National Institute of Standards and Technology

Role of Nano-Additives in Fire Science: High Performance Fabrics and Foams

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Fire Research Division
NIST

Building and Fire Research Laboratory

...dedicated to improving performance and safety of constructed facilities

Challenges

1) <u>Furniture and mattress fires</u> still cause ~1000 deaths/yr and cost $ 500 M/yr

   1) **Objective:** to evaluate the effectiveness of <u>nanoadditive based flame retardants</u> in reducing the flammability of flexible foams.

   2) **Objective :** To improve the ability of barrier fabrics to prevent flame spread in mattresses and furniture using <u>nanoadditives</u>.

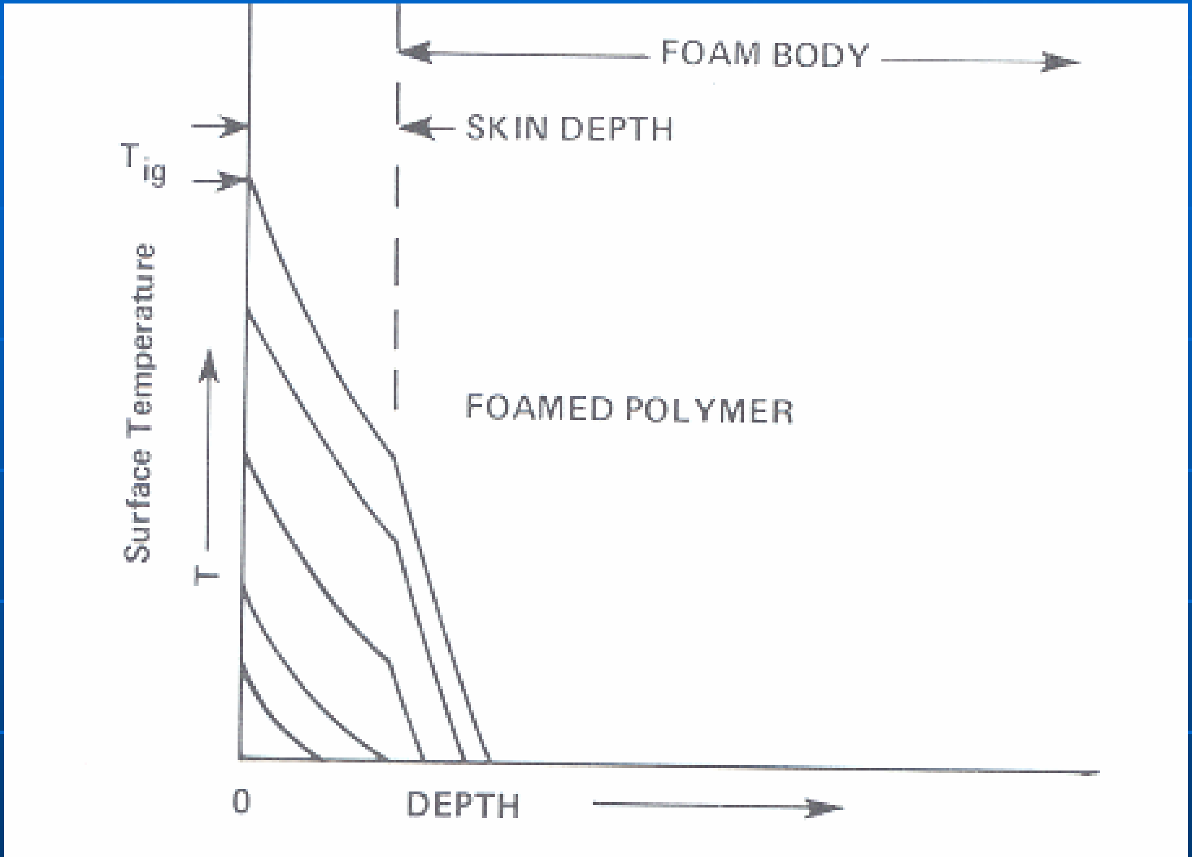
2) <u>Environmental degradation</u> (UV, oxidation) In <u>fire fighter turnout gear.</u>

   1) Objective : to evaluate the ability of carbon nanotubes to stop these degradation mechanisms in turnout gear

Flammability of Foam

- The special flammability characteristics of foamed polymers have been recognized for more than 25 years
  - Due to:
    - low density (ρ)
    - low thermal conductivity (k)
    - high surface area (SA)

Flammability of Foam



Low thermal inertia (kρc) results in short ignition times for foams

Foam sample reaches ignition temperature ~10 x faster than solid polymer sample

Source: Fire Research on Cellular Plastics: Final Report of the Products Research Committee, 1980

Flammability of Foam

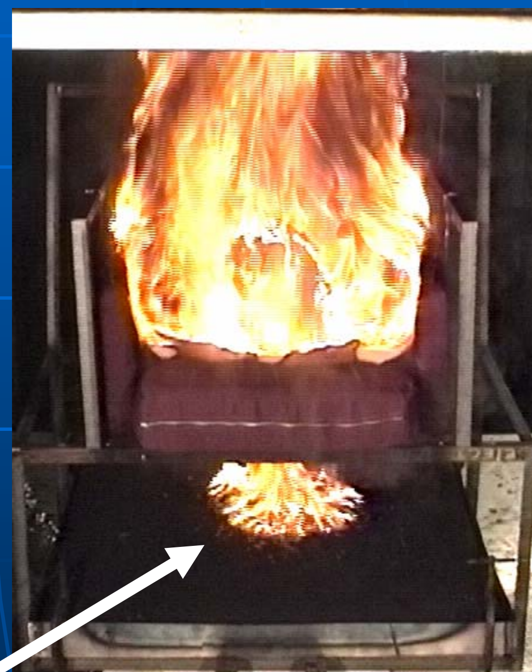
- **Rapid heating means:**
  - **Faster flame spread rate**
    - **flame spread rate ~ flame height / ignition time**
- **This combination implies the potential for fast development of a large fire**

Flammability of Foam

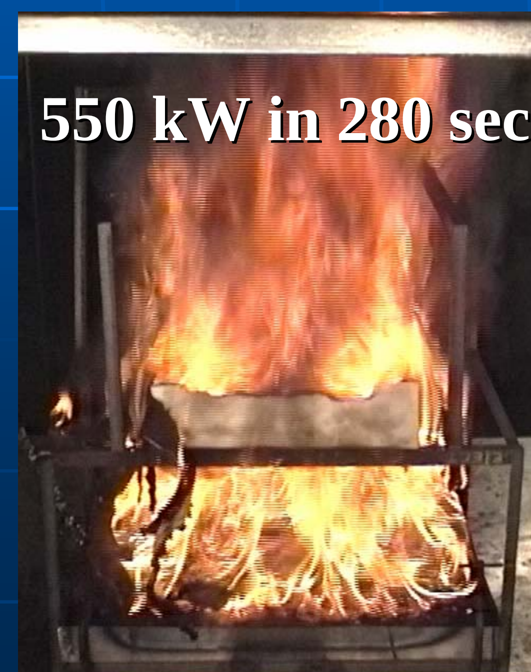
- Remedies for this tendency to rapid fire growth, in the case of flexible PU foams:
  - Barrier fabrics
  - Coatings
  - Fire resistant foam layer
  - Flame retardant additives

Furniture Mock-Up Behavior –PP fabric

PP Fabric/CAL-117 PU foam
Match size ignition
Full size cushion mock-up

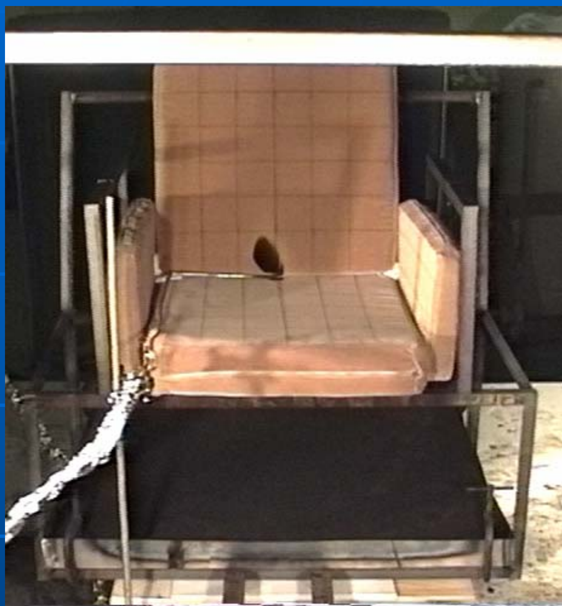


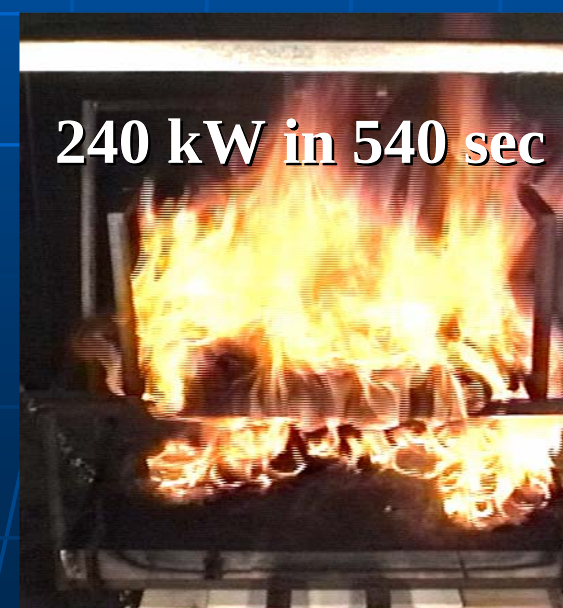
Melt pool fire



Furniture Mock-Up Behavior – Cotton Fabric

Cotton Fabric/CAL-117 PU foam
Match size ignition
Full size cushion mock-up

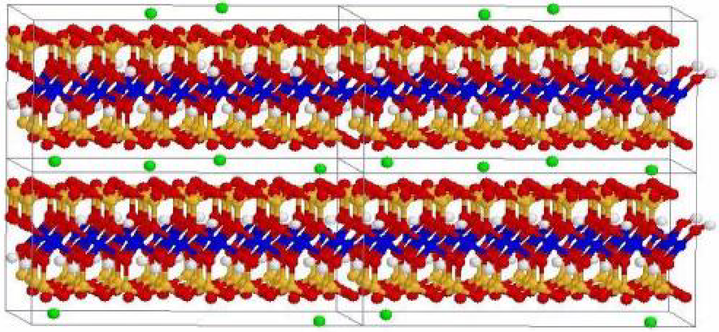


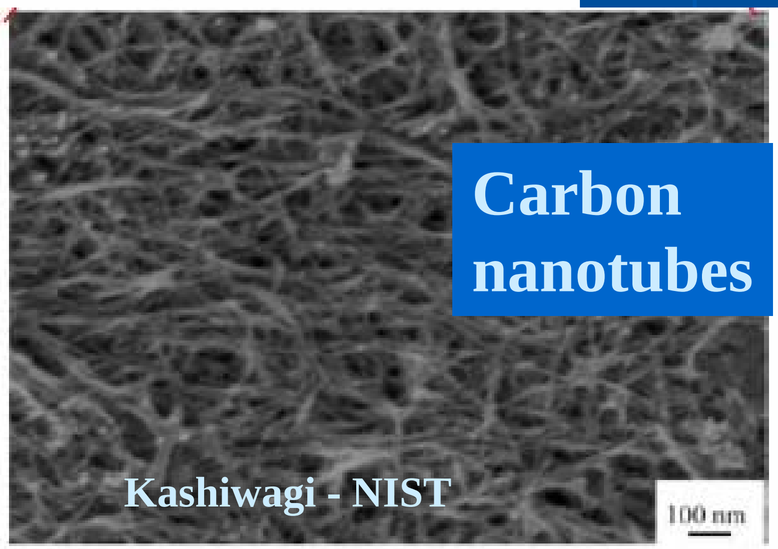


Melt pool fire starts later fabric absorbs foam melt prevents dripping

Nano-additives in Foam

Layered Silicates

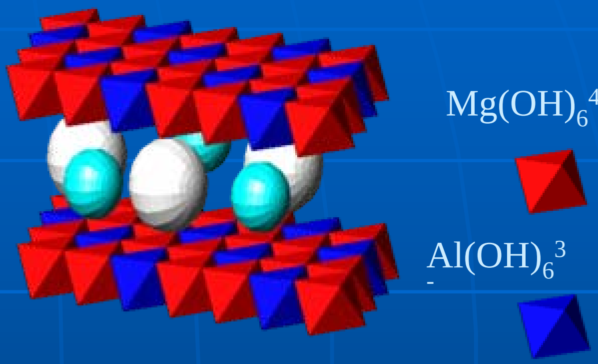




Carbon nanotubes

Kashiwagi - NIST

Layered Double Hydroxide



Zammarano-NIST/Cimteclab

POSS

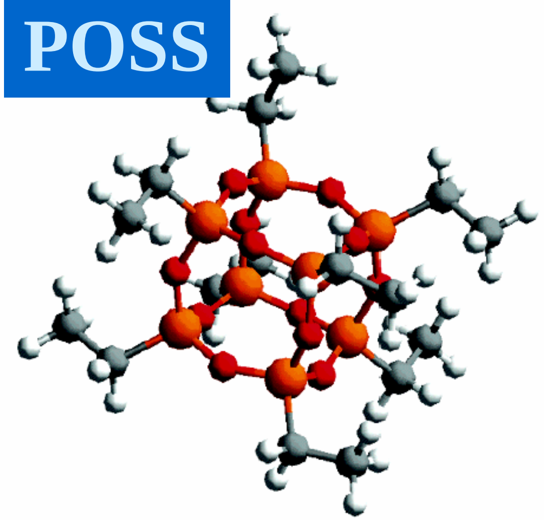
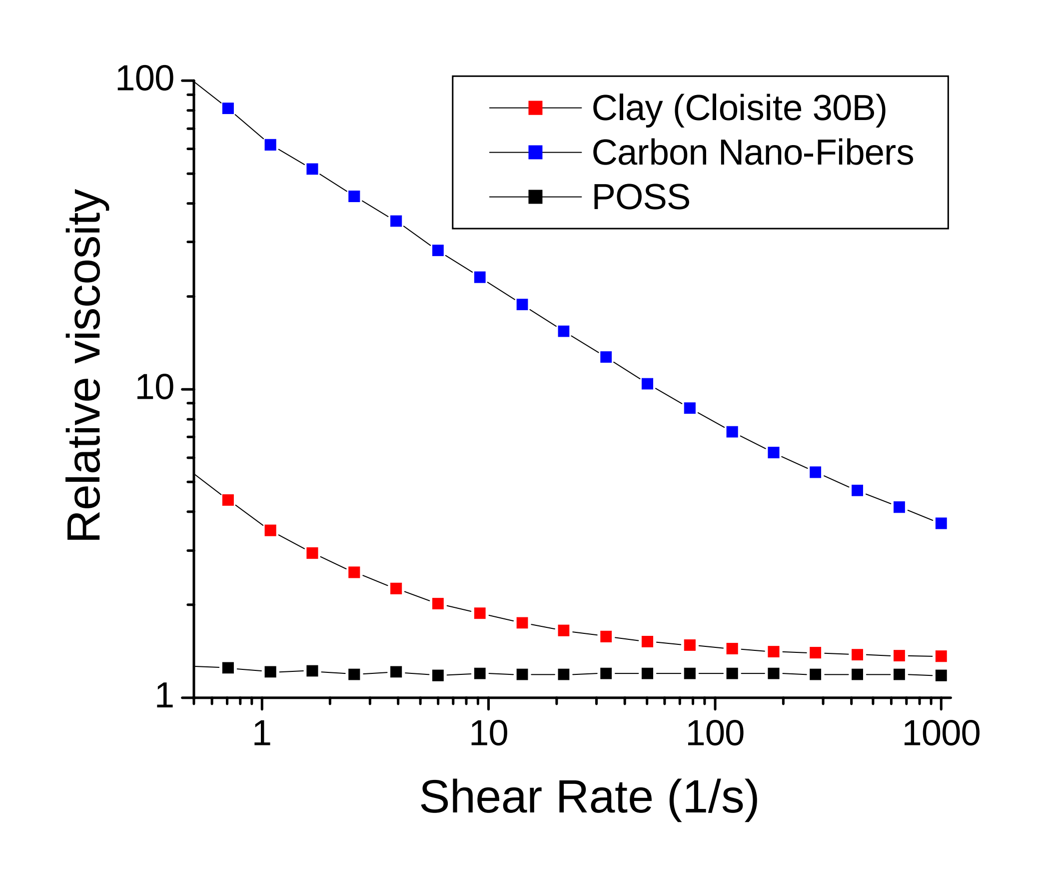


Image -Coughlin-U Mass

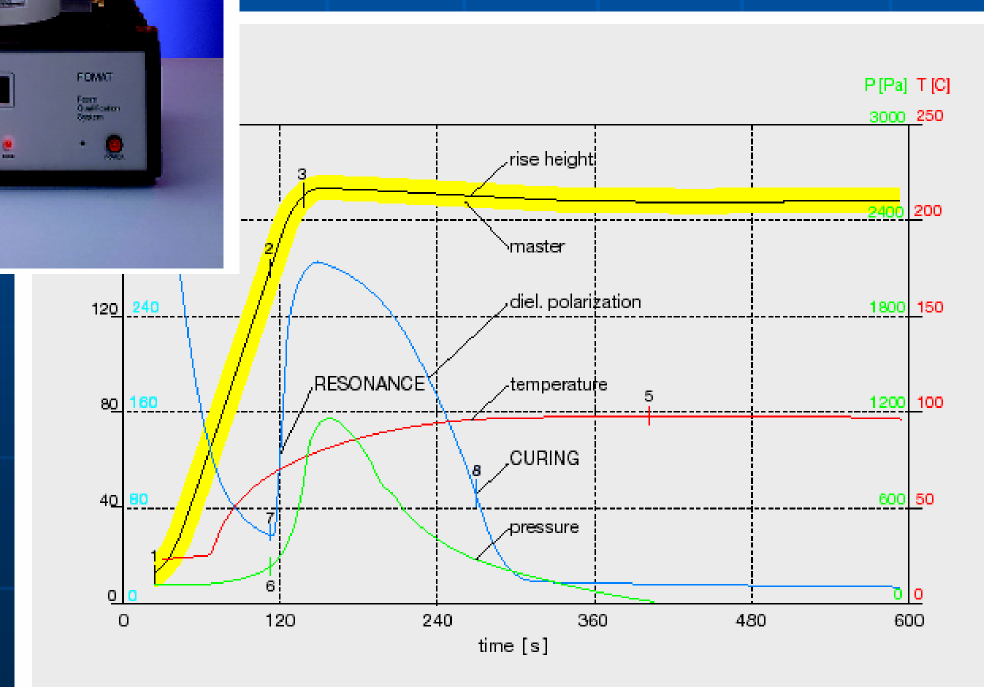
Foam Processing



FOAM PROCESSING OPTIMIZATION STEPS:

1. **Dispersion of the nanoparticles in the polyether polyol by high shear forces.**
2. **Adjustment of the polyol – nanoparticle dispersion viscosity by coupling agents.**
3. **Optimization of the curing and blowing reaction through suitable catalysis ratios.**
4. **Prevention of collapse and shrinkage by appropriate surfactants and cell openers.**
5. **Monitoring of the foam rise and curing with a FOAMAT foam qualification system.**
6. **Evaluation of the foam quality by optical analysis, density and air flow measurements.**

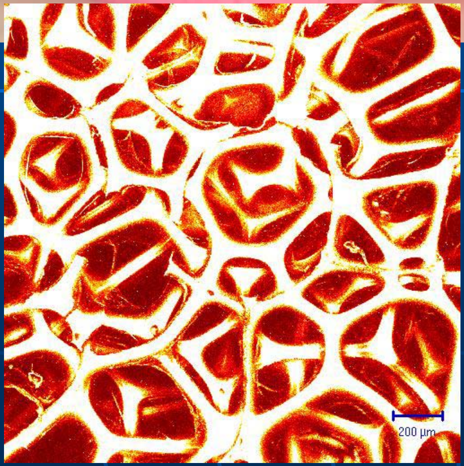
Foam Process Characterization

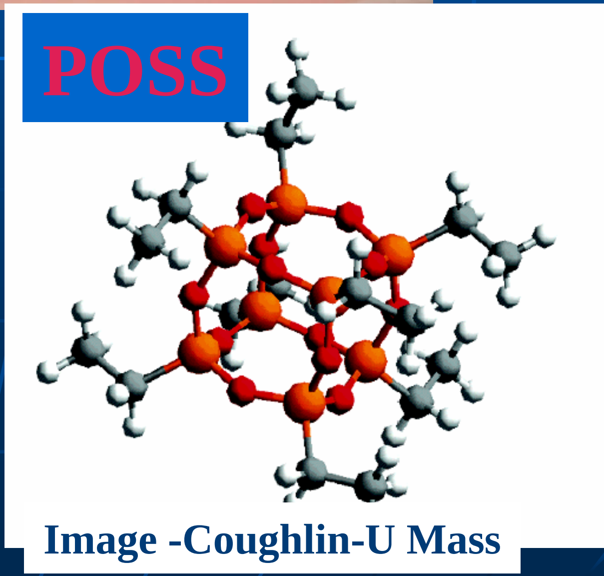


POSS Foam Samples

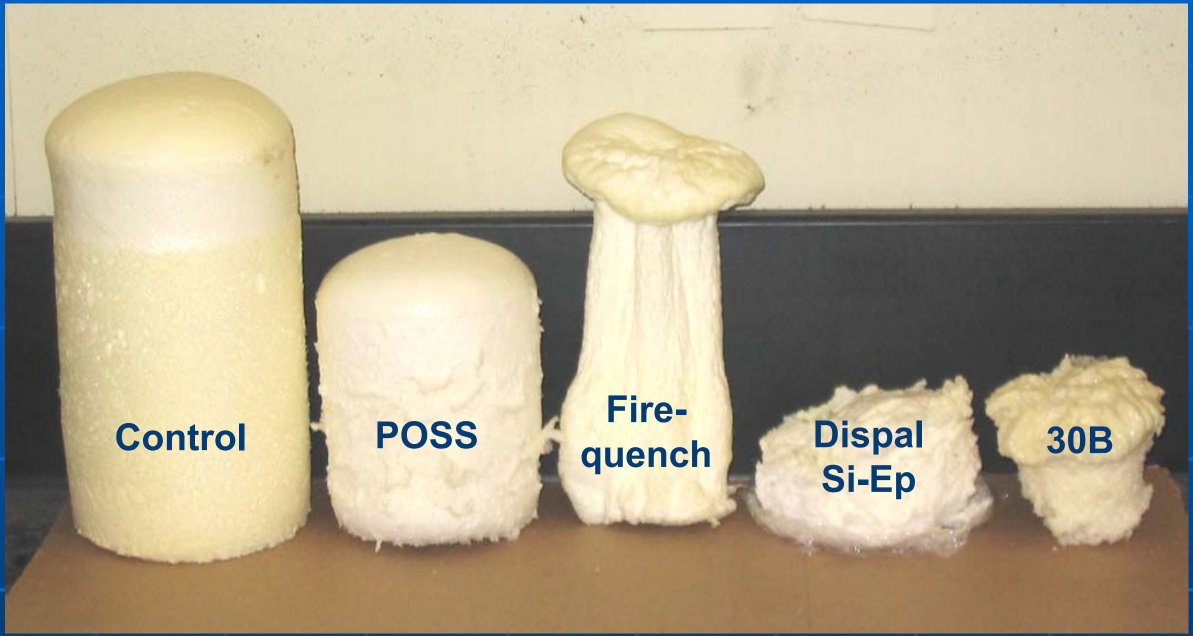
Control	Control + Fluorescent Dye	Fluorescent Dye + POSS Formulation 1	Fluorescent Dye + POSS Formulation 2

Confocal Image of foam cell structure





Foam Processing



Non-optimized foam samples with various additives.
Each formulation needs
to be individually tuned to match the control formulation.

FOAM PROCESSING OPTIMIZATION STEPS:

1. Dispersion of the nanoparticles in the polyether polyol by high shear forces.
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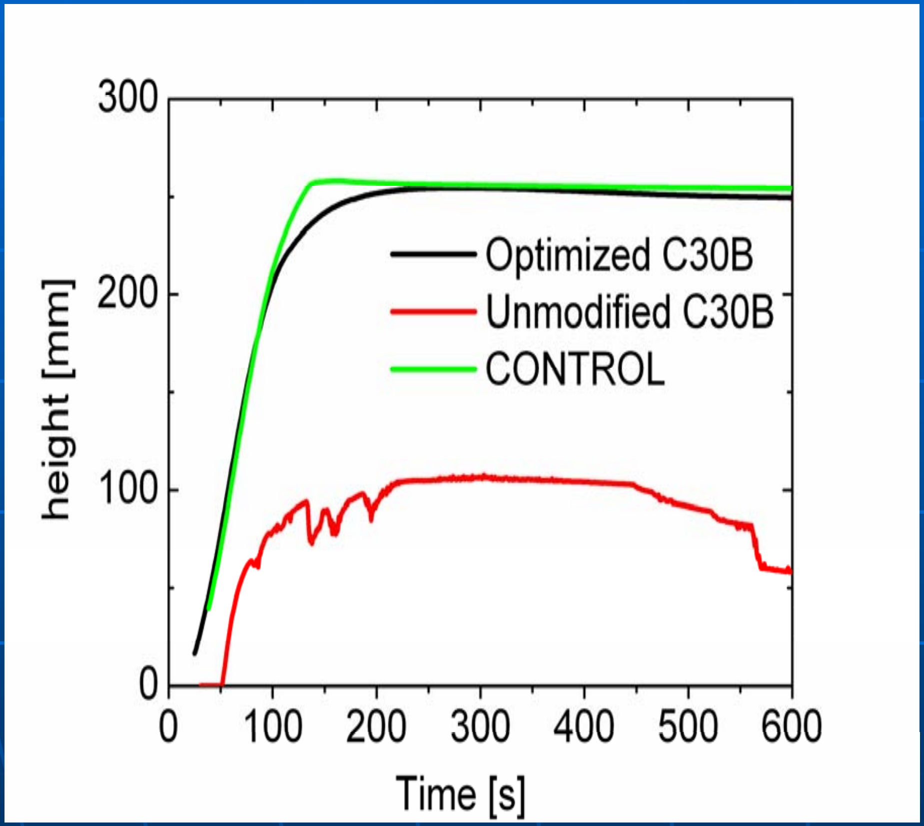
Foam Processing



Rise profile of a clay composite foam before (red) and in the process of optimization of the formulation (black) as compared to the unmodified foam (green)

FOAM PROCESSING OPTIMIZATION STEPS:

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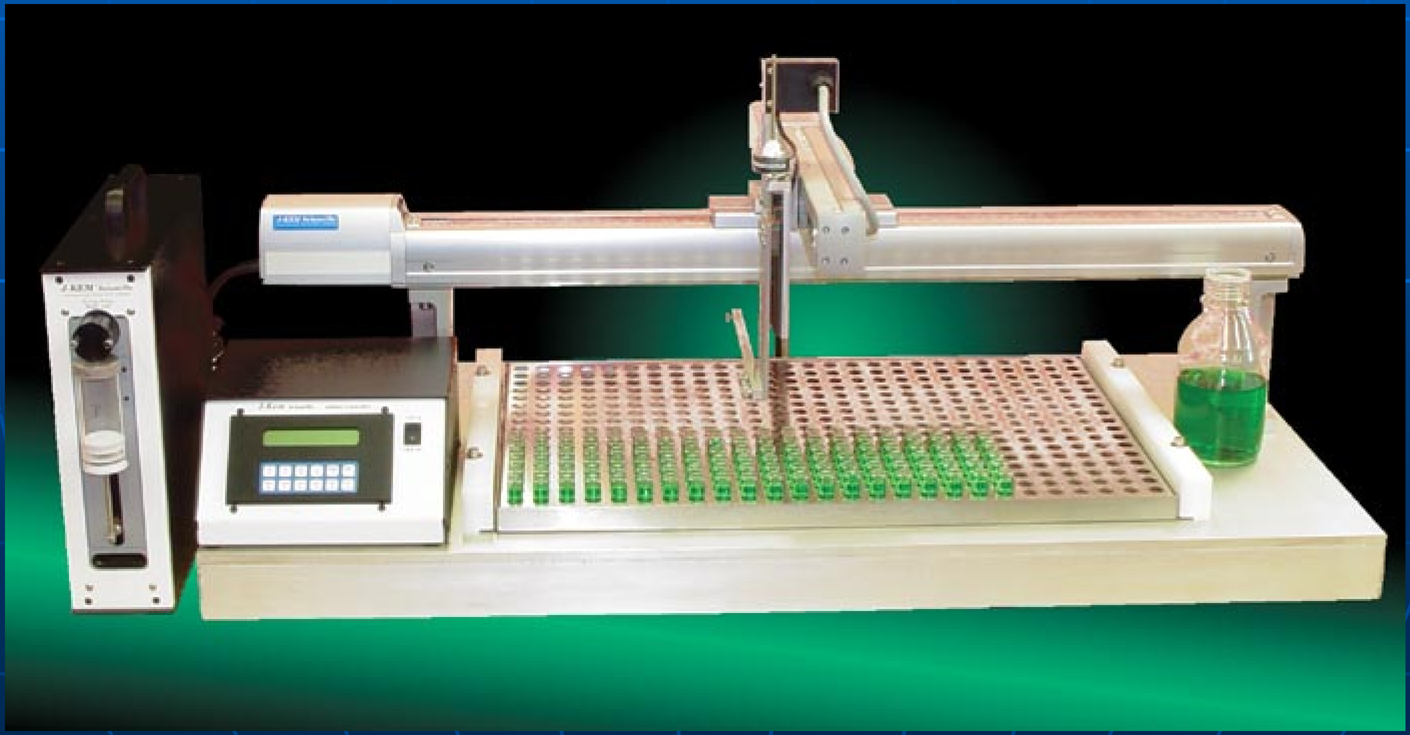
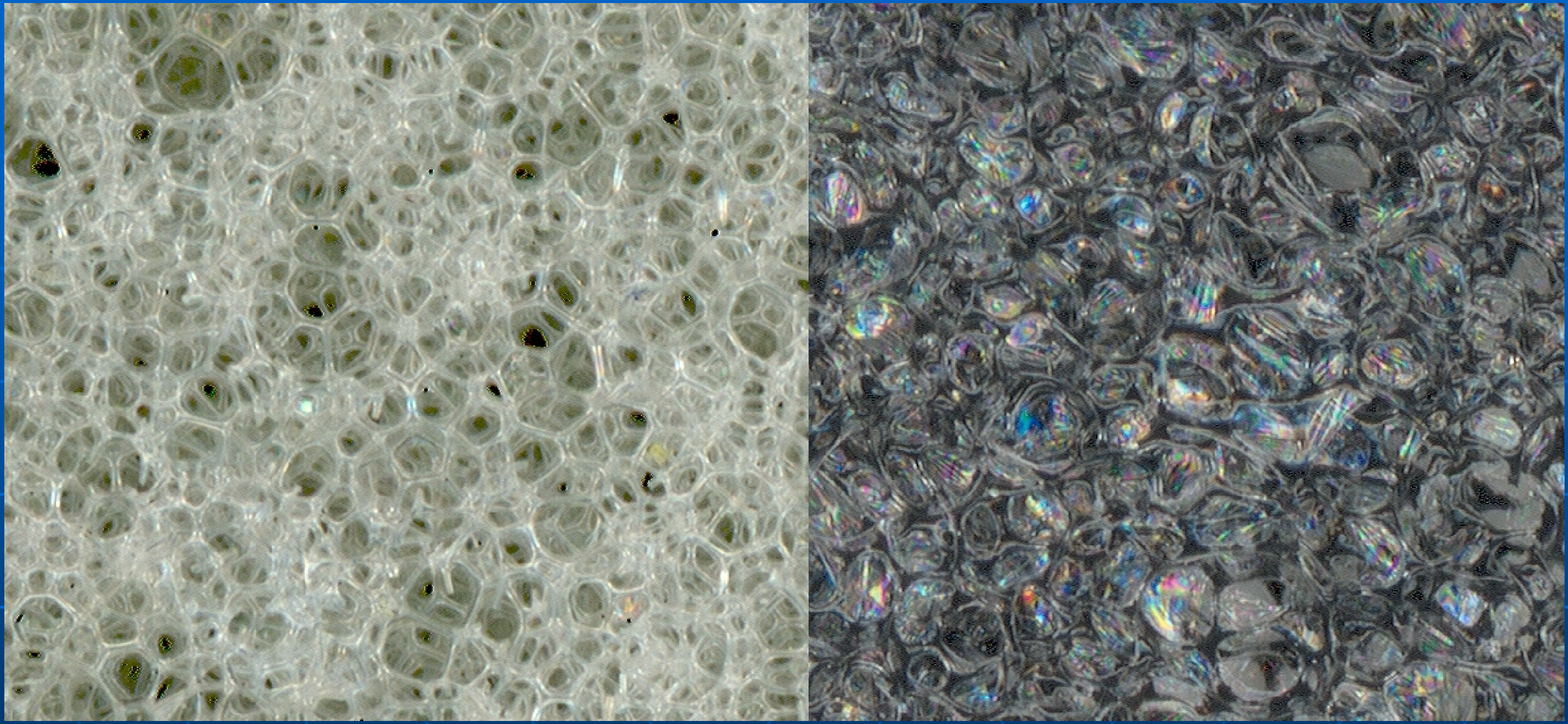
5. **Monitoring of the foam rise and curing with a FOAMAT foam qualification system.**
6. **Evaluation of the foam quality by optical analysis, density and air flow measurements.**

Automated Nano-dispersion

- We have designed 2 automated high throughput liquid handling platform with the capability of mixing dozens of polyol, nanoadditive combinations to screen for nanoscale mixing



Foam Characterization

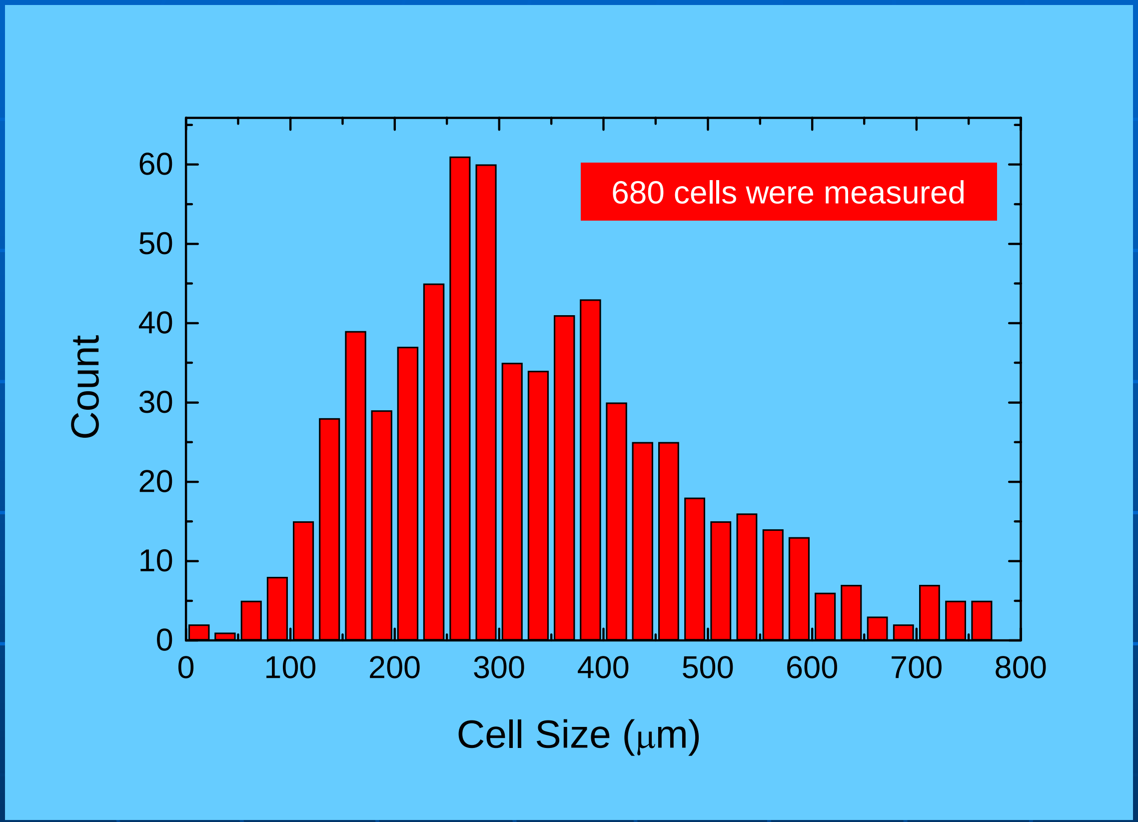


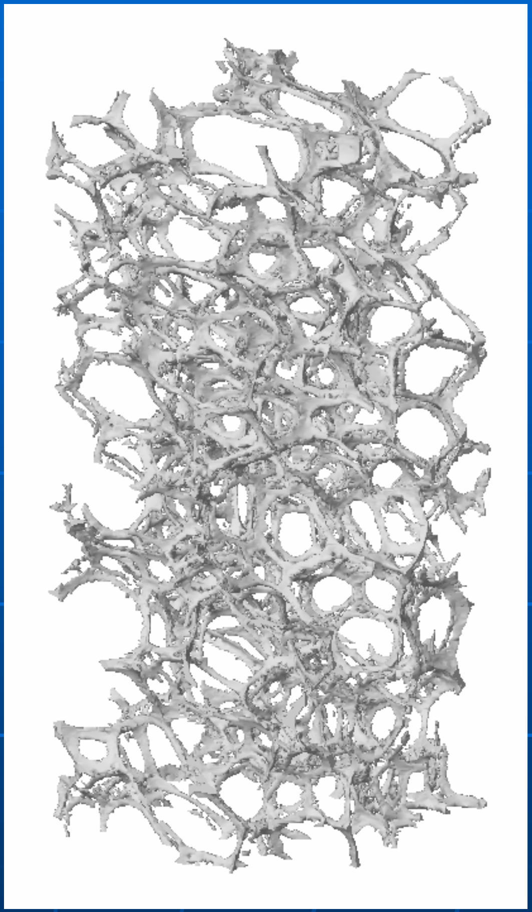
Optical analysis of cell structure for unmodified foam (left) and carbon nanofiber composite foam (right). The formulation has to be adapted to prevent a closed cell structure (right).

FOAM PROCESSING OPTIMIZATION STEPS:

6 Evaluation of the foam quality by optical analysis, density and air flow measurements.

Foam Characterization



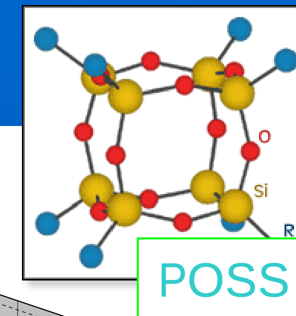


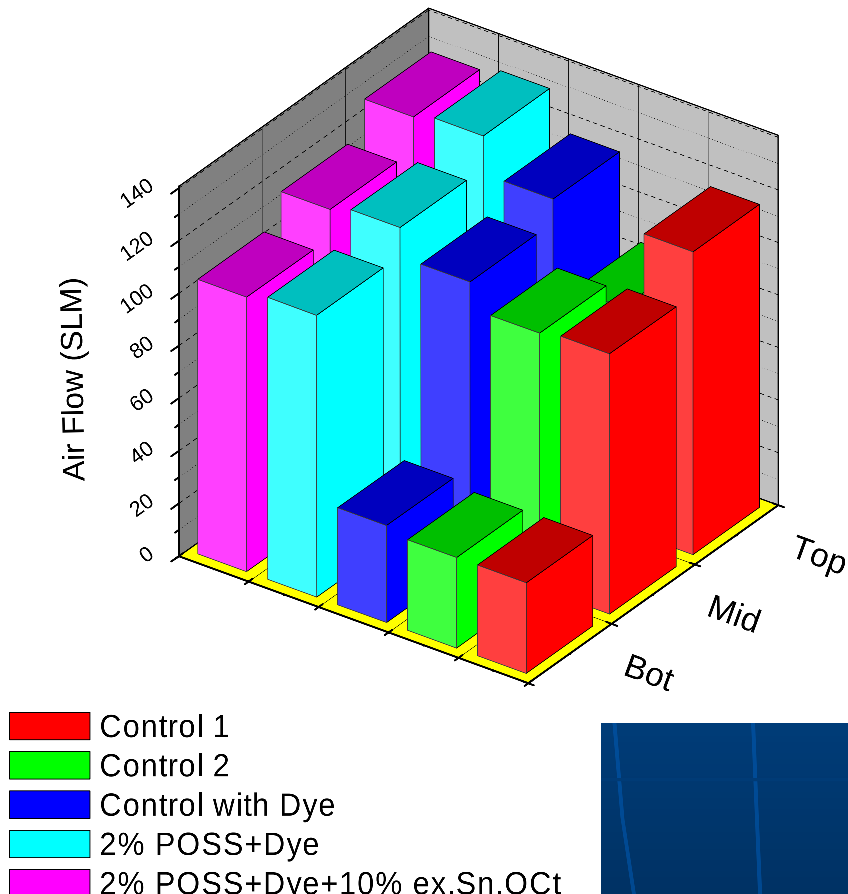
Cell size distribution in foam (left) from modeling of x-ray tomographic image of foam (right).

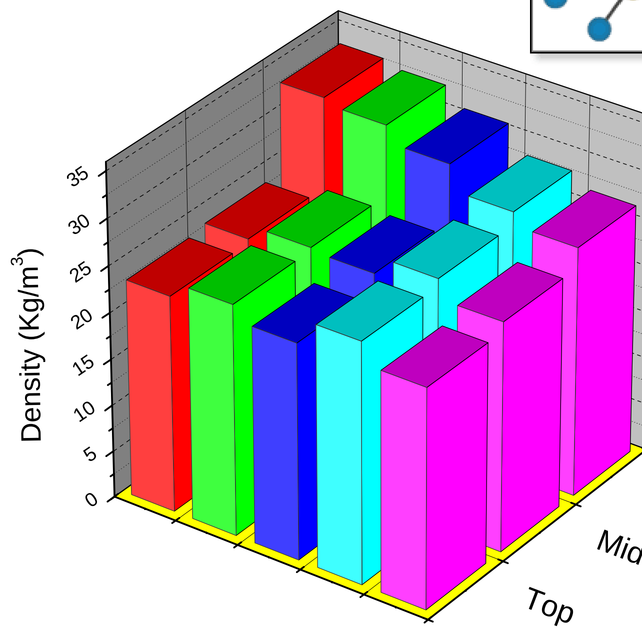
FOAM PROCESSING OPTIMIZATION STEPS:

6 Evaluation of the foam quality by optical analysis, density and air flow measurements.

Foam Characterization





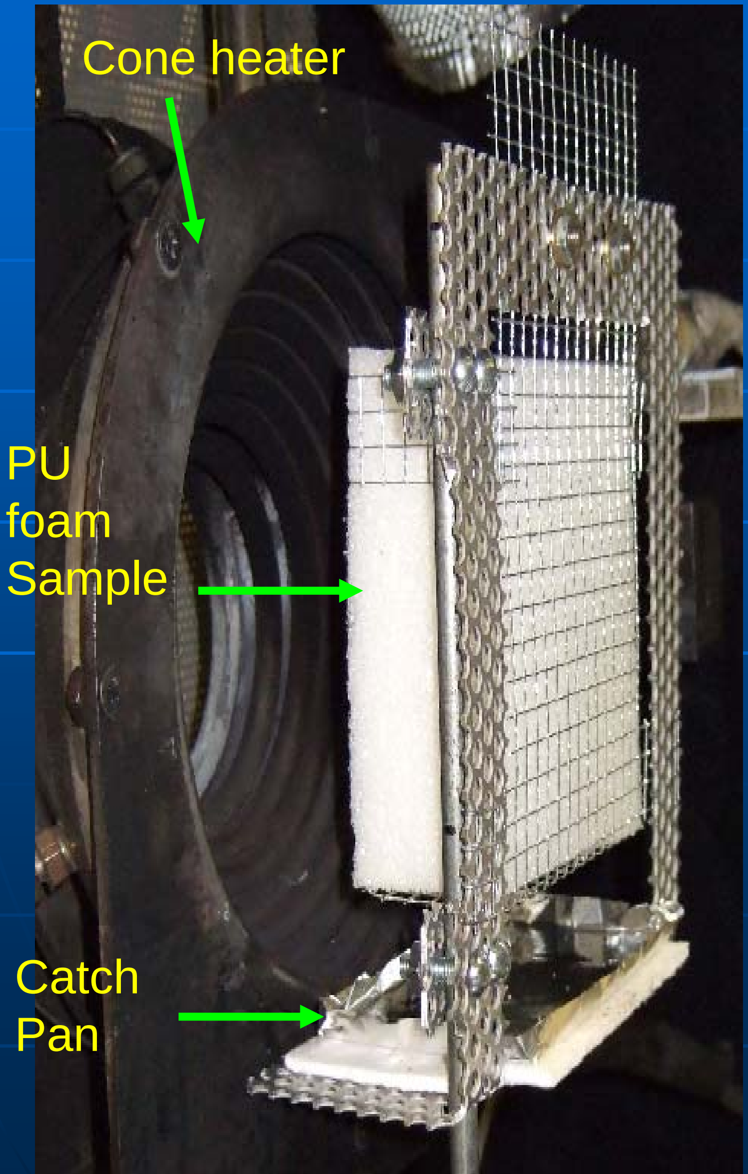


Air Flow (left) and Density (right) of POSS and Control foams

FOAM PROCESSING OPTIMIZATION STEPS:

6 Evaluation of the foam quality by optical analysis, density and air flow measurements.

Flammability of Foam

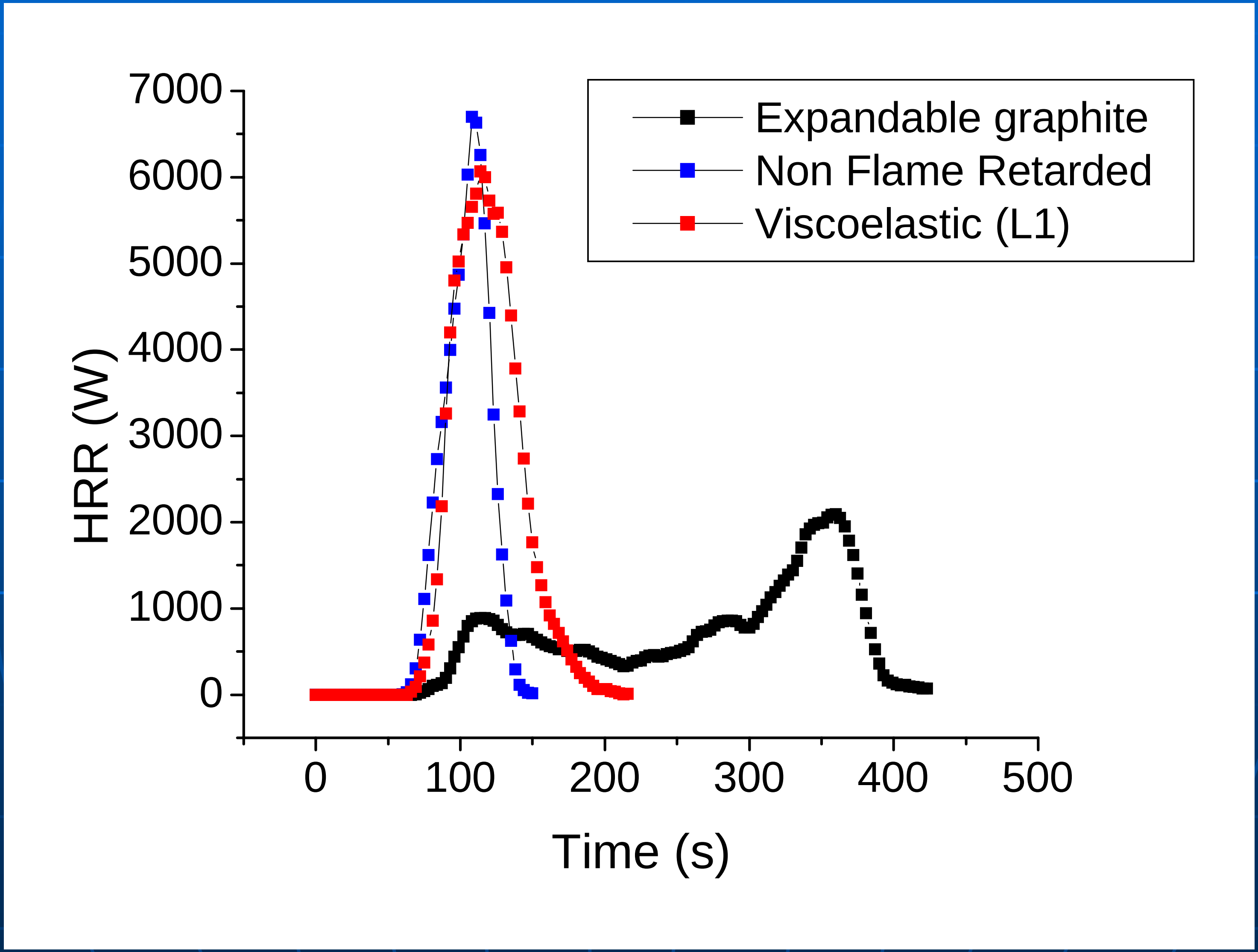


Goal:
measure the heat release rate of small samples taking into account the possible feedback effect due to dripping and formation of a pool-fire

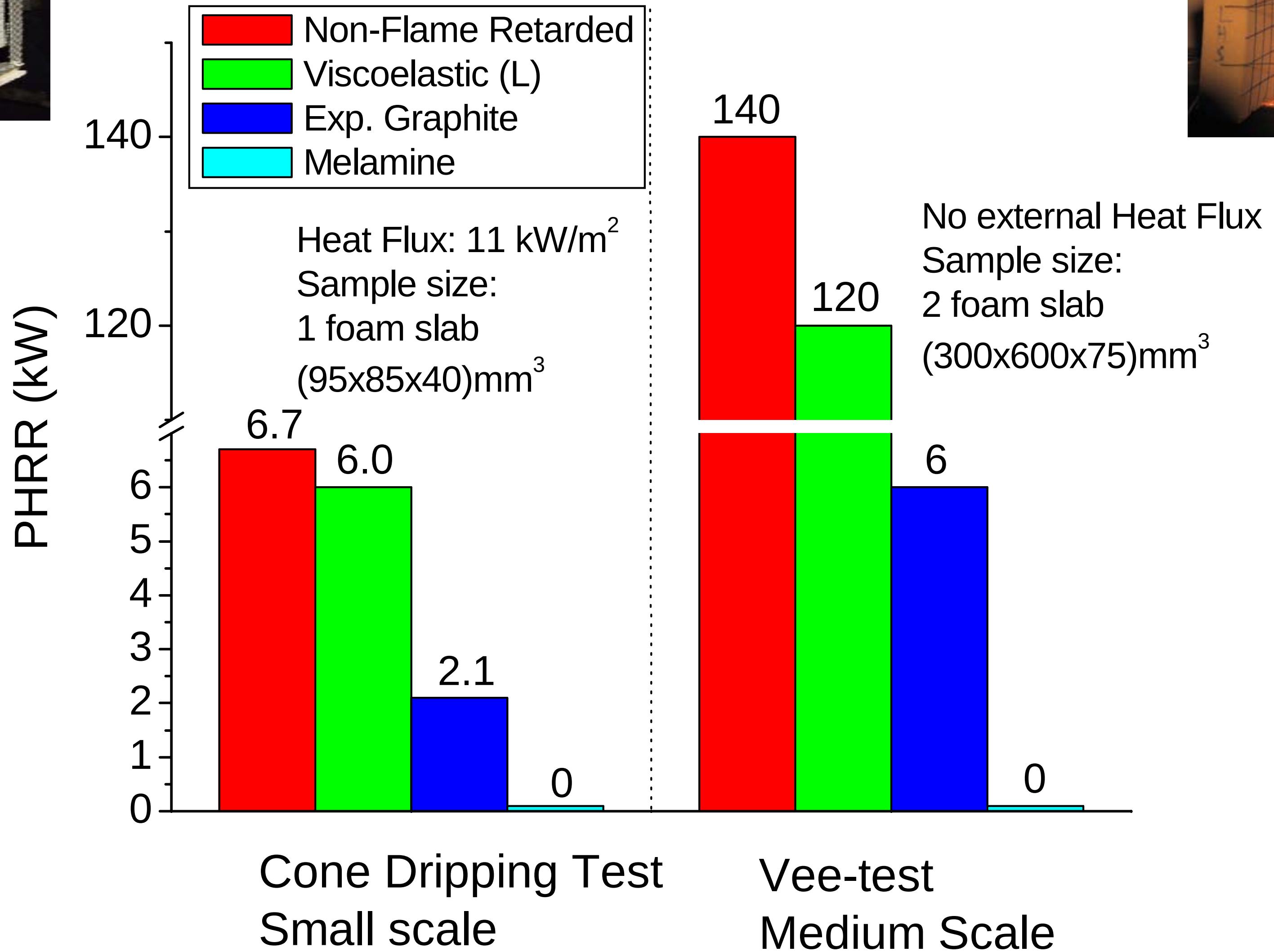
Note:
The catch pan is preheated by cone irradiation to minimize the heat-sink effect

Output:
- Heat Release Rate
- Mass loss Rate
- Video

Flammability of Foam

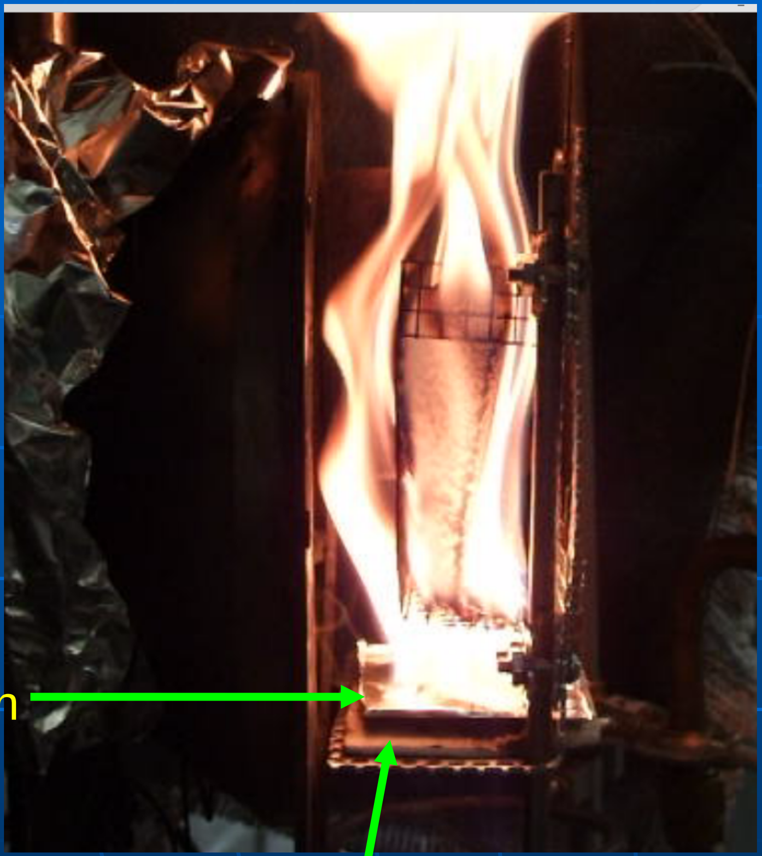


Flammability of Foam



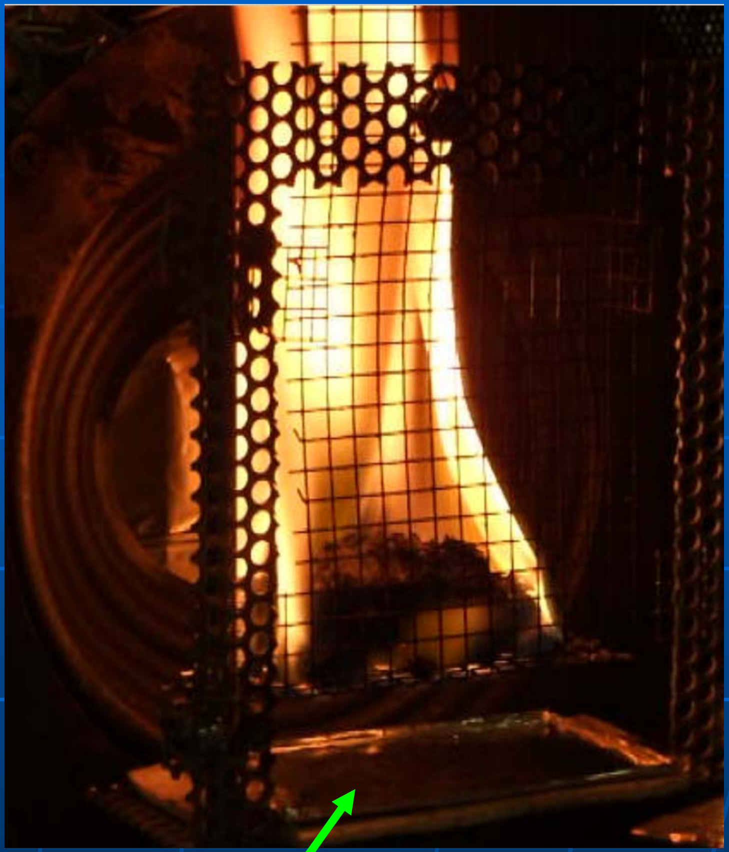
Nanoadditive Flame Retardants for Polyurethane Foam

Catch
Pan



Pool-fire

PU FR-foam control



<u>no</u> Pool-fire

PU FR-foam + 4% Carbon Nano-Fibers:

**Tom Ohlemiller, Richard Harris, J. Randy Shields,
Mauro Zammarano (GR), Roland Krämer (GR)**

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   2) **Objective :** To improve the ability of barrier fabrics to prevent flame spread in mattresses and furniture using nanoadditives.

2) Environmental degradation (UV, oxidation) In fire fighter turnout gear.

   1) Objective : to evaluate the ability of carbon nanotubes to stop these degradation mechanisms in turnout gear

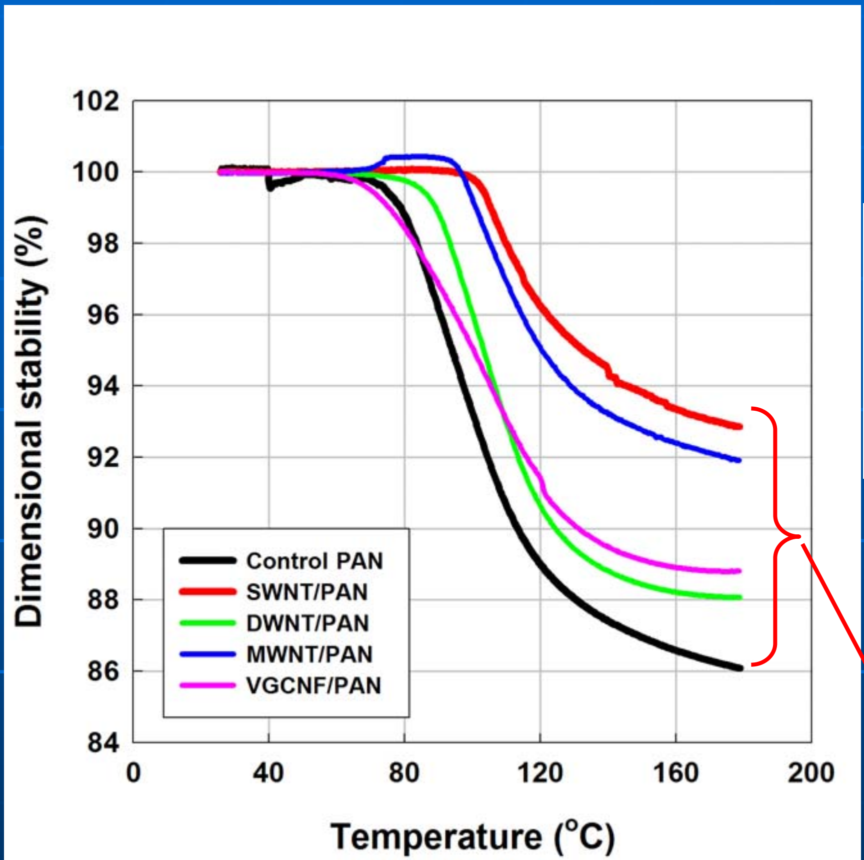
Barrier Materials

1) Fabric combustion creates high heat flux exposure
2) Polymers shrink when burned so barriers crack and fail
3) Fabric costs focus industry on low performing commodity polymers
4) Water insoluble environmentally additives required
5) No suitable bench-scale test currently exists for barriers

Barrier Materials

cotton, rayon, PAN, novoloid, aramid

Carbon Nanotubes in Barrier Fabrics



Satish Kumar-Georgia Tech

1. Use nanocomposite spinning
2. Spin fabrics using electro-spinning
3. Use bi-component spinning wih CNT-rich jacket material

CNT-skin

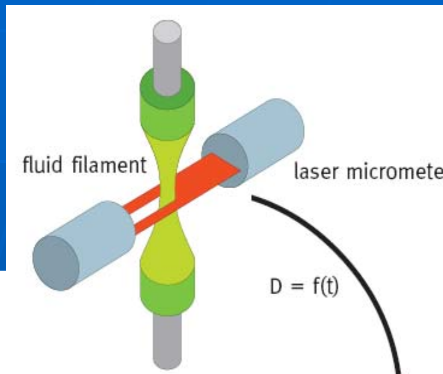
CNT Nanocomposite

Use CNT in fiber to reduce shrinkage in char fabric during barrier burning, and to increase strength.

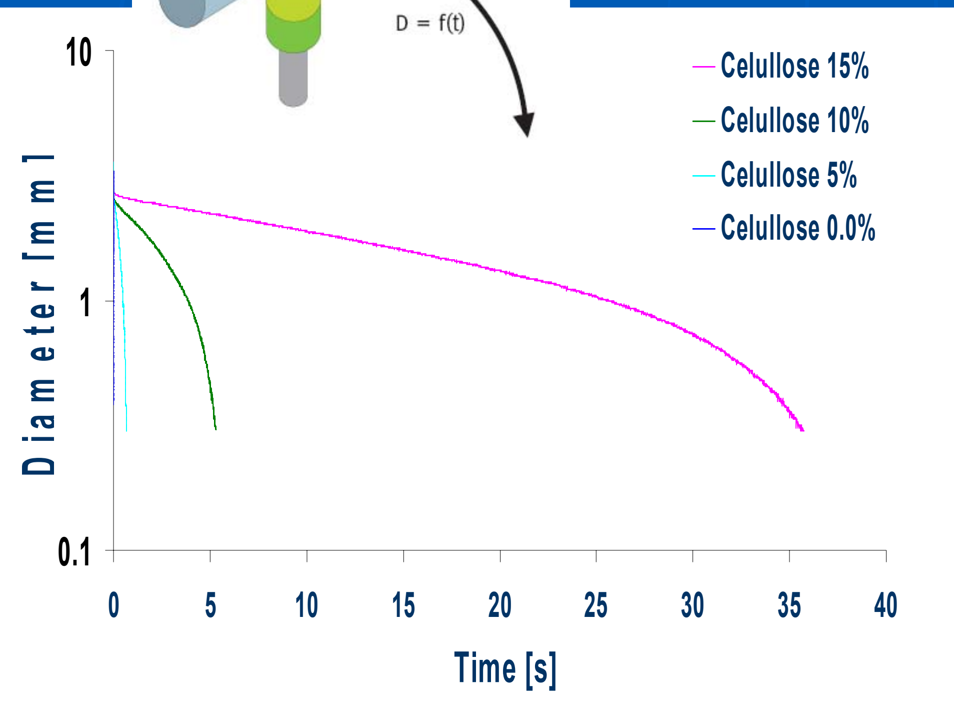
PAN/Carbon Nanotube Composite Fiber:
Thermal Shrinkage Data (S. Kumar-Ga. Tech – Fire Grant)

Carbon Nanotubes in Barrier Fabrics

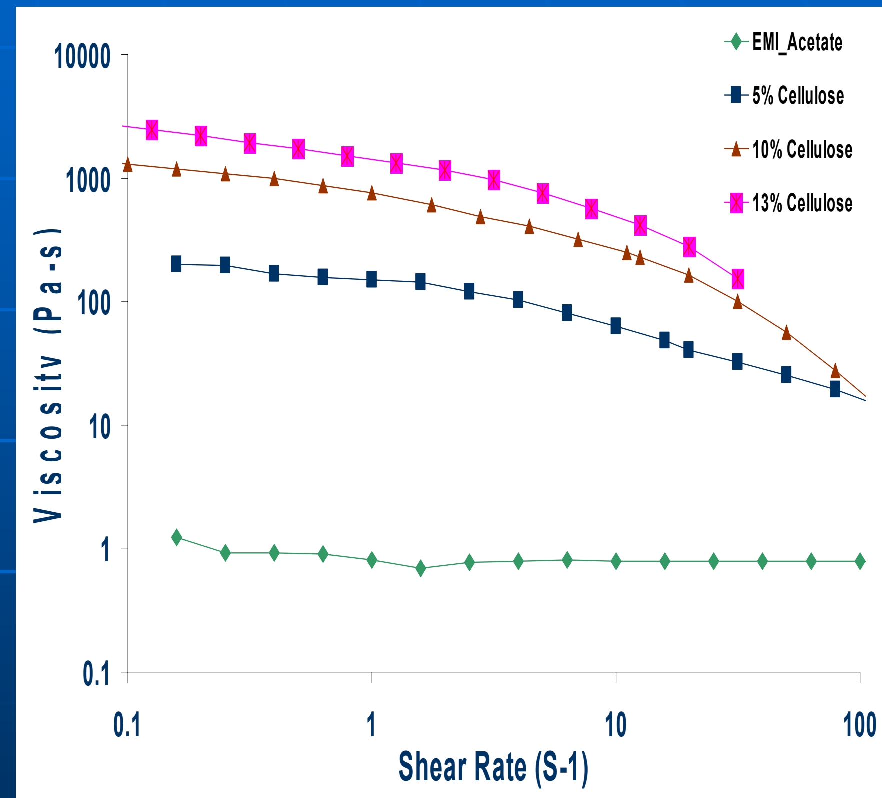
Extensional Viscosity Measurement



$$\eta_e = -\rho \Big/ \frac{d[D(t)-D_o]}{dt}$$



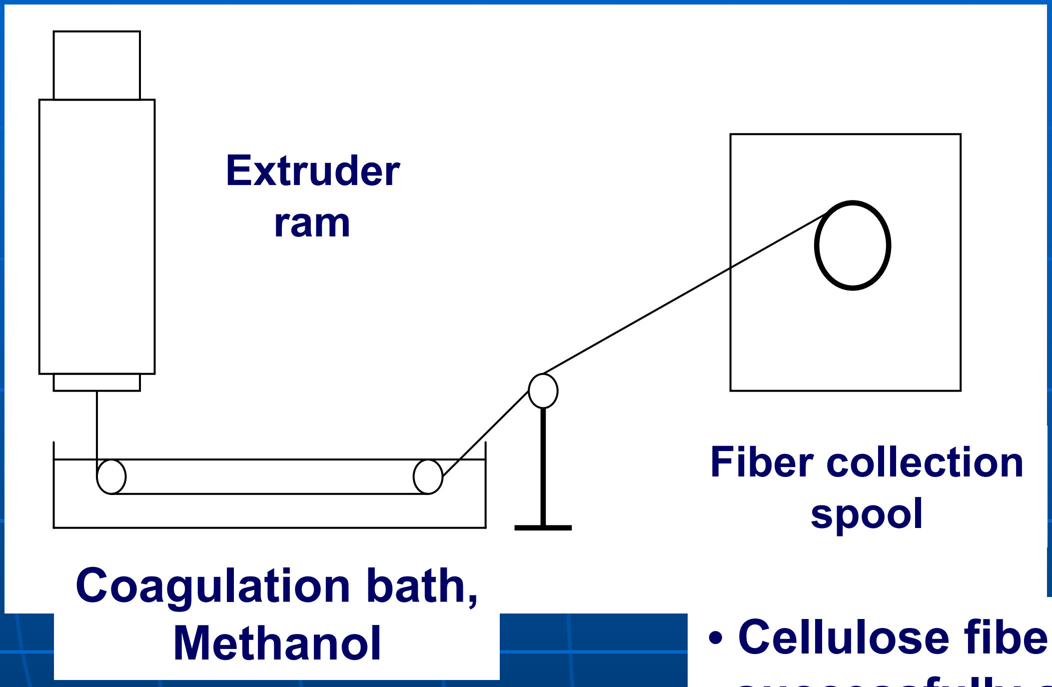
Shear Viscosity Measurement

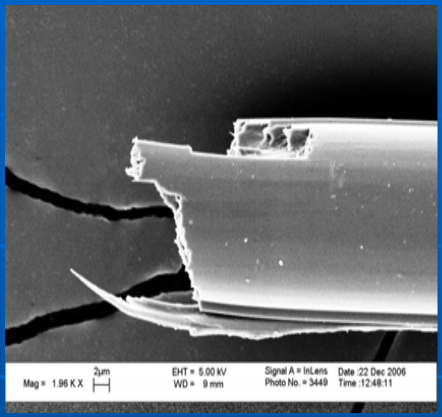


- We used EMI Acetate to dissolve cellulose (degree of polymerization 240)
- Twenty times increase in the relaxation time between 10 and 15 % cellulose

- Cellulose degree of polymerization 820 was dissolved in EMI acetate
- Low Shear viscosity is used as a guideline to find right concentration for fiber spinning

Carbon Nanotubes in Barrier Fabrics



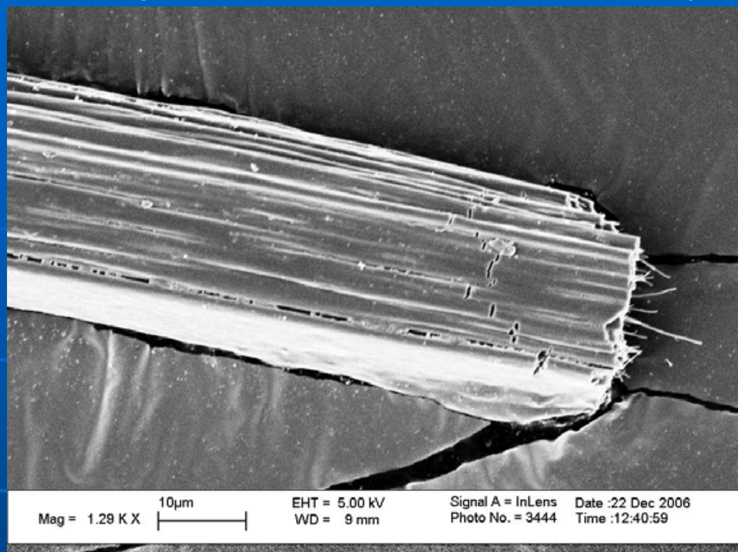


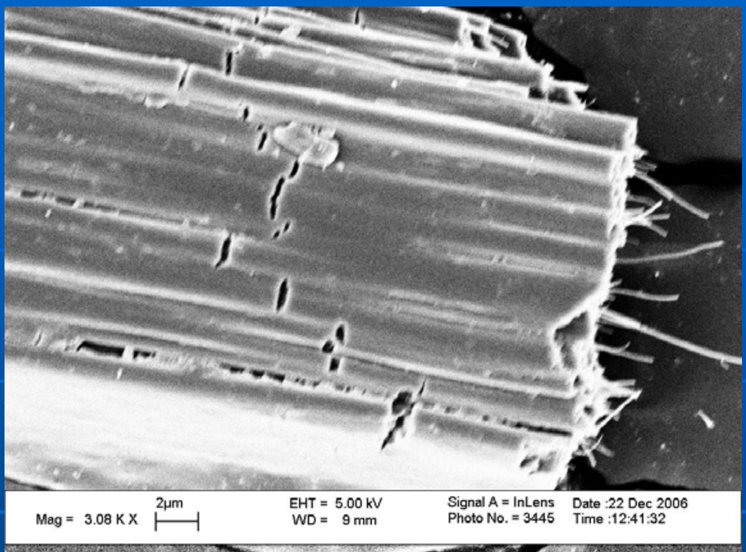
- Cellulose fibers of DP 500 and 820 were successfully spun using EMI Acetate as solvent
- Methanol was used for coagulation of cellulose during fiber spinning
- Fibers average diameter obtained as 26µm

(S. Kumar-Ga. Tech – Fire Grant)

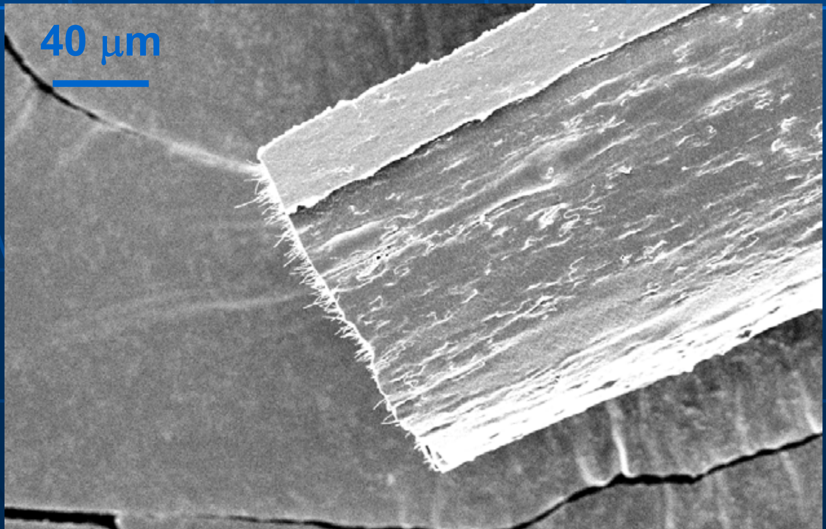
SEM and Mechanical Properties of Cellulose/MWCNT Composite Fibers

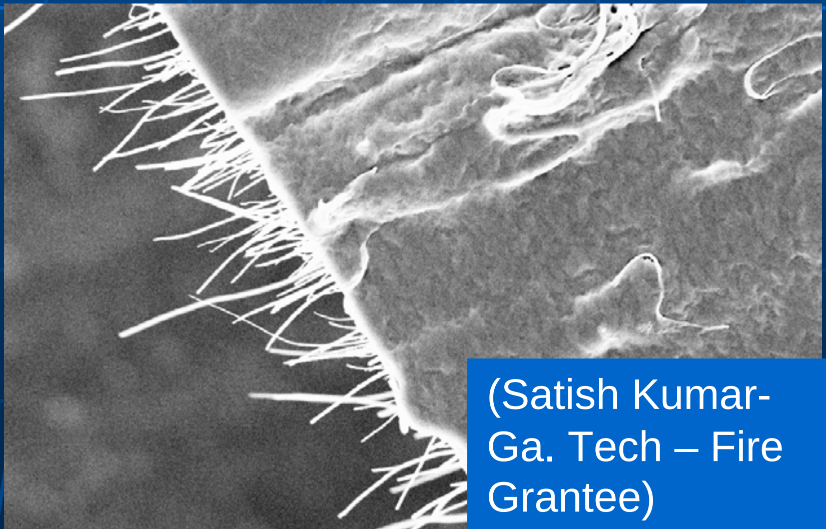
SEM images of 1wt% of MWCNT/Cellulose composite fibers





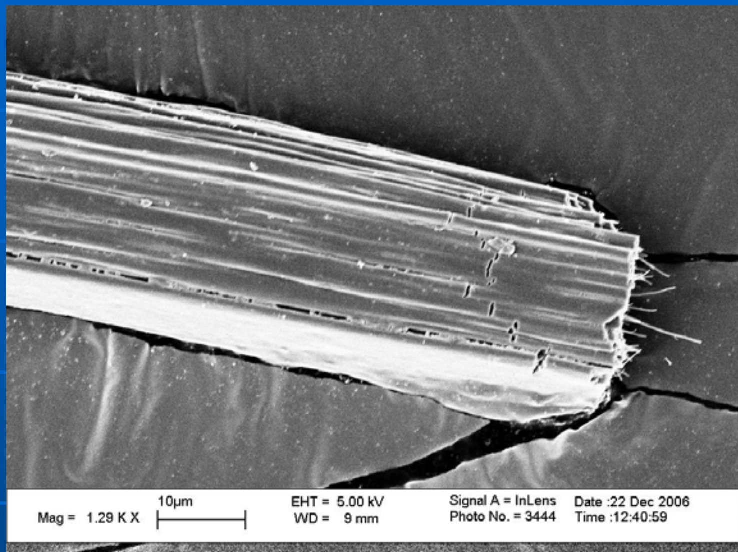
SEM images of 1wt% of MWCNT/Silk composite fibers

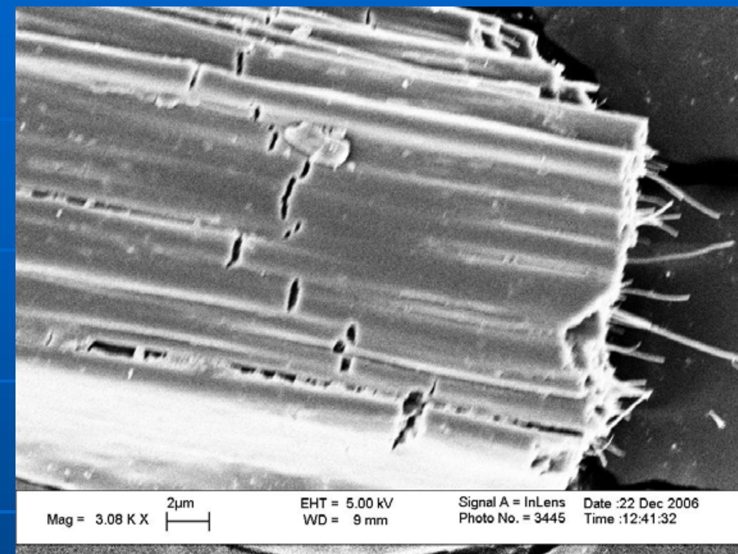




(Satish Kumar- Ga. Tech – Fire Grantee)

SEM and Mechanical Properties of Cellulose/MWCNT Composite Fibers





SEM images of 1wt% of MWCNT/Cellulose composite fibers

(Satish Kumar- Ga. Tech – Fire Grantee)

	Fiber Dia (micron)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Strain to Failure (%)
Cellulose	29.2 ± 4.1	113 ± 26	8.4 ± 1.7	5.2 ± 0.92
Cellulose+1 %MWNT	26.2 ± 1.2	137 ± 7.5	10.8 ± 0.5	7.4 ± 1.7

Mechanical Properties of cellulose fibers are comparable to the cellulose films* processed by ionic liquids (*Zhang *et al. Macromolecules* **2005,** *38,* 8272-8277)

Challenges

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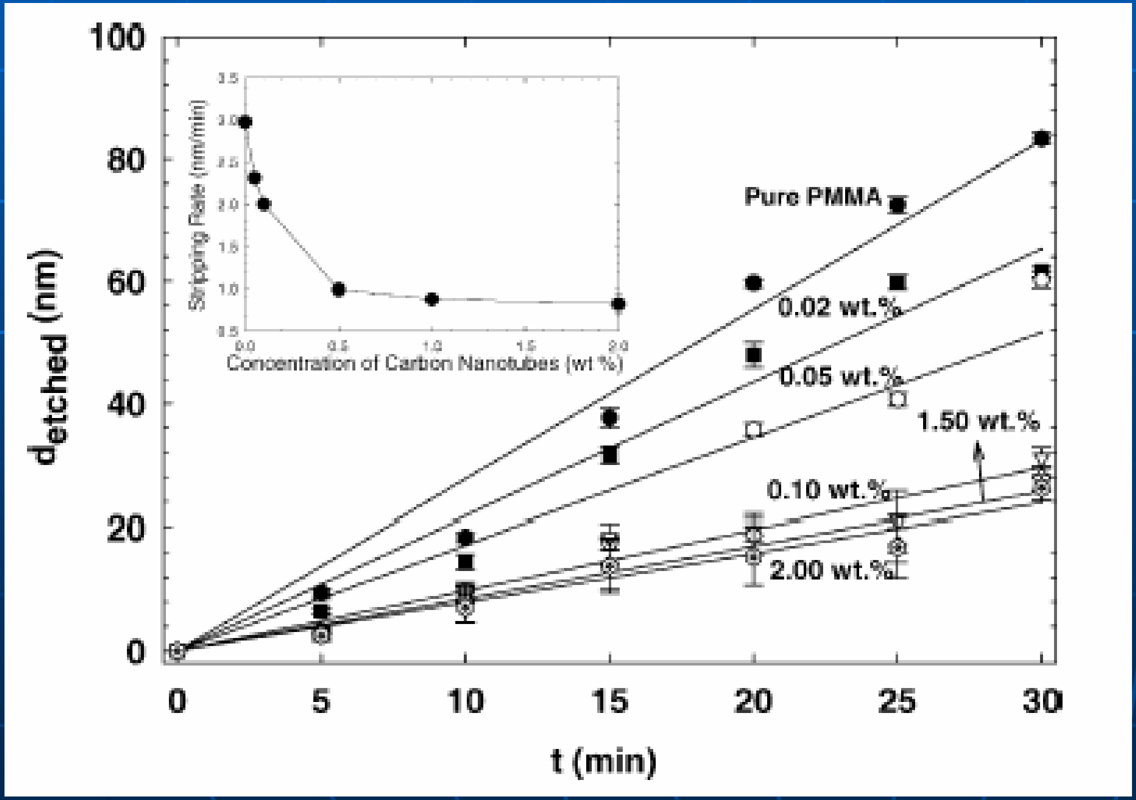
1)Objective : to evaluate the ability of carbon nanotubes to stop these degradation mechanisms in turnout gear



Shin et al. *Colloids and Surfaces A,* 2006

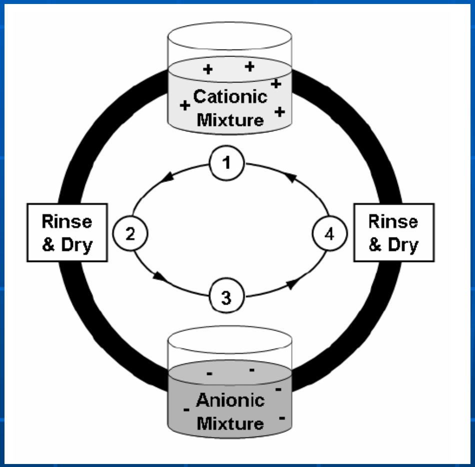
CNT reduce degradation rate

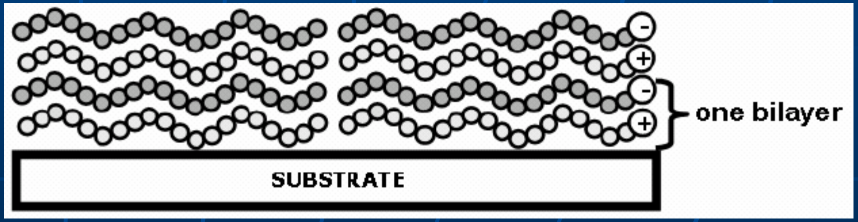
Joannie Chin
– Polymeric Materials Group,BFRL

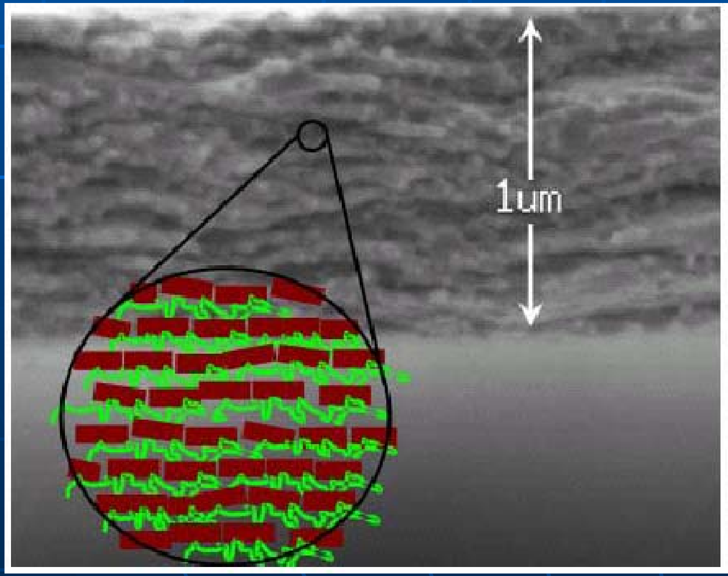
Layer-by-layer Nanocomposite Coatings on PBO Moisture Barrier

Coat current fabrics with 100 nm thick nanocomposite coating
- Jamie Grunlan – Texas A&M

Layer-by-layer nanocomposite coatings







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Building and Fire Research Laboratory

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School of Polymer, Textile and Fiber Engineering,

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Krzysztof K K Koziol, Alan H Windle

Department of Materials science and Metallurgy, University of Cambridge, UK

Paul Trulove and Wesley Henderson

Chemistry Department, US Naval Academy

Hugh DeLong, Air Force Office of Scientific Research

Douglas Fox, Chemistry Department, American University