# Layer by layer assembly of PET textile fabrics with flame retardant properties

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# Outline

- ***Introduction:***

  ***Layer by layer deposition technique***

- ***Materials and methods:***

  ***Sample preparation***

  ***Vertical flame test***

  ***Cone calorimetry***

- ***Results and discussion:***

  ***Surface morphology***

  ***Flammability***

  ***Combustion behavior***

- ***Conclusions***

# Layer-by-Layer (LbL) Deposition Technique

- The principle was apparently first described by Iler in 1966 [*]
- A practical method for LbL was developed only in the early 1990s by the group of Decher [**]
- Nowadays….

…. It's studied and used
in a wide range of application fields
with a thousands of variations[***]

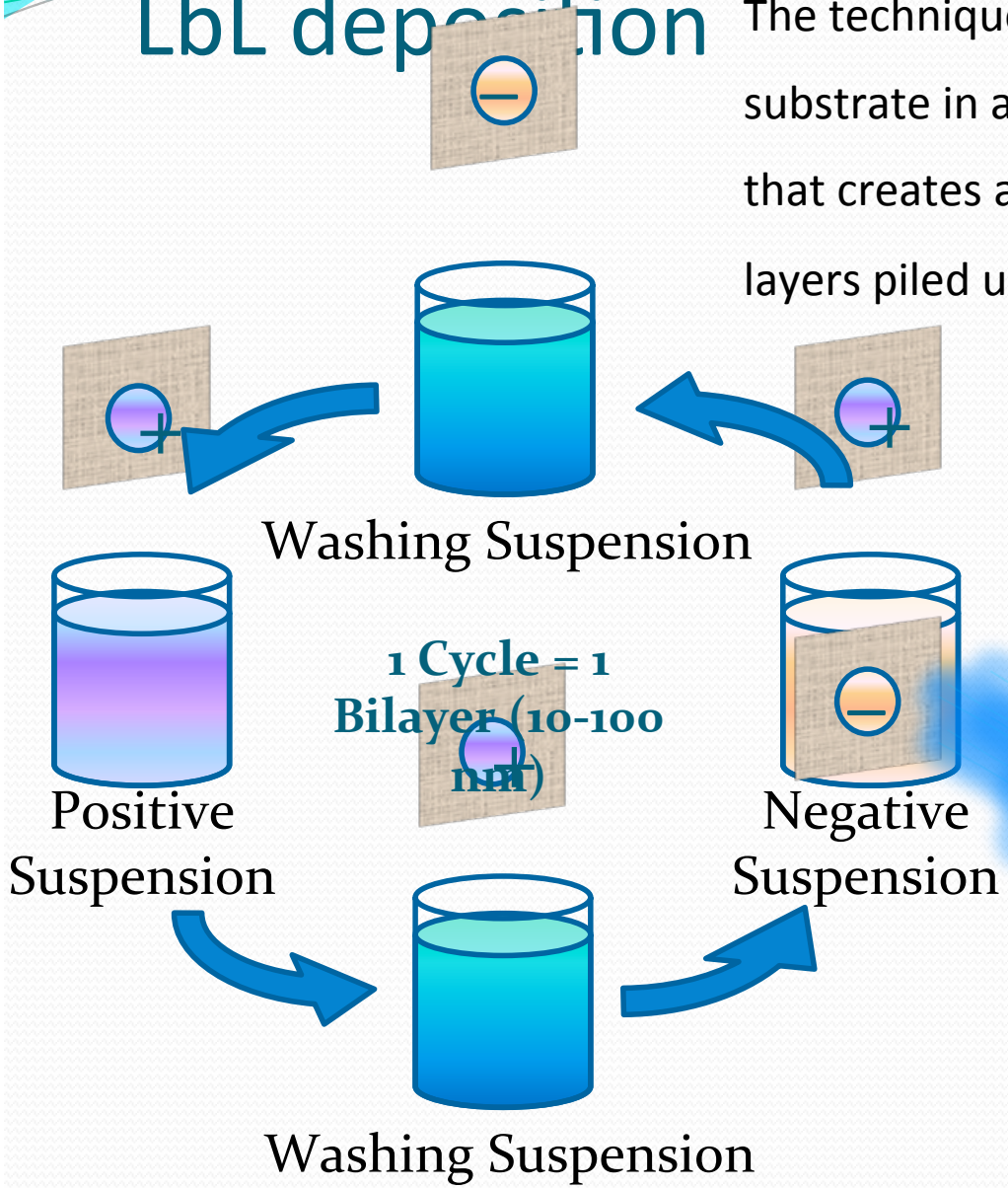
[*] Iler, R. K., *Multilayers of Colloidal Particles*, J. Colloid Interface Sci. 1966, 21, 569.

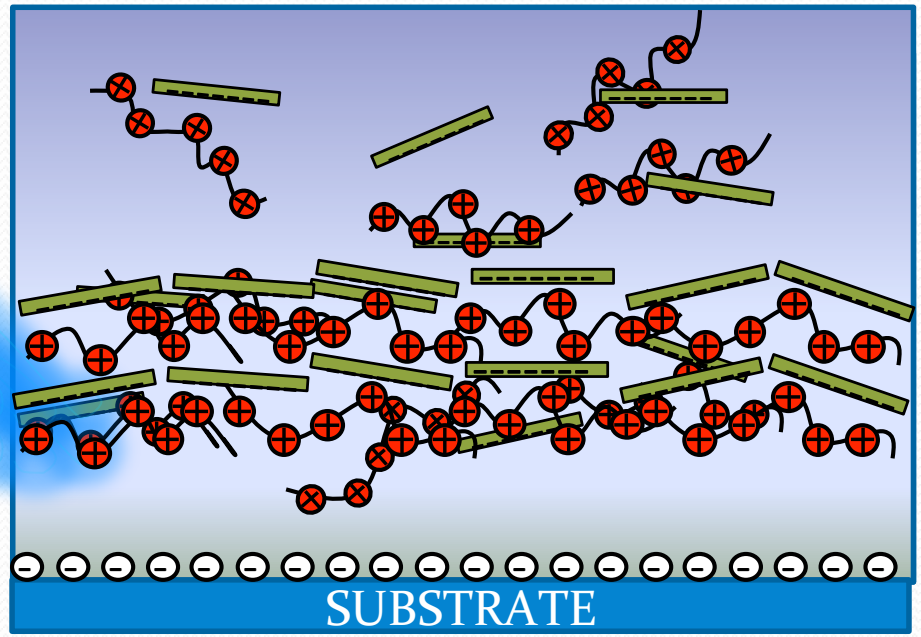
[**] Decher, G., Hong, J.-D., *Buildup of Ultrathin Multilayer Films by a Self-Assembly Process: I. Consecutive Adsorption of Anionic and Cationic Bipolar Amphiphiles*, Makromol. Chem., Macromol. Symp. 1991, 46, 321.

[***] Ariga, K., Hill, P. H., Ji, Q.; *Layer-by-layer assembly as a versatile bottom-up nanofabrication technique for exploratory research and realistic application,* Phys. Chem. Chem. Phys. 2007, 9, 2319.

# LbL deposition

The technique consists in an alternate immersion of the substrate in an oppositely charged polyelectrolyte solutions that creates a coating of positively and negatively charged layers piled up on the substrate surface

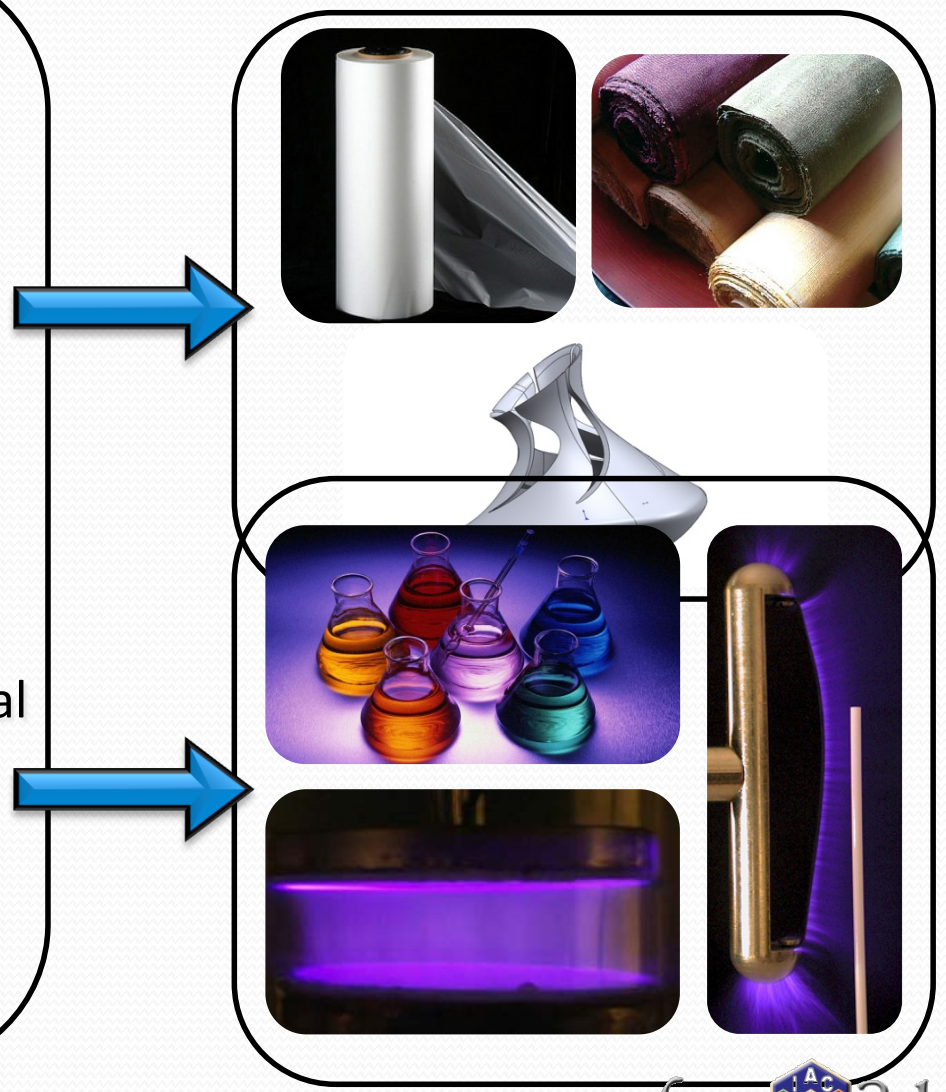


# LbL Deposition: Substrate outlook

**Substrate**:

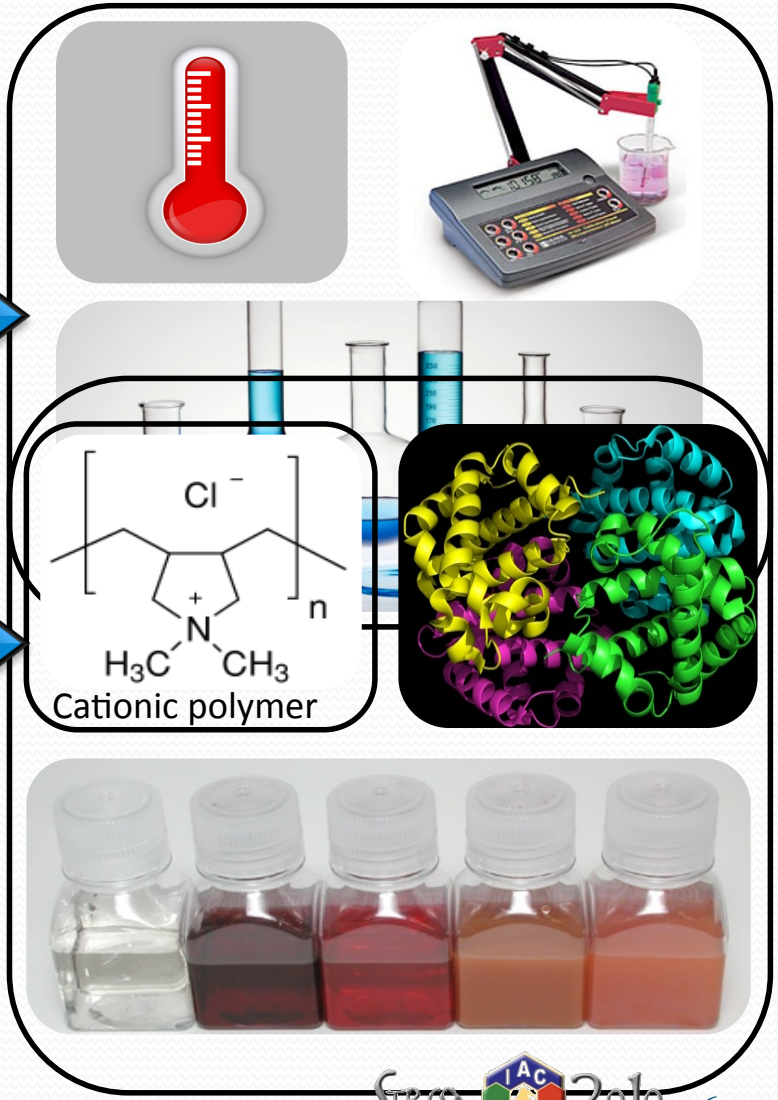
- Wide range of substrates(polymers, metals, textiles…)
- Simple and complex shapes
- Surfaces can be pre-treated using classical process (chemical activation, corona treatment, plasma etching...)



# LbL Deposition: Coating outlook

**Coating**:

- The roughness, thickness and porosity of the film can be controlled adjusting experimental parameters
- Thousand of reagents can be used for layer building



# Coatings and characterization

CL/TM system


**5, 10, 20 Bilayers**

***Negative silica nanoparticles:***

Average size 30 nm

Zeta potential -39.4 mV

***Positive silica (coated with Alumina) nanoparticles:***

Average size 10 nm

Zeta potential 32.2 mV

CL/SM system


**5, 10, 20 Bilayers**

***Negative silica nanoparticles:***

Average size 10 nm

Zeta potential -19.2 mV

***Positive silica (coated with Alumina) nanoparticles:***

Average size 10 nm

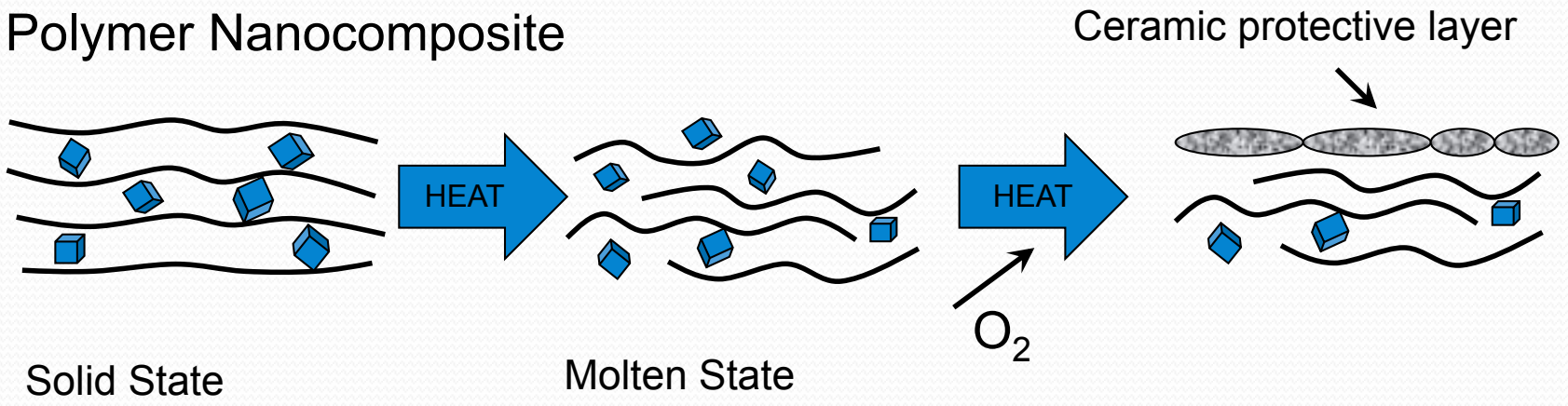
Zeta potential 32.2 mV

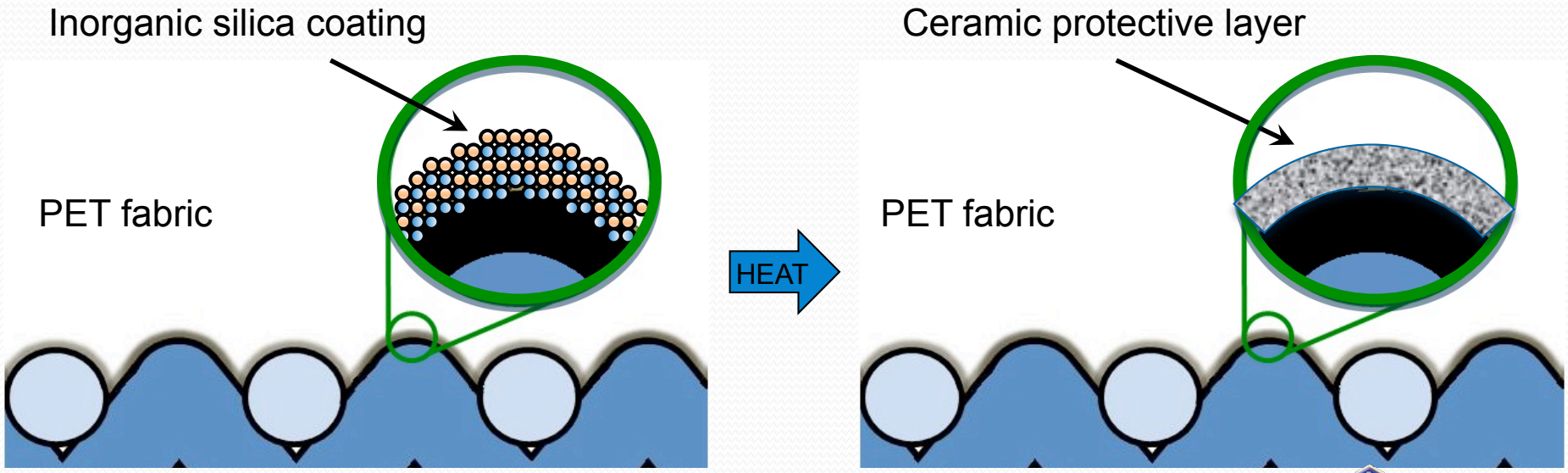
*SEM*

*Vertical Flame test*

*Cone Calorimetry*

# Coating effect



# Vertical Flame Test

ASTM D6413-08

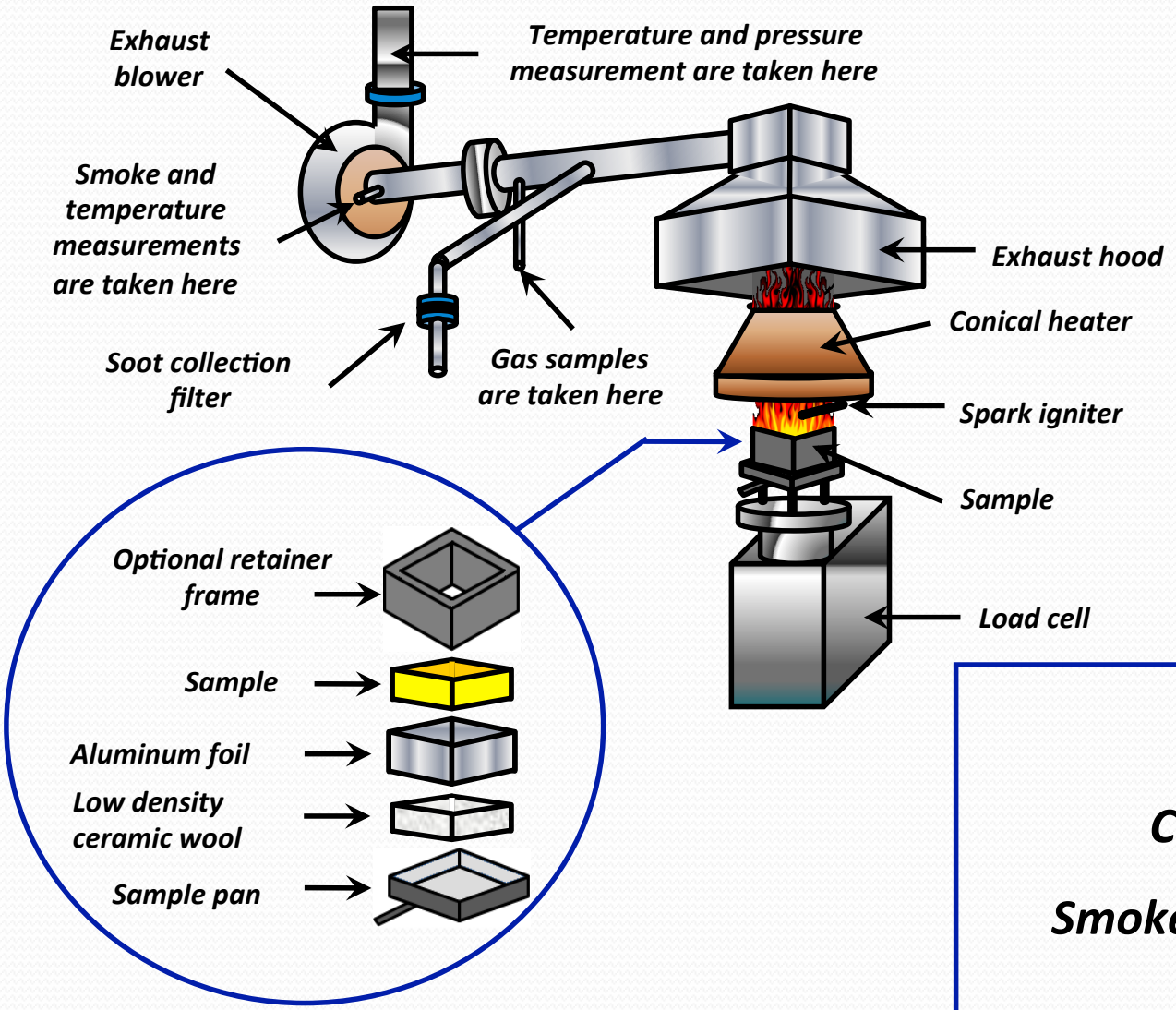
Sample size
30.5 x 7.6 cm

Characteristics observed:

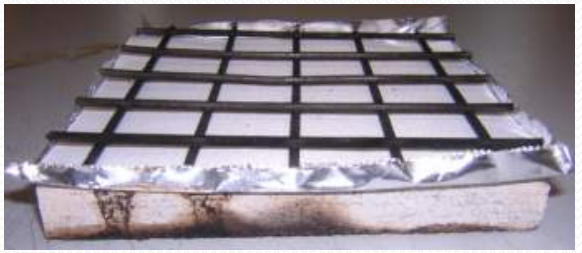
- Afterflame and Afterglow time
- Dripping
- Char formation
- Weight loss

ASTM D 6413 – 08 , *Standard Test Method for Flame Resistance of Textiles (Vertical Test)*

# Cone calorimetry




**Specimen size:**
**100x100x0.5 mm**
**Heat Flux: 35 kW/m²**



***Time to ignition***

***Combustion kinetics***

***Smoke production and optical density***

# Results and discussion

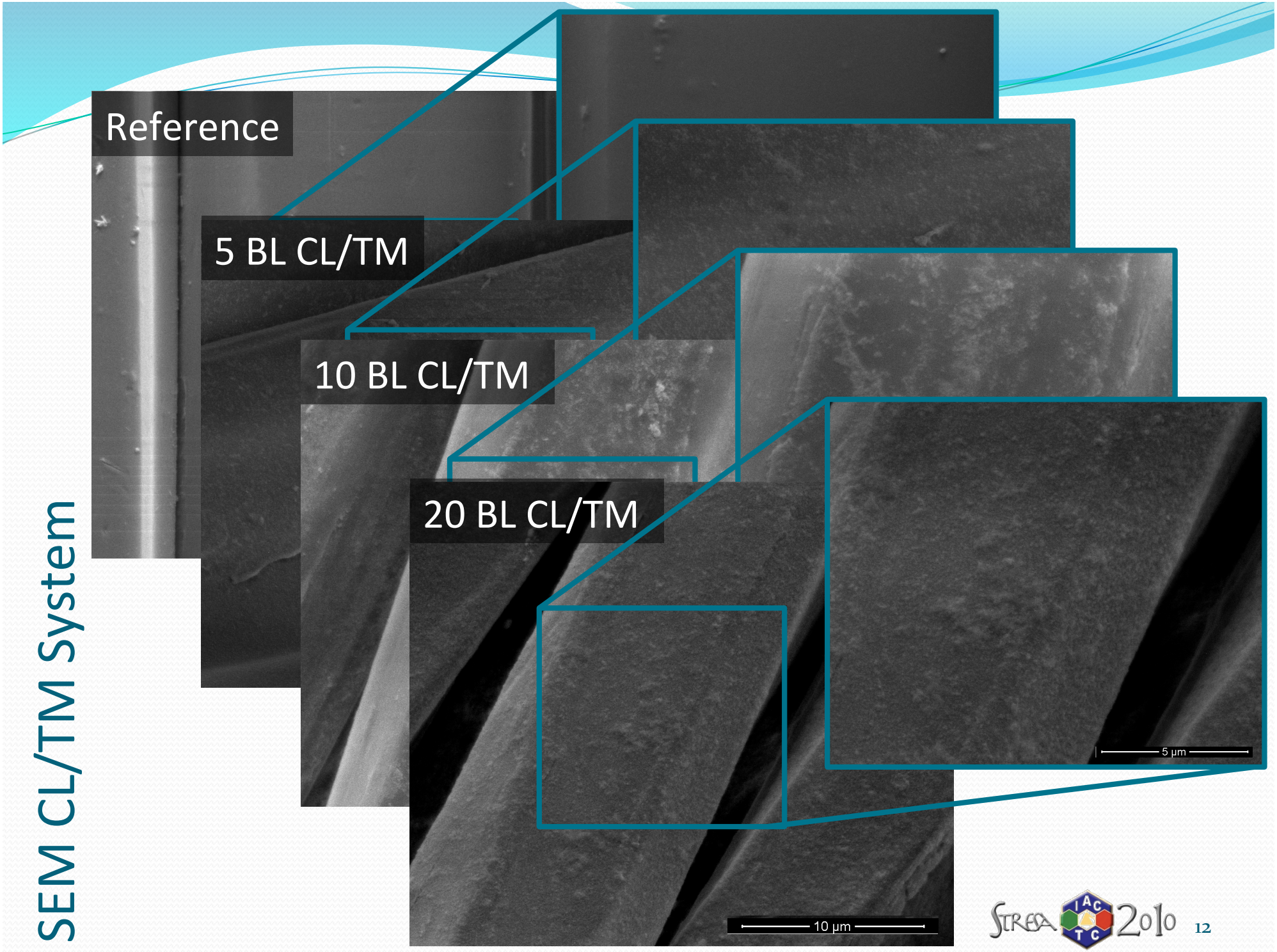
- *PET CL/TM System:*

*Surface morphology*

*Vertical flame test*

*Cone calorimetry*

# SEM CL/TM System



# Vertical Flame Test CL/TM System





| | Reference | 5 BL CL/TM | 10 BL CL/TM | 20 BL CL/TM |
|---|---|---|---|---|
| Burning time [sec] | 32 | 6 | 9 | 22 |
| Δ % | - | -81% | -71% | -29% |
| Δ wt % | -7.6% | -2.4% | -1.2% | -2.7% |
| Dripping | Yes | Yes | Yes | Yes |

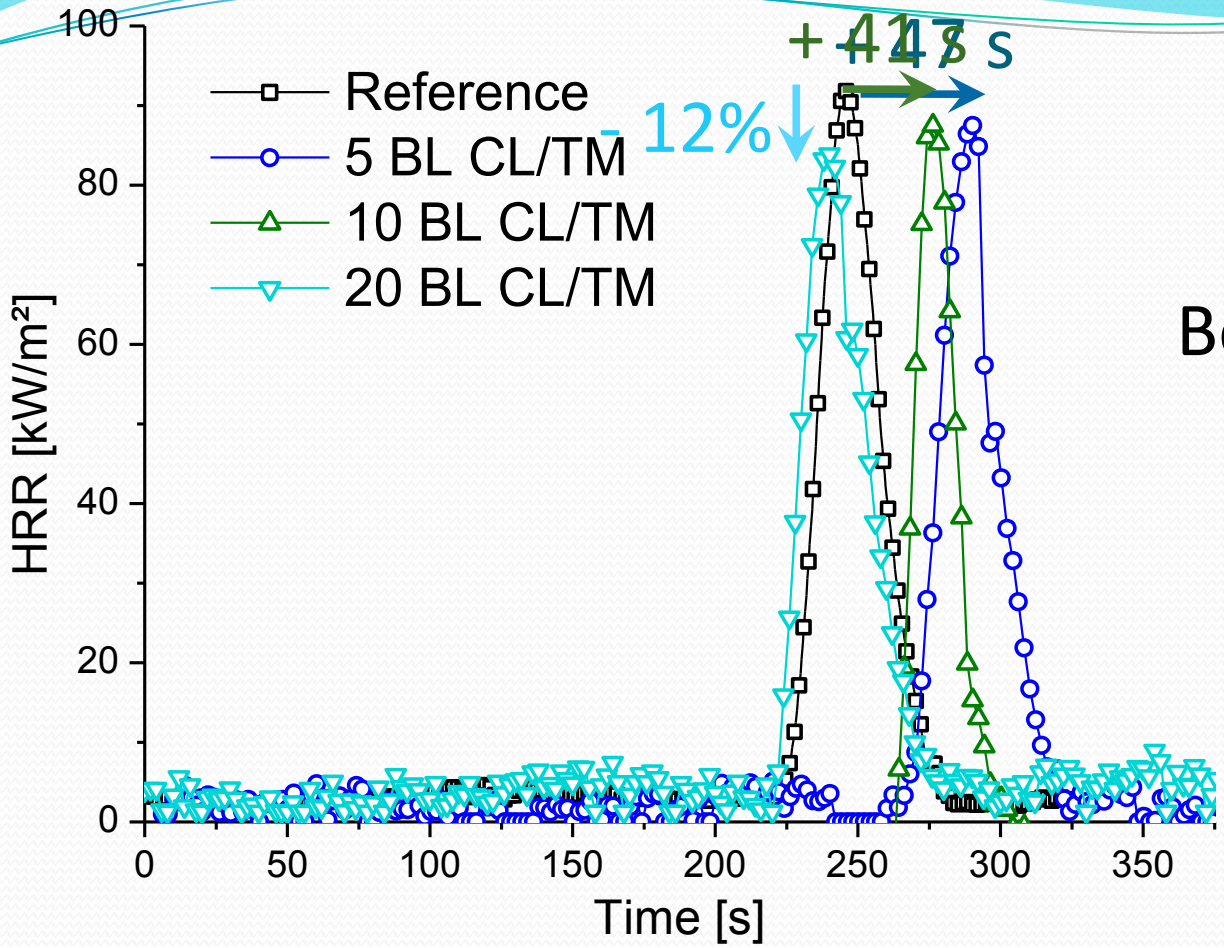
# Vertical Flame Test CL/TM System



| Reference | |
|---|---|
| Burning time [sec] | 32 |
| Δ % | - |
| Δ wt % | -7.6% |
| Dripping | Yes |

| 5 BL CL/TM | |
|---|---|
| Burning time [sec] | 6 |
| Δ % | -81% |
| Δ wt % | -2.4% |
| Dripping | Yes |

# Cone Calorimetry CL/TM System




Best system 10 BL

+ 41 s on TTI

- 6% on HRR

| | *Reference* | *5 BL CL/TM* | *10 BL CL/TM* | *20 BL CL/TM* |
|---|---|---|---|---|
| *TTI±σ [s]* | 222±3 | 269±21 | 263±10 | 218±3 |
| *Δ [s]* | - | +47 | +41 | -4 |
| *Peak HRR±σ [kW/m²]* | 93±7 | 88±2 | 86±9 | 82±5 |
| *Δ[%]* | - | -5% | -6% | -12% |

# Results and discussion

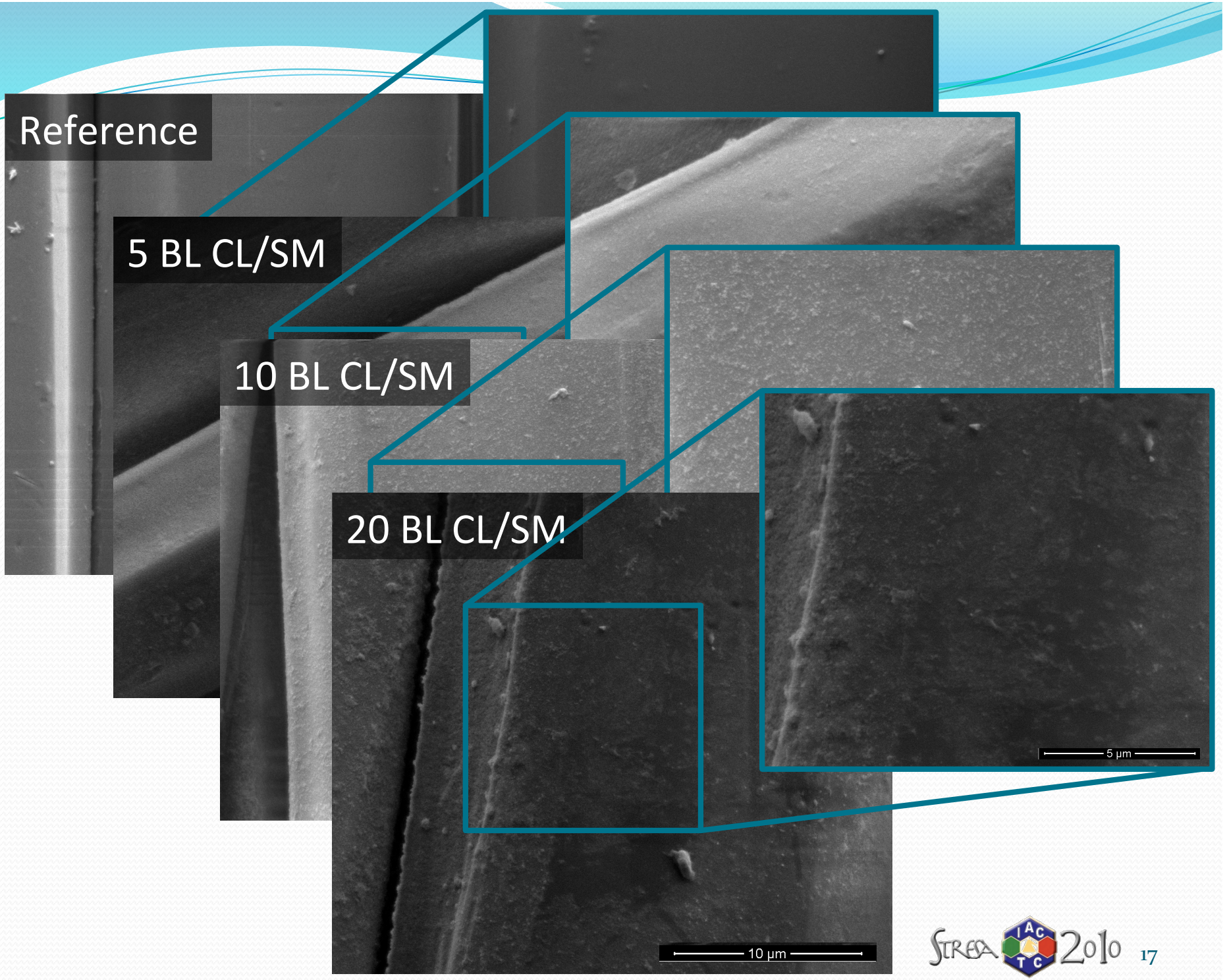
- *PET CL/SM System:*

*Surface morphology*

*Vertical flame test*

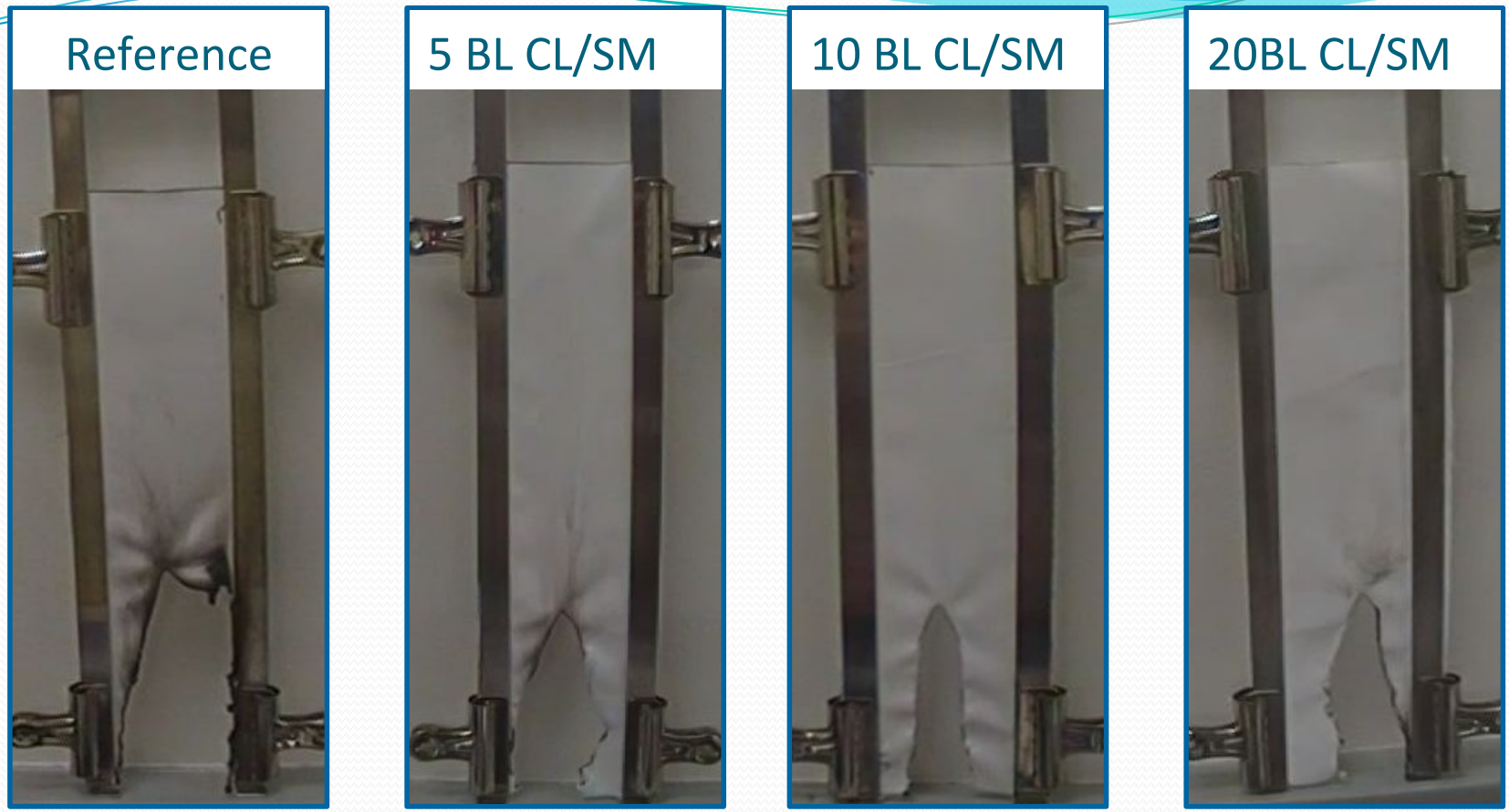
*Cone calorimetry*

# SEM CL/SM System



# Vertical Flame Test

CL/SM System



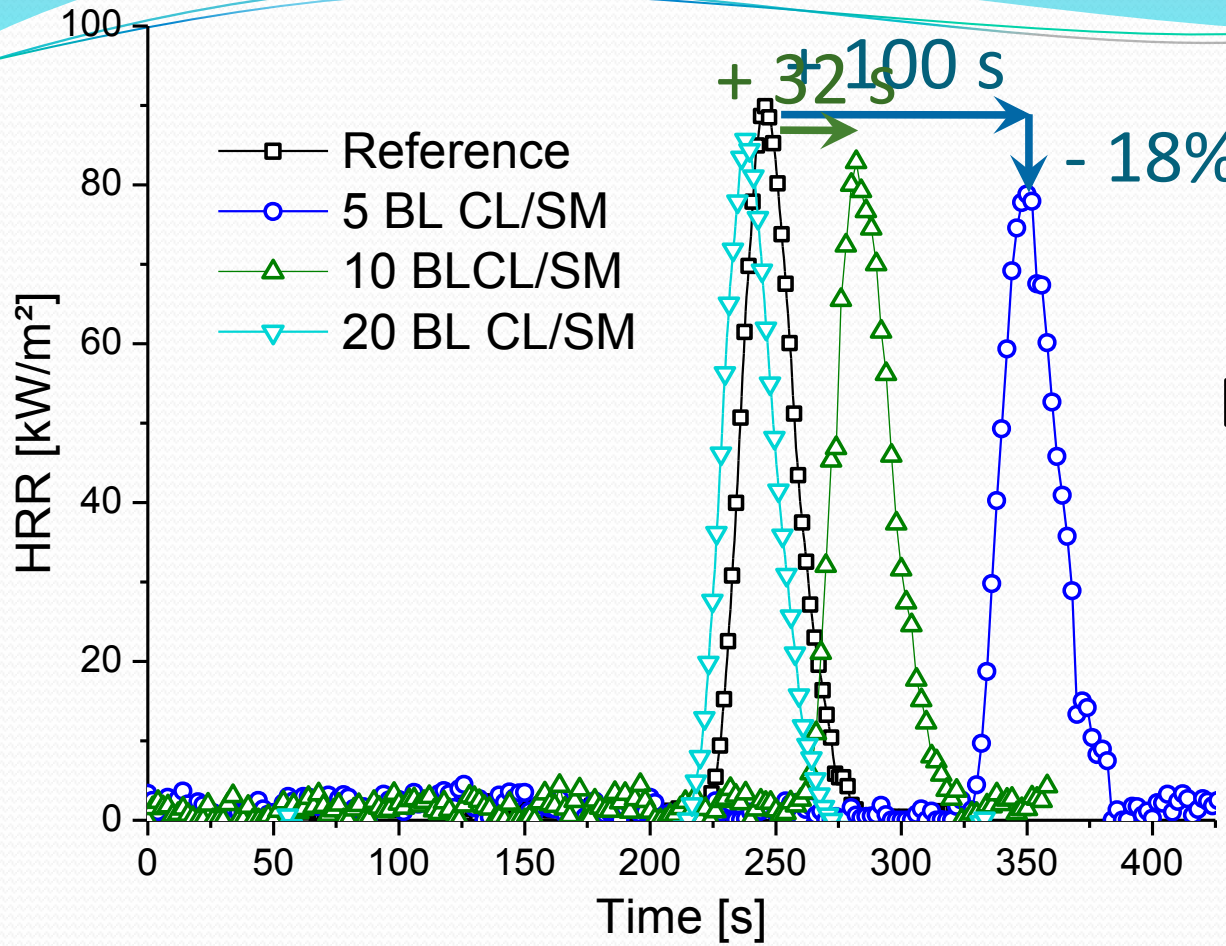

| | Reference | 5 BL CL/SM | 10 BL CL/SM | 20 BL CL/SM |
|---|---|---|---|---|
| Burning time [sec] | 32 | 10 | 2 | 10 |
| Δ % | - | -69% | -94% | -69% |
| Δ wt % | -7.6% | -0.8% | -0.2% | -1.9% |
| Dripping | Yes | No | No | Yes |

# Vertical Flame Test CL/SM System


| Reference | |
|---|---|
| Burning time [sec] | 32 |
| Δ % | - |
| Δ wt % | -7.6% |
| Dripping | Yes |

| 10 BL CL/SM | |
|---|---|
| Burning time [sec] | 2 |
| Δ % | -94% |
| Δ wt % | -0.2% |
| Dripping | No |

# Cone Calorimetry CL/SM System




Best system 5 BL

+ 100 s on TTI

- 18% on HRR

| | *Reference* | *5 BL CL/SM* | *10 BL CL/SM* | *20 BL CL/SM* |
|---|---|---|---|---|
| *TTI±σ [s]* | 222±3 | 322±31 | 254±32 | 212±3 |
| *Δ [s]* | - | +100 | +32 | -10 |
| *Peak HRR±σ [kW/m²]* | 93±7 | 76±1 | 89±5 | 90±8 |
| *Δ[%]* | - | -18% | -4% | - |

# Conclusions

- LbL was succesfuly used to make inorganic coatings of different size silica nanoparticles on PET fabrics
- SEM analysis showed a change in surface morphology for treated fabrics with an increased presence of the coating as a function of bilayer number
- Flammability and combustion properties were found to be highly affected by the morphology of the coating and its physical and solid stability during the test
- Best sample on vertical flame test had a combustion of 2 seconds and no dripping of incandescent drops
- Best sample on cone calorimetry had an increase of 100 seconds in TTI and a reduction of 18% in HRR

# Thank you for your attention