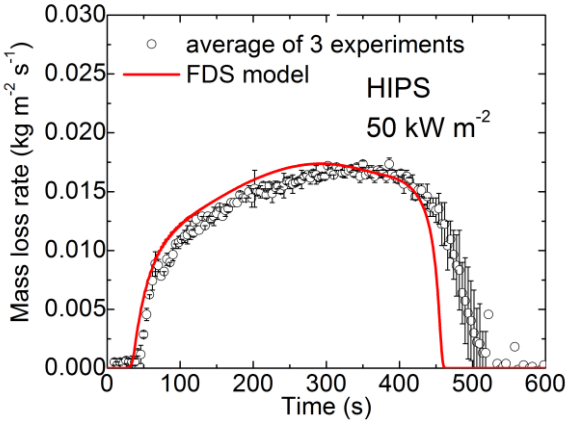

average of 3 experiments
FDS model
PMMA
60 kW m-2
Mass loss rate (kg m-2 s-1)
Time (s)

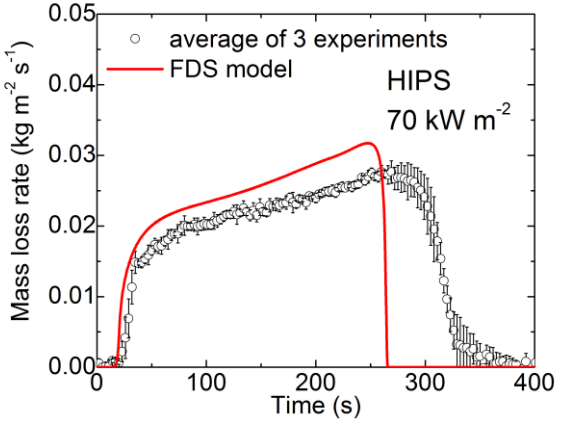

average of 3 experiments
FDS model
POM
30 kW m-2
Mass loss rate (kg m-2 s-1)
Time (s)


average of 3 experiments
FDS model
POM
50 kW m-2
Mass loss rate (kg m-2 s-1)
Time (s)


average of 3 experiments
FDS model
POM
70 kW m-2
Time (s)


average of 3 experiments
FDS model
HIPS
30 kW m-2
Mass loss rate (kg m-2 s-1)
Time (s)


average of 3 experiments
FDS model
HIPS
50 kW m-2
Mass loss rate (kg m-2 s-1)
Time (s)


average of 3 experiments
FDS model
HIPS
70 kW m-2
Mass loss rate (kg m-2 s-1)
Time (s)

Conclusions

- First systematic approach that yields a global reaction model that simultaneously reproduces both TGA and DSC measurements.
- Temperature-dependent thermal conductivity of a solid material is extracted from material bottom surface temperature data in a computationally efficient way.
- Combination of experiments and modeling represents a routine that generates complete property sets and provides validation procedure at a modest experimental cost.

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Q&A