ENVIRONMENTALLY-BENIGN FLAME RETARDANT COATINGS FOR POLYMERS

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(Presented by Natalie Vest)

**DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING,
DEPARTMENT OF MECHANICAL ENGINEERING,
& DEPARTMENT OF CHEMISTRY
TEXAS A&M UNIVERSITY**

10th Triennial International Aircraft Fire and Cabin Safety Research Conference – Atlantic City, NJ – 18 October 2022

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

Jaime Grunlan's Research Thrusts

Scientific Pillars:

- **Polyelectrolyte complexation / assembly**
- **Polymer-nanoparticle interactions**
- **Water-based processing**
- **Renewable chemistry**

Nature Rev. Mater. **2020**	*Adv. Mater. Interf.* **2019**	*Adv. Electronic Mater.* **2019**
ACS Mater. Lett. **2020**	*Macro. Rapid Comm.* **2017**	*Advanced Materials* **2018**
ACS AMI **2018**	*Green Materials* **2016**	*Nano Energy* **2016**
J. Mater. Sci. **2017**	*Macromolecules* **2015**	*Adv. Energy Mater.* **2016**
Adv. Mater. Interf. **2015**	*Langmuir* **2015**	*Advanced Materials* **2015**
Advanced Materials **2011**	*Macro. Rapid Comm.* **2015**	*ACS Nano* **2010**
ACS Nano **2009**	*ACS Macro Lett.* **2014**	*Nano Letters* **2008**

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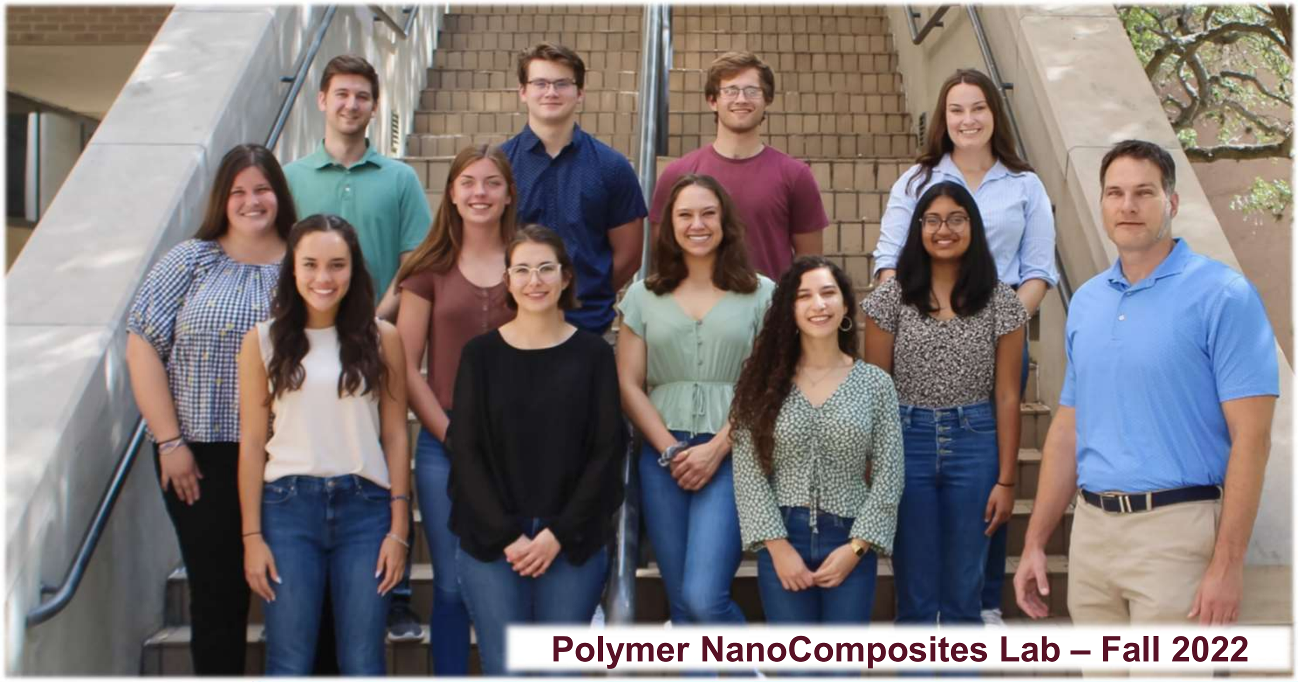
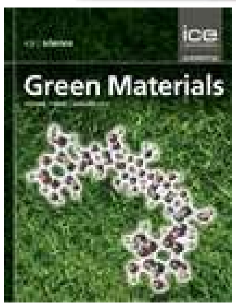
Acknowledgements





NATO OTAN

This activity is supported by: The NATO Science for Peace and Security Programme

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Presentation Outline

- Overview of <u>polyelectrolyte complexes</u> (PEC) in water
- <u>Flame retardant</u> treatments from "complex" coatings
- <u>Heat shielding</u> from layer-by-layer nanobrick wall coatings

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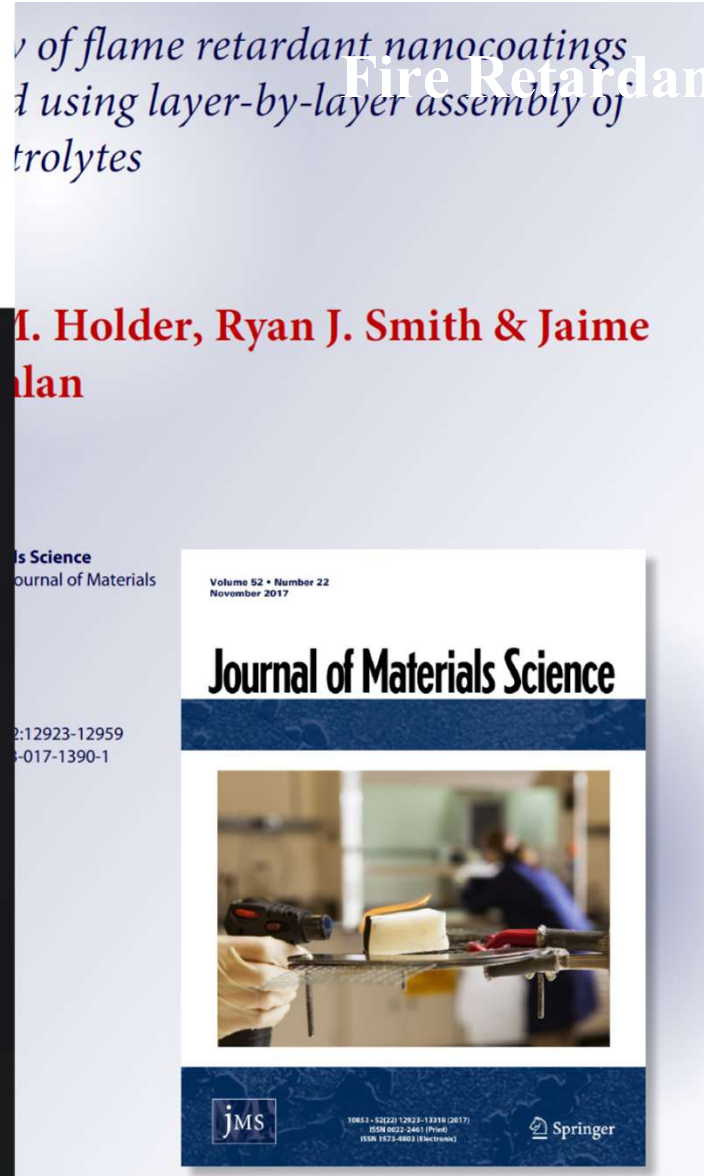
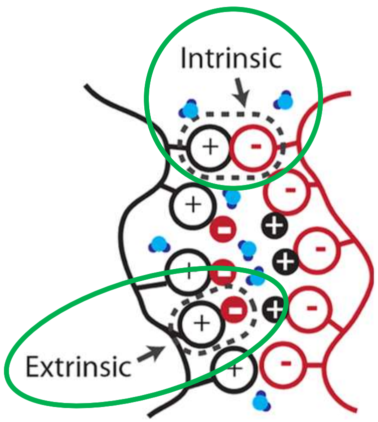
April 2020 volume 5 no. 4
www.nature.com/natrevmats
Review of flame retardant surface treatments
nature reviews materials

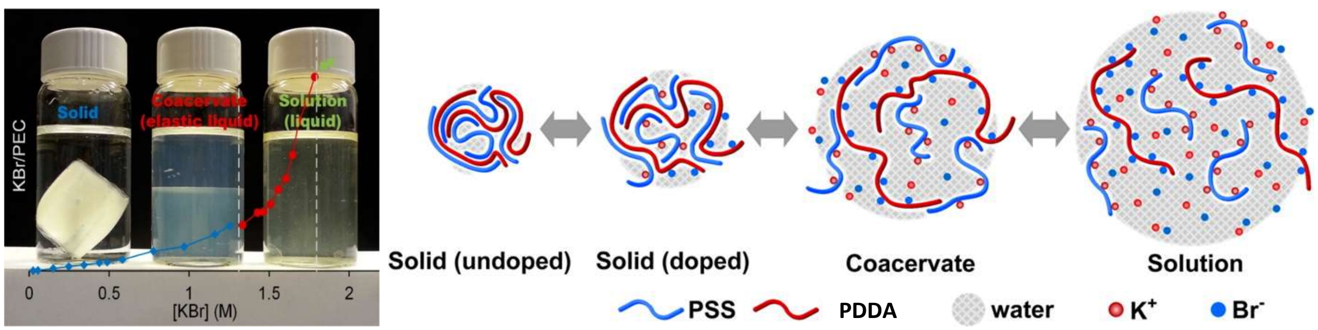

of flame retardant nanocoatings
using layer-by-layer assembly of
trolytes
I. Holder, Ryan J. Smith & Jaime
lan
ls Science
ournal of Materials
:12923-12959
-017-1390-1
Volume 52 • Number 22
November 2017
Journal of Materials Science
JMS
Springer

Polyelectrolyte Complexes



Coulombic interactions cause polyelectrolyte complexation (PEC)

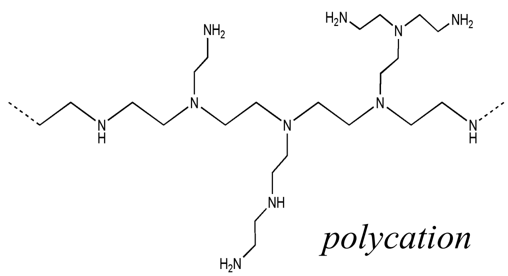
- Entropic driving force through expulsion of small counter ions and water
- PEC form along a spectrum from insoluble complex to soluble solution



Zhang, Y., et al. *ACS Cent. Sci.* **2018**, *4*, 638.
Wang, Q., et al. *Macromolecules*, **2014**, *47*, 3108.
Chiang, H.-C.; Grunlan, J. C.; et al. *Macromol. Rapid Comm.* **2021**, *42*, 2000540.

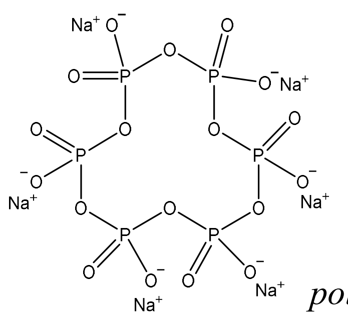
Flame Retardant PEC

Polyethylenimine (PEI)



polycation

Sodium hexametaphosphate (PSP)



polyanion

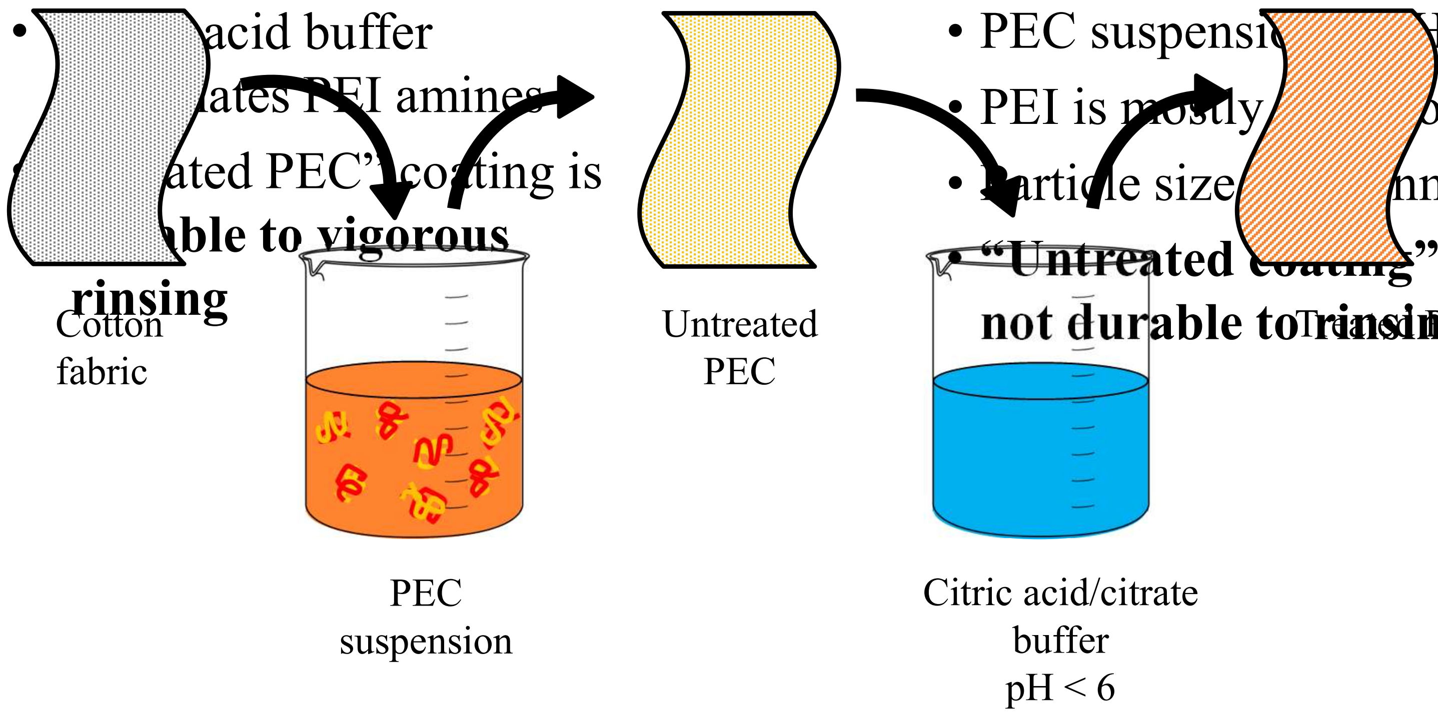
- Chemistry helps to form insulating char
- pH affects PEI degree of protonation
- Polyelectrolytes flocculate at pH ≤ 8, but mutually suspended above pH 9

M. Haile, C. Fincher, S. Fomete, J. C. Grunlan, *Polym. Degrad. Stab*. **2015**, 114, 60–64.
J. C. Grunlan, "Aqueous Polyelectrolyte Complex as One Pot Nanocoating Solution to Impart Antiflammable Behavior to Various Substrates," **U.S. Patent 9,840,629**.

PEC Coating of Cotton Fabric

- acid buffer lates PEI amines
- ated PEC" coating is ble to vigorous rinsing

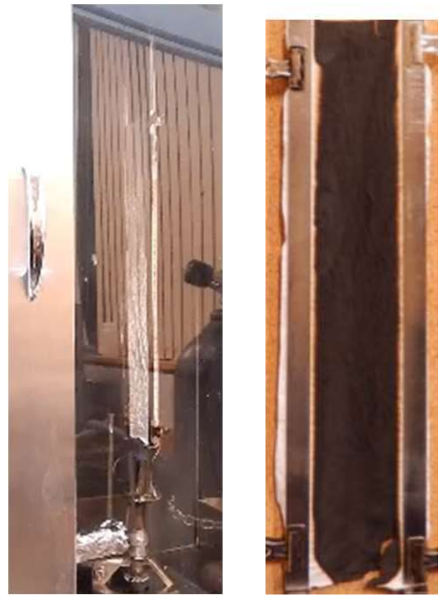
- PEC suspensi H 9
- PEI is mostly onated
- Particle size nm
- "Untreated coating" is not durable to rinsing



M. Haile, C. Fincher, S. Fomete, J. C. Grunlan, *Polym. Degrad. Stab.* **2015**, 114, 60–64.
J. C. Grunlan, "Aqueous Polyelectrolyte Complex as One Pot Nanocoating Solution to Impart Antiflammable Behavior to Various Substrates," **U.S. Patent 9,840,629**.

Flame Testing of Cotton

Uncoated control

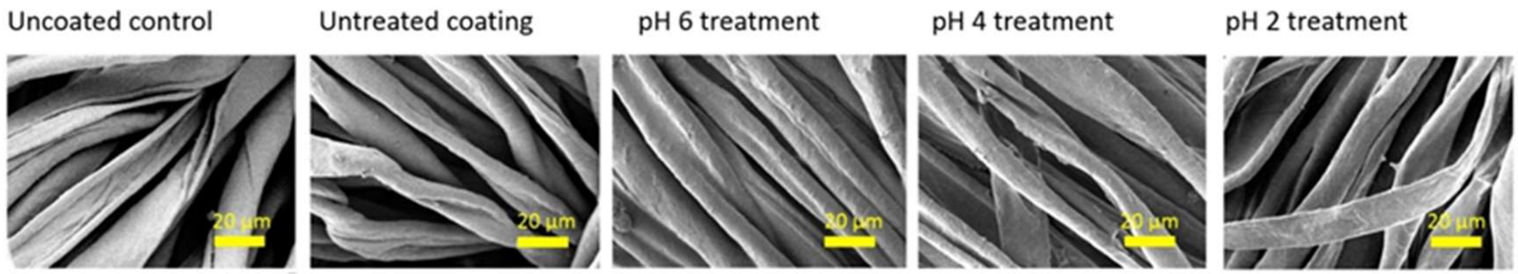


Untreated PEC coating

PEC coating treated by pH 2 buffer

M. Haile, C. Fincher, S. Fomete, J. C. Grunlan, *Polym. Degrad. Stab*. **2015**, 114, 60–64.
J. C. Grunlan, “Aqueous Polyelectrolyte Complex as One Pot Nanocoating Solution to Impart Antiflammable Behavior to Various Substrates,” **U.S. Patent 9,840,629**.

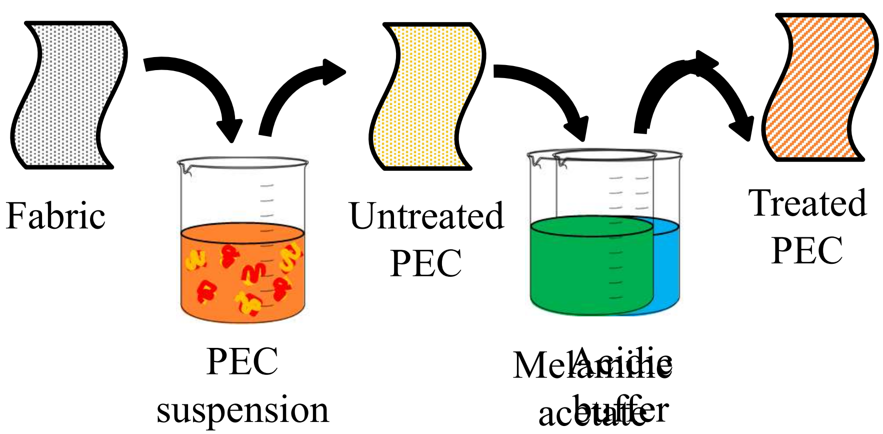
Microscopy of Coated Cotton



M. Haile, C. Fincher, S. Fomete, J. C. Grunlan, *Polym. Degrad. Stab*. **2015**, 114, 60–64.
J. C. Grunlan, "Aqueous Polyelectrolyte Complex as One Pot Nanocoating Solution to Impart Antiflammable Behavior to Various Substrates," **U.S. Patent 9,840,629**.

PEC for Nylon-Cotton

- Nylon-cotton (NYCO) fabric particularly challenging substrate
- Phosphate acts to catalyze the charring of cellulose
- Melamine polyphosphate can add further FR protection



M. Leistner, M. Haile, S. Rohmer, A. Abu-Odeh, J. Grunlan, *Polym Degrad Stab,* **2016,** *122,* 1-7.

Flammability of NYCO

No coating

19 wt% (PEC + Mel[2%])

M. Leistner, M. Haile, S. Rohmer, A. Abu-Odeh, J. Grunlan, *Polym Degrad Stab,* **2016,** *122,* 1-7.
J. C. Grunlan, "Aqueous Polyelectrolyte Complex as One Pot Nanocoating Solution to Impart Antiflammable Behavior to Various Substrates," **U.S. Patent 9,840,629**.

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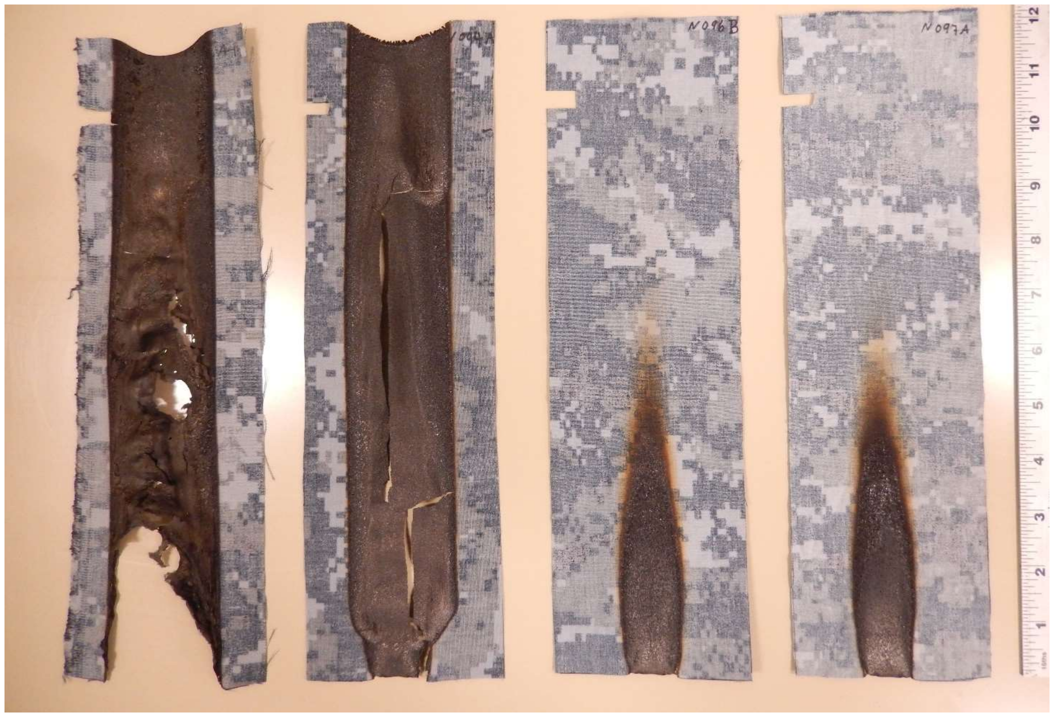
Flammability of NYCO

control PEC PEC + Mel$^{2\%}$ PEC + Mel$^{5\%}$

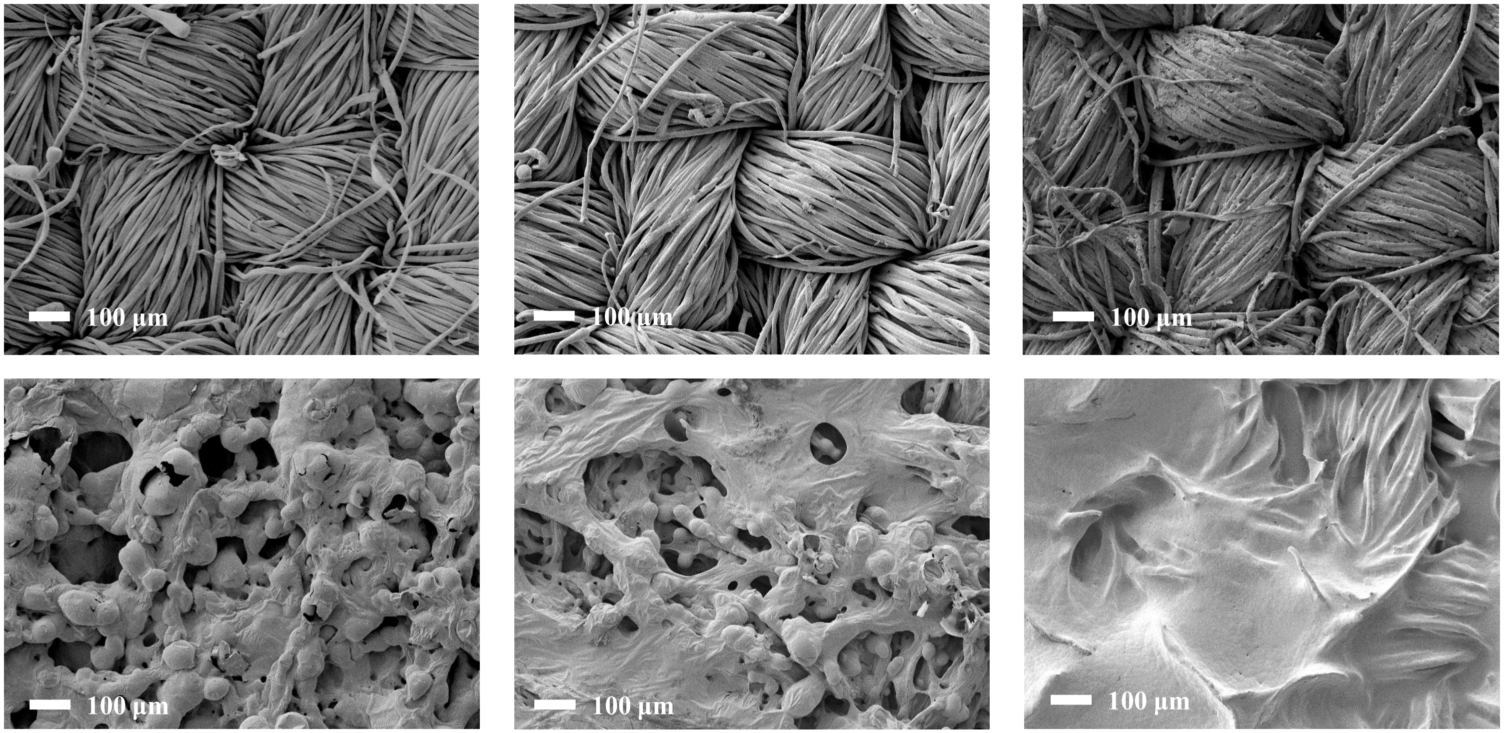


PEC: 7 wt% PEI + 14 wt% APP

M. Leistner, M. Haile, S. Rohmer, A. Abu-Odeh, J. Grunlan, *Polym Degrad Stab,* **2016,** *122,* 1-7.
J. C. Grunlan, "Aqueous Polyelectrolyte Complex as One Pot Nanocoating Solution to Impart Antiflammable Behavior to Various Substrates," **U.S. Patent 9,840,629**.

Melamine for Char-Improvement

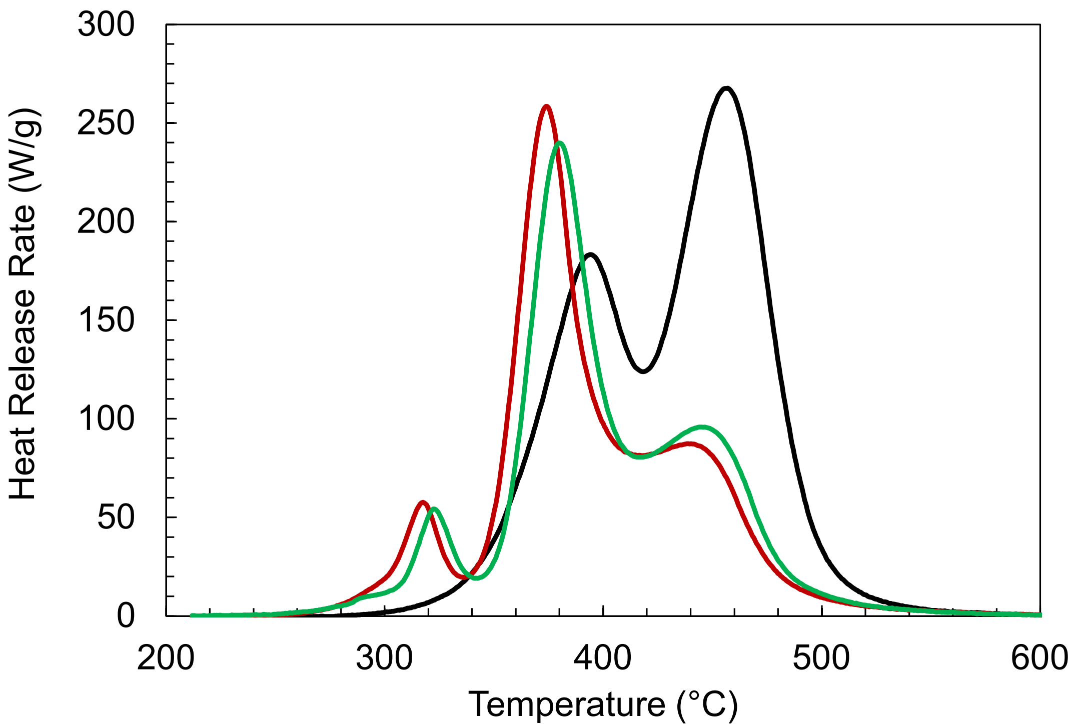
No coating | PEC | PEC + Mel$^{2\%}$



Melamine addition creates strong, dense char that acts as heat shield and barrier to oxygen and volatiles.

M. Leistner, M. Haile, S. Rohmer, A. Abu-Odeh, J. Grunlan, *Polym Degrad Stab,* **2016,** *122,* 1-7.
J. C. Grunlan, "Aqueous Polyelectrolyte Complex as One Pot Nanocoating Solution to Impart Antiflammable Behavior to Various Substrates," **U.S. Patent 9,840,629**.

Heat Release of NYCO



No coating
2 peaks
THR: 19.1 kJ/g

PEC
3 peaks
THR: 13.6 kJ/g

PEC + Mel$^{2\%}$
3 peaks
THR: 13.7 kJ/g

PCFC (aka MCC) not able to detect char density or cooling effects.

M. Leistner, M. Haile, S. Rohmer, A. Abu-Odeh, J. Grunlan, *Polym Degrad Stab,* **2016,** *122,* 1-7.
J. C. Grunlan, "Aqueous Polyelectrolyte Complex as One Pot Nanocoating Solution to Impart Antiflammable Behavior to Various Substrates," **U.S. Patent 9,840,629**.

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Heat Sink during Pyrolysis

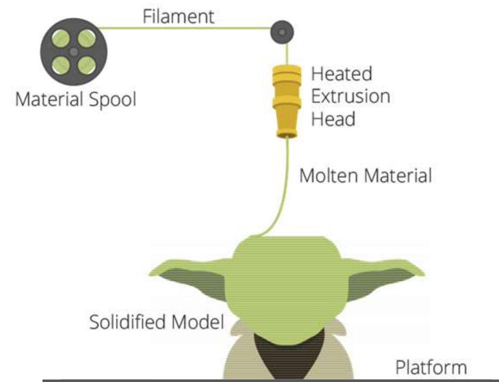
	VFT	THR (by PCFC)	Energy balance* (260 – 500°C)
no coating	burned off	19.1 kJ/g	+ 340 J/g
PEC	burned off	13.6 kJ/g	+ 70 J/g
PEC + Mel$^{2\%}$	self-extinguishing	13.7 kJ/g	– 60 J/g

* measured by DSC in N_2 at a heating rate of 10 K/min

DSC reveals a change in the energy balance during pyrolysis that reveals melamine addition making a more endothermic situation.

M. Leistner, M. Haile, S. Rohmer, A. Abu-Odeh, J. Grunlan, *Polym Degrad Stab,* **2016,** *122,* 1-7.
J. C. Grunlan, "Aqueous Polyelectrolyte Complex as One Pot Nanocoating Solution to Impart Antiflammable Behavior to Various Substrates," **U.S. Patent 9,840,629**.

- Fused Filament Fabrication
  - Filaments are flammable thermoplastics
    - Causes fires, limits part applications



https://3dprintingindustry.com/3d-printing-basics-free-beginners-guide

s counterproductive for filaments

retardant not localized to surface of part

3D printer blamed for fire inside Cain Building on Texas A&M campus

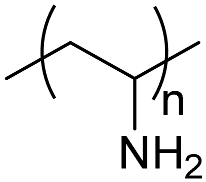
Firefighters say a 3D printer started a fire inside a classroom Wednesday afternoon inside the James J. Cain Building on the Texas A&M campus.

https://kbtx.com

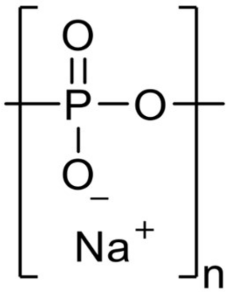
C. B. Sweeney, B. A. Lackey, M. J. Pospisil, T. C. Achee, V. K. Hicks, A. G. Moran, B. R. Teipel, M. A. Saed, M. J. Green, *Sci. Adv.* **2017**, *3*, e1700262.

Flame Retardant Filament

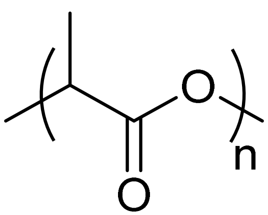
- Polyvinylamine (PVA)
  - BASF Lupamin 9095
  - Estimated M ~ 205 kDa



- Sodium hexametaphosphate (PSP)
  - M_n ~ 3 kDa (estimated)

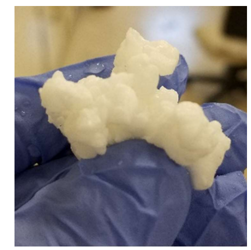


- Polylactic acid (PLA)
  - 3D Solutech filament
  - Most common 3D printing filament

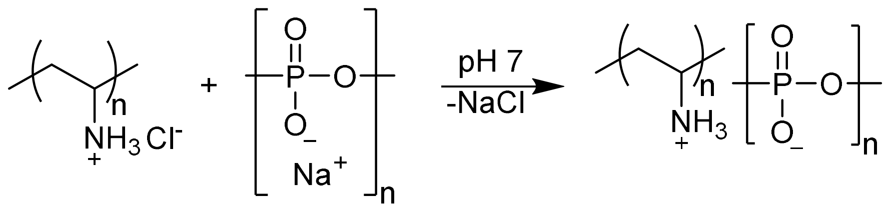


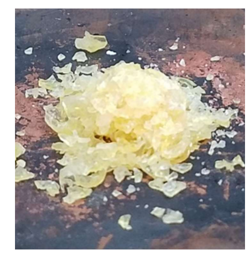
T. J. Kolibaba, C.-C. Shih, S. Lazar, B. L. Tai, J. C. Grunlan, *ACS Materials Letters* **2020**, *2*, 15.

PEC Production and Processing



- Mix PVA & PSP
  - Separate solutions each pH 7, 0.25 M





  - Dried overnight at 120 °C

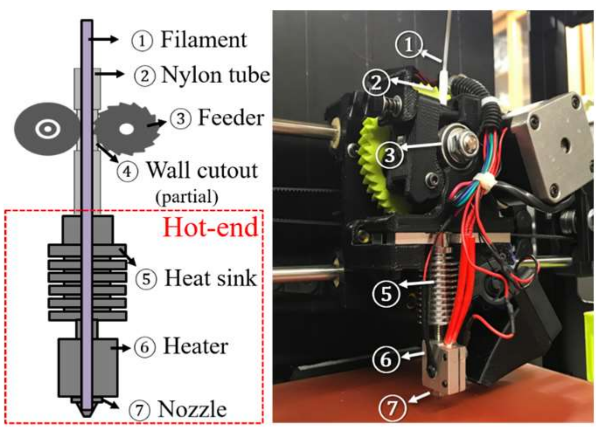
- Resultant PEC can be extruded
  - Plasticize with DI water, extrude at 90 °C
- Intrinsically flame retardant

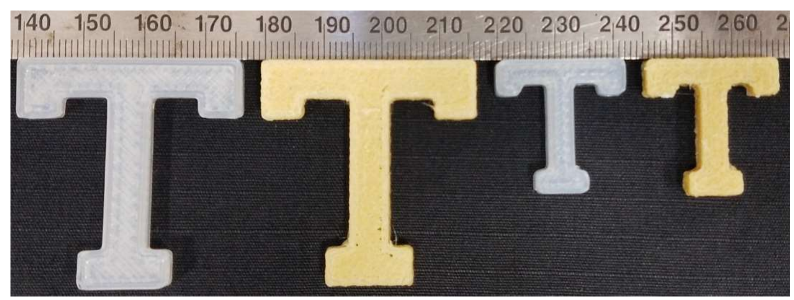
T. J. Kolibaba, C.-C. Shih, S. Lazar, B. L. Tai, J. C. Grunlan, *ACS Materials Letters* **2020**, *2*, 15.

3D Printing

- Filament
  - 25% PEC, 75% PLA
  - Mixed in microcompounder/extruder
    - Plasticized with DI water prior to extrusion
  - Printed at 200 °C, 3000 mm/min
    - Identical to 'normal' parameters for PLA

MI-LAB
MANUFACTURING
INNOVATION
LABORATORY





PLA

PLA-PEC

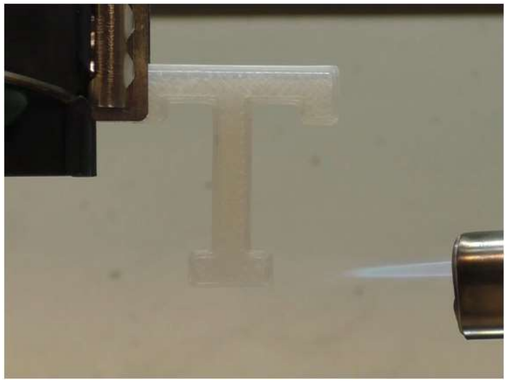
T. J. Kolibaba, C.-C. Shih, S. Lazar, B. L. Tai, J. C. Grunlan, *ACS Materials Letters* **2020**, *2*, 15.

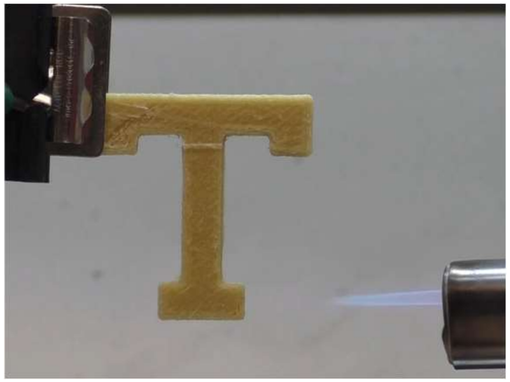
Printed Part Flame Retardancy

- Microscale Combustion Calorimetry

Sample	Char Yield (wt%)	pkHRR (W/g)	pkHRR Temp (°C)	THR (kJ/g)
PLA	0.8 ± 0.2	530 ± 40	392 ± 5	16.8 ± 0.1
PLA-PEC	13.6 ± 0.3	309 ± 3	391	13.6 ± 0.1
Change	***+1600%***	***-42%***	***-***	***-19%***

- Open flame test

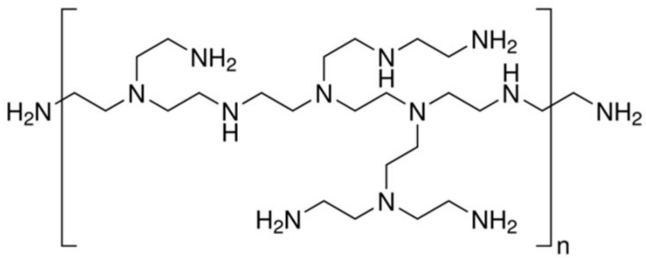




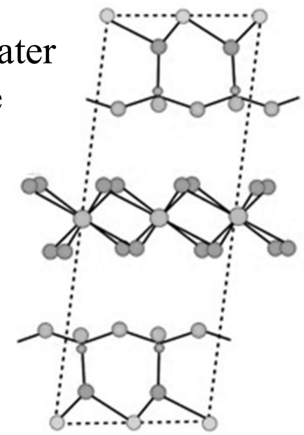
T. J. Kolibaba, C.-C. Shih, S. Lazar, B. L. Tai, J. C. Grunlan, *ACS Materials Letters* **2020**, *2*, 15.

Nanobrick Wall Thermal Shielding Coating

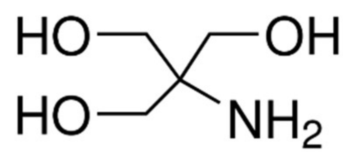
5 wt % Polyethylenimine, Branched (PEI)
Adjusted to pH 6
Sigma-Aldrich
M_w= 25,000 g/mol



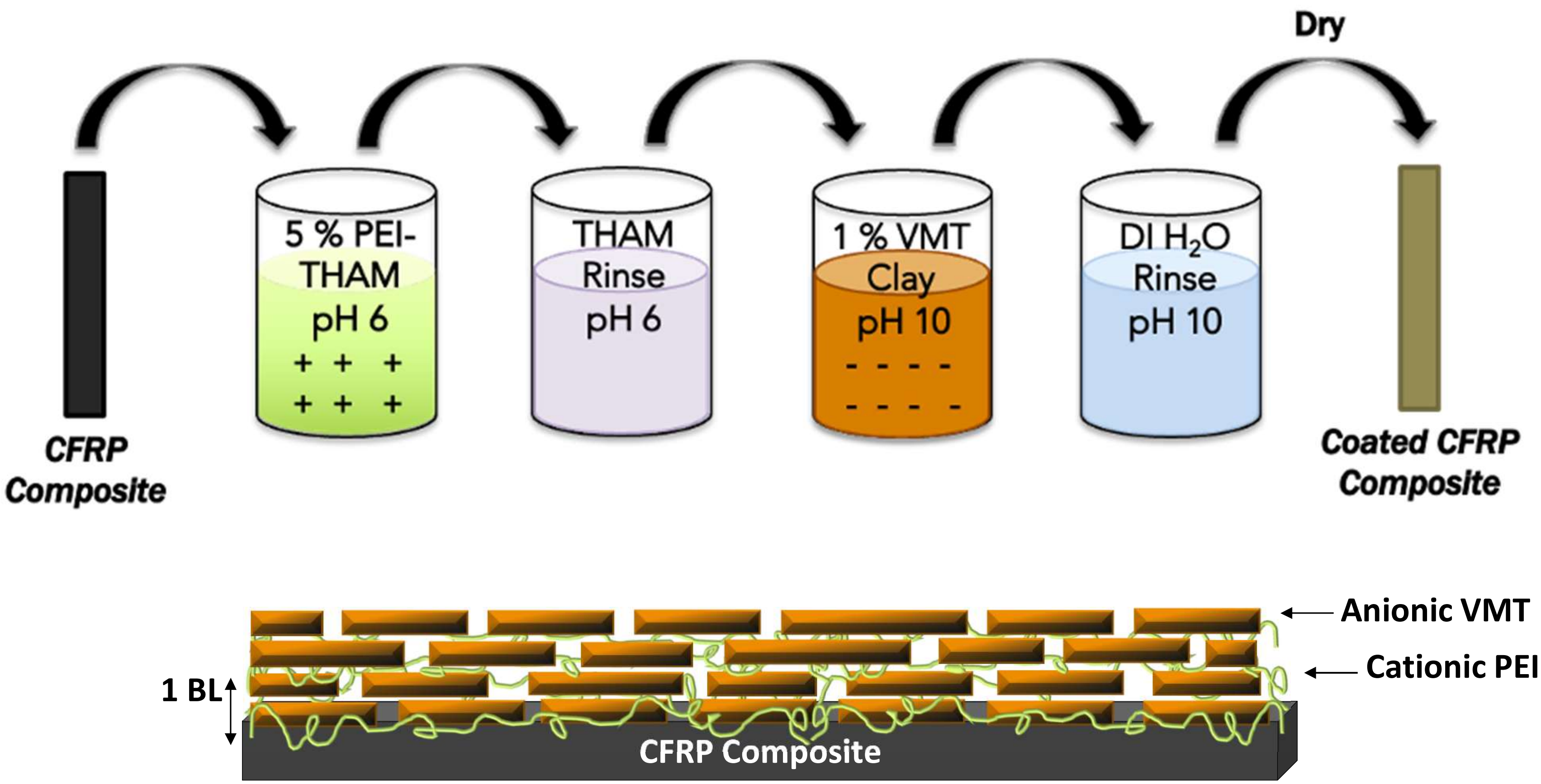
1 wt % Vermiculite Clay (VMT)
Adjusted to pH 10
963++, 7.8 wt% in water
Specialty Vermiculite



50 mM Tris (hydroxymethyl) aminomethane (THAM)
Adjusted to pH 6
Sigma-Aldrich



Deposition of Aqueous Heat Shielding System



Protection of Polystyrene Plate

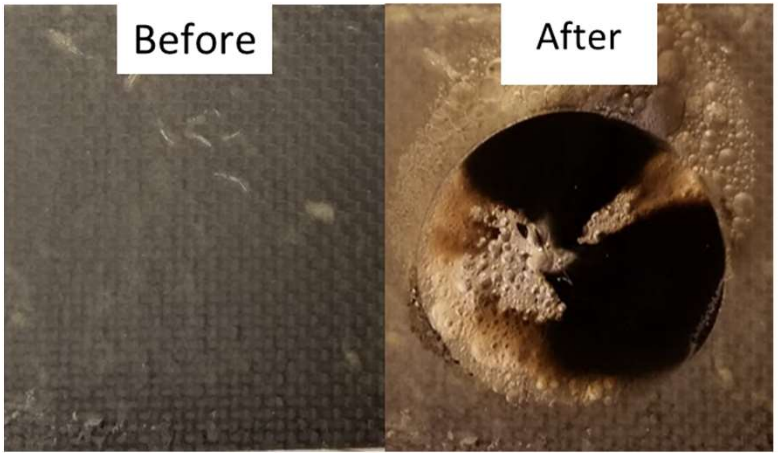
3.2 mm Polystyrene Plate

Polystyrene Plate with 8 BL Clay/Polymer Coating (4 mm thick)

Guin, Grunlan et al. *Advanced Materials Interfaces* **2015**, *2*, 1500214.

Early Demonstration of Shielding CFRP

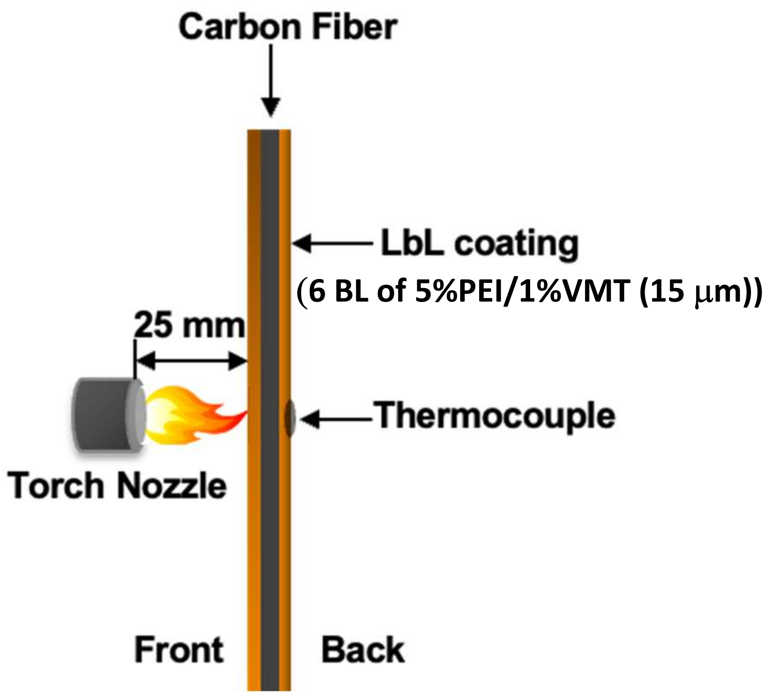
- Carbon Fiber Reinforced Polymer
  - 6 BL: 0.1% CH + 50 mM THAM (pH 6) / 1% VMT (pH 10)
    - Dip rinses in 50 mM THAM (pH 6) / pH 10 water
  - Torch test 120 s test with butane blowtorch (2.5 cm away, ~2.5 cm flame)
    - Plate approx. 7.6 x 10 x 0.16 cm^3



CFRP	% Mass Loss	Backside* Temp (°C)
Uncoated	4.8	353
Coated	2.0	257

*Backside temp is maximum temperature achieved by a thermocouple in contact with the backside of the substrate during the test

Tensile Testing with Torch Exposure



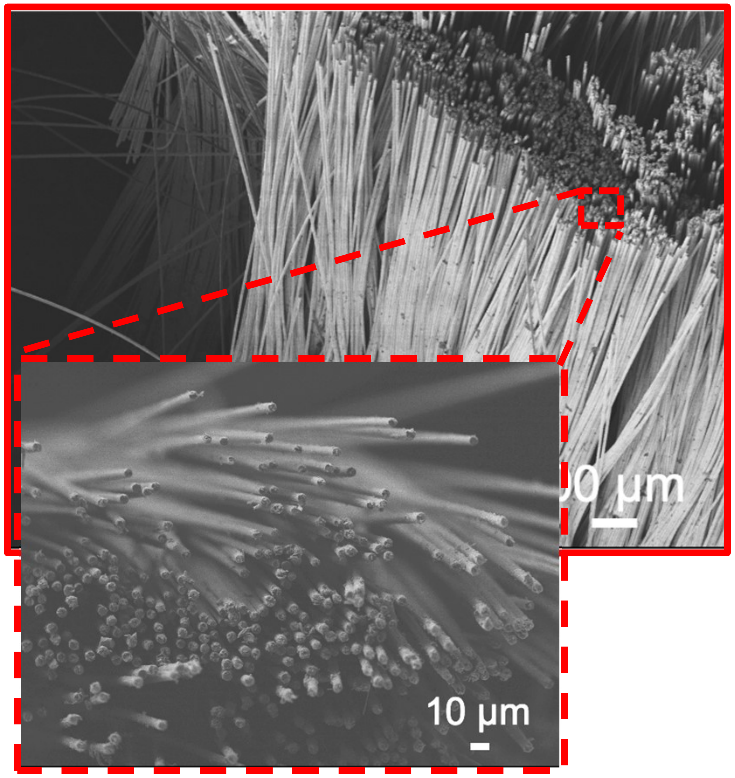
Setup

Uncoated

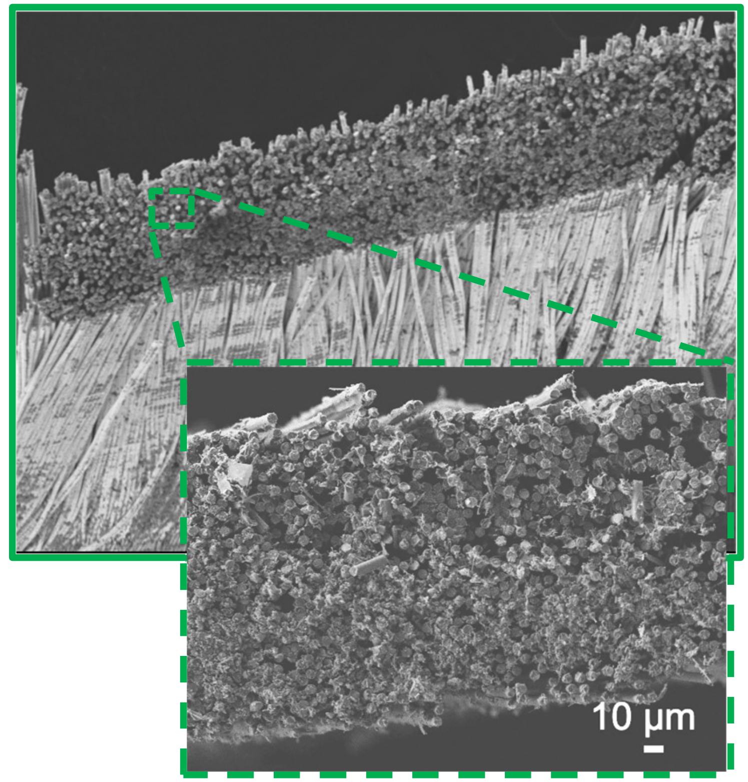
Coated

SEM of Torched Composites

Uncoated

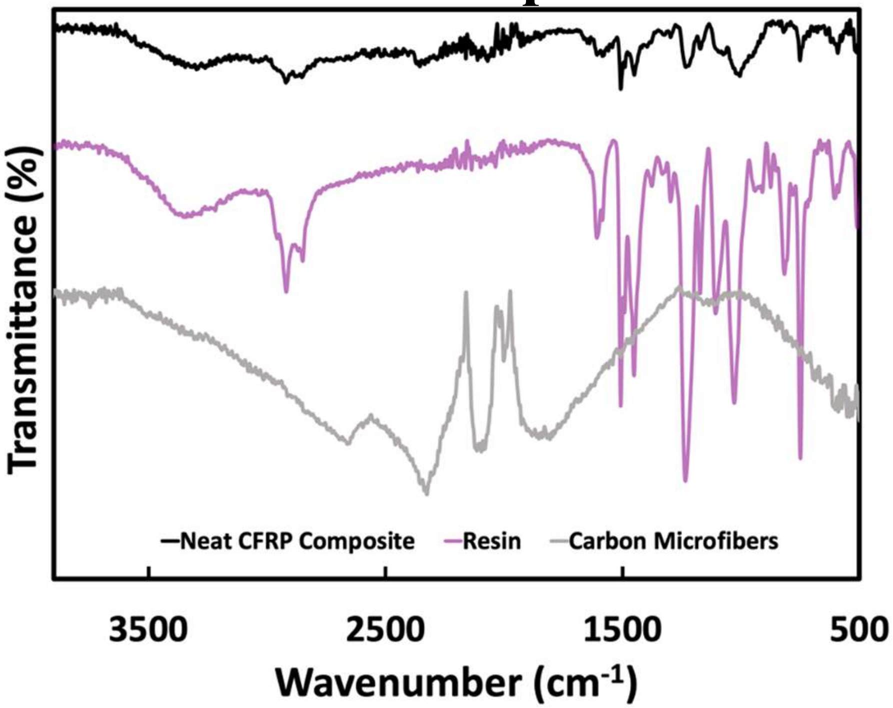


Coated (coating removed)

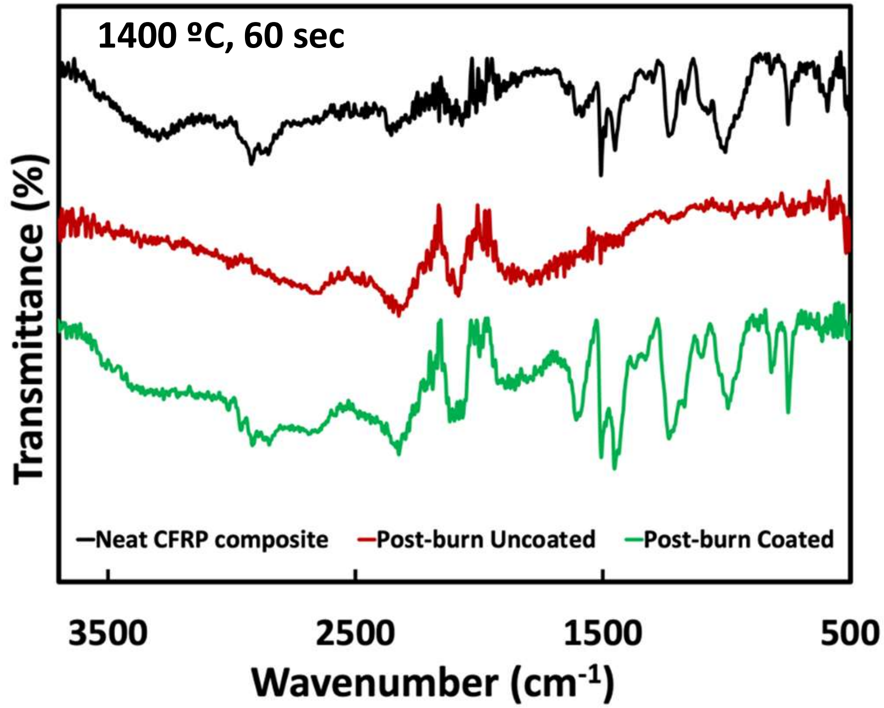


Post-Burn FTIR of Composites

CFRP Components

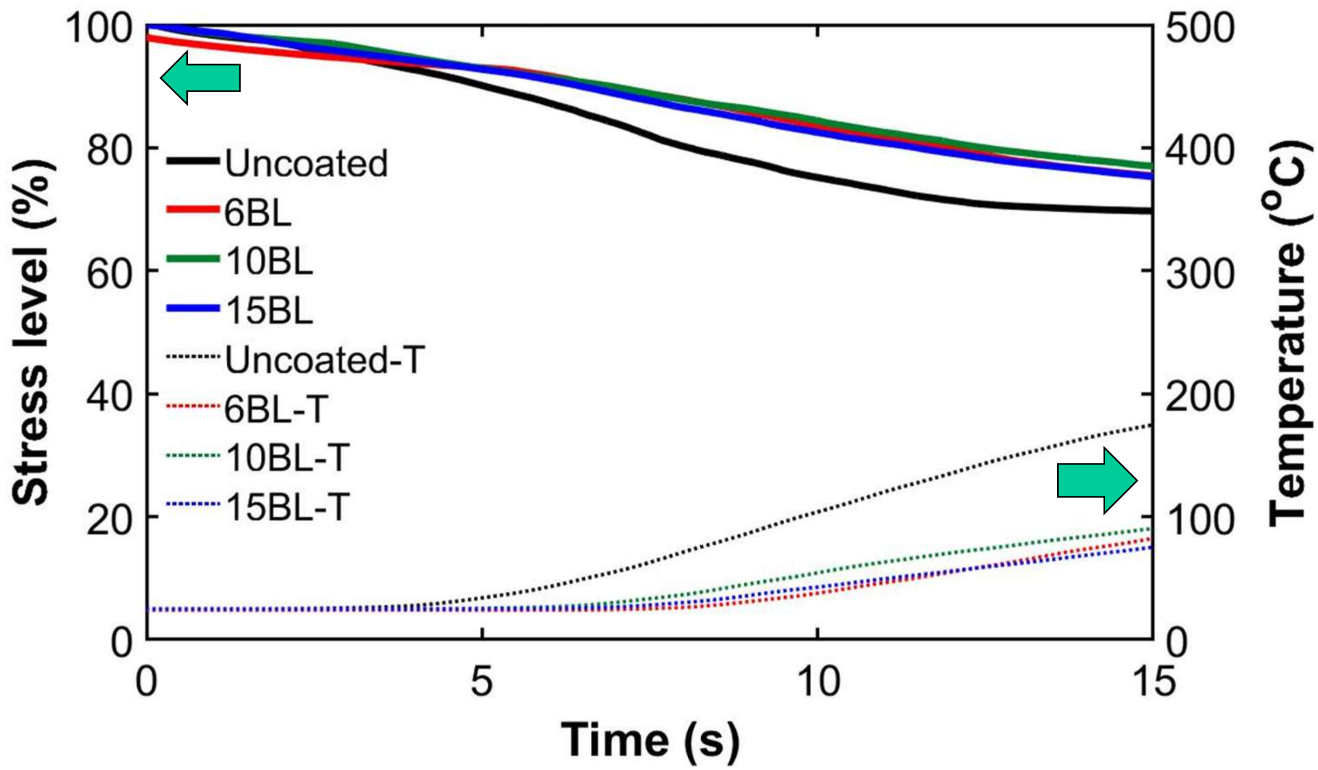


Post-burn CFRP Composites



Epoxy matrix preserved after 1-minute exposure to 1400 ^{o}C flame.

Maintaining Strength at High Temperature



Composite feels lower temperature and maintains strength for longer time upon flame exposure.

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Coated Composites Do Not Oxidize in Flame

Sample	Atomic Ratio (%) C	Atomic Ratio (%) O	O / C ratio (%)
Pre-burn uncoated	89.56	10.55	12
Post-burn uncoated	81.80	11.98	15
Post-burn coated*	89.15	10.27	12

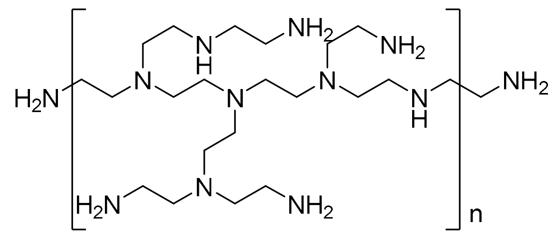
*Coating was removed

Post-flame XPS analysis suggests the coated composites did not oxidize.

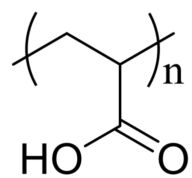
Materials for Halloysite-Based FR Treatment

- Branched Polyethylenimine (BPEI)
  - 0.1 wt% in water
  - Purchased from Sigma Aldrich
- Poly(acrylic acid) (PAA)
  - 0.1 wt% in water
  - Purchased from Sigma Aldrich
- Halloysite (HNT)
  - 0.5% in BPEI and PAA solutions, unaltered pH
  - Ultrasonication to achieve stable suspensions
  - Applied Minerals Inc.

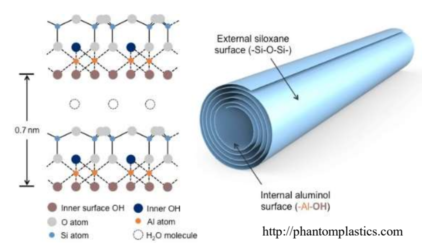
BPEI



PAA



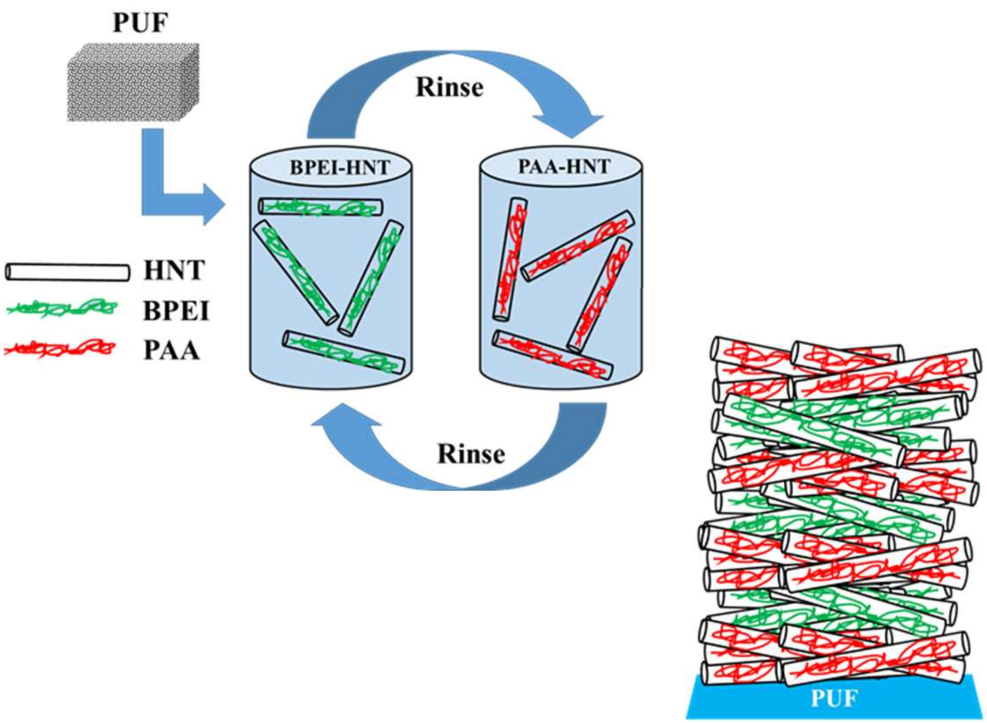
HNT

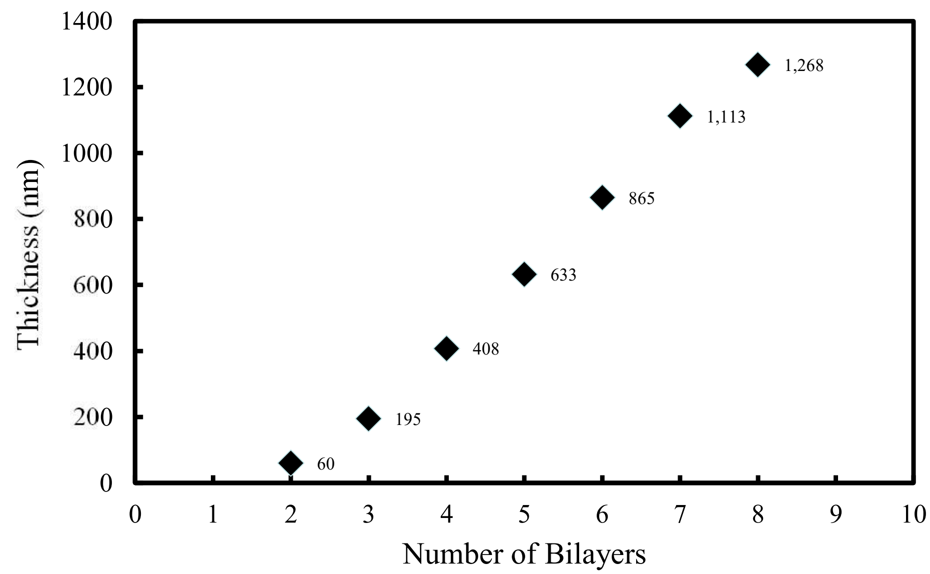


http://phantomplastics.com

Smith, R. J.; Grunlan, J. C.; et al. *Adv. Funct. Mater.* **2018**, *28*, 1703289

Coating Deposition and Growth



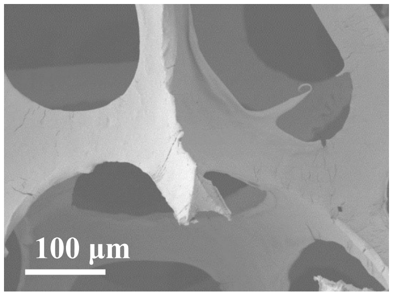


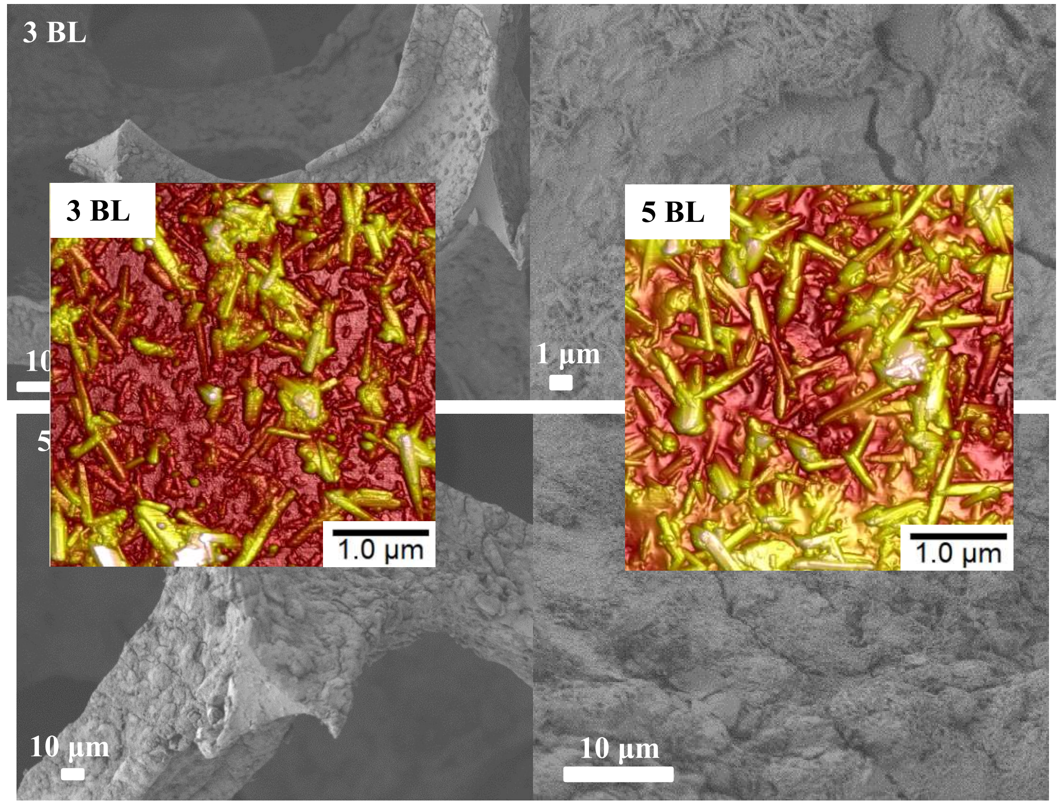
Linear growth observed: 3 BL ~200 nm and 5 BL ~600 nm.

Smith, R. J.; Grunlan, J. C.; et al. *Adv. Funct. Mater.* **2018**, *28*, 1703289

Conformal Coating of Open-Celled Foam

5 BL BPEI/PAA

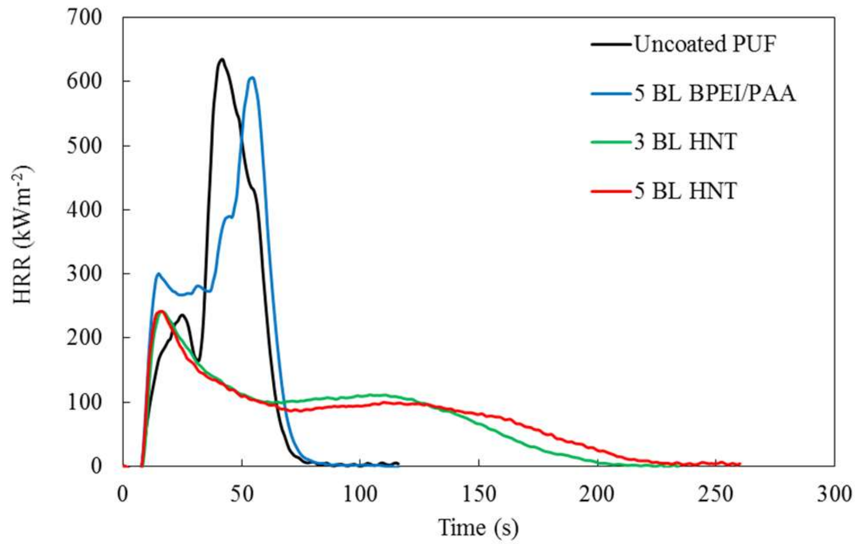




Uniform coating with HNT nanotube bundles observed in SEM and AFM.

Smith, R. J.; Grunlan, J. C.; et al. *Adv. Funct. Mater.* **2018**, *28*, 1703289

Heat and Smoke Release Behavior



Halloysite reduces flammability

- pkHRR 61% reduction
- TSR 60% at 5 bilayers
- Prevents melt pool formation

Coating	Weight Gain [%]	HNT [%]	pkHRR [kWm^{-2}]	THR [MJm^{-2}]	TSR [m^2m^{-2}]
Uncoated	N/A	N/A	634 ± 31	18.4 ± 0.1	178 ± 7
5 BL PEI/PAA	10.6 ± 0.5	N/A	621 ± 11	20.2 ± 0.3	217 ± 4
3 BL HNT	26.2 ± 0.6	91	244 ± 2	18.1 ± 0.2	93 ± 8
5 BL HNT	34.2 ± 0.5	86	243 ± 2	18.8 ± 0.2	71 ± 7

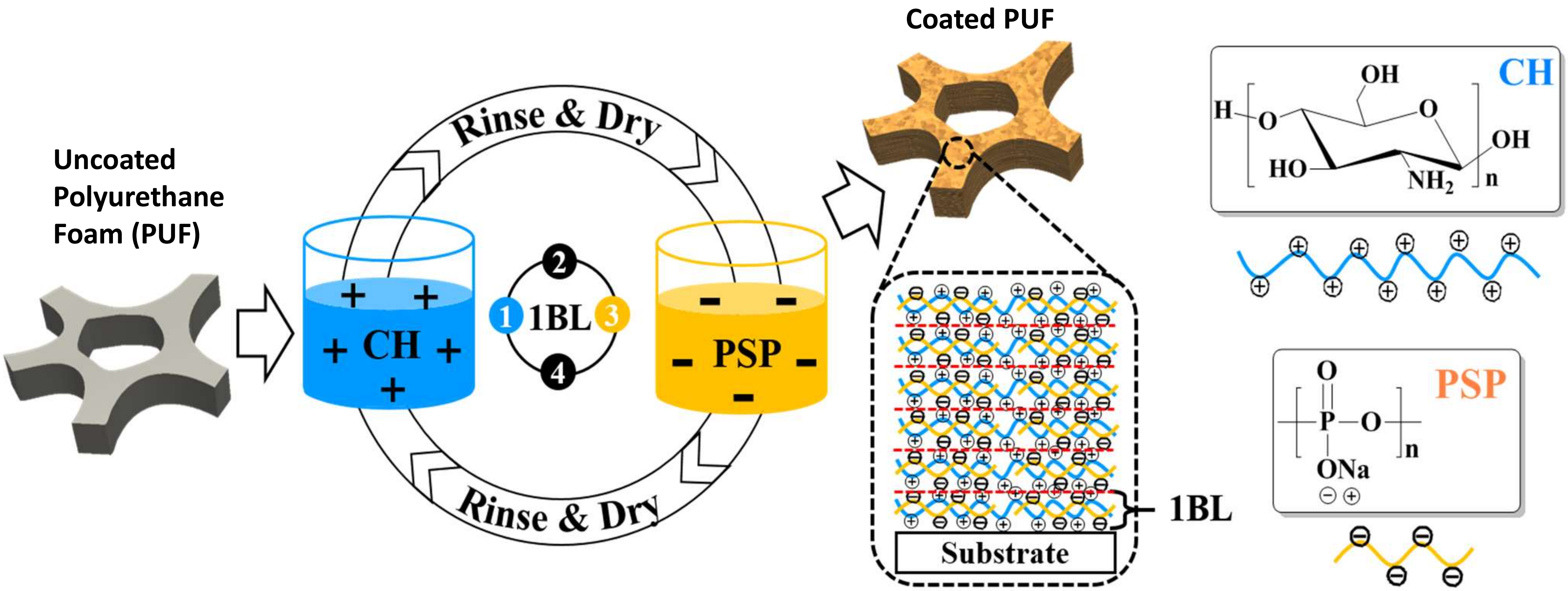
Smith, R. J.; Grunlan, J. C.; et al. *Adv. Funct. Mater.* **2018**, *28*, 1703289

Open Flame Testing of 5 BL Coated Foam

5BL BPEI-HNT/PAA-HNT
5x Speed

Smith, R. J.; Grunlan, J. C.; et al. *Adv. Funct. Mater.* **2018**, *28*, 1703289

Self-Extinguishing Polyurethane Foam



- Completely polymeric intumescent nanocoating
- CH and PSP both at pH 6
- PSP promotes dehydration of CH to form protective char layer

M.-J. Chen, S. Lazar, T. J. Kolibaba, R. Shen, Y. Quan, Q. Wang, H.-C. Chiang, B. Palen, J. C. Grunlan, *Appl. Mater. Interfaces* **2020**, *12,* 41930.

Direct Torch Flame on Foam

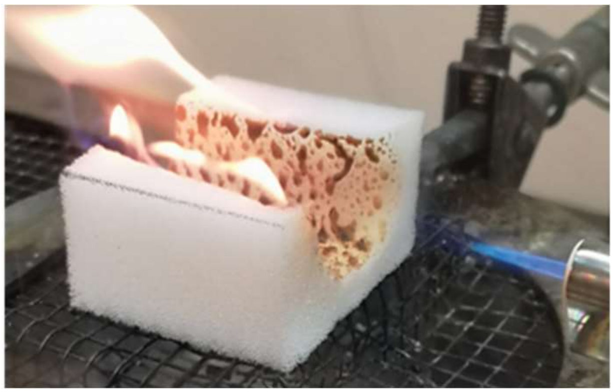
Uncoated Polyurethane Foam

6 BL CH/PSP

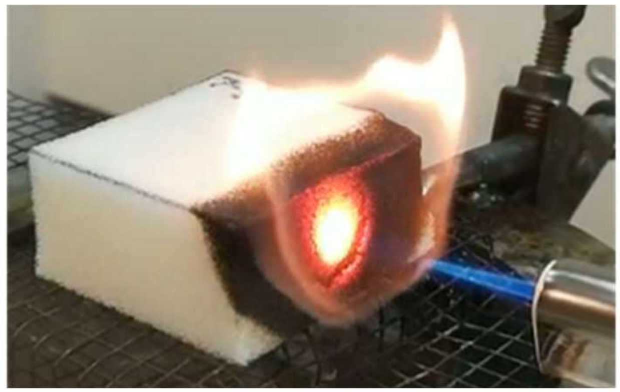
M.-J. Chen, S. Lazar, T. J. Kolibaba, R. Shen, Y. Quan, Q. Wang, H.-C. Chiang, B. Palen, J. C. Grunlan, *Appl. Mater. Interfaces* **2020**, *12,* 41930.

Self-Extinguishes and Maintains Form w/o Clay

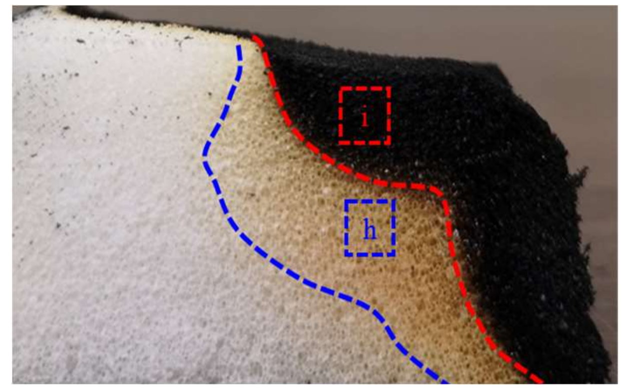
Uncoated



6 BL CH/PSP



Post-burn 6 BL CH/PSP cross-section



This clay-free nanocoating exhibits self extinguishing behavior after being exposed to a 1400^{o}C direct flame for 10 s, while preserving structure of the foam.

M.-J. Chen, S. Lazar, T. J. Kolibaba, R. Shen, Y. Quan, Q. Wang, H.-C. Chiang, B. Palen, J. C. Grunlan, *Appl. Mater. Interfaces* **2020**, *12,* 41930.

Conclusions

- Polyelectrolyte complexes (PEC) provide an opportunity to quickly deposit "LbL-like" films
- Effective flame-retardant coatings deposited in 1 or 2 steps from water-based solution
- LbL films with few bilayers can yield tremendous properties

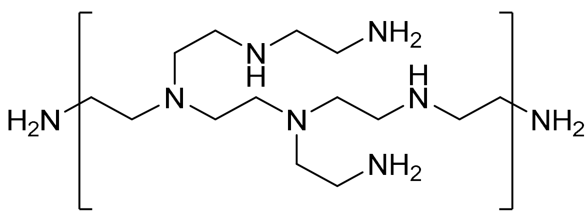
Polymer NanoComposites (PNC) Lab (http://nanocomposites.tamu.edu)

Questions?

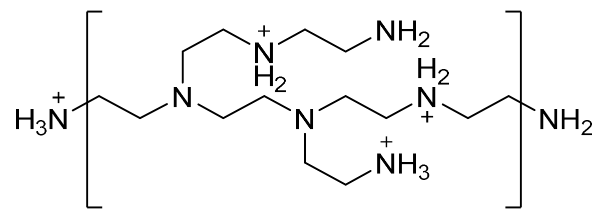
TEXAS A&M UNIVERSITY

Weak Polyelectrolytes

- Polyelectrolyte with pH-dependent charge
  - Example: polyethylenimine



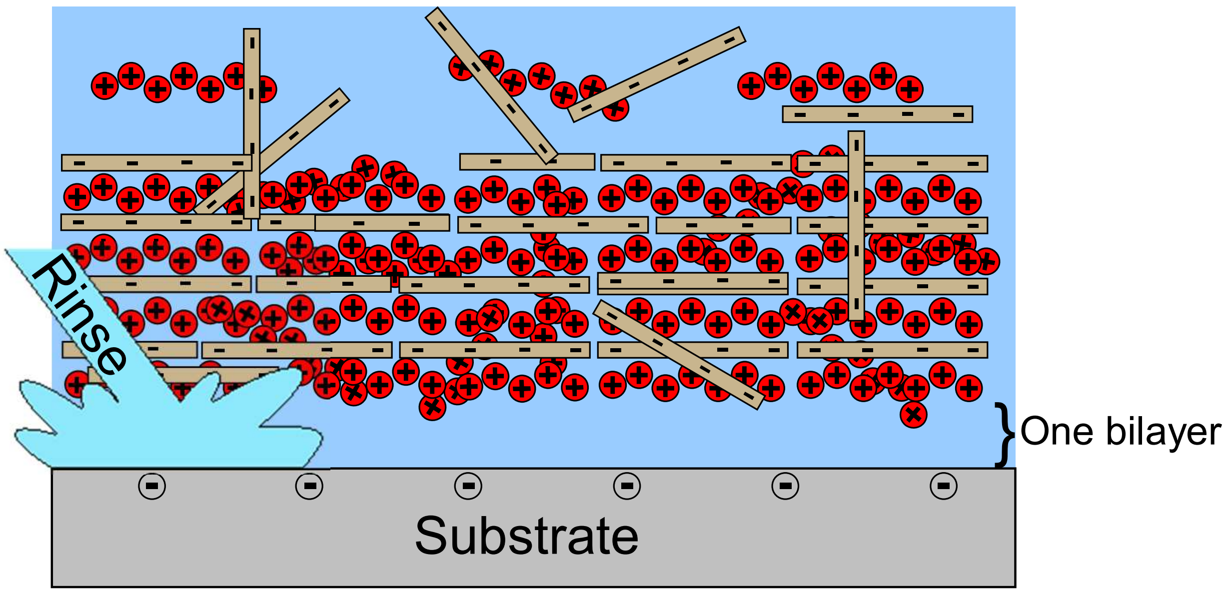
High pK_a
High pH = Low Charge



High pK_a
Low pH = High Charge

- Solution pH can serve as a stimulus to form a PEC on demand

Layer-by-Layer Assembly

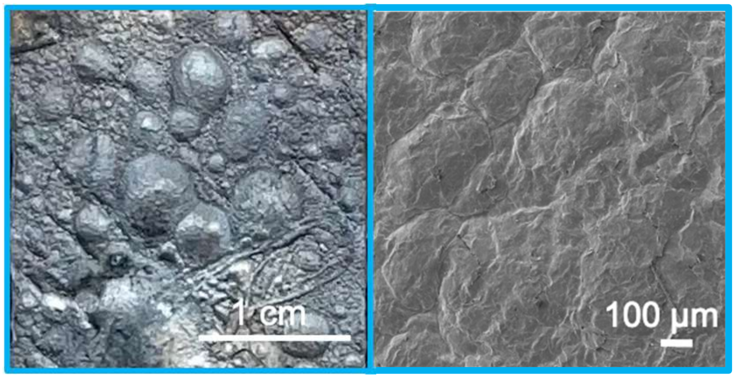


Ambient Processing ✇ **Tunable Properties** ✇ **Nanoscale Control**

Bertrand, P., Jonas, A., Laschewsky, A., Legras. R. *Macromol. Rapid Comm.* **2000**, *21*, 319.
Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials, 2nd Ed., Decher, G., Schlenoff, J. B., Eds., Wiley: New York **2012**.
Ariga, K., Yamauchi, Y., Rydzek, G., Ji, Q. M., Yonamine, Y., Wu, K. C. W. Hill, J. P. *Chemistry Letters* **2014**, *43*, 36.

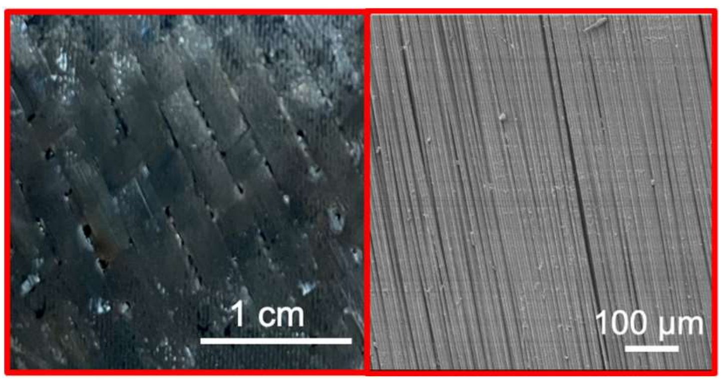
Post-Burn CFRP Composites

Coated



All images are following one minute exposure to butane torch flame.

Uncoated



Coated (coating removed)