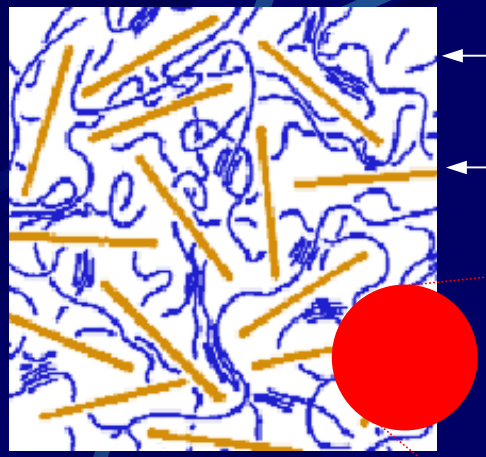
# Improved Thermal Stability of Imidazolium Treatments for Polymer Layered-Silicate Nanocomposites

Rick Davis*[1], Jeffrey W. Gilman[1], Walid H. Awad[1], Alexander B. Morgan[1], Paul C. Trulove[2], Hugh C. DeLong[3], Thomas E. Sutto[4], Lon Mathias[5], Cher Davis[1] and David Schiraldi[6]

[1]National Institute of Standards and Technology, Gaithersburg, MD
[2]Air Force Office of Scientific Research, Arlington, VA
[3]Chemistry Department, U.S. Naval Academy, Annapolis, MD
[4]Naval Research Laboratory, Chemistry Division, Washington, DC
[5]University of Southern Mississippi, Hattiesburg, MS
[6]KoSa, Charlotte, NC

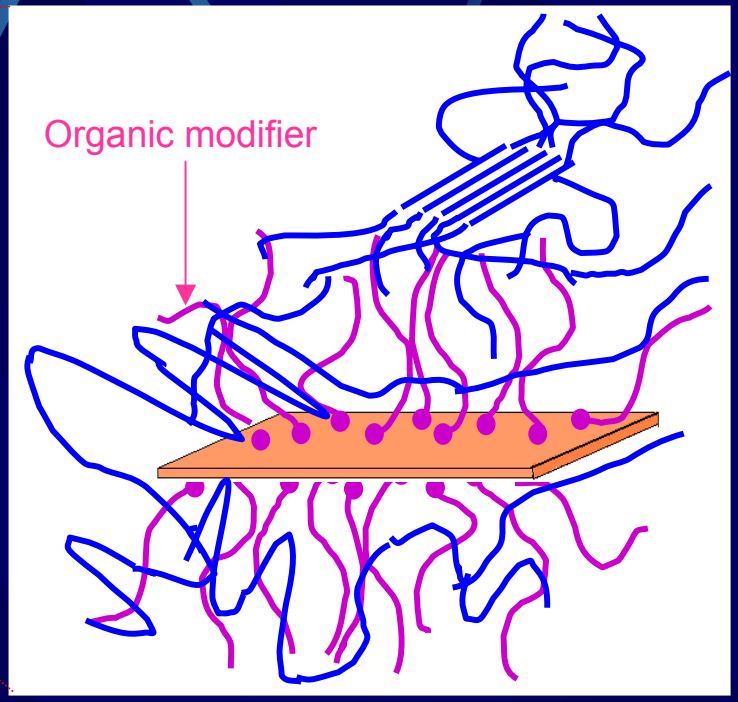
**201st Meeting of The Electrochemical Society**
**13th International Symposium on Molten Salts**
**May 14, 2002**

# Polymer Layered-Silicate Nanocomposites



Polymer

Organically treated clay sheets (50 nm x 50 nm x 1 nm)




Advantages:
- decreased flammability
- increased properties
- inexpensive

Problems with degradation
- limited recycling – toxic
- decreased mechanical properties
- increased flammability
- limited commercialization

# Unique Mechanism

**Clay reinforced Carbonaceous Char**

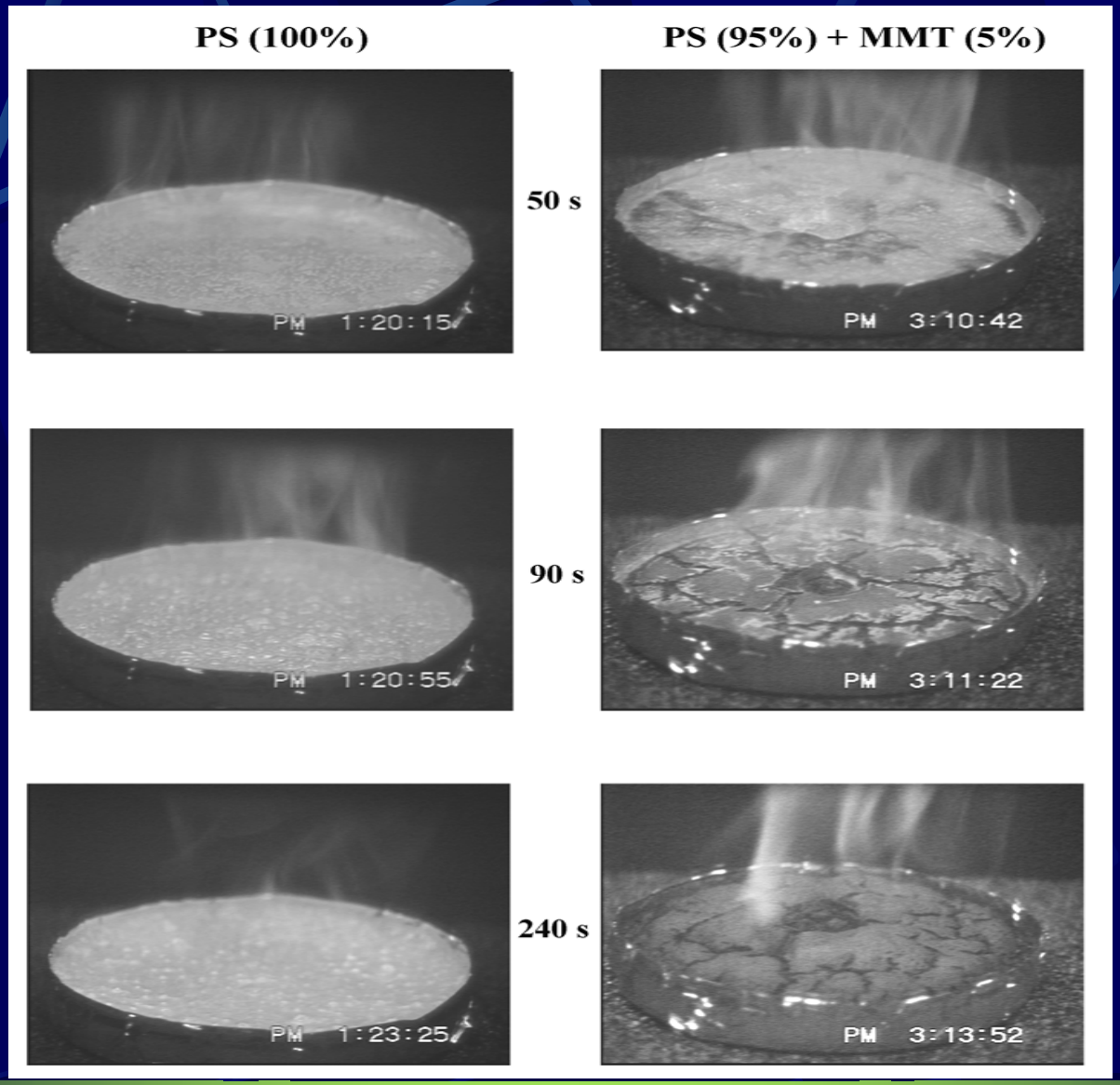
TEM

**Polymer/Clay Nanocomposite**

Improved Flammability
with
Improved
Mechanical Properties

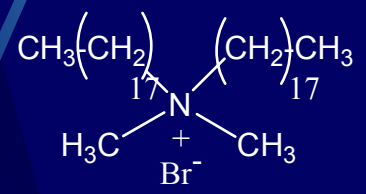
Gilman et al, *SAMPE Journal*, **1997**
Gilman, et al, *Chem Mater,* **2000**
Vaia et al, *Chem Mater,* **2000**

# Gasification of PS/Clay Nanocomposite

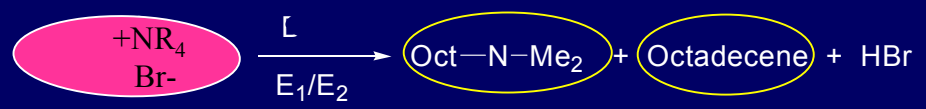


# DMDODA Thermal Degradation

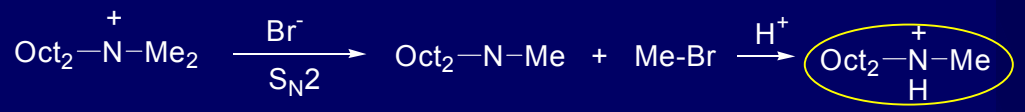
Me = $-CH_3$  Oct = $CH_3(CH_2)_{17}$  Octadecene = $CH_3(CH_2)_{15}CH{=}CH_2$



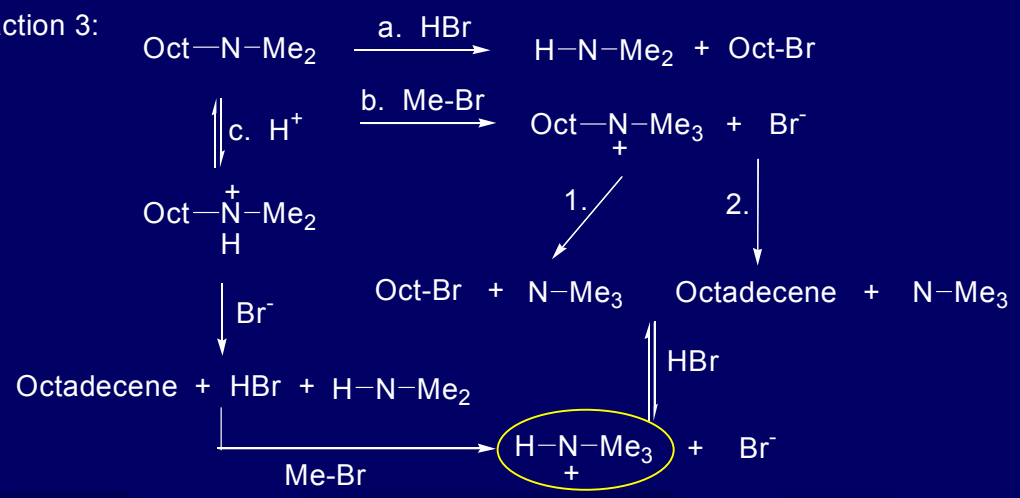
Reaction 1:



Reaction 2:

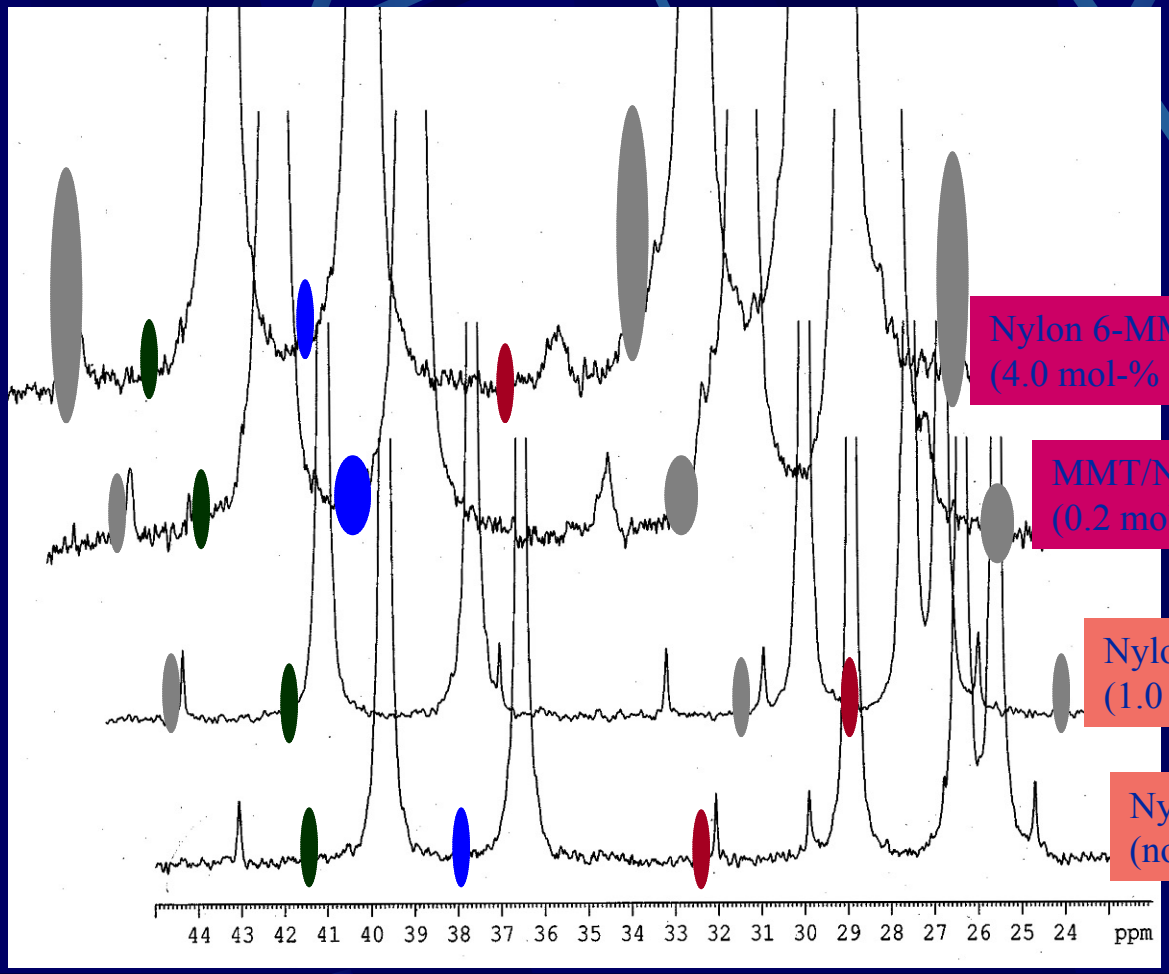


Reaction 3:



Davis, R. D.; Gilman. J. W.; Suttos, T.E.; Callhan, J.; Improving the Thermal Stability of Organically Modified Layered Silicates, *in preparation.*

# Nanocomposite Processing Degradation - Solution $^{13}C$ NMR Spectroscopy




Nylon 6-MMT - Injection Molded
(4.0 mol-% caprolactam, 7,490 g/mol)

MMT/Nylon 6
(0.2 mol-% caprolactam, 13,670 g/mol)

Nylon 6 - Injection Molded
(1.0 mol-% caprolactam, 12,310 g/mol)

Nylon 6
(no caprolactam, 13,620 g/mol)

ε-Caprolactam

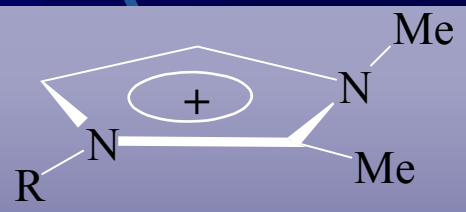
$\alpha NH_2$

$\beta CO_2H$

$\beta NH_2$

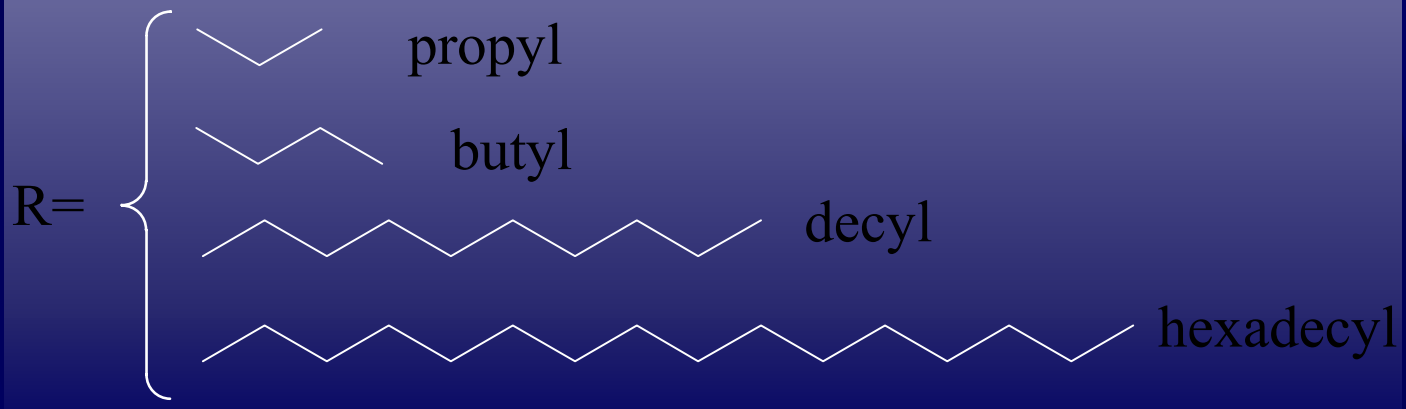
Davis, R. D.; Gilman, J. W.; VanderHart, D. L.; Processing Degradation of Polyamide 6-Montmorillonite Nanocomposites and Clay Organic Modifier, *submitted to Chem. Mater.*

# Imidazolium Salts




$X^- = Cl^-, BF_4^-$

**Dimethyl alkyl imidazolium salts**



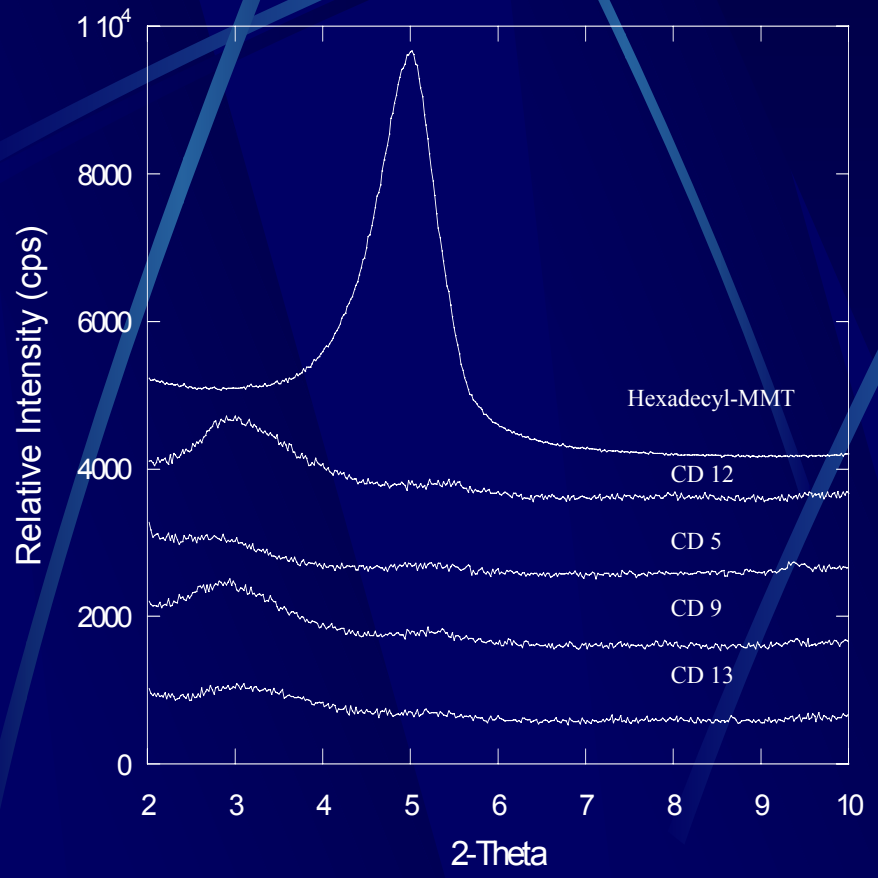
# TGA of Alkyl-Imidazolium- and Alkyl Quaternary-MMT

| Sample | TGA, °C ($N_2$) | | TGA, °C (air) | | Imidazolium content | | | Δ in d-spacing vs. Na-MMT (nm) |
|---|---|---|---|---|---|---|---|---|
| | $T_{onset}$ | $T_{peak}$ | $T_{onset}$ | $T_{peak}$ | Theoretical | Under Air | Under $N_2$ | |
| DMDODA/MMT | 280 | 308 | 226 | 299 | 34.11 | 34.43 | 31.15 | 1.49 |
| MHEtIM/MMT | 325 | 492 | 290 | 482 | 9.39 | 8.65 | 8.10 | |
| DMPIM/MMT | 340 | 445 | 305 | 422 | 11.57 | 10.30 | 8.77 | 0.2 |
| DMBIM/MMT | 340 | 448 | 303 | 381 | 12.59 | 11.60 | 9.17 | 0.16 |
| DMDIM/MMT | 320 | 432 | 234 | 312 | 18.26 | 17.14 | 13.63 | 0.49 |
| DMHDIM/MMT | 343 | 406 | 250 | 298 | 23.21 | 23.50 | 20.53 | 0.72 |
| DMEiIM/MMT | 308 | 409 | 250 | 317 | 26.20 | 27.10 | 26.09 | |
| DMMeOEtOEtIM/MMT | 250 | 319 | 233 | 320 | | | | |
| DMEtBIM/MMT | 262 | 418 | 235 | 384 | | | | |

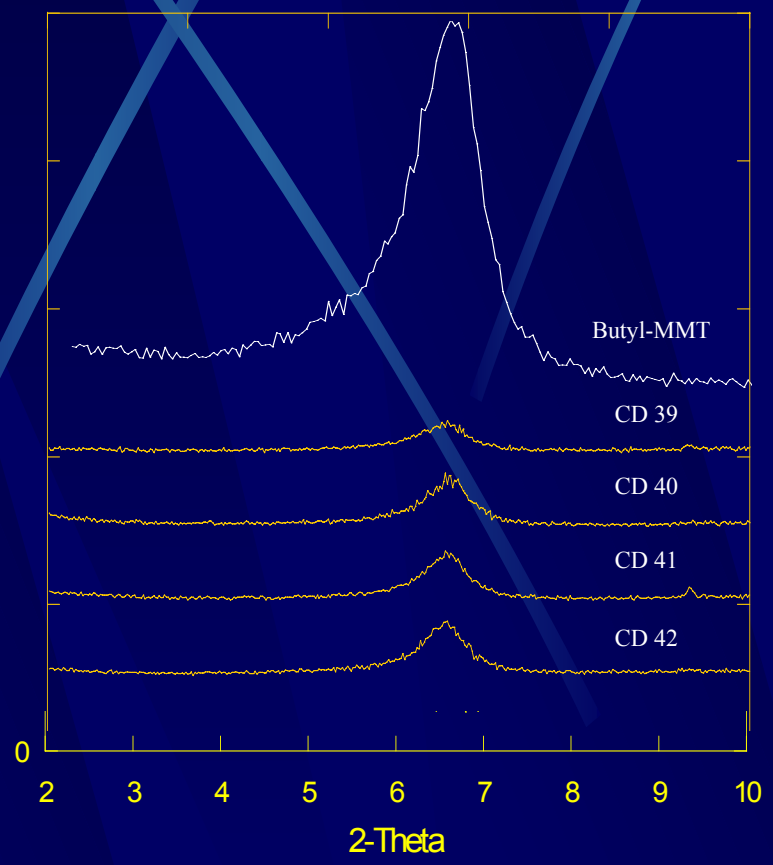
Uncertainty ± 1.2 °C (2 sigma)

BF4, ht xtr\suin

# Effect of Varying Imidazolium Organic Modifier



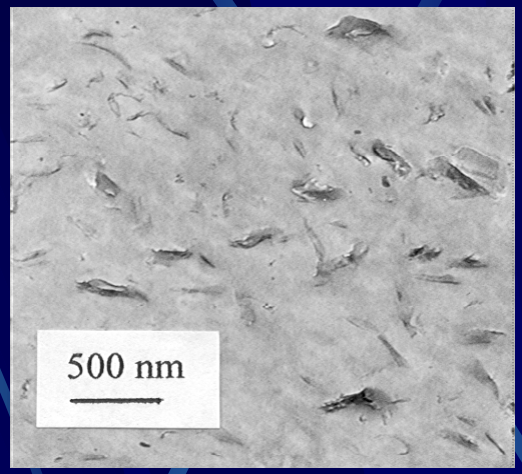

Hexadecyl-MMT/PET nanocomposites

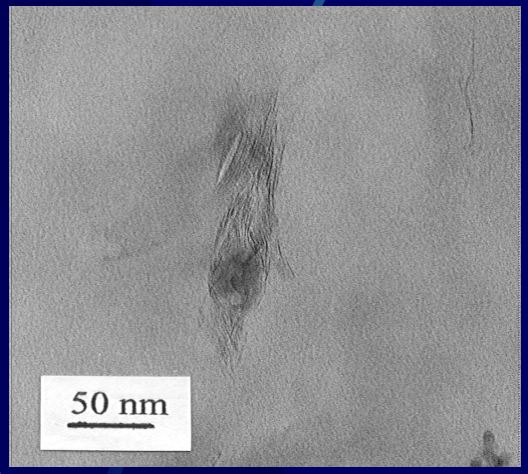



Butyl-MMT/PET nanocomposites

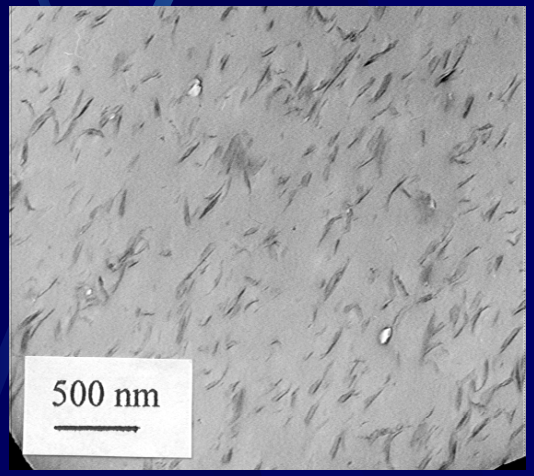
# Effect of Varying Processing Conditions

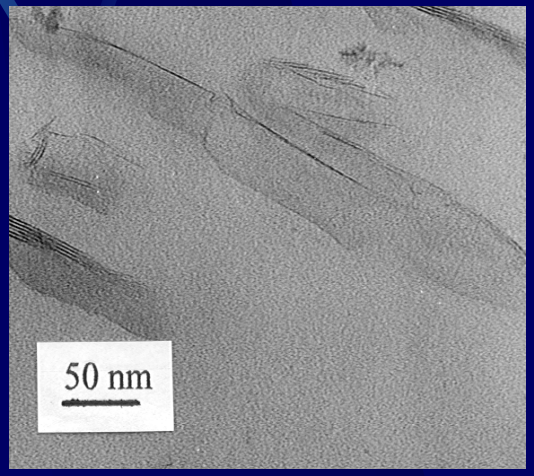
CD 29: hexadecyl-MMT/PET-OD nanocomposite
Screw speed: 300 rpm
Residence time: 2 minutes
**CD 29 is representative of samples set III

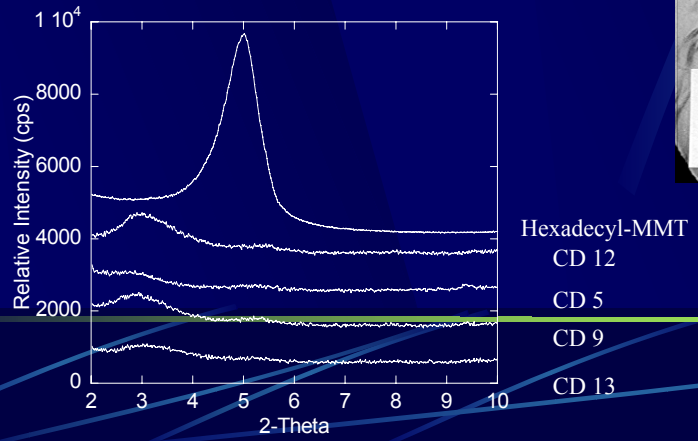



CD 12: hexadecyl-MMT/PET nanocomposite
Screw speed: 200 rpm
Residence time: 2 minutes

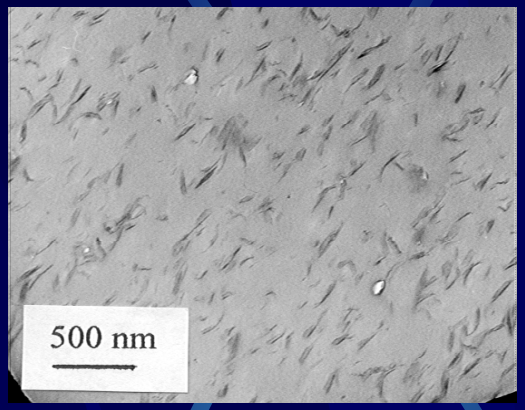


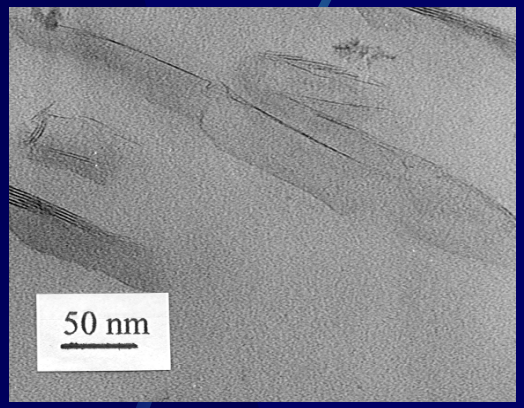



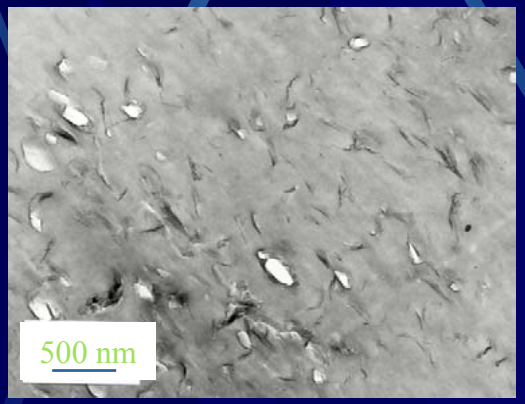
# Effect of Varying PET Copolymers

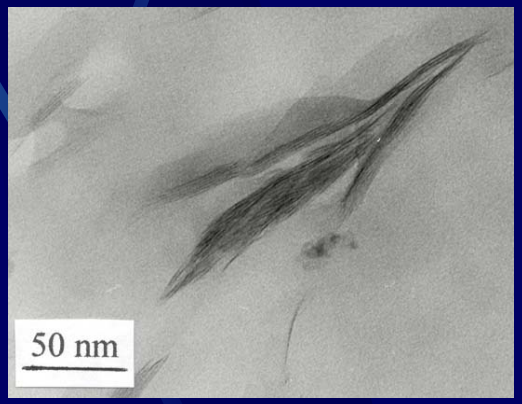
CD 12: hexadecyl-MMT/PET nanocomposite
Screw speed: 200 rpm
Residence time: 2 minutes



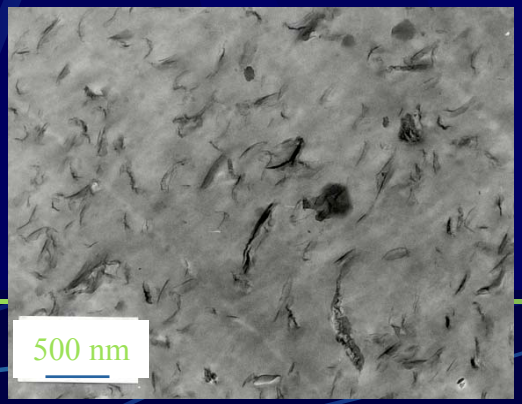



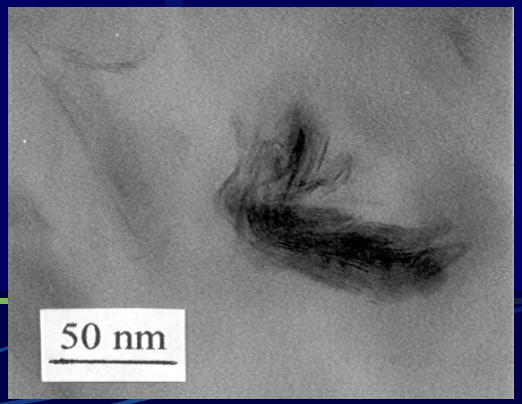

CD 10: hexadecyl-MMT/PET-OD nanocomposite
Screw speed: 200 rpm
Residence time: 2 minutes



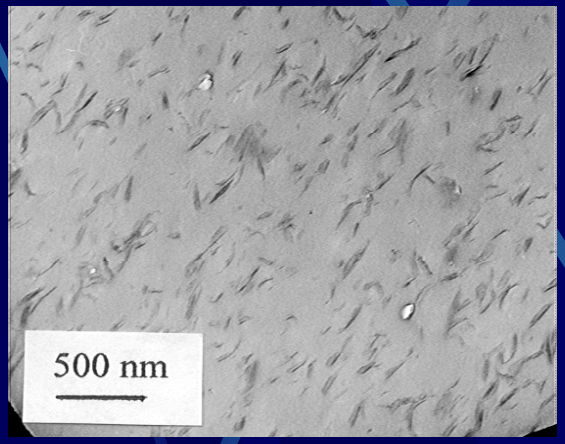

CD 15: hexadecyl-MMT/FR-PET nanocomposite*
Screw speed: 200 rpm
Residence time: 2 minutes

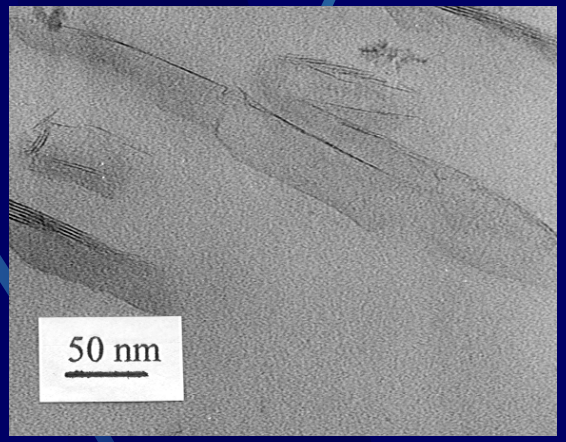


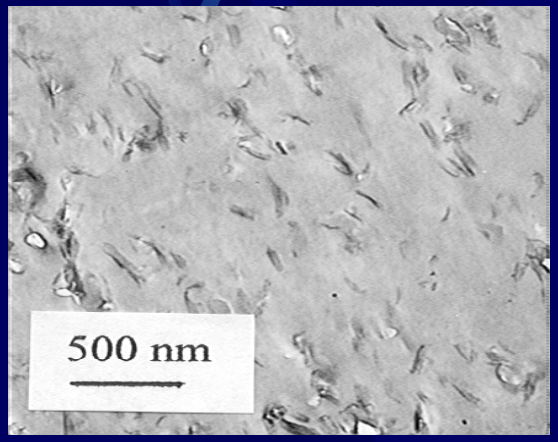
# Optimal Melt Blend Processing Conditions

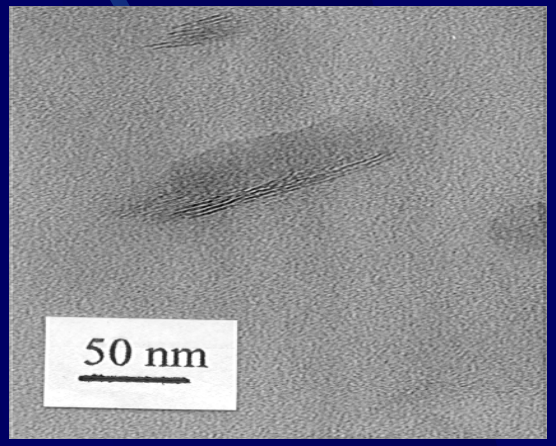
CD 12: hexadecyl-MMT/PET nanocomposite
Screw speed: 200 rpm
Residence time: 2 minutes




CD 13: hexadecyl-MMT/PET nanocomposite
Screw speed: 300 rpm
Residence time: 5 minutes



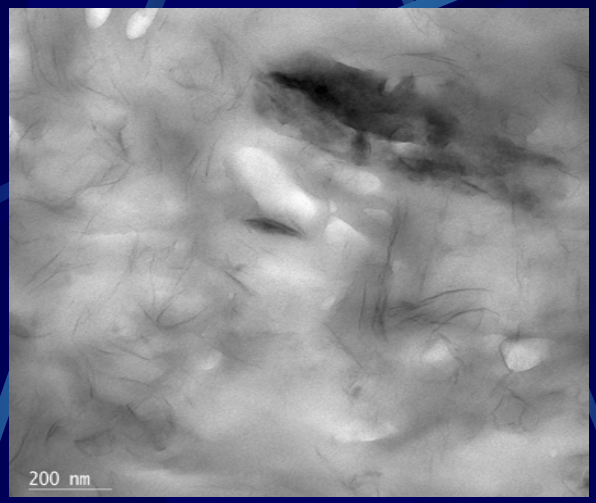



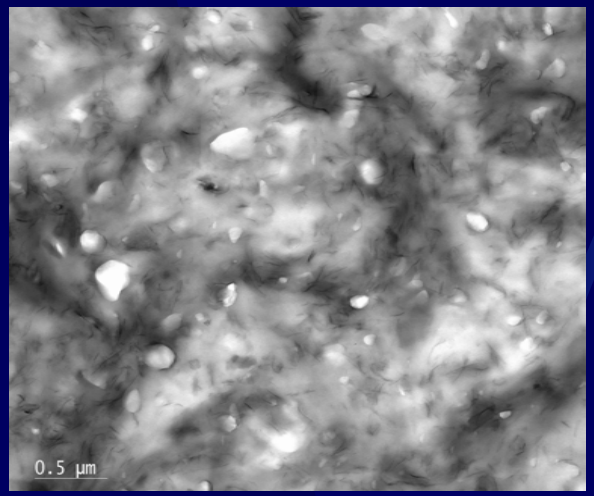
# DMHDIM-MMT/PA-6: Dispersion Using NMR Spectroscopy

| PA-6 and PA-6 nanocomposites | $T_1^H$ (ms) |
|---|---|
| DMHDIM-MMT/PA-6 at 250 °C / 2 min | 361 |
| DMHDIM-MMT/PA-6 at 250 °C / 5 min | 343 |
| DMHDIM-MMT/PA-6 at 300 °C / 2 min | 388 |
| DMHDIM-MMT/PA-6 at 300 °C / 5 min | 381 |
| Pure PA-6* | 529 |
| Medium exfoliation of MMT in PA-6* | 400 |
| Very good exfoliation MMT in PA-6* | 327 |

# DMHDIM-MMT/PA-6: Dispersion Using TEM Images

A

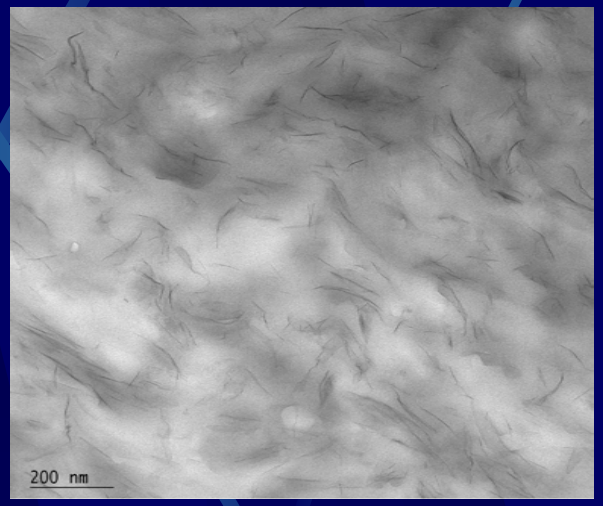


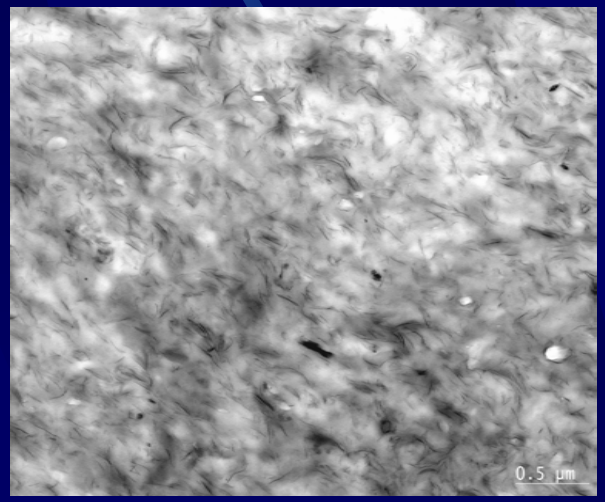




B

A and B: processed at 250 °C for 2 min.

A

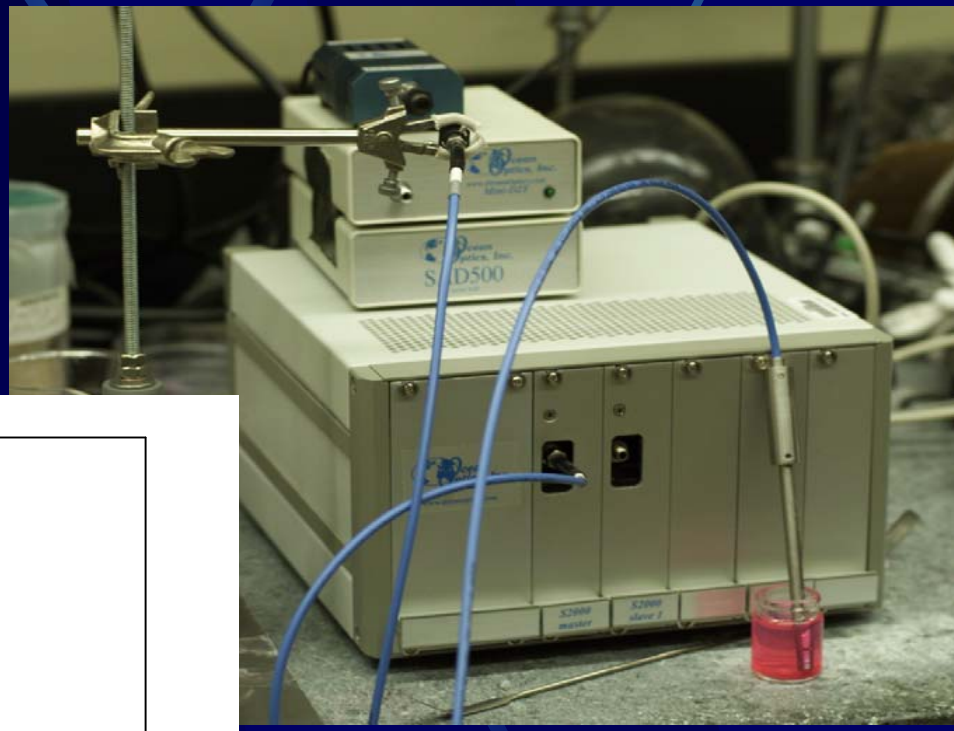


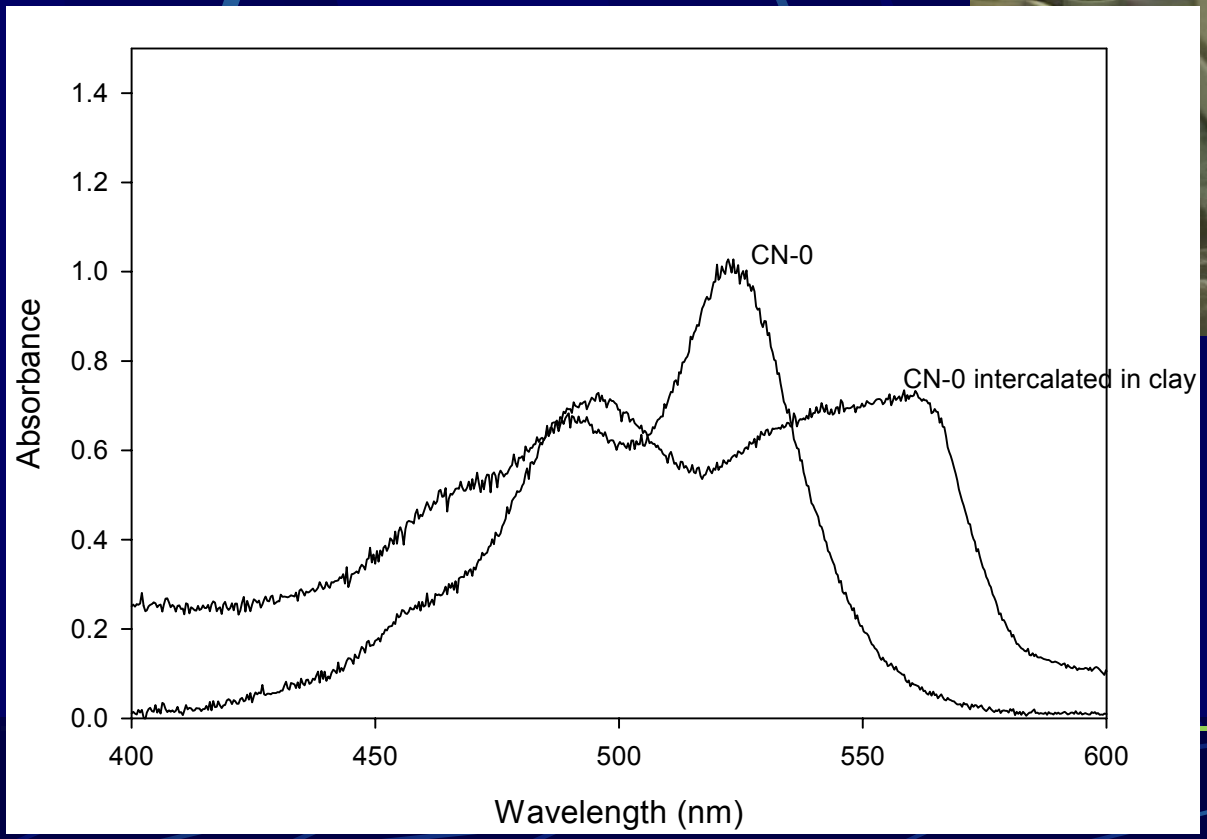




B

A and B: processed at 250 °C for 5 min.

# Sample Characterization





# Parameter Space for Polymers and Additives

| Polymer | Nano-additive | Counter-Ion | Organic Treatment | Processing Conditions | Other additives | Flame Retardant |
|---|---|---|---|---|---|---|
| PE<br>PP<br>PS<br>PA6<br>PU<br>PVC<br>PC<br>PEO<br>PMMA<br>EVA<br>… | MMT<br>Mica<br>POSS<br>graphite<br>silica | Na<br>Ca<br>Cu<br>Fe… | Alkylammonium<br>Imidazolium<br>Crown Ether<br>Silated<br>Carboxylate | Temperature<br>Shear<br>Residence time | Stabilizers<br>Processing<br>UV<br>Antioxidant<br>Fillers<br>Pigments<br>Toughening agents | Phosphate<br>Halogenated<br>Silicon Based |
| ~ 10 | ~ 5 | ~ 5 | ~ 10 | ~ 10 | ~ 10 | ~ 10 |

**(~ $10^6$ Experiments)**

# High Throughput Technology

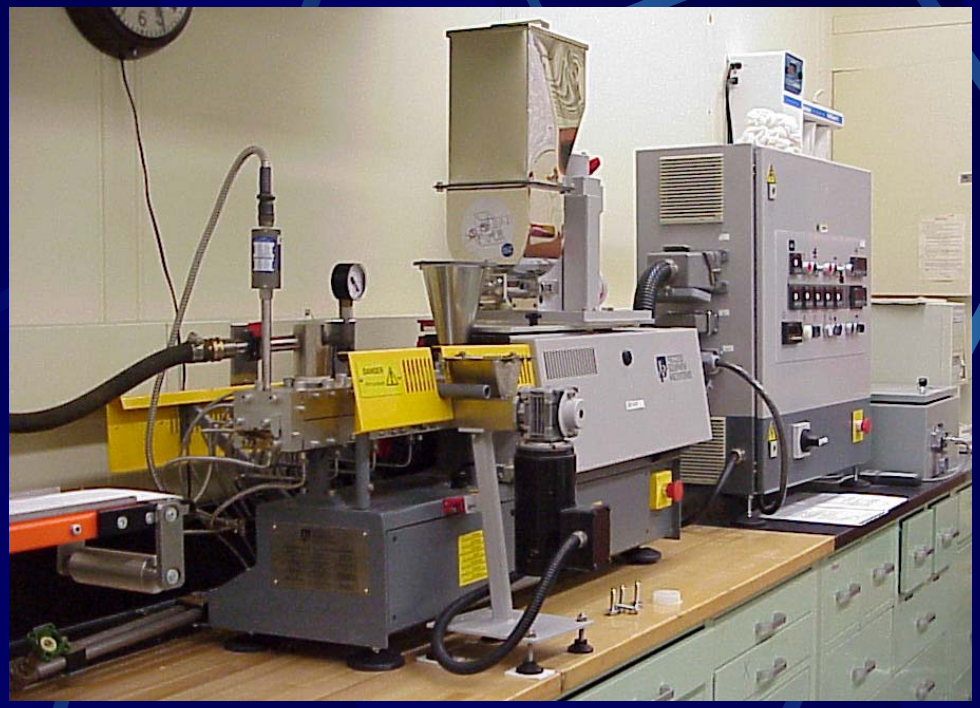
**Properties**
**Characterization**
•XRAS
•UV/VIS Probe
•Dielectric Sensor
•*Microhotplates*

**Structure**
**Flammability**
•HRR
•Flame spread
**Physical**
•Nanoindenter

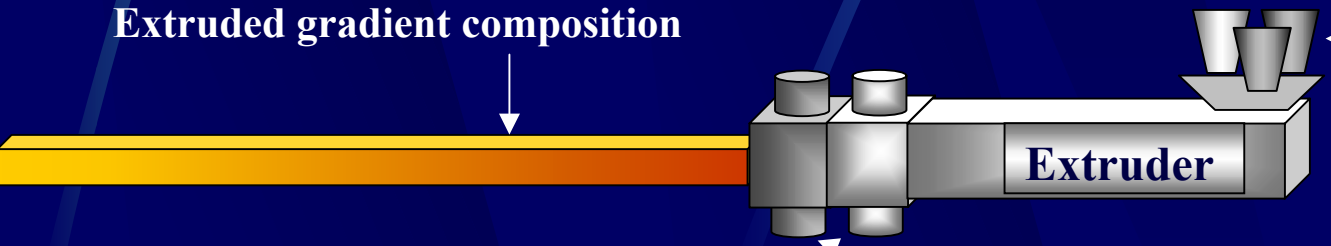
**Extrusion**
•Single composition
•Gradients composition

Step 1: Small scale
Step 2: Larger scale

# Fabrication and Measurements



Extruded gradient composition




Gravimetric feeders

In-line sensors
- UV/VIS probe
- FTIR
- Dielectric

# Radiation Panel

**Constant composition and gradient flux**

**Different critical fluxes for flame-spread**

# Combinatorial Methods Center at NIST

## New Consortium:
## High-Throughput Methods for Flammability

Team Project

will work with project teams, consisting of 3 or more companies, to develop generic tools for high-throughput formulation, characterization, and flammability performance screening of materials and fire retardant systems.

# Conclusions

By combining nanotechnology with high-throughput experimentation, we can maximize the effect of additives and thereby provide industry with a powerful tool for the development of a new generation of high performance, low flammability materials.

# Acknowledgements


David VanderHart, Atsuchi Asano
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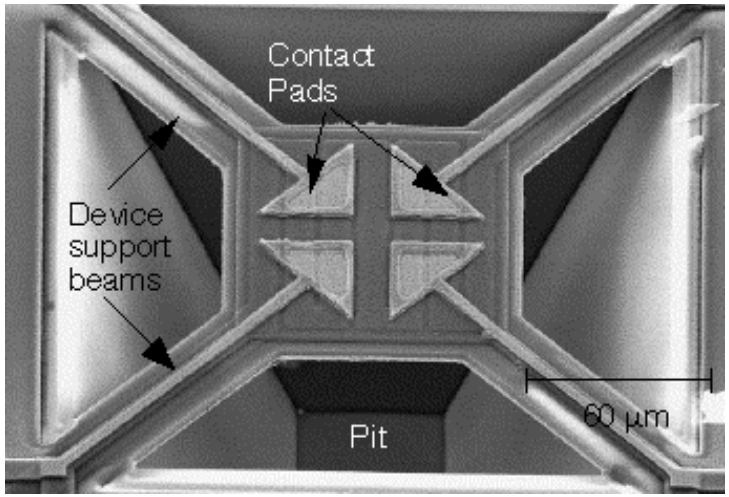
Air Force Office of Scientific Research (ISSA - AFOSR- ISSA-01-0001 )

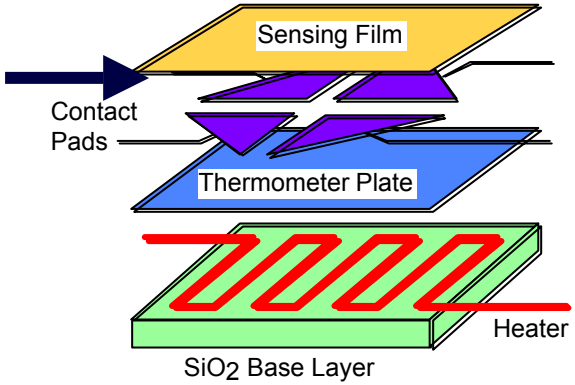
# Materials and Products Group

Group Leader: Jeff Gilman
Researchers: Takashi Kashiwagi, Tom Ohlemiller, Marc Nyden, Rick Davis, Kathy Butler, Greg Linteris
Technicians: Lori Brassell, John Shields, Michael Smith, Richard Harris, Ruth Perkins, Roy McClane
Guest Researchers: Walid Awad
Students: Wes Demory, David Wentz

# Measurements - Microhotplates

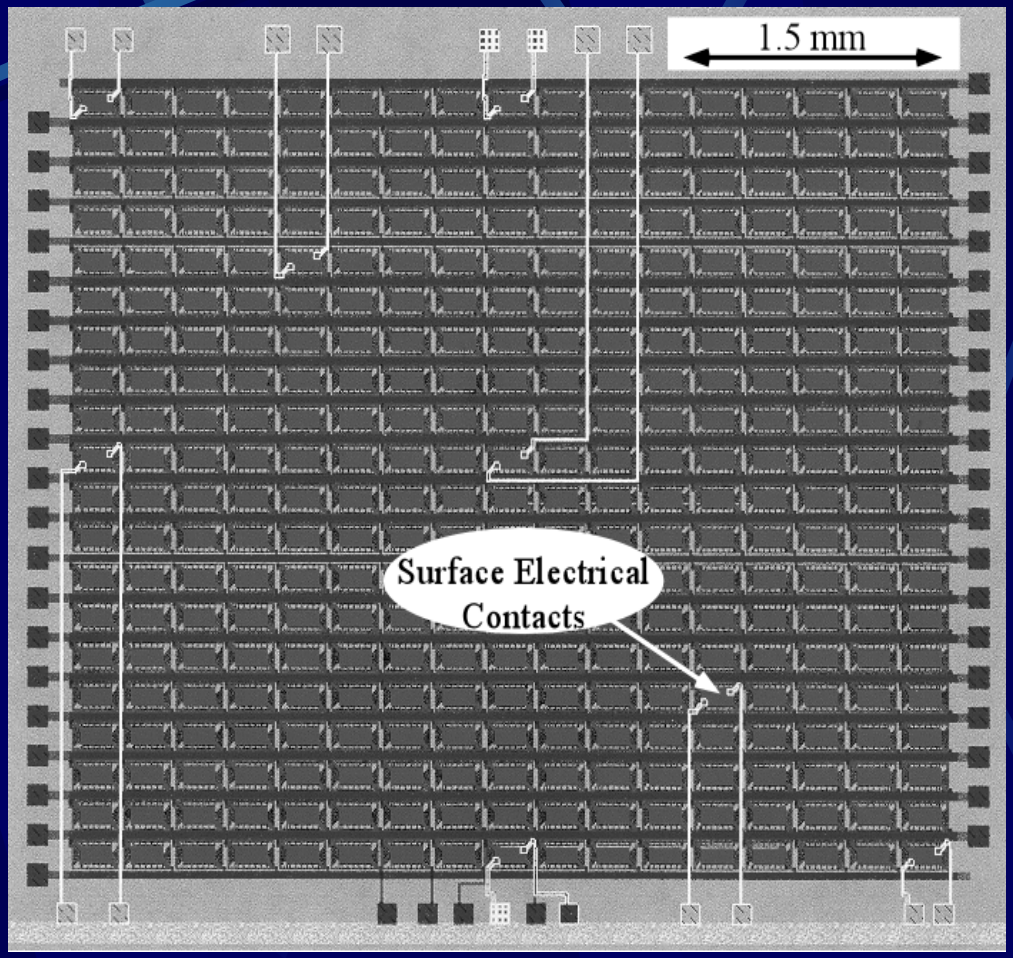



Coat sensing film with test material



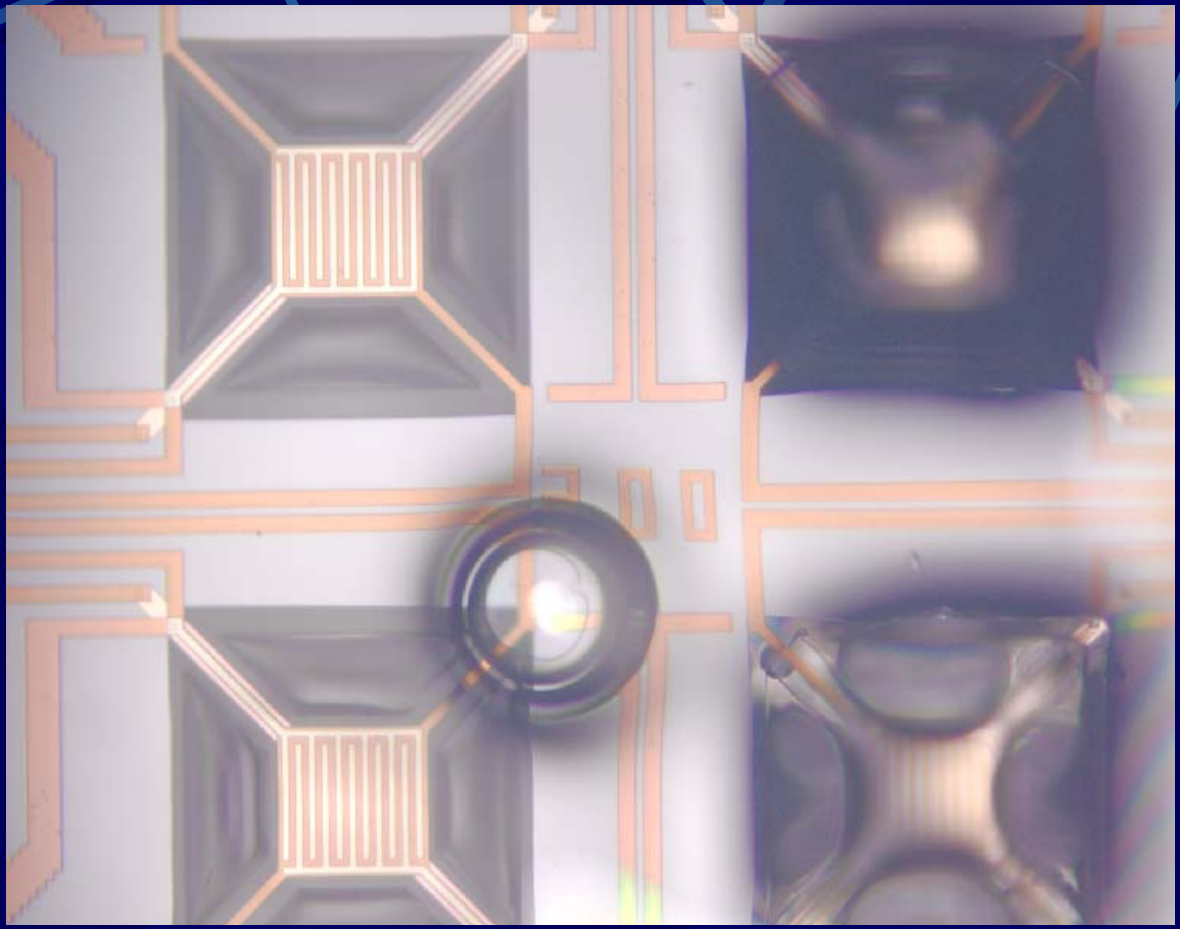

Correlate changes in power demand needed to maintain the specified heating rate with mass loss from degrading polymer

# Measurements - Microhotplates

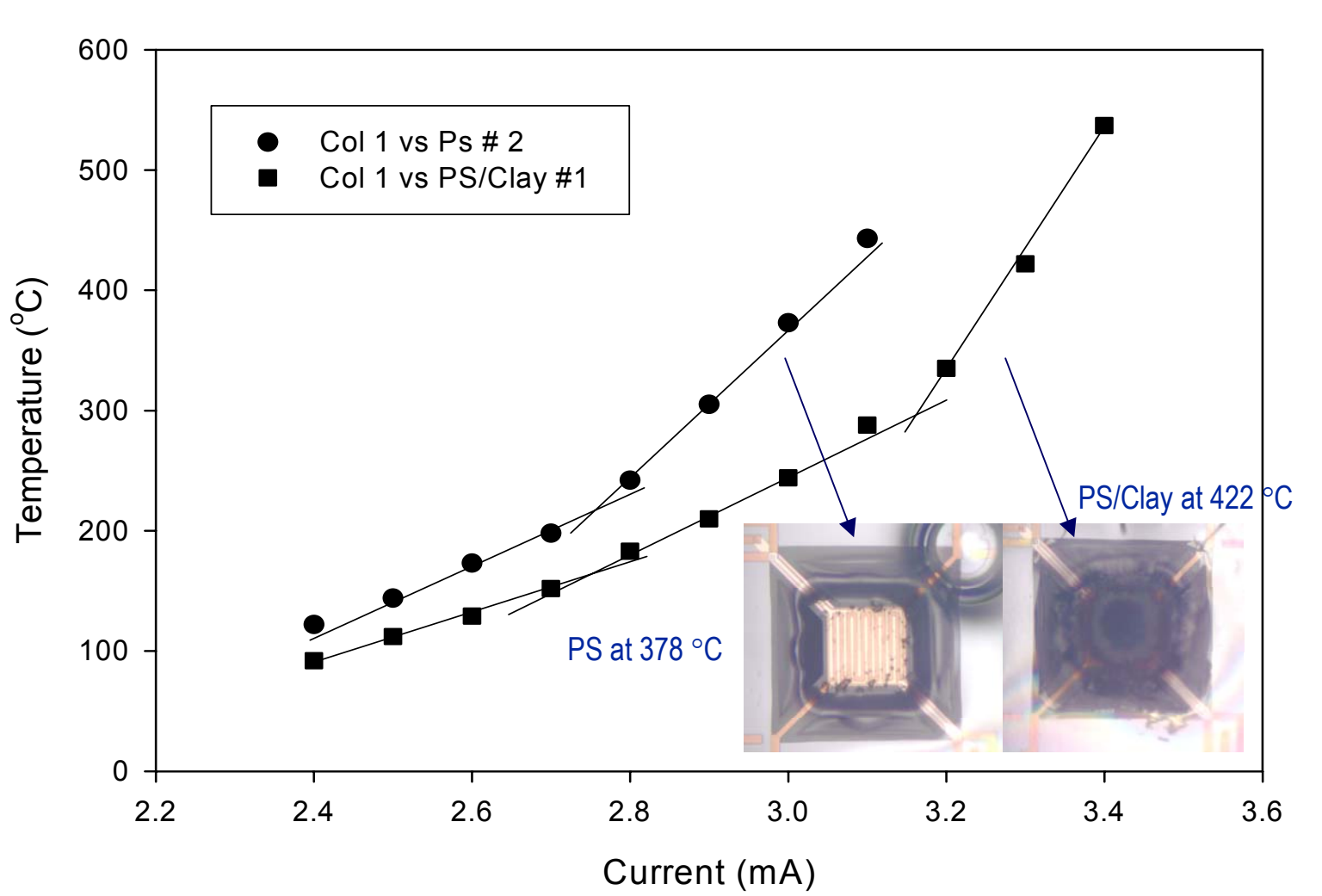



High throughput flammability screening on small (~ 1 μg) samples

# Measurements - Microhotplates



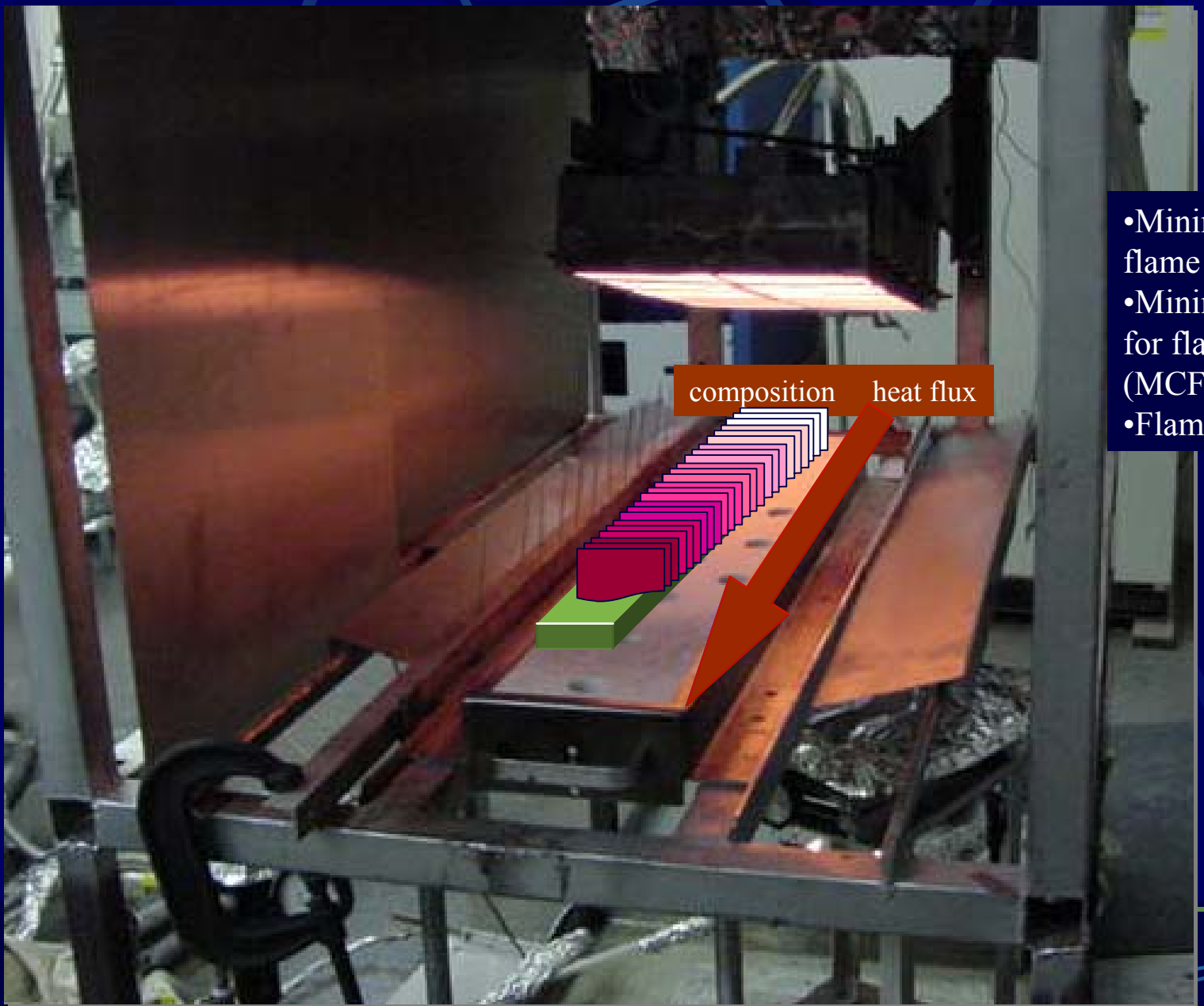
# Measurements - Microhotplates



# Measurements – Radiation Panel

Polystyrene
APP/PER (3:1)

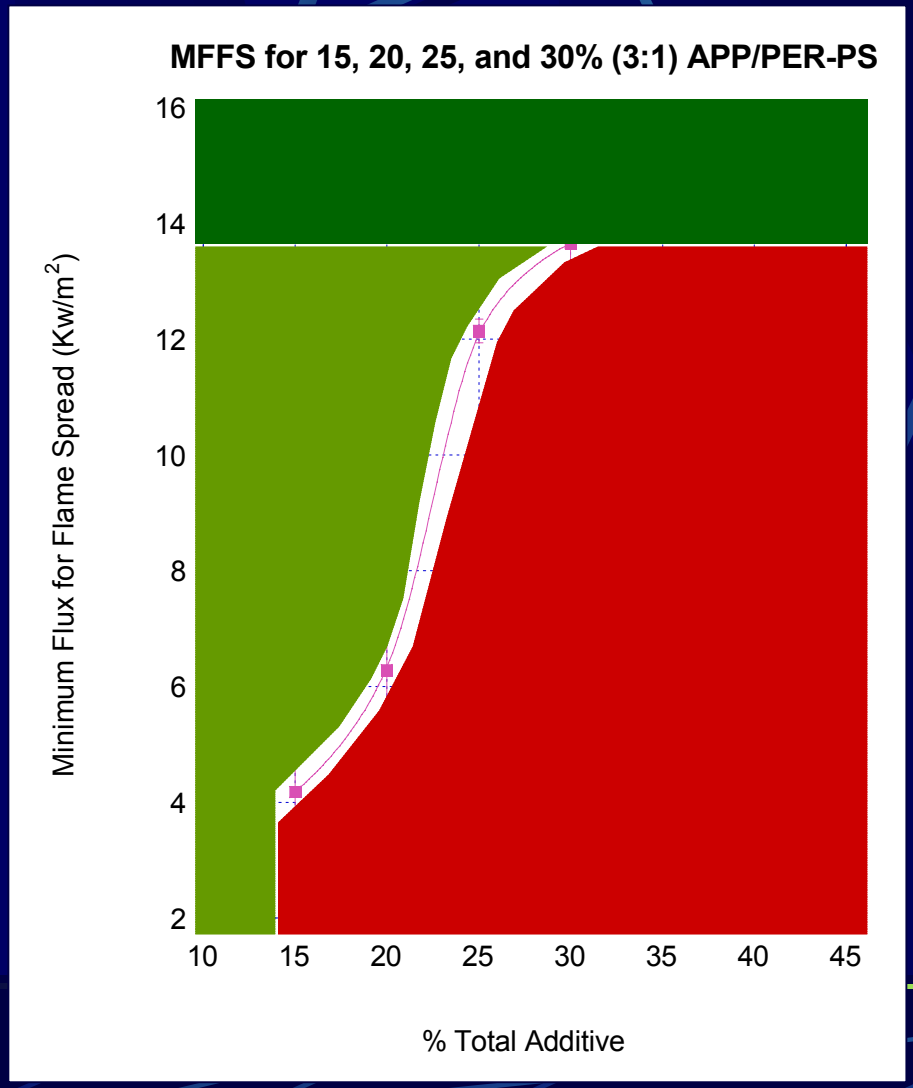
# Measurements – Radiation Panel




- Minimum heat flux for flame spread (MFFS)
- Minimum composition for flame spread (MCFS)
- Flame spread velocity

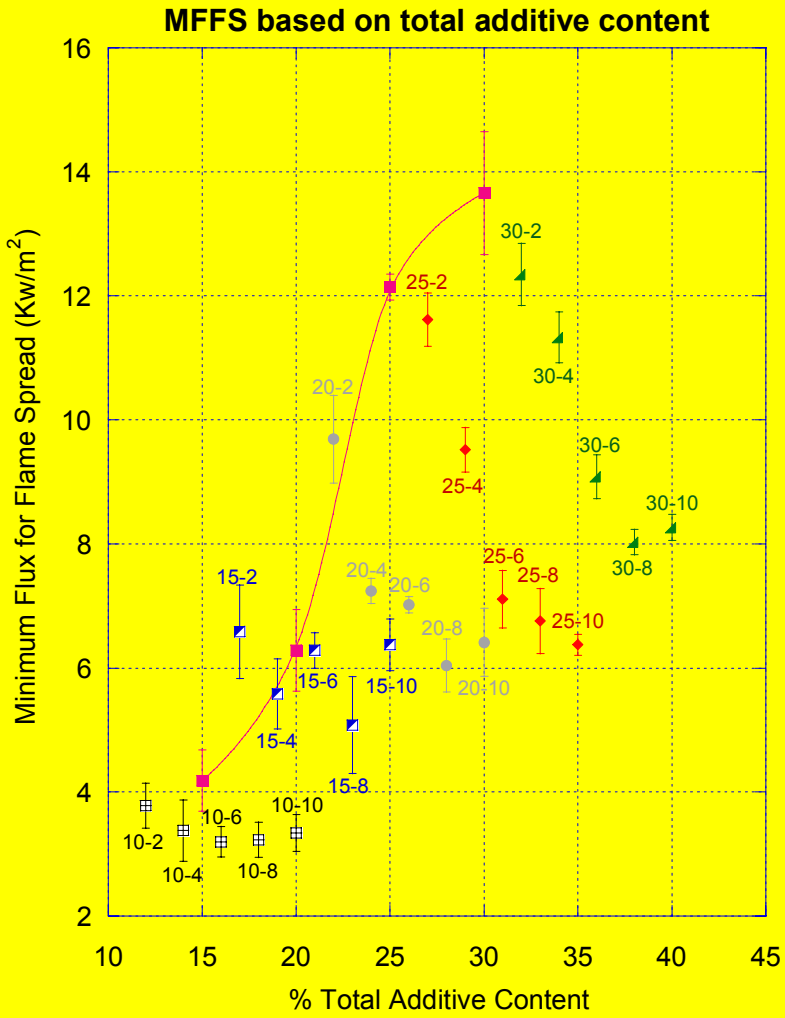
# Radiation Panel

# Additive Synergy



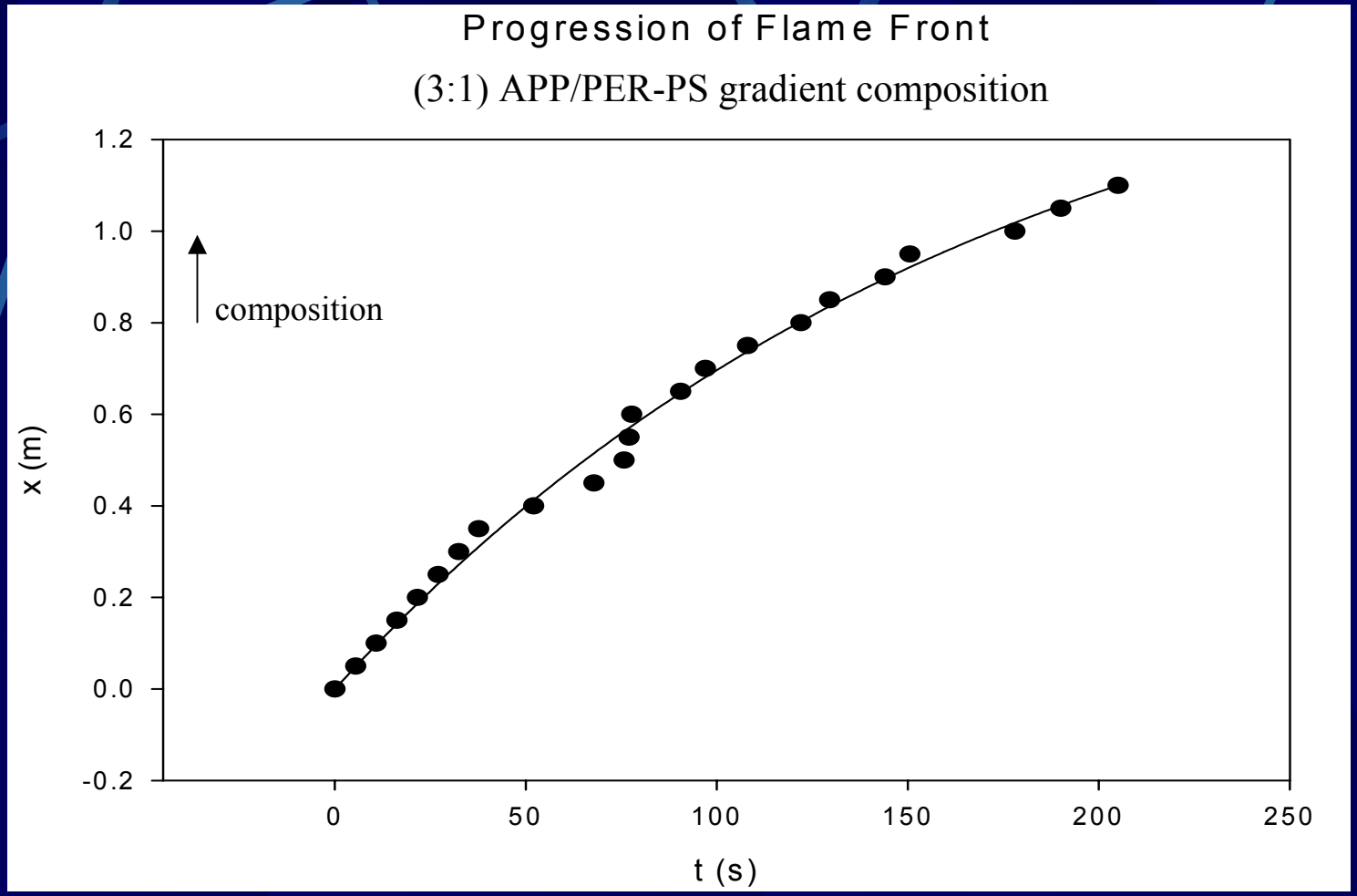

15, 20, 25, and 30% (3:1) APP/PER-PS
10% APP/PER with 2, 4, 6, 8, or 10% 15A -PS
15% APP/PER with 2, 4, 6, 8, or 10% 15A -PS
20% APP/PER with 2, 4, 6, 8 or 10% 15A -PS
25% APP/PER with 2, 4, 6, 8, or 10% 15A -PS
30% APP/PER with 2, 4, 6, 8, or 10% 15A -PS

**Did not self extinguish:**
0, 5, and 10% (3:1) APP/PER-PS
2, 4, 6, 8, and 10% 15A-PS



# High Throughput Flammability Test

# Gradient Composition - Constant Flux: Flame Spread




slower flame spread as composition increases