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DI INGEGNERIA
CIVILE E AMBIENTALE


# Applicazioni ingegneristiche dei materiali nanocompositi

Nanotecnologie in Umbria, Perugia 25 Ottobre 2021

Prof. Luigi Torre

**Biomateriali nanostrutturati per packaging e biomedicale**

**Materiali a cambio di fase nanostrutturati per solare termico**

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**Materiali nanostrutturati per alte temperature e per l'aerospazio**

**Nano-materiali per il monitoraggio delle deformazioni e rilevamento di danni**

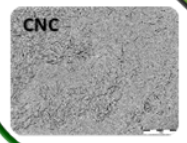
# Biomateriali nanostrutturati per packaging e biomedicale

# NANOCOMPOSITI BIODEGRADABILI MULTIFUNZIONALI

## PACKAGING

**Objectives:** production of biodegradable multifuncional nanocomposites reinforced with cellulose nanocrystals extracted from different cellulosic sources and wastes combined with antimicrobical nanoparticles or essentials oils in order to obtain a reinforcement effect and also an anti-bacterical response.

**REVALORIZATION OF WASTE**



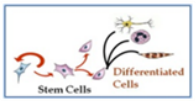

**Cellulose and lignin extraction**

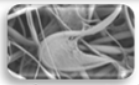
**FOOD ACTIVE PACKAGING**

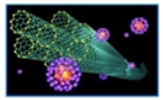
- Biodegradable Polymers
- Essential Oil
- Antimicrobial
- Antioxidant

## BIOMEDICAL

**Objectives:** production of biodegradable bi-dimensional (*films*) and tri-dimensional (*scaffolds* and *mats*) nanocomposites reinforced with specific nanoparticles (metal nanoparticles, biopolymeric nanoparticles, carbon nanotubes, hydroxyapatite, cellulose nanocrystals, etc) able to modulate differentiate or stem-cell activities for biomedical and pharmaceutical applications.



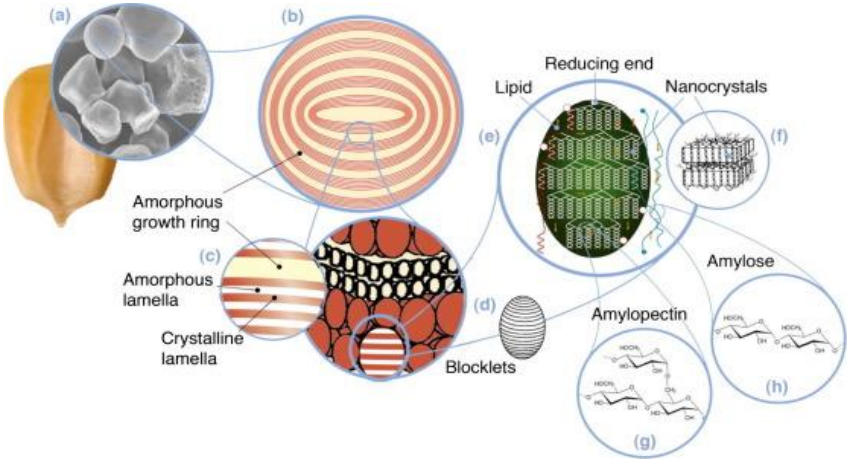
- Antibacterical
- Osteoconductive

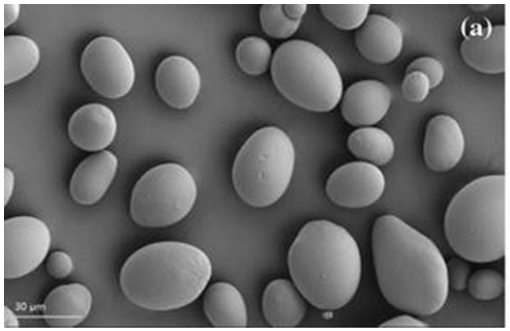
- Mechanical
- Electrical

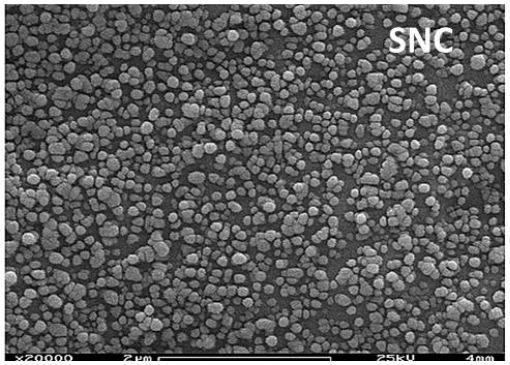
i) MULTIFUNCTIONAL POLYMERIC **BIONANOCOMPOSITES**
ii) MULTIFUNCTIONAL BIODEGRADABLE **BLENDS**

(**STARCH**, **CELLULOSE** , **LIGNIN** AND ACTIVE INGREDIENTS)

# BIONANOFILLERS - AMIDO



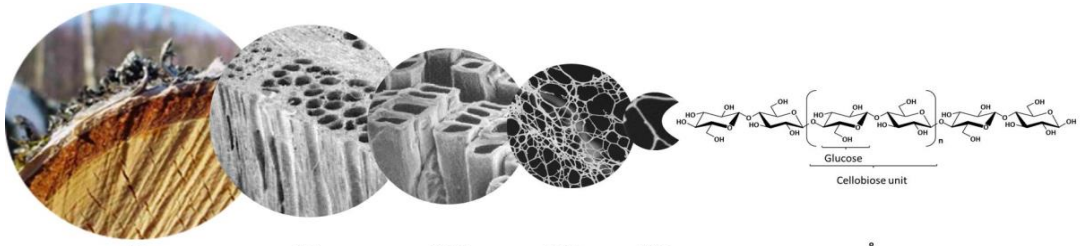

***BARLEY starch (waxy - no waxy)***

*starch characterized by granules of smaller dimensions (WS) gave nanoparticles (WNP) with reduced mean diameter and thermal stability with respect to NPs obtained from non-waxy barley flour*

***PVA*** + ***Starch NC or NP*** + ***HTyr***

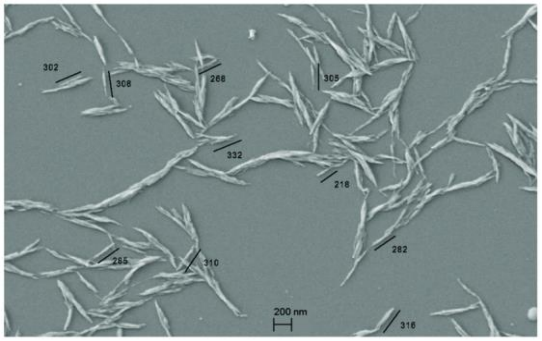

- **ternary films based on PVA, nanostructured starch and a strong antioxidant compound such as HTyr**, represent very promising novel combinations for active food packaging applications
- nanostructured starch-based formulations were able to **tune a prolonged release of HTyr** from the films over the time.

# BIONANOFILLERS - CELLULOSA

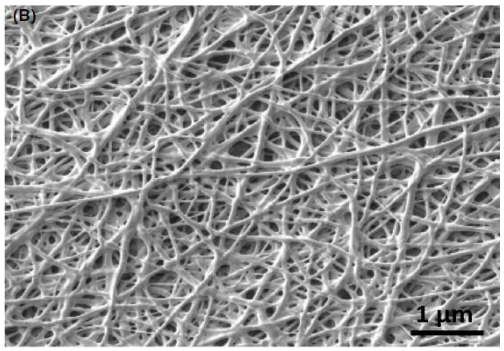



| m | cm | mm | µm | nm | Å |
|---|---|---|---|---|---|
| Wood or plants | Fibers in wood matrix | Cellulose Fiber | Micro Fibrils | Nano Fibrils | Molecular Structure |

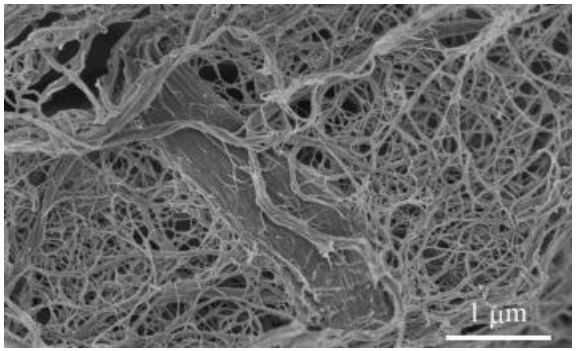
**CNC**




**BC**

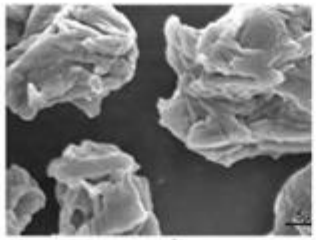



**MFC**

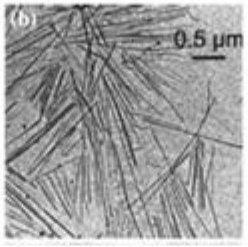


# BIONANOCOMPOSITI BASE CNC - ESTRUSIONE

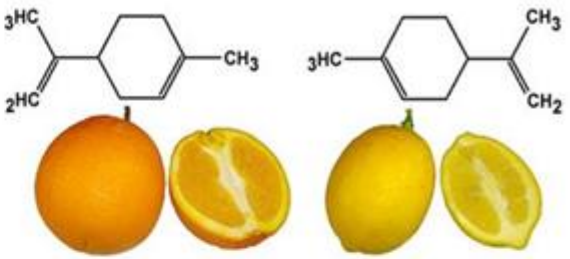
## PLA + Cellulose + Active Agents

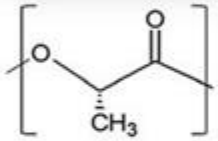


MCC

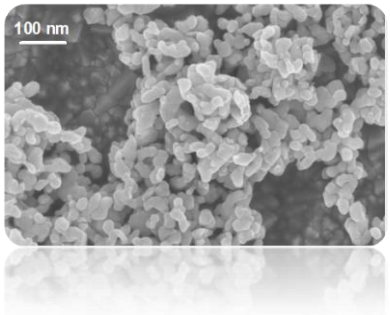



CNC

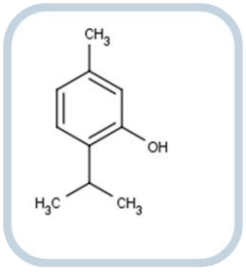


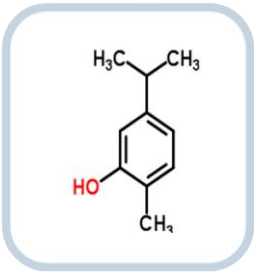

**Metal nanoparticles**




**Natural additive**



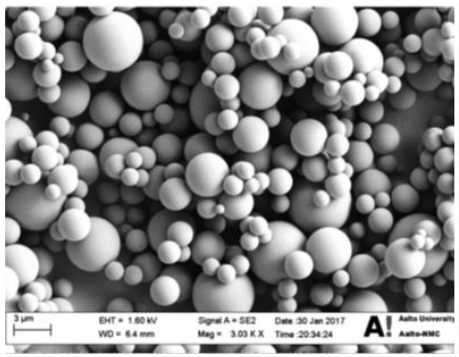

Thymol

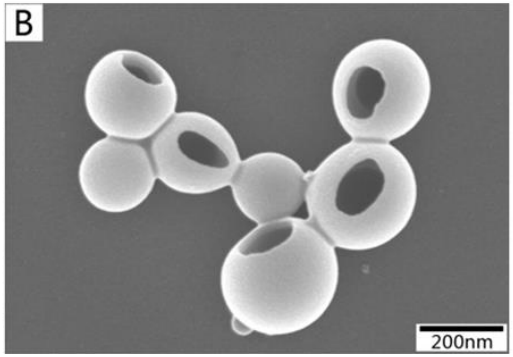


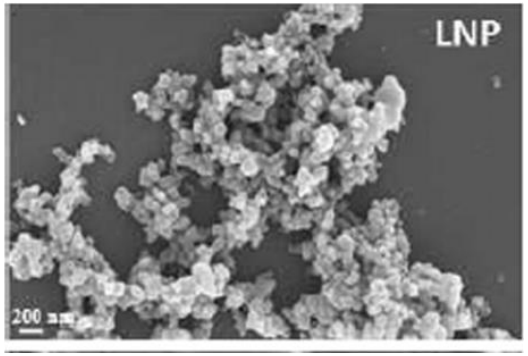

Carvacrol

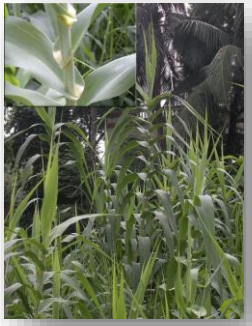
- *Essential oil*
- *Antioxidant agents*
- *Antimicrobial agents*
- *Metal nanoparticles*
- *Silicates*

# BIONANOFILLERS - NANOLIGNINA

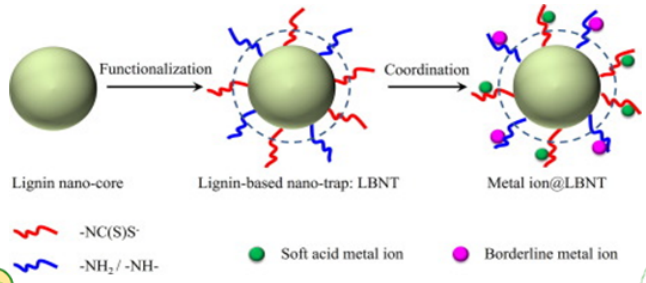



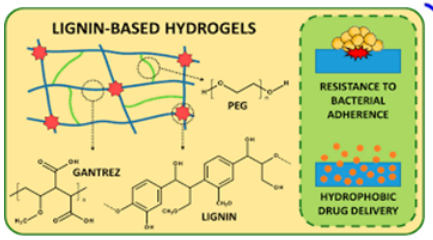


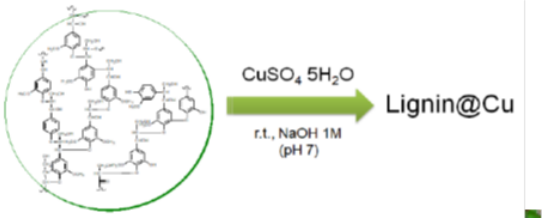



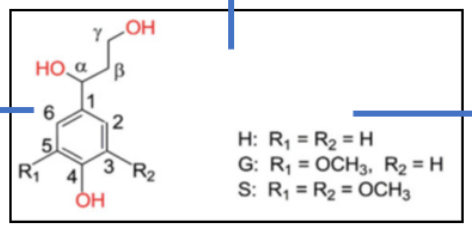
# NANOLIGNINA - APPLICAZIONI

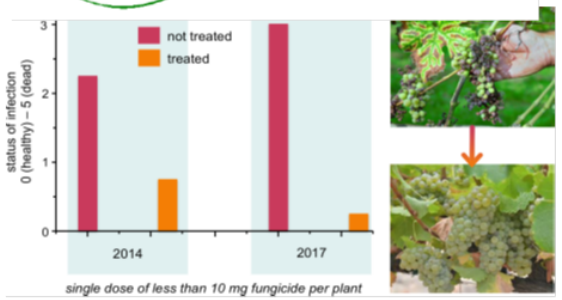




***Environmental remediation***

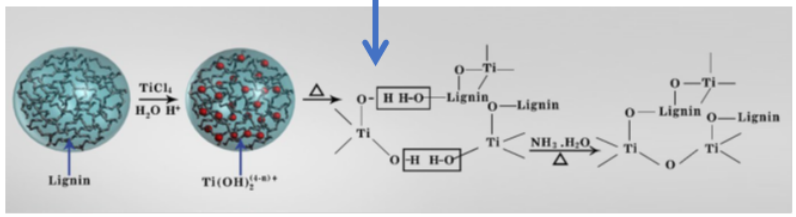


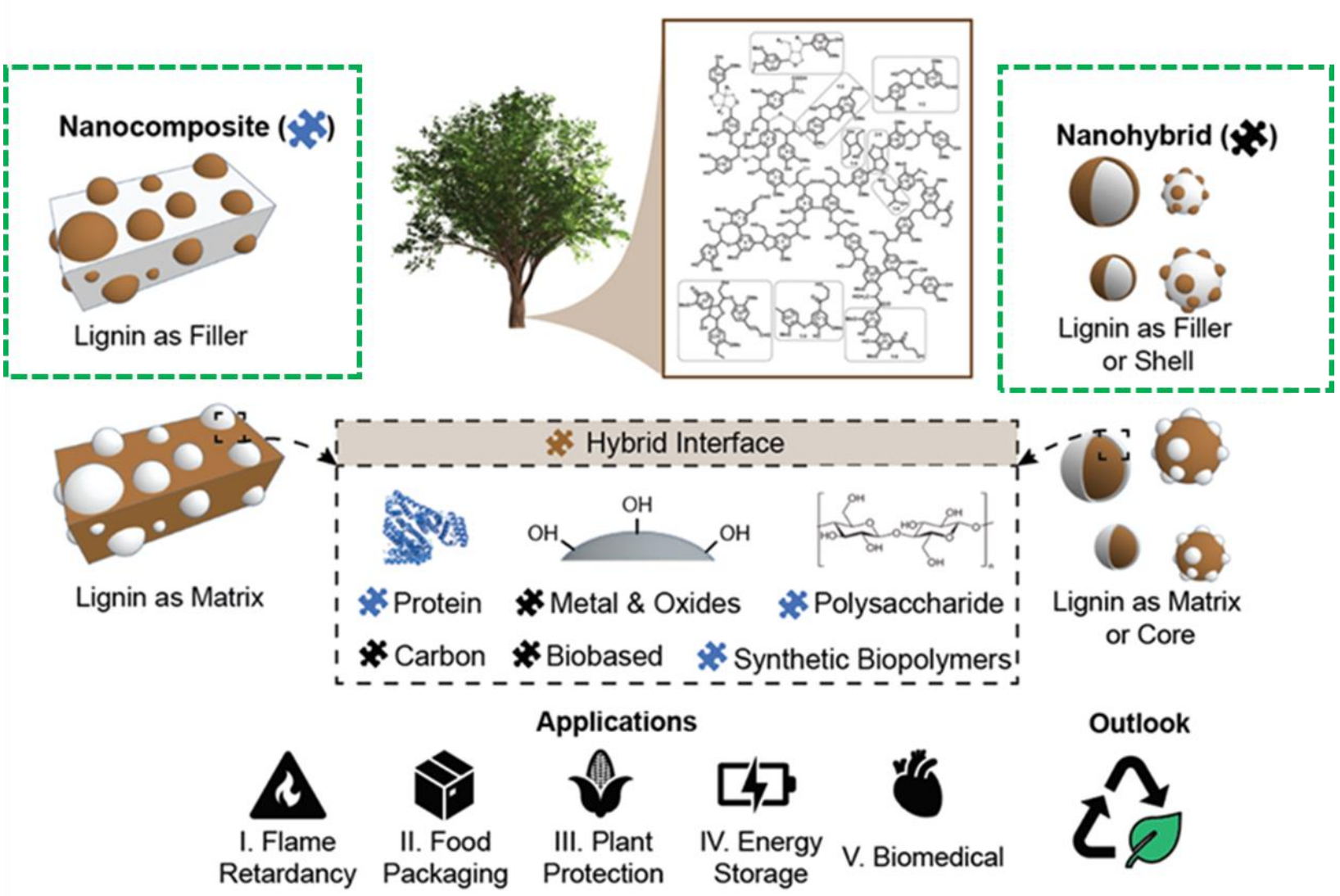

***Antimicrobial/drug delivery***

***Smart Drug Delivery in Crop Protection***

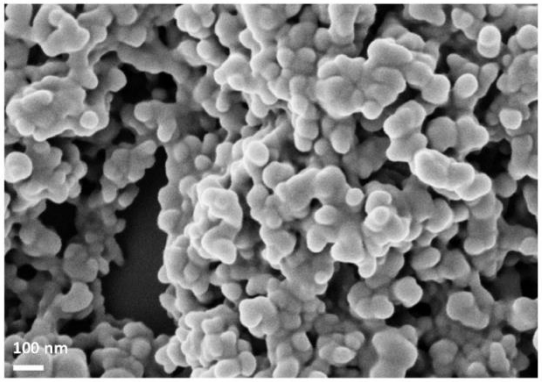


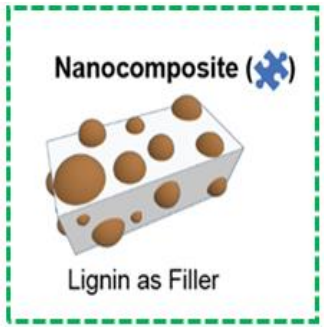

***Lignin-Based Composite Materials for Photocatalysis and Photovoltaics***

# NANOLIGNINA – IBRIDI E NANOCOMPOSITI



# NANOLIGNINA E IBRIDI NANOCOMPOSITI @ UNIPG

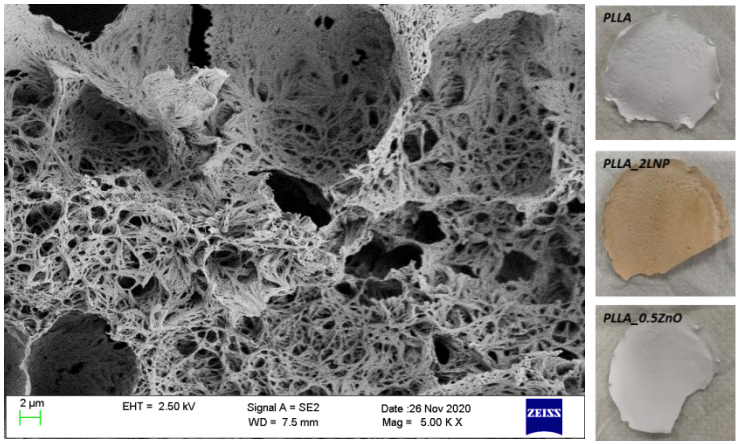



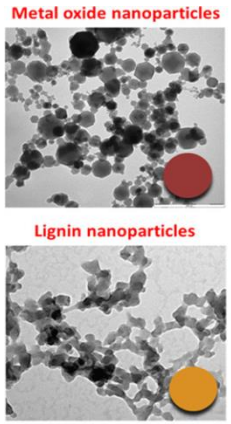

*LNP, ZnO and hybrid ZnO@LNP for:*

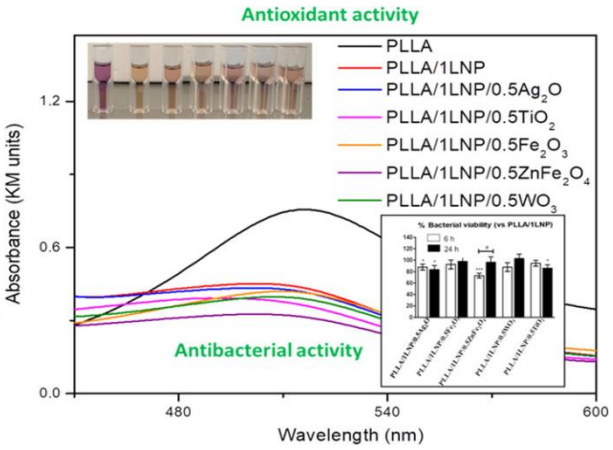
- ***Food packaging*** and ***Biomedical applications*** *(scaffold)*
- ***Seed priming*** *(plant growth)*

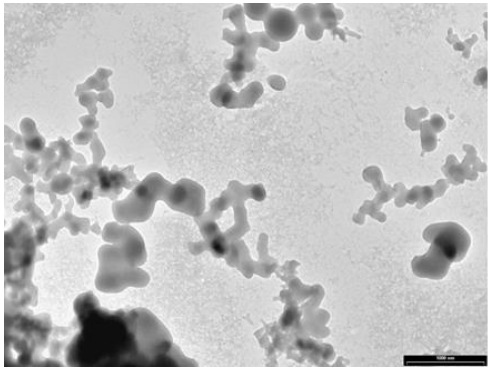
*(4) LNP and metal oxides in PLLA*

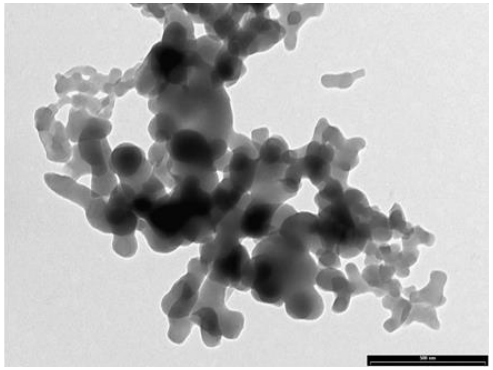
- ***UV resistance***
- *Synergic fillers role* ***(UV, antioxidant, antibacterial)***



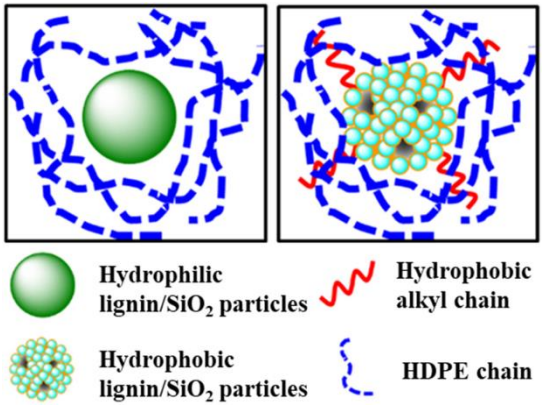



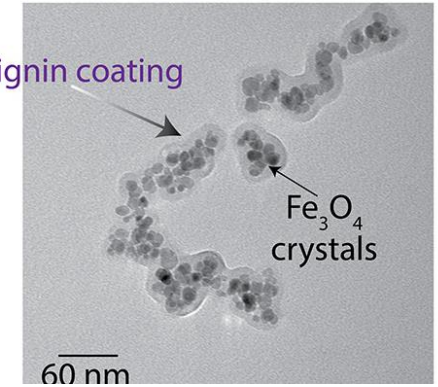




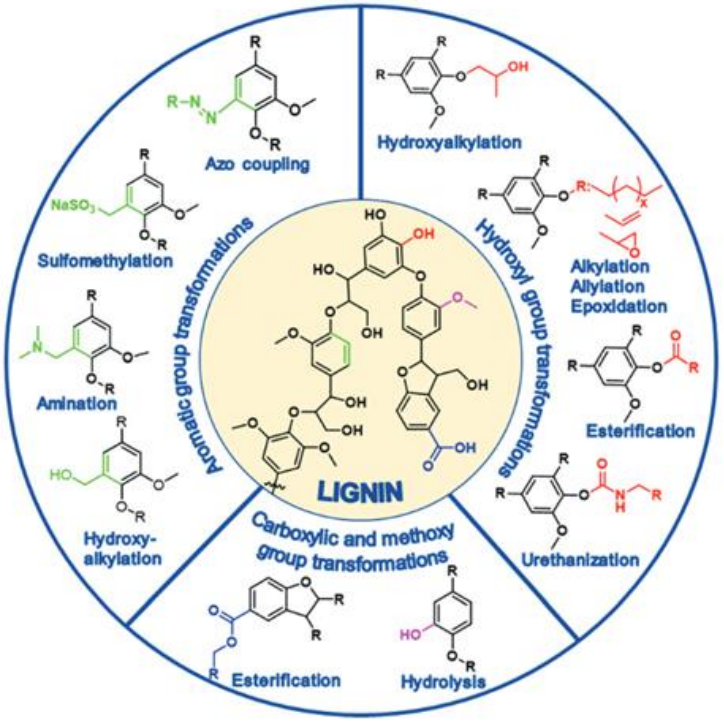
## *Attività in corso*
## *Ibridi Nanolignina/MeO*

- *binders for phenolic resins*
- *Bio-Based sorbents for metal ion recycling*
- *new catalytic materials*

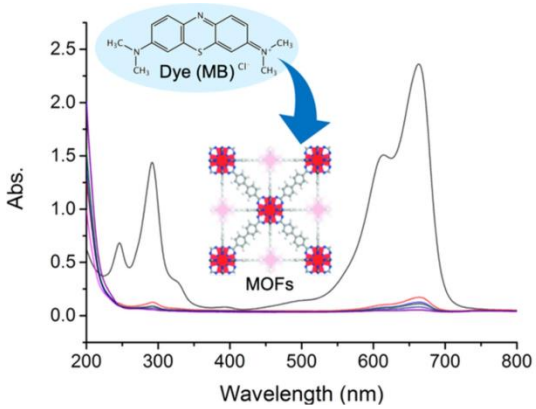


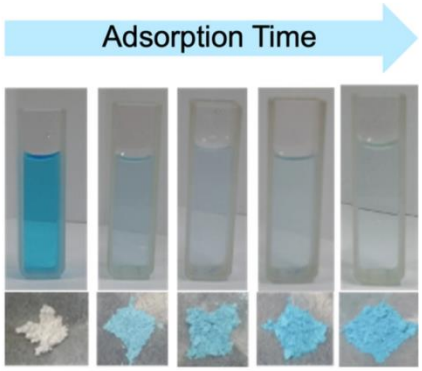







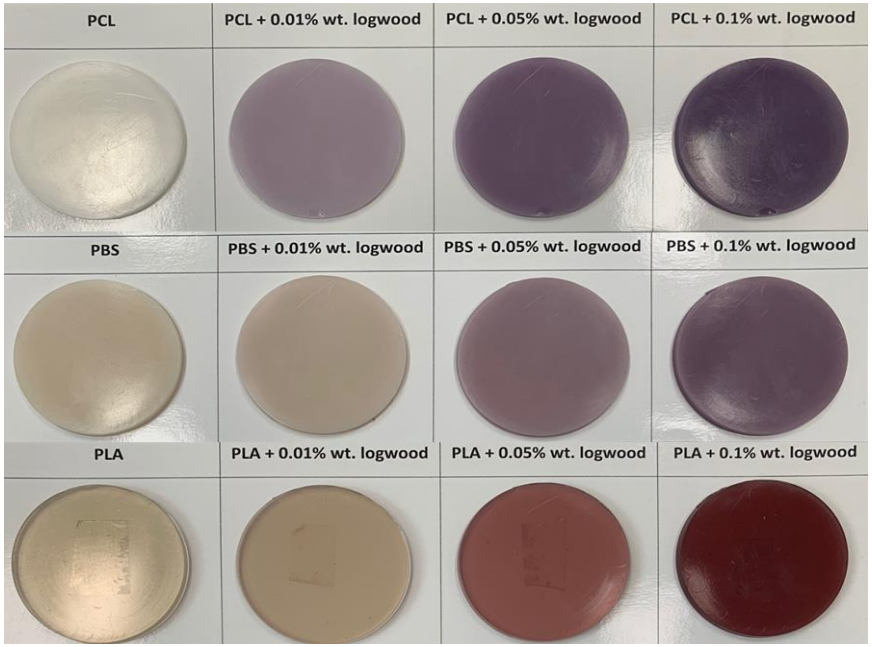

*Dr. Alessandro Di Michele - UNIPG*

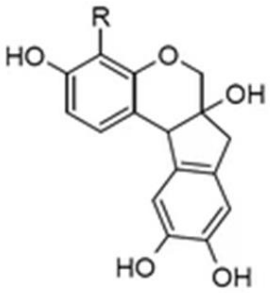


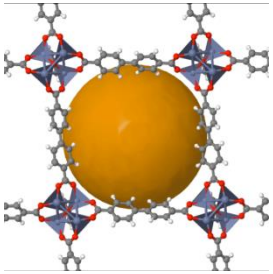

## *Attività in corso*
## *Ibridi Nanolignina e colore*

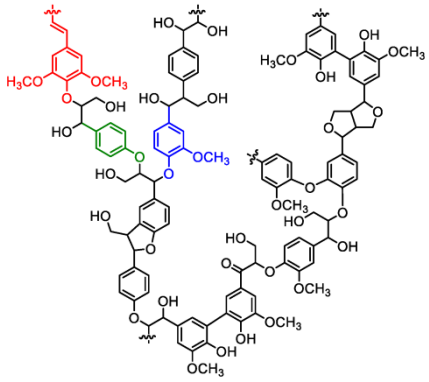
- Water based at $T_{room}$ synthesis of Al MOF
- Lignin intermediate and hybrid natural dye/lignin, thermal stabilization by MOF




*Logwood extract*





*Prof. Loredana Latterini, Dr. Catia Clementi - UNIPG*

- Colouring effect at different % wt. On PCL (low melting), high T melting semicrystalline (PBS) and amorphous PLA

# Materiali a cambio di fase nanostrutturati per solare termico

# Nano Enhanced Phase Change Materials NEPCM

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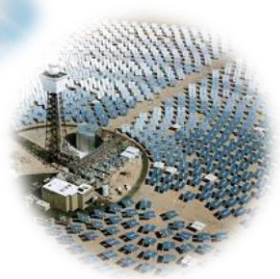
ENEA
Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile

Thermal Energy Storage TES

Concentrating Solar Plants CSP

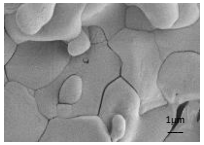
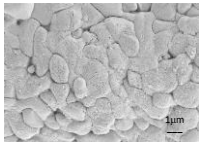
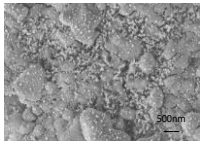
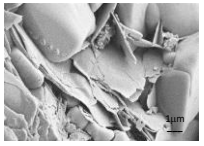
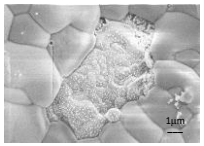
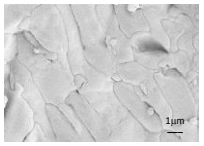
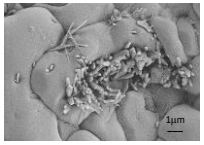
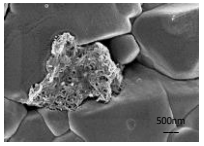


Heat Transfer Fluid HTF

## Nanofillers selection / synthesis

| Sample | Nano Filler (% wt.) | Notes |
|---|---|---|
| Solar Salt | - | $NaNO_3$ / $KNO_3$ 60/40 % wt. |
| SS_02Al | 1% Cok 84 | Cok 84 – Evonik, Nano Particles $SiO_2/Al_2O_3$ ,mix ratio 8:2 |
| SS_04Al | 1% SIRAL 40 | Siral 40 – Sasol, Nano Pareticles of hydrated silicon and aluminum oxides, mix ratio 6:4 |
| SS_06Al | 1% Disperal P2 | Disperal P2 – Sud Chemie, Nano sized boehmite $SiO_2/Al_2O_3$ ratio 4:6 |
| SS_08Al | 0.1% A200 - 0.1% A300 - 0.8% Al2O3 | Aerosil 200 - Aerosil 300 – Evonik, Nanometric hydrophilic fumed silicas with BET area 200 - 300 m2/g respectively - **UNIPG post-synthesis** Al2O3 Nano Particles – **UNIPG synthesis** |
| SS_1Al | 1% $Al_2O_3$ | $Al_2O_3$ Nano Particles synthesized by aluminum nitrate nona-hydrate in a melt of solar salts - **UNIPG synthesis** |
| SS_Cu | 1% EC_Cu_OFE | Copper Nano Particles EC_Cu_OFE – Numanova - **UNIPG post-synthesis** |
| SS_Cu12Sn | 1% EB_CuSn12 | Bronze Nano Particles EB_CuSn12 – Italeaf- **UNIPG post-synthesis** |
| SS_CATAS | 1% Ca(BDC) | MOF - Calcium Terephthalate Anhydrous Salts (CATAS) – **UNIPG synthesis** |
| SS_ALTAS | 1% MIL 53 (Al) | MOF - Aluminum Benzene Di-Carboxylates Salts (ALTAS) – **UNIPG synthesis** |
| SS_05CNT | 0.5% MWCNT | Graphistrength C100 – Arkema, Multi Wall Carbon Nano Tubes (MWCNT) |

## NEPCM morphology

| Sample | FESEM 25-50 KX | | Sample |
|---|---|---|---|
| Solar Salt (SS) |  |  | SS_Cu12Sn |
| SS_0.2Al |  |  | SS_CATAS |
| SS_0.8Al |  |  | SS_ALTAS |
| SS_Cu |  |  | SS_05CNT |

# Nano Enhanced Phase Change Materials NEPCM

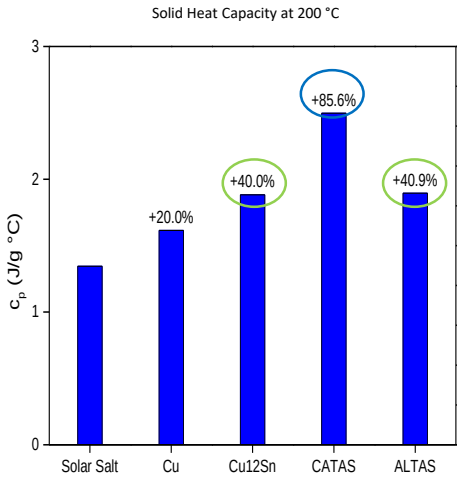
A.D. 1308 unipg
UNIVERSITÀ DEGLI STUDI DI PERUGIA

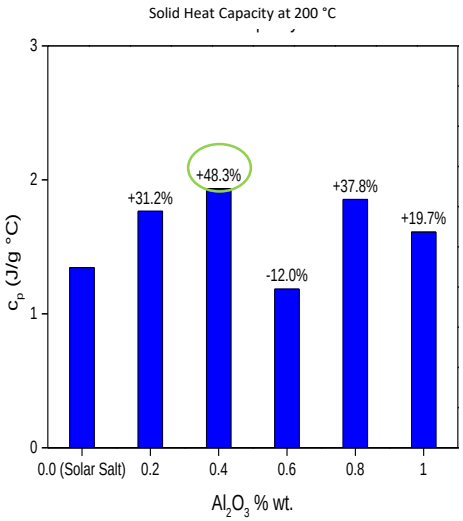
NEPCM Suitable both as
- LHSM Latent Heat Storage Media
- HTF Heat Transfer Fluid

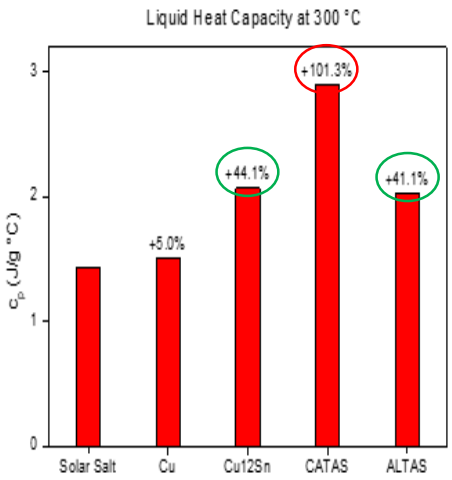
ENEA
Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile

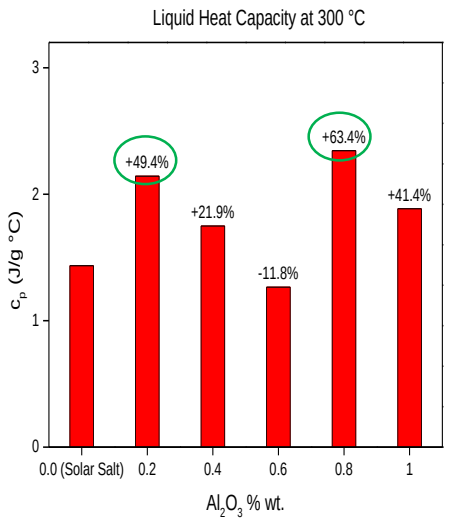
Solid $C_p$ @200 °C
Improvement
SS_CATAS **+85.6%**
SS_ALTAS, SS_Cu12Sn, SS_04Al **> +40%**

Liquid $C_p$ @300 °C
Improvement
SS_CATAS **+101.3%**
SS_ALTAS, SS_Cu12Sn, SS_02Al, SS_08Al, SS_1Al, **> +40%**



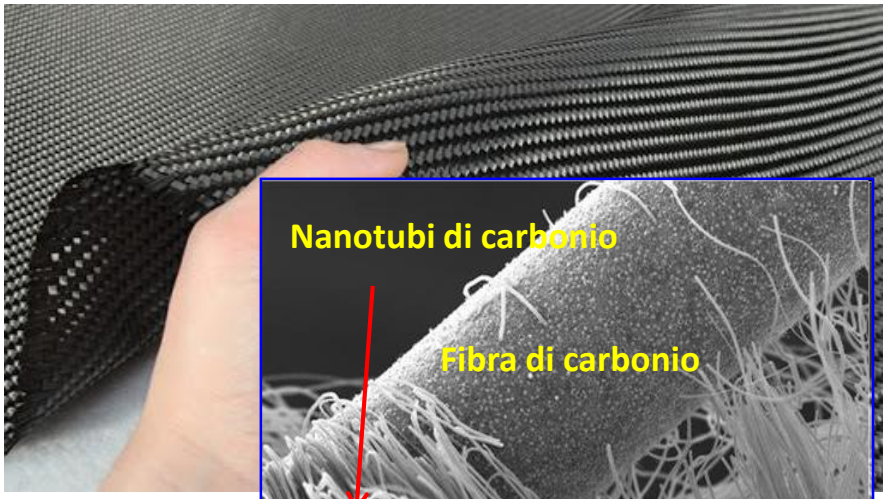



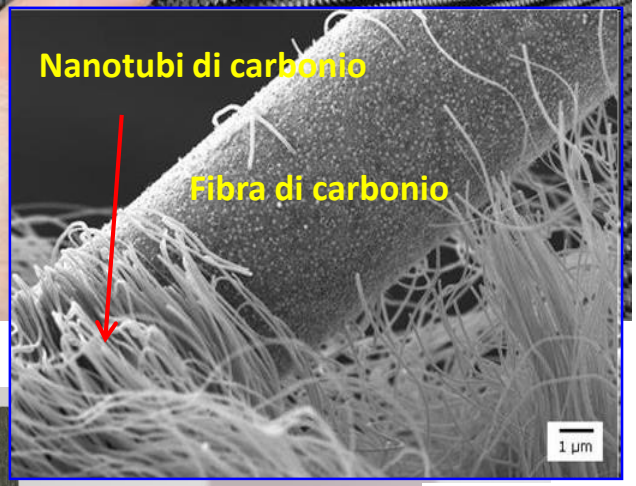



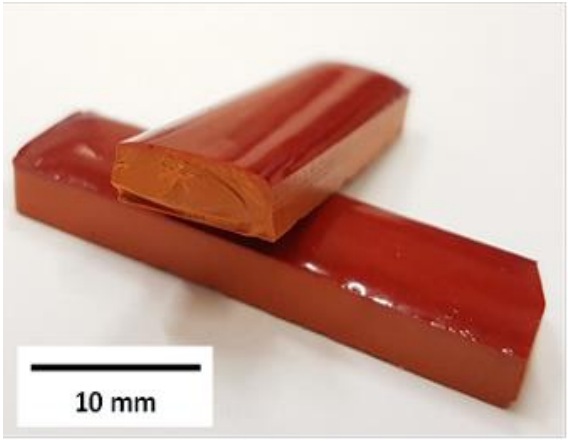



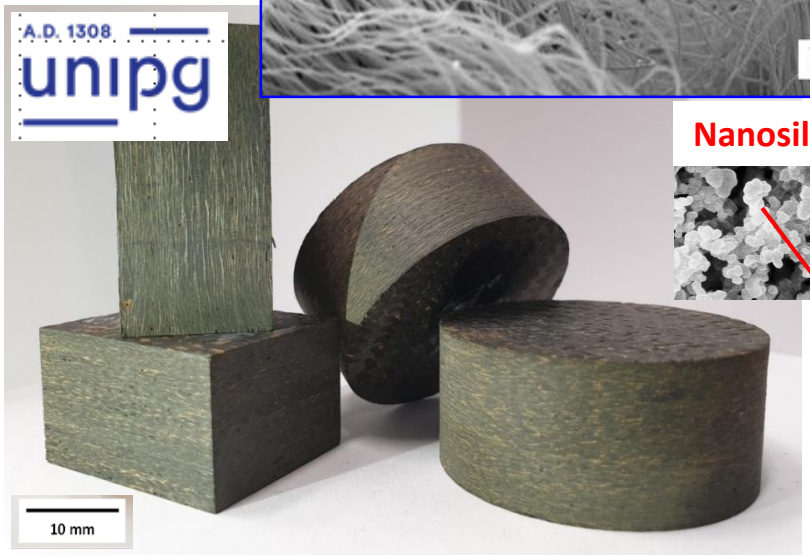
# Materiali nanostrutturati per alte temperature e per l'aerospazio

# Materiali compositi carbonio/fenolica nano-strutturati

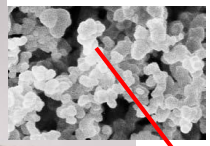


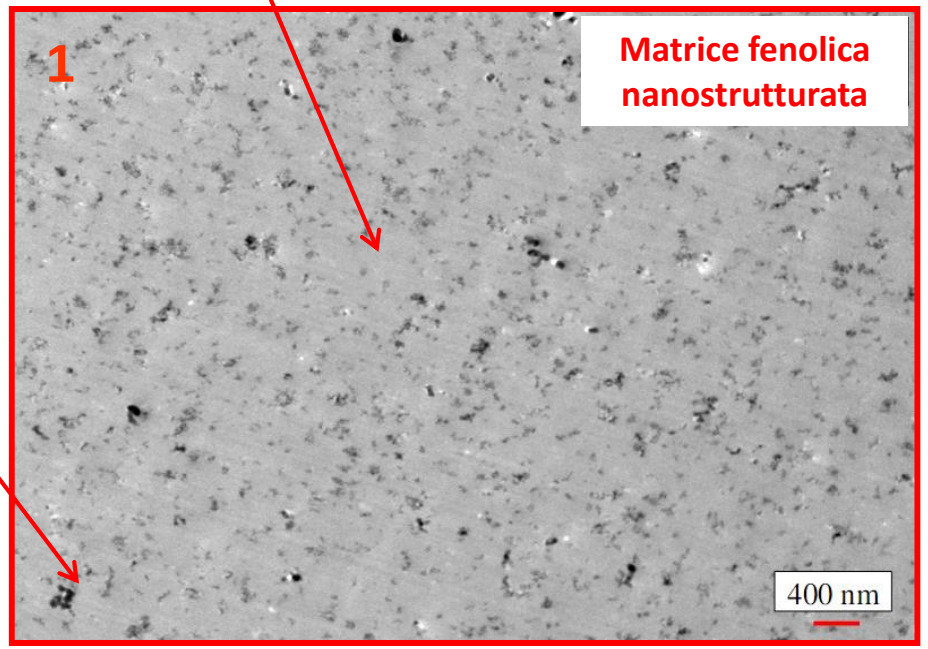



Nanosilice

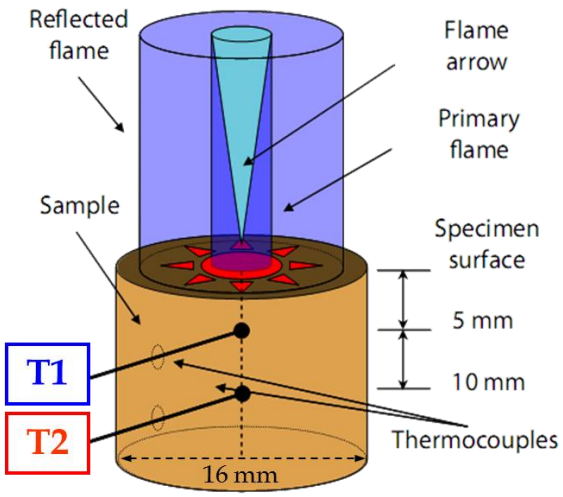


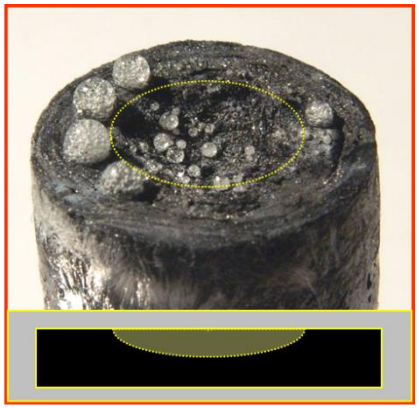


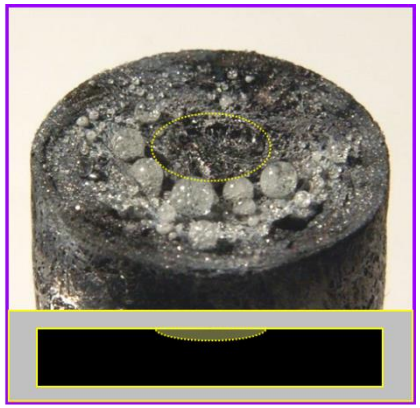


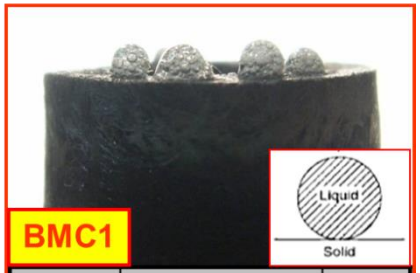

materiali nanocompositi

# Compositi nano-strutturati con nanosilice - test alla torcia



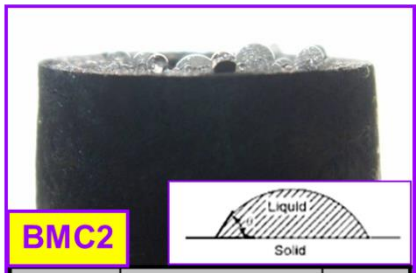







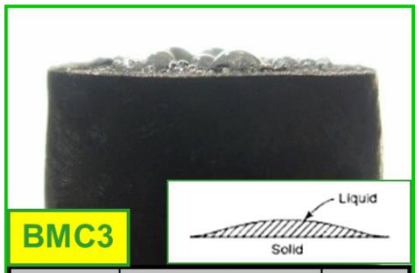

BMC1

| Resin | E-Glass CS | NS |
|---|---|---|
| 40% | 60% | 0% |




BMC2

| Resin | E-Glass CS | NS |
|---|---|---|
| 38% | 60% | 2% |



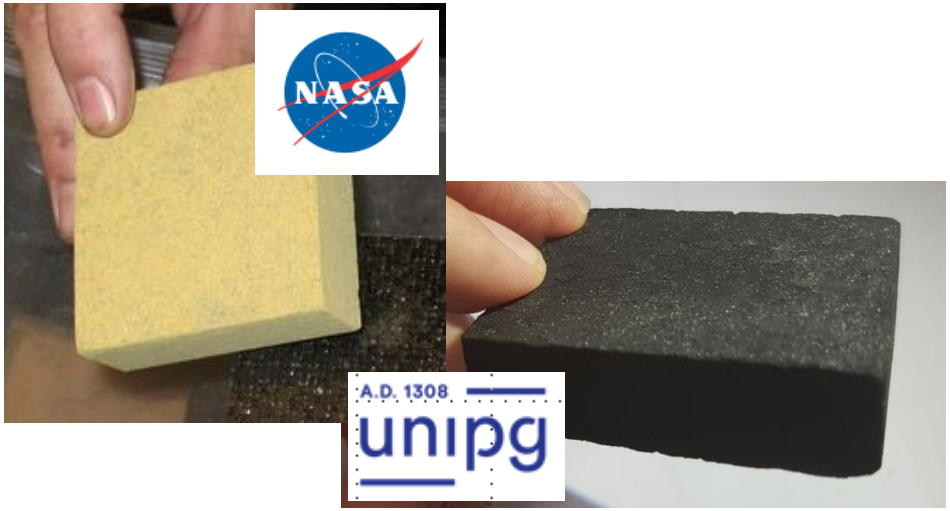

BMC3

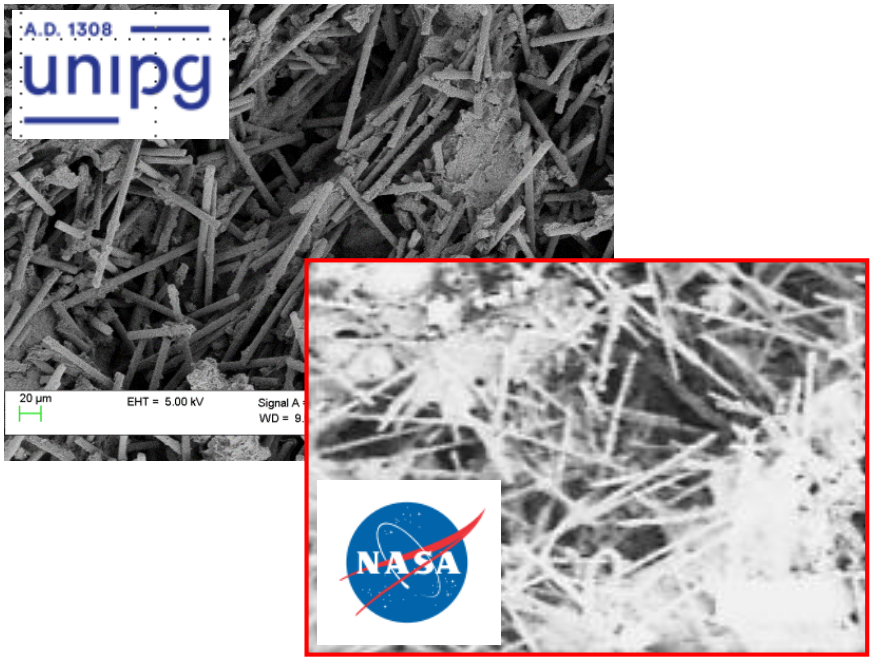
| Resin | E-Glass CS | NS |
|---|---|---|
| 32% | 60% | 8% |

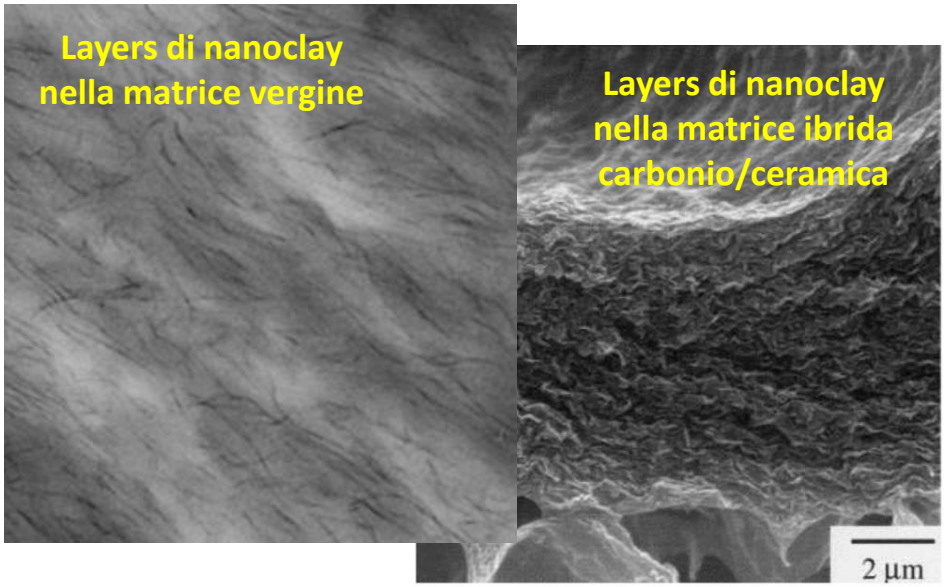
| Nanosilica content [%] | T1max [°C] | T2max [°C] | W [mg] | Wn [%] |
|---|---|---|---|---|
| 0 | 581.1 ± 7.9 | 223.1 ± 2.2 | 261.5 ± 7.1 | 100 ± 2.7 |
| 2 | 555.2 ± 11.6 | 217.4 ± 14.0 | 257.8 ± 8.2 | 98.6 ± 3.2 |
| 8 | 534.6 ± 8.3 | 208.1 ± 13.3 | 218.9 ± 12.5 | 83.7 ± 4.8 |

# Phenolic Impregnated Carbon Ablators nano-strutturati - produzione

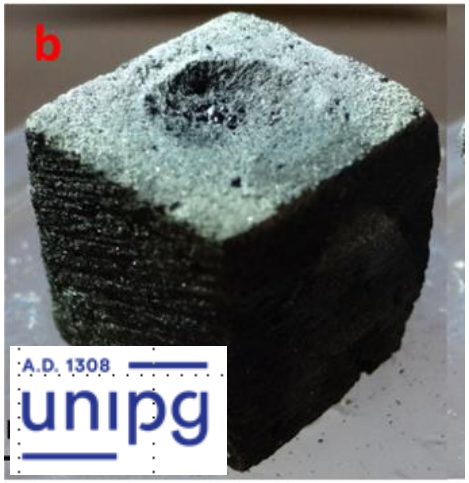
| Formulation | Nanoclay/MWCNT ratio | Density ($g/cm^3$) |
|---|---|---|
| PICA 1 | 1/1 | 0.36 ± 0.01 |
| PICA 2 | 2/1 | 0.47 ± 0.01 |
| PICA 3 | 1/2 | 0.29 ± 0.01 |

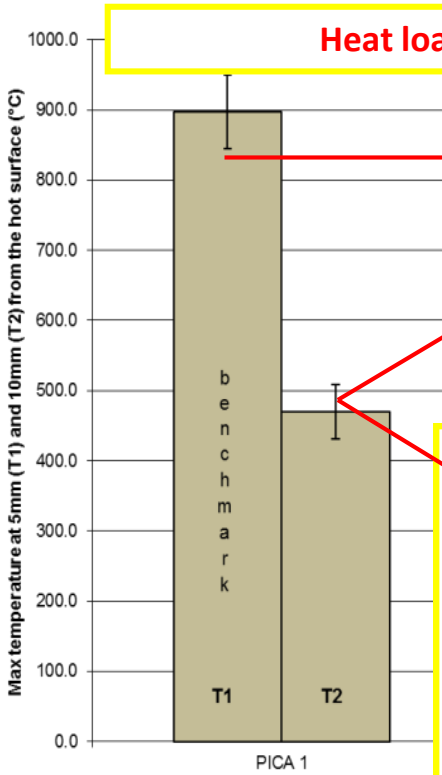


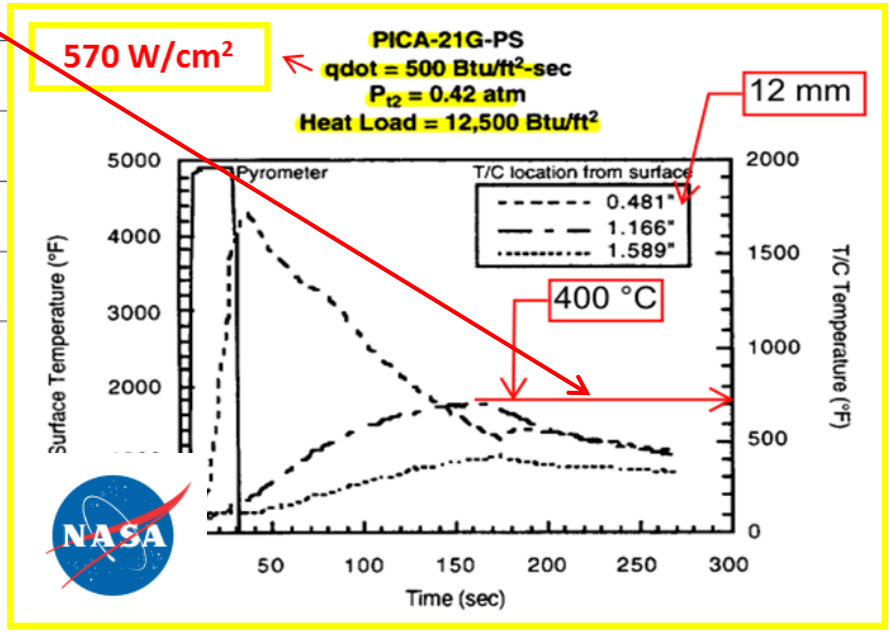



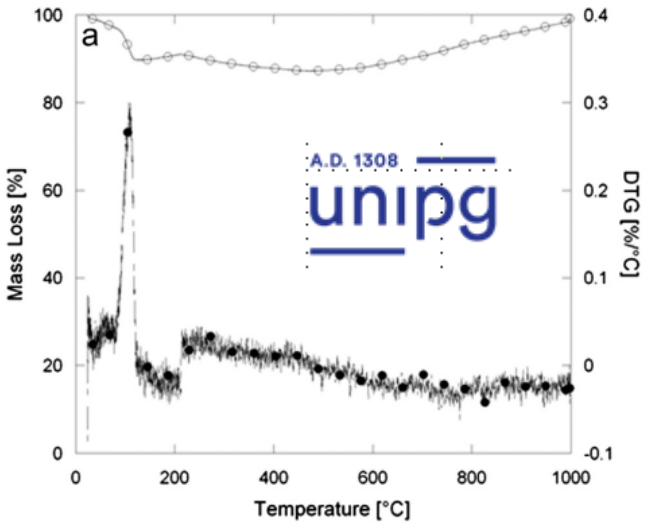
# Phenolic Impregnated Carbon Ablators nano-strutturati - test avanzato

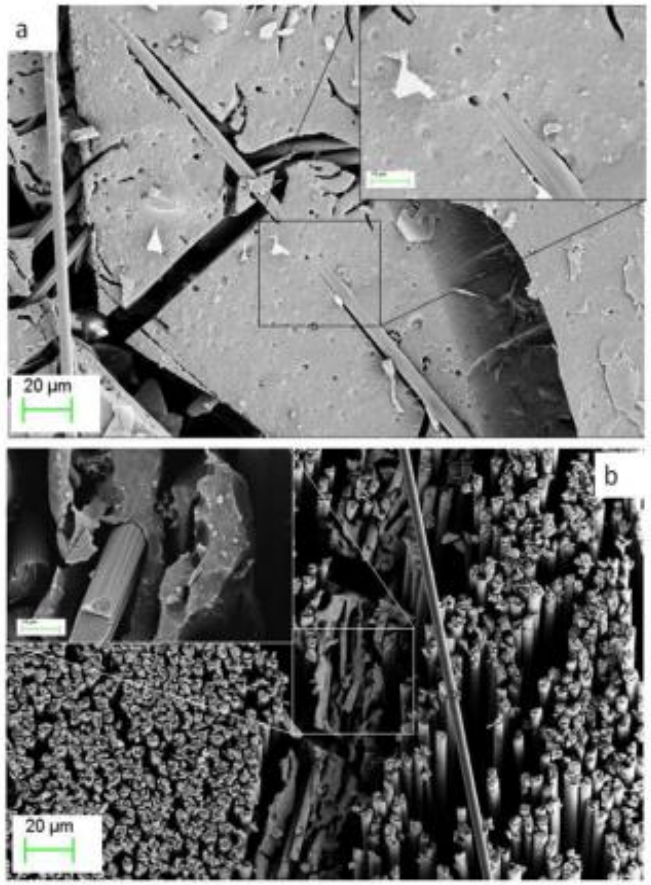


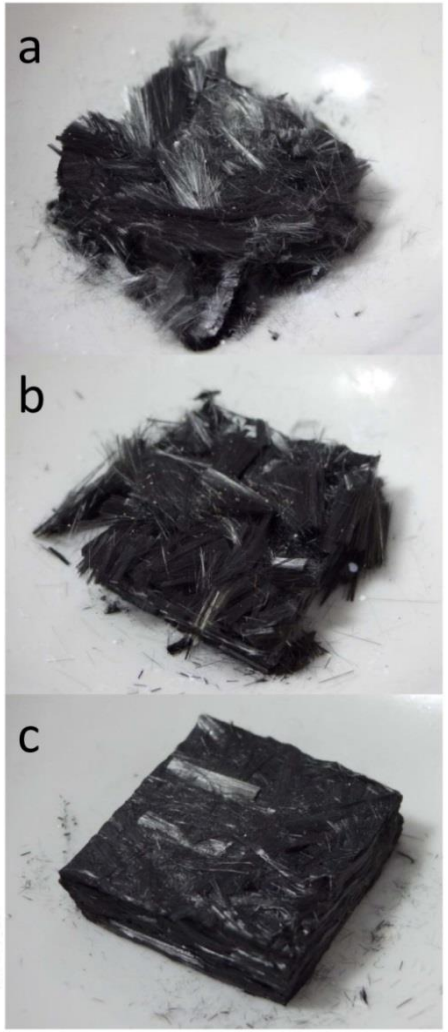



# Nano-carburo di boro come adesivo ad alta temperatura



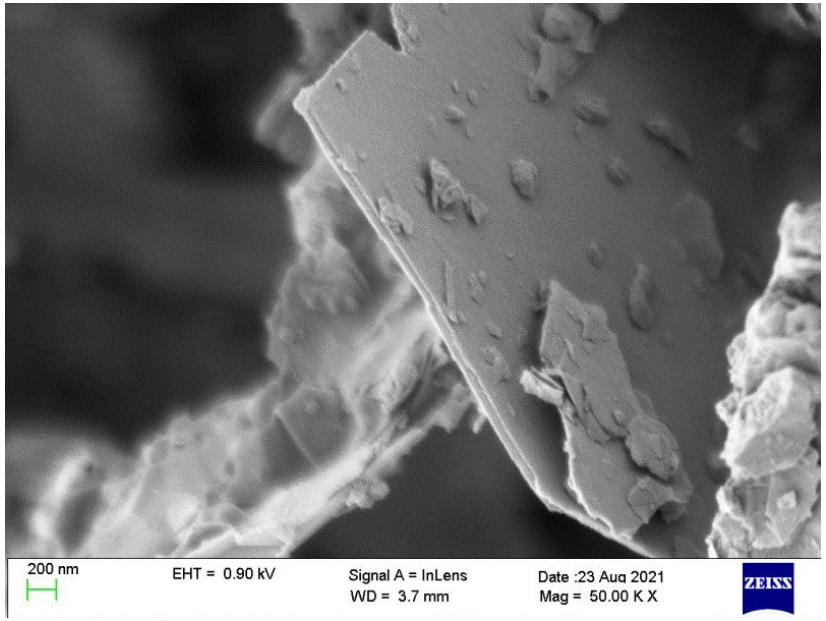

$B_4C\ (s) + 4O_2\ (g) \rightarrow 2B_2O_3\ (l) + CO_2\ (g)$

$B_4C\ (s) + 6CO\ (g) \rightarrow 2B_2O_3\ (l) + 7C\ (s)$

$B_4C\ (s) + 6H_2O\ (g) \rightarrow 2B_2O_3\ (l) + C\ (s) + 6\ H_2\ (g)$

# Nanocompositi a base di Grafene

# Grafene - Applicazioni




- Proprietà elettriche e termiche
- Proprietà meccaniche
- Peso Specifico

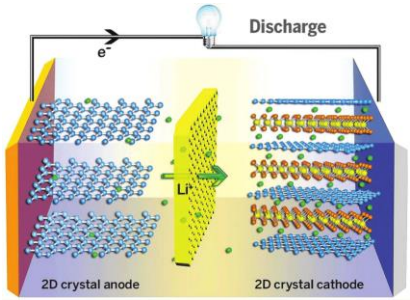
## Nanocompositi Polimerici

Aumento Proprietà Meccaniche
Aumento proprietà Elettriche
Tribologiche e di barriera

## Energy Storage

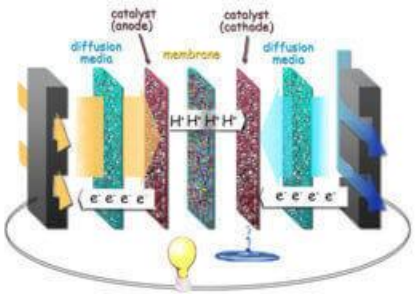
**Batterie al grafene**

Elevata capacità e
velocità di ricarica

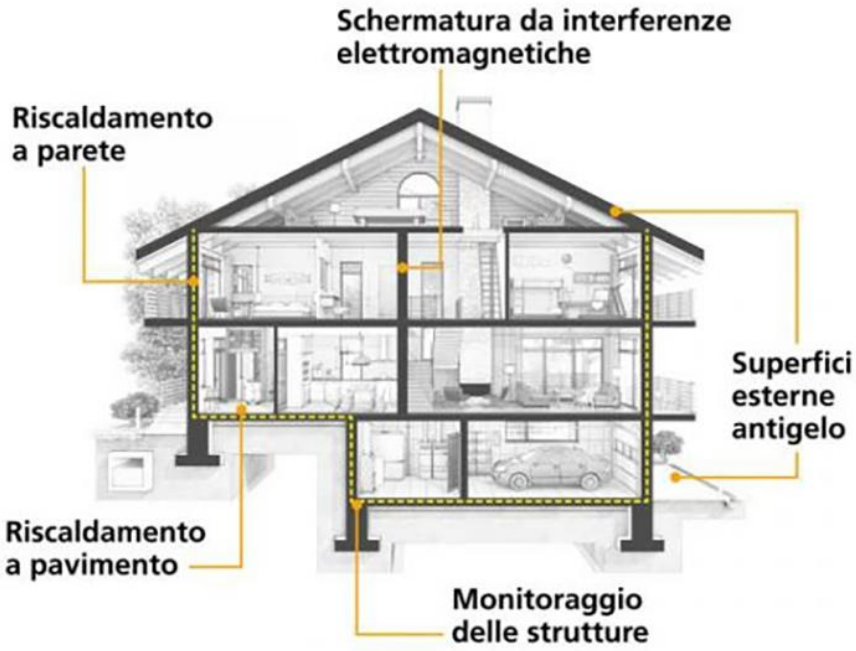



**Fuel Cell al grafene**

Elettrodi al grafene
anche nelle celle
a combustibile



# Grafene - Applicazioni




## Calcestruzzi al Grafene

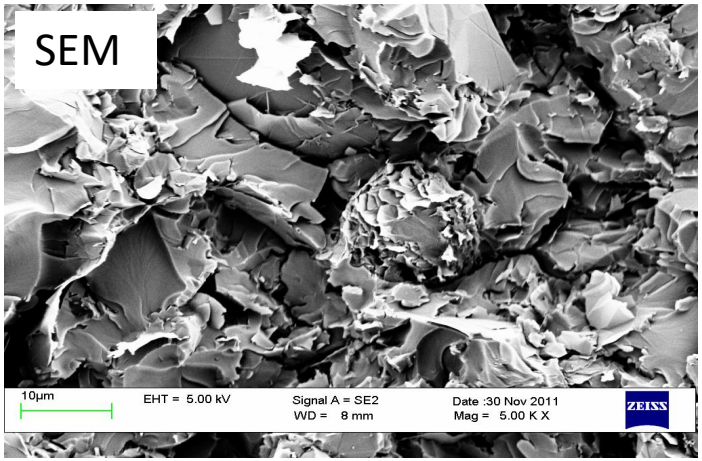
Incremento delle proprietà meccaniche (riduzione armature e quantità cemento – migliore impatto ambientale)

Conduce il calore (sistemi di riscaldamento radianti)

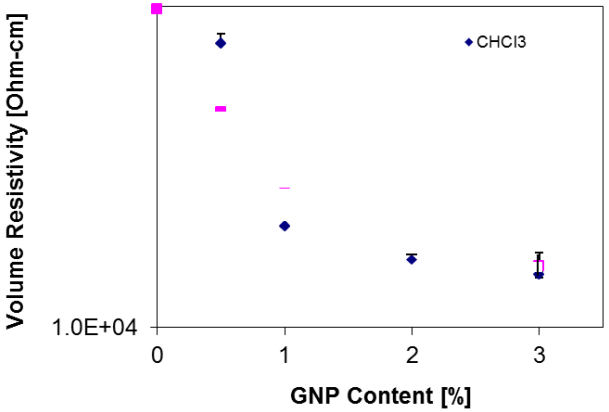
Schermatura elettromagnetica

Conduce elettricità (possibili impieghi nel monitoraggio strutture)

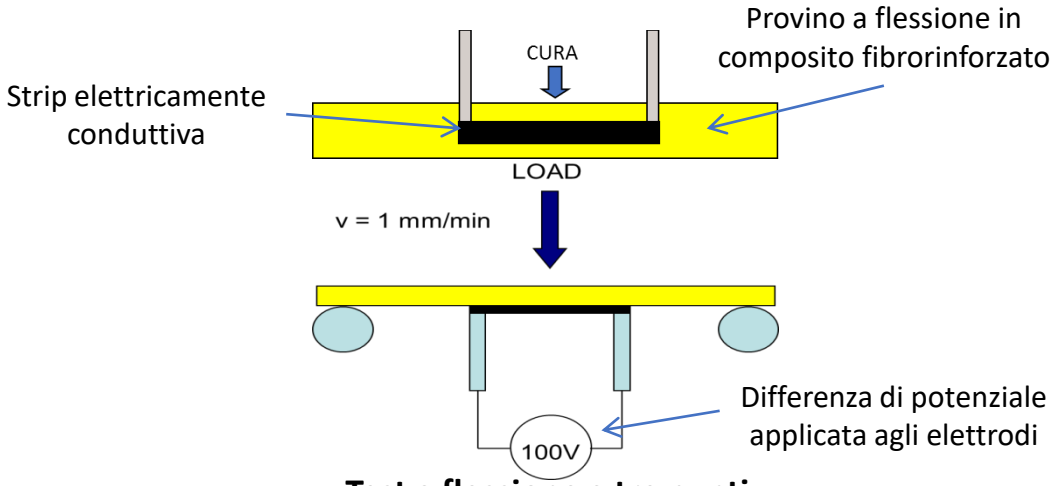
# Nanocompositi grafene/epossidica per la realizzazione di sensori per il monitoraggio di deformazioni e rilevamento di danni



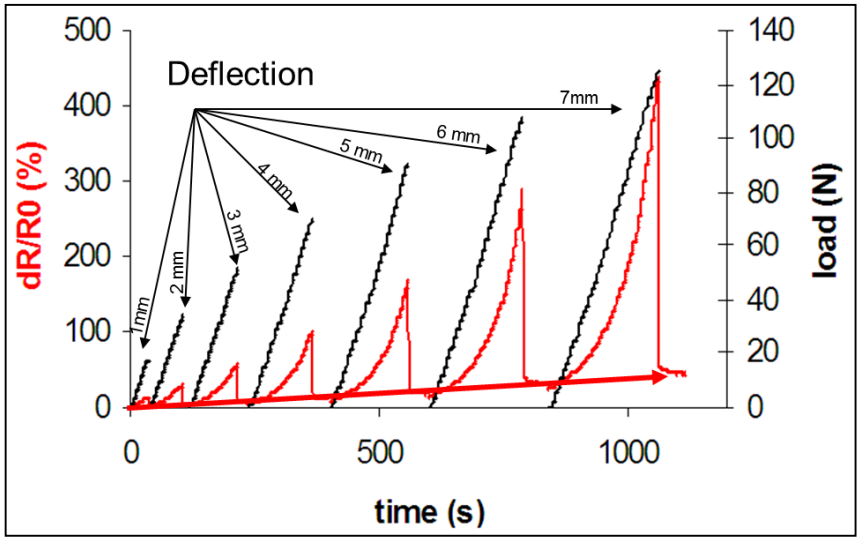

**Grafene (Cheap Tube Inc) in Epossidica**




**Soglia percolativa (2 wt%)**




**Test a flessione a tre punti**




**Variazione della resistenza elettrica nel tempo a diversi livelli di deflessione**