Flammability Properties of Polymer Nanocomposites

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- **New FR Approach**
  - **Nanocomposites:** **particle-filled polymers where at least one dimension of the dispersed particle is nanometer scale.**
    - **Layered silicate (clay) : large aspect ratio - 1D**
    - **Tube : large aspect ratio - 2D**
    - **Sphere : aspect ratio of 1 - 3D**

Exceptional physical properties.

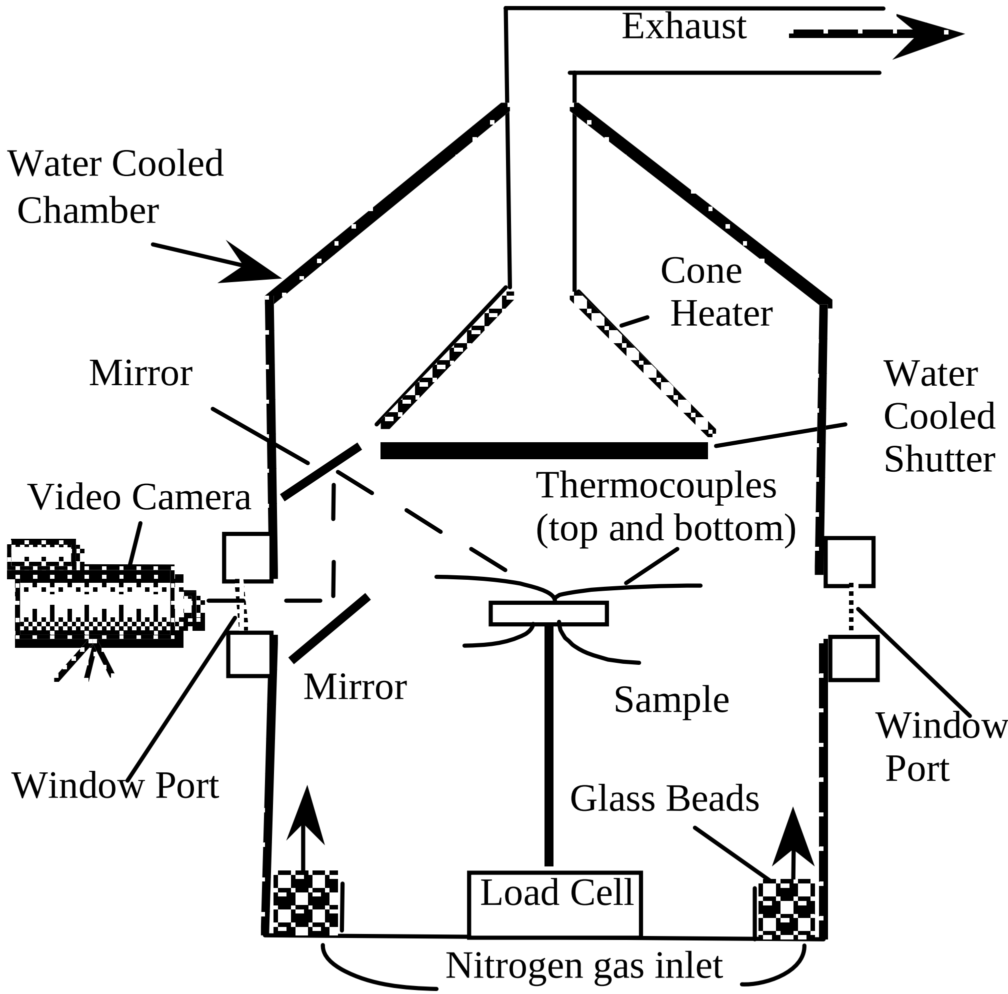
- **How about their FR performance ?**

If effective, what are the effects of the shape of nanoparticles on FR performance ?

- **If effective, what are their FR mechanisms ?**

Measurement of Flammability Properties

- **Cone Calorimeter**
  - Oxygen consumption measurement under external thermal radiation (up to 100 kW/m^2), ignition delay time, heat release rate, CO, soot, sample mass loss rate, ..
- **Radiative Gasification Device**
  - Mass loss rate measurement in **nitrogen**



Effects of Shape of Nanoparticles

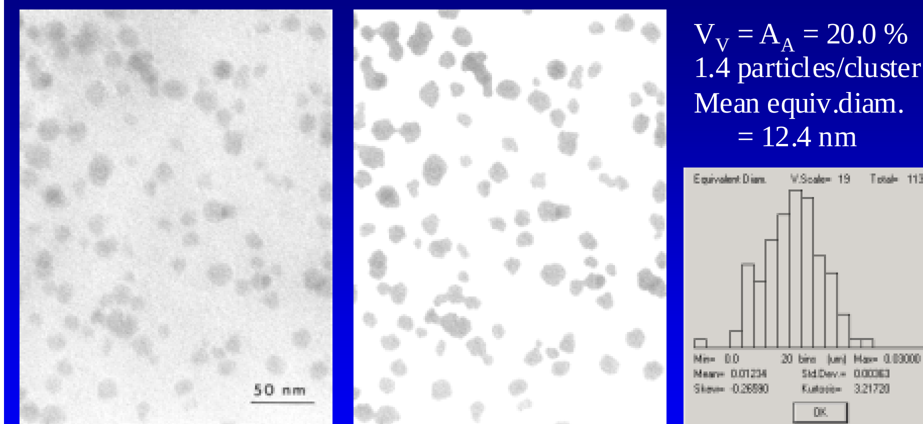
- **Sphere -** Nano silica particles

Sample Preparation of Silica-PMMA

1. Mix 14 g of MEK-ST(30% by weight colloidal silica with average 12 nm diameter in MEK, Nissan Chemical) in 40 mL of MMA(Sigma-Aldrich).
2. MEK was removed using a rotary evaporator at 62 ºC in low vacuum.
3. Additional MMA was added and mixed in a sonic bath.
4. BPO (1.7% by weight of MMA) was added to make free
radical polymerization.
6. The sample was then transferred to a vacuum oven at 80 ºC for 72 hours.
7. Control sample was made by substituting MEK-ST with MEK and followed exactly the same procedure.

Kashiwagi, et.al. *J. Apply. Polym. Sci.*, 89, 2072, 2003.

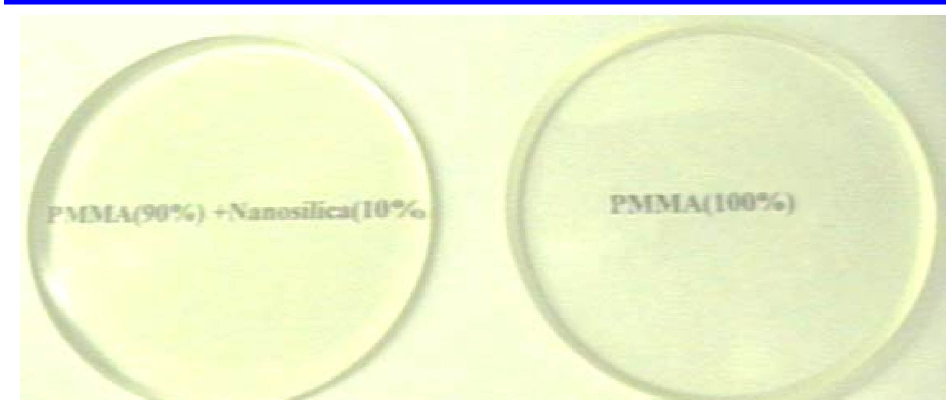
PMMA with SiO2 – 300 kx

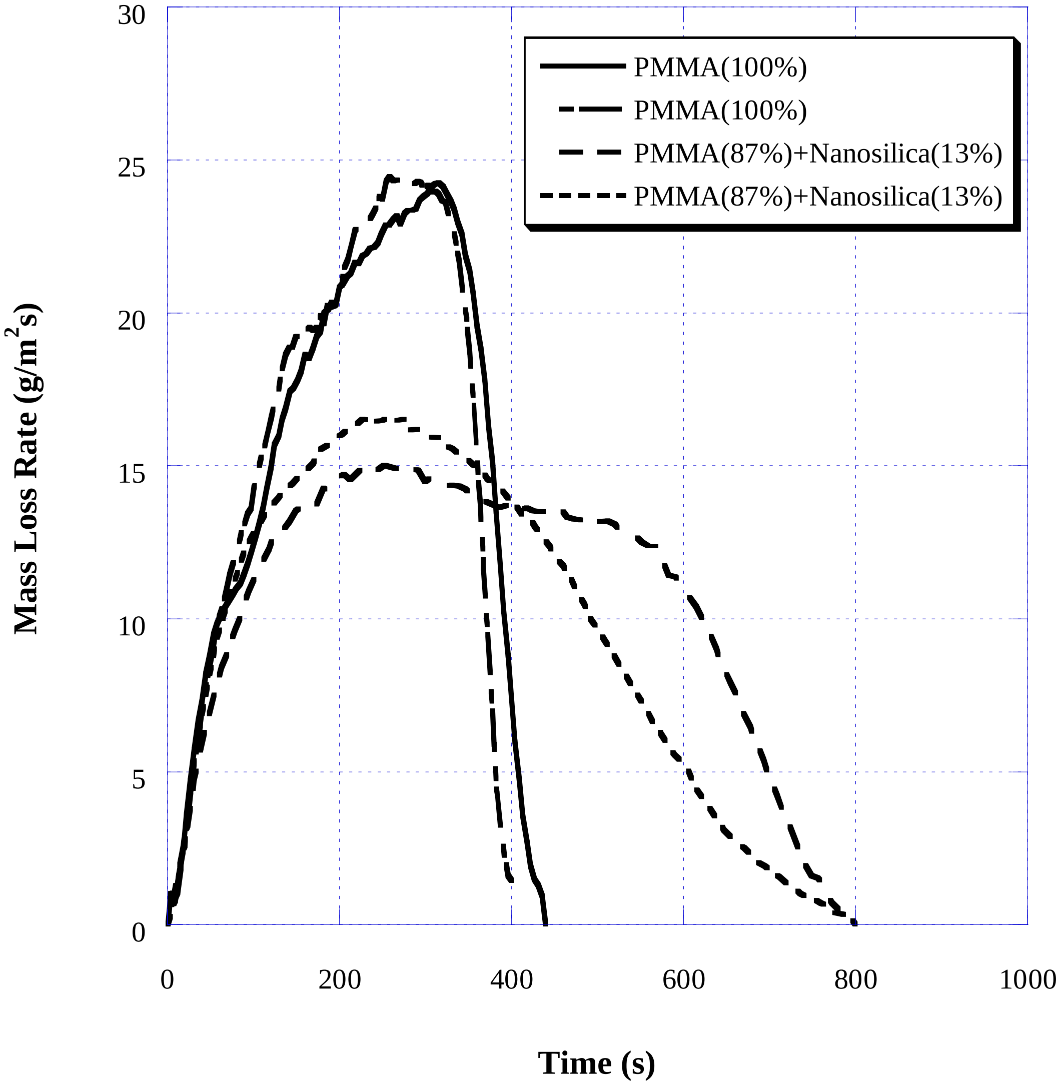


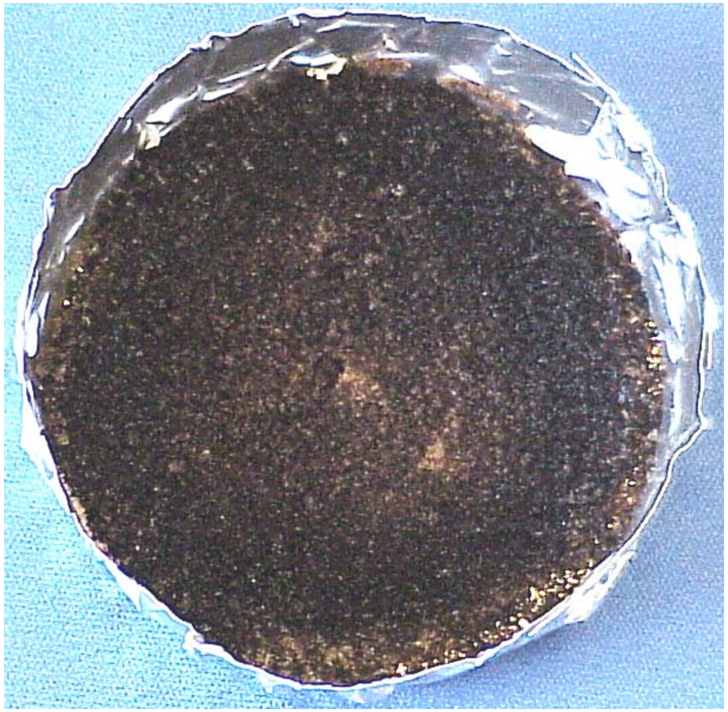
$V_V = A_A = 20.0$ %
1.4 particles/cluster
Mean equiv.diam.
= 12.4 nm

Original

Clusters: 78
Primary particles: 112







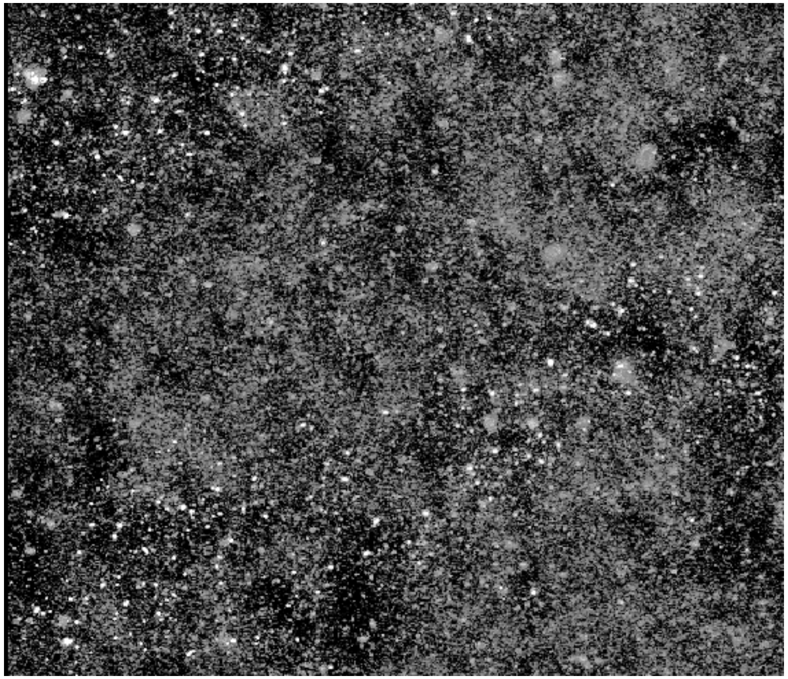
Picture of the residue of PMMA/Nanosilica

Granular particles

Effects Shape of Nanoparticles

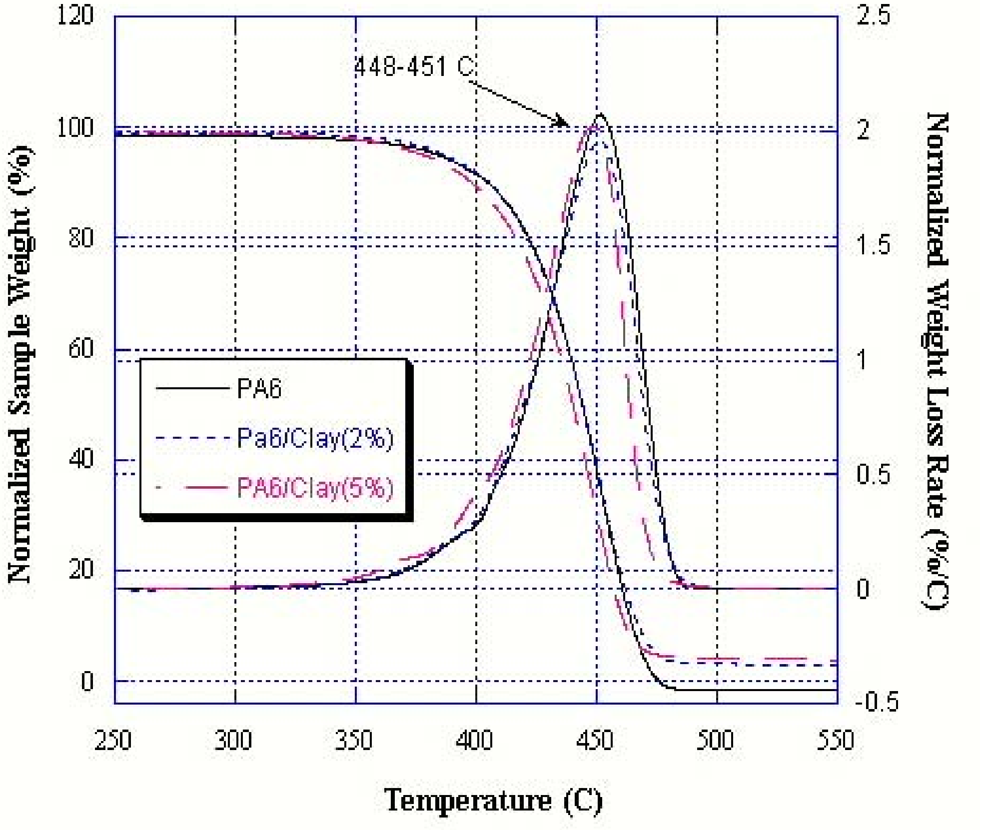
- **Plate -** Clay particles
- **UBE 1015 series of PA6 with 2 % and 5 % MMT.**

TEM

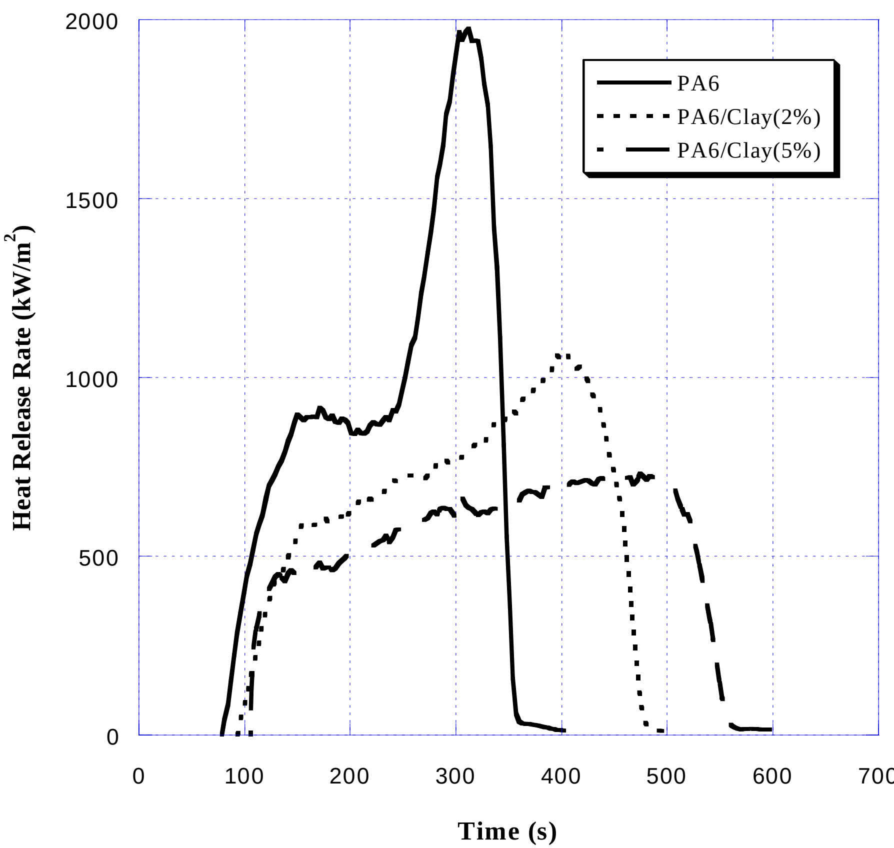


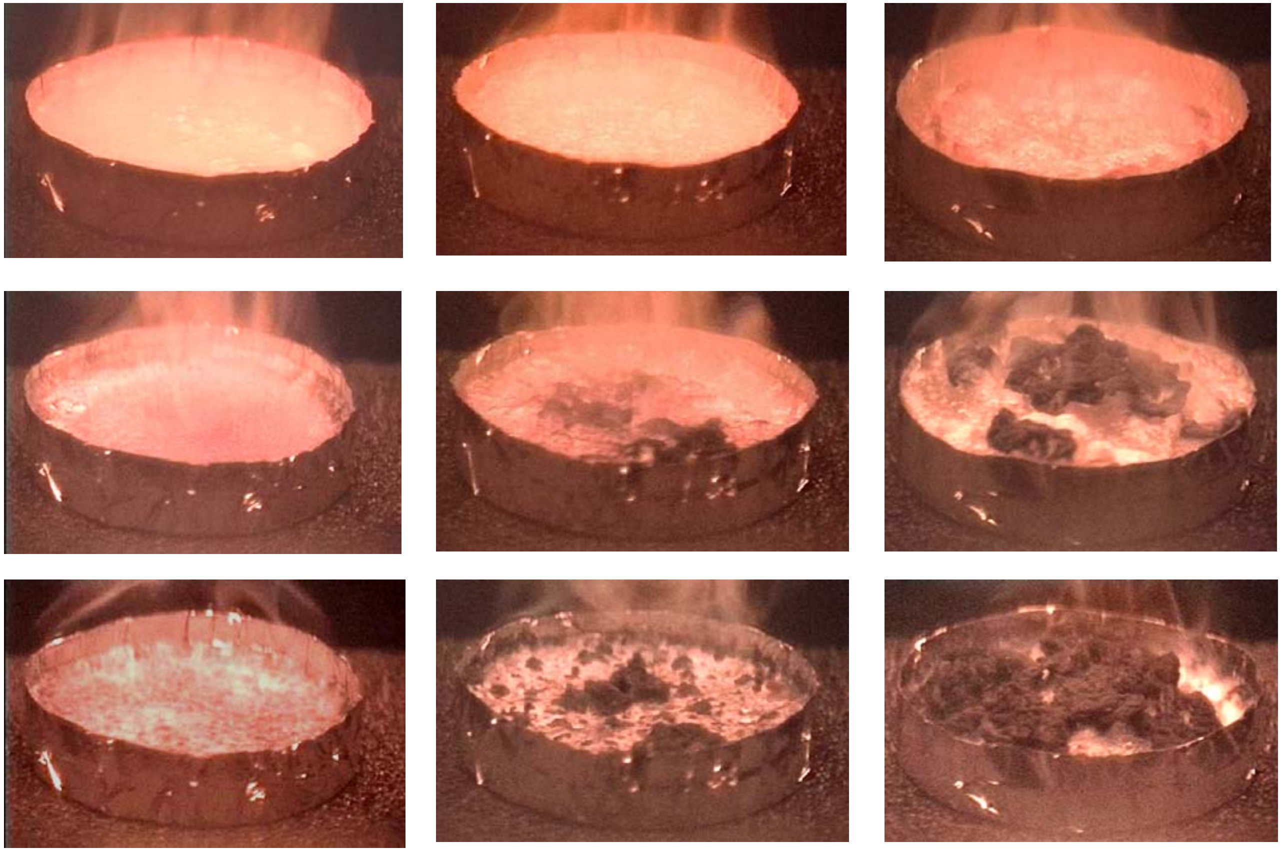
Confocal Microscope

Kashiwagi, et.al. *Polymer*, 45, 881, 2004.



Normalized sample weight and weight loss rate curves in N_2 at 10°C/min.





PA6 PA6/Clay(2%) PA6/Clay(5%)

Selected video images at 100s, 200s, and 400s in nitrogen at 50 kW/m^2.

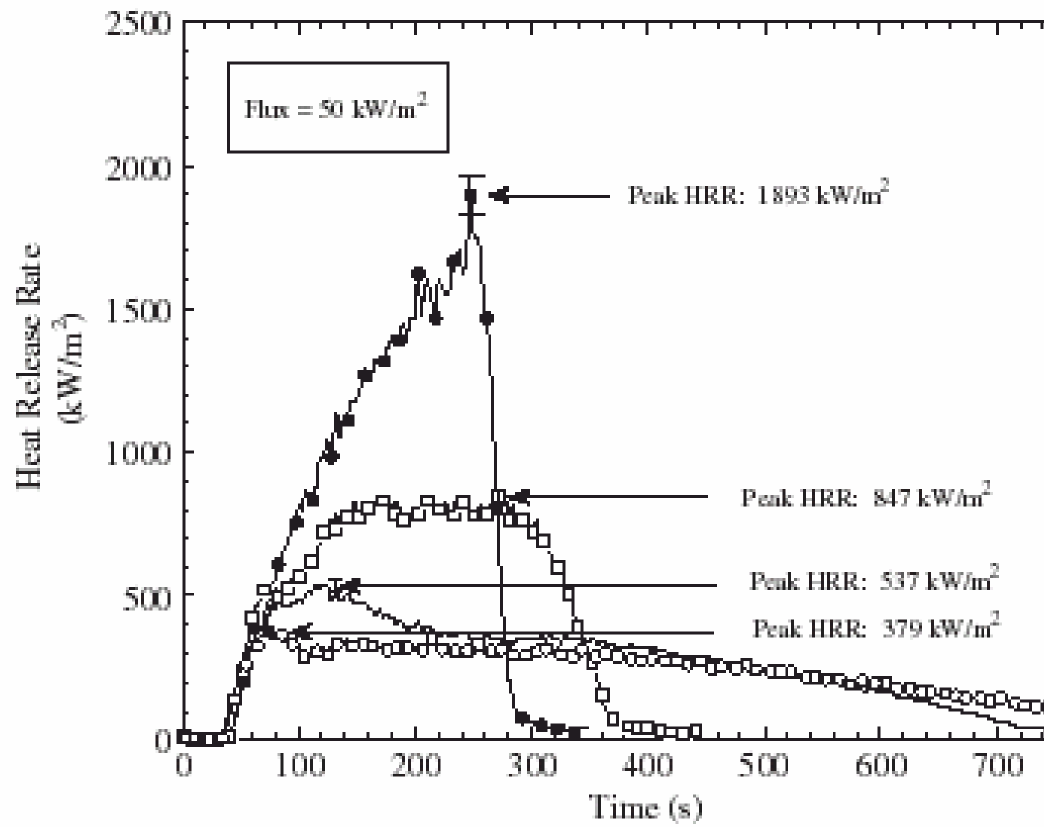
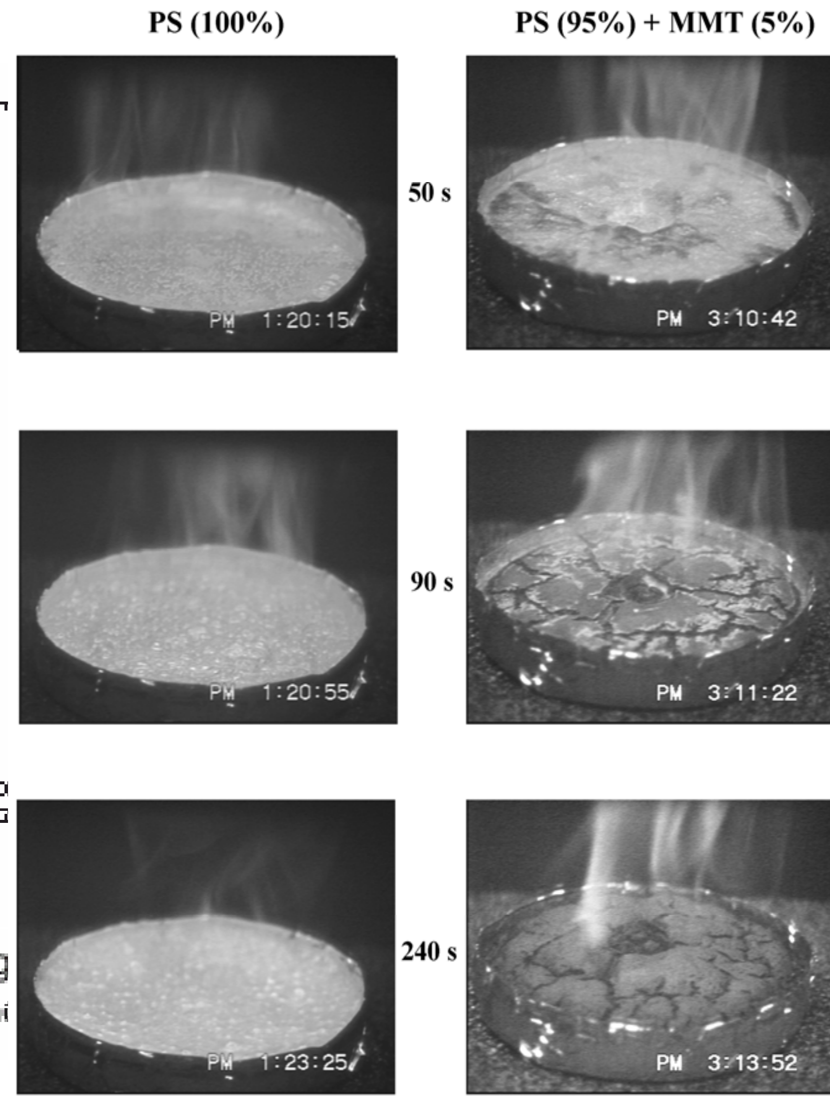
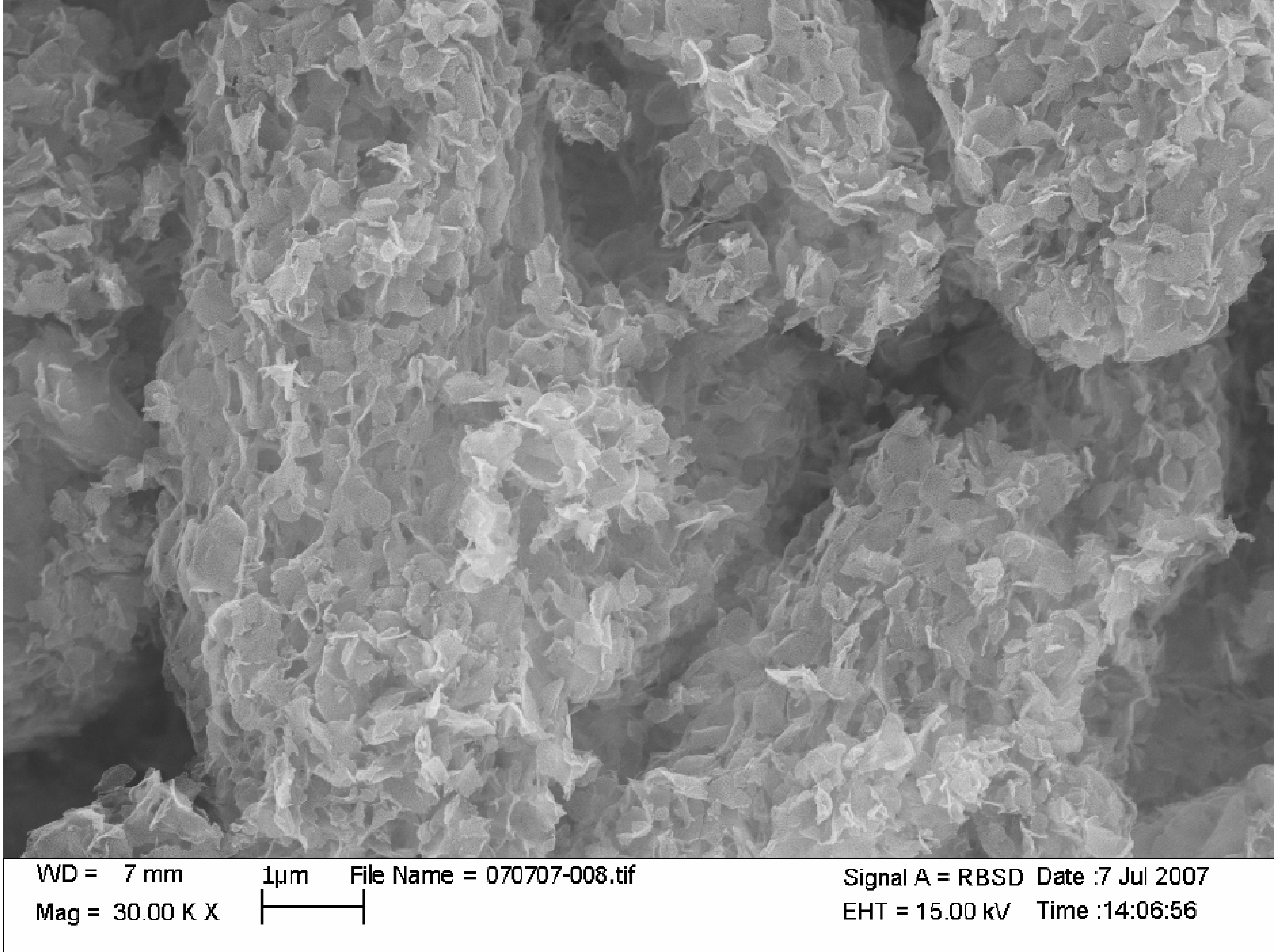


Figure 8. HRR plots for the high M_n pure PS, and the hig
PS/MMT nanocomposites with 2%, 5%, and 10% clay loa



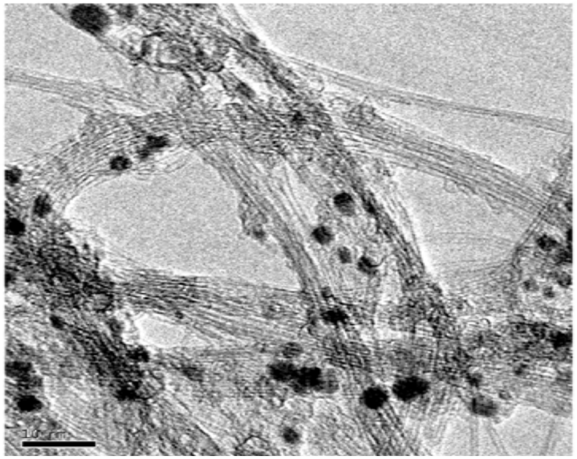
Gilman, et.al. *Chem. Mater.* 12, 1866, 2000.

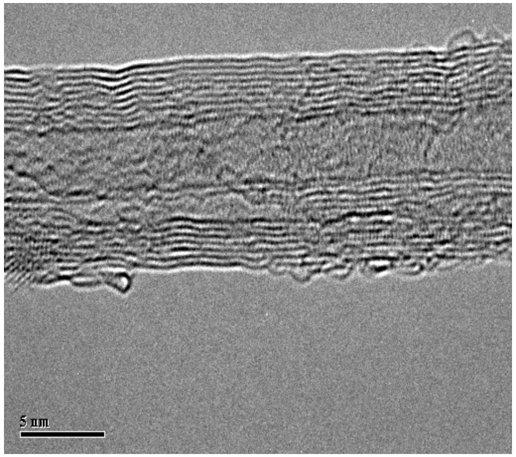

WD = 7 mm
Mag = 30.00 K X
1µm
File Name = 070707-008.tif
Signal A = RBSD
EHT = 15.00 kV
Date :7 Jul 2007
Time :14:06:56

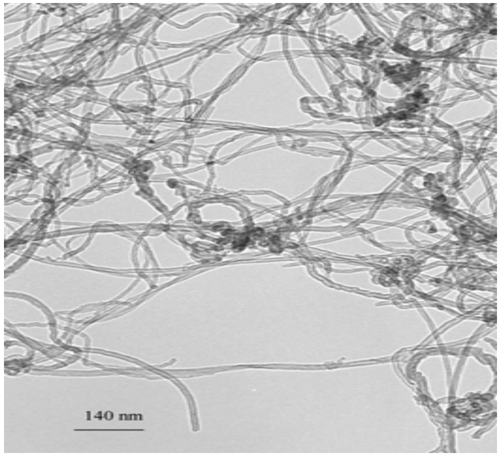
Park, SC, 2007

Effects of Shape of Nanoparticles

- **Tube** – Carbon nanotubes

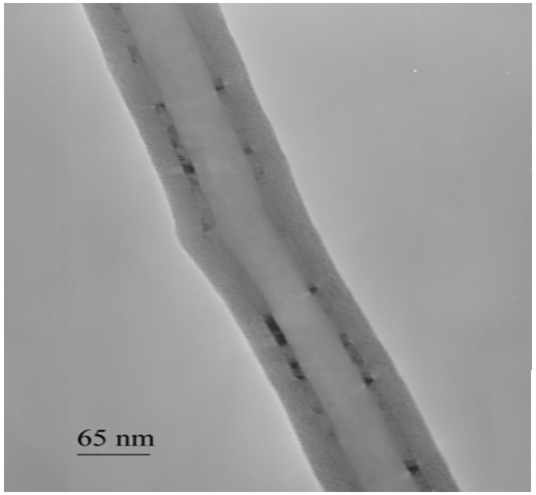


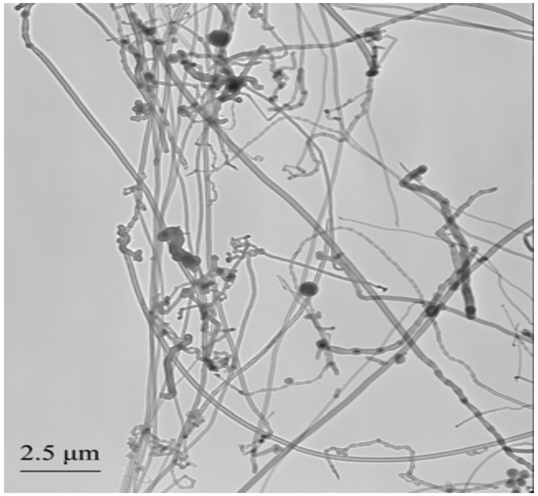




SWNT

MWNT





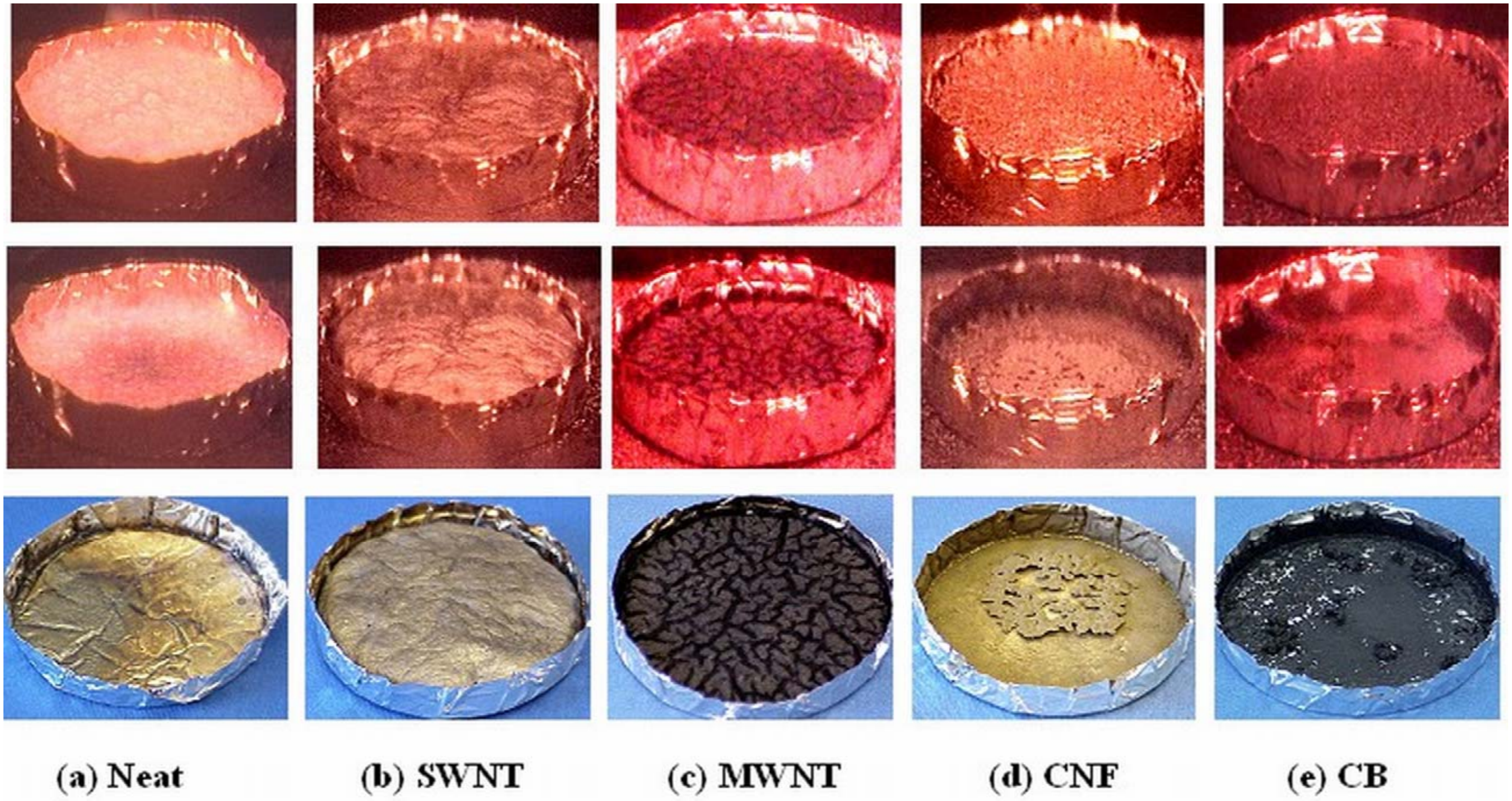
CNF

Kashiwagi, et al. Nature Mater, *4, 928, 2005*

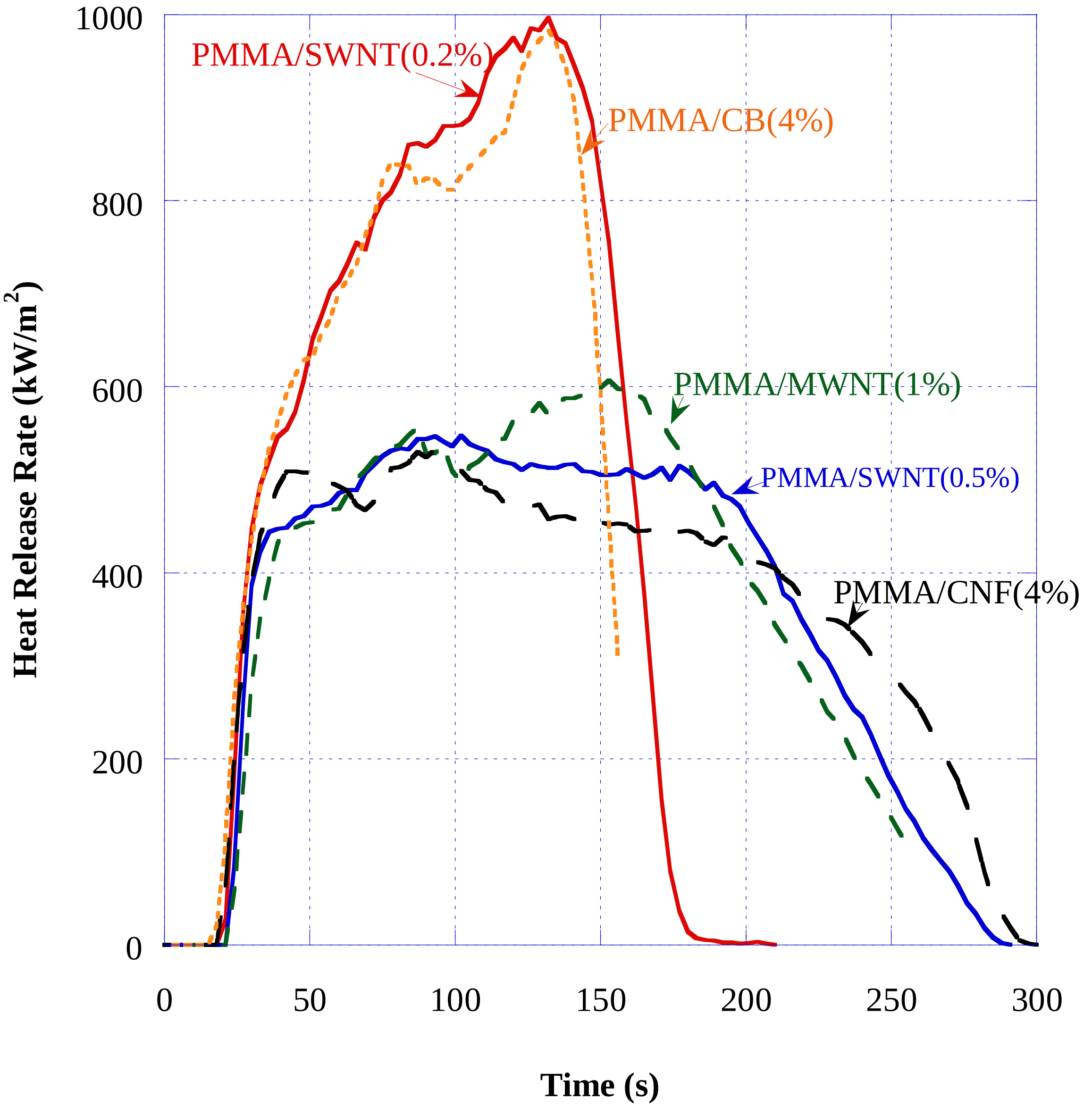
- **Effects of type of nanotubes ?**

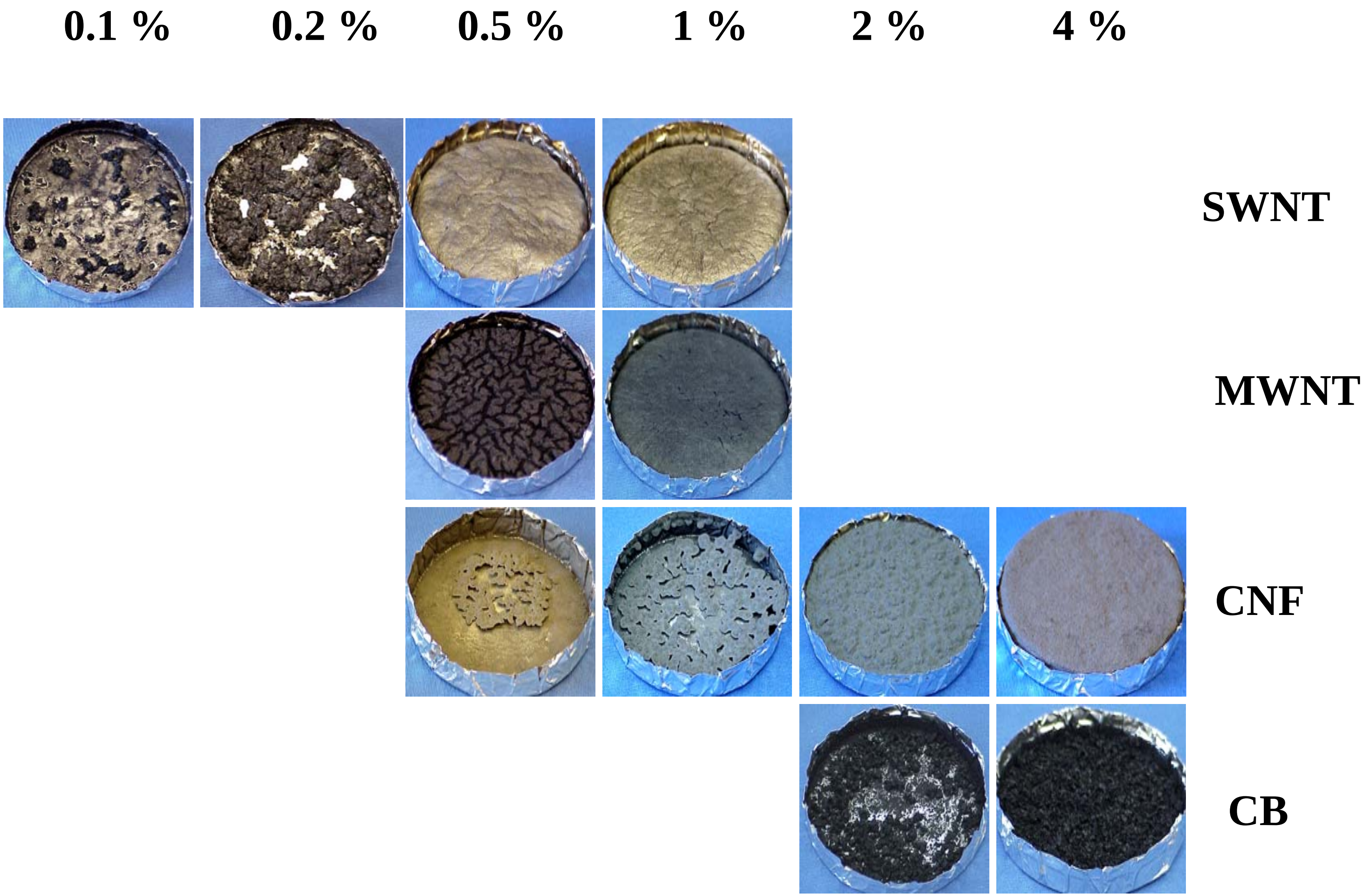
Sample behavior during gasification in nitrogen at 50 kW/m²

PMMA/CNT(0.5 %)



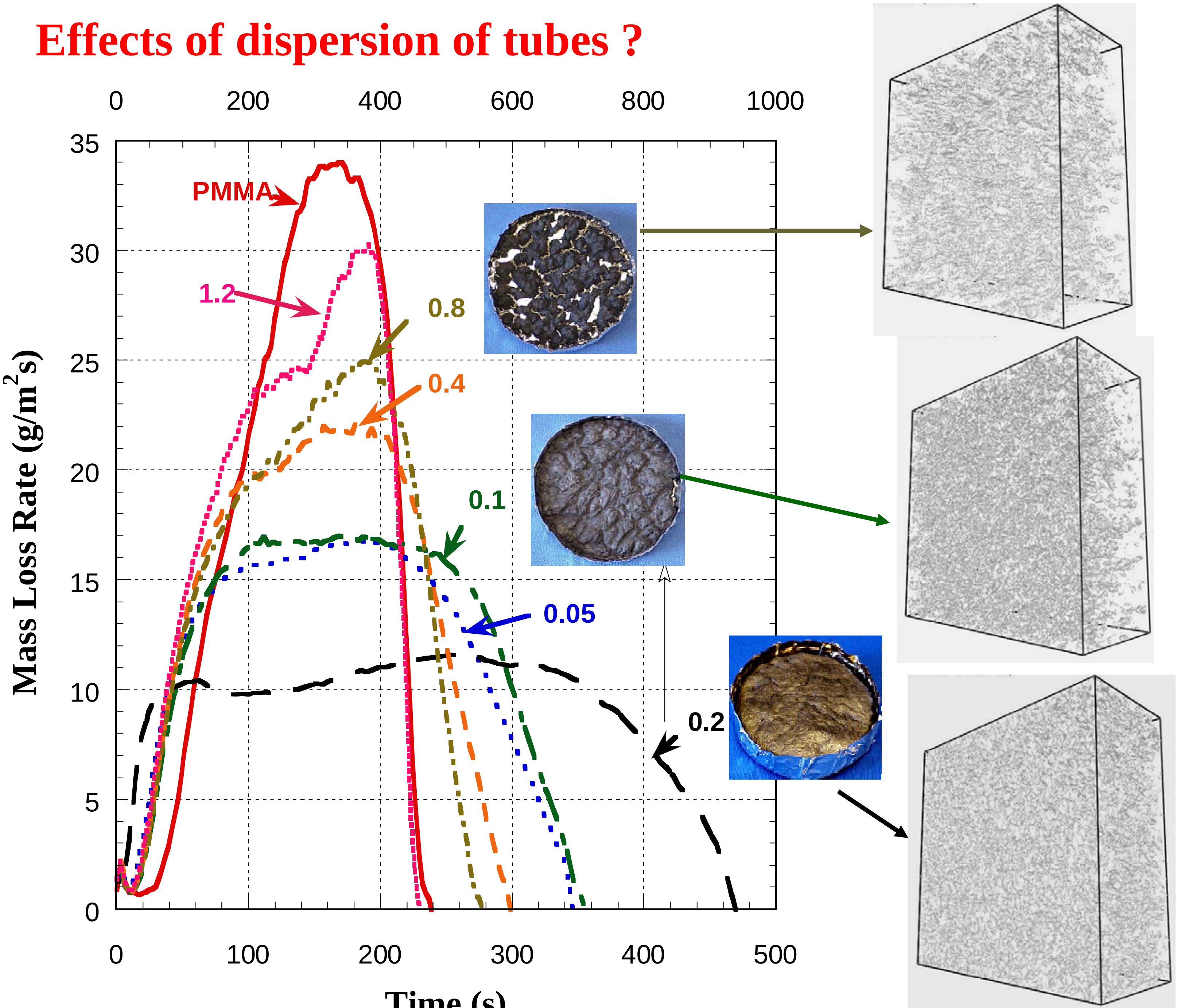
In Cone Calorimeter at 50 kW/m^2





Residues collected after nitrogen gasification tests at 50 kW/m^2

Effects of dispersion of tubes ?

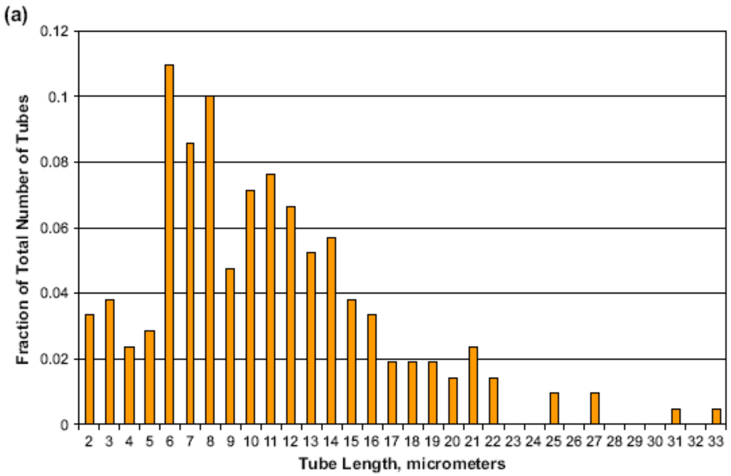


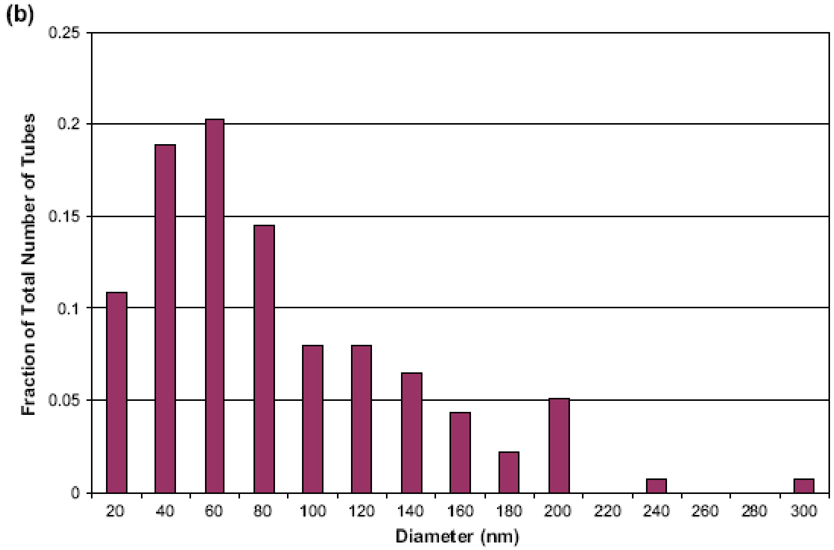
Kashiwagi, et al.

Polymer, 48, 4855, 2007

Cipiriano, et al. *Polymer*, 48, 6086, 2007.

Effects of aspect ratio ?





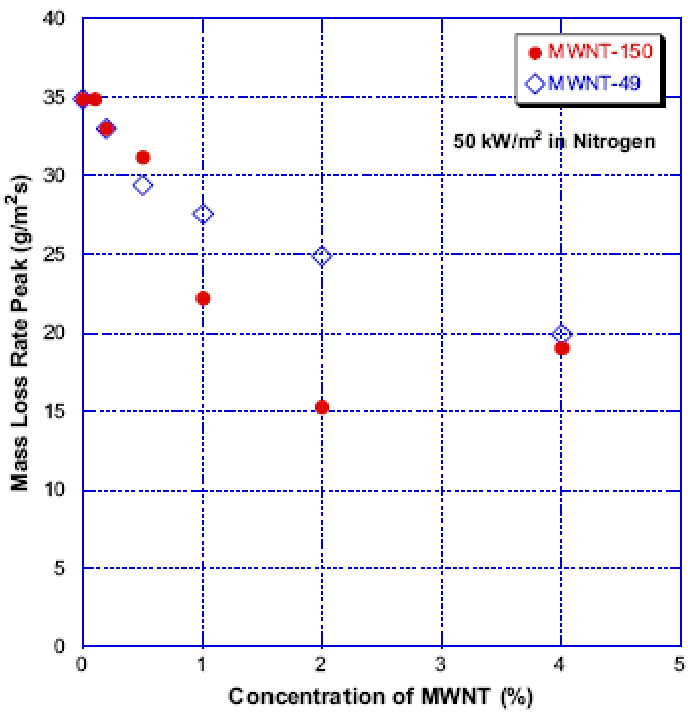
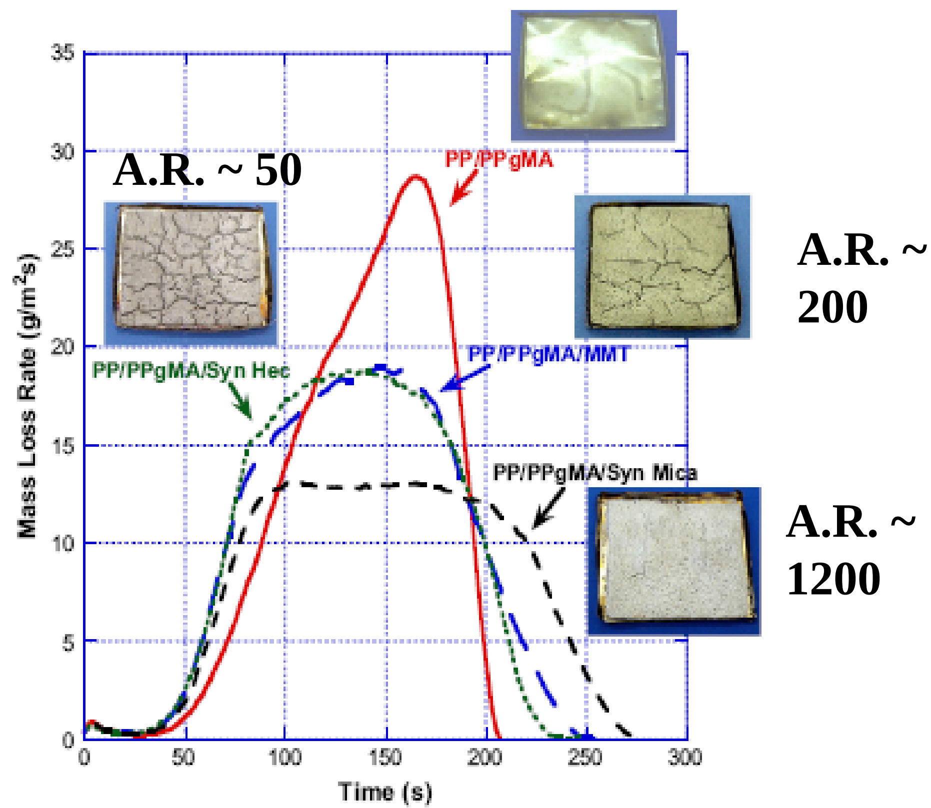
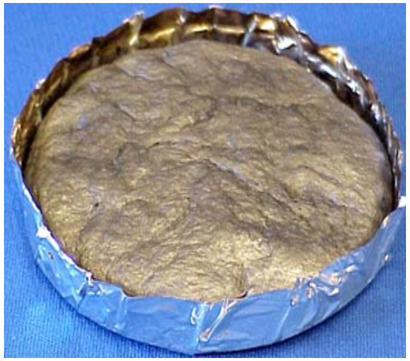


Fig. 11. The effects of aspect ratio of MWNT on the relationship between mass loss rate peak and mass concentration of MWNT.



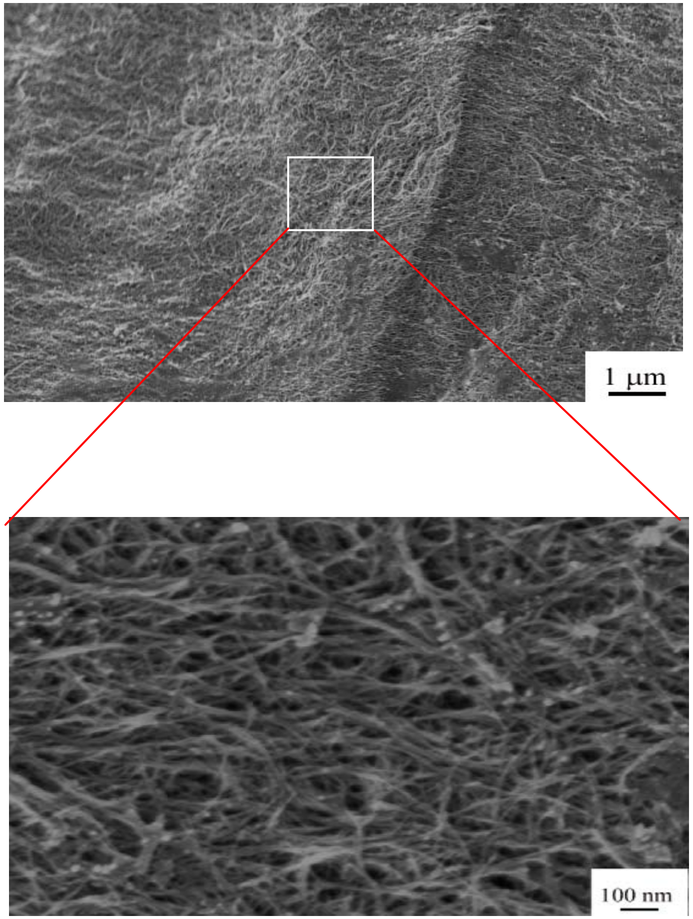
• FR Mechanisms



SWNT(0.5%)

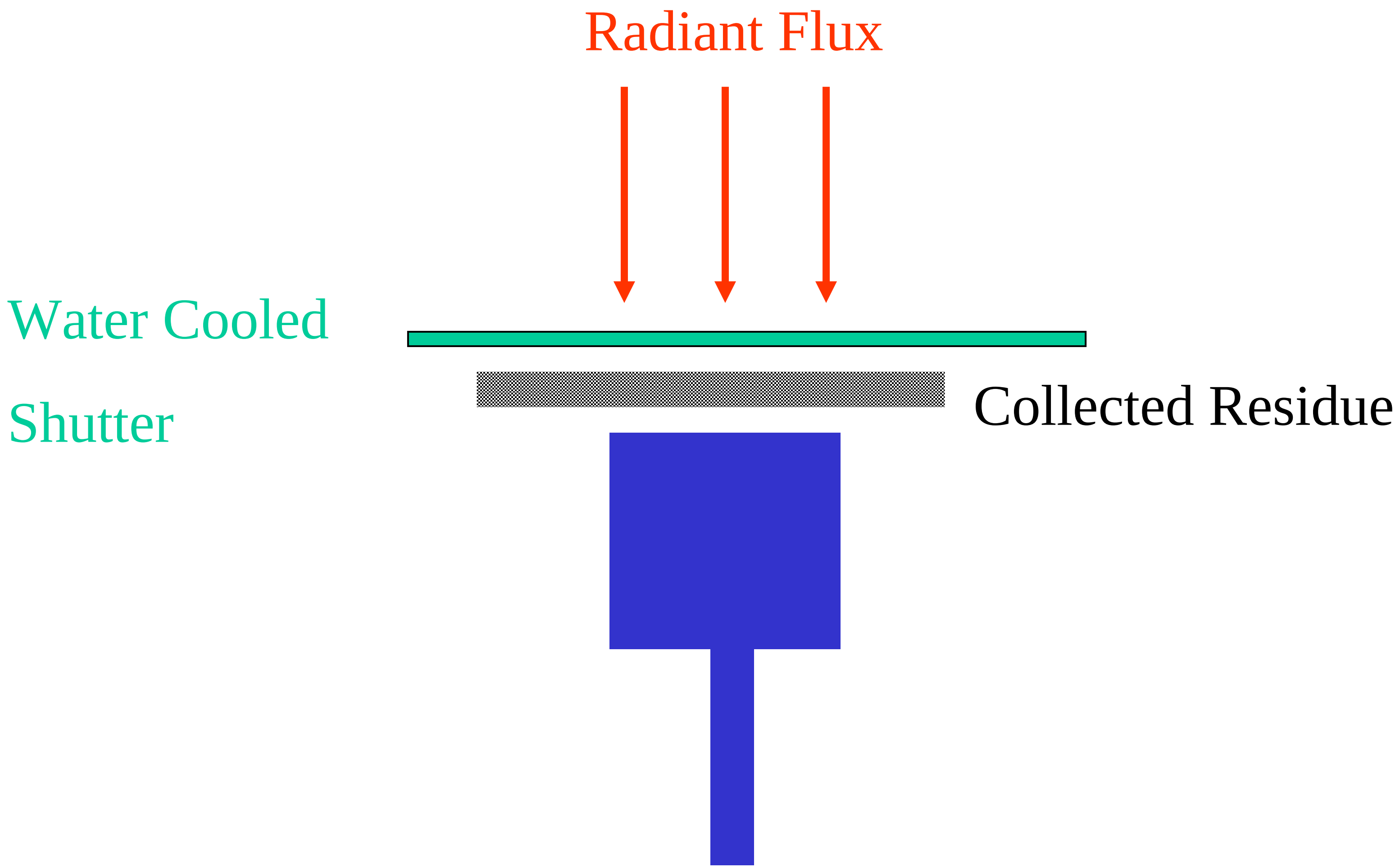
MWNT(1%)

CNF(4%)

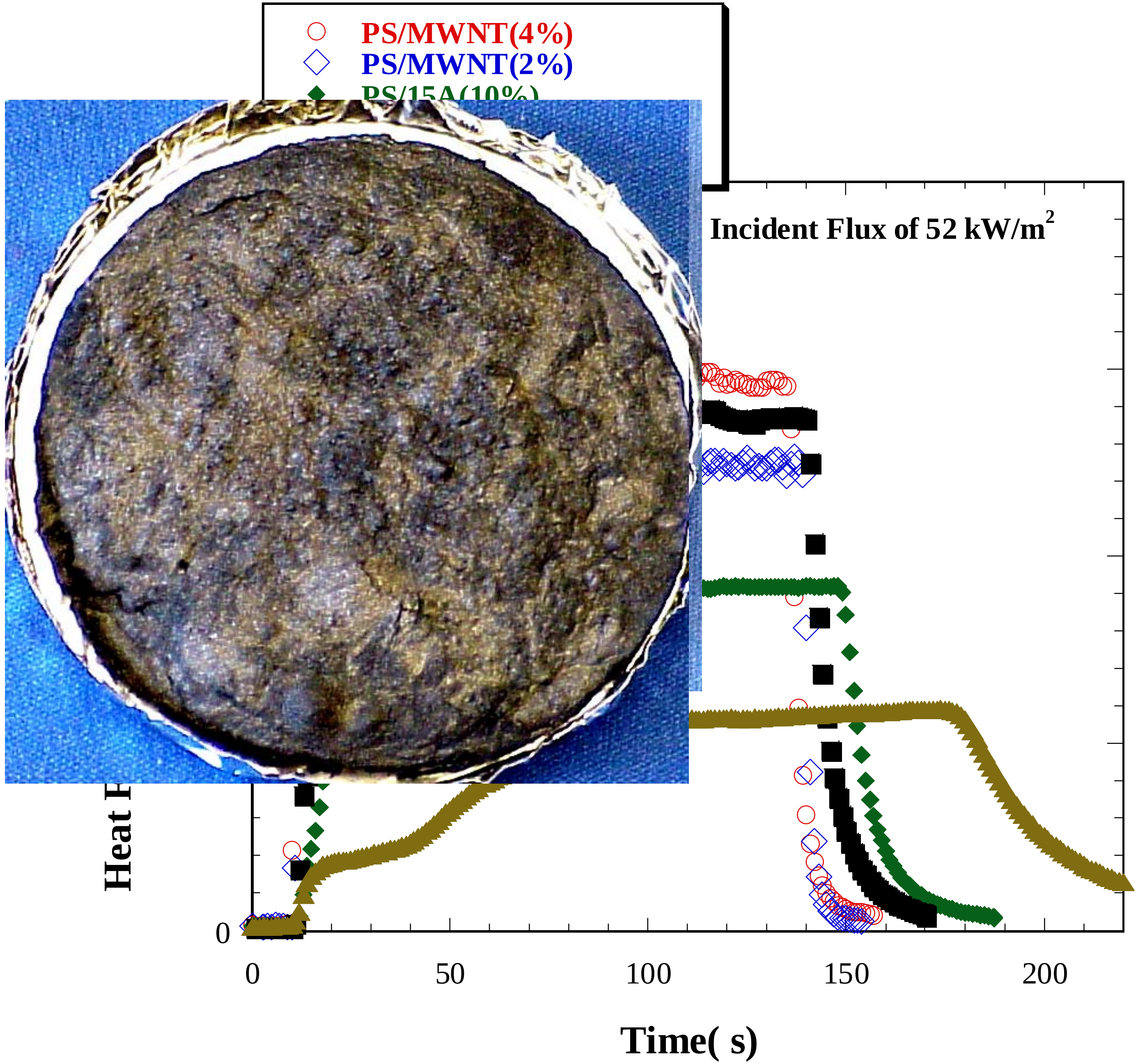


SEM image of the residue of PMMA/SWNT(1%) collected after nitrogen gasification indicating a randomly interlaced structure.

Kashiwagi, et al. *Polymer*, 46, 471, 2005.

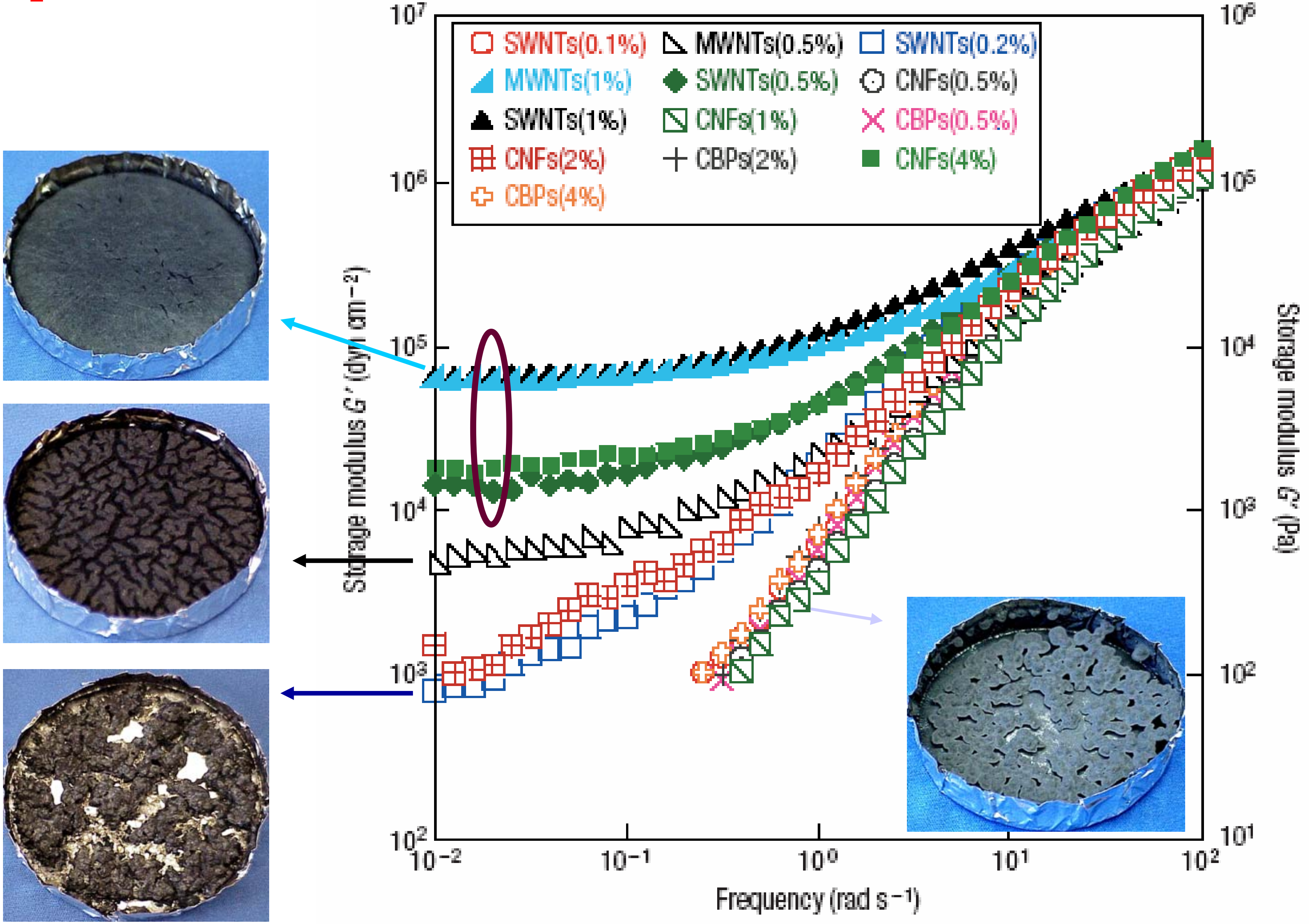


Radiant Flux
Water Cooled
Shutter
Collected Residue



PS/MWNT(4%)
PS/MWNT(2%)
PS/15A(10%)
Incident Flux of 52 kW/m2
Heat R
0
0
50
100
150
200
Time(s)

Any relationship between viscoelastic property and FR performance ?



Kashiwagi, et al.,*Nature Mater*. 4, 928, 2005.

Requirements for high FR polymer nanocomposites - to form network structure

- Good dispersion of nanoparticles
- High aspect ratio of nanoparticles
- Need minimum concentration of nanoparticles
- High Mn of resin

- Possible Screening Test
- Viscoelastic measurement to determine the formation of jammed network of initial sample

- **Flammability of Polymer nanocomposites:**
- **reduce peak heat release rate**
- **do not reduce total heat release**
- **need further reduction in heat release rate**

How ?

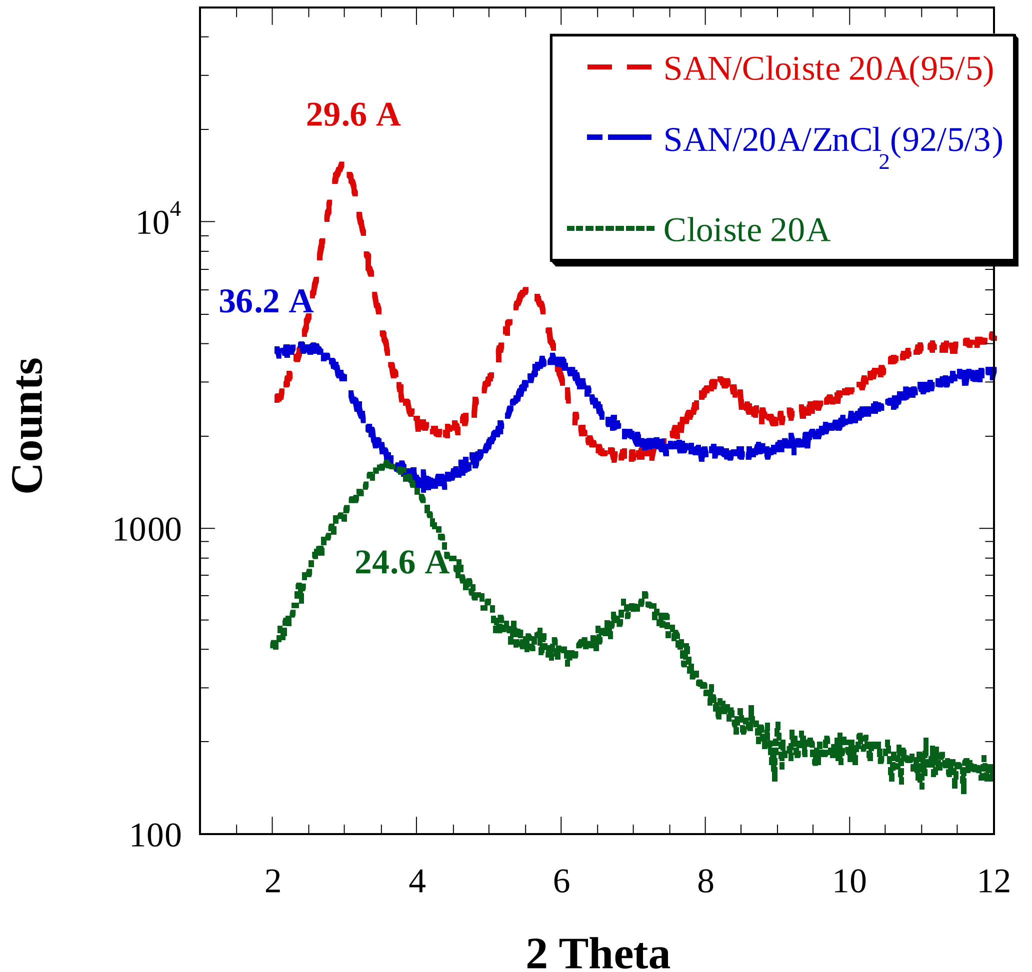
1. Nanocomposites plus existing FR additives

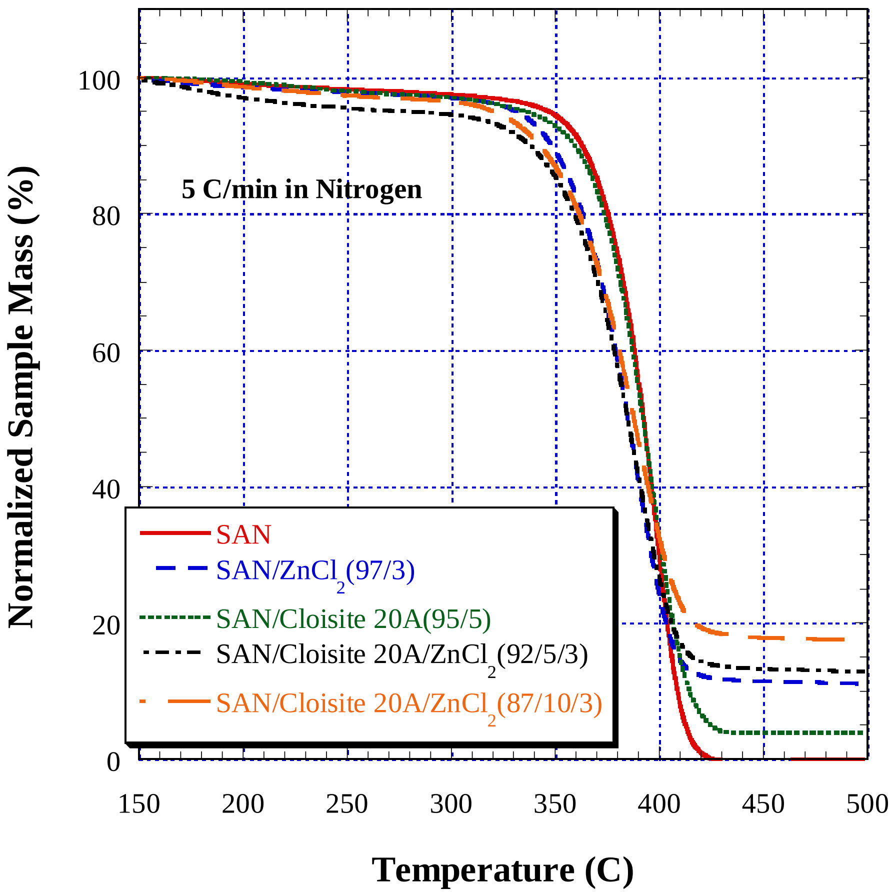
2. Enhance char formation (our approach)

- **Combination of clay with catalysts**
- **Special functionalization on clay surface**

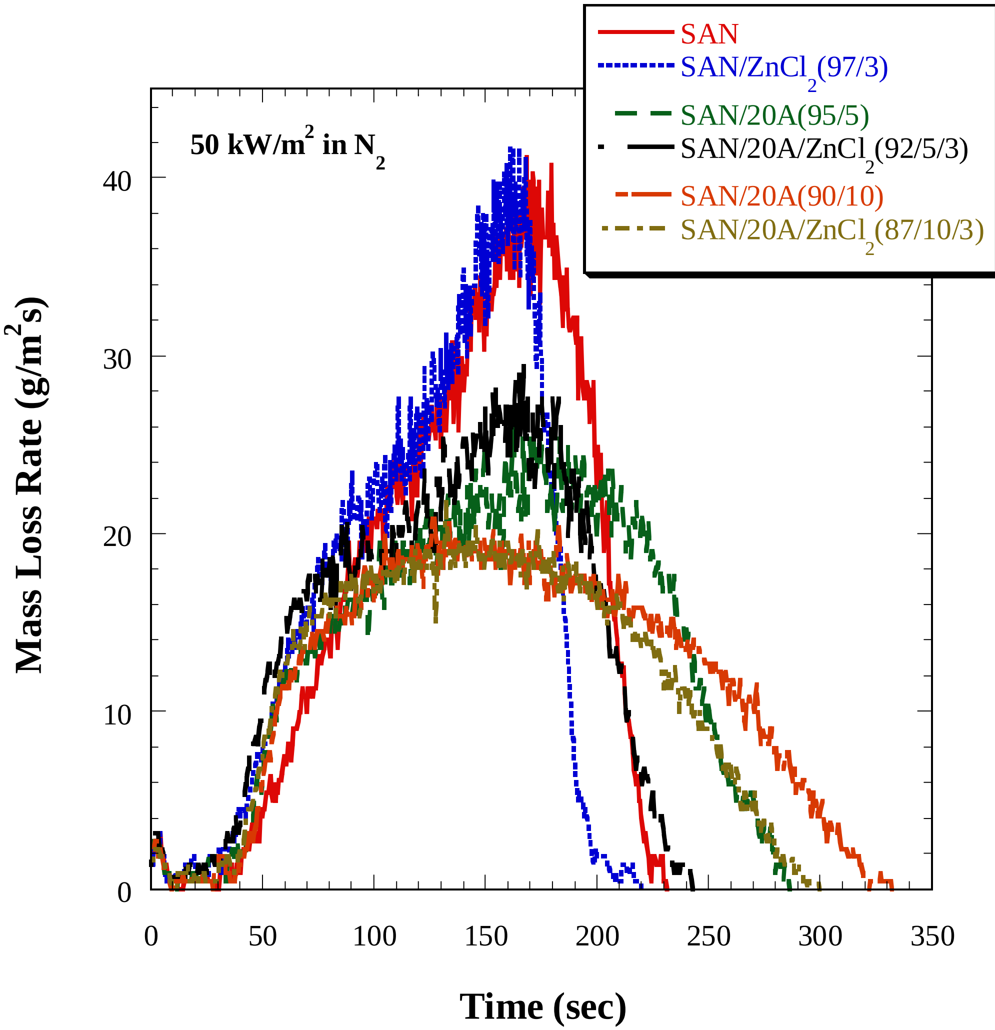
SAN/clay/$ZnCl_2$

- **SAN(PS/PAN(75/25))**
- **Solvent (THF) blending**
  - **18 g of SAN in 200 ml of THF**
  - **1 g of cloisite 20A and 0.6 g of $ZnCl_2$ in 100 ml of THF**
  - **Sonication and stiring**
  - **Drying and annealing**
- **SAN, SAN/20A(95/5), SAN/$ZnCl_2$(95/3), SAN/20A/$ZnCl_2$(90/5/3), SAN/20A(90/10), SAN/20A/$ZnCl_2$(87/10/3**





5 C/min in Nitrogen
Normalized Sample Mass (%)
Temperature (C)
0
20
40
60
80
100
150
200
250
300
350
400
450
500
SAN
SAN/ZnCl$_2$(97/3)
SAN/Cloisite 20A(95/5)
SAN/Cloisite 20A/ZnCl$_2$(92/5/3)
SAN/Cloisite 20A/ZnCl$_2$(87/10/3)



50 kW/m^2 in N$_2$
Mass Loss Rate (g/m^{2}s)
Time (sec)
0
10
20
30
40
0
50
100
150
200
250
300
350
SAN
SAN/ZnCl$_2$(97/3)
SAN/20A(95/5)
SAN/20A/ZnCl$_2$(92/5/3)
SAN/20A(90/10)
SAN/20A/ZnCl$_2$(87/10/3)

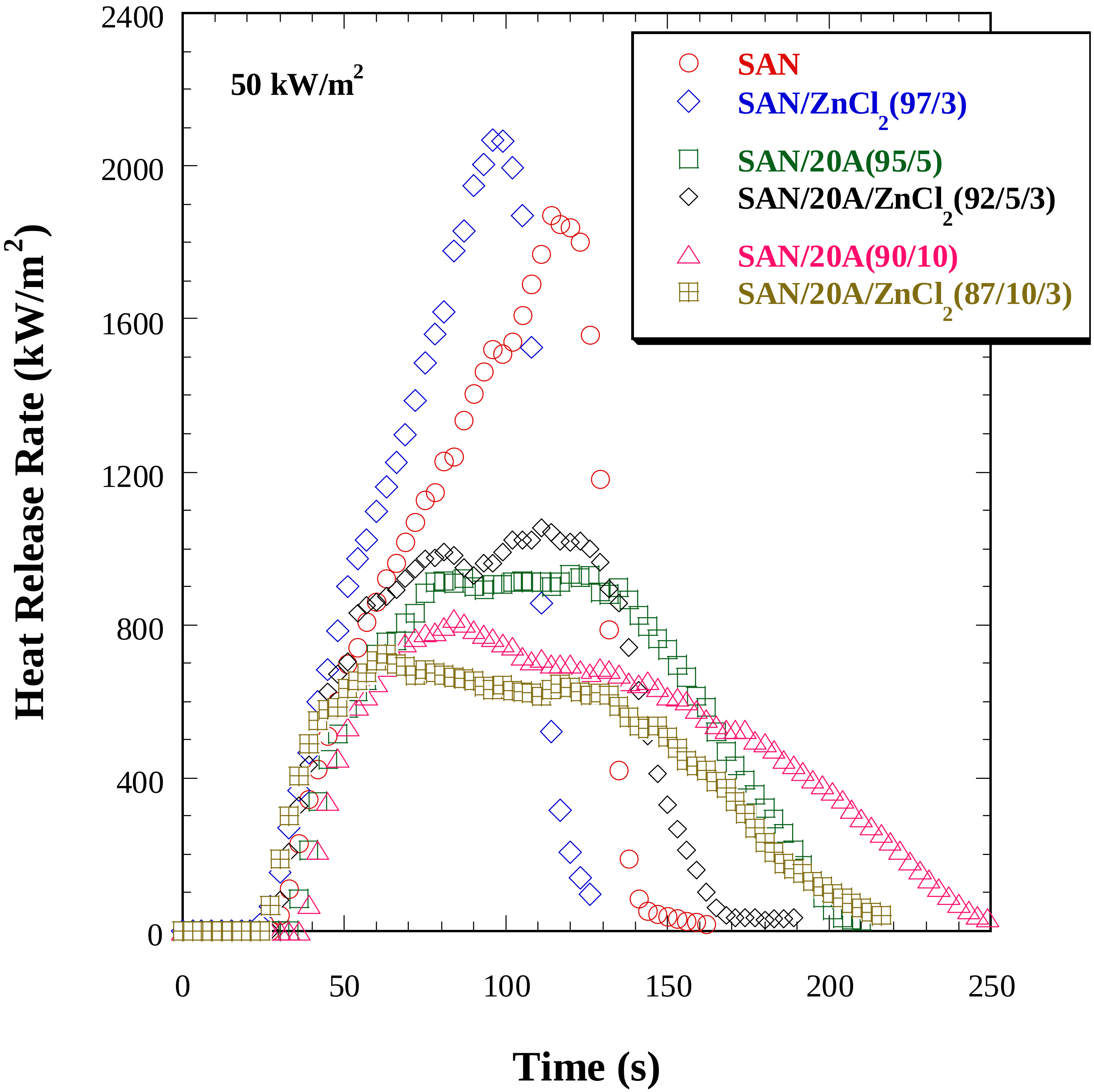
Videos Deleted

SAN/$ZnCl_2$(97/3)

SAN/20A/$ZnCl_2$(87/10/3)

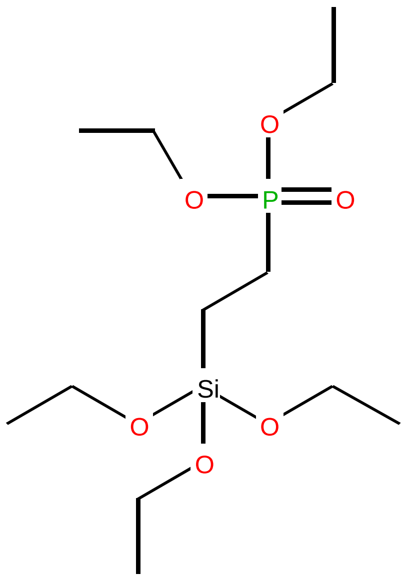
Pictures of residues of SAN with additives collected after gasification tests at 50 kW/m^2 in a nitrogen atmosphere

SAN	SAN/$ZnCl_2$ 97/3	SAN/20A 95/5	SAN/20A/$ZnCl_2$ 92/5/3	SAN/20A 90/10	SAN/20A/$ZnCl_2$ 87/10/3



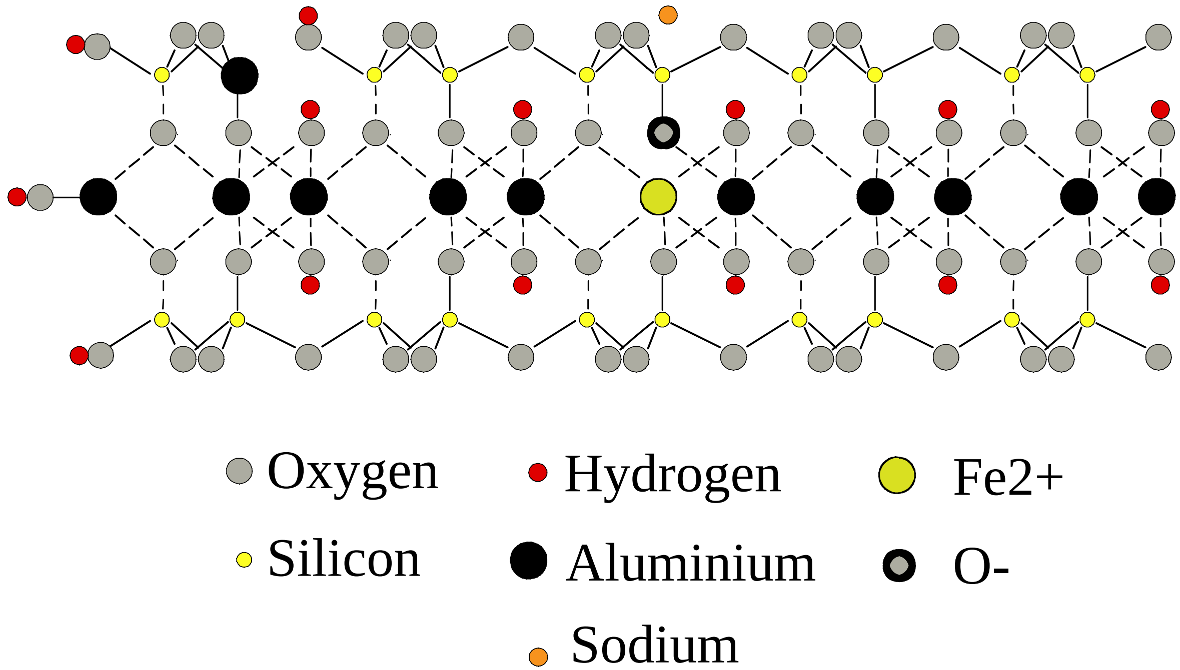
2400
2000
1600
1200
800
400
0
0
50
100
150
200
250
Heat Release Rate (kW/m2)
Time (s)
50 kW/m2
SAN
SAN/ZnCl2(97/3)
SAN/20A(95/5)
SAN/20A/ZnCl2(92/5/3)
SAN/20A(90/10)
SAN/20A/ZnCl2(87/10/3)

Clay modification background

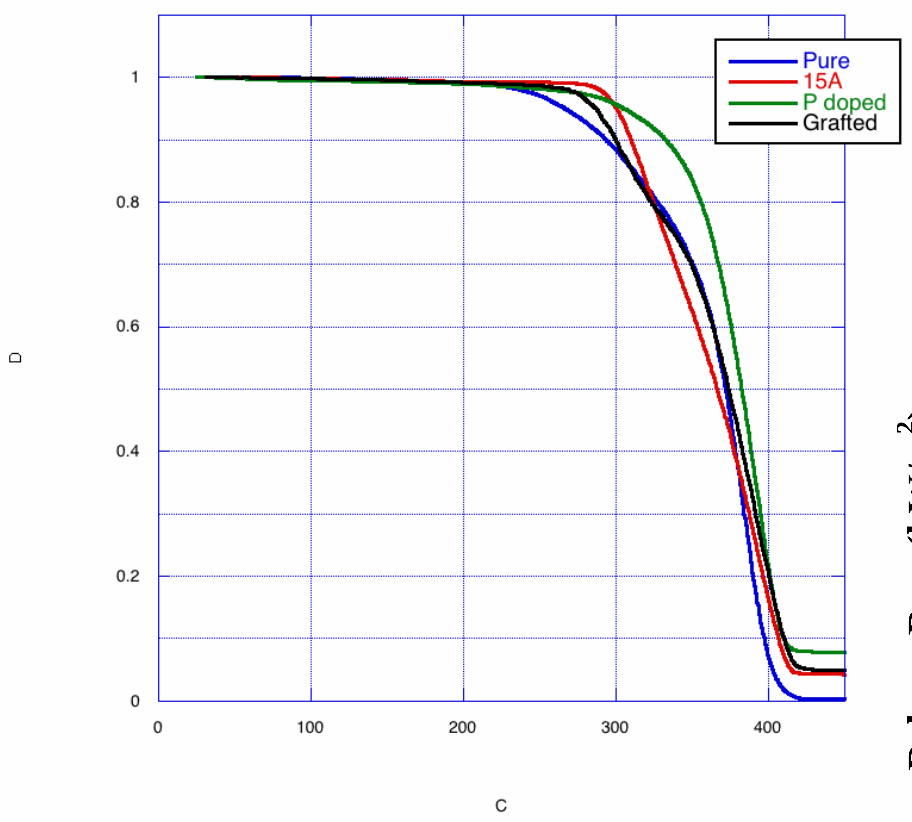


Diethylphosphatoethyl triethoxysilane

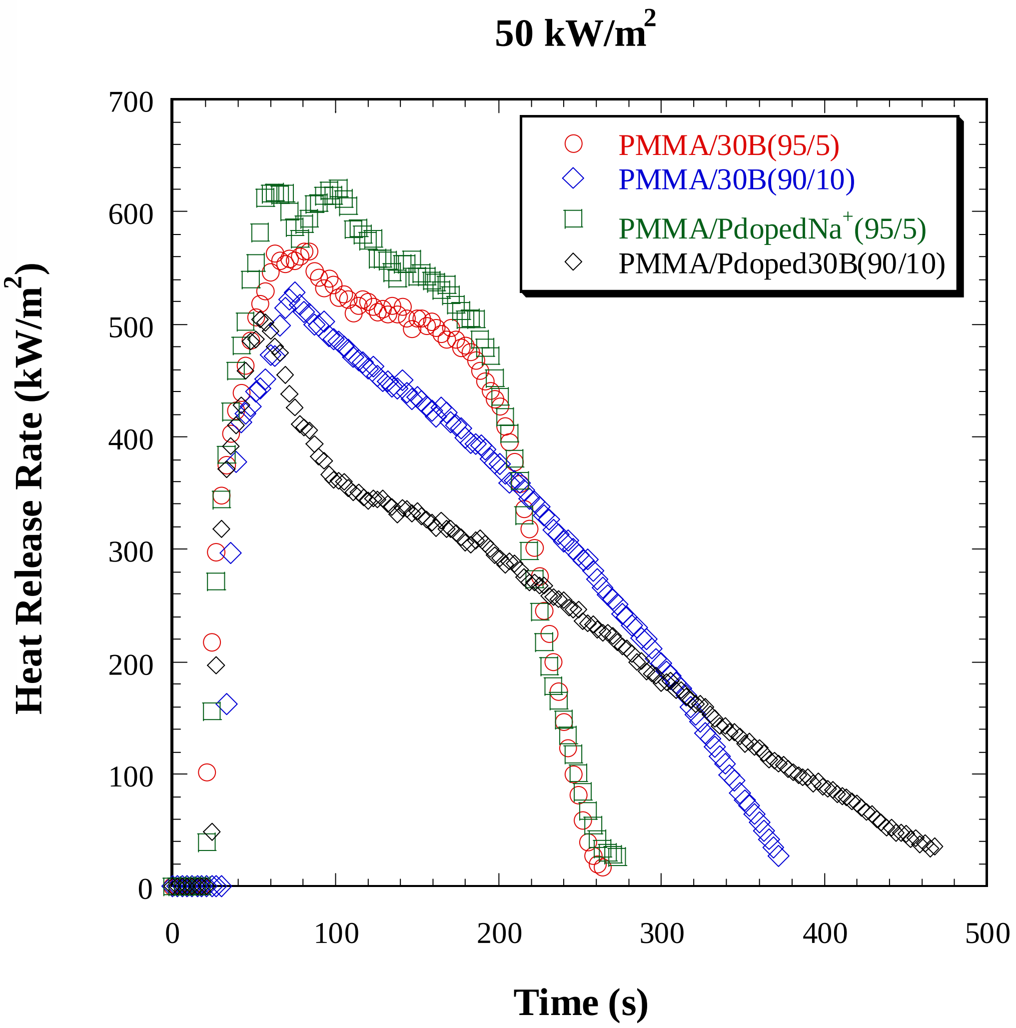
Potential sites for silane to attach

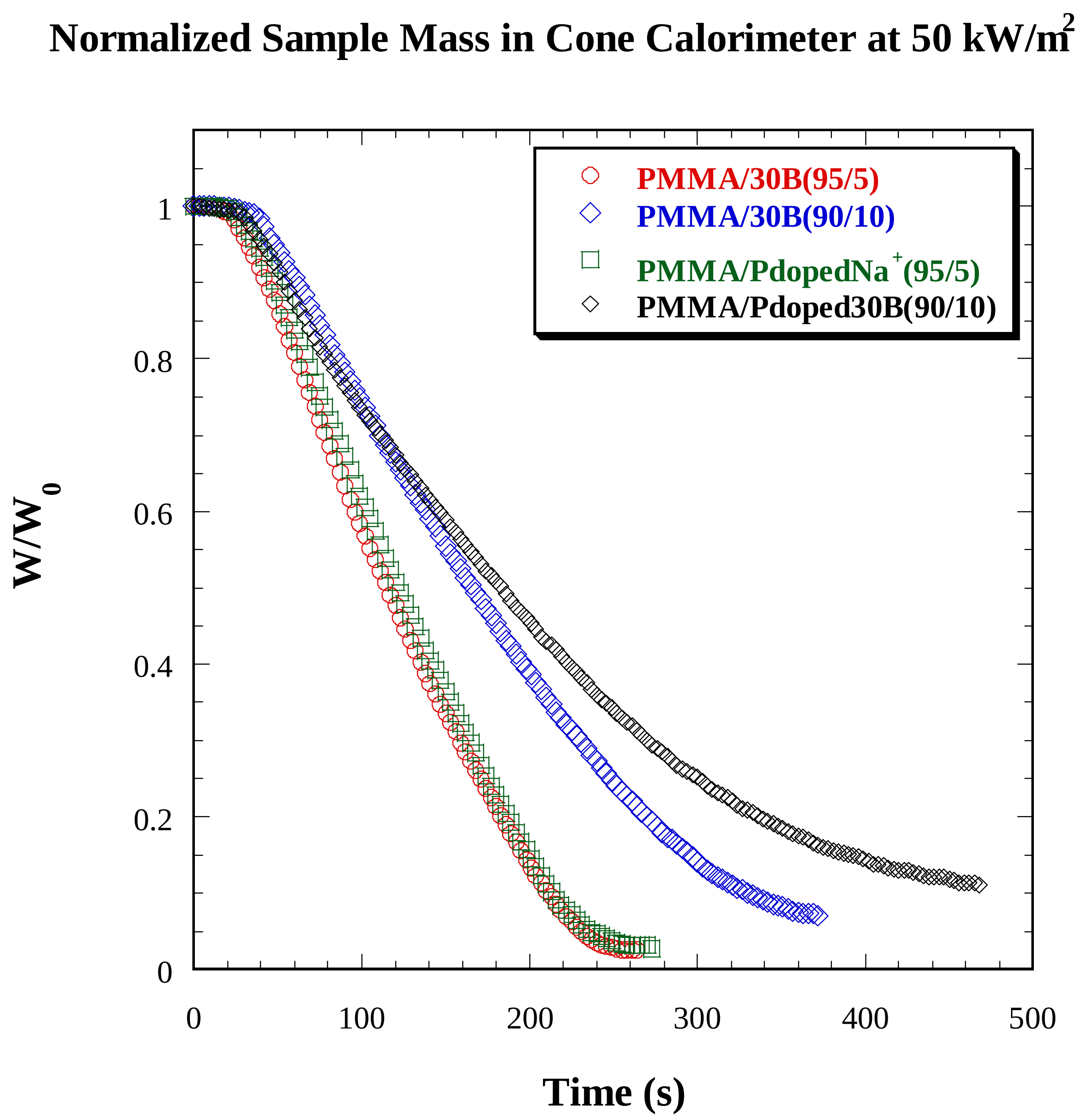


Clay Structure with hydroxy group on edge or aluminum sites (A sites)



•P containing silane improved the thermal stability of the nanocomposites





Normalized Sample Mass in Cone Calorimeter at 50 kW/m2
W/W0
Time (s)
PMMA/30B(95/5)
PMMA/30B(90/10)
PMMA/PdopedNa+(95/5)
PMMA/Pdoped30B(90/10)
0
0.2
0.4
0.6
0.8
1
0
100
200
300
400
500

Acknowledgement

Richard Harris, John Shields, Jeffrey Gilman, Alex Morgan (currently Dayton Research Inst.), Tom Ohlemiller,
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Jenny Hilding, Xing Ying, Eric Grulke – University of Kentucky

Bani Cipiriano, Srini Raghavan– University of Maryland