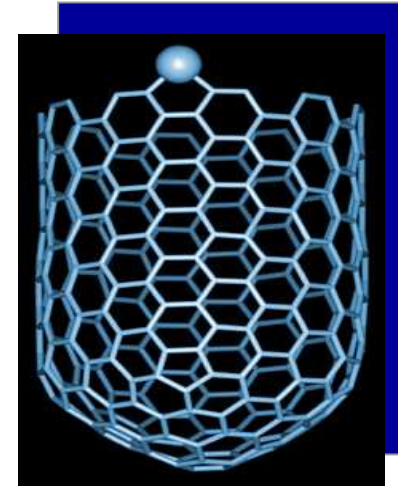


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APPLICAZIONE DI CNT IN NANOCOMPOSITI POLIMERICI: CASI DI STUDIO

Prof. Michele MODESTI

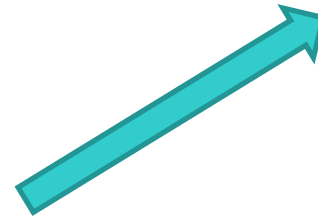
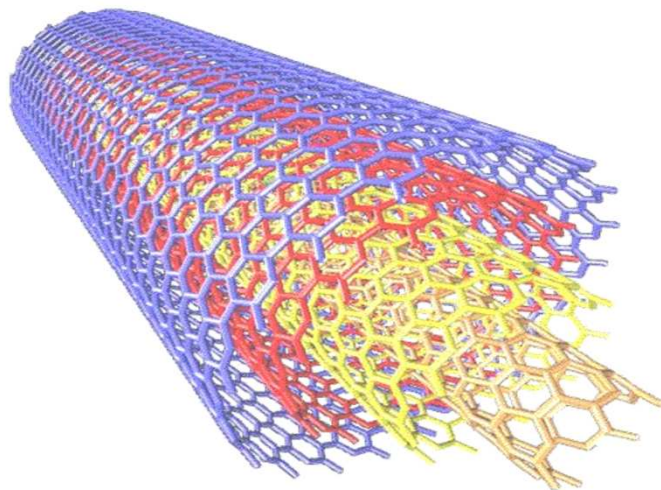
Dipartimento di Ingegneria Industriale - Università di Padova



Dipartimento Ing. Chimica Giulio Natta – Politecnico di Milano, 16 Maggio 2013



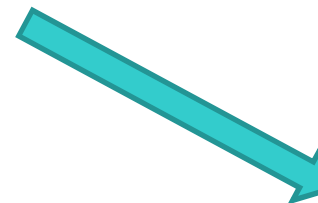
DII: ATTIVITA' R&D CON CNTs



PC/ABS-CNTs:
Il settore automotive



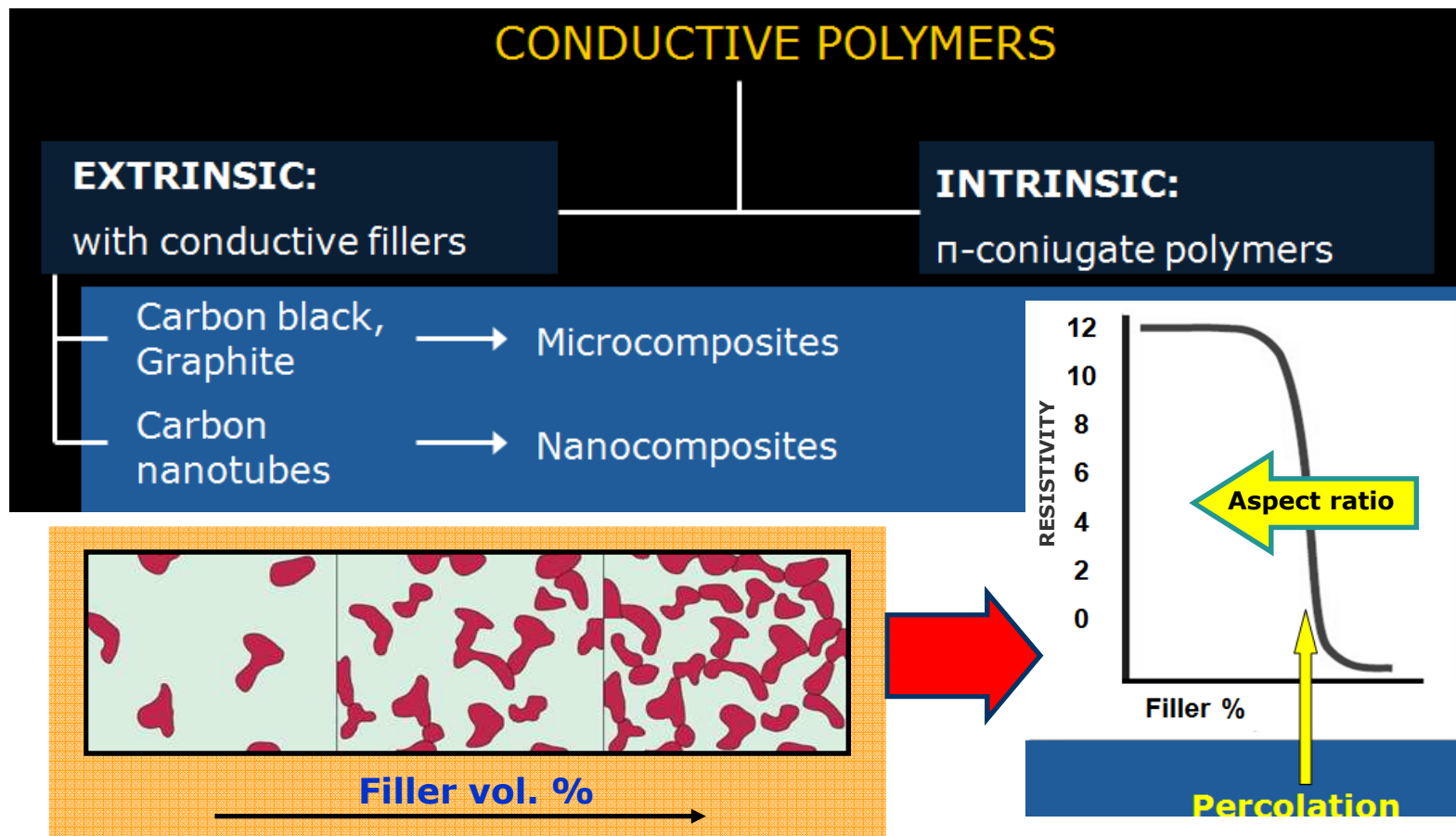
PP-CNTs:
Masterbatch ad elevate
prestazioni



ELETTROSPINNING:
Membrane nanostrutturate
elettricamente conduttive



CONDUCTIVE POLYMER COMPOSITES (CPC)





Caso studio #1

Cromatura di componenti per automotive

NON CONDUCTIVE POLYMERS

Chemical treatments

| |
|---------------------|
| PRE-MORDANTING |
| WASHING |
| MORDANTING |
| RECOVERY |
| WASHING |
| NEUTRALIZER |
| DROPPER |
| ACTIVATOR |
| WASHING |
| ACCELERATOR |
| WASHING |
| CHEMICAL Ni (or Cu) |
| WASHING |
| NICKEL STRIKE |
| WASHING |



AUTOMOTIVE



Electrolytic treatments

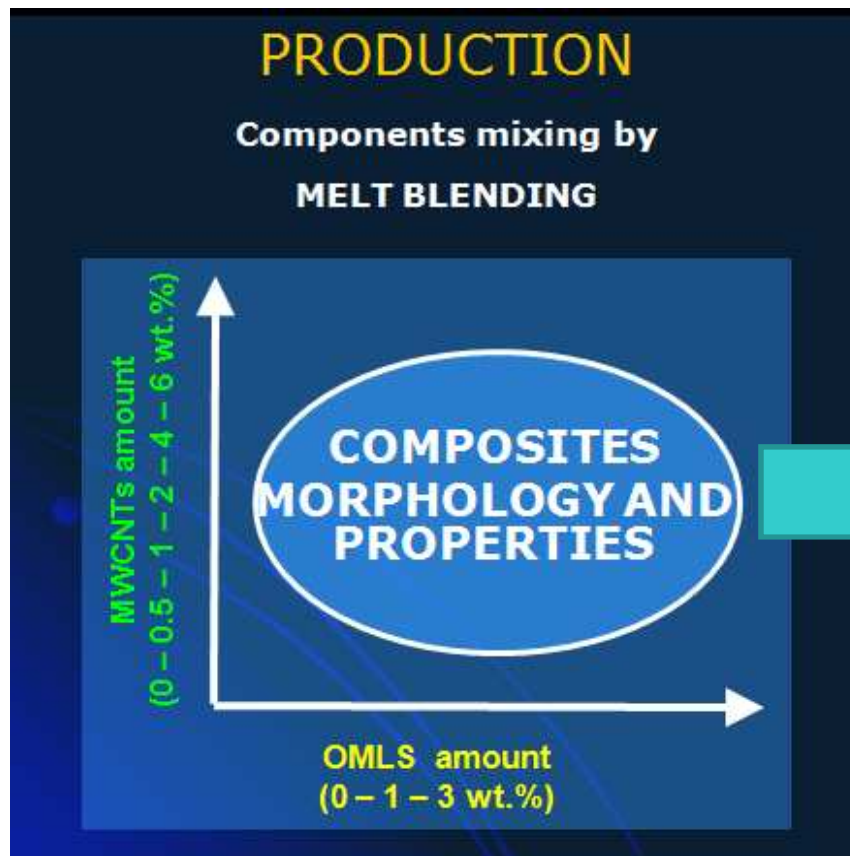
| |
|-------------------------|
| DRYING |
| WASHING |
| RECOVERY |
| CHROME |
| PRE-CHROME |
| WASHING |
| MICROCRAPORES NICKEL |
| MICROCRACKED NICKEL |
| WASHING |
| SATINY Ni |
| WASHING |
| SHINY Ni |
| WASHING |
| SEMI-SHINY Ni |
| ACTIVATION |
| WASHING |
| ACID COPPER |

CONDUCTIVE POLYMERS



Caso studio #1

Scopo del lavoro



CHARACTERIZATION

Electric properties

Mechanical properties

Thermal properties

Raman spectroscopy

Morphology



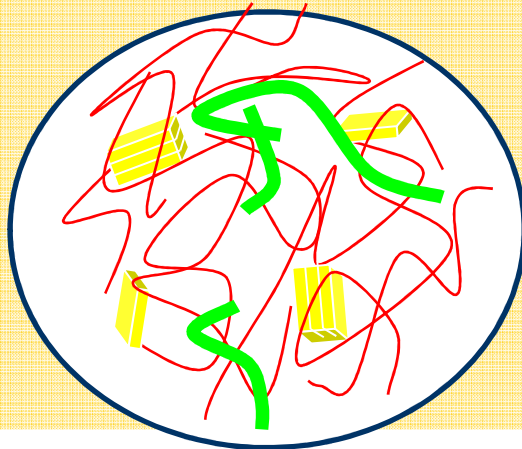
Caso studio #1

Materie prime

POLYMER: Blend PC/ABS (45:55)

BAYBLEND T45, Bayer Material Science

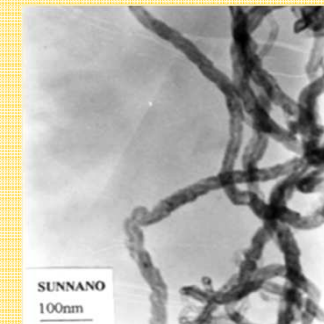
MVR 260°C, 5 kg = 12 cm³/10'



CNTs: MWCNTs (CVD) 0.5 to 6.0 wt%

Sun Nano Co. Ltd. – PRC

- Carbon vapor deposition (CVD)
- >90% purity (after purification)
- average diameter of 10-30 nm
- average length of 1-10 μm.



OMLS: SYNTHETIC FLUORO MICA + 3-N-OCTYL, 1-METHYL AMMONIUM CHLORIDE

SOMASIF MTE, CO-OP Chem.– JP: 1 and 3 wt%

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PC/ABS-CNTs: PROCESSO

PC - ABS

GRINDING

OMLS

DRY BLEND

MWCNTs

TWIN SCREW EXTRUDER
Melt temp.=260°C, screws speed=100rpm

**PC/ABS/MWCNT/OMLS
PELLETS**

INJECTION MOULDING

COMPRESSION MOULDING

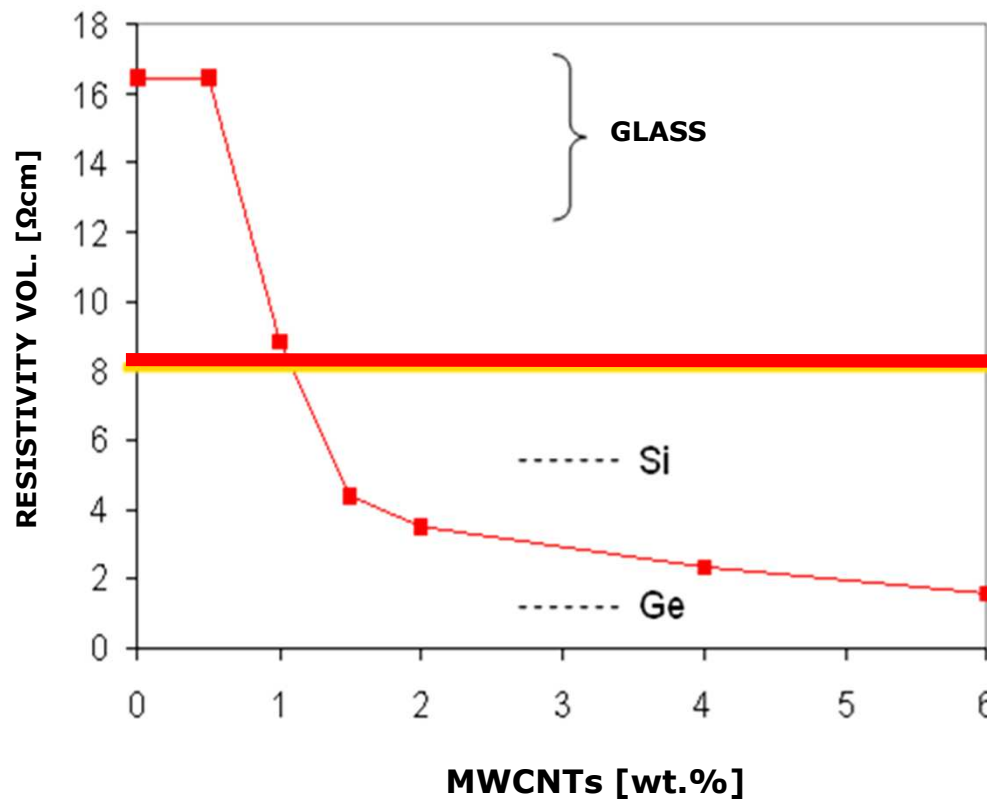
Specimens for physical and
morphological characterization

Specimens (thin disk) for
electrical characterization



Caso studio #1

PC/ABS-CNTs: PROPRIETA' ELETTRICHE



Electrometer:
Keithley 8009
Samples: disks with
60 mm diameter and
0.4 to 0.6 mm
thickness

INSULATORS



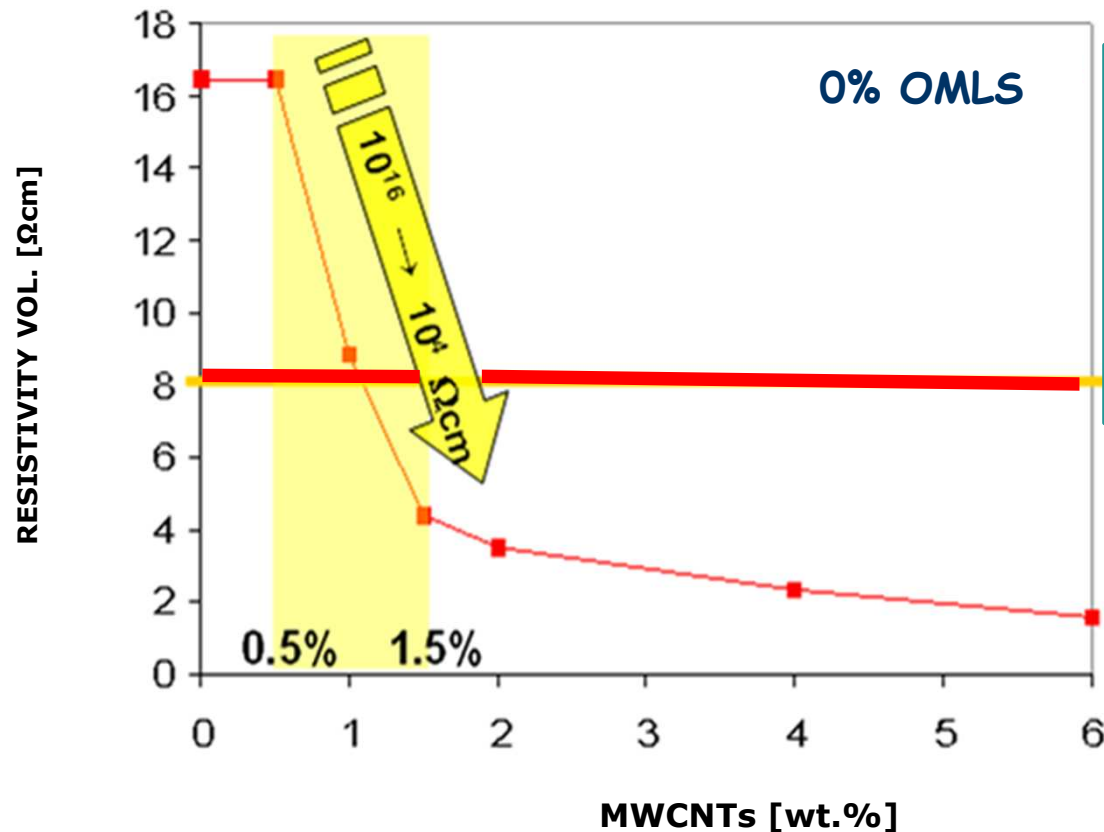
Electrometer:
Keithley DMM 2000
Samples: strips with
dimensions of 50x10
mm²

SEMICONDUCTORS



Caso studio #1

PC/ABS-CNTs: PROPRIETA' ETTRICHE



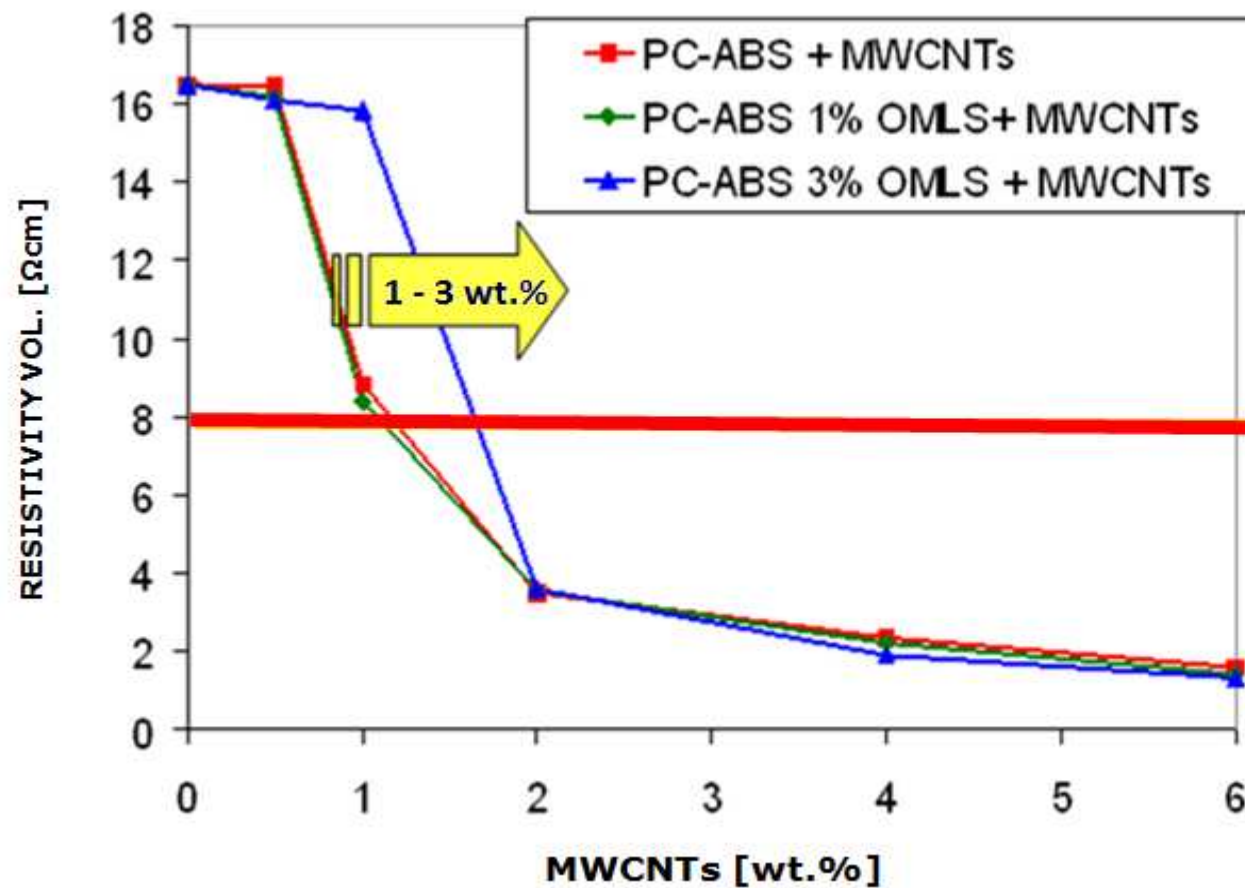
Sotto lo 0.5 % di MWCNTs, i nanocompositi si comportano come isolanti elettrici, mentre sopra 1.5-2.0 % essi diventano elettricamente conduttivi.

Caso studio #1



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PC/ABS-CNTs: PROPRIETA' ELETTRICHE



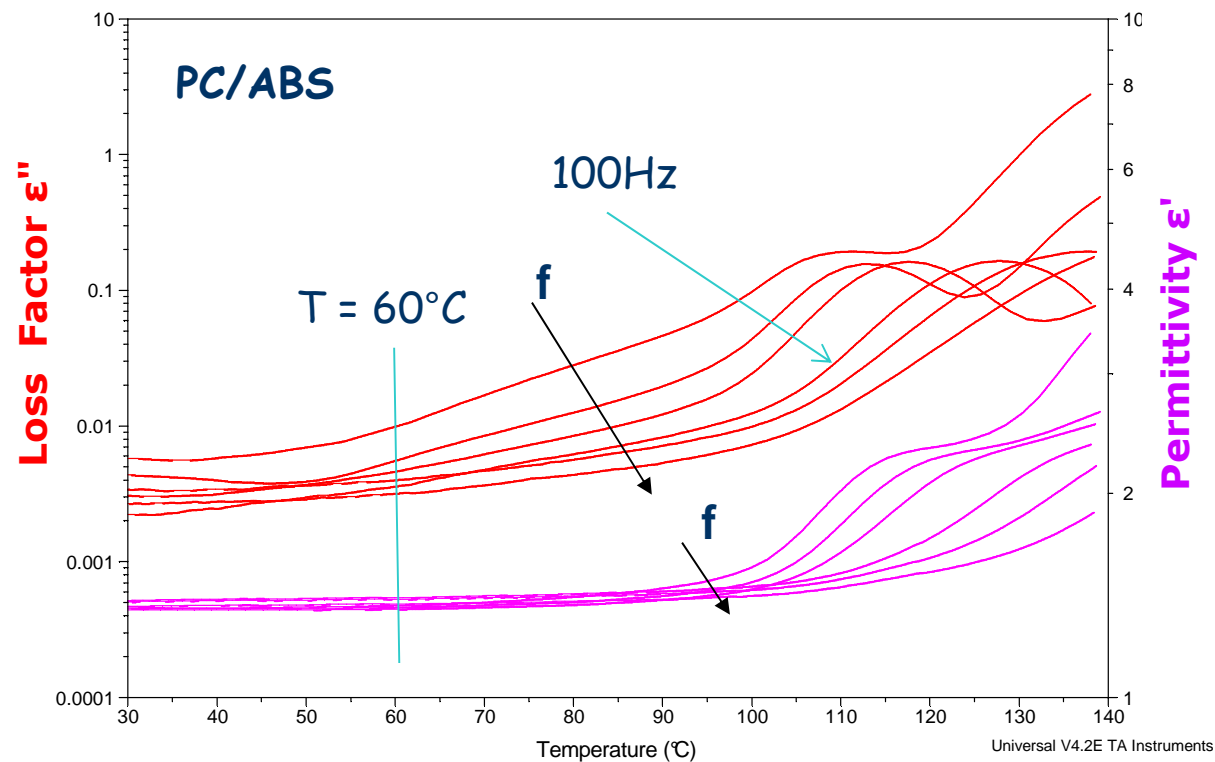


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Caso studio #1

PC/ABS-CNTs: PROPRIETA' DIELETTRICHE

Frequencies: 0.1, 1.0, 10, 100, 1000 and 10.000 Hz



TA Instruments
mod. 2970

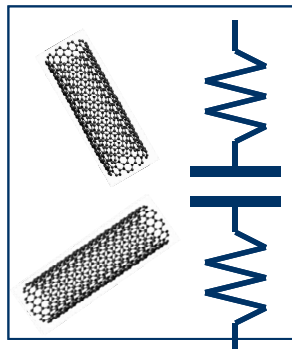


Caso studio #1

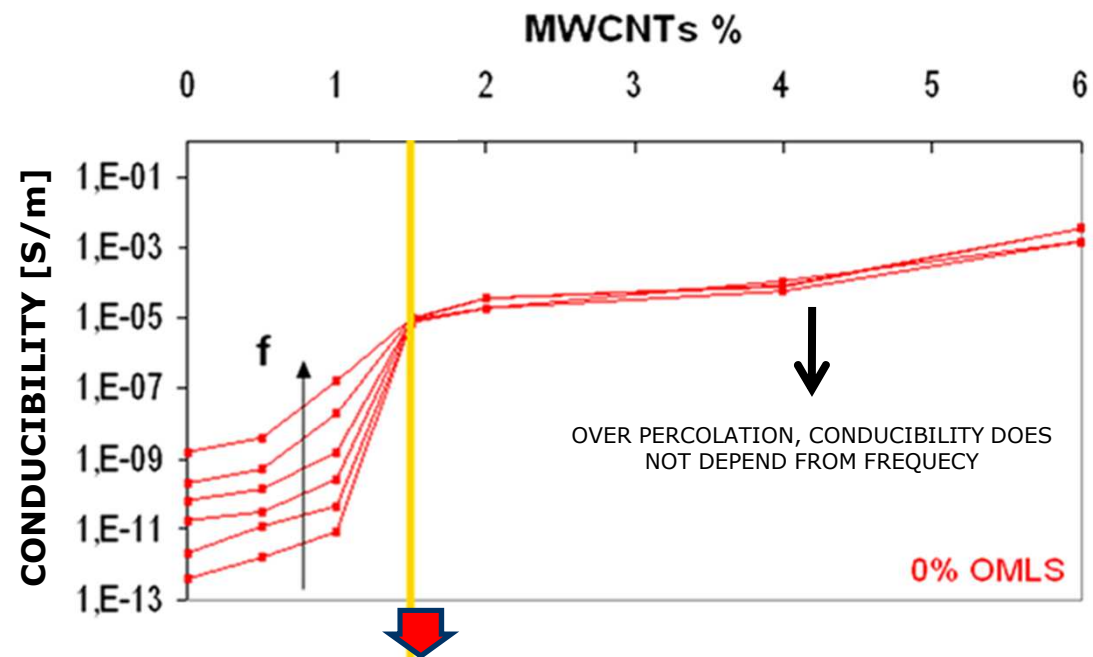
PC/ABS-CNTs: PROPRIETA' DIETTRICHE

DA 0.1Hz A 10,000 Hz - T=60°C

$$\sigma = \varepsilon'' \cdot 2\pi f \cdot \varepsilon_0$$



MWCNTs form
nano-capacitor

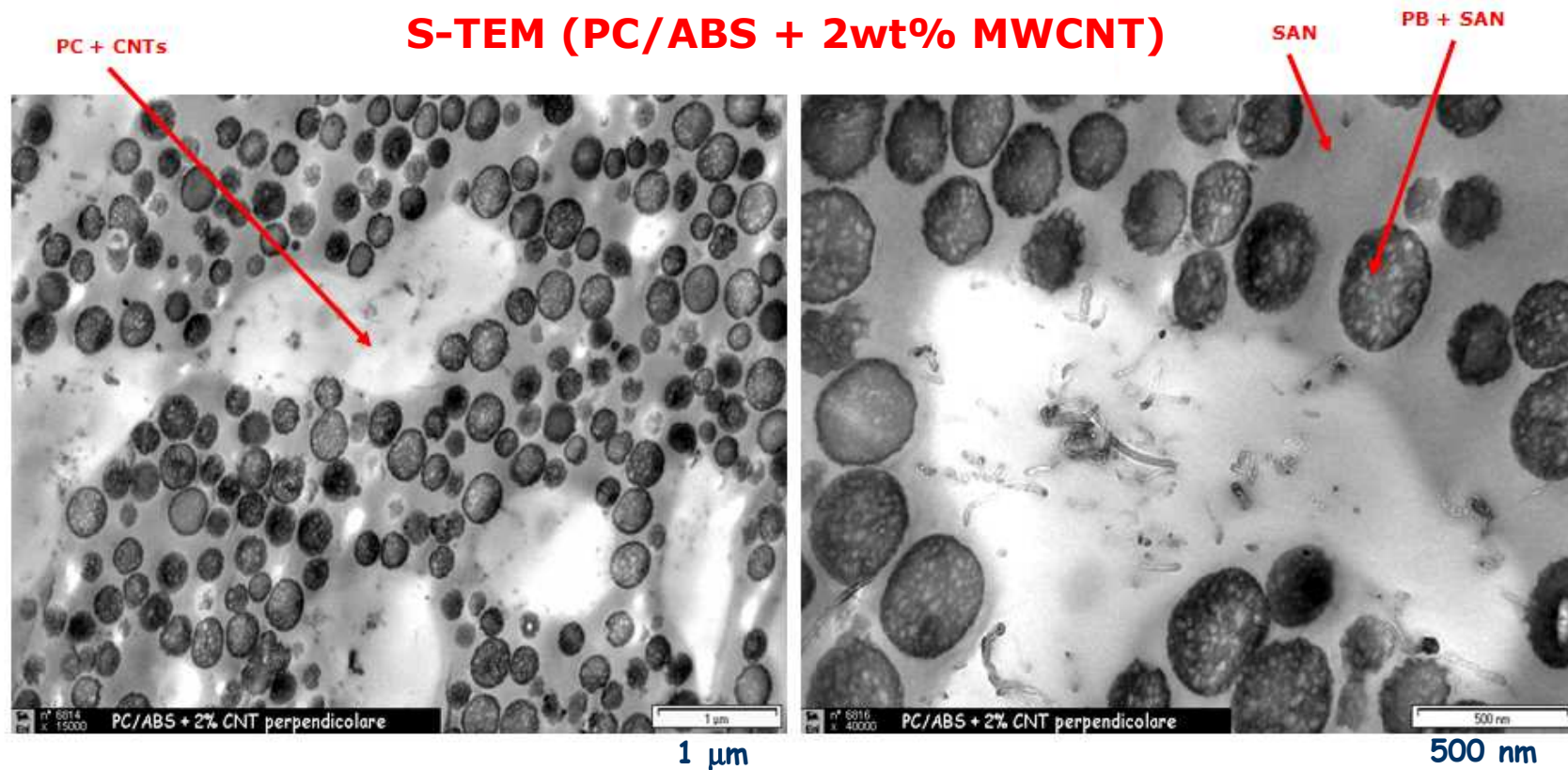


ELECTRIC PERCOLATION



Caso studio #1

PC/ABS-CNTs: MORFOLOGIA

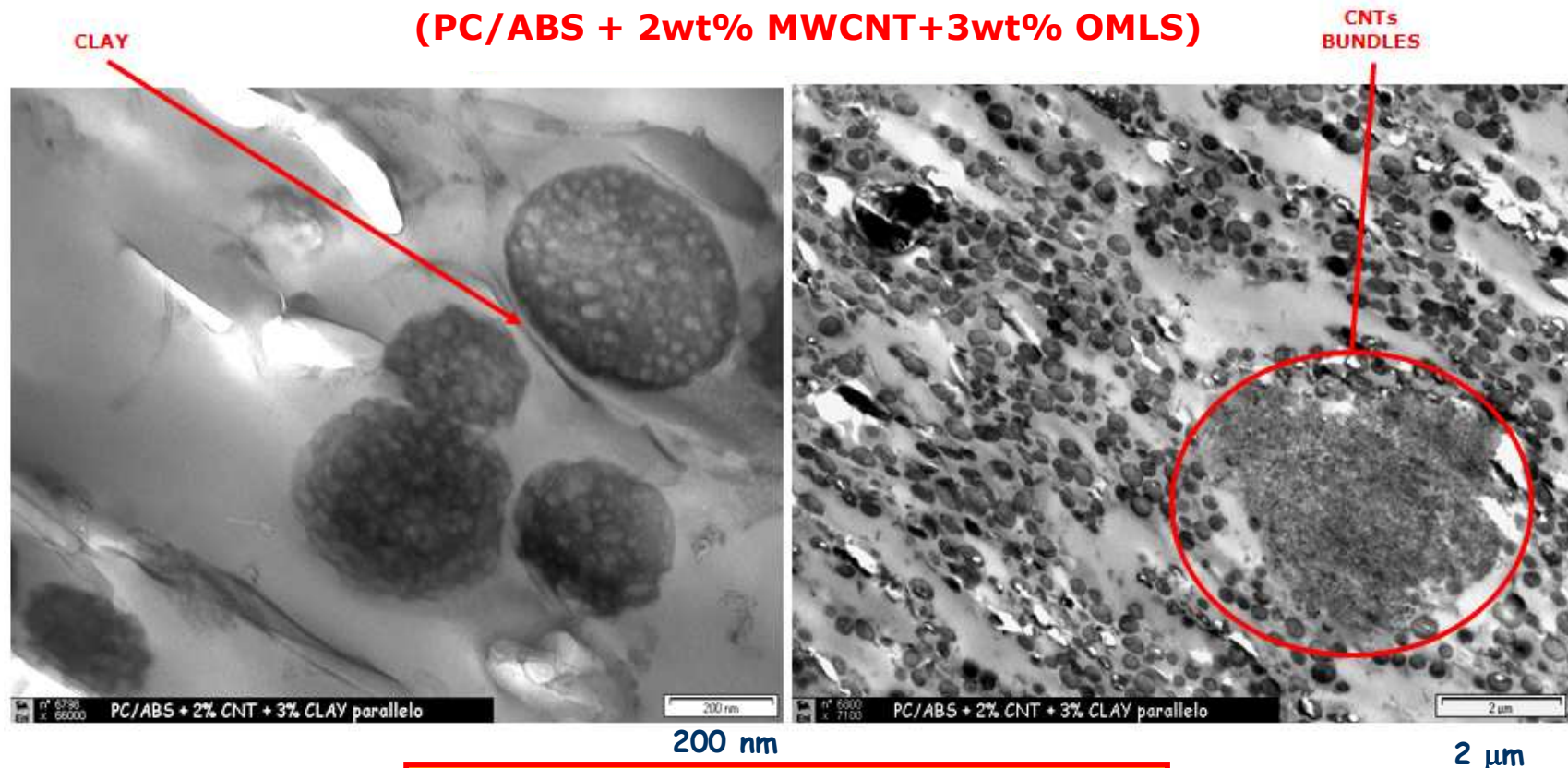


PERCOLAZIONE SELETTIVA



Caso studio #1

PC/ABS-CNTs: MORFOLOGIA



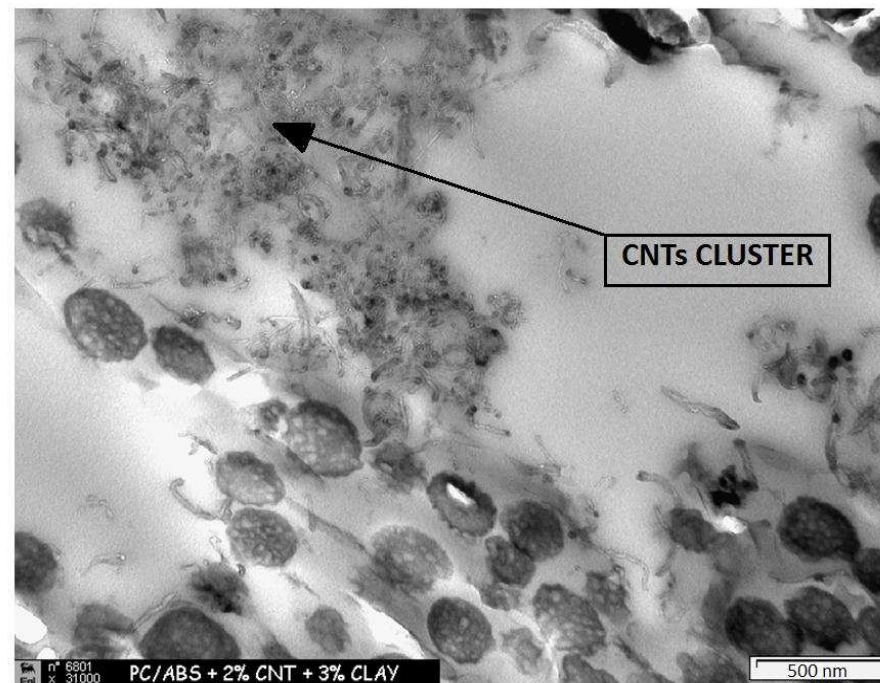
CLAY'S platelets / MWCNTs bundles



Caso studio #1

PC/ABS-CNTs: MORFOLOGIA

(PC/ABS + 2wt% MWCNT + OMLS 3WT.%)

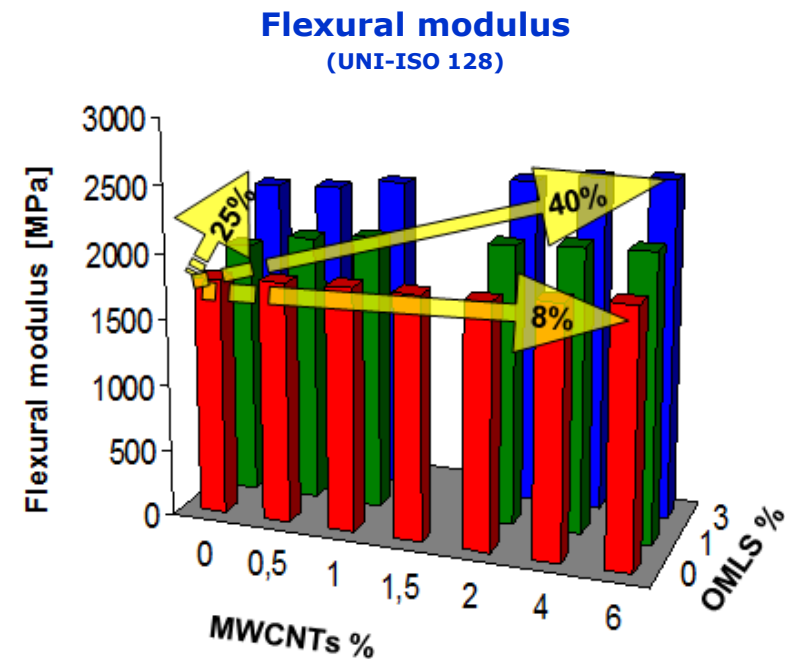
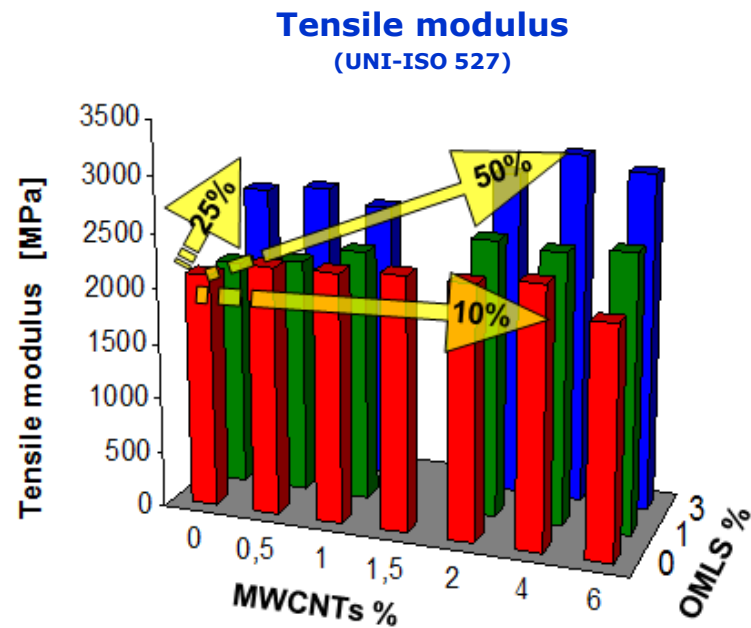


**MWCNTs MIGRATION TOWARDS PC BOUNDARIES +
BUNDLES FORMATION**



Caso studio #1

PC/ABS-CNTs-OMLS: PROPRIETA'



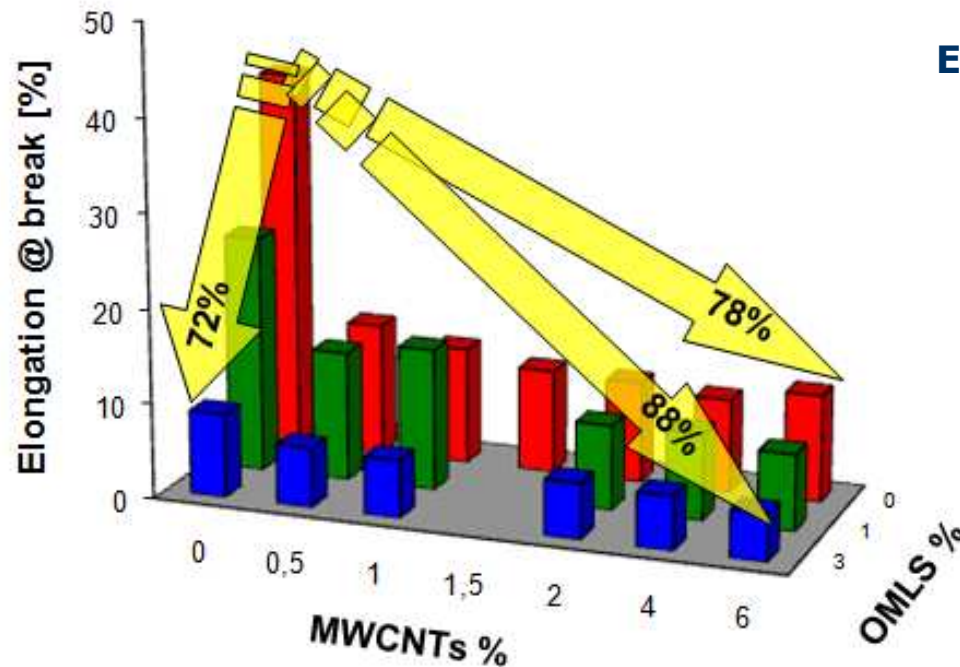
MECHANICAL STIFFNESS

SYNERGIC EFFECT OF MWCNTs and OMLS



Caso studio #1

PC/ABS-CNTs-OMLS: PROPRIETA'



Tensile elongation at break [%]
(UNI-ISO 527)

Elongation at break drops adding
OMLS and MWCNTs



LOSS DUCTILITY

DUCTILE-FRAGILE TRANSITION
Weidisch et al., Comp. Sci and Tech. 67
(2007) 867-879

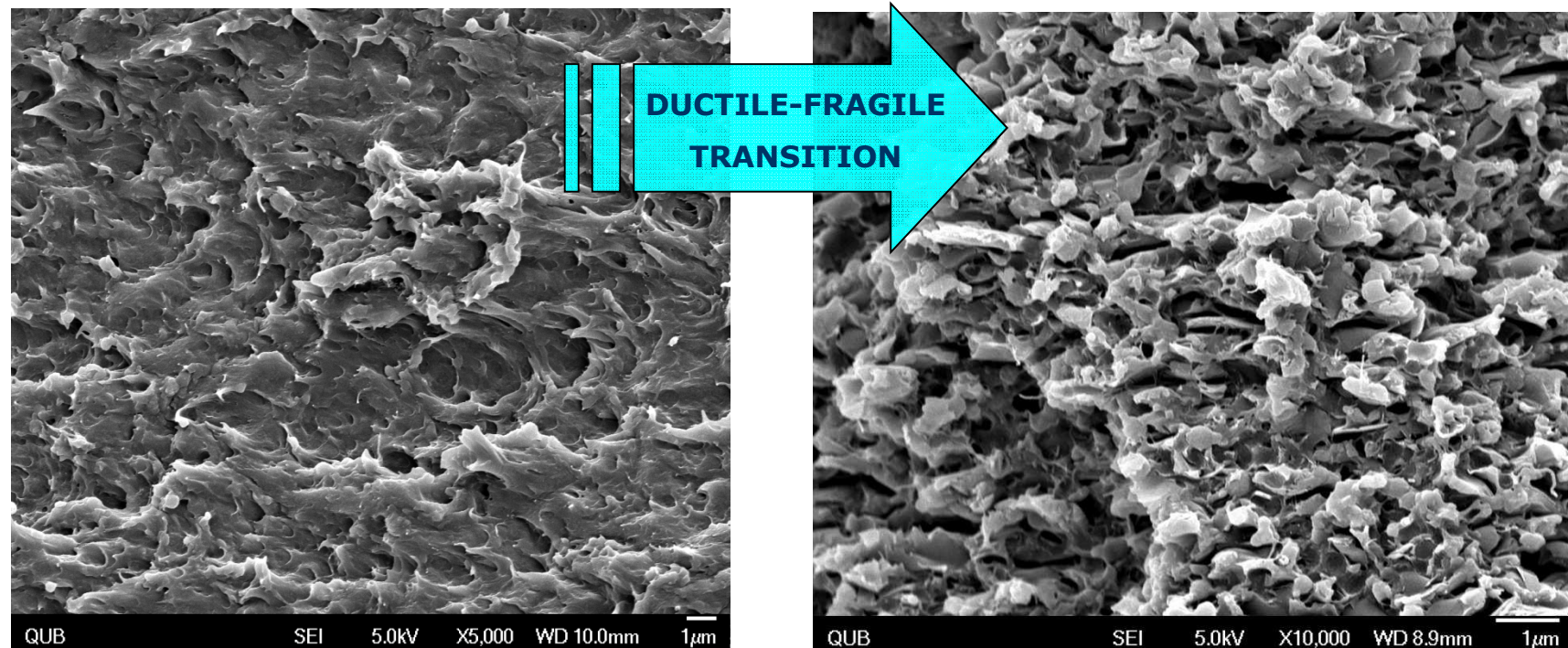


...Morphological
investigations needed...



Caso studio #1

PC/ABS-CNTs-OMLS: MORFOLOGIA



MWCNTs 0.5wt.%

MWCNTs 4wt.%

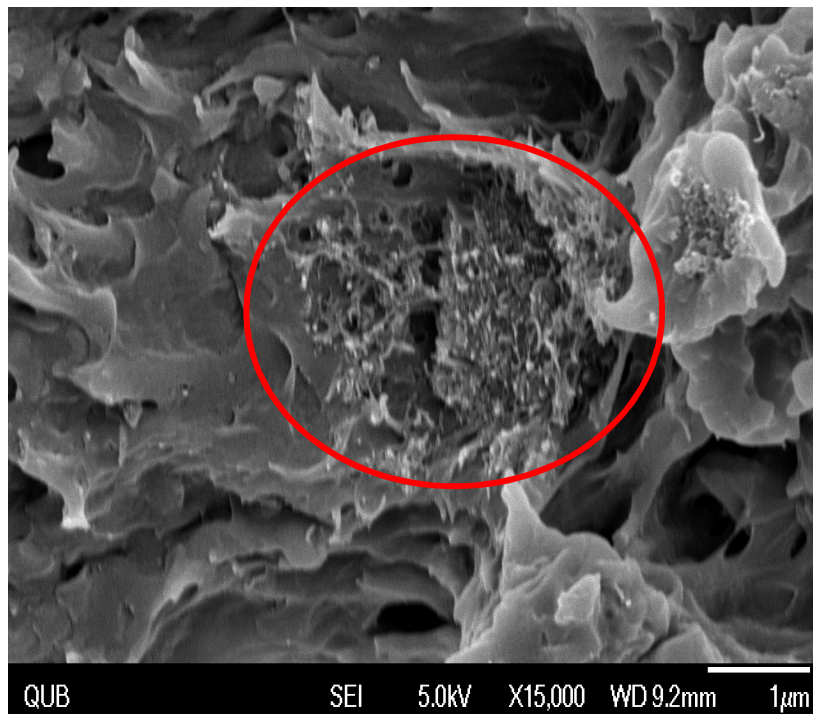
SINGLE MWCNTs / MECH. BEHAVIOR TRANSITION



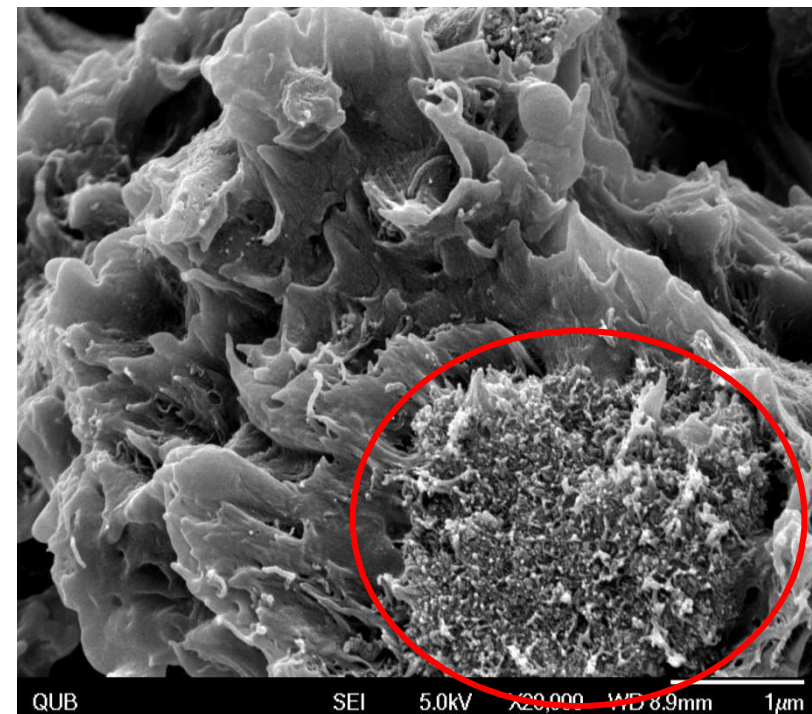
Caso studio #1

PC/ABS-CNTs: MORFOLOGIA

HR-SEM



MWCNTs 4wt.%



MWCNTs 4wt.% + OMLS 3wt.%

MWCNTs AGGLOMERATES (HIGHEST CNTs CONTENTS)

Caso studio #1



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Conclusioni e sviluppi

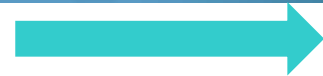
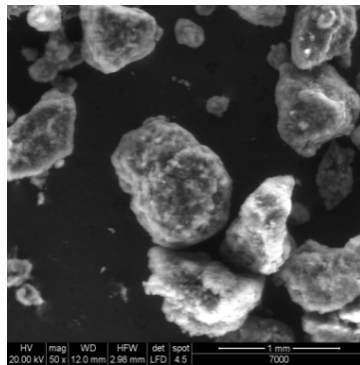
- ✓ OTTENIMENTO SI NANOCOMPOSITI A BASSA SOGLIA DI PERCOLAZIONE MEDIANTE MECCANISMO DI DOPPIA PERCOLAZIONE
- ✓ POSSIBILITA' DI SVILUPPI NELL'IMPIEGO PER VERNICIATURA ELETTROSTATICA
- ✓ PRIMI TEST DI CROMATURA GALVANICA : RISULTATI PROMETTENTI, NECESSARIA OTTIMIZZAZIONE
- ✓ SVILUPPI: NUOVI TEST DI CROMATURA GALVANICA PREVIO TRATTAMENTO CHIMICO SEMPLIFICATO



Caso studio #2

PP-CNTs: PROGETTO

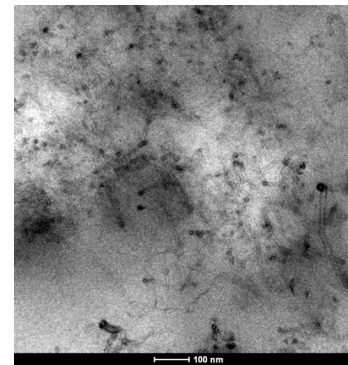
POLIPROPILENE



MASTERBATCH 10%

+

**CONDIZIONI DI
DILUIZIONI CON PP**



Caratterizzazione

- Analisi elettrica
- Analisi dielettrica (DEA)
- Prove meccaniche a flessione
- Calorimetria a scansione differenziale (DSC)
- Analisi dinamica meccanica (DMA)
- Analisi termogravimetrica (TGA)
- Analisi morfologica (SEM, TEM)



Caso studio #2

PP-CNTs: PROCESSING

PP modificato
90wt.%



MWCNTs
10wt.%

PP3=2

0.25, 0.5, 1, 2, 4, 6
%CNTs



PP2=35

0.25, 0.5, 1, 2, 4, 6
%CNTs



PP1=450

0.25, 0.5, 1, 2, 4, 6
%CNTs



Caso studio #2



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PP-CNTs: MATERIE PRIME

MATRICI POLIMERICHE:

- 1) PP modificato alta fluidità per masterbatch
- 2) PP commerciali per test diluizione:
 - a) PP MFI 2 - Basell (PP3)
 - b) PP MFI 35 - Aldrich (PP2)
 - c) PP MFI 450 - Borealis (PP1)

CNTs: NANOCYL NC7000

| PROPERTY | UNIT | VALUE | METHOD OF MEASUREMENT |
|------------------|-------------------|---------|-----------------------|
| Average Diameter | nanometers | 9.5 | TEM |
| Average Length | microns | 1.5 | TEM |
| Carbon Purity | % | 90 | TGA |
| Metal Oxide | % | 10 | TGA |
| Amorphous Carbon | - | * | HRTEM |
| Surface Area | m ² /g | 250-300 | BET |

* Pyrolytically deposited carbon on the surface of the NC7000

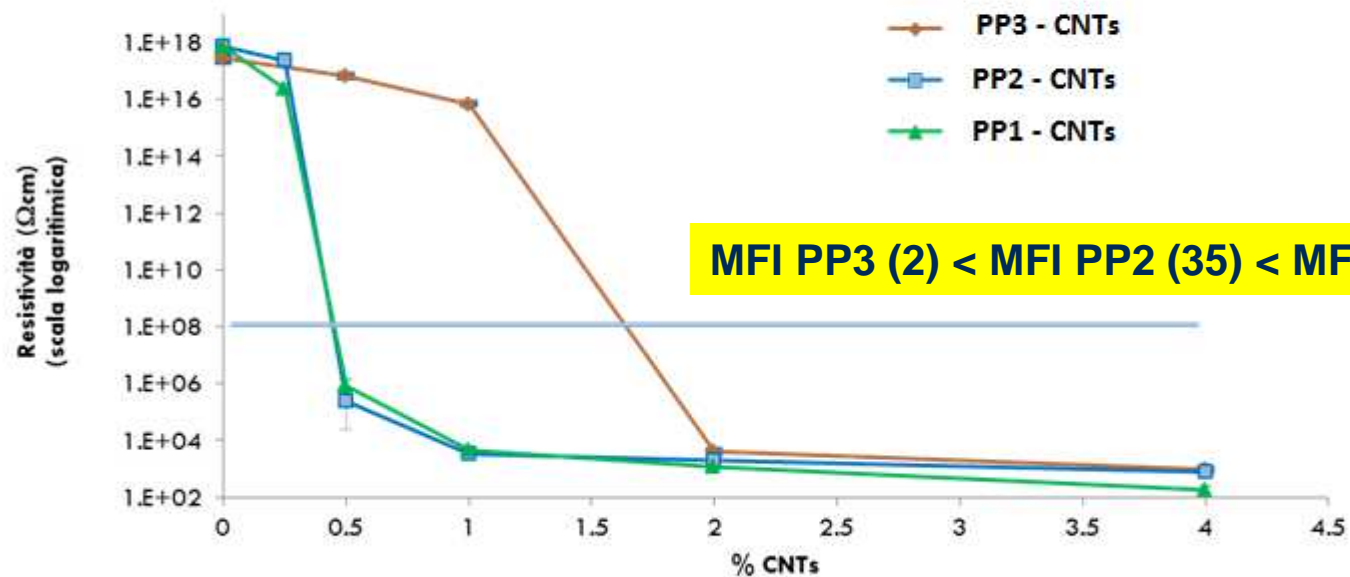
Caso studio #2



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PP-CNTs: PROPRIETA' ELETTRICHE

Curve di percolazione PP - CNTs



Caso studio #2



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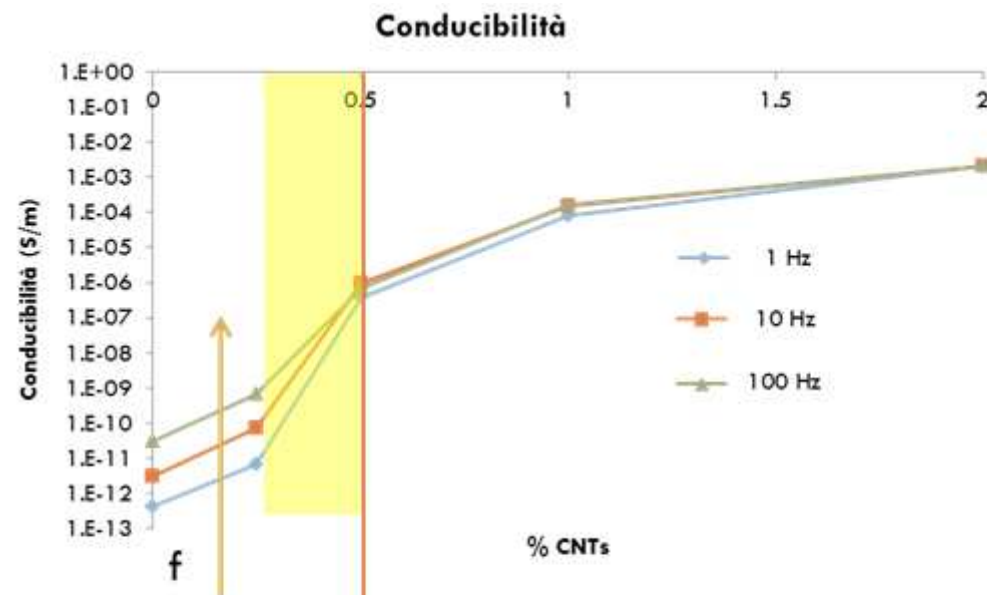
PP-CNTs: PROPRIETA' DIELETTICHE

Temperatura costante
Frequenza: 1-10-100 Hz

Conducibilità =
f(loss factor ε'')

$$\sigma = \varepsilon'' \cdot 2\pi f \cdot \varepsilon_0$$

PP MFI PP1



MWCNTs distanti tra loro

⇒ Prevale contributo capacitivo

Frequenza dipendente

MWCNTs vicini tra loro

⇒ Prevale contributo conduttivo

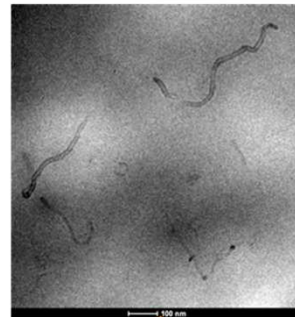
Frequenza indipendente



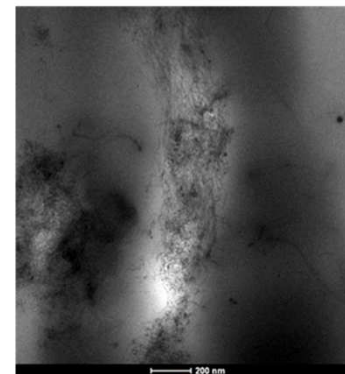
Caso studio #2

PP-CNTs: MORFOLOGIA

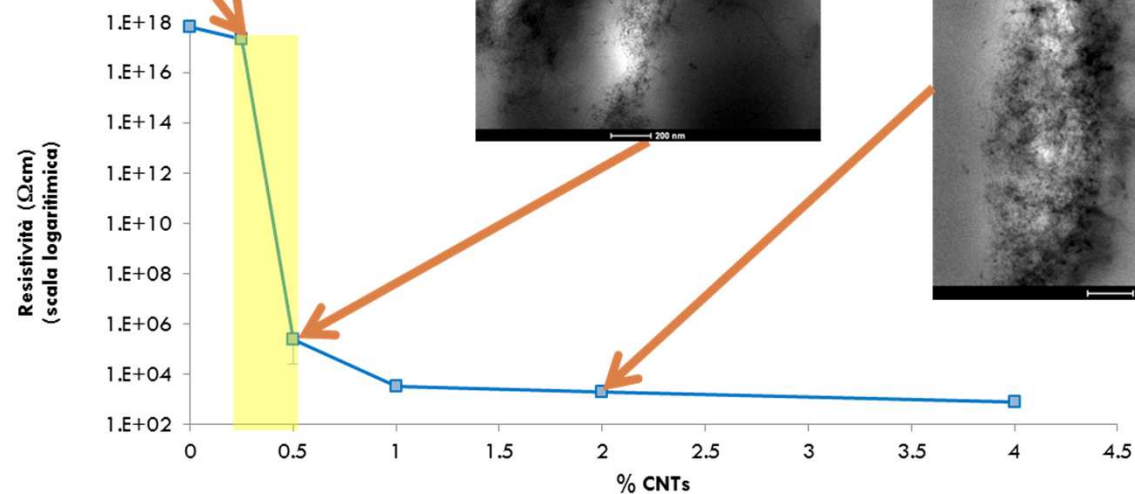
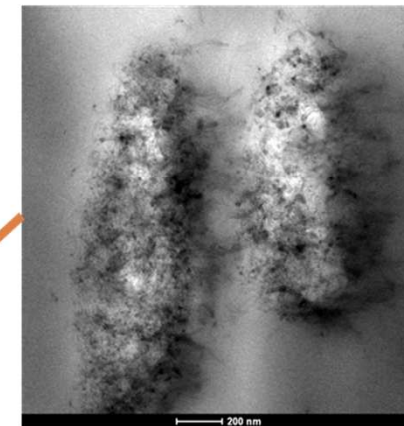
Strutture isolate



Network conduttivo



Agglomerati

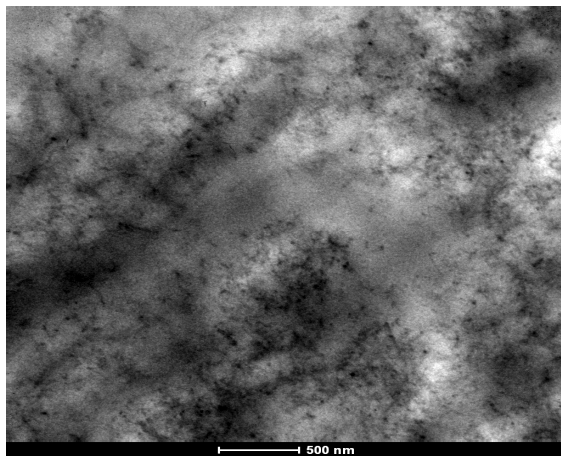


Caso studio #2



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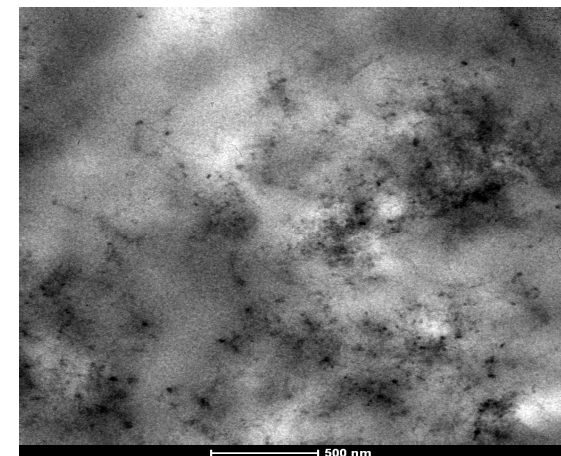
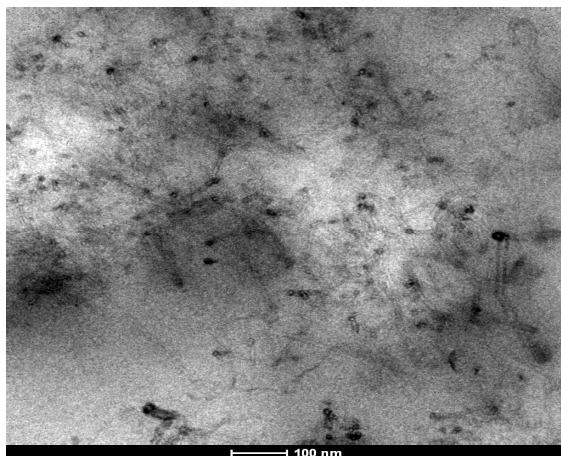
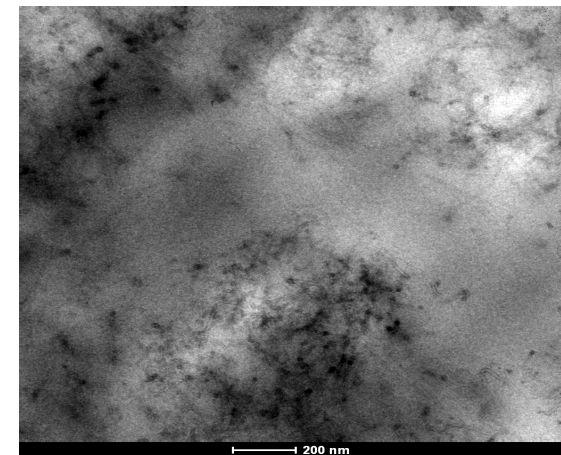
PP-CNTs: MORFOLOGIA MASTERBATCH



**ECCELLENTE DISPERSIONE
CNTs MASTERBATCH**



**NOTEVOLE ABBASSAMENTO
SOGLIA PERCOLAZIONE**



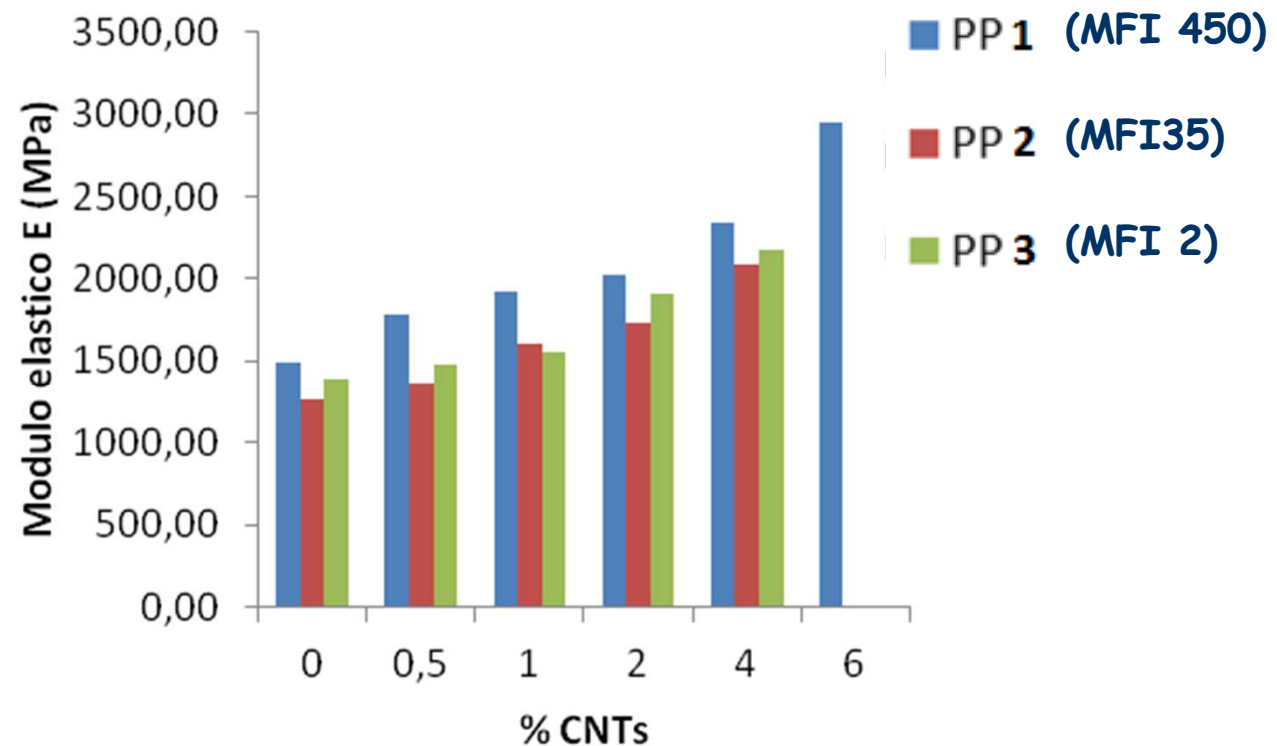
Caso studio #2



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PP-CNTs: PROPRIETA' MECCANICHE

Test ISO 178 – Flessione su tre punti



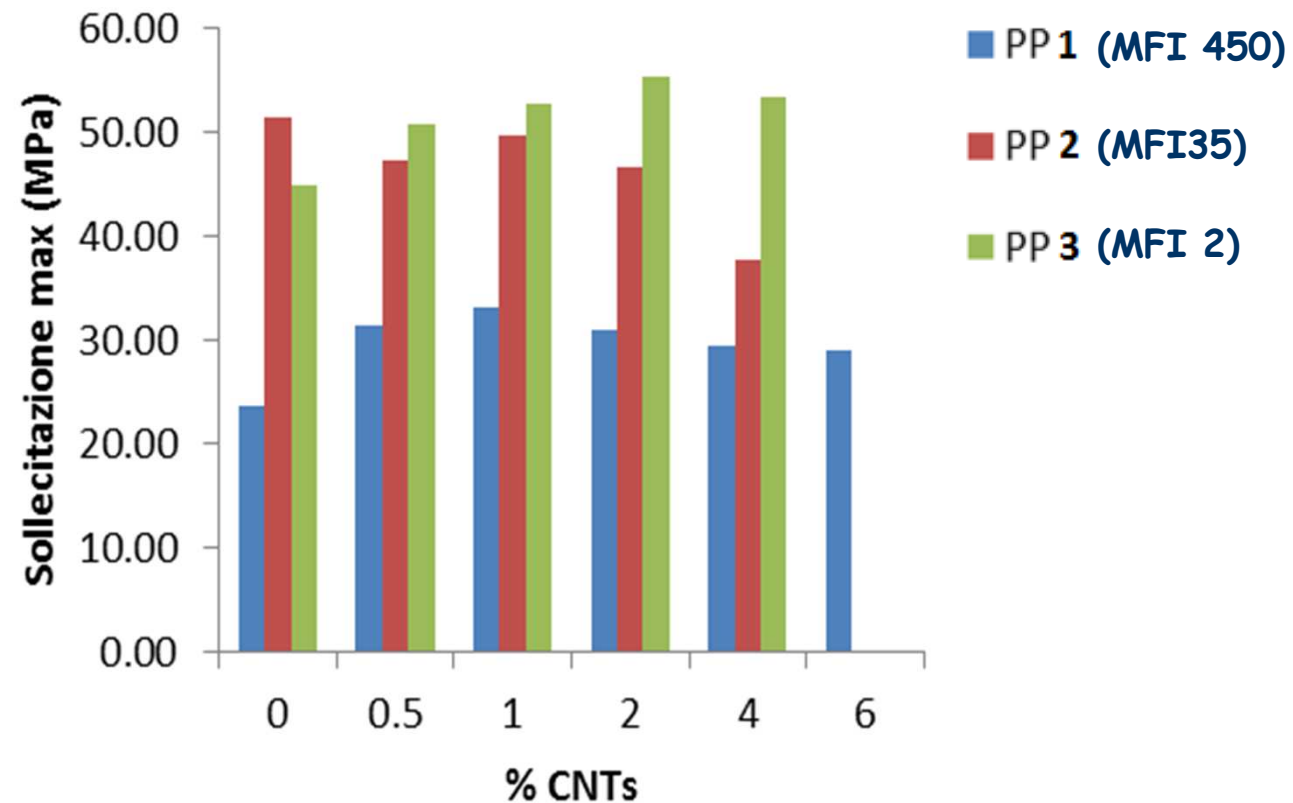
Caso studio #2



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PP-CNTs: PROPRIETA' MECCANICHE

Test ISO 178 – Flessione su tre punti



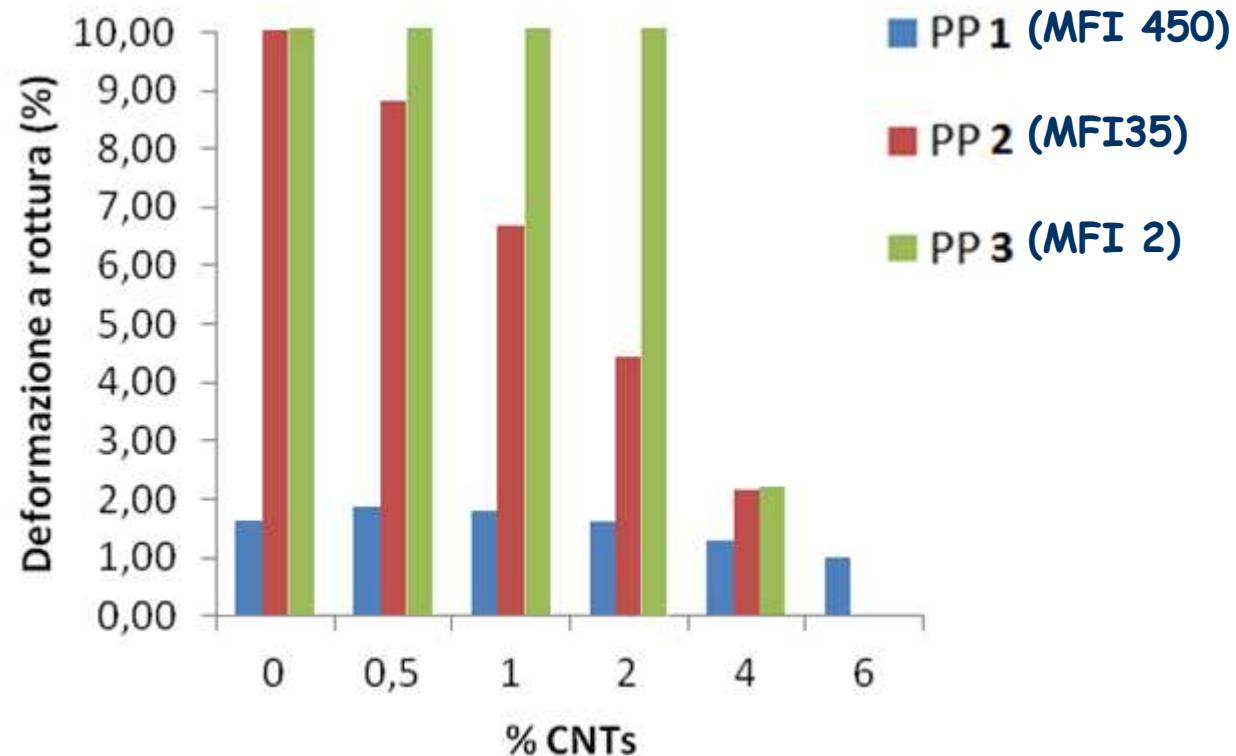
Caso studio #2



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PP-CNTs: PROPRIETA' MECCANICHE

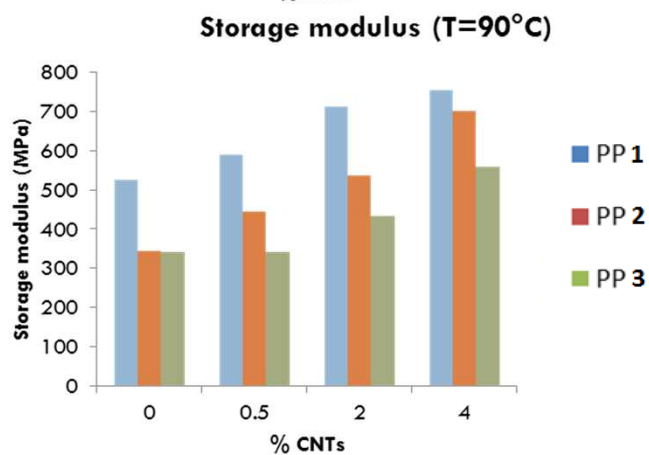
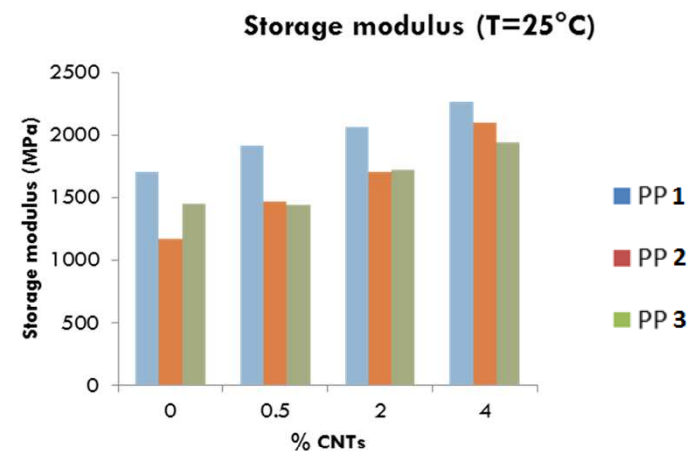
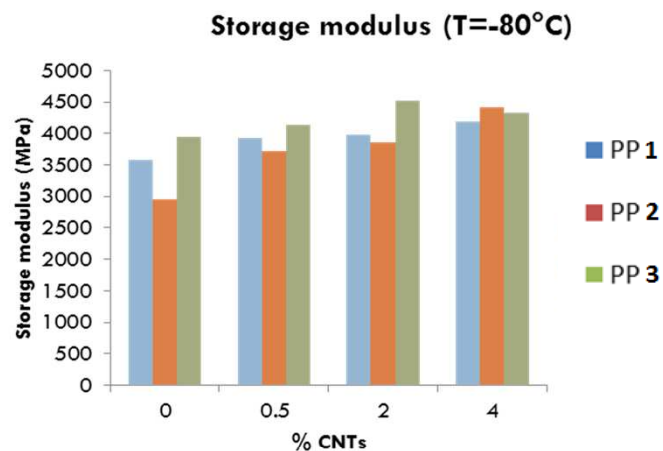
Test ISO 178 – Flessione su tre punti





Caso studio #2

PP-CNTs: analisi dinamico-meccanica



- Lo storage modulus aumenta all'aumentare del contenuto di CNTs
- Si conferma quanto determinato con le prove meccaniche (cfr. modulo elastico)

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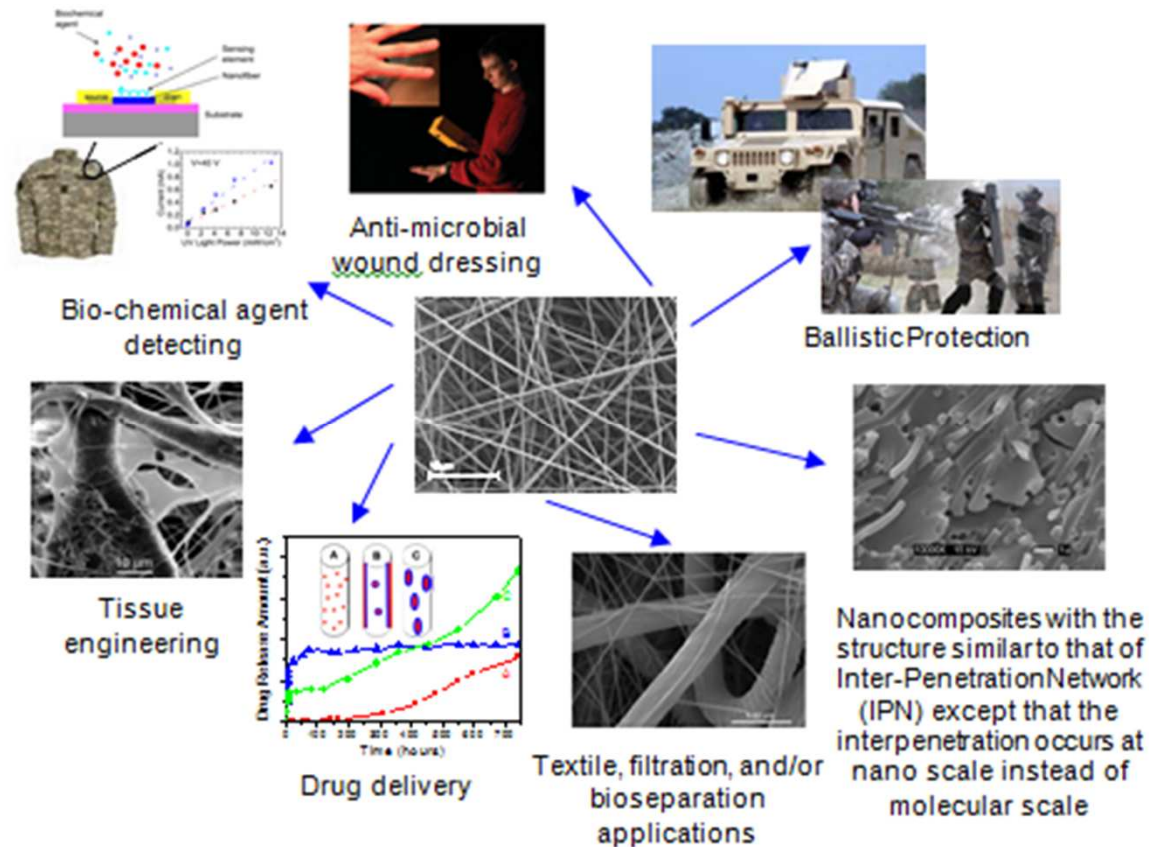
Conclusioni e sviluppi

- ✓ OTTENIMENTO DI UN MASTERBATCH CON EFFICACE DISPERSIONE DEI MWCNT NELLA MATRICE POLIMERICA
- ✓ OTTIMI RISULTATI NELLA DILUIZIONE CON PP GRADO FIBRE E STAMPAGGIO
- ✓ VERIFICA DELL'IMPORTANZA DELLE CONDIZIONI E MODALITA' DI DILUIZIONE DEL MASTERBATCH
- ✓ POSSIBILI APPLICAZIONI NEL CAMPO DELLE DEPOSIZIONI PER VIA GALVANICA E DELLE MEMBRANE CON CARATTERISTICHE ESD



Caso studio #3

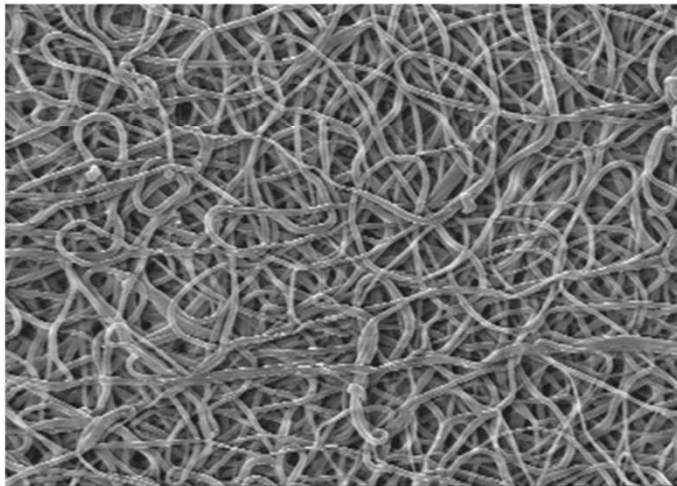
Membrane nanostrutturate elettricamente conduttive a base di nanofibre



Caso studio #3

Nanofibre

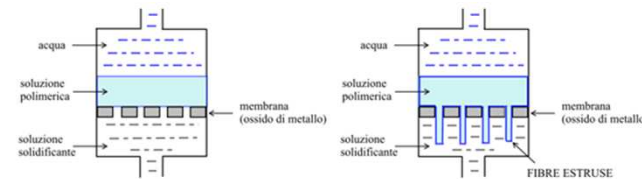
Diametro $10 \text{ nm} < \varnothing < 1 \text{ }\mu\text{m}$
Lunghezza $\gg 1 \text{ m}$
Superficie specifica $> 1000 \text{ m}^2/\text{g}$
Modulo elastico più elevato



Membrana a base TPU



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Template Synthesis

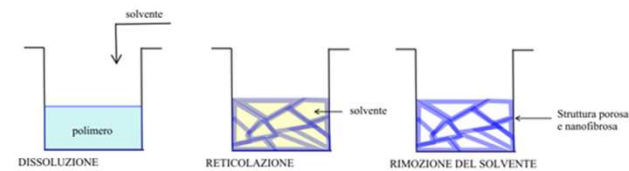
Drawing

Electro-Hydro-Dynamic

Self Assembly

Melt Blown

Phase Separation

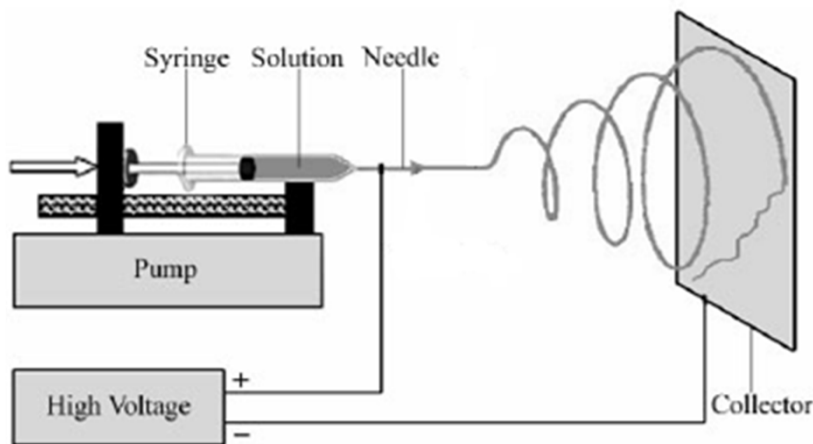


Caso studio #3



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Il processo di elettrospinning



•Processo Versatile

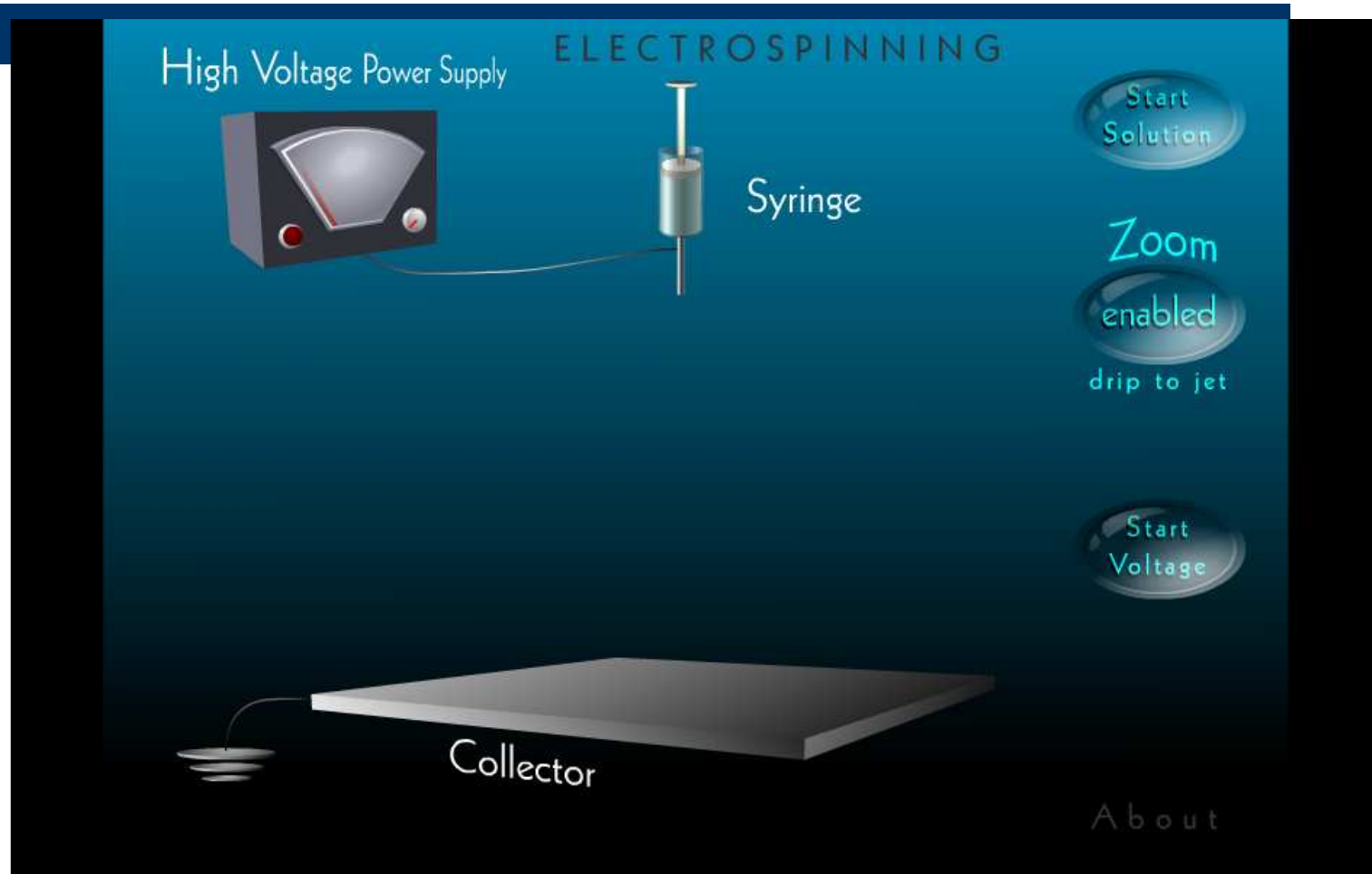
- ✓ Nanofibre → **Electrospinning**
- ✓ Aerosol → **Electrospray**

•Apparato Strumentale

- ✓ Pompa per siringa
- ✓ Generatore di alta tensione
- ✓ Collettore a terra



Tecnica di elettrospinning: Funzionamento

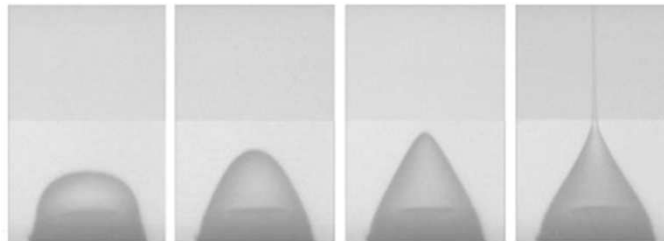




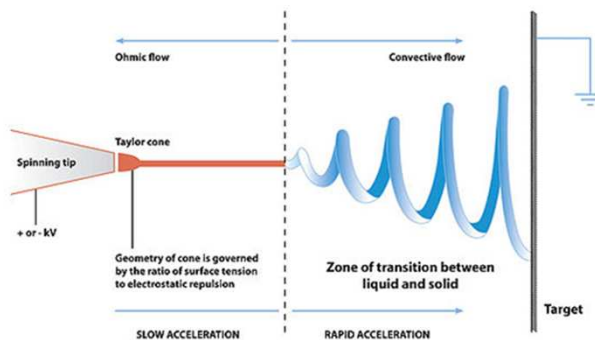
Caso studio #3

Cenni di teoria

Cono di Taylor



$$V_C^2 = \left(\frac{2L}{h}\right)^2 \left[\ln\left(\frac{2h}{R}\right) - 1.5\right] (0.117 \pi RT)$$



II legge di Newton

$$m \frac{d^2 P}{dt^2} = f_C + f_E + f_V + f_S + f_A + f_G$$

Forza di Coulomb

$$f_C = \frac{e^2}{L^2}$$

Forza elettrodinamica

$$f_E = -\frac{eV}{L}$$

Forza viscoelastica

$$f_V = \frac{d\sigma_V}{dt} = \frac{G}{l} \frac{dl}{dt} - \frac{G}{\mu} \sigma_V$$

Tensione superficiale

$$f_S = \frac{\alpha \pi R^2 k}{\sqrt{x_i^2 + y_i^2}} [i|x| \text{sign}(x) + j|y| \text{sign}(y)]$$

Attrito dell'aria

$$f_A = 0.65 \pi R \rho_{aria} v^2 \left(\frac{2vR}{v_{aria}}\right)^{-0.81}$$

Forza gravitazionale

$$f_G = \rho g \pi R^2 \quad \text{Reneker et al. (2000)}$$

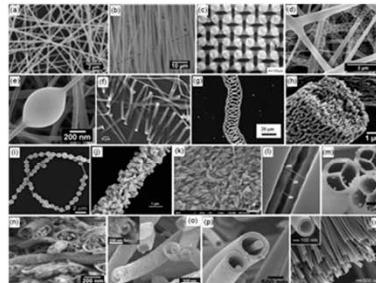


Caso studio #3

Parametri di processo

Parametri della soluzione

- ✓ viscosità e peso molecolare
- ✓ tensione superficiale
- ✓ conducibilità
- ✓ costante dielettrica

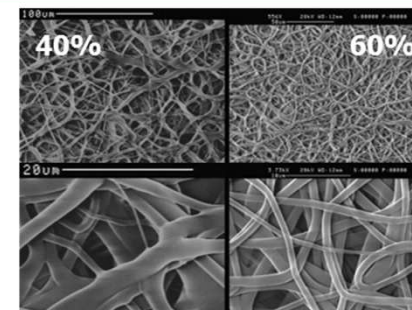


Parametri di processo

- ✓ tensione di polarizzazione
- ✓ portata della pompa
- ✓ dimensione dell'ago
- ✓ distanza del collettore

Condizioni ambientali

- ✓ temperatura
- ✓ umidità
- ✓ pressione
- ✓ tipo di atmosfera

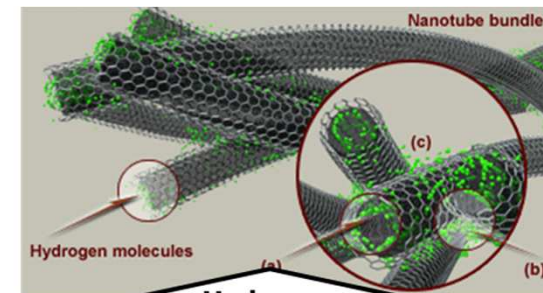
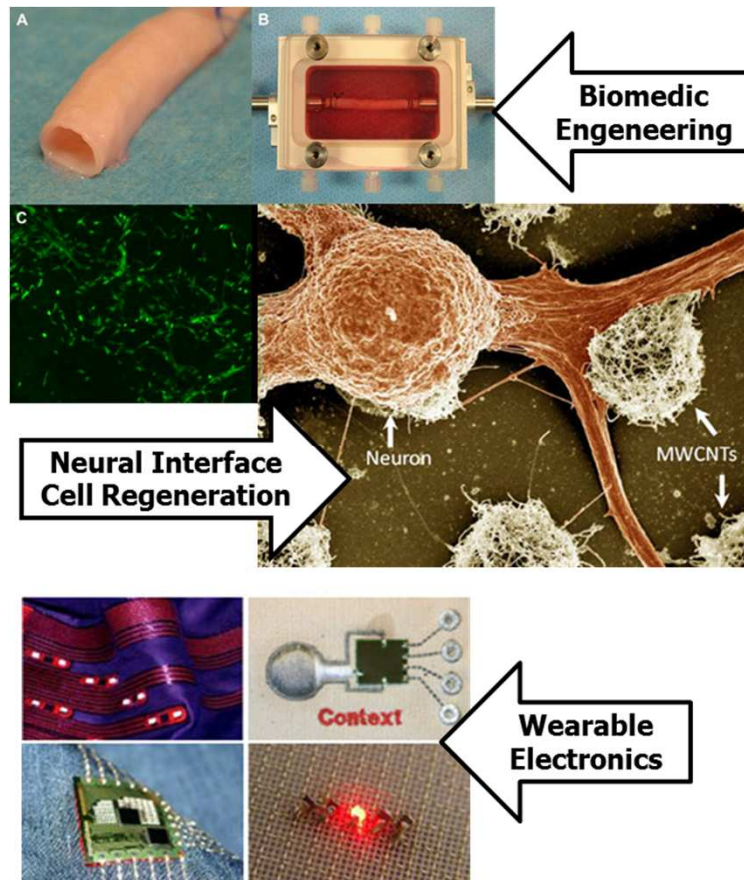




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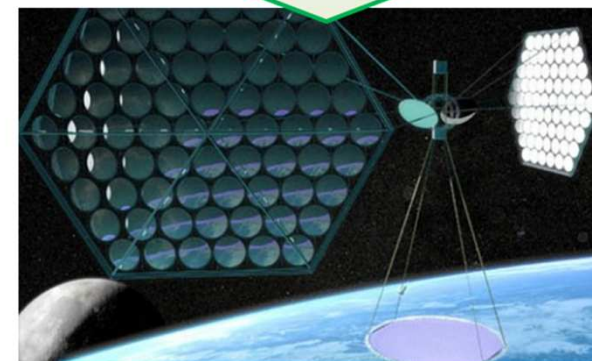
Caso studio #3

Nanofibre + nanotubi



Hydrogen Storage

Future ?





Caso studio #3

Obiettivi

Preparazione e caratterizzazione di membrane polimeriche nanostrutturate elettricamente conduttive

Poliuretano ($\rho=10^{15} \Omega \cdot cm$)



Nanotubi ($\rho = 10^{-5} \Omega \cdot cm$)

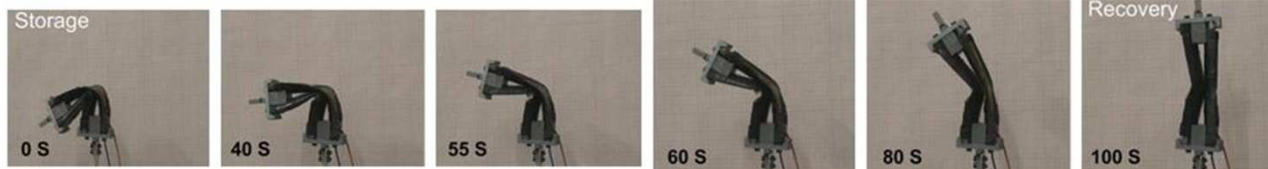


Sistemi antistatici ($\rho \leq 10^5 \Omega \cdot cm$)

Protezione RF ($\rho \leq 10^2 \Omega \cdot cm$)



Attuatori SMP comandabili elettricamente



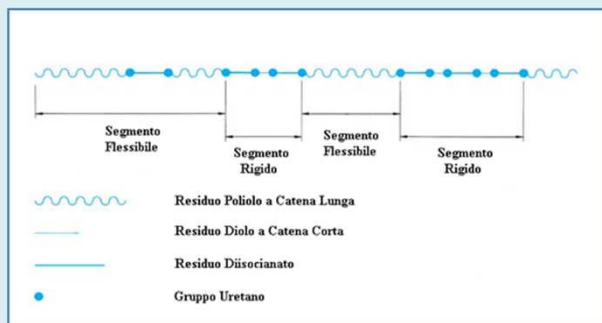
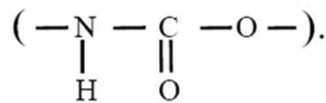


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Obiettivi

Elastollan® B70D

Poliuretano
Termoplastico
Base Estere
Elastomero

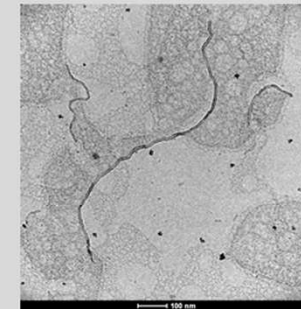


Solventi: **THF, DMF**

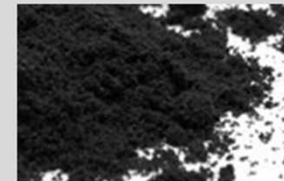
Nanocyl® NC7000

Multi Wall Carbon Nanotubes
C.V.D.

Ø = 10 nm
A.R. = 150
Purezza 90%



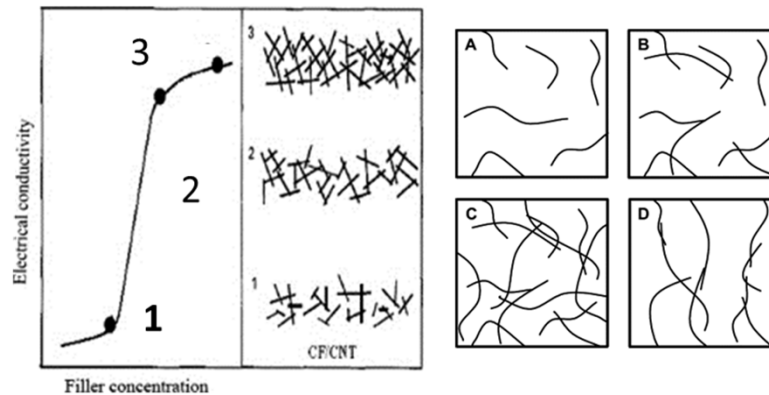
$\rho = 10^{-5} - 10^{-6} \Omega \cdot \text{cm}$





Caso studio #3

Obiettivi



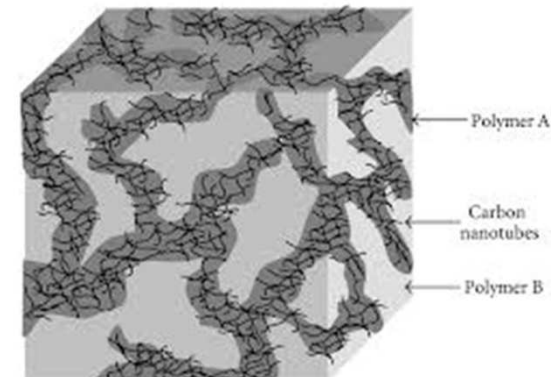
Doppia Percolazione

Percolazione in polimero A
Polimero B immiscibile
Sistema bifasico

[CNT] finale molto bassa

Curva di Percolazione

- 1) Bassa Conducibilità
- 2) Cammini Percolativi
- 3) Percolazione → **Network Conduttivo**



Caso studio #3



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1) Filatura di una sospensione contenente i nanotubi

- **Fibre nanocomposite**
- **Nanotubi allineati all'interno delle fibre**

2) Electrospray di nanotubi

- **Fibre rivestite di nanotubi**
- **Nanotubi in contatto diretto con l'esterno**



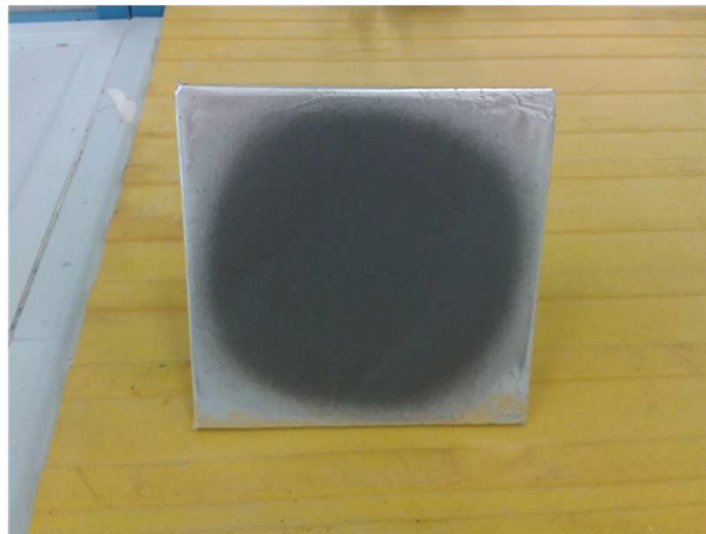
Caso studio #3

Preparazione delle membrane

Sospensioni Polimeriche:

[TPU] = 20% (p) in DMF

$0,1 < \mathbf{[MWCNT]} < 5\%$ (p) su TPU



Elettrospinning:

Collettore Piano Rotante

Tensione **15-18 kV**

Portata ~ **1 ml/h**

Distanza collettore ~ **20 cm**

Umidità ambientale **55-65%**

Membrane TPU puro

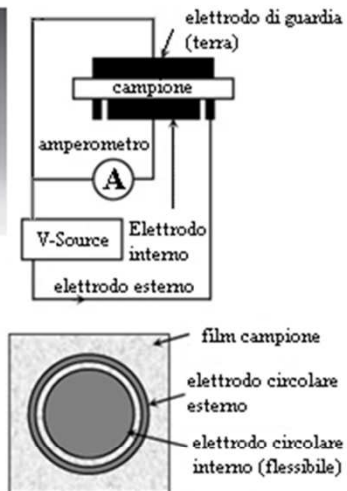


Caso studio #3

Proprietà elettriche

∅ min film > 5,5 - 6 cm

$R \text{ (max)} \approx 10^{16} \Omega$



TPU Puro

$\rho \approx 1,5 \cdot 10^{14} \Omega \cdot \text{cm}$

$R_S \approx 1,0 \cdot 10^{15} \Omega / \blacksquare$

TPU + Nanotubi

$\rho = 1,7 \cdot 10^{14} \Omega \cdot \text{cm}$

$R_S = 5,5 \cdot 10^{15} \Omega / \blacksquare$

[CNT]

0,5%

1%



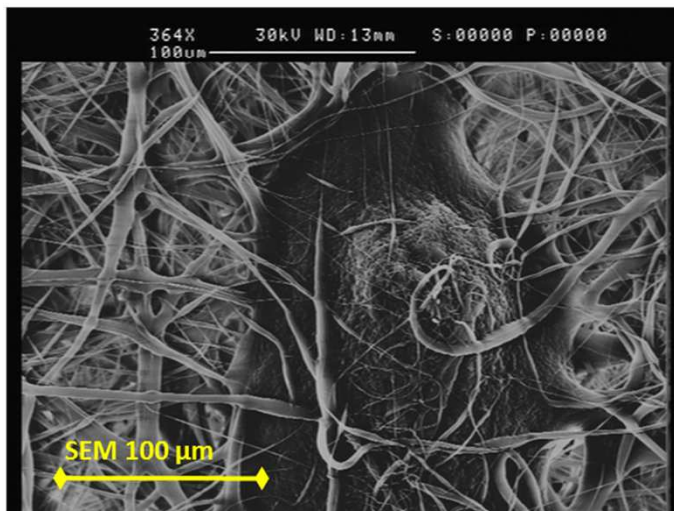
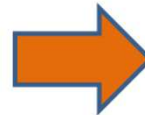
Caso studio #3

Morfologia

**Aggregati macroscopici
visibili ad occhio nudo.**



**Minore concentrazione
di nanotubi dispersi
disponibili alla conduzione.**



**Interruzione continuità
della membrana**

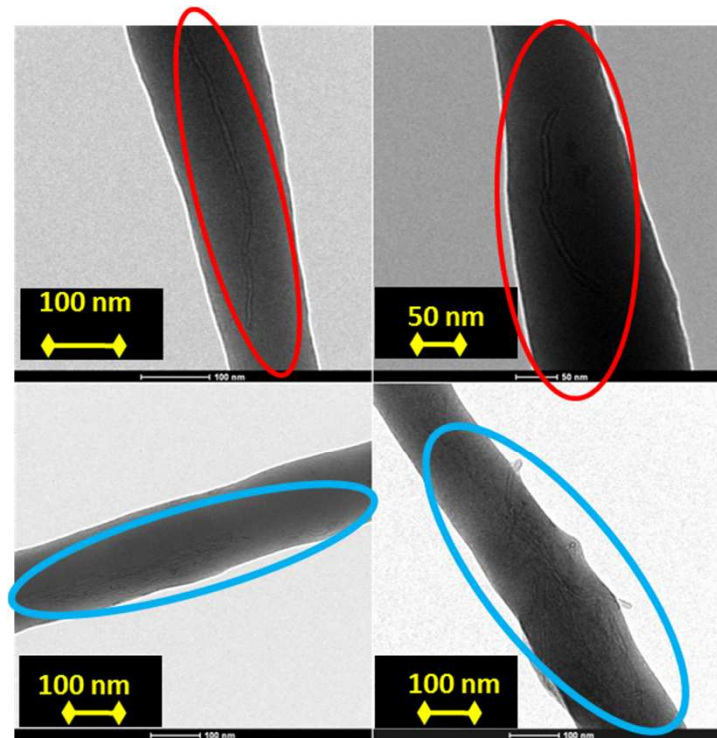


**Infragilimento della
struttura**

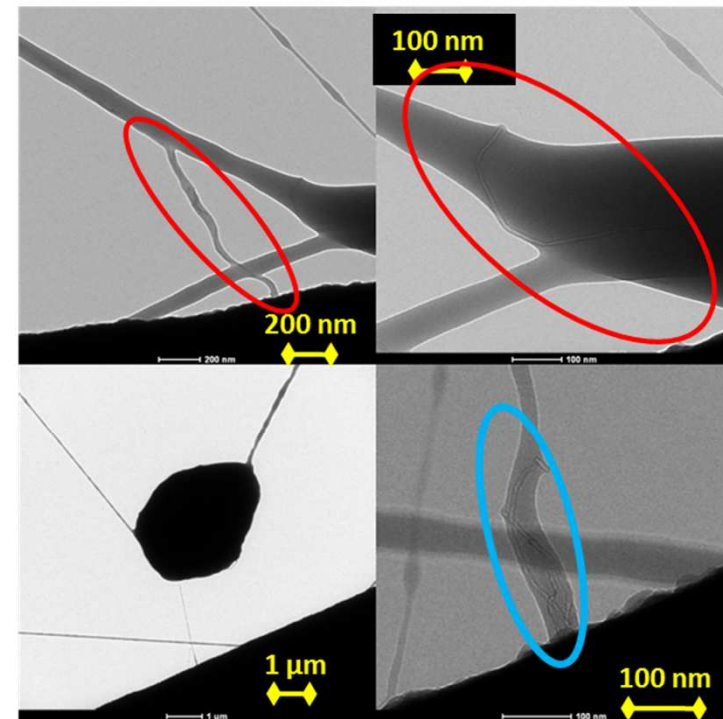


Caso studio #3

Morfologia - TEM



0.5% [CNT]



5% [CNT]

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1) Filatura di una sospensione contenente i nanotubi

➤ **Fibre nanocomposite**

➤ **Nanotubi allineati all'interno delle fibre**

2) Electropray di nanotubi

➤ **Fibre rivestite di nanotubi**

➤ **Nanotubi in contatto diretto con l'esterno**



Caso studio #3

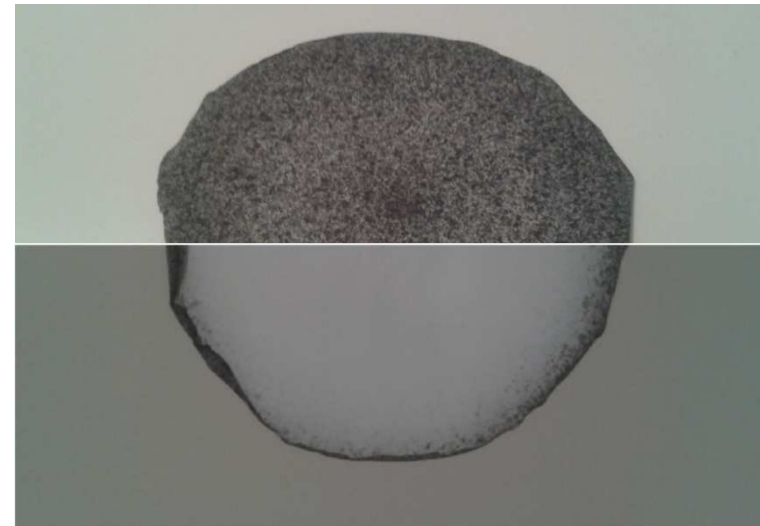
Metodo spray-coating

Sospensioni

[CNT] { 0,05%
0,1%
0,25%

Penetrazione

30 μm



$$R_s = 1,01 \cdot 10^5 \Omega / \blacksquare$$

Test di Stabilità → 30' Sonicazione (70 W)

$$R_s = 1,12 \cdot 10^5 \Omega / \blacksquare$$

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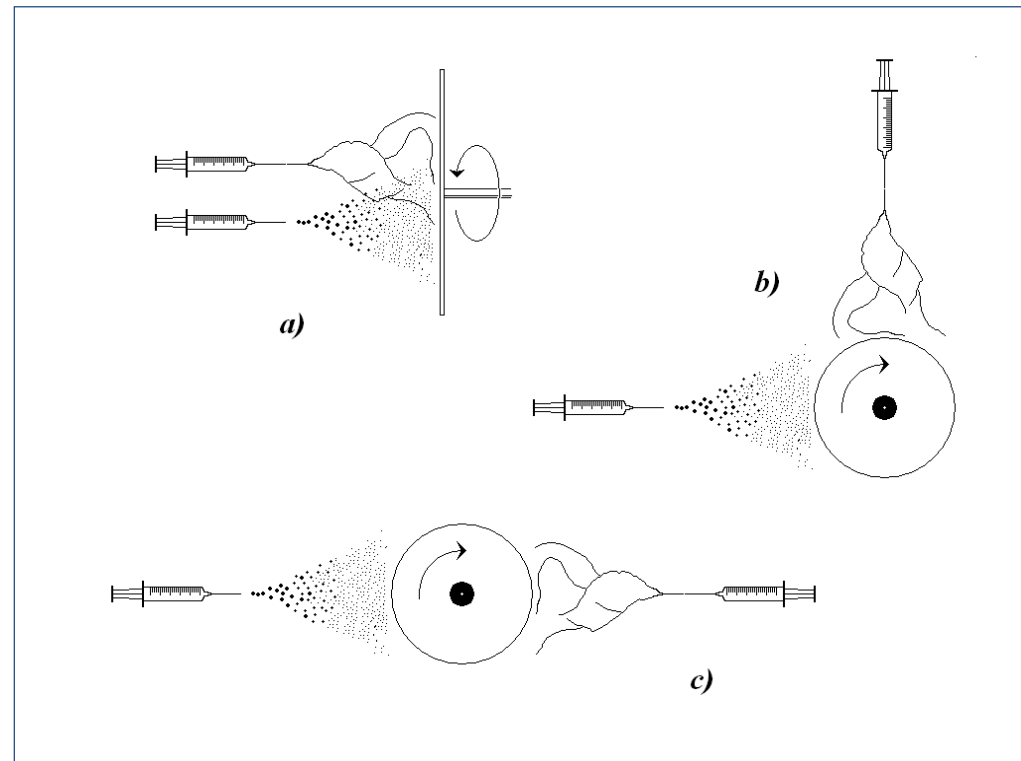


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Metodo a deposizione simultanea

Configurazioni per deposizione simultanea:

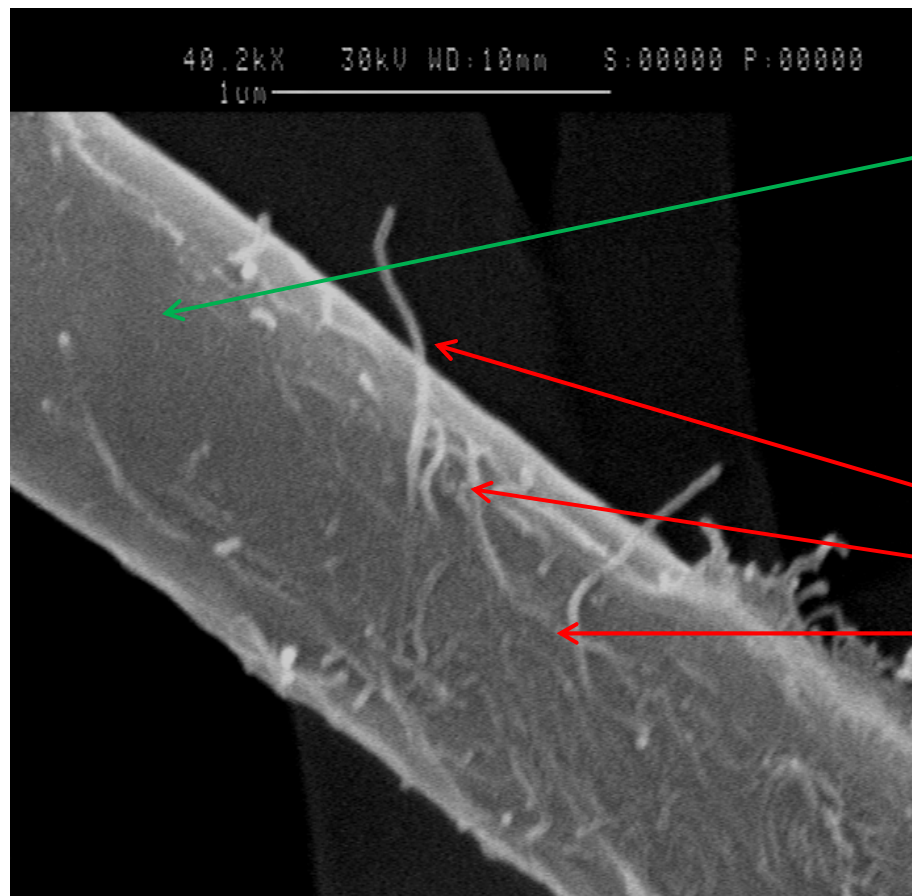
- a) Parallela ($\sim 0^\circ$) su piastra rotante*
- b) Ortogonale (90°) su cilindro rotante*
- c) Antiparallela (180°) su cilindro rotante*



Caso studio #3



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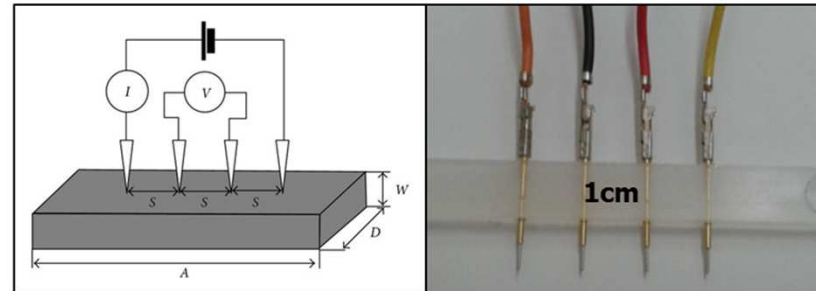
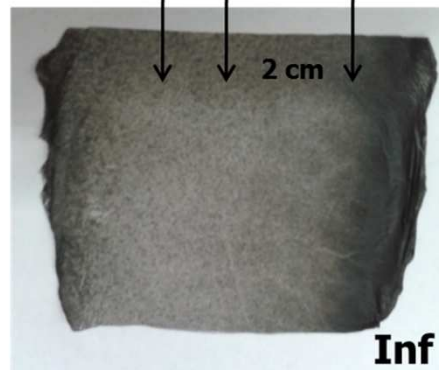
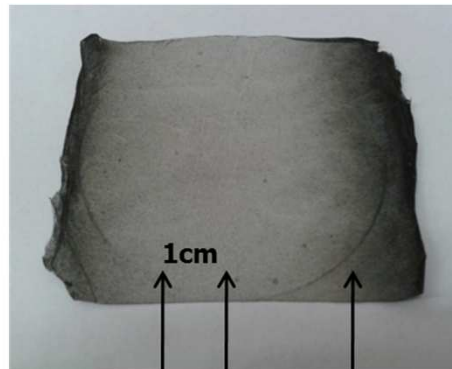
FIBRA (TPU)

MWCNT



Caso studio #3

Proprietà elettriche



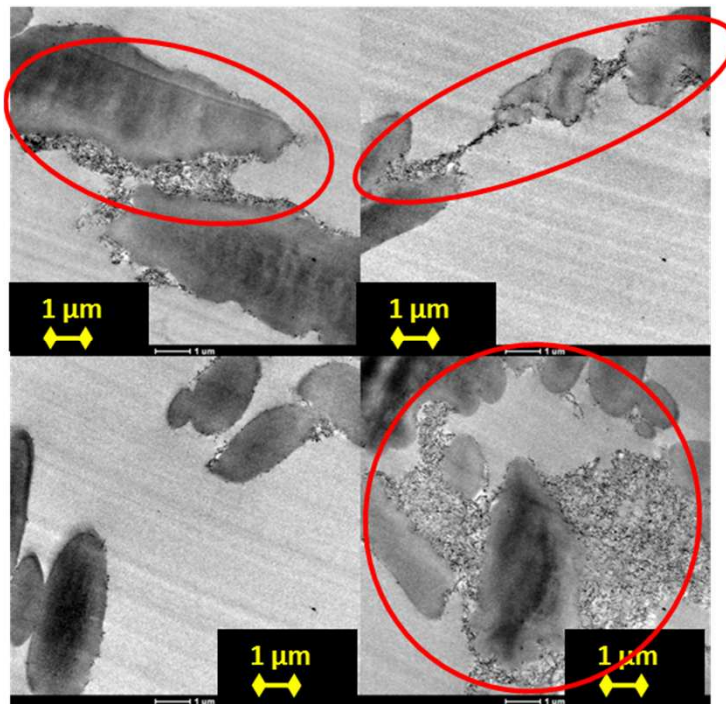
| | F. Superiore | F. Inferiore |
|----------|--|--|
| a | $150 \cdot 10^3 \Omega / \blacksquare$ | $50 \cdot 10^3 \Omega / \blacksquare$ |
| b | $70 \cdot 10^3 \Omega / \blacksquare$ | $15 \cdot 10^3 \Omega / \blacksquare$ |
| c | $6,5 \cdot 10^3 \Omega / \blacksquare$ | $2,5 \cdot 10^3 \Omega / \blacksquare$ |



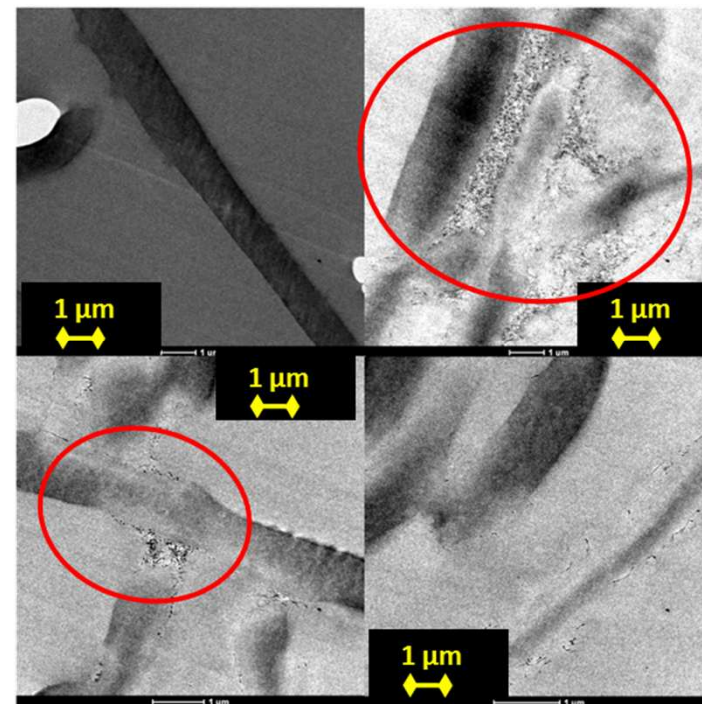
Caso studio #3

Morfologia TEM

Inglobamento in resina e sezionamento al microtomo



Sezione Perpendicolare alle fibre

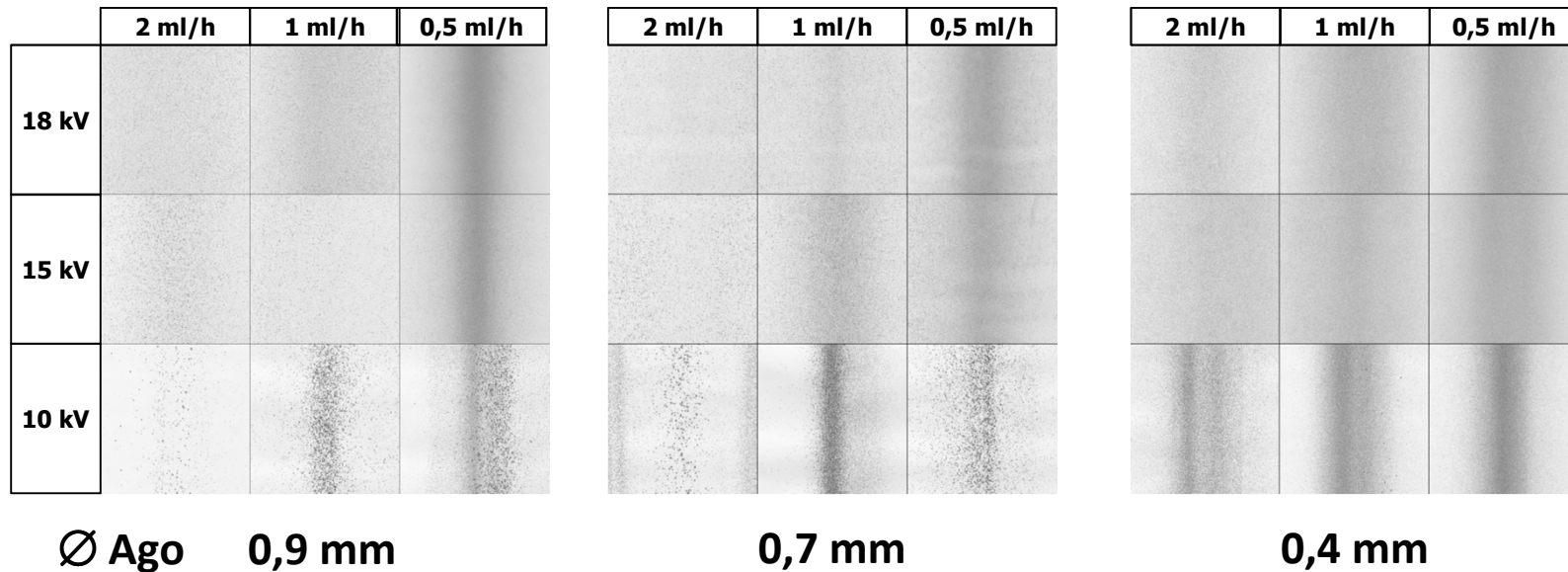


Sezione Parallela al piano della membrana



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Ottimizzazione dei parametri



Aumento di Tensione applicata

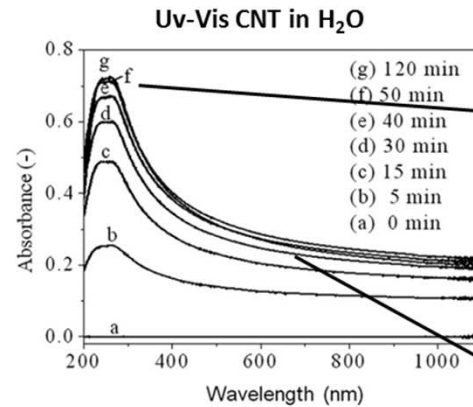
Diminuzione diametro dell'ago

Portata della pompa



Caso studio #3

Misura [CNT] – UV-vis



λ (CNT) = 260 nm

$\lambda_{\text{cutoff}}(\text{H}_2\text{O}) = 190 \text{ nm}$

$\lambda_{\text{cutoff}}(\text{DMF}) = 300 \text{ nm}$

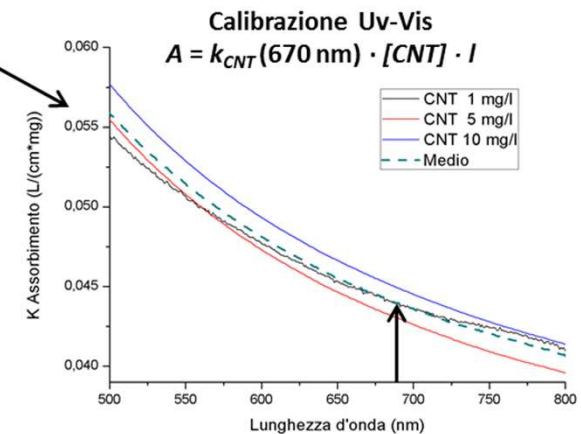
$\lambda_{\text{cutoff}}(\text{Xilene}) = 350 \text{ nm}$

Concentrazioni Misurate

Sim 180° 1 [CNT] = **1,1%**

Sim 180° 2 [CNT] = **0,9%**

Covered [CNT] = **0,28% (0,01 mg / cm²)**





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Misura [CNT] – ICP plasma

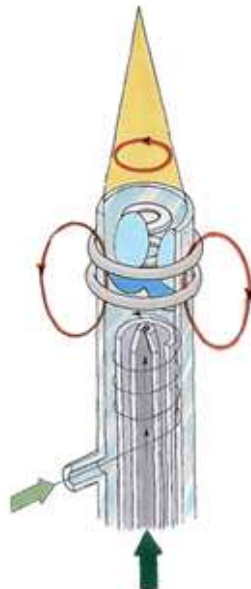
Catalizzatore CNT

| | |
|--------------------------------|--------------|
| Al ₂ O ₃ | 10,14% |
| Fe | 0,44% |
| Co | 0,22% |

Contaminazione

Preparativa Campioni

- Dissoluzione in **HNO₃** concentrato
- 40 min con reattore a **microonde**
- diluizione con acqua **MilliQ**



Campione

Covered
Sim 180° 1
Sim 180° 2

R_S (Ω / ■)

1,12 · 10³
1,5 · 10³
2 · 10³

Uv-Vis ICP-MS

0,28% 0,301
1,1% 1,578
0,9% 1,32

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Conclusioni e sviluppi

- ✓ OTTENIMENTO DI MEMBRANE NANOSTRUTTURATE AD ELEVATA CONDUCIBILITA' GIA' BASSI CONTENUTI DI MWCNT
- ✓ MESSA A PUNTO E OTTIMIZZAZIONE DI UN PROCESSO DI DEPOSIZIONE SIMULTANEA POLIMERO/MWCNT NONCHE' DI TECNICHE SPERIMENTALI PER LA VALUTAZIONE DELLA %MWCNT
- ✓ POSSIBILI APPLICAZIONI NEL CAMPO DELLE CELLE A COMBUSTIBILE E DEI TESSUTI INTELLIGENTI



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Grazie per l'attenzione!

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