Coatings based on TiO_2 nanoparticles and biomacromolecules as a new flame retardant approach for cotton fabrics

Simona Ortelli

ISTEC-CNR, Institute of Science and Technology for Ceramics, National Research Council - Via Granarolo, 64 Faenza (RA) Italy

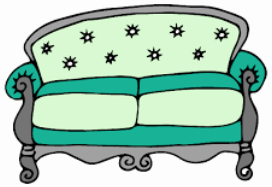
simona.ortelli@istec.cnr.it

Dipartimento Scienze Chimiche e Tecnologie dei Materiali

Young Investigator Award 2019

The burning of textiles has always been considered a major hazard: indeed, most fibers and fabrics, which play an important role in everyday life are flammable and potentially dangerous materials.






DEVELOPMENT of **Flame Retardant (FR) materials** in order to :

- limit the risk of fire;
- reduce the rate of flame spread;
- inhibit the fabric ignition.

The flame retardant finishing that can be counted among the most important textile finishes is doubtless the noblest technical treatment.

DEVELOPMENT of 'GREEN' Flame Retardant

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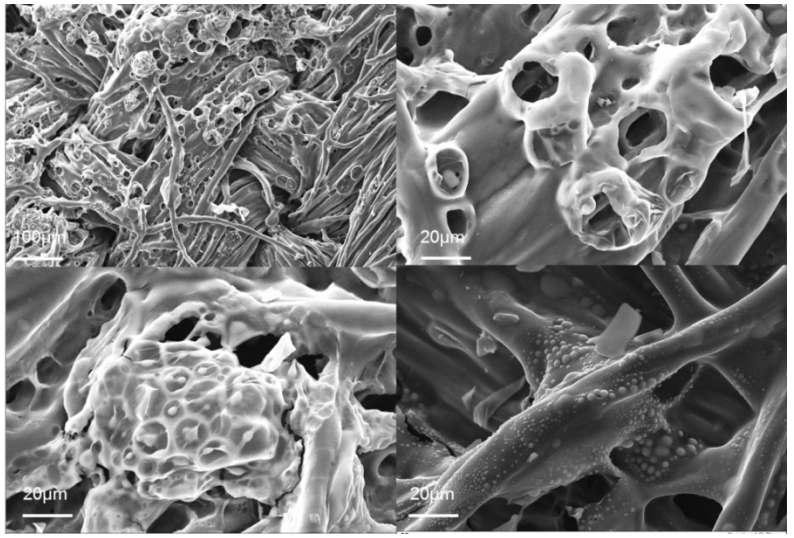
INTUMESCENT MATERIALS

THREE MAIN COMPONENENTS

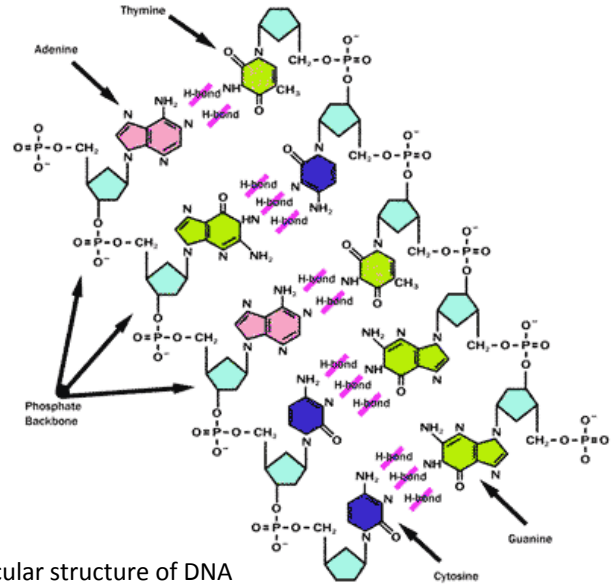
1. an acid-generating catalyst
2. a carbon (C) source
3. a blowing agent



BIOMACROMOLECULES as 'GREEN' FLAME RETARDANT

- **WHEY PROTEINS (WP): FR elements = S and N**
- **CASEINS: FR elements = P and N**
- **DEOXYRIBONUCLEIC ACID (DNA): 'all in one' molecule that naturally contains the three ingredients of intumescent formulation**

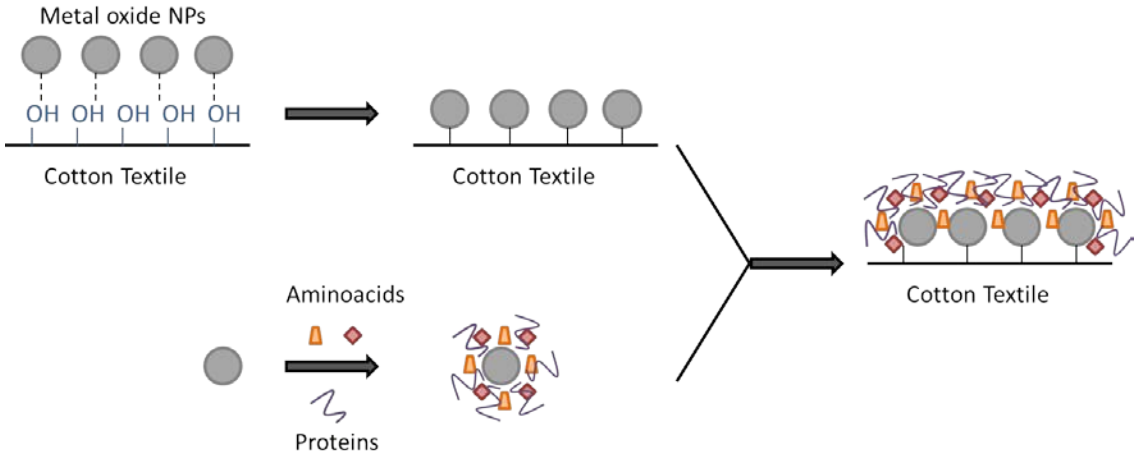
1. **PO_4^- groups** produce phosphoric acid
2. **Deoxyribose units** are carbon (C) source and blowing agents
3. **Groups containing N** can release ammonia



Molecular structure of DNA

BIOMACROMOLECULES as flame retardant coating on textile supports show VERY LOW washing fastness

DESIGN STRATEGY = COUPLING of Intumescent material + Ceramic Layer (inorganic nanoparticles)

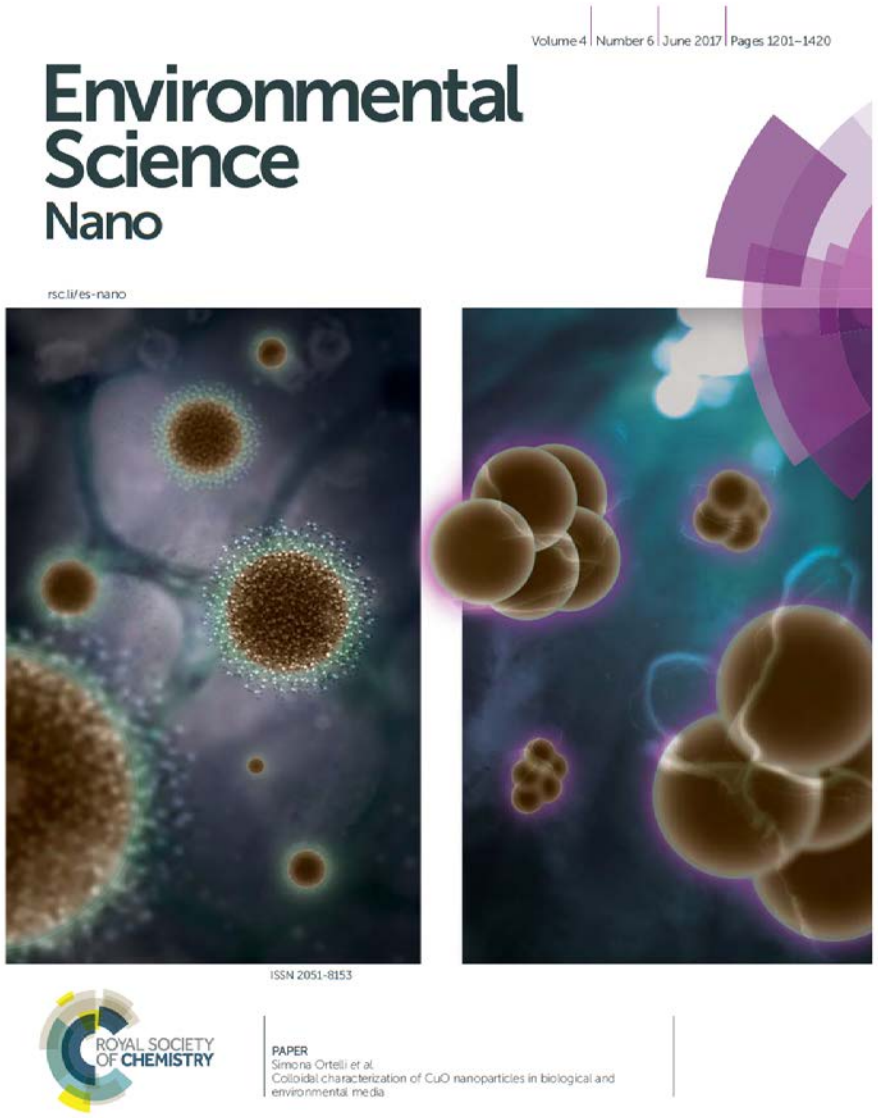


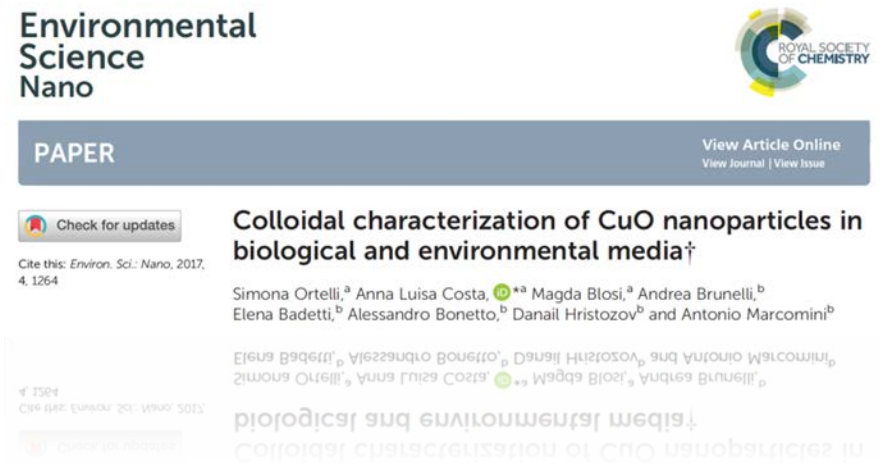
1) **Ability of proteins and amino acids to irreversibly cover nanoparticles**
2) **Affinity of inorganic NPs for the natural hydrophilic fibers**

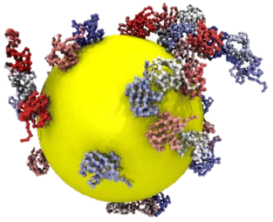
'GREEN' HYBRID COATING

with promising flame-retardant and washing fastness properties

1) Ability of proteins and amino acids to irreversibly cover nanoparticles







Nanoparticle Protein Corona

2) Affinity of inorganic NPs for the natural hydrophilic fibers

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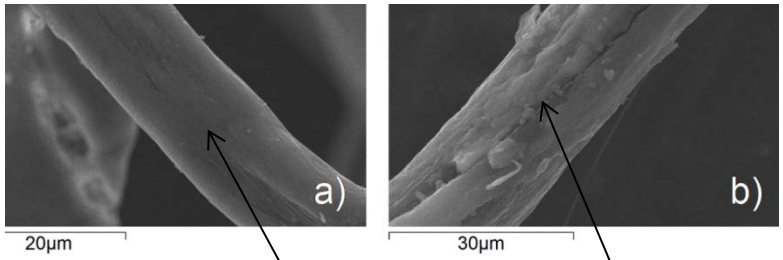
TiO_2 based nano-photocatalysis immobilized on cellulose substrates

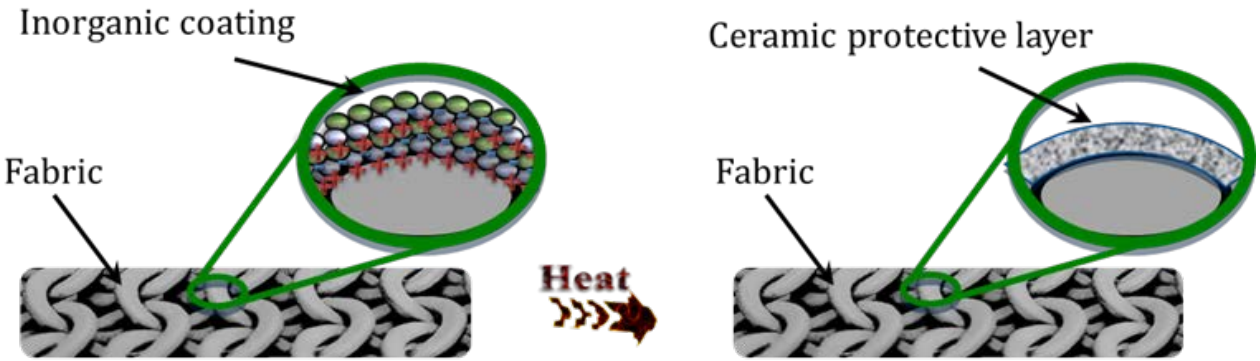
S. Ortelli[a], M. Blosi[a], S. Albonetti[b], A. Vaccari[b], M. Dondi[a], A.L. Costa[a,*]

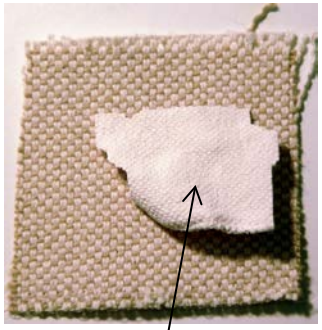
[a] Institute of Science and Technology for Ceramics (CNR-ISTEC), National Research Council of Italy, Via Granarolo 64, 48018 Faenza, RA, Italy
[b] Department of Industrial Chemistry "Toso Montanari", ALMA MATER STUDIORUM – Università di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy



Smooth texture of the uncoated fiber

The coated fiber shows a certain surface roughness due to the presence of nano-TiO_2





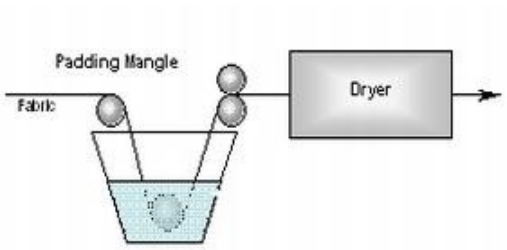
TiO_2 layer perfectly mimicking the texture of the fabric

Sample produced:

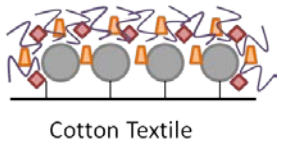
'GREEN' HYBRID SAMPLES based on TiO_2 NP coupled with

1) **Whey Proteins (TiO_2/WP)**
2) **Caseins (TiO_2/Caseins)**
3) **DNA (TiO_2/DNA)**

Hybrid suspension sample



Dip-padding-curing process



Coated cotton fabric

Cellulose
https://doi.org/10.1007/s10570-018-1745-z

ORIGINAL PAPER

Coatings made of proteins adsorbed on TiO_2 nanoparticles: a new flame retardant approach for cotton fabrics

Simona Ortelli · Giulio Malucelli · Fabio Cuttica · Magda Blosi · Ilaria Zanoni · Anna Luisa Costa

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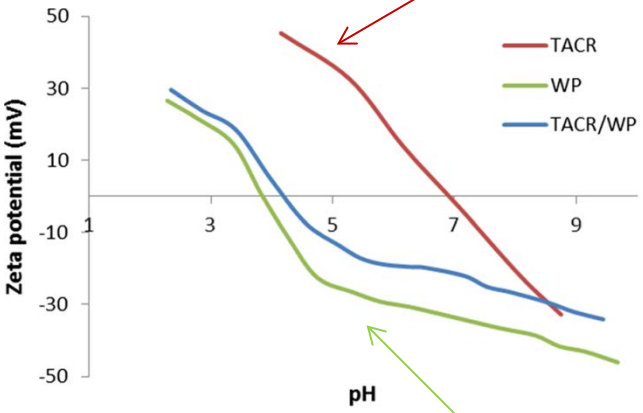
Regular Article

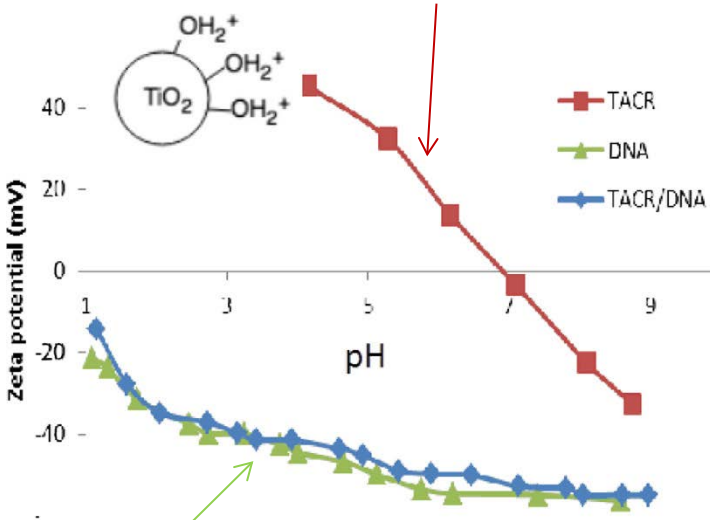
NanoTiO$_2$@DNA complex: a novel eco, durable, fire retardant design strategy for cotton textiles

Simona Ortelli [a], Giulio Malucelli [b], Magda Blosi [a], Ilaria Zanoni [a,c], Anna Luisa Costa [a,*]

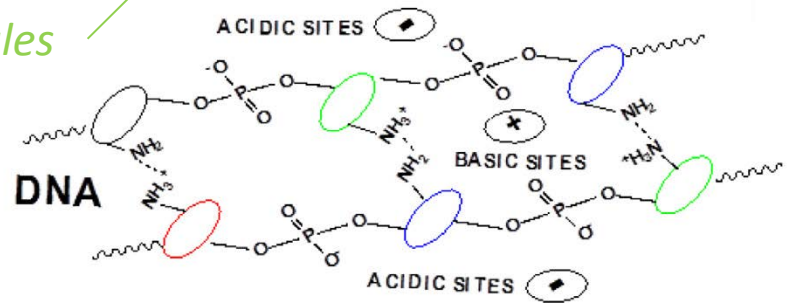
[a] ISTEC-CNR, Institute of Science and Technology for Ceramics – National Research Council of Italy, Via Granarolo 64, I-48018 Faenza, RA, Italy
[b] Politecnico di Torino, Department of Applied Science and Technology, and Local INSTM Unit, Viale Teresa Michel 5, I-15121 Alessandria, Italy
[c] Clinical Unit of Occupational Medicine, Department of Medical and Surgical Sciences, University of Trieste, Via della Pietà 2/2, 34129 Trieste, Italy

Positively charged TiO_2 NP



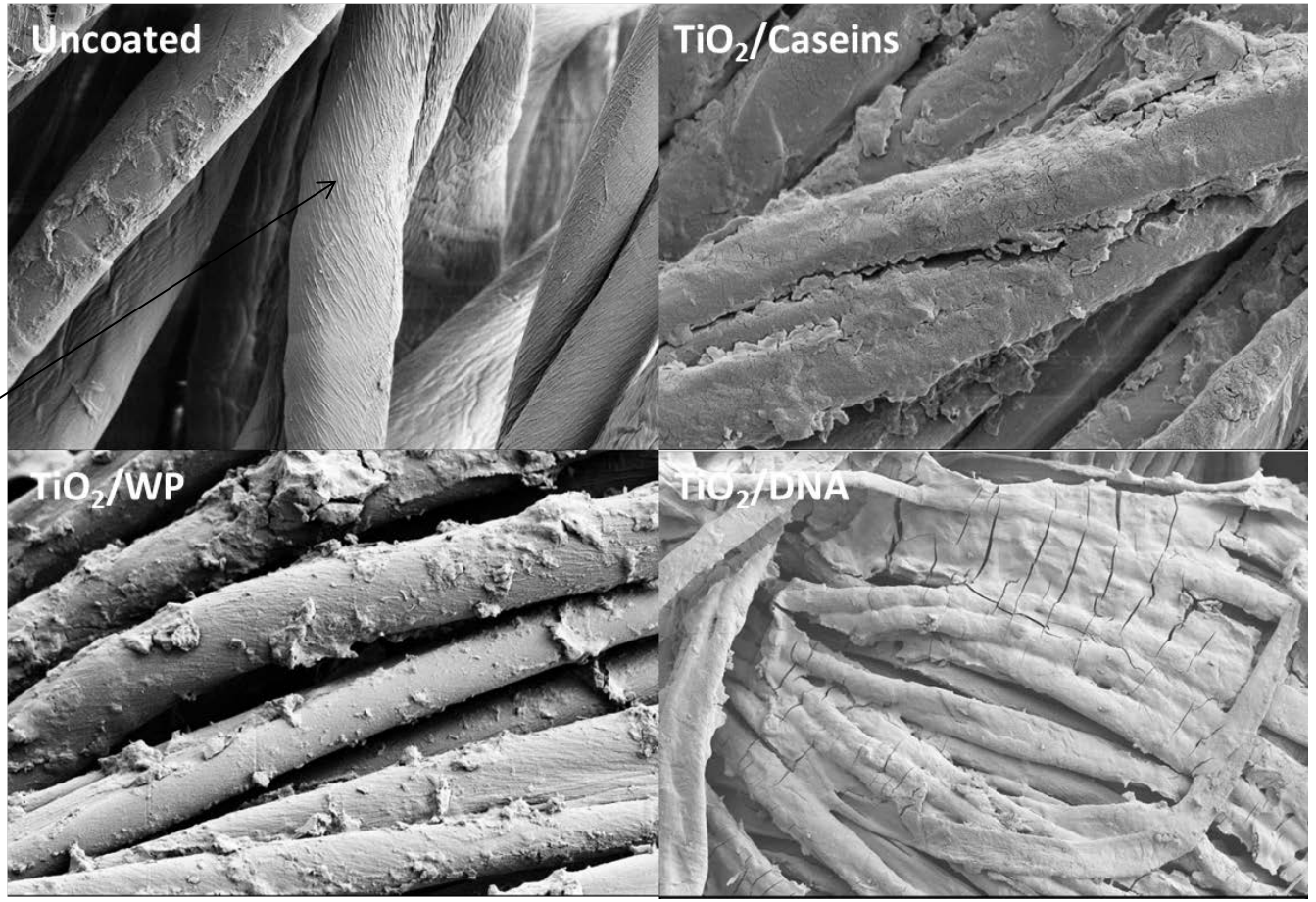


Negatively charged biomacromolecules



Strong electrostatic interactions between positively charged TiO_2 NPs and negatively charged proteins.

High correspondence found in hybrid nanosuspensions (TiO_2/biomacromolecules – blue curves) and biomacromolecules (green curves) curves ensures the covering of TiO_2 NPs by protein.



Smooth texture of the uncoated fibers

*FESEM analysis shows the **surface morphology change** induced by hybrid coatings. Unlike the smooth texture of the uncoated, the coated fibers show a certain **surface roughness** due to the presence of nano-TiO_2/protein layers attached on cotton substrate fibers.*

RELEASE TEST

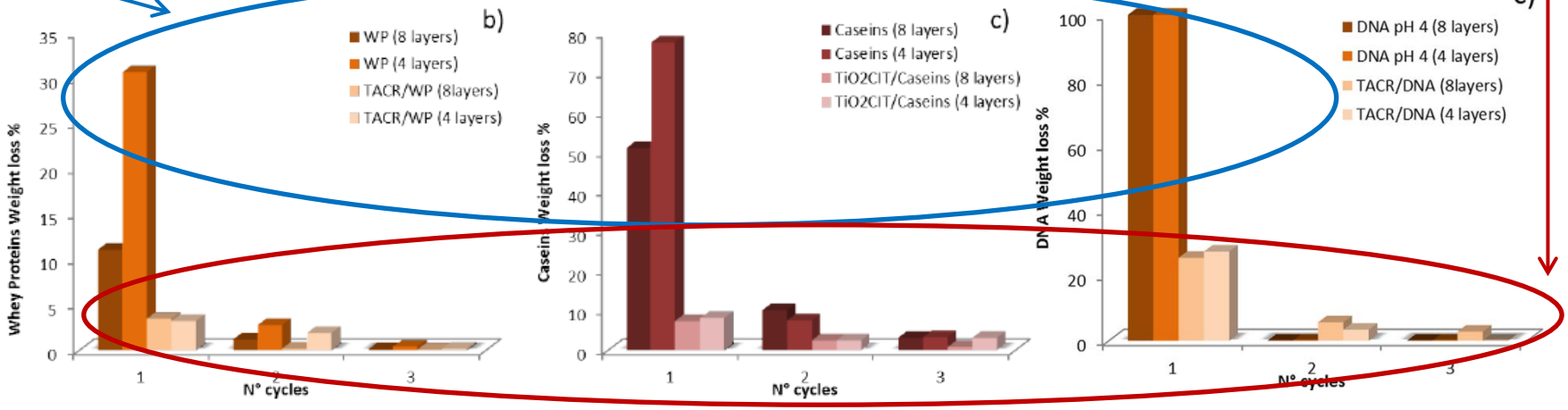
After 1, 4 and 6 days

Washing water → ICP analysis

RESULTS

High proteins weight loss % in monophasic biomacramolecules based-samples

Low proteins weight loss % in hybrid NPs/biomacromolecules based-samples



VERY LOW release of hybrid coatings

Confirming the cross-linking action of TiO_2 NP

FLAME SPREAD TESTS in horizontal configuration

Flame spread tests in horizontal configuration were carried out by applying a methane flame for 3 s on the short side of the specimens (50 x 100 mm^2)

Sample	Total burning time (s)	Burning rate (mm/s)	Residue (%)
Uncoated	52	1.92	0
TiO_2 NP/WP	63	1.59	7.9
TiO_2 NP /Caseins	64	1.60	41.3
TiO_2 NP/DNA	29	1.72	61.6

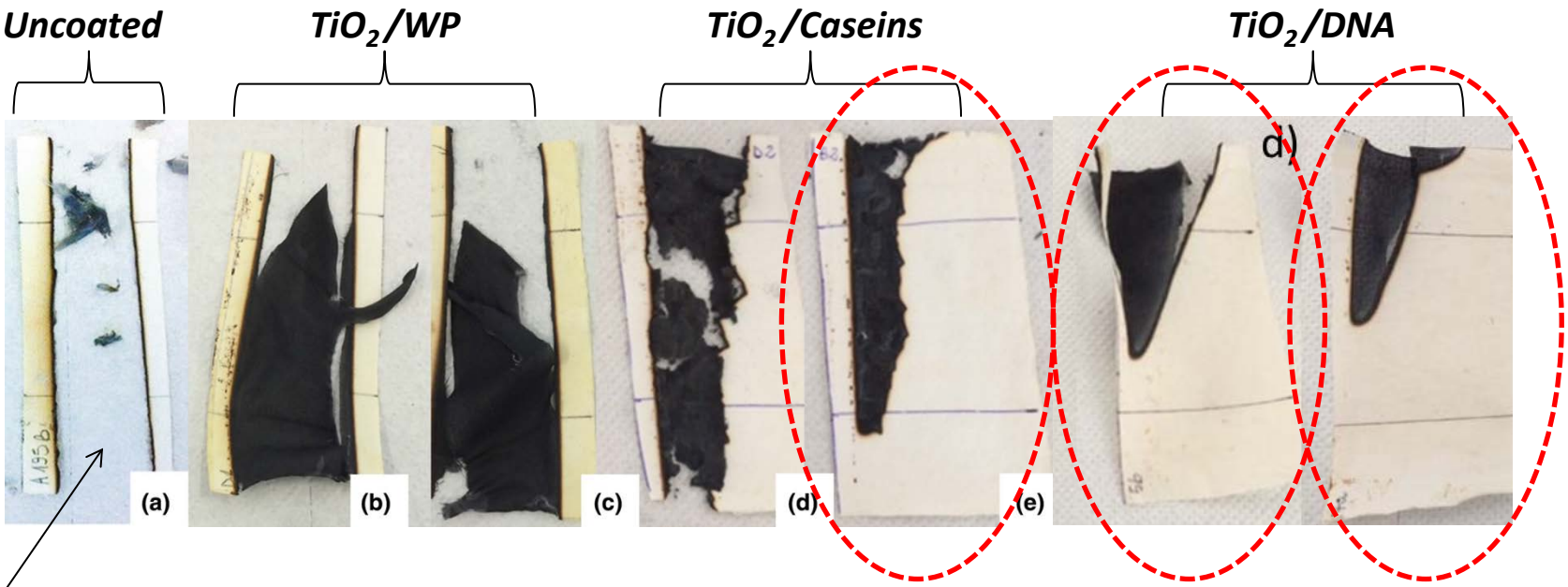
Decrease of the total burning time due to self-extintion.

***Increase** of the total burning time and **decrease** of the burning rate.*

Increase of residue.

***Protection** of the underlying cellulosic substrate from flame spread, **slowing down flame propagation**.*

FLAME SPREAD TESTS in horizontal configuration



Vigorous and quick combustion. No residue.

*TiO_2/Caseins e TiO_2/DNA coatings were able to **self-extinguish**.*
*The final residues are **remarkably higher** as compared to that of the untreated fabric.*

COMBUSTION TESTS by cone calorimetry

The resistance of the fabrics towards heat flux (35 kW/m²) has been assessed by means of forced combustion tests using the cone calorimeter.

Sample	HRR (kW/m²)	pkHRR (kW/m²)	THR (kJ/m²)	Residue (%)
Untreated	7.7	47.1	1.0	1.0
TiO_2 NP/WP	10.8	52.4	1.2	7.3
TiO_2 NP /Caseins	No ignition			7.0
TiO_2 NP/DNA	No ignition			12.5

*It is confimed that TiO_2/Caseins and TiO_2/DNA coatings were able to **self-extinguish**.*

*The increase of the residues at the end of the test indicates the **high char-forming character** of biomacromolecules in combination with TiO_2 nanoparticles in the layered assembly.*

- Simple innovative design solution for the production of **environmentally-friendly** intumescent hybrid coatings was presented, making a significant step forward towards the obtainment of flame resistant textiles with improved washing fastness.

- The high affinity developed between biomacromolecules and NPs **enhance the washing fastness** of protein-based coatings, allowing the production of **durable** flame retardant **coatings**.

- The proposed hybrid coatings show very good flame retardant properties, being effective in **slowing down (or even impeding) the flame propagation**, **increasing the final residue**, thus indicating the **protection effect** exerted by the deposited char forming coatings.

DSCTM

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Environmental Nanotechnologies Group

Anna L. Costa (researcher)
Davide Gardini (researcher)
Magda Blosi (researcher)
Simona Ortelli (researcher)
Carlo Baldisserri (researcher)
Felice C. Simeone (researcher)
Lara Faccani (Ph.D. student)
Ilaria Zanoni (Ph.D. student)

and
Anna Tampieri (Director of ISTEC)

Politecnico di Torino

Prof. Giulio Malucelli

THANK YOU!!