NANOCOMPOSITE THIN FILMS FOR REDUCED FLAMMABILITY FOAM AND FABRIC

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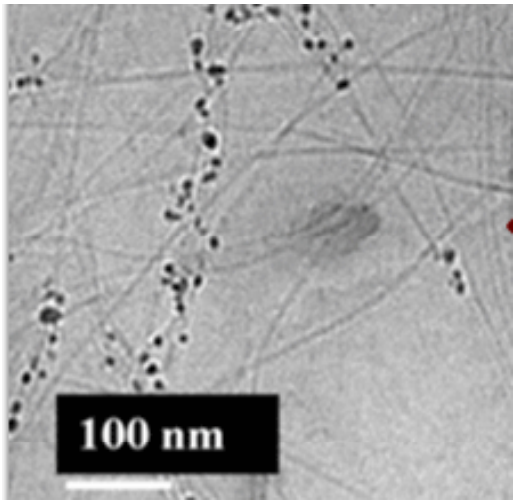
6th Triennial IFCSRC – Atlantic City, NJ – 27 October 2010

Polymer NanoComposites (PNC) Lab (http://nanocomposites.tamu.edu)

Polymer NanoComposites (PNC) Lab

Nanoparticle Stabilization

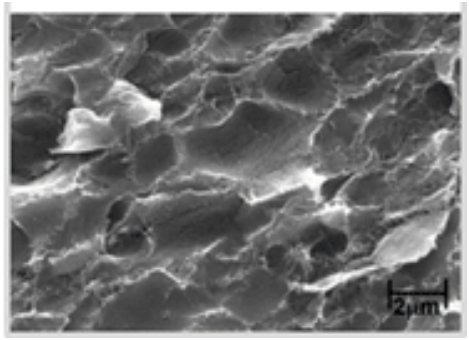


pH-Responsive
Nano Letters **2006** (featured in *Nature Materials* **2006**)
J. Coll. Interf. Sci. **2008**

Thermoresponsive
J. Am. Chem. Soc. **2009**

"Solid Surfactant"
Carbon **2009**

Polymer Composites

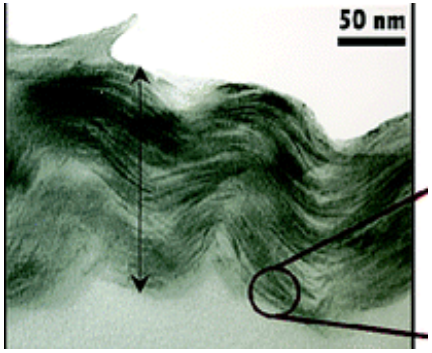


Clay-Carbon-Epoxy
Adv. Functional Mater. **2007**
Macromol. Rapid Comm. **2009**
Carbon **2009**

Conductive Emulsions
Advanced Materials **2004**
Polymer **2008**
Macromol. Chem. Phys. **2008**

Energy Harvesting
Nano Letters **2008**
ACS Nano **2010**

Thin Film Assemblies



Gas Barrier
ACS Appl. Mater. Interf. **2010**
(featured in *C&EN* 11 Jan **2010**)

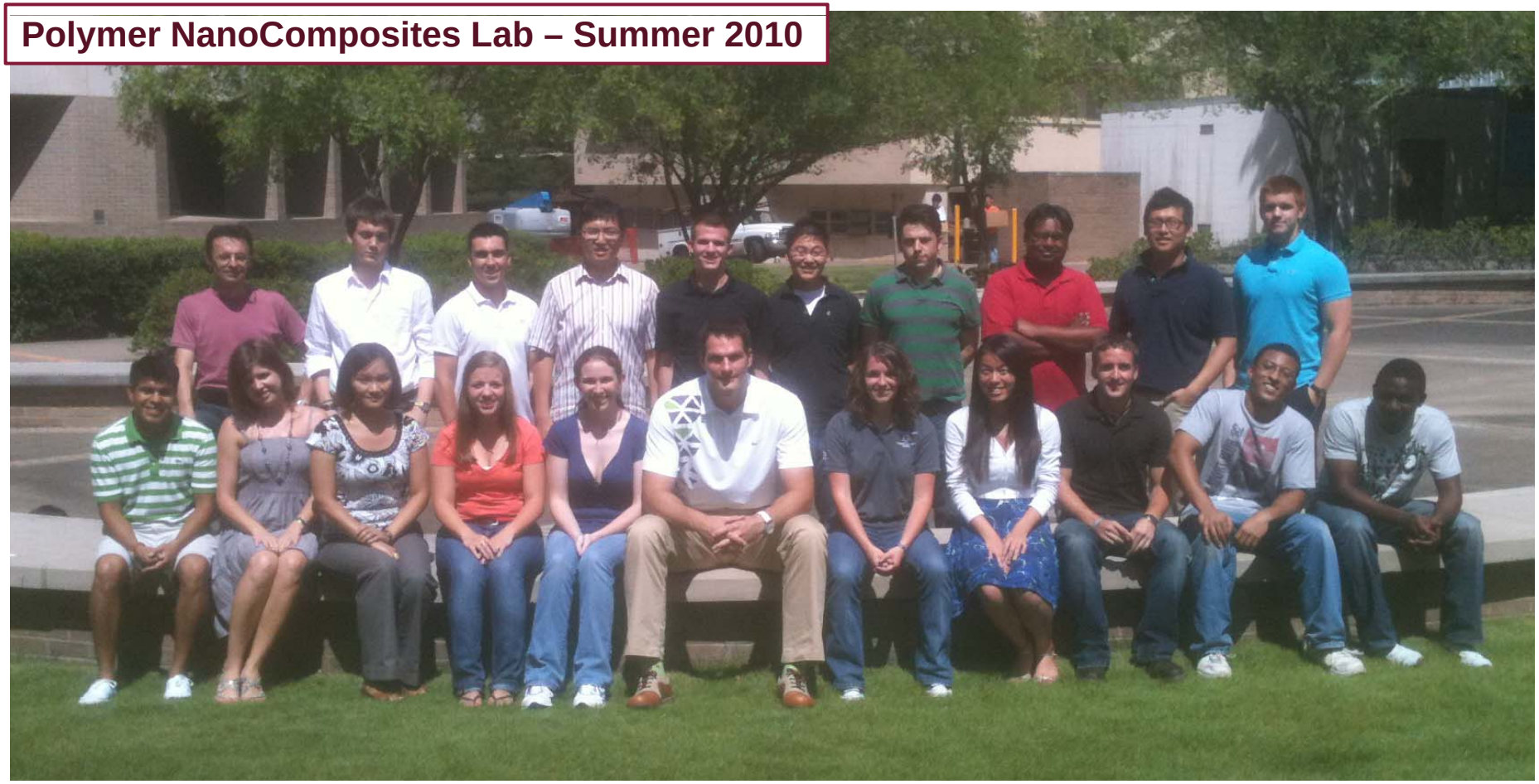
Anti-Flammable
ACS Nano **2010**
(featured in *C&EN* 7 June **2010**)

Antimicrobial
Langmuir **2008**

Electrically Conductive
Langmuir **2008**
J. Phys. Chem. C **2010**

Acknowledgements

Polymer NanoComposites Lab – Summer 2010



Building and Fire Research Laboratory

NIST

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

USDA

Southern Regional Research Center

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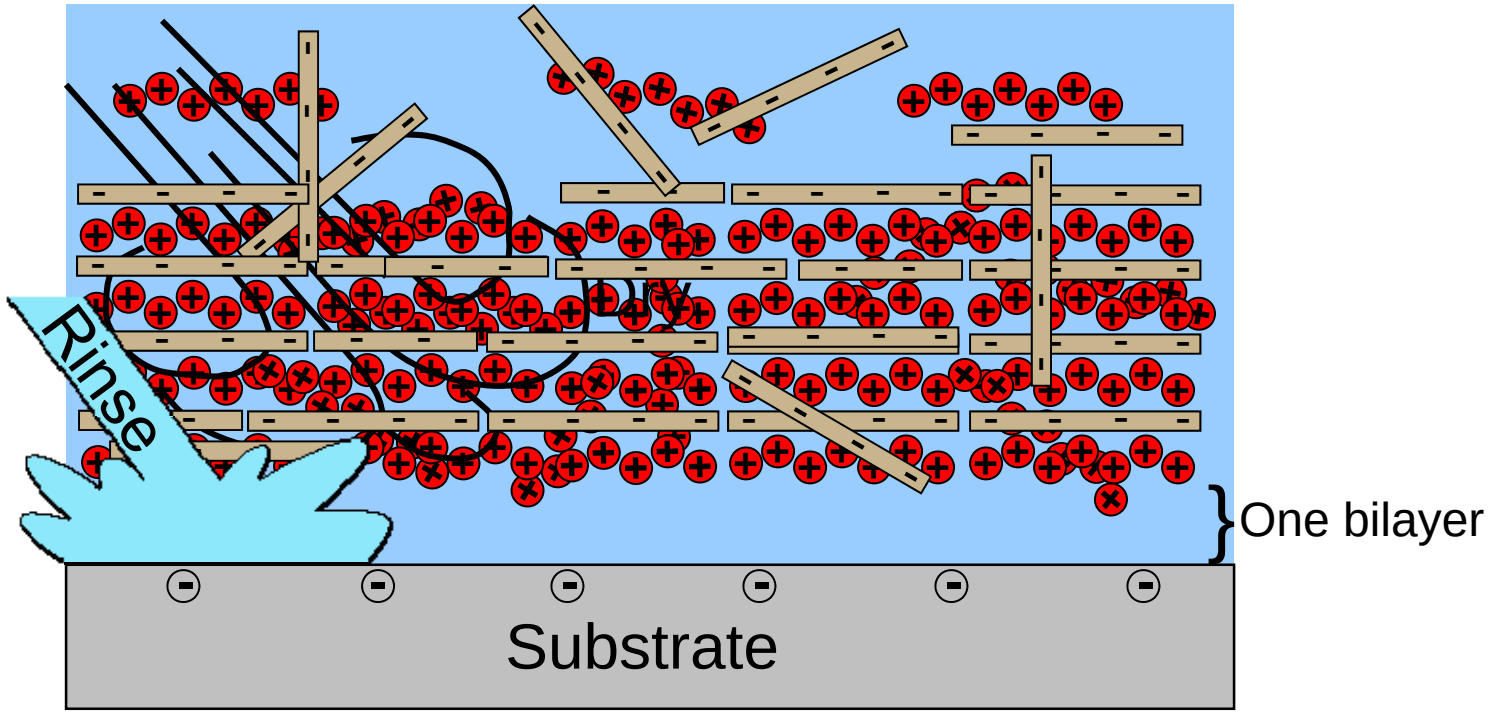
Outline

- **Overview of layer-by-layer (LbL) assembly**
- **Growth and microstructure of clay-based assemblies**
- **Flame retardant behavior of coated substrates**
- **Initial results with new systems…**
- **Conclusions**

Layer-by-Layer Deposition Overview

Layers of positively and negatively charged materials are alternately deposited from water to create functional thin films.



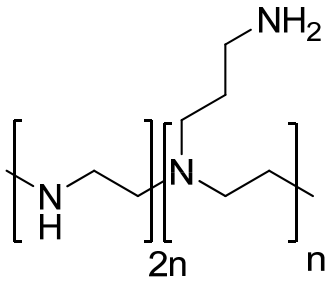
Ambient Processing ☞ **Tunable Properties** ☞ **Nanoscale Control**

Decher, G. *Science* **1997**, *277*, 1232.
Bertrand, P., Jonas, A., Laschewsky, A., Legras. R. *Macromol. Rapid Comm.* **2000**, *21*, 319.

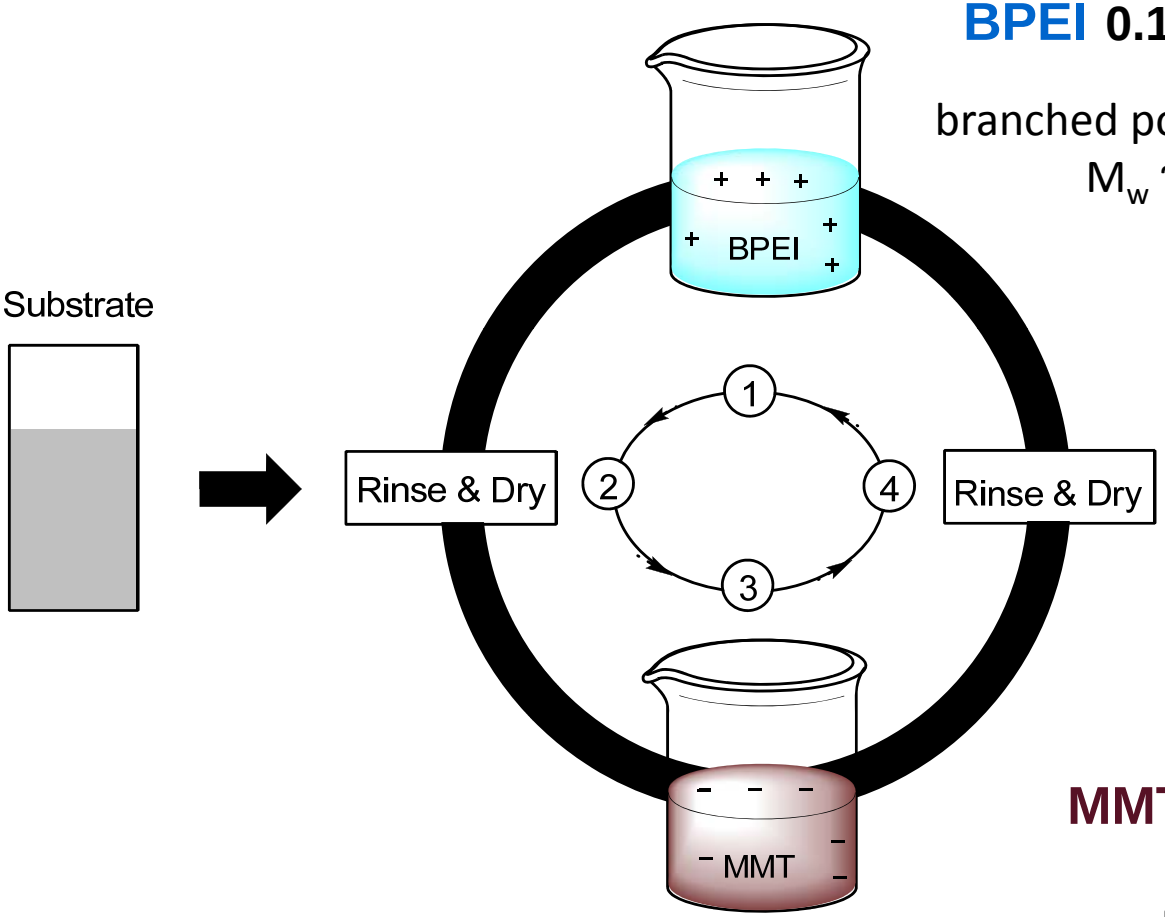
Layer-by-Layer Assembly of Clay and PEI

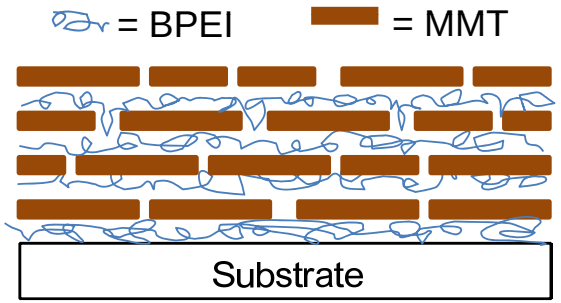
BPEI 0.1 wt.%

branched polyethylenimine
M_w ~25,000



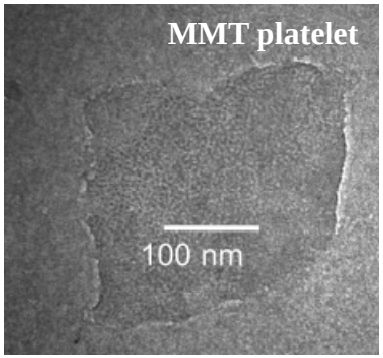
Substrate





MMT 0.2 wt. %

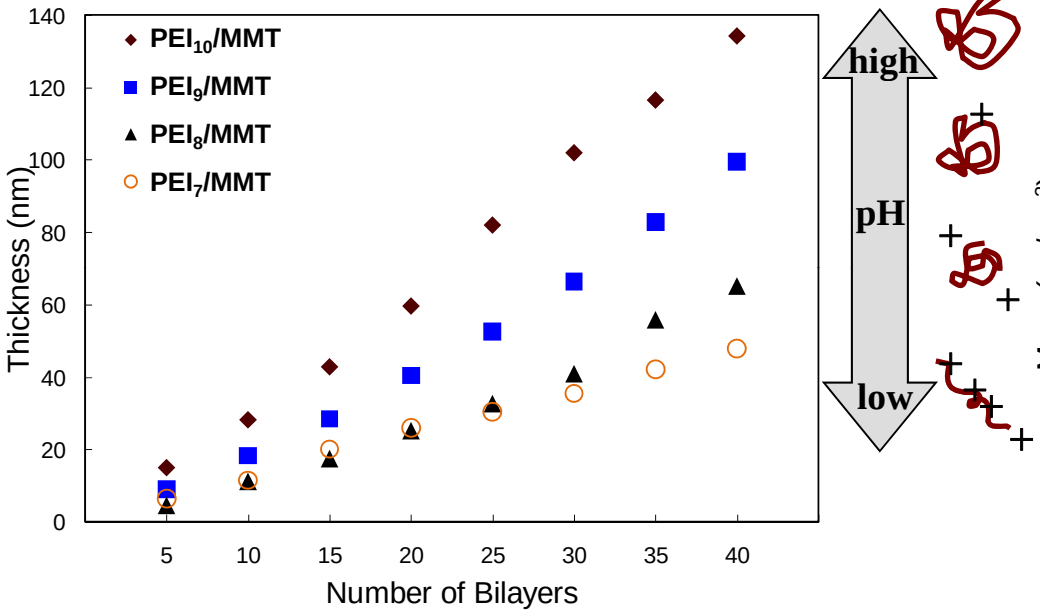
Montmorillonite
$Si_8(Al_{3.33}Mg_{0.67})O_{20}(OH)_4],0.67Na^+ \cdot nH_2O$



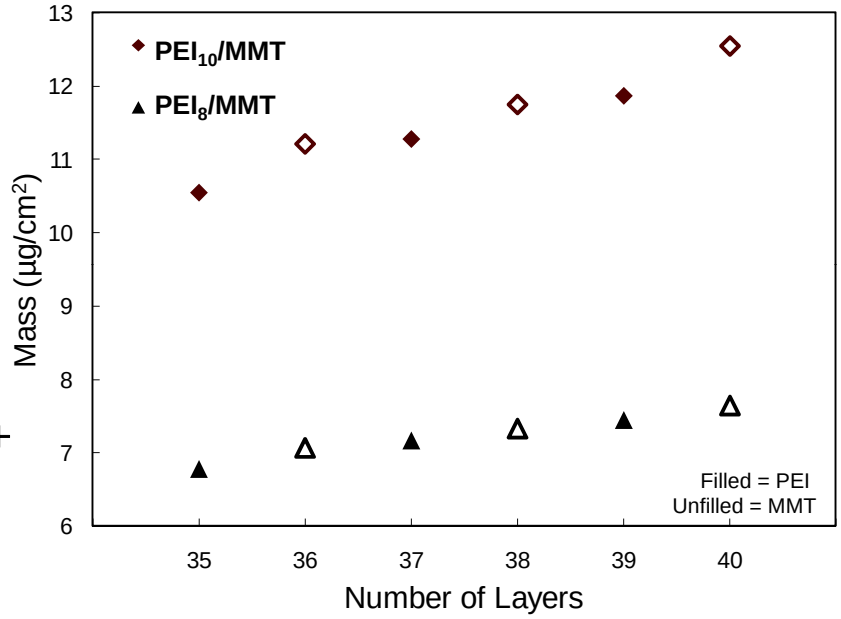
Suh, J.; Paik, H. J.; Hwang, B. K., *Bioorg. Chem.* **1994**, *22*, 318.
Grim, R. E., *Science* **1962**, *135*, 890.
Ploehn, H. J.; Liu, C., *Ind. Eng. Chem. Res.* **2006**, *45*, 7025.
Annabi-Bergaya, F., *Microporous Mesoporous Mater.* **2008**, *107*, 141.

pH Tailored Film Growth of PEI-MMT

Ellipsometric Growth



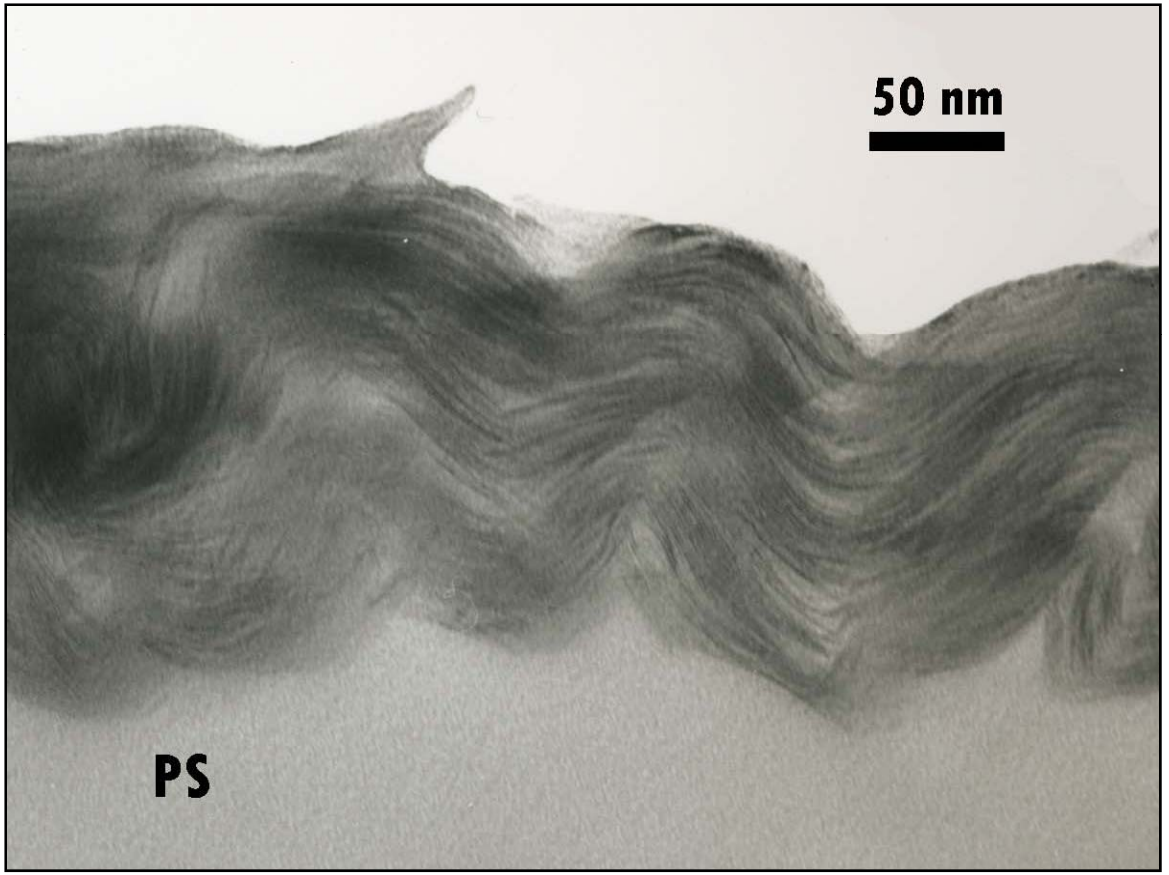
Mass Deposited (QCM)



Thin Film Assembly	MMT (vol. %)	MMT (wt. %)	Density (g/cc)
PEI_8/MMT	66.0	84.3	2.50
PEI_{10}/MMT	54.1	76.6	2.27

Grunlan. et al., *ACS Applied Materials & Interfaces* **2010**, *2*, 312.

TEM Cross-Sections of PEI-MMT Films



40 BL films of pH 10 PEI-MMT were grown on polystyrene and cured in epoxy prior to sectioning.

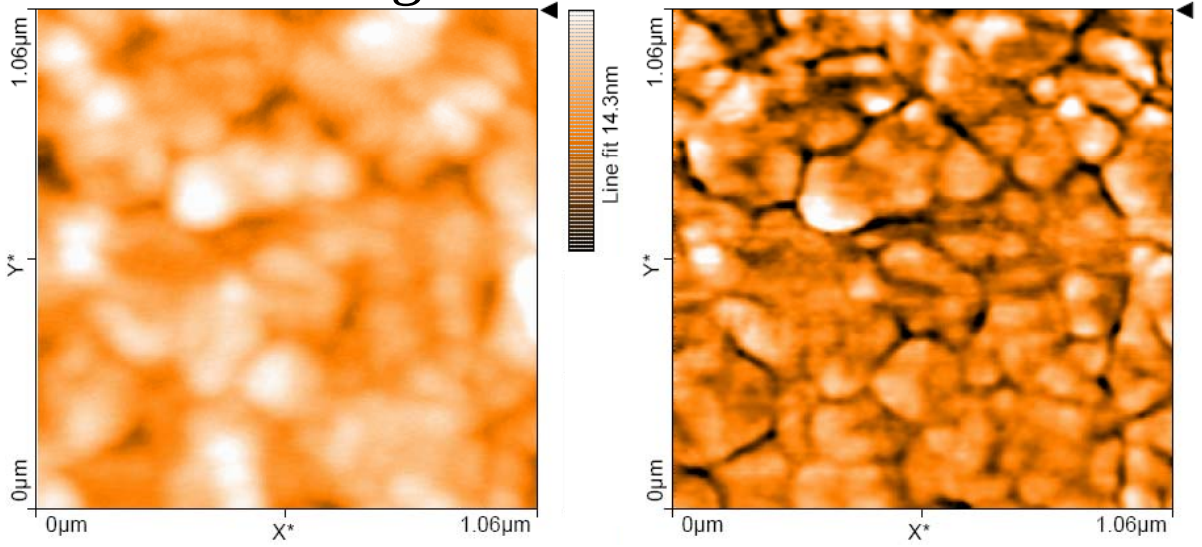
Grunlan. et al., *ACS Applied Materials & Interfaces* **2010**, *2*, 312.

Surface Microstructure via AFM

Height Phase

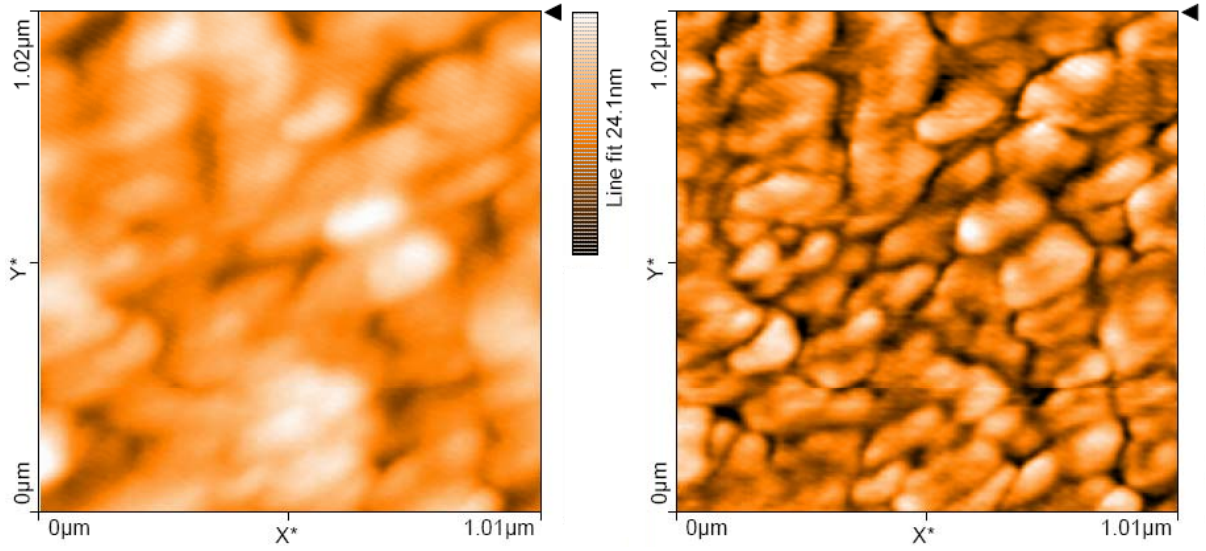
$(PEI_8/MMT)_{10}$

RMS Surface Roughness: 2.1nm

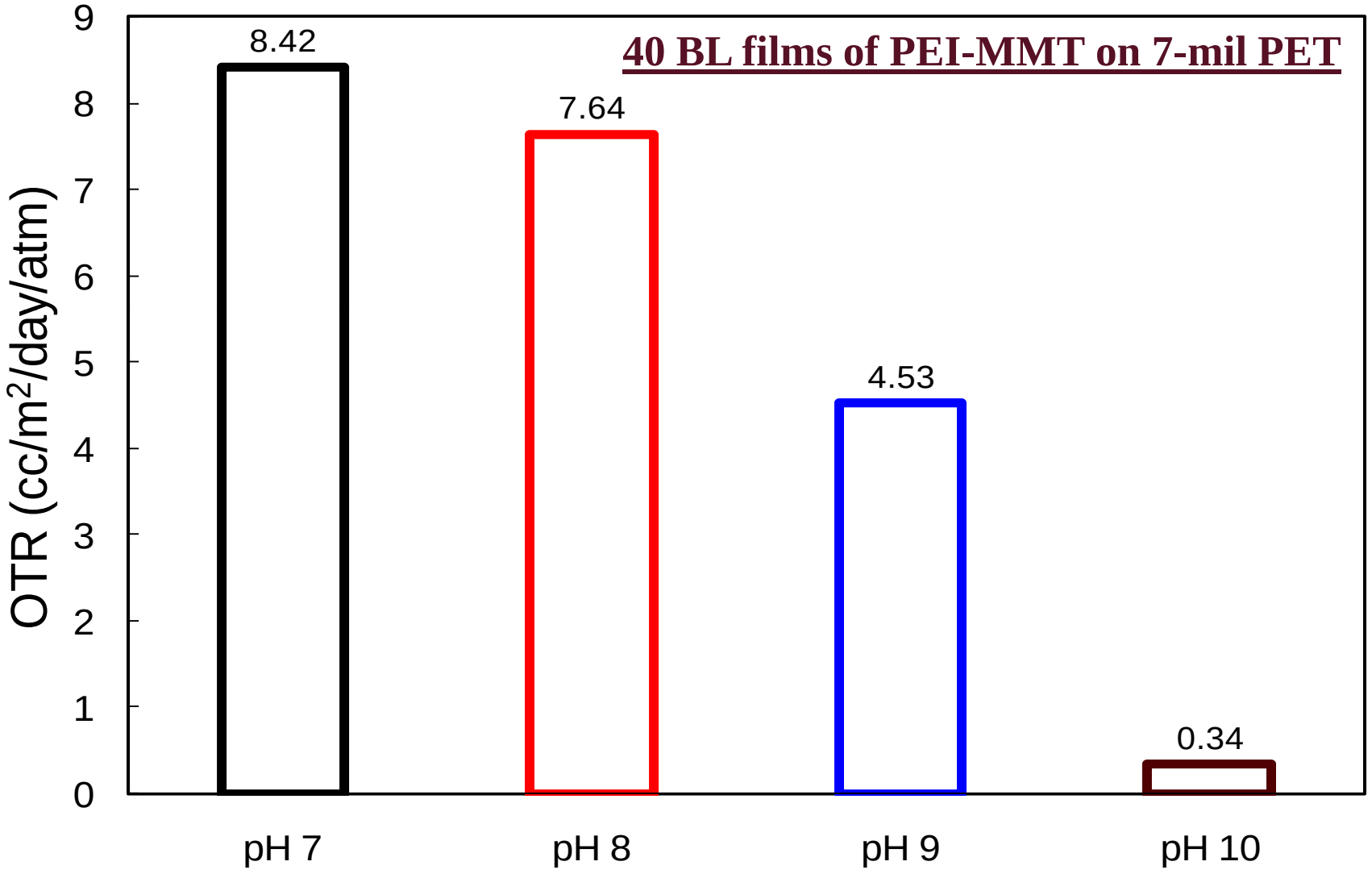


$(PEI_{10}/MMT)_{10}$

RMS Surface Roughness: 3.6nm

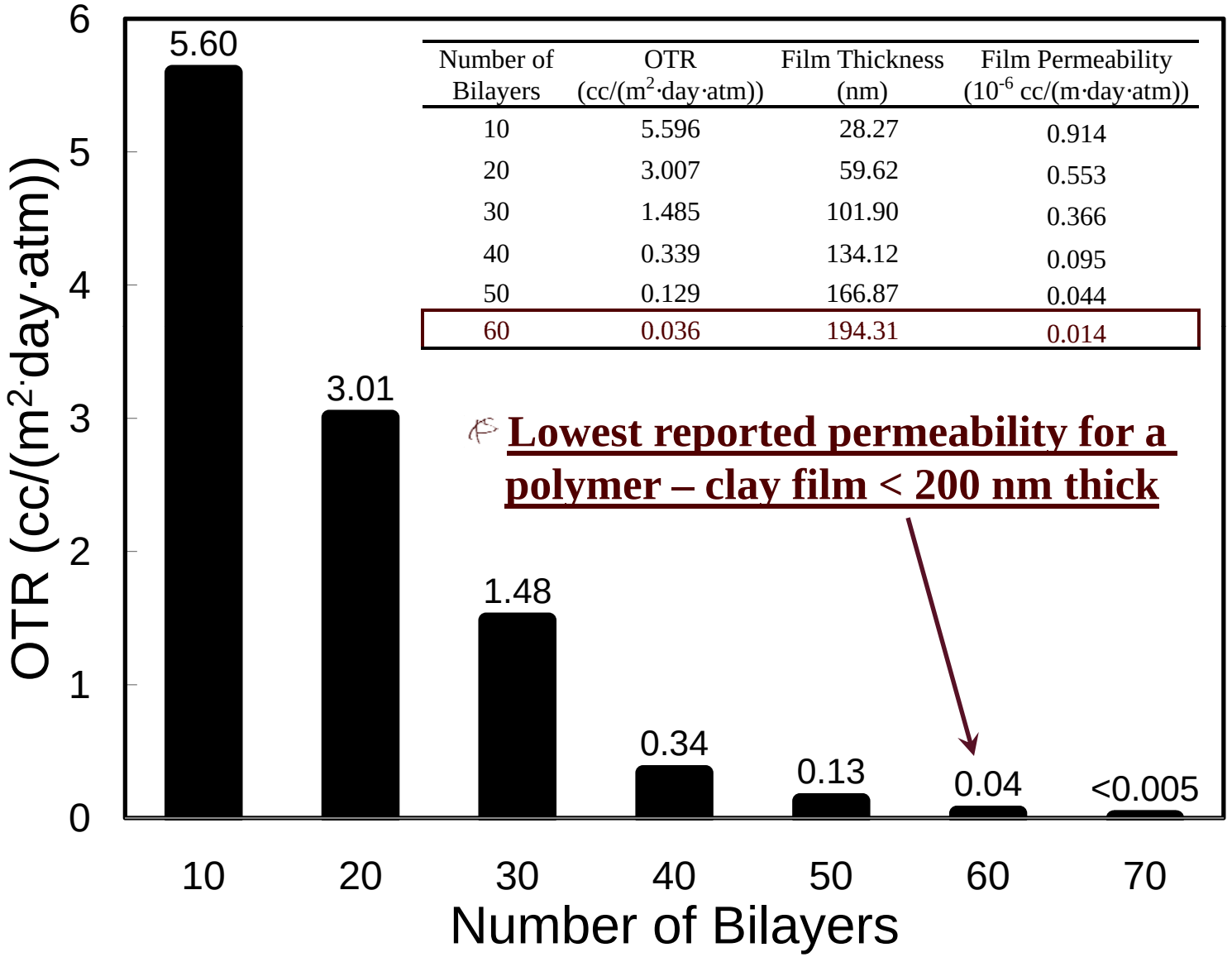


pH Tailored Oxygen Barrier



Grunlan. et al., *ACS Applied Materials & Interfaces* **2010**, *2*, 312.

Oxygen Transmission Rate of PEI-MMT at pH 10



Number of Bilayers	OTR (cc/(m^2·day·atm))	Film Thickness (nm)	Film Permeability (10^{-6} cc/(m·day·atm))
10	5.596	28.27	0.914
20	3.007	59.62	0.553
30	1.485	101.90	0.366
40	0.339	134.12	0.095
50	0.129	166.87	0.044
60	0.036	194.31	0.014

Lowest reported permeability for a polymer – clay film < 200 nm thick

Grunlan. et al., *ACS Applied Materials & Interfaces* **2010**, *2*, 312.

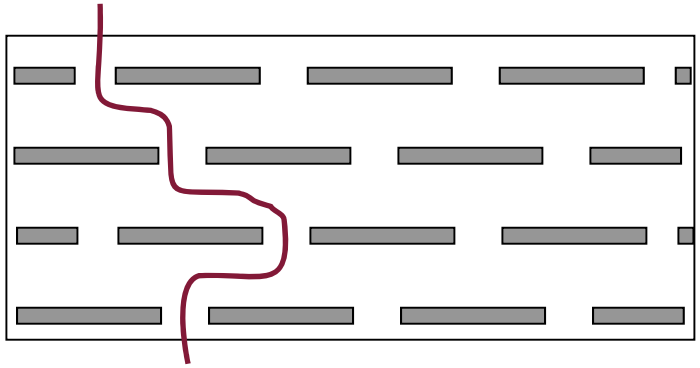
Barrier Mechanism

Classical Tortuosity

Nielsen, L. E. *J. Macromol. Sci.* **1967**, *A1*, 929.

dilute (ϕ<<1 and $\alpha\phi$<1)

$$\frac{P_o}{P} = 1 + \alpha\phi$$

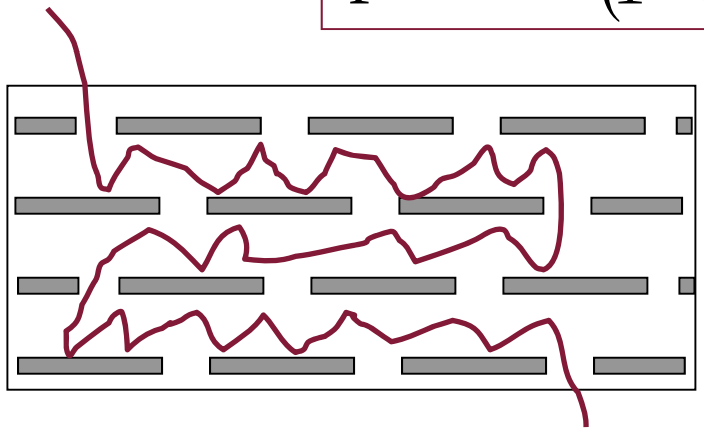


Reflective Tortuosity

Cussler et al. *J. Membrane Sci.* **1988**, *38*, 161.

semi-dilute (ϕ<<1 and $\alpha\phi$>1)

$$\frac{P_o}{P} = 1 + \mu\frac{\alpha^2\phi^2}{(1-\phi)}$$



Brick wall microstructure with staggered "slits" limits diffusion in three ways:

- ✓ **tortuous wiggles to get around platelets**
- ✓ **tight slits between platelets**
- ✓ **resistance when transitioning from wiggle into slit**

α = aspect ratio

μ = geometric factor

ϕ = vol. fraction

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Flame Retardant Foam and Fabric

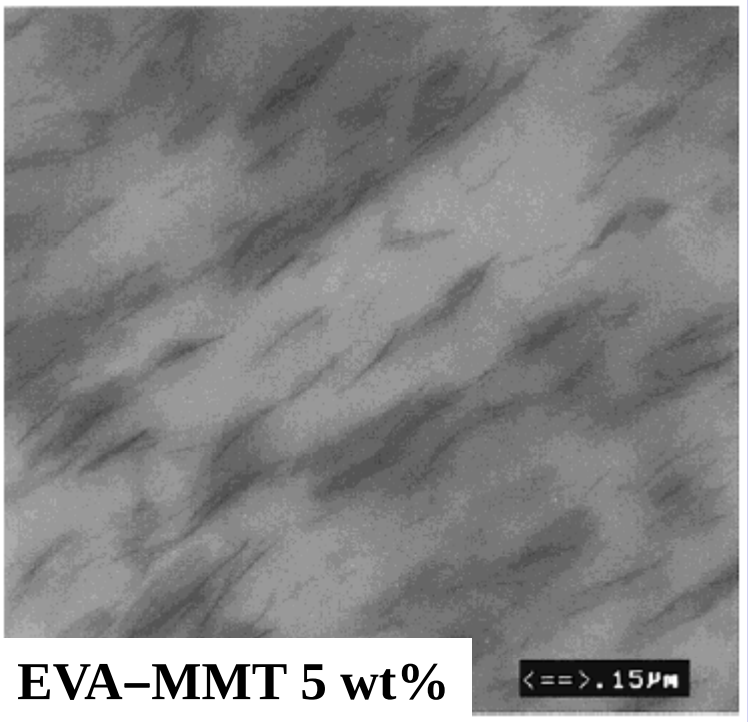
Our recent paper on this topic was featured on the ACS website and highlighted in *C&EN* on 7 June 2010.

"Creation of a barrier surface layer is believed to be a key mechanism in flame retardancy imparted by the addition of clay."

Gilman et al. *Polym. Adv. Technol.* **2006**, *17*, 263.

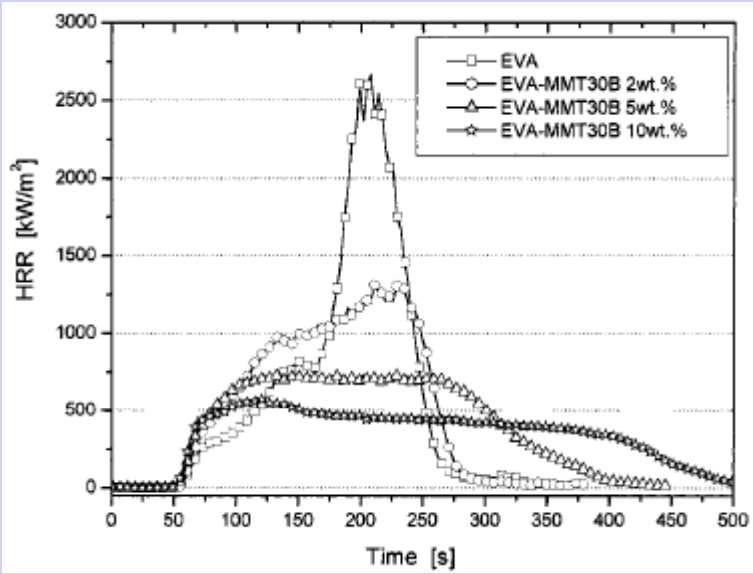
Clay Reduction of Peak Heat Release

TEM of nanocomposite



EVA–MMT 5 wt%

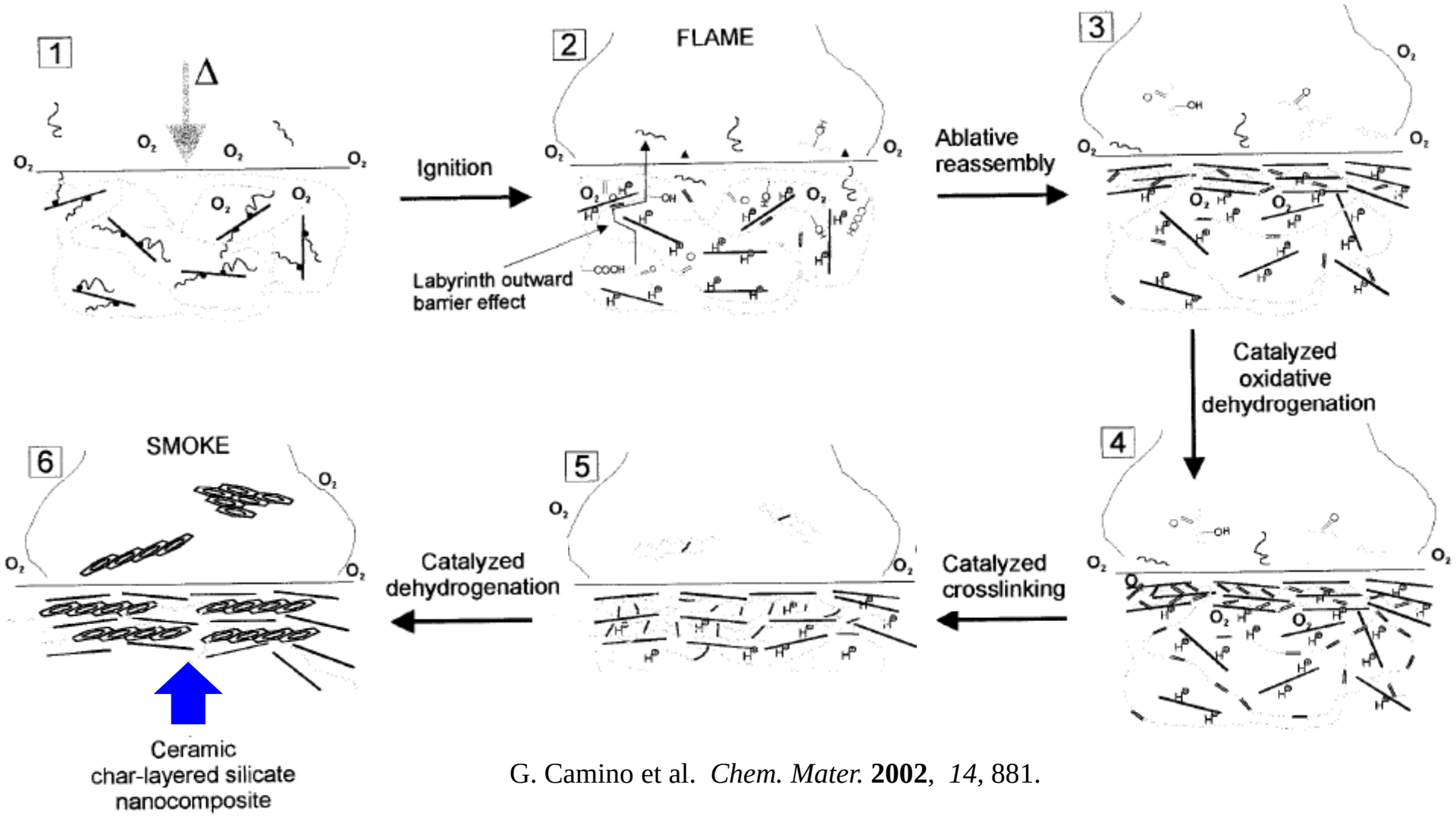
Combustion studies



- **2~5 % clay loading resulted in 70–80 % reduction of peak HRR.**
- **Charred ceramic surface act as an insulator during burning.**

G. Camino et al. *Chem. Mater.* **2002**, *14*, 881.

Mechanism of Clay Flame Suppression



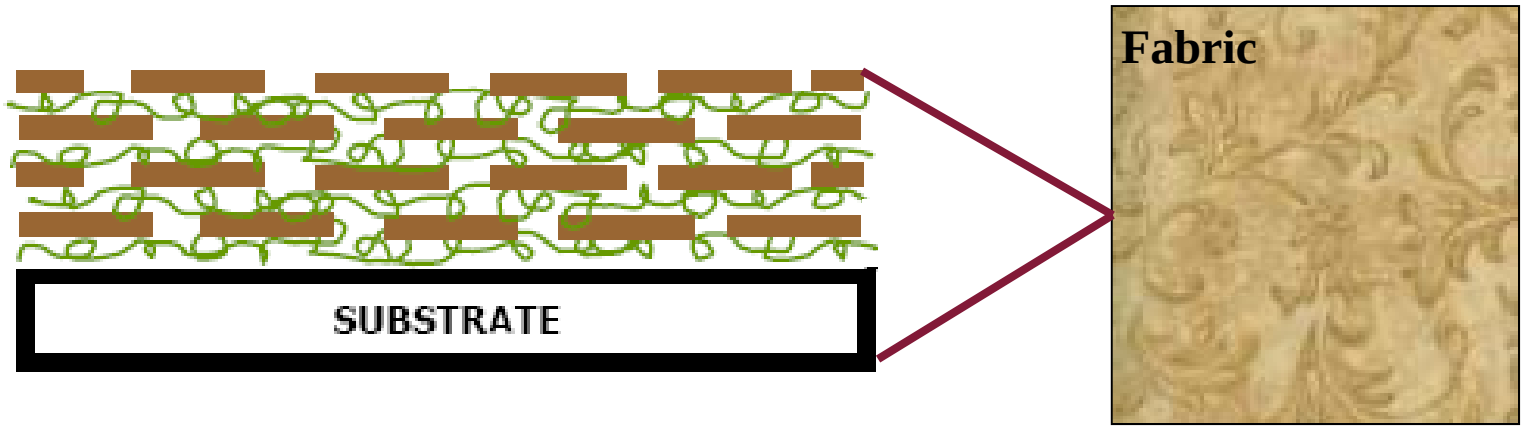
G. Camino et al. *Chem. Mater.* **2002**, *14*, 881.

Why LbL of Clay and Polymer?

- halogenated compounds-harmful for environment
- carbon nanotubes and clays-increase processing viscosity and alter mechanical properties of final foam or fabric when used *in-situ*

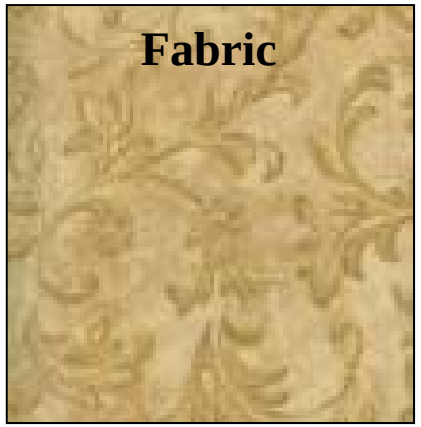
Kashiwagi, K. et al. *Nat. Mater.* **2005**, *4*, 928.
Gilman, J. W. et al. *Chem. Mater.* **2000**, *12*, 1866.

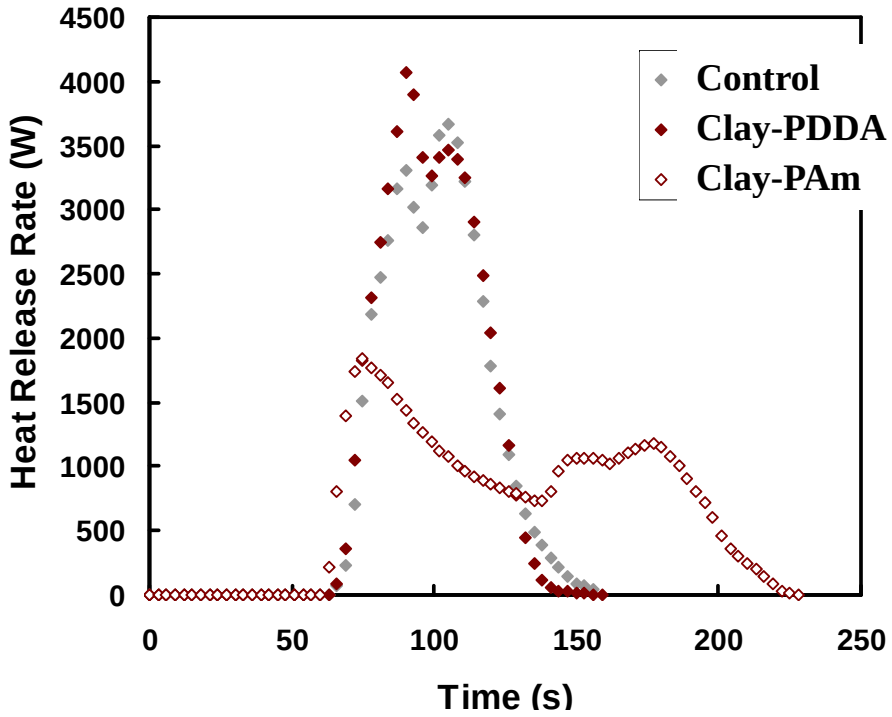
- **Layer-by-layer assembly provides the benefits of clay without the drawbacks**



Cone Calorimeter Results for Foam

The thin, conformal clay coating can easily coat three-dimensional objects (e.g., foam) to render them flame resistant without altering any other intrinsic properties.





<u>Polyurethane foam was coated with 20-bilayers</u> of two different clay-polymer compositions.

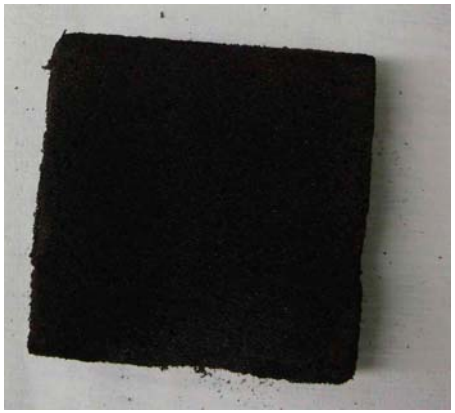
The PDDA coating is just 25 nm, while the PAm coating is 150 nm.

Gilman, Rahatekar, Zammarano (NIST)

Grunlan et al. "Layer-by-layer assembly of flame retardant coating for foam" *Polym. Mater. Sci. Eng.* **2008**, *98*, 772.

Foam Appearance After Cone Test

Foam squares were exposed to an external heat flux of 11 kW/m from the cone heater and a direct flame for 20 seconds.



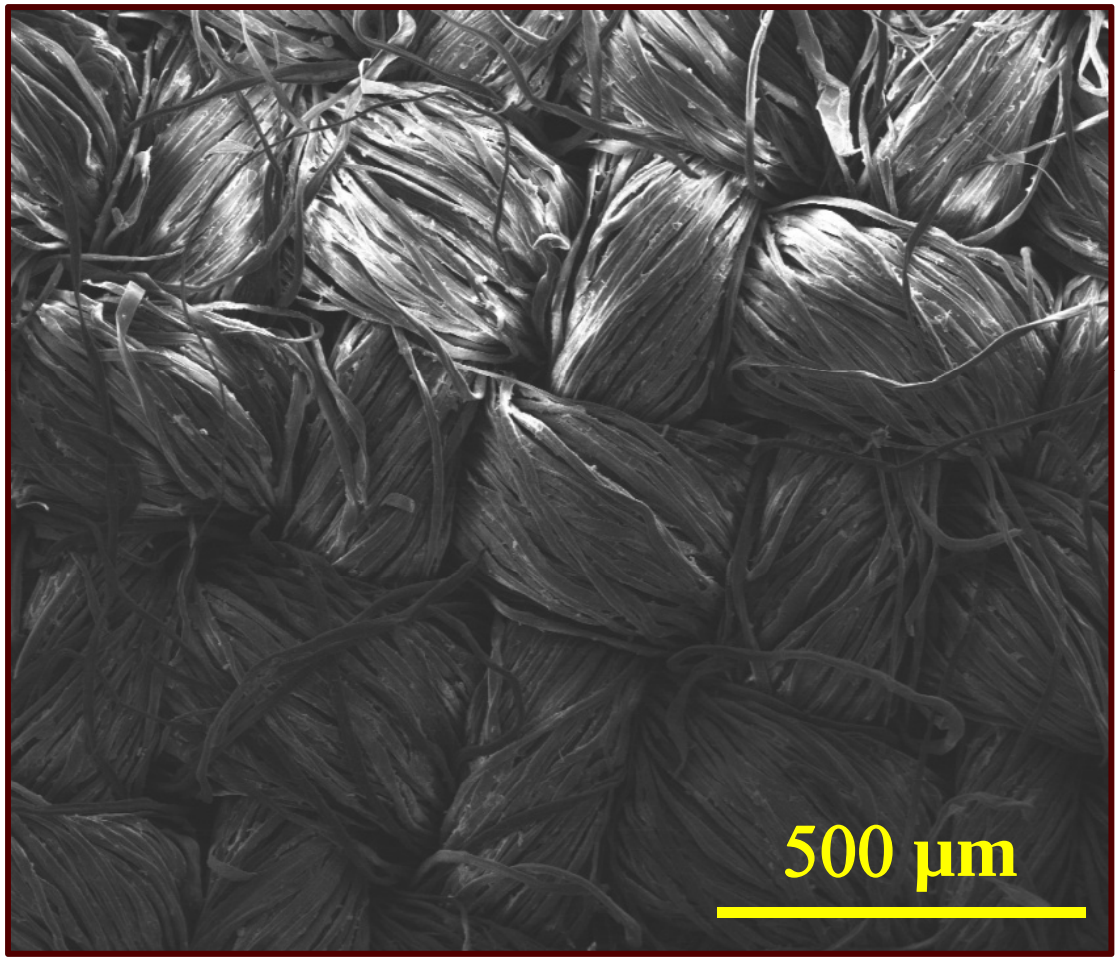
20 BL Clay-PAm
150 nm thick coating

Bare Foam
no coating

20 BL Clay-PDDA
25 nm thick coating

Gilman
Rahatekar
Zammarano
(NIST)

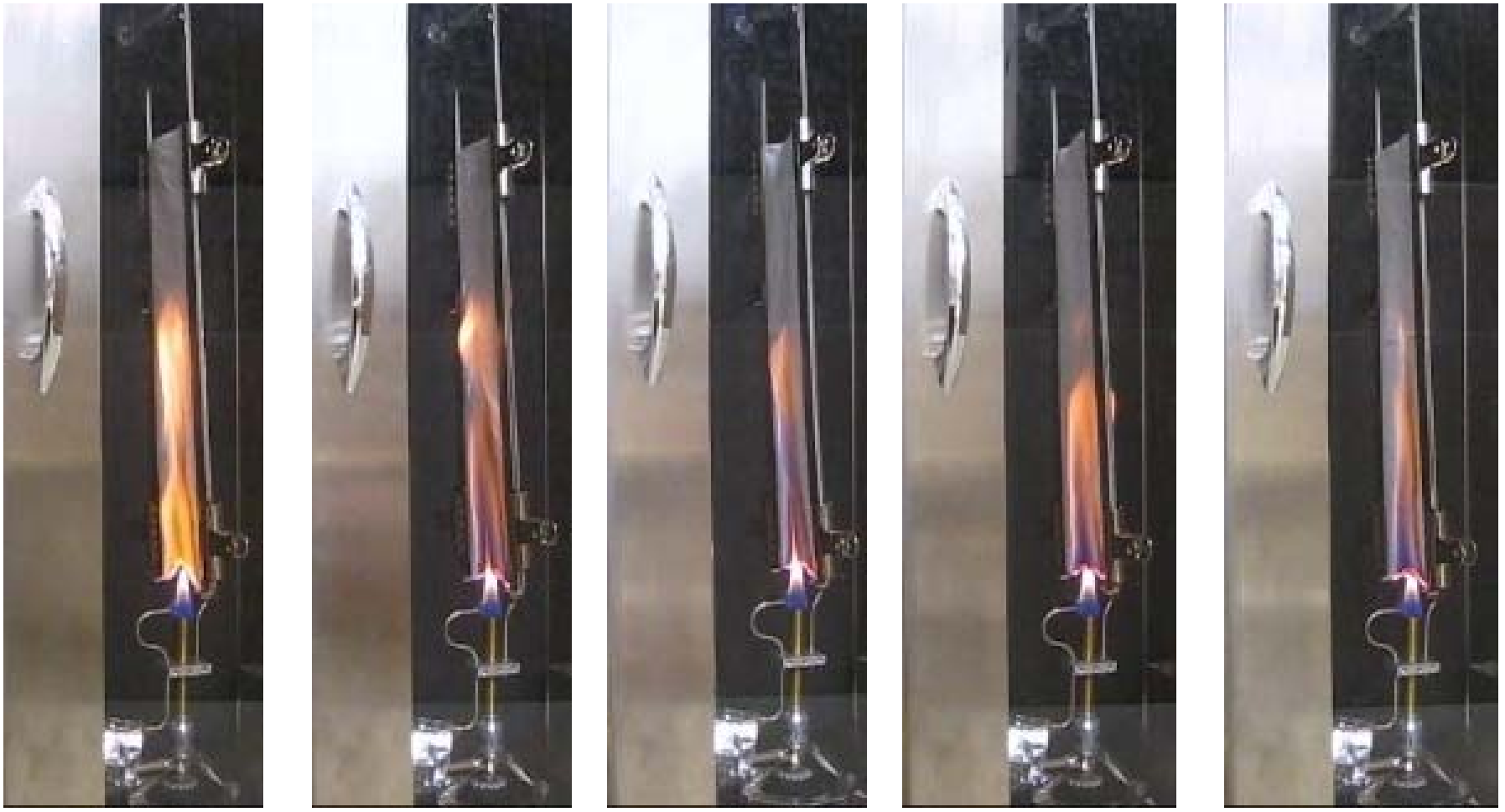
Coated Cotton Fabric Before Burning



Fabric coated with 5 BL of 0.1% BPEI pH 7/ 1% MMT

Li, Y. -C., Schulz, J., Mannen, S., Zammarano, M., Grunlan, J. C. *ACS Nano* **2010**, *4*, 3325.

Vertical Flame Test of Coated Fabrics

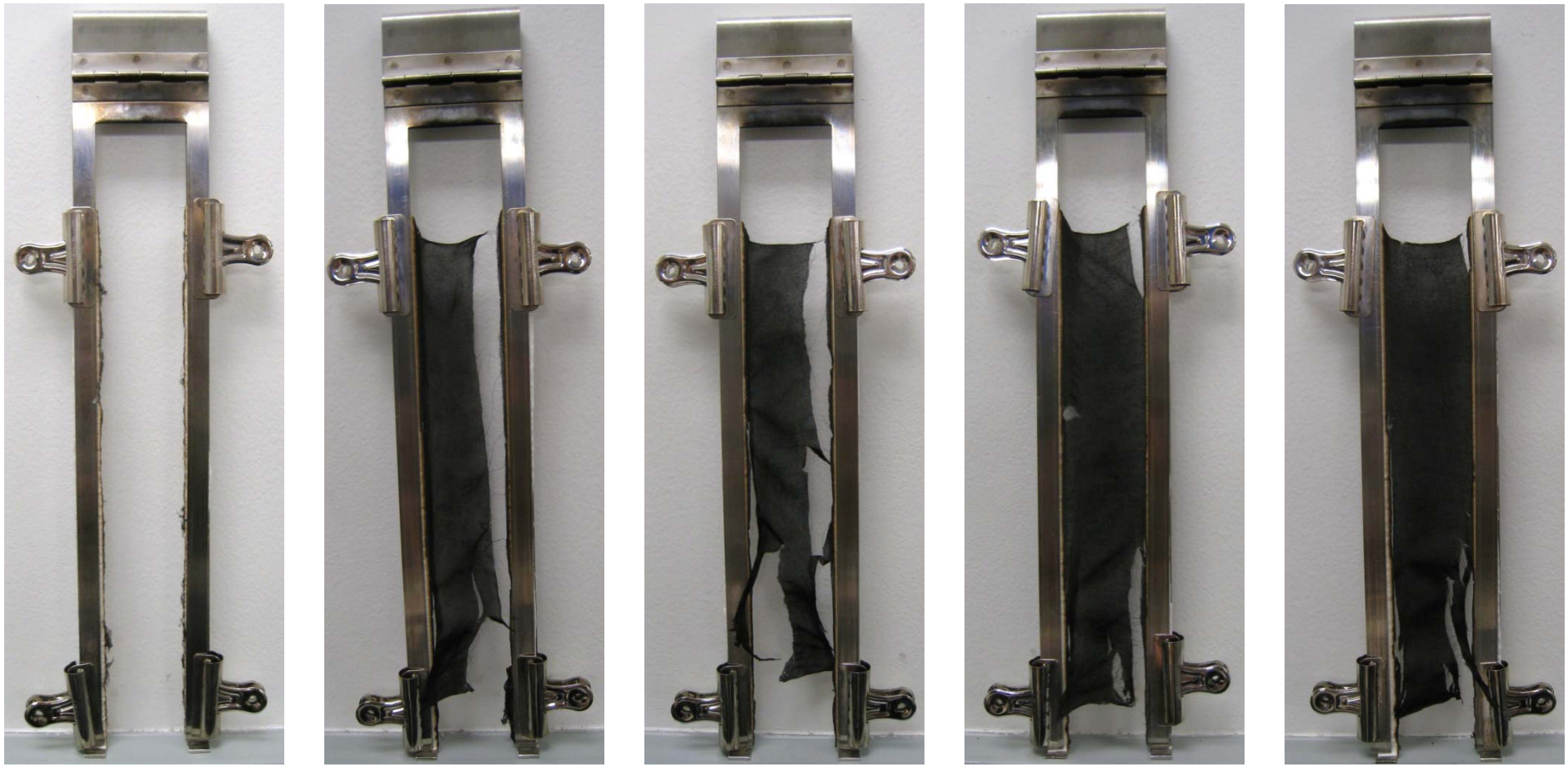


Test shown at 5 seconds after ignition on 20 BL films. *ASTM D 6413- 08*

Li, Y. -C., Schulz, J., Mannen, S., Zammarano, M., Grunlan, J. C. *ACS Nano* **2010**, *4*, 3325.

Vertical Flame Test – Post Burn

Control	BPEI pH 10/ MMT 0.2wt%	BPEI pH 7/ MMT 0.2wt%	BPEI pH 10/ MMT 1.0 wt%	BPEI pH 7/ MMT 1.0 wt%

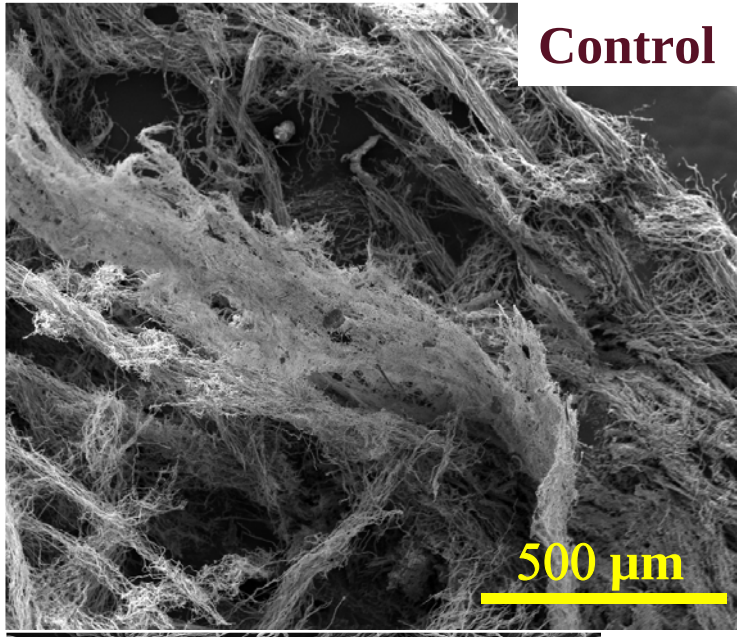


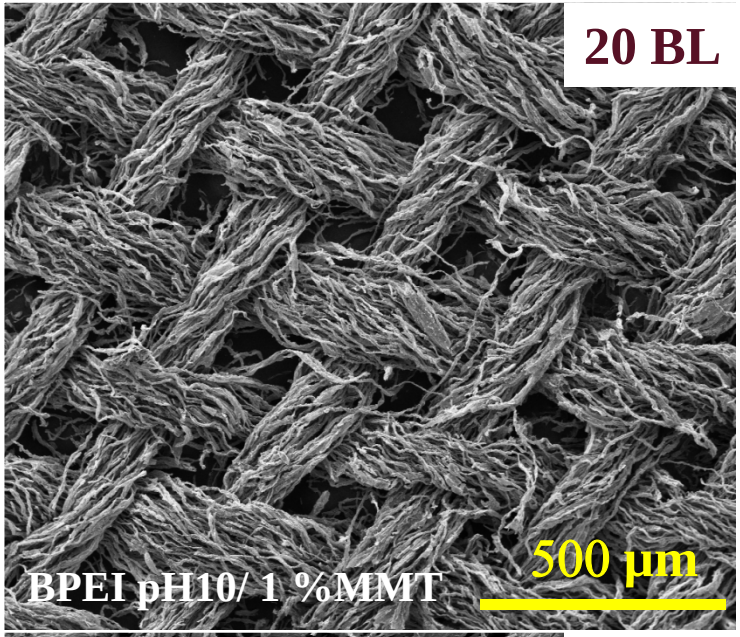
Post burn images on 20 BL films.

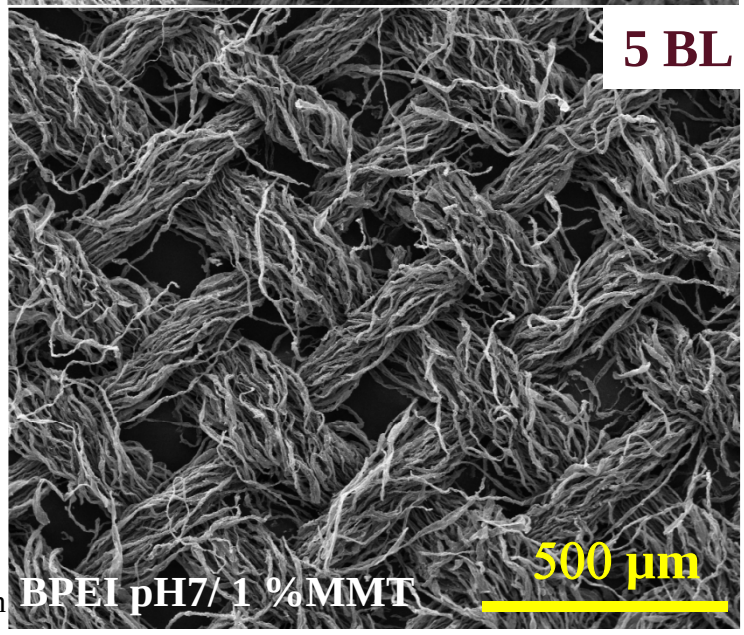
ASTM D 6413- 08

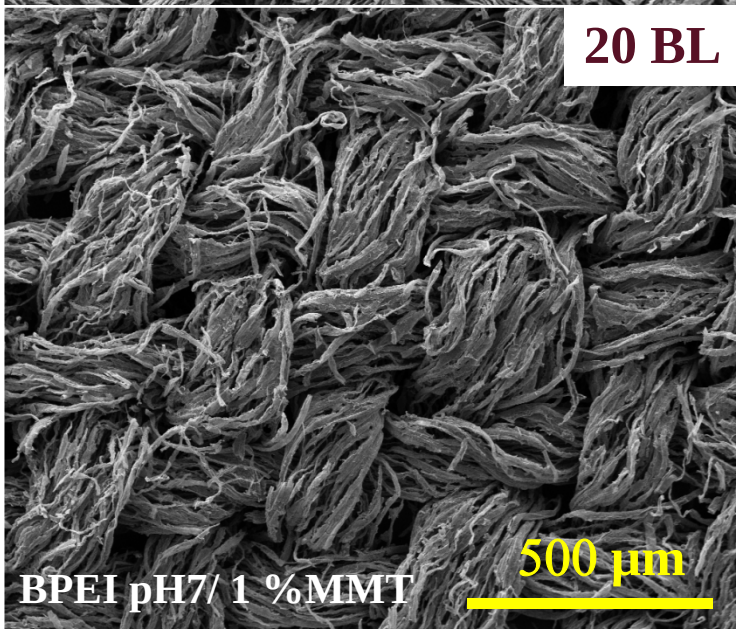
Li, Y. -C., Schulz, J., Mannen, S., Zammarano, M., Grunlan, J. C. *ACS Nano* **2010**, *4*, 3325.

Images of Fabric After Vertical Flame Test









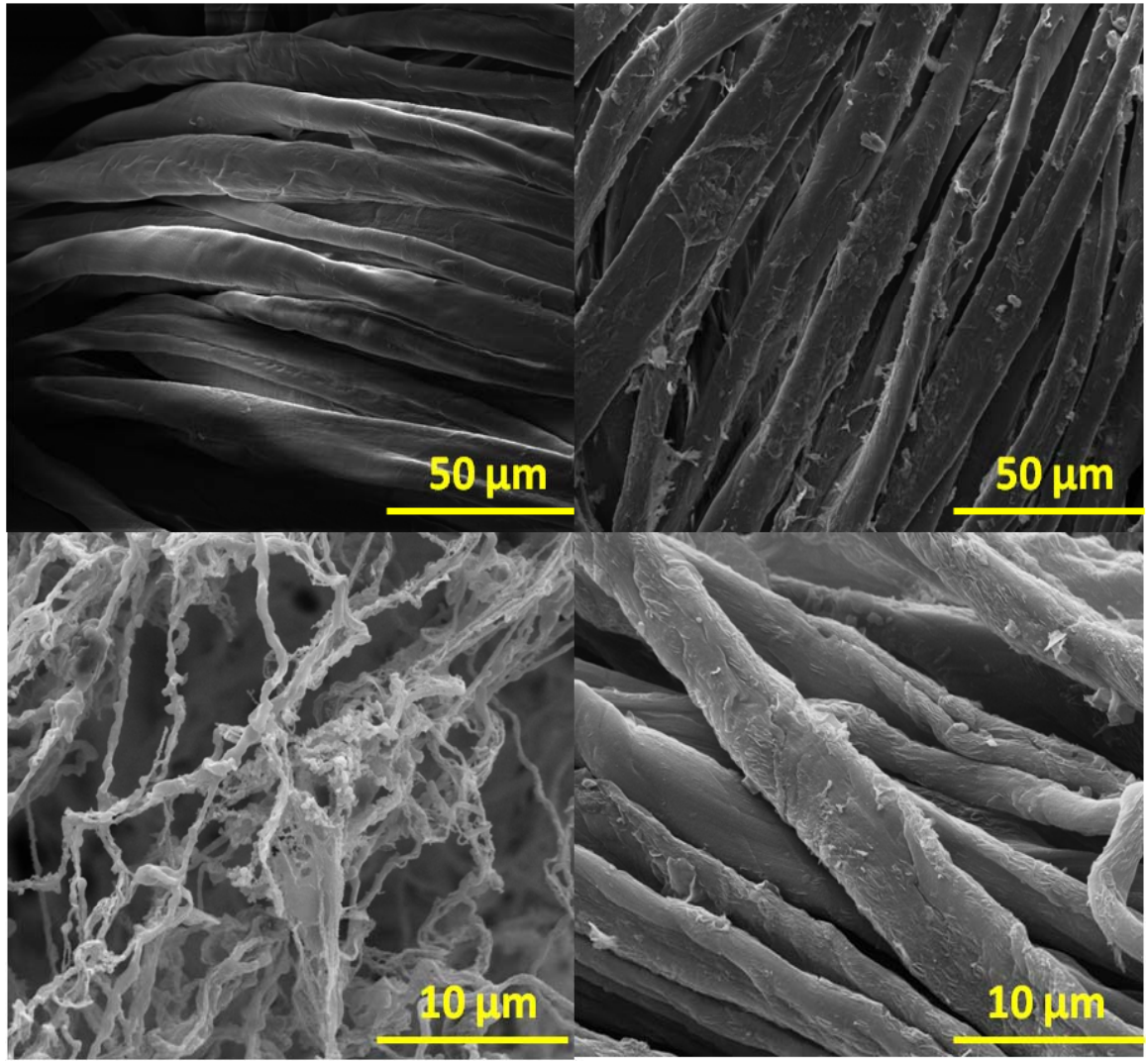
SEM Images of Virgin and Coated Fabric

Uncoated

5 BL
BPEI pH10/ 0.2 %MMT

Before burning

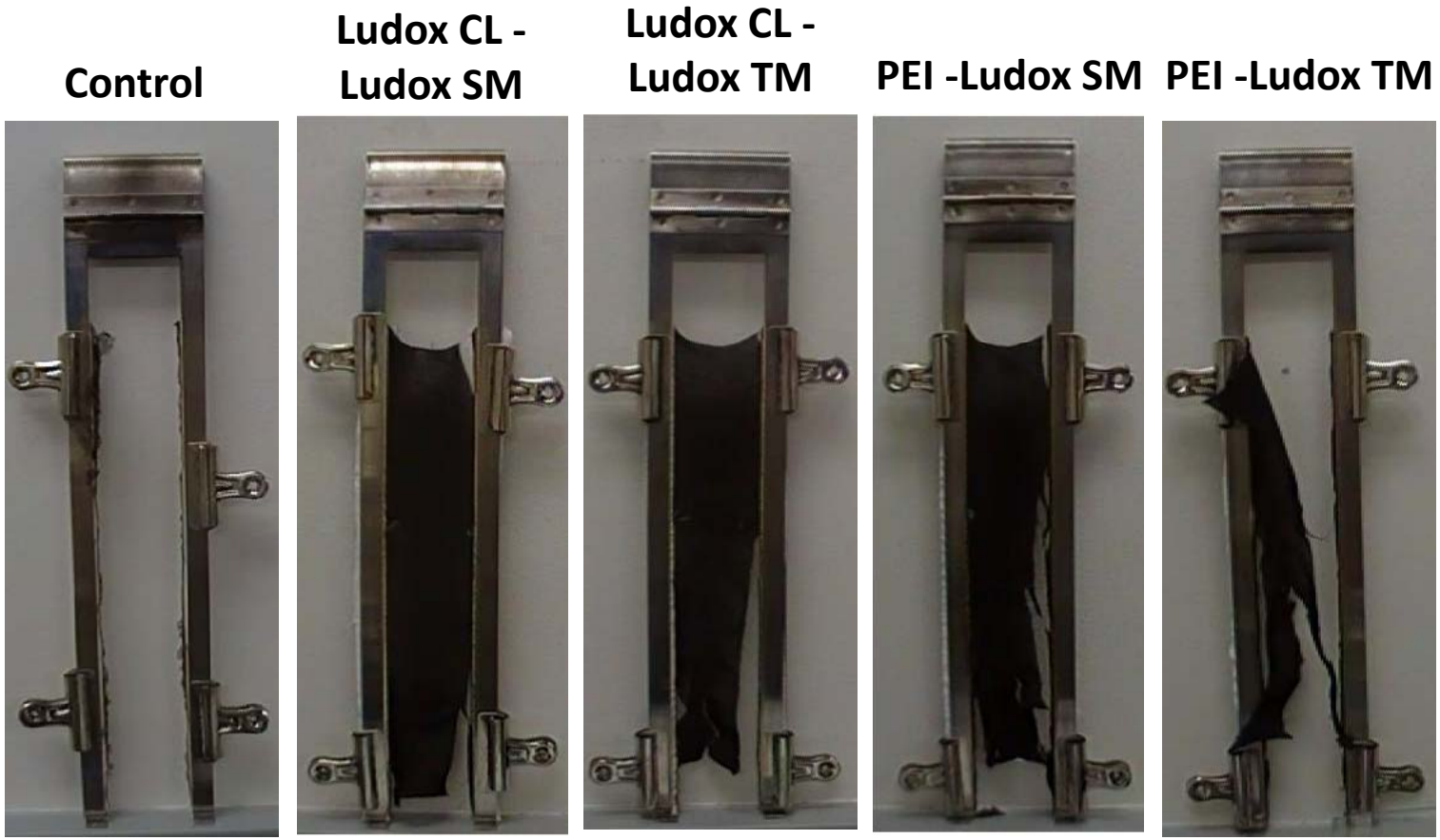
After burning



 Li, Y. -C., Schulz, J., Mannen, S., Zammarano, M., Grunlan, J. C. *ACS Nano* **2010**, *4*, 3325.

Colloidal Silica-Based Assemblies

Vertical Flame Testing of Coated Fabric

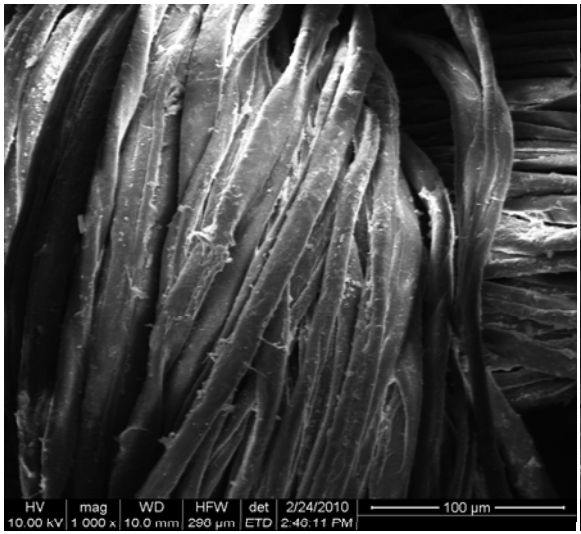
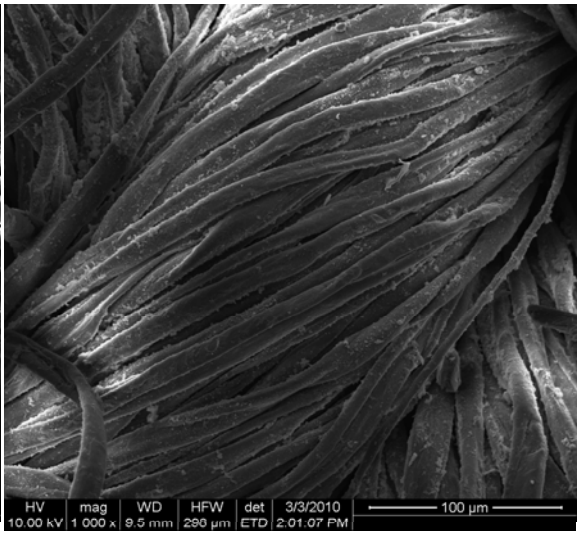
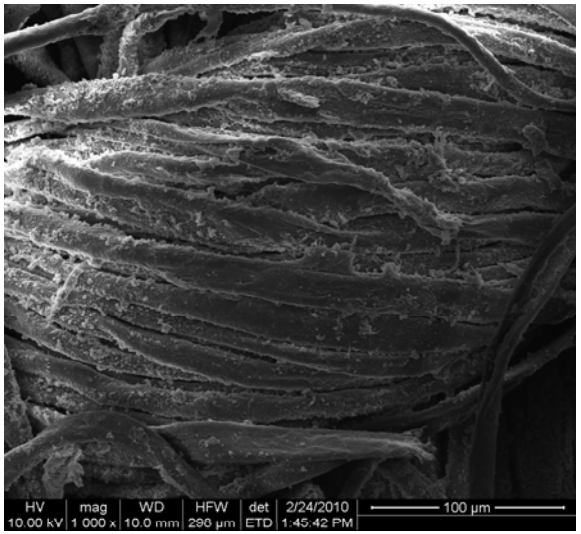
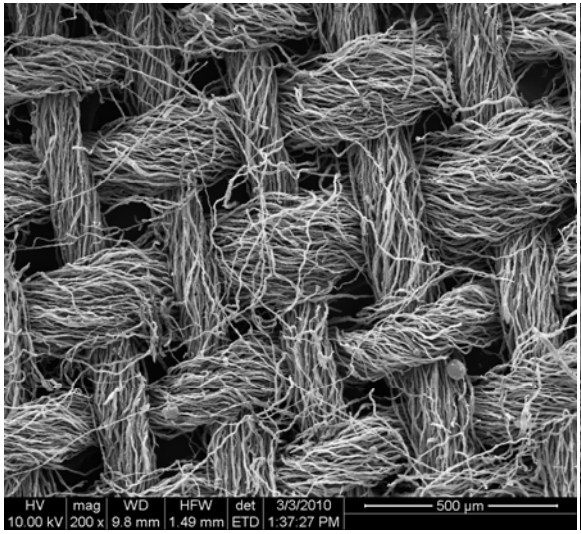
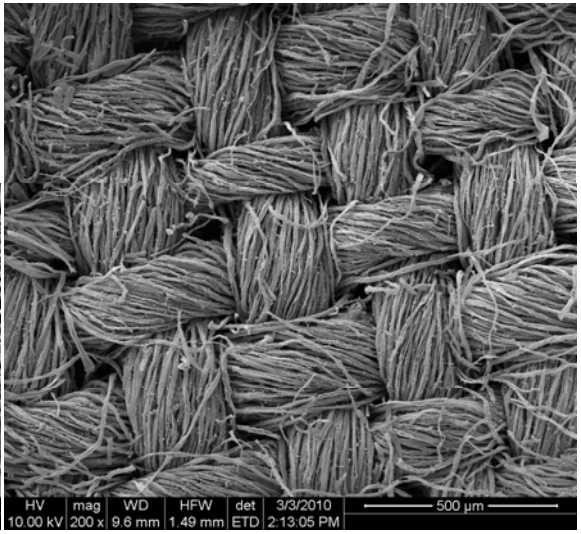
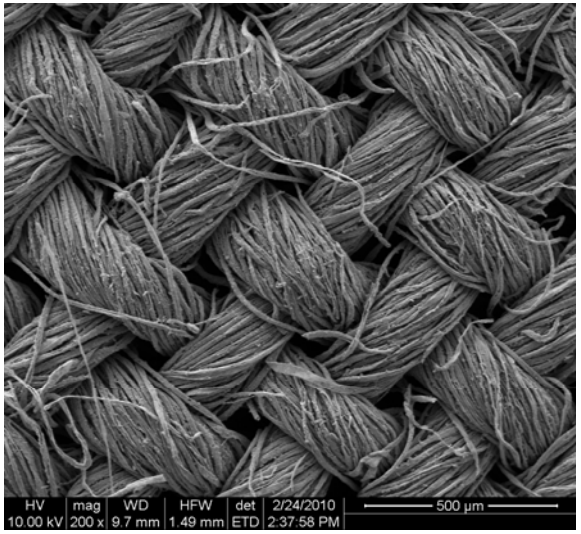


Post burn images on 10 BL films.

ASTM D6413

POSS-Based Assemblies

SEM of AP-POSS Coatings

	5BL	10BL	20BL
Before burning			
after burning			

Li, Y. C.; Mannen, S.; Schulz, J.; Grunlan, J. C., *to be submitted*.

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Conclusions

- **Clay-based assemblies can exhibit extremely low oxygen transmission rates (foil replacement)**
- **Processing is environmentally friendly (green)**
- **Ability to conformally coat complex geometries**
- **Renders foam and fabric/fibers flame retardant**