Recenti applicazioni delle NANOTECNOLOGIE nel ritardo alla fiamma di fibre e tessuti

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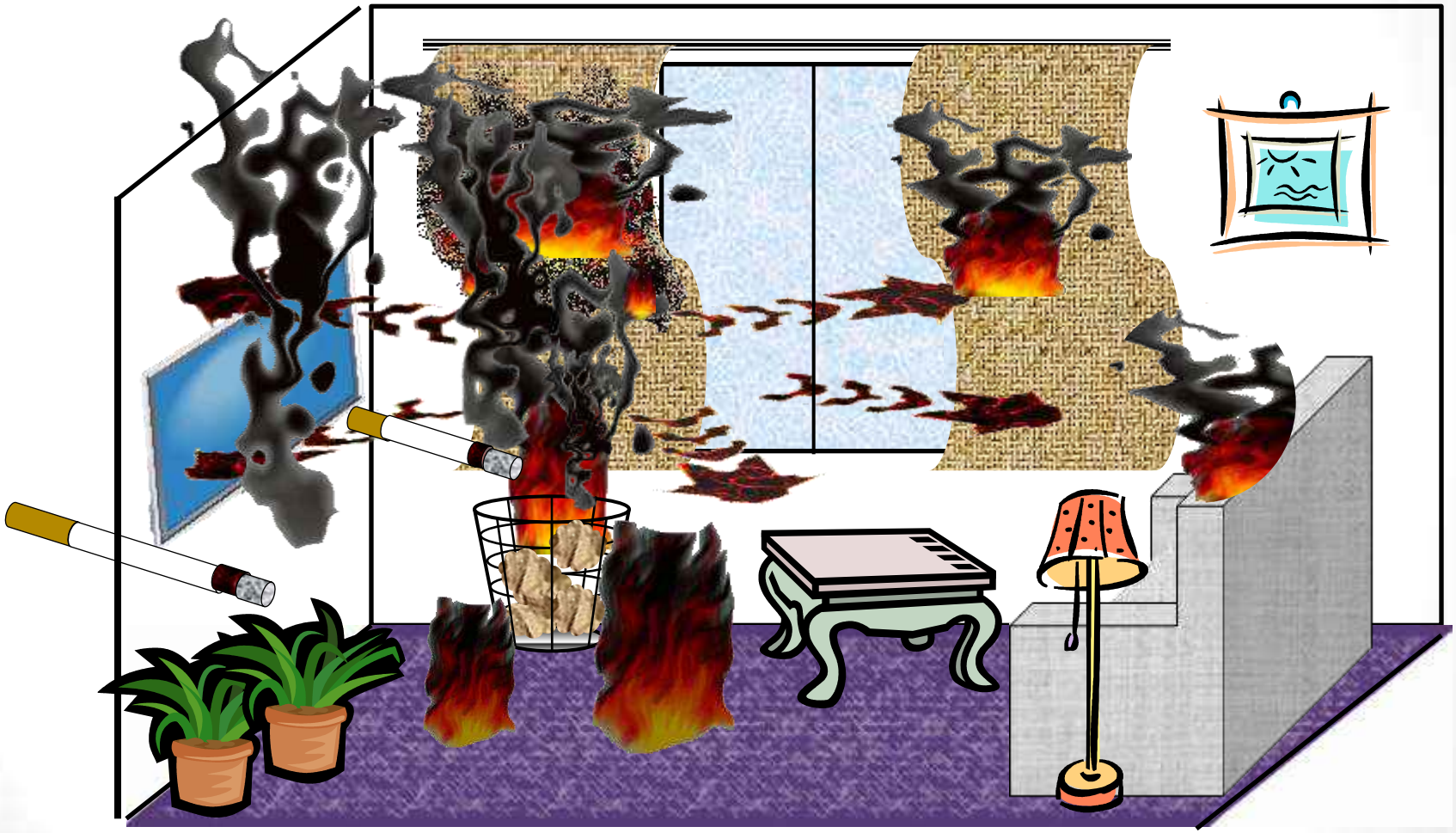
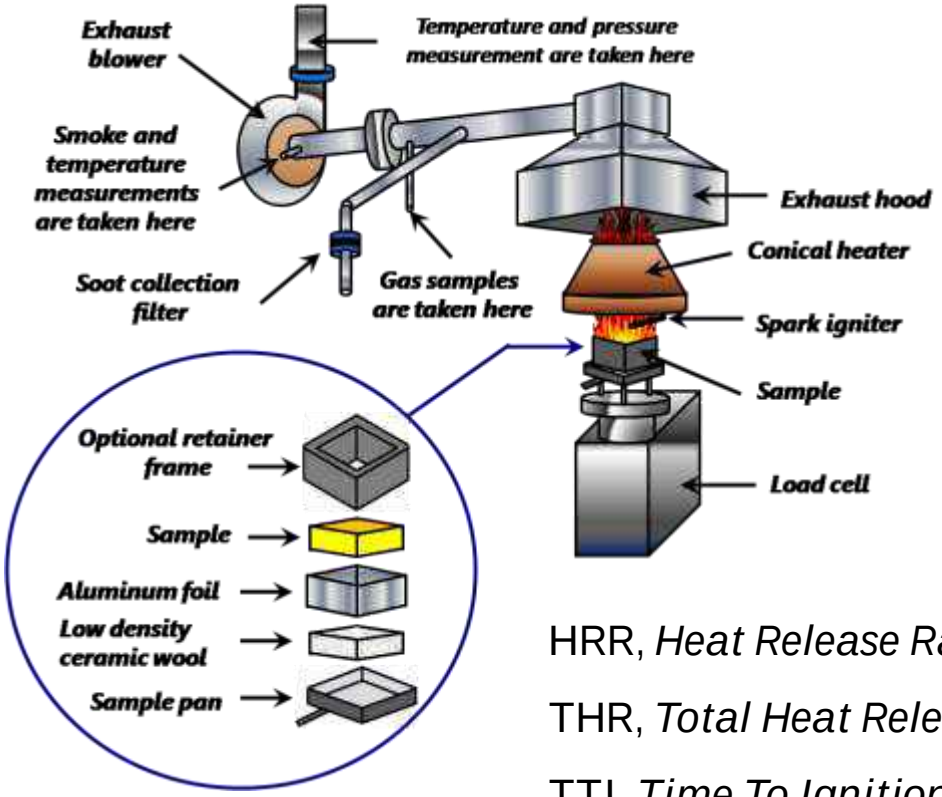


Vertical flame tests

LOI
ISO 4589

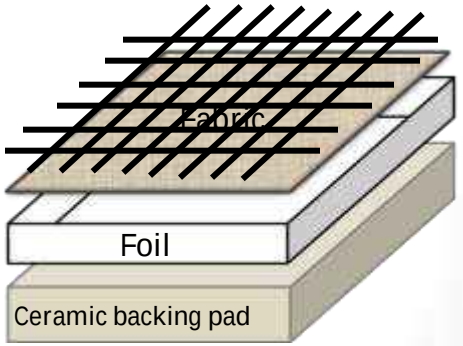
Flammability
ASTM D6413

Cone calorimetry



THE PRINCIPLE OF OXYGEN CONSUMPTION CALORIMETRY

Specimen size: 100 x 100 x 0.5 mm
Heat Flux: 35 kW/m^2



$$FPI = \frac{TTI}{pkHRR}$$

HRR, *Heat Release Rate*

THR, *Total Heat Release*

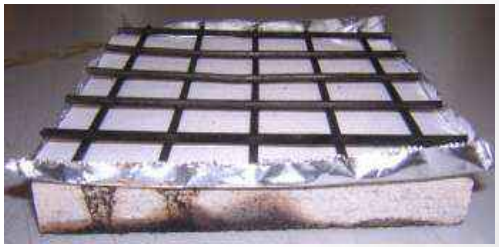
TTI, *Time To Ignition*

TSR, *Total Smoke Release*

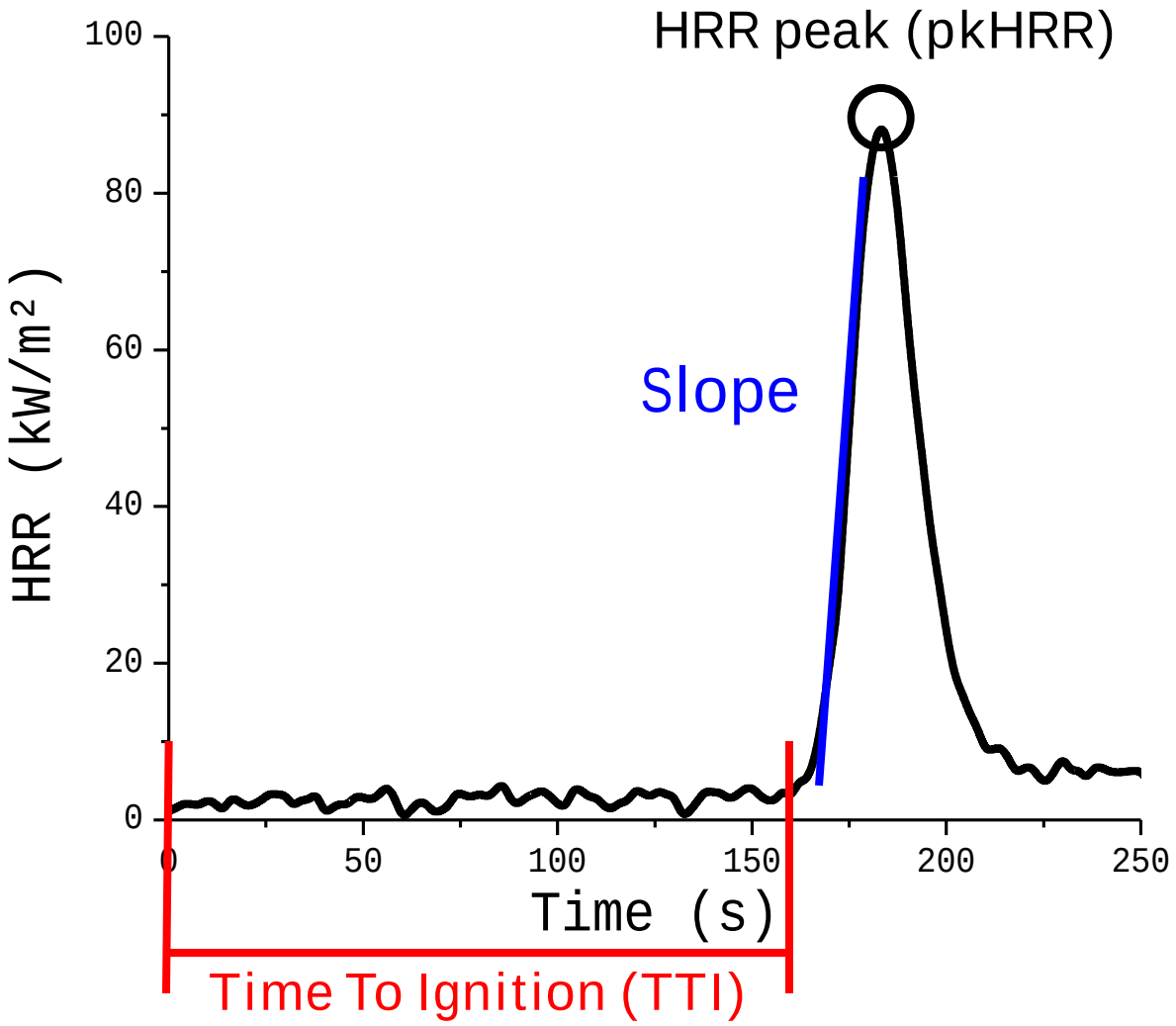
OD, Optical Density

Mass or residue

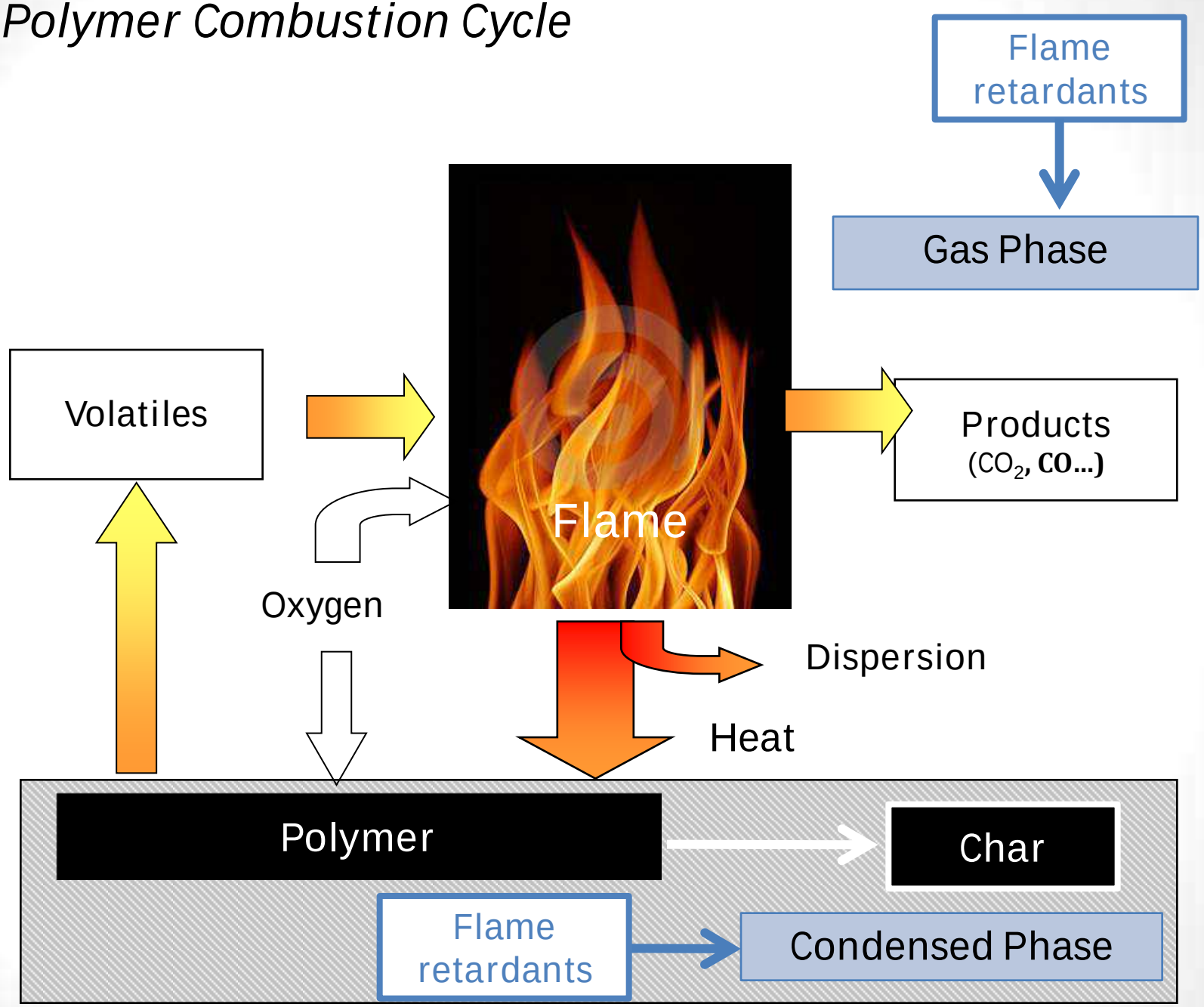
CO_2 and CO amount



Heat Release Rate (HRR) *vs.* time

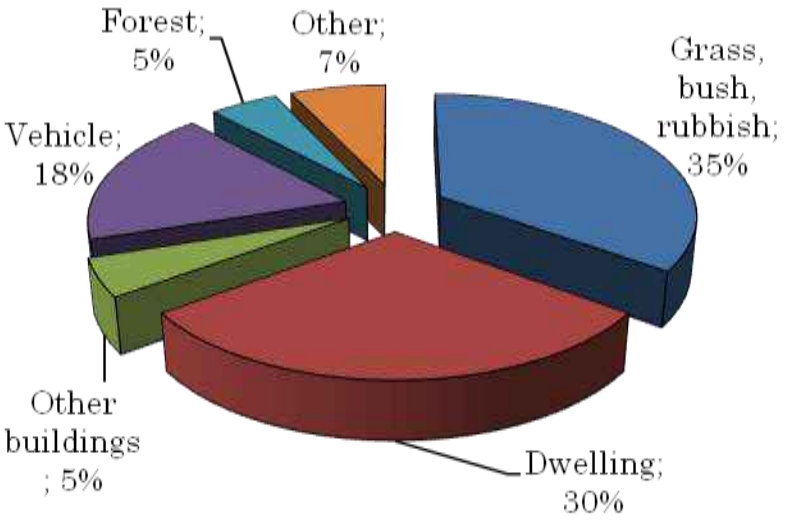


Polymer Combustion Cycle

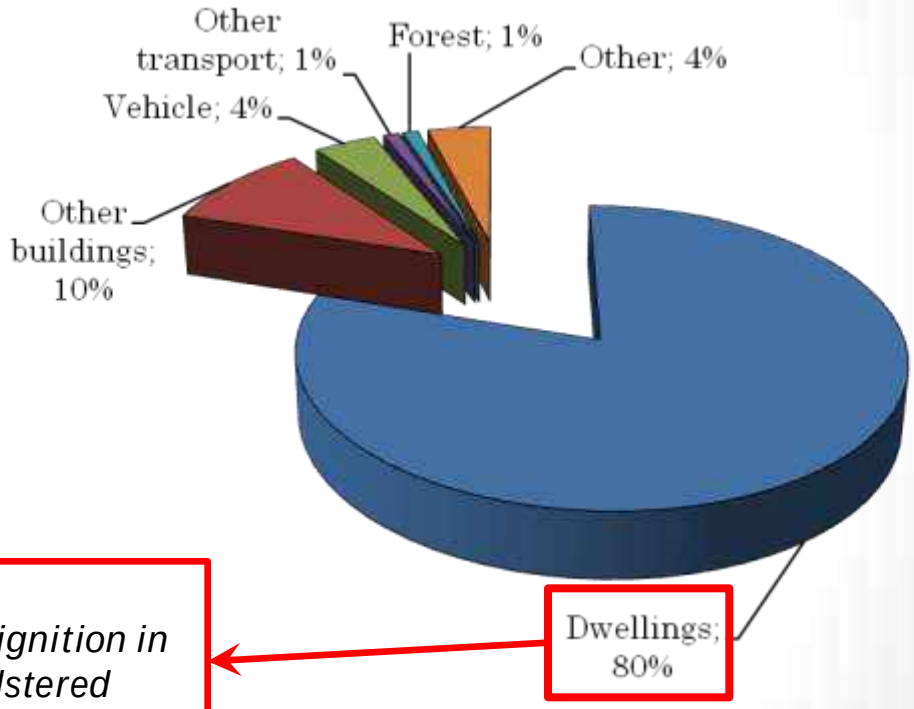


Fire statistics

World annual fires:7 Millions



World annual fire deaths: 75 Thousands



Cigarettes and small flames turn out to be the most common source of ignition in combination with the presence of upholstered furniture and textile

N.N. Brushlinsky, S.V. Sokolov, P. Wagner , J.R. Hall World fire statistics Report № 10 of Centre of Fire Statistics of CTIF

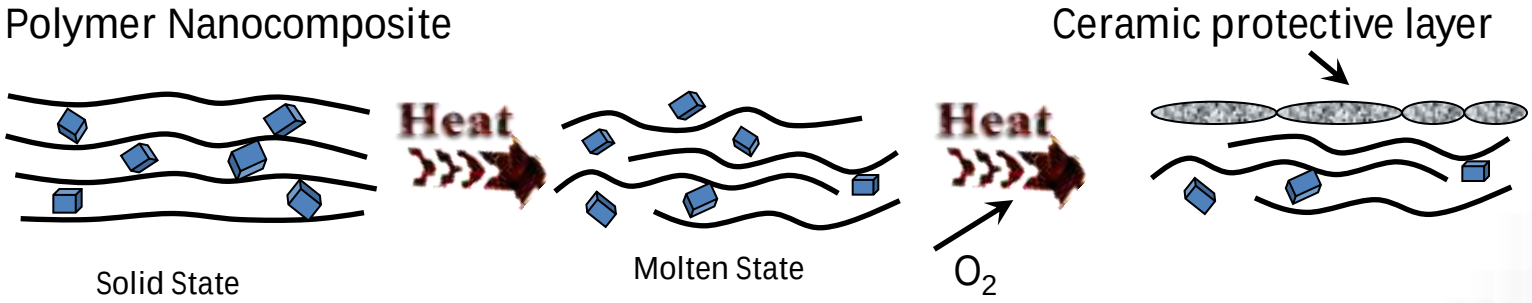
Netherlands Institute for Safety Nibra Consumer fire safety:European statistics and potential fire safety measures Versie: 431N8032/3.0, January 2009

*AIM:

to enhance the flame retardancy of (natural and synthetic) textile fabrics by using nanoparticles

POLYMER NANOCOMPOSITES:

1st STRATEGY



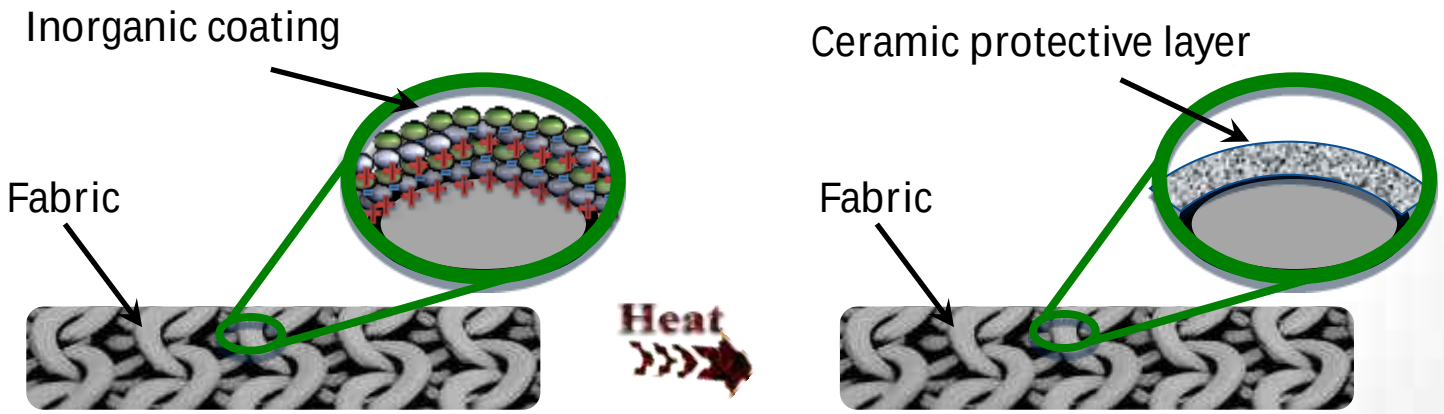
*AIM:

To FORM a COATING on the FABRIC

ABLE TO ACT as PHYSICAL BARRIER to HEAT and OXYGEN TRANSFER

MIMICkING WHAT OCCURS in BULK POLYMER NANOCOMPOSITES:

2nd STRATEGY



OUTLINE:

1. SOL-GEL processes
2. DUAL-CURE processes
3. NANOPARTICLE adsorption
4. LAYER BY LAYER assembly

• SOL-GEL processes

Formation of an oxide network through hydrolysis/condensation reactions of an inorganic precursor.

→ a USEFUL WAY to OBTAIN OXIDIC PHASES (i.e. (NANO)PARTICLES or COATINGS)

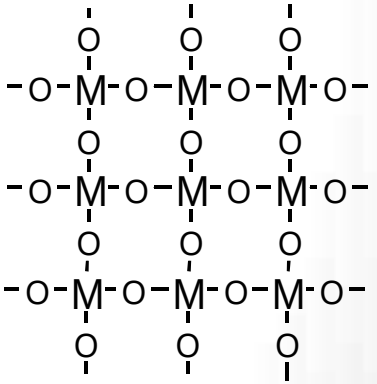
Hydrolysis:

$$M(OR)_4 + 4\,H_2O \rightleftharpoons M(OH)_4 + 4\,ROH \qquad (1)$$

Condensation:

$$\equiv M\text{-}OH + HO\text{-}M\equiv \rightleftharpoons \equiv M\text{-}O\text{-}M\equiv + H_2O \qquad (2a)$$

$$\equiv M\text{-}OH + RO\text{-}M\equiv \rightleftharpoons \equiv M\text{-}O\text{-}M\equiv + ROH \qquad (2b)$$



M = (semi)metal

→ a USEFUL WAY to OBTAIN SILICA (NANO)PARTICLES or COATINGS

Step 1: hydrolysis

Step 2: condensation

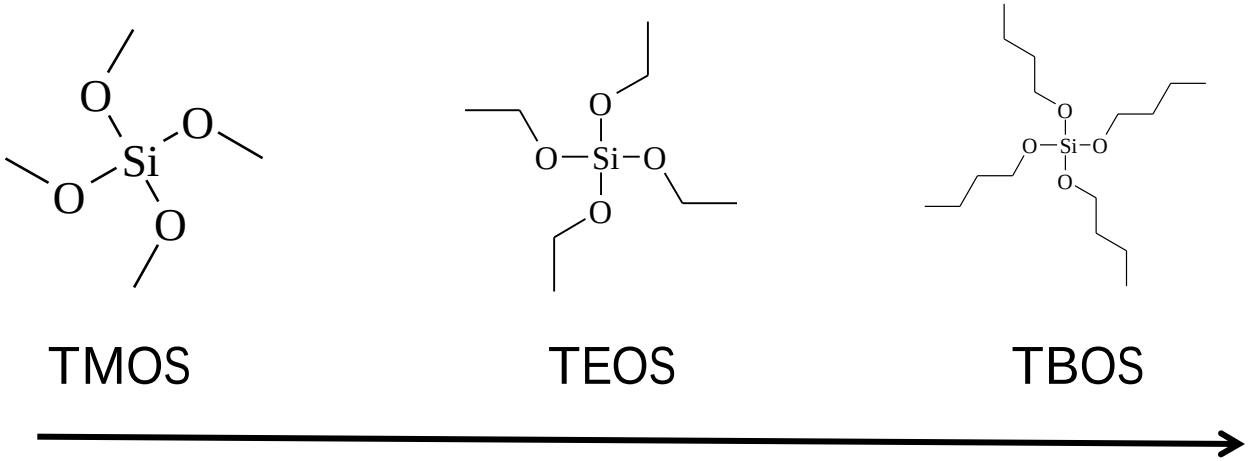
Aqueous condensation

Alcoholic condensation

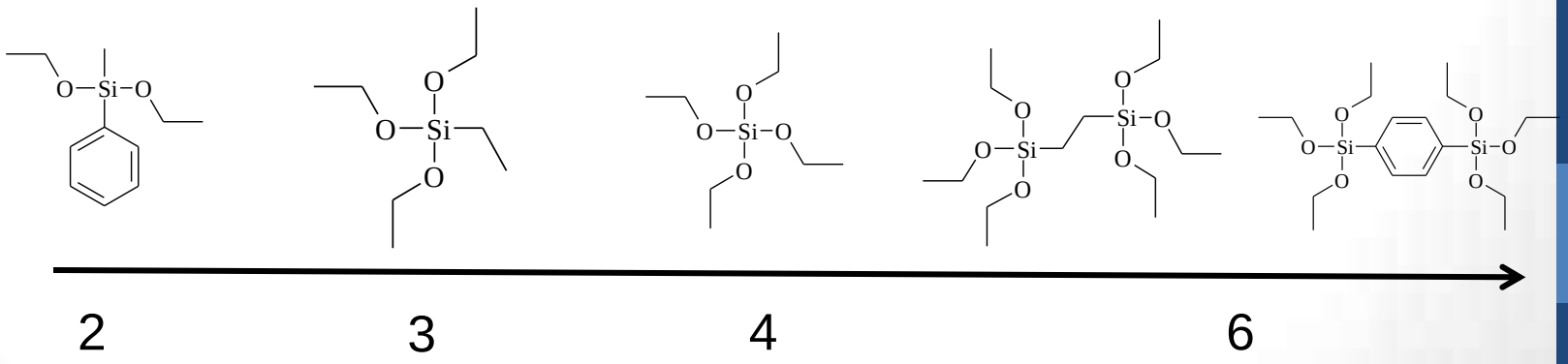
SILICA PRECURSORS

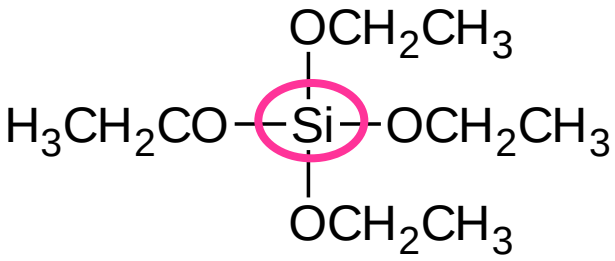
TWO KEY FACTORS:

1. CHAIN LENGTH OF ALKOXY GROUPS

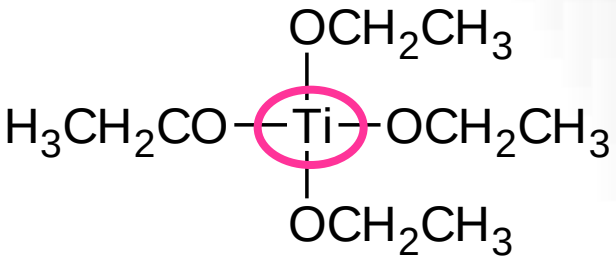


2. NUMBER OF HYDROLYSABLE GROUPS

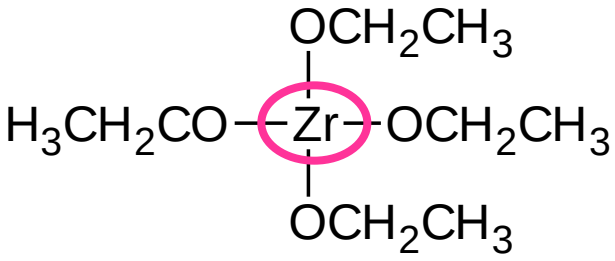




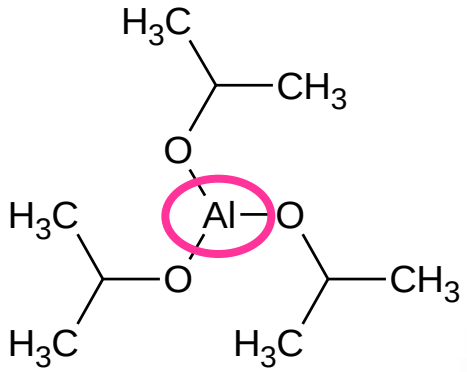
Tetraethylorthosilicate



Tetraethylorthotitanate



Tetraethylorthozirconate



Aluminium isopropylate

STATE OF ART:
application of sol-gel for FABRICS

EFFECTS on HYDROLYSIS RATE:

- ✓ pH effect (*acid or basic conditions*)
- ✓ Precursor type (*substituent effect*)
- ✓ Precursor hydrophobicity
- ✓ Precursor:water molar ratio
- ✓ Sintering mechanism

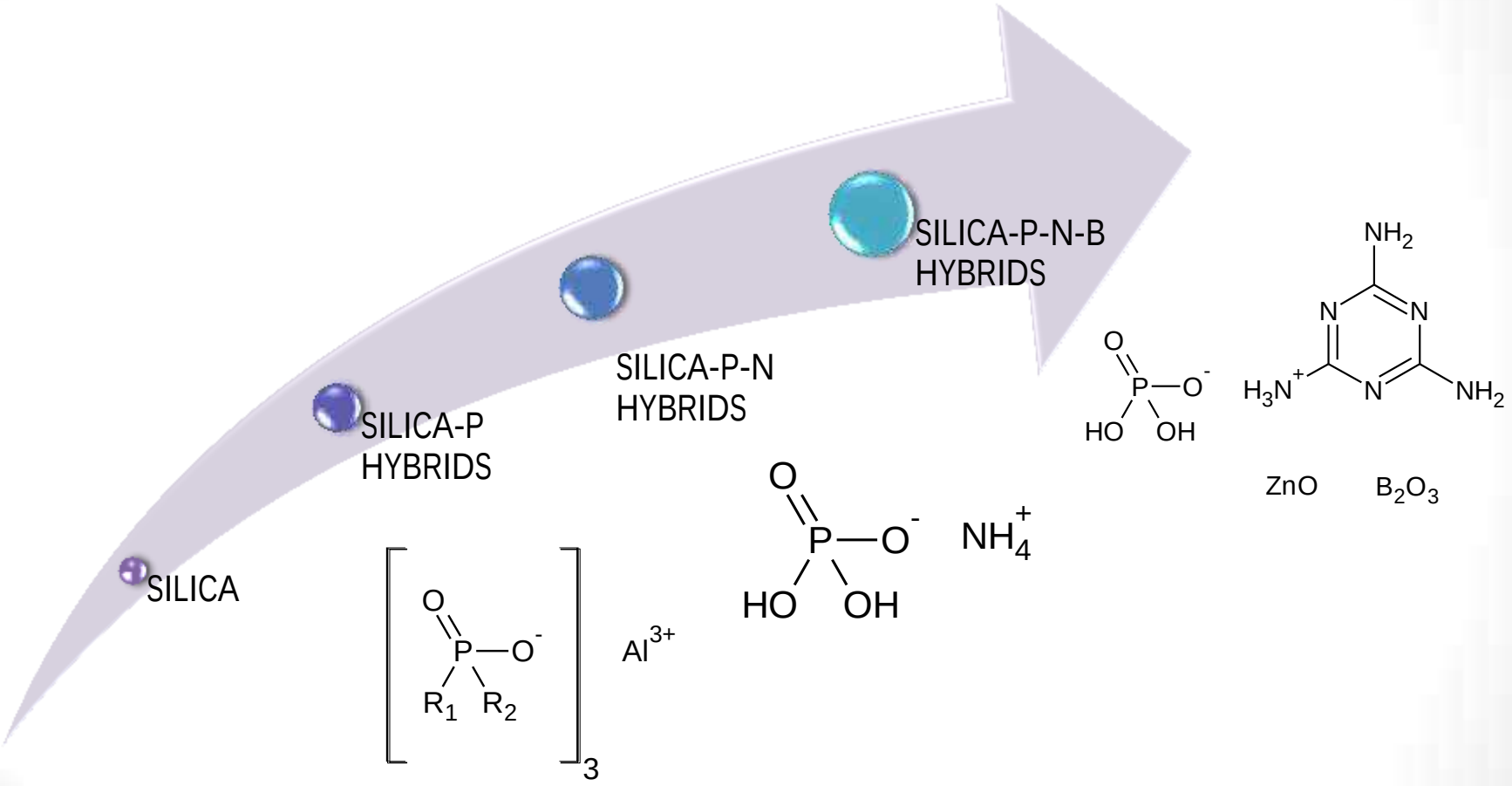
PET and COTTON CAN BE PARTIALLY HYDROLYZED BY ACID or BASIC CONDITIONS: ☹

A PART OF THE USED PRECURSOR IS ABSORBED BY FABRIC TEXTURES: ☹

THE PRESENCE OF FABRIC TEXTURE CAN BLOCK THE OXIDE FORMATION AFFECTING KINETICS: ☹

→ Necessity to study *ab initio*
the sol-gel process for the application in the textile field

SYNERGY

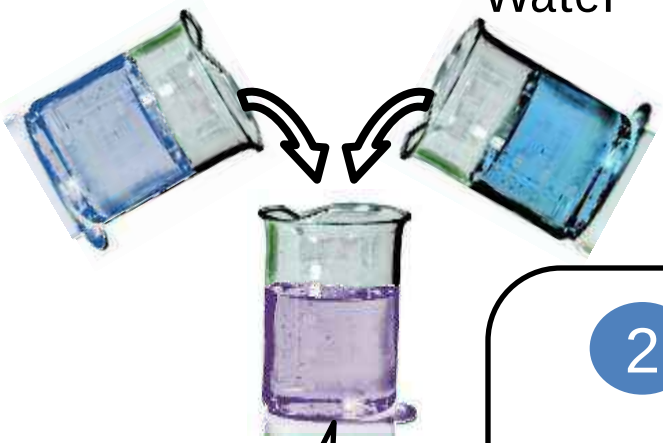

SILICA-P-N-B HYBRIDS
SILICA-P-N HYBRIDS
SILICA-P HYBRIDS
SILICA
ZnO
B_2O_3
Al^{3+}
NH_4^+
3

Method

1 Sol-gel preparation

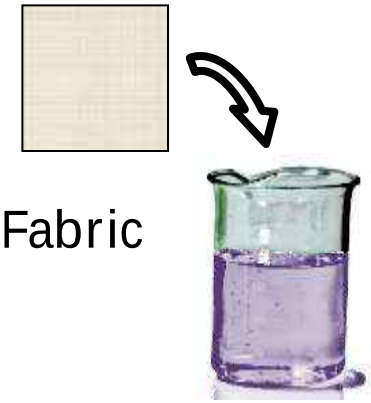
Precursor

Water



Sol

2 Fabric immersion

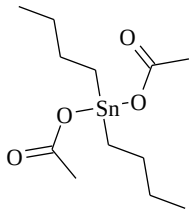


Fabric

Sol

3 Thermal treatment

DBTA



as condensation catalyst
and EtOH

COTTON treated with SILICA (I)

after20s after 35s

COT

Residue= ca.2%

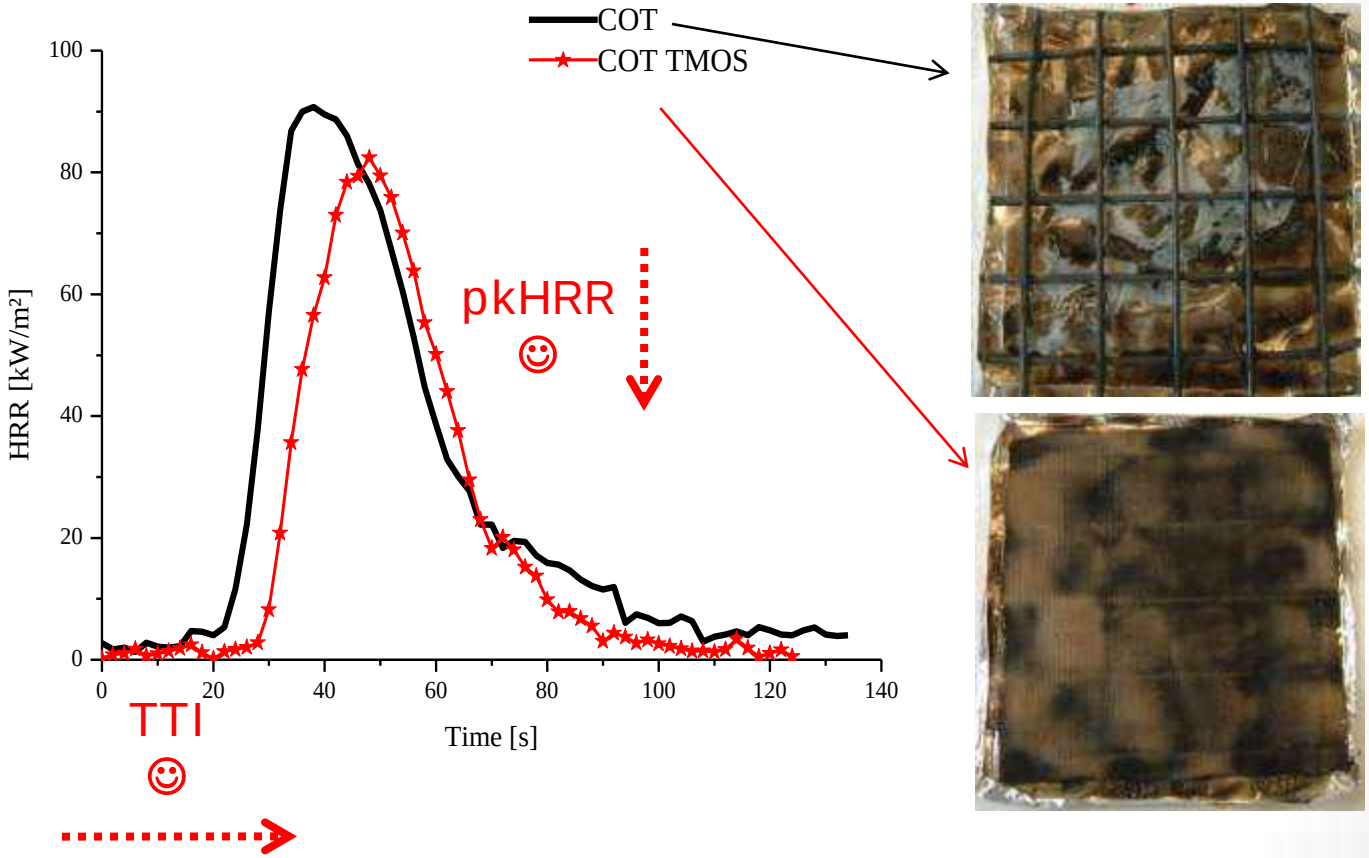
LOI=19%

SOL-GEL TREATED COT

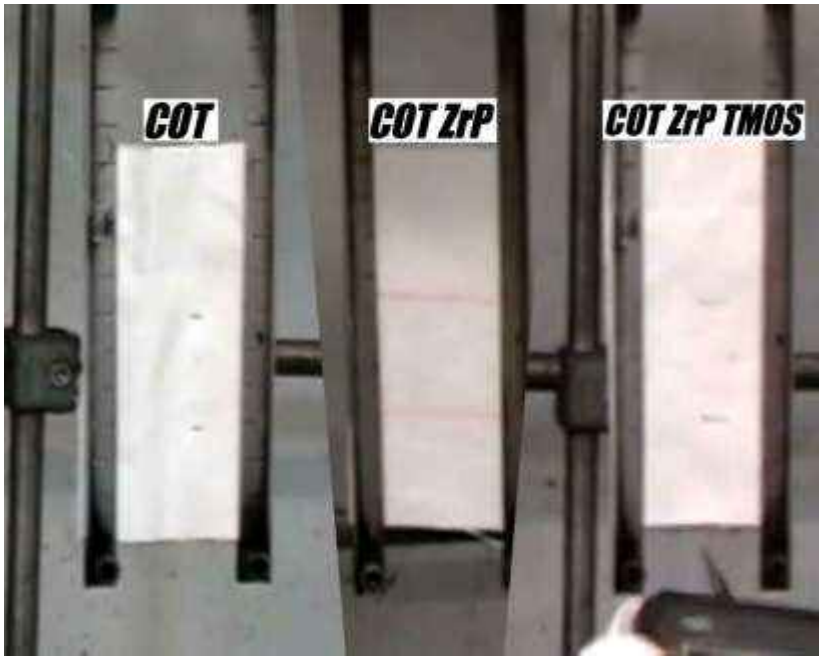
Residue= ca. 40%

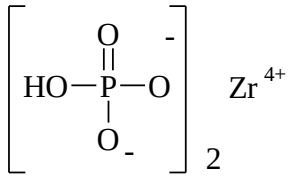
LOI=20%

COTTON treated with SILICA (II)



COTTON treated with SILICA and P-based DERIVATIVE (I)



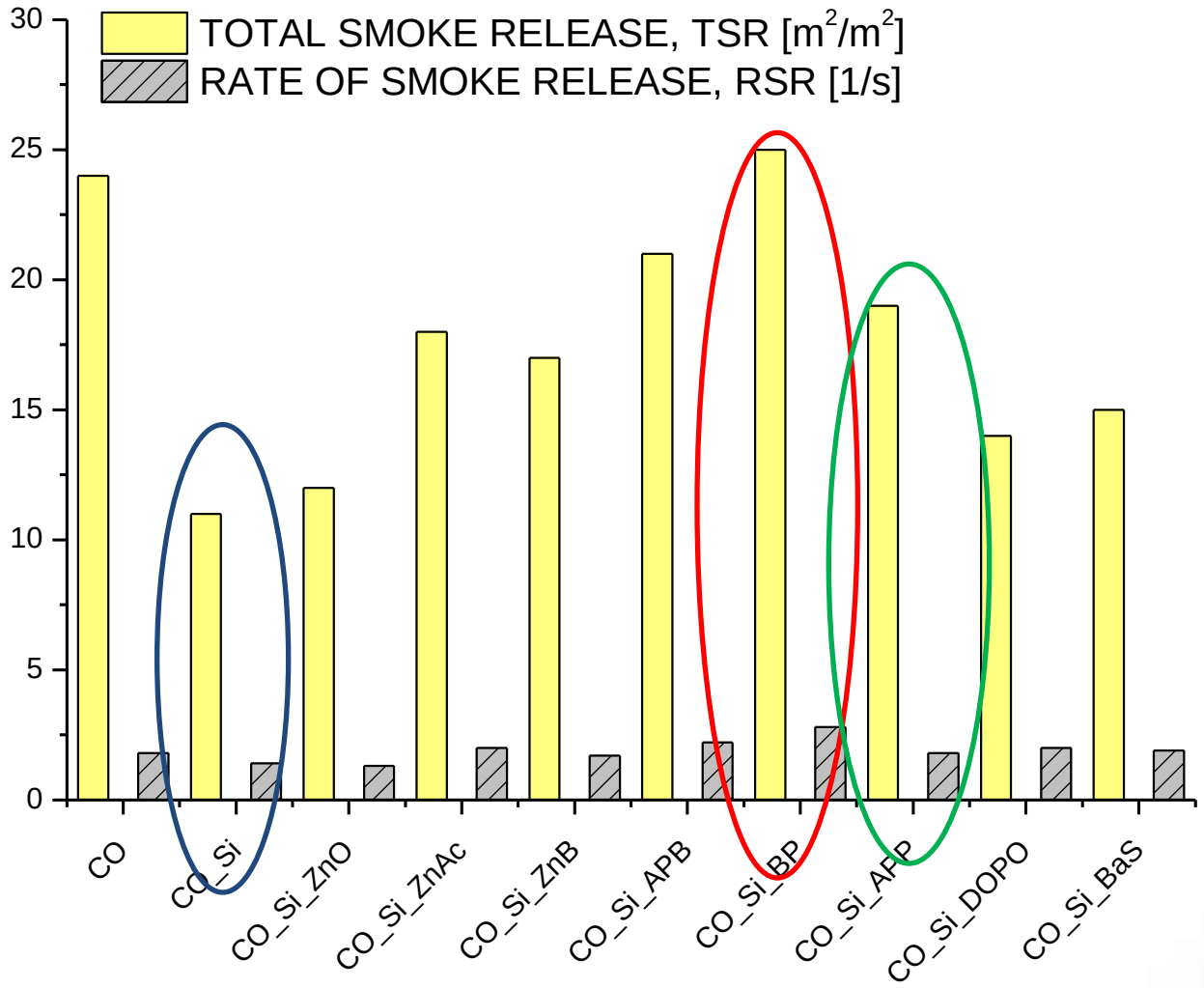


ZrP

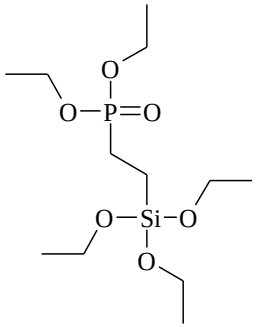
Residue ca. 96%,

LOI=30%

COTTON treated with SILICA and P-based DERIVATIVE (II)

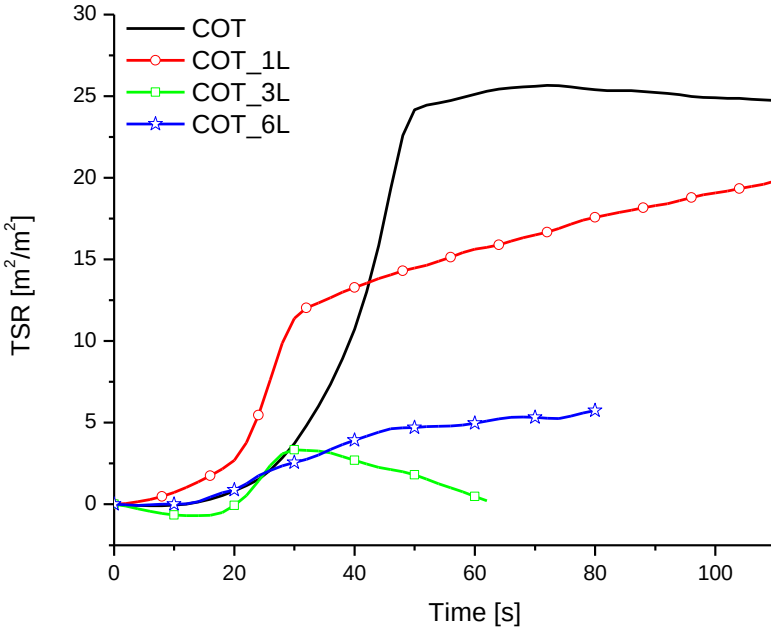


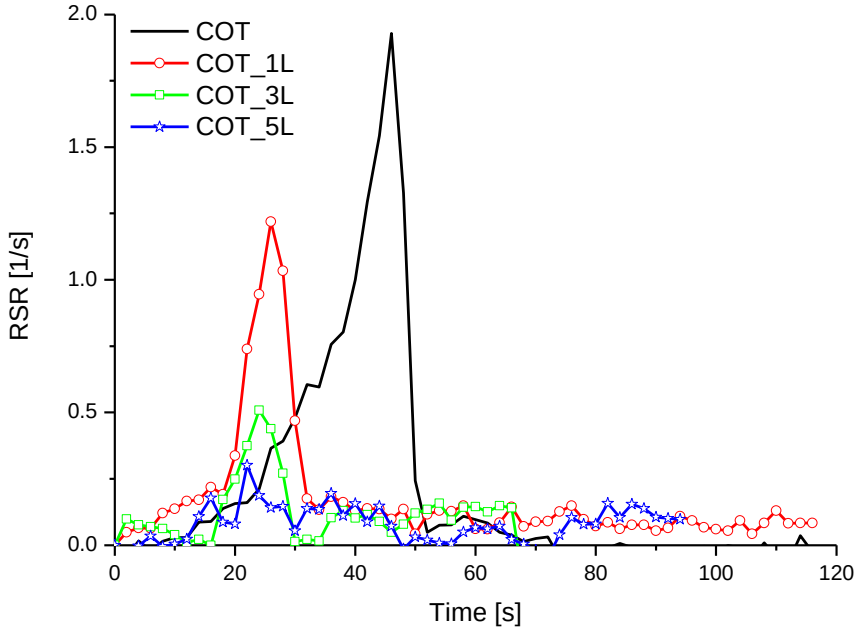
COTTON treated with a Si and P-based PRECURSOR



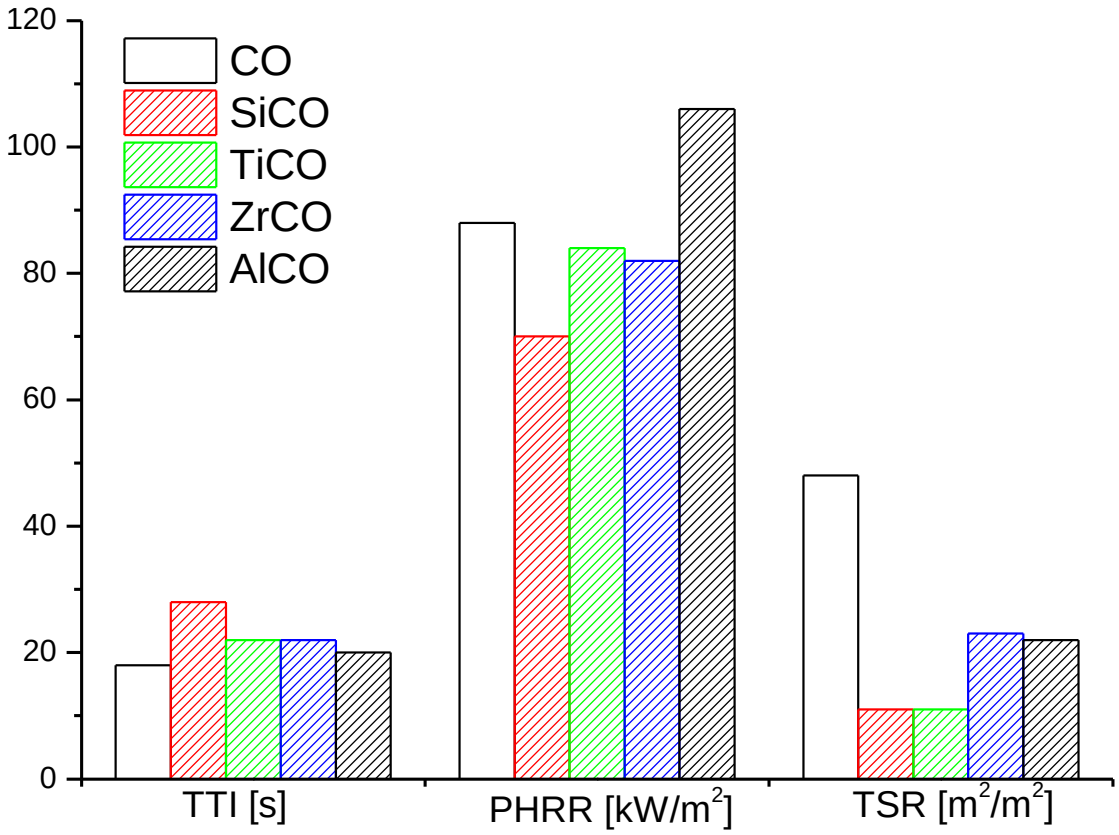
multistep process, consisting of consecutive depositions for obtaining architectures with a different number of layers (1, 3 or 6 layers)

CONE CALORIM

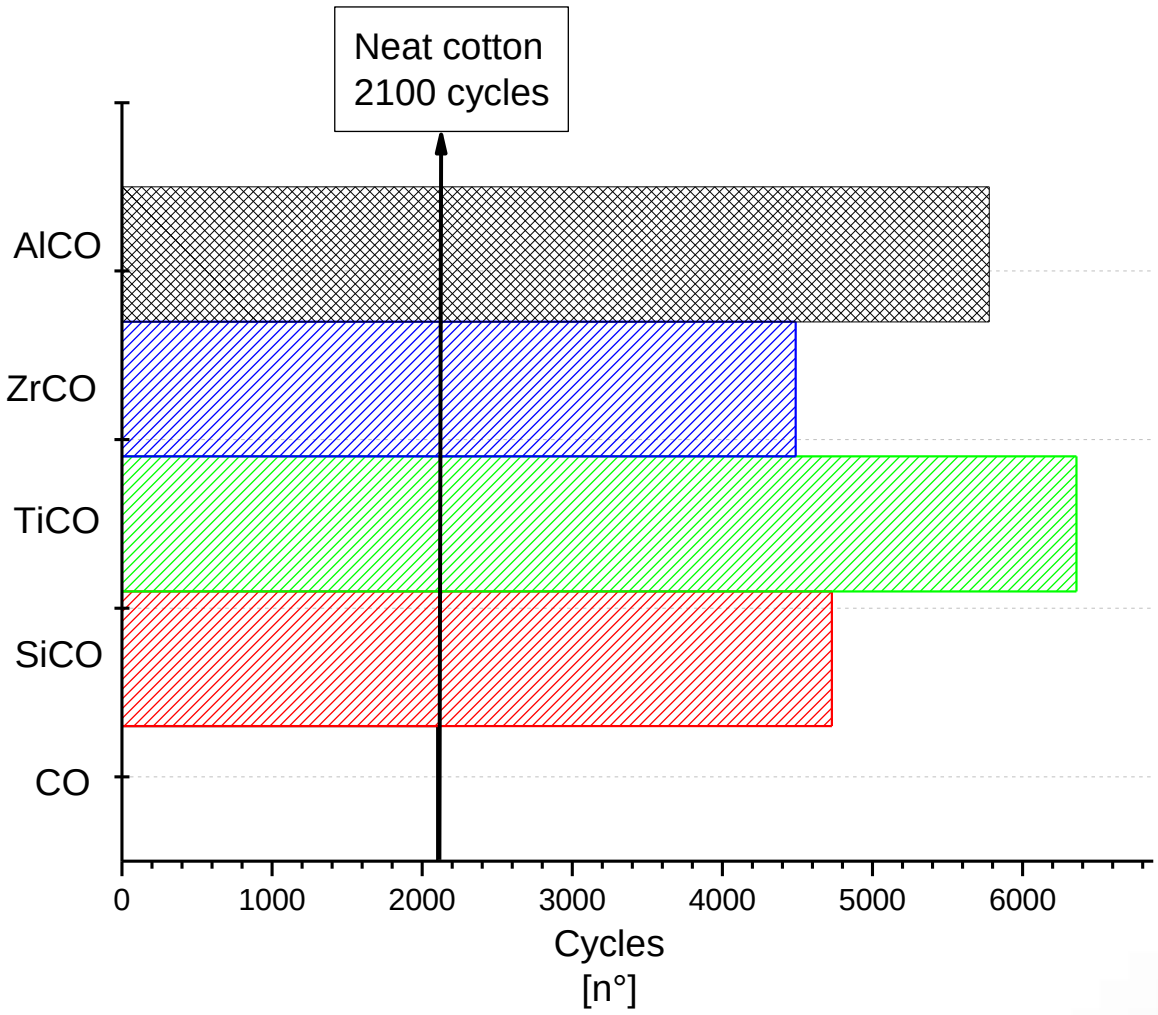




COTTON treated with SILICA, TITANIA, ZIRCONIA and ALLUMINA (I)



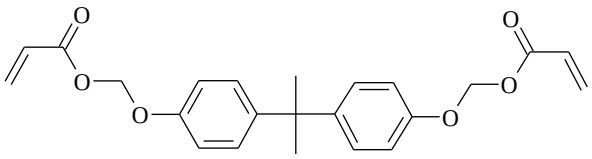
COTTON treated with SILICA, TITANIA, ZIRCONIA and ALLUMINA (II)



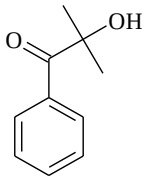
2 • DUAL-CURE processes

PHOTOPOLYMERIZATION REACTION FOLLOWED BY A THERMAL TREATMENT FOR PROMOTING THE FORMATION OF SILICA PHASES THROUGH A SOL-GEL PROCESS.

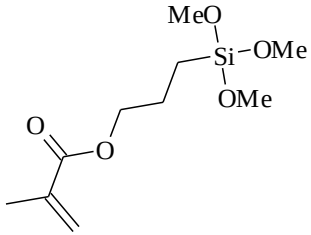
Different amounts of a silica precursor were added to an acrylic UV-curable formulation in the presence of a suitable coupling agent.



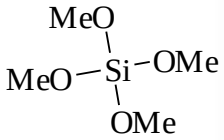
RESIN



PHOTOINITIATOR



COUPLING AGENT



TMOS

HIGH PERFORMANCES in FLAMMABILITY TESTS (HORIZONTAL and VERTICAL CONFIGURATION)

3

• NANOPARTICLE adsorption

* FRONT project: *Flame Retardant On Textile*

2 years- Collaborative Project in 7°FP

Contract n° 222486

The use of preformed nanoparticles in aqueous suspension has been exploited for polyester, cotton and polyester-cotton blends, aiming to mimic the impregnation/exhaustion steps currently employed as finishing treatments for industrial applications.

EUROPIZZI

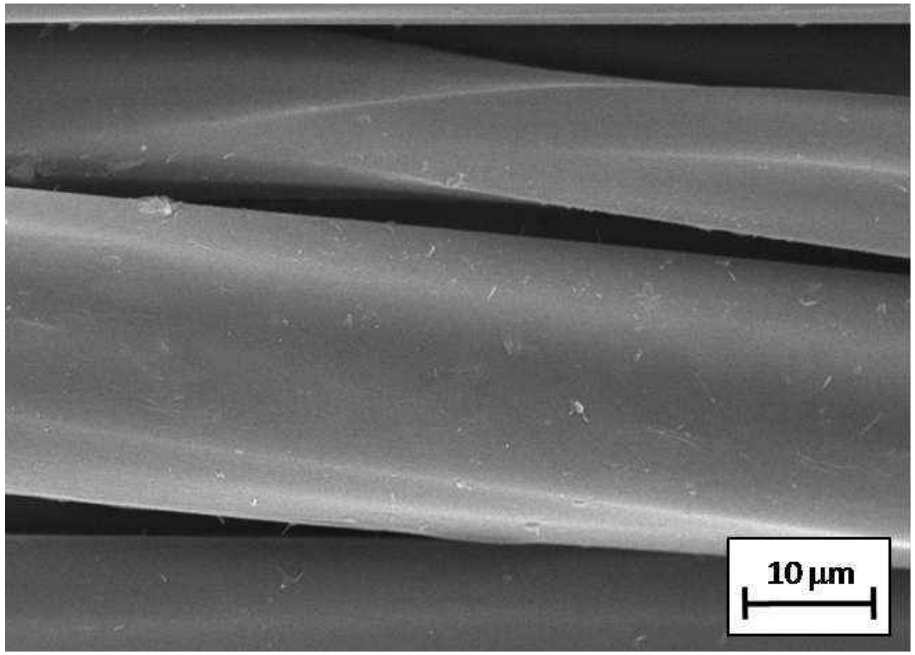
KLOPMAN International

CENTRO TESSILE COTONIERO e ABBIGLIAMENTO S.p.A.

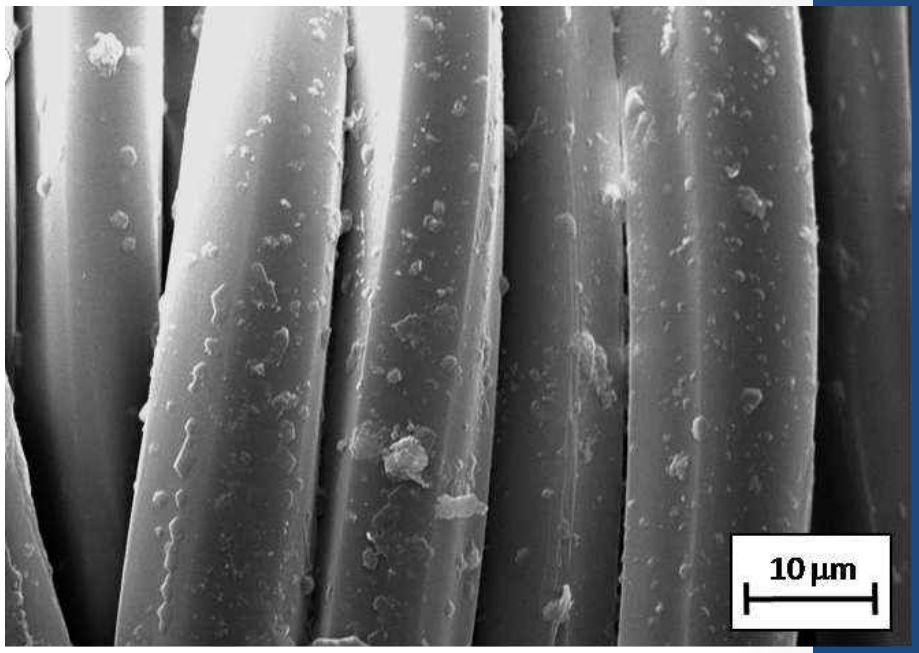
* Nanoparticles investigated

Family	Nanoparticle	Chemical formula
Lamellar nanoparticles		
Montmorillonite	Sodium cloisite	$M_x[Al_{4-x}Mg_x](Si)_8O_{20}(OH)_4$
Hectorite	Flourohectorite	$M_x[Mg_{6-x}Li_x](Si)_8O_{20}(OH)_4$
Hydrotalcite	Carbonate hydrotalcite	$Mg_6Al_2(CO_3)(OH_{16}).4(H_2O)$
Bohemite	Sulphonate bohemite	AlO(OH)
Globular nanoparticles		
Titania (anatase form)	Titania	TiO_2
Silica	Silica	SiO_2
Polyhedral oligomeric silsesquioxane	Octapropylammonium POSS®	R(SiOx)

PET



PET-Sodium Cloisite



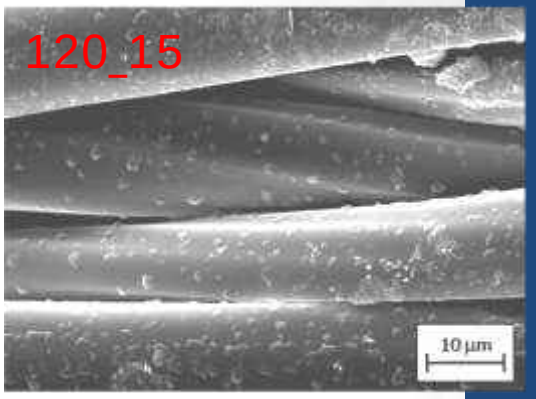
Sample	TTI±σ [s]	pkHRR±σ [kW/m^2]
PET	158±4	90±9
PET+cloisite	198±8	105±2

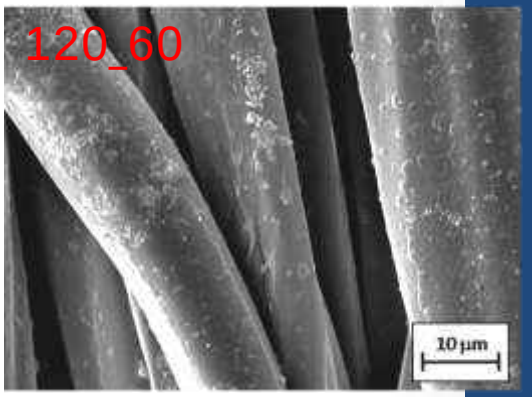
Oxygen cold plasma pre-treatment: power *vs.* time

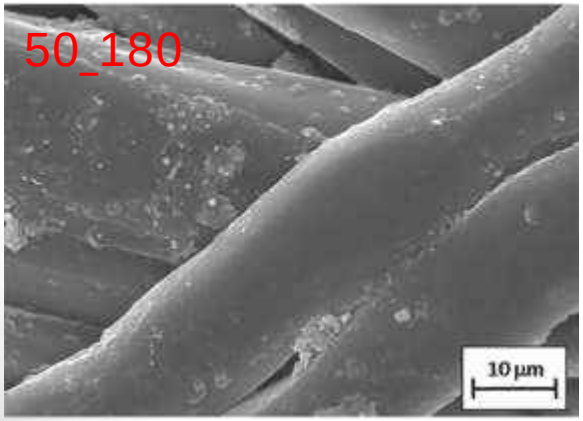
Sample	TTI±σ [s]	pkHRR±σ [kW/m^2]
PET	158±4	90±9
PET+cloisite	198±8	105±2
120_15	244±21	85±7
120_60	261±10	89±2
120_180	192±34	94±12
50_180	241±10	92±9
80_180	322±29	81±18

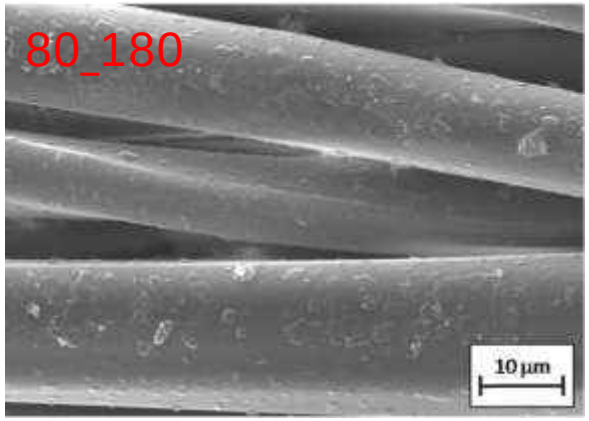
> power

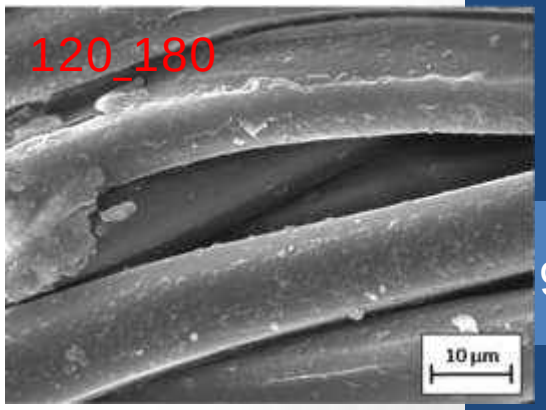
> time





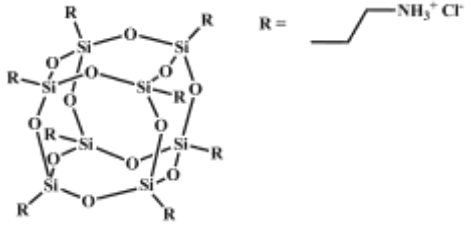




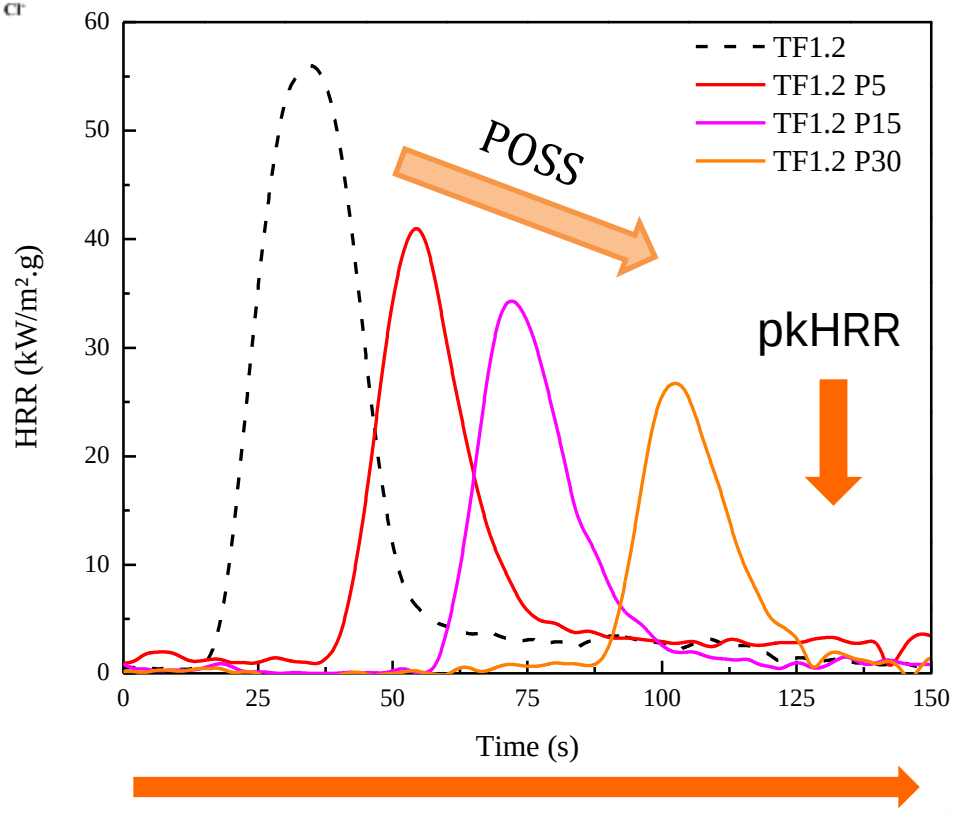


EXAMPLE OF GLOBULAR NANOPARTICLE-BASED FINISHING

Sample	POSS [wt.-%]	TTI [s]	Δ [s]	pkHRR [kW/m².g]	Δ [%]
PET-COT	0	11	-	57	-
PET-COT P5	5	36	+25	41	-28
PET-COT P15	15	56	+45	35	-39
PET-COT P30	30	86	+75	27	-53



Octapropylammonium POSS®

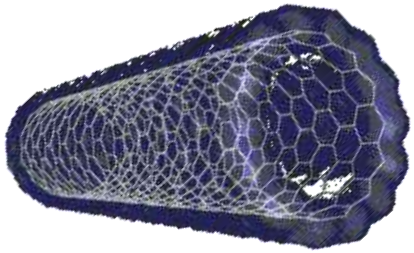


4 • LAYER BY LAYER assembly

- ✓ 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 is studied and used in a wide range of application fields with thousands of variations[***]

APPLICATIONS



Carbon Nanotubes

Metal nanoparticles

Bio-medical

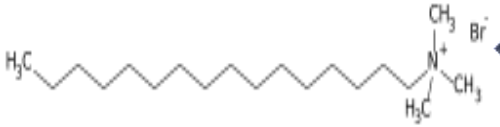
Anti-bacterial

Electrical properties

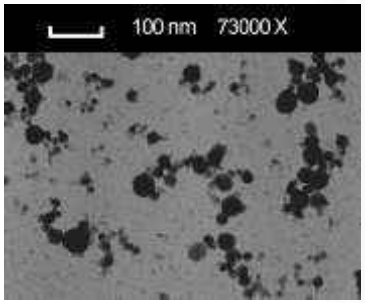
Gas barrier properties

Optical properties

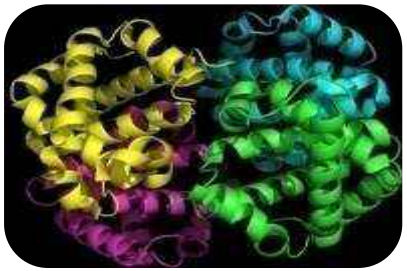
Flame retardancy



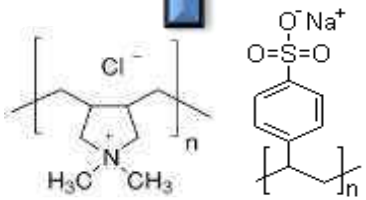
Surfactants



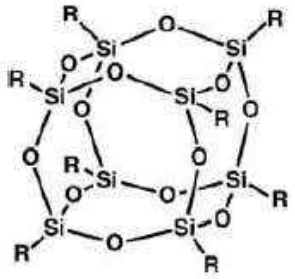
Ceramic nanoparticles



Bio-macromolecules

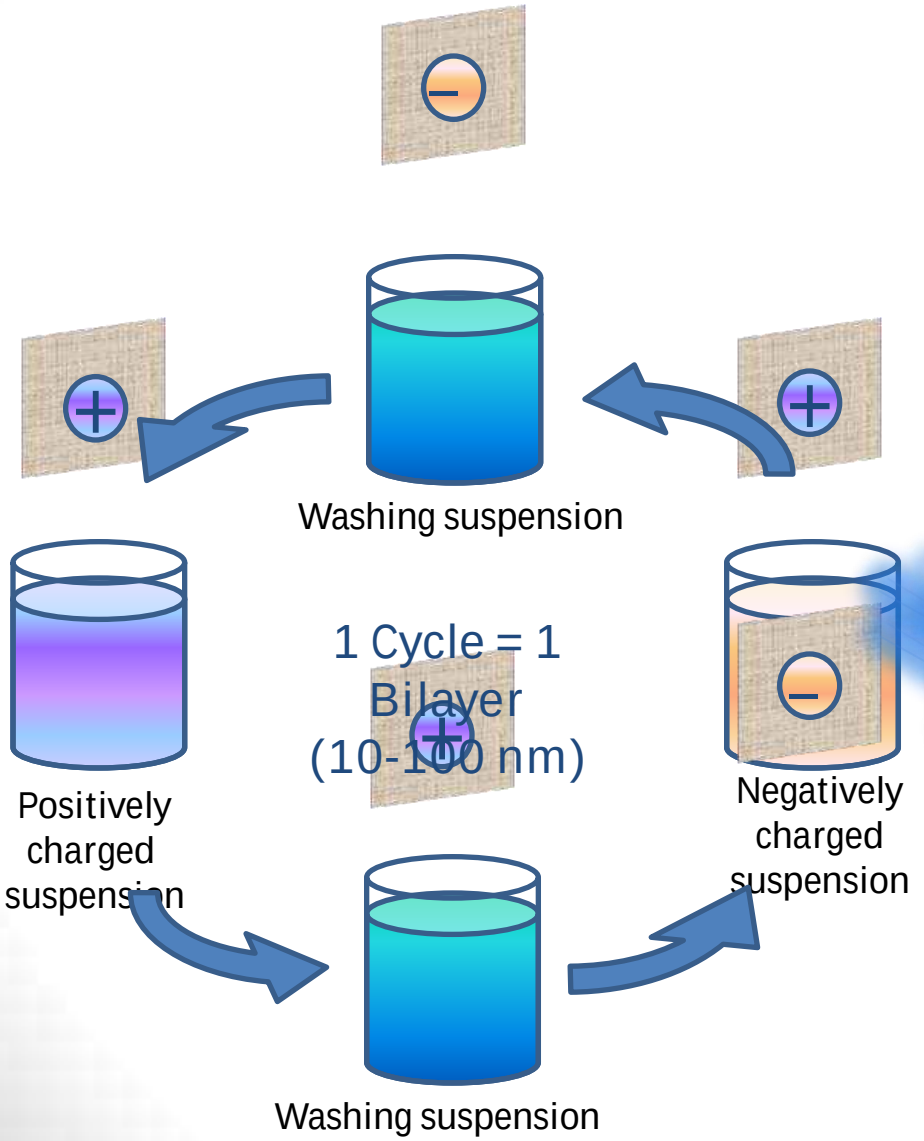


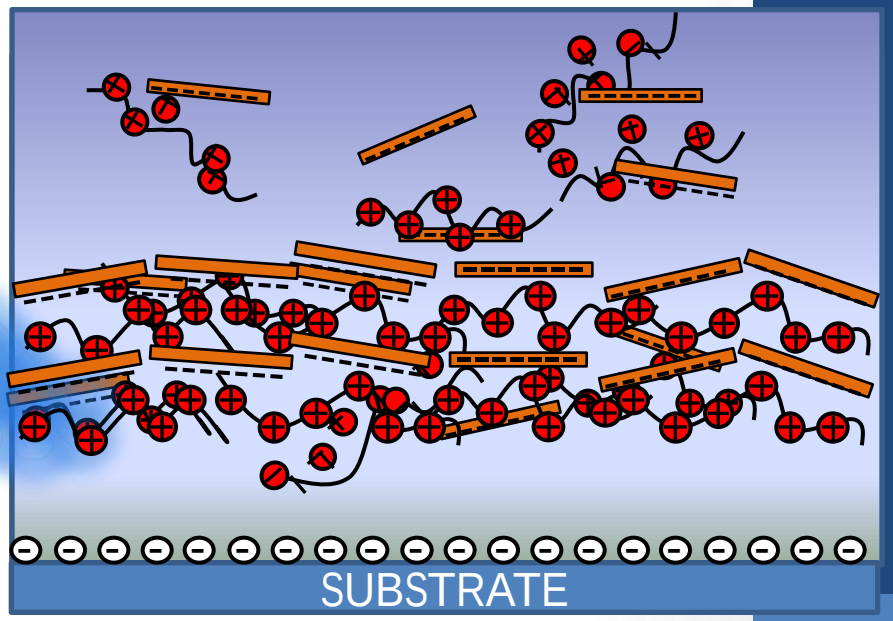
Polyelectrolytes



Organic-inorganic nanoparticles

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.





ADVANTAGES

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

IT IS POSSIBLE TO SELECT SUITABLE REAGENTS IN ORDER TO ACHIEVE THE DESIRED PROPERTIES

SOME EXAMPLES

Silica-based treatments

Inorganic coating → Barrier effect

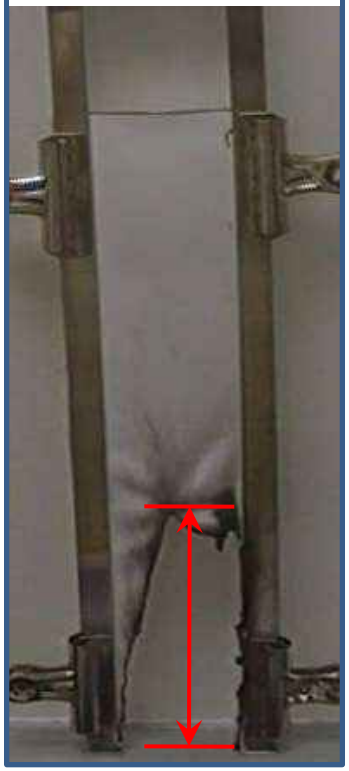
Zirconium phosphate-based treatments

Inorganic coating → Barrier effect + Release of P-based flame retardants

Ammonium polyphosphate-based treatments

Organic-inorganic coating → Barrier effect + Release of P-based flame retardants

PET



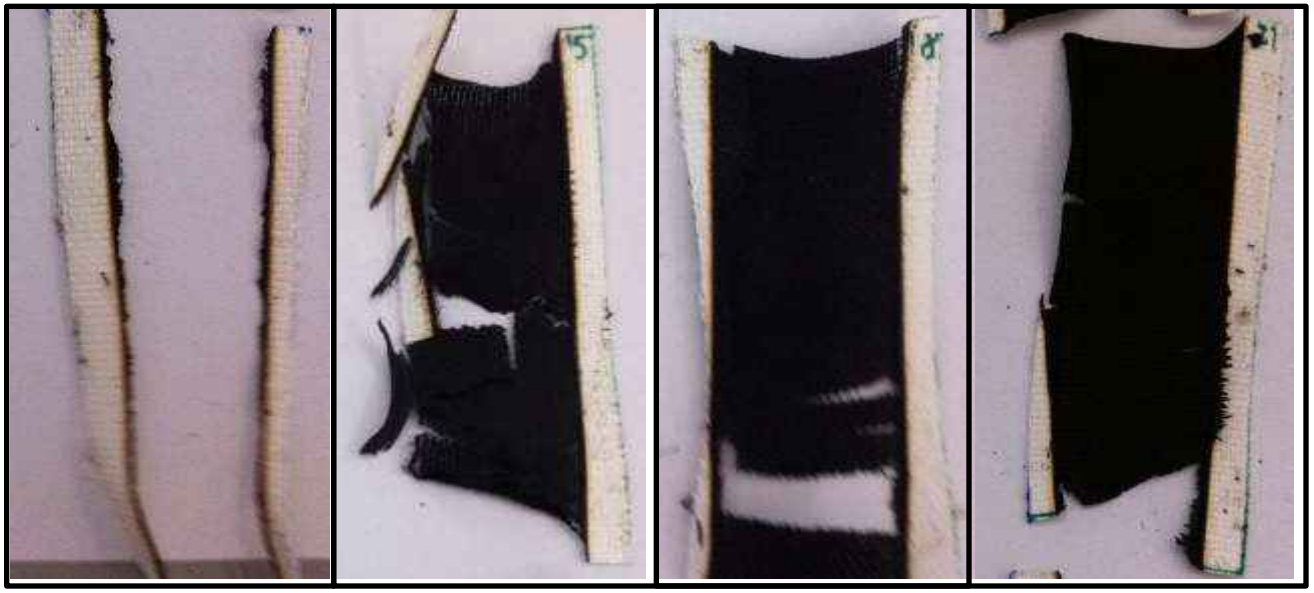
5 BL SiO_2

10 BL SiO_2

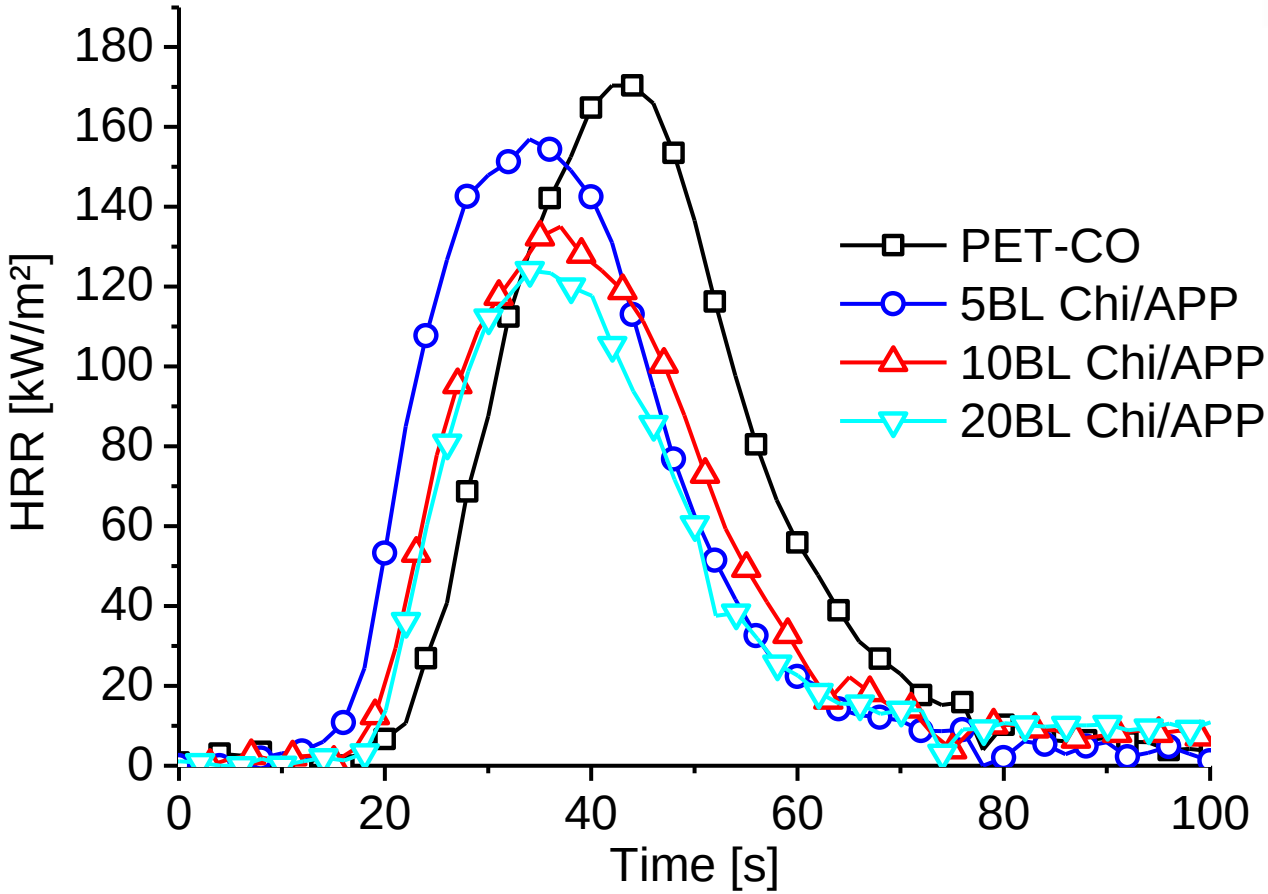
	PET	5 BL SiO_2	10 BL SiO_2
Burning time [sec]	32	10	2
Δ wt.-%	-7.6%	-0.8%	-0.2%
Dripping	Yes	No	No

	PET	5 BL SiO_2/ZrP	10 BL SiO_2/ZrP
CO [ppm]	418±55	298±12	293±18
Δ [%]	-	-28%	-30%
SPR	0.12±0.01	0.09±0.01	0.09±0.01
Δ [%]	-	-20%	-20%
TSR	247±4	219±6	233±4
Δ [%]	-	-11%	-6%

PET-CO 5BL Chi/APP 10BL Chi/APP 20BL Chi/APP

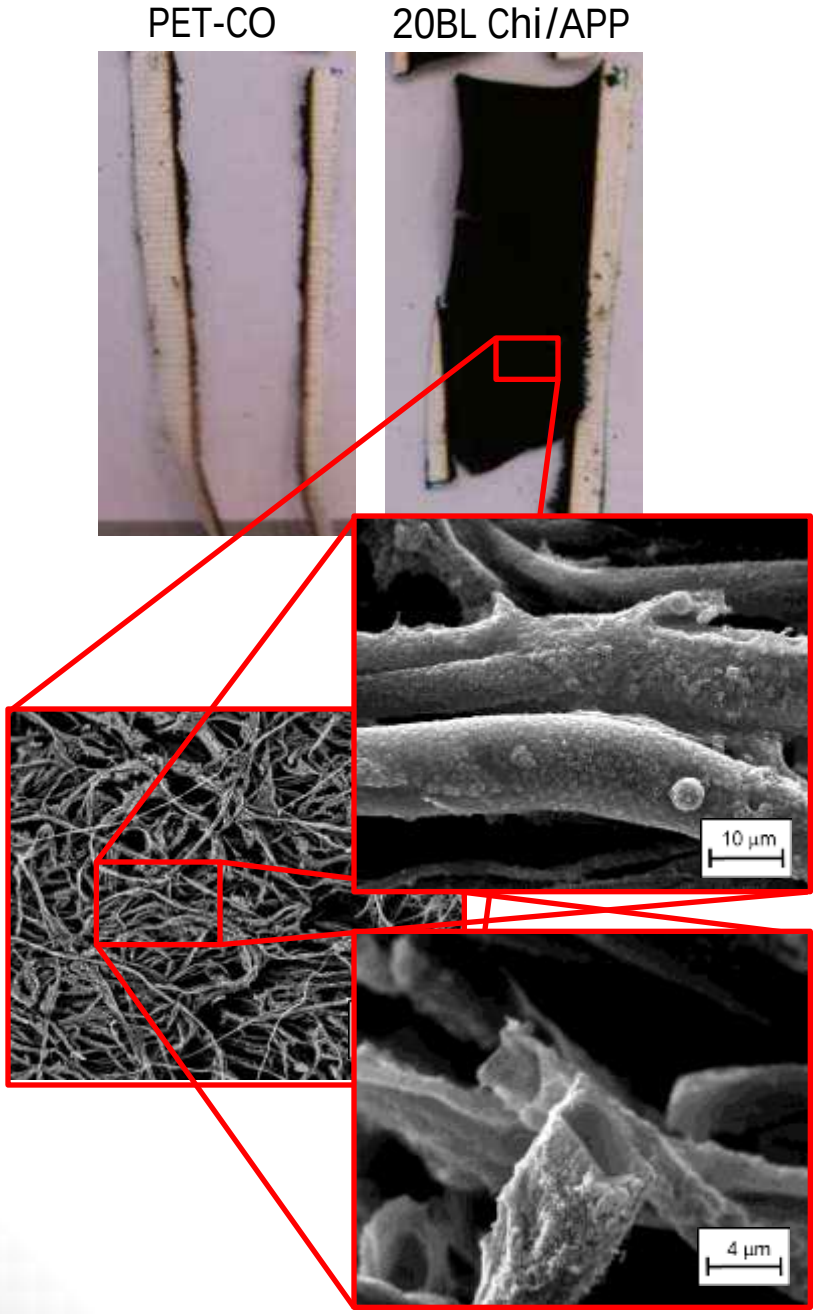


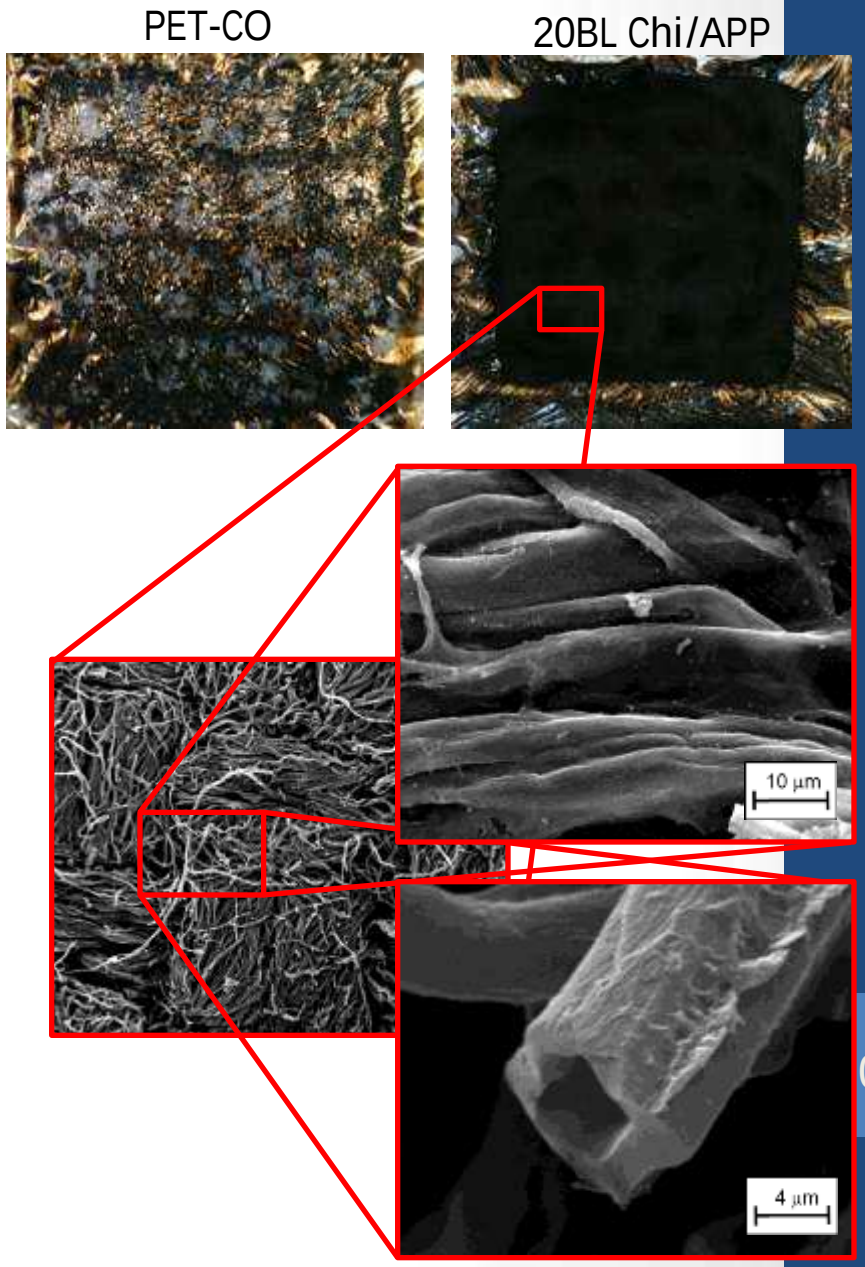
	PET	5 BL Chi/APP	10 BL Chi/APP	20 BL Chi/APP
Burning time [sec]	35	35	34	34
Afterflame time [sec]	36	-	-	-
Residue [%]	0	4.5	5.8	7.1



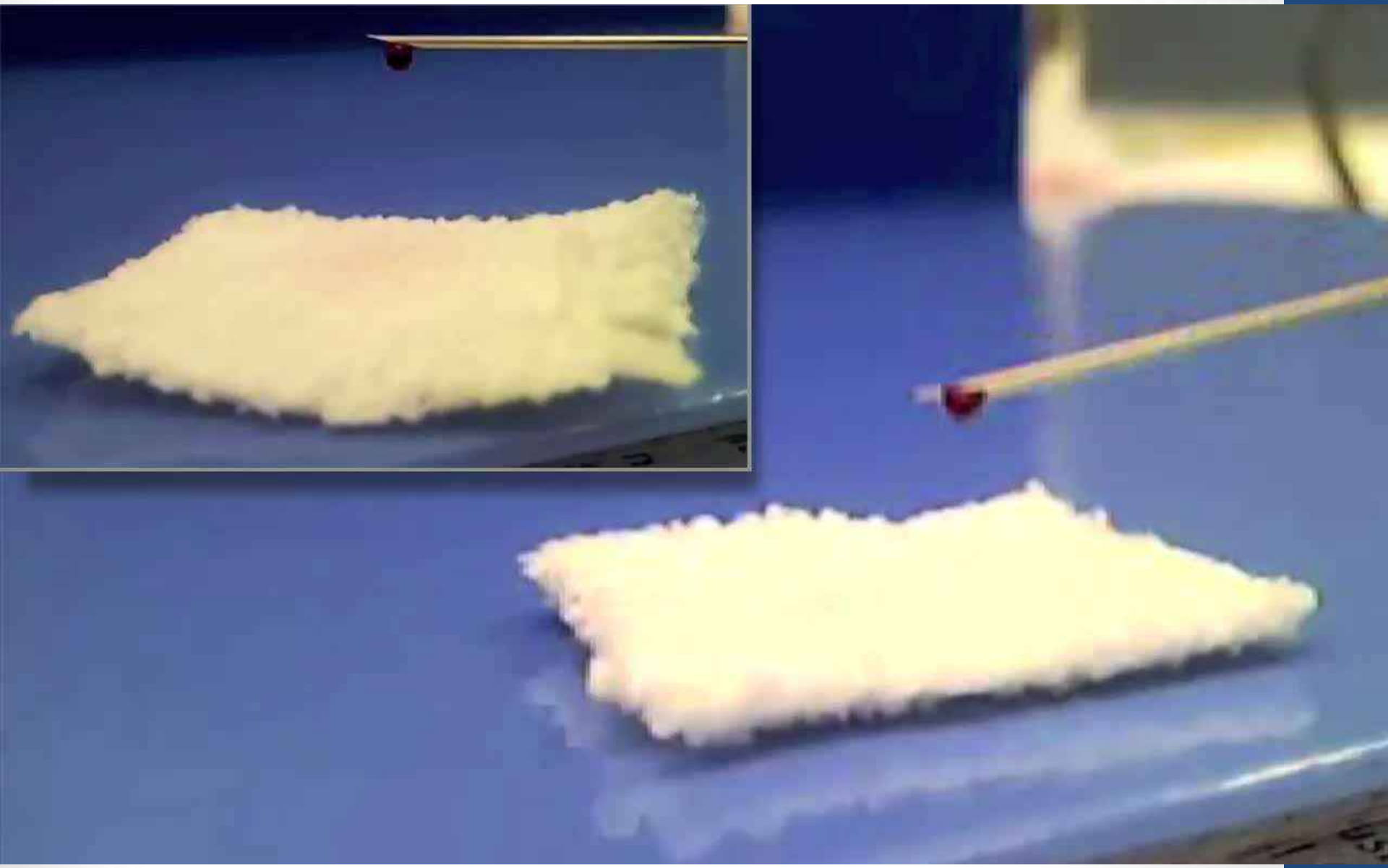
	PET-CO	5 BL Chi/APP	10 BL Chi/APP	20 BL Chi / APP
TTI±σ [s]	22±2	12±3	17±6	17±4
Δ [s]	-	-	-	-
Peak HRR±σ [kW/m^2]	170±3	162±6	138±16	128±3
Δ[%]	-	-5%	-19%	-25%

After combustion: residues





SMART-NANOCOATINGS?



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Thank you for your kind attention