Tunable Piezoelectric and Thermoelectric Properties of Polymer-Based Composites

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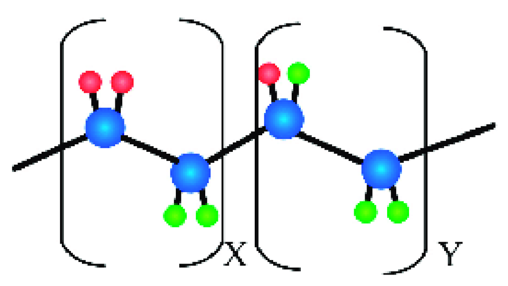
INTRODUCTION

Energy harvesting is the process of converting ambient sources such as solar, mechanical (human motion), or thermal (heat losses) energy into useful energy, which is becoming interesting for sustainable technologies. Piezoelectricity converts mechanical energy into electrical energy from local dipoles, while thermoelectricity uses thermal gradients to generate electricity from the Seebeck effect. Conventional piezoelectric materials are ceramics (electrical insulators), whereas thermoelectrics are inorganic semiconductors (electrical conductors). Polymer-based nanocomposites filled with conductive nanofillers have attracted interest given their lightweight, tunable properties and potential flexibility.

OBJECTIVE

POLYMER MATRIX

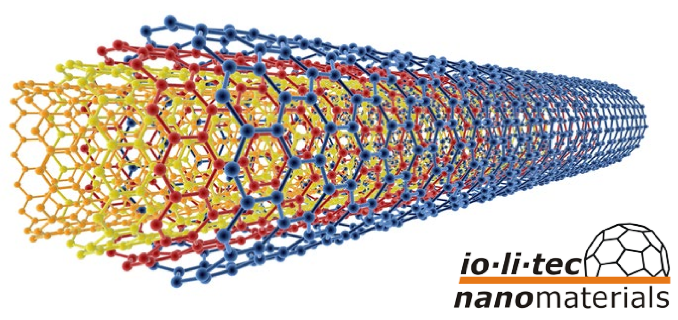


Poly(vinylidene fluoride-co-trifluoroethylene)
P(VDF-co-TrFE) 80/20

Intrinsic piezoelectric properties

+

CONDUCTIVE FILLERS

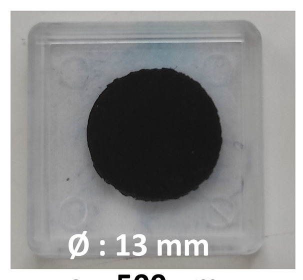


MultiWalled Carbon Nanotubes
(MWCNT)

High electrical conductivity

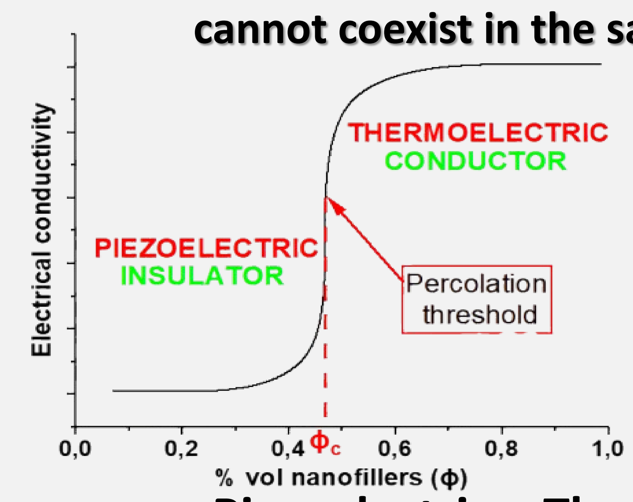
Solution Mixing

COMPOSITES



e ≈ 500 µm

Piezoelectric and thermoelectric effects cannot coexist in the same material



By simply adjusting the fillers content

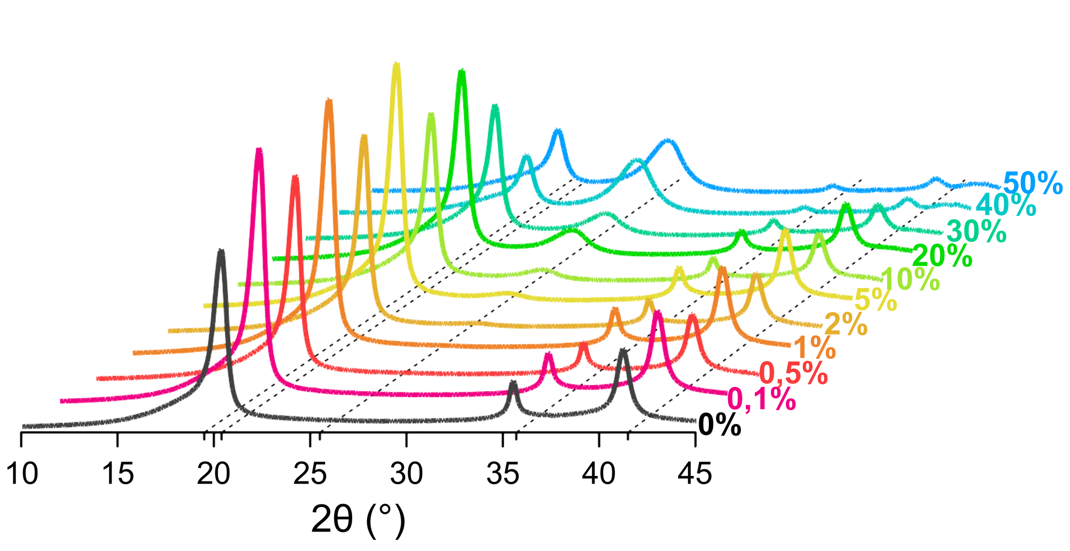
Piezoelectric or **Thermoelectric**

$\phi<\phi_c$ $\phi>\phi_c$

CNTs can enhance PE(1) or TE(2) properties in polymer-based composites

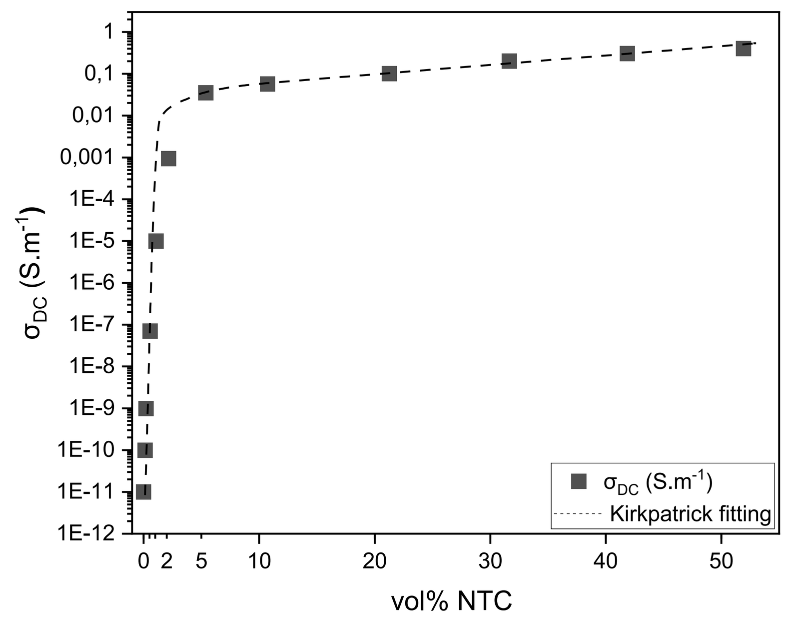
RESULTS

❖ Impact of CNT on structure (WAXS)



- Crystalline structure is preserved : Presence **of ferroelectric phases** (19,5°) and no sign of paralectric phase (18,5°) => essential to preserve **ferroelectric & piezoelectric behavior** from the polymer
- **Degree of crystallinity is decreased** (from 51% to 40%)

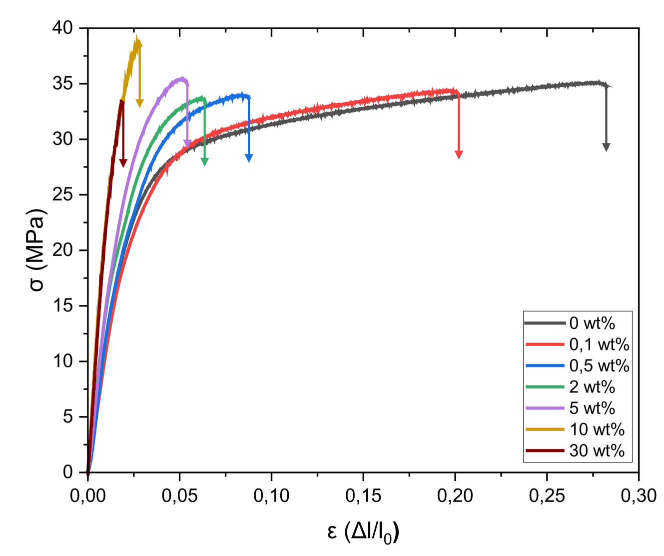
❖ Electrical properties



- CNT impart **electrical conductivity** to the composite
- σ values ≈ 10^{-1} S.m^{-1} **(Semi-conductor)**
- **Percolation threshold = 0,906vol%** (Kirkpatrick)

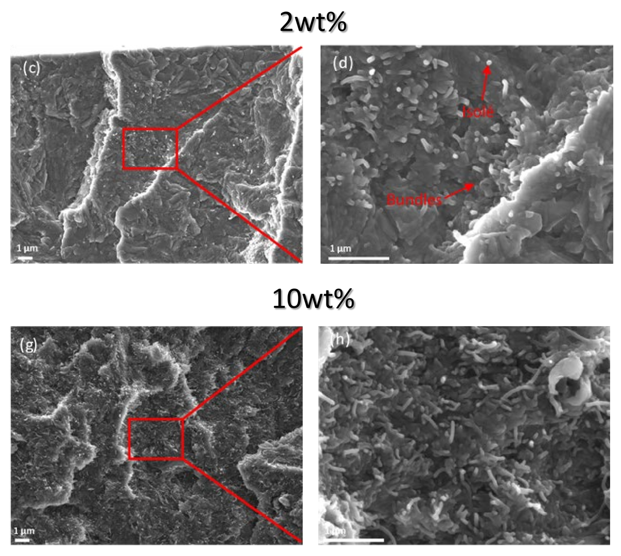
PE < 0,84 wt% < TE

❖ Mechanical properties



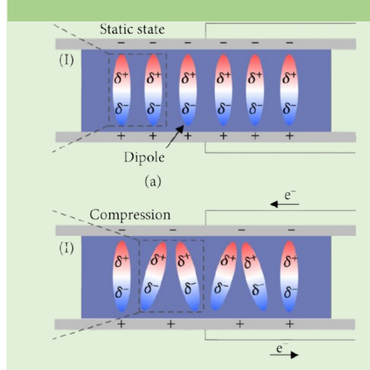
- Composite maintains **flexibility** from the matrix up to **5wt%** of carbon nanotubes
- Young Modulus in increased from 1,11 to 2,47 GPa

❖ SEM images



- Carbon nanotubes appear to **be well-dispersed within polymer matrix**
- While some bundles are observed, they remain well distributed, even at high content fillers

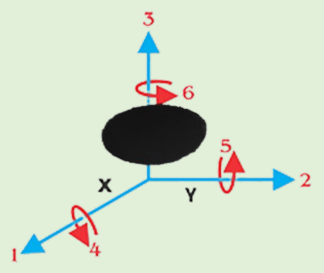
Piezoelectric properties



Piezoelectric coefficient

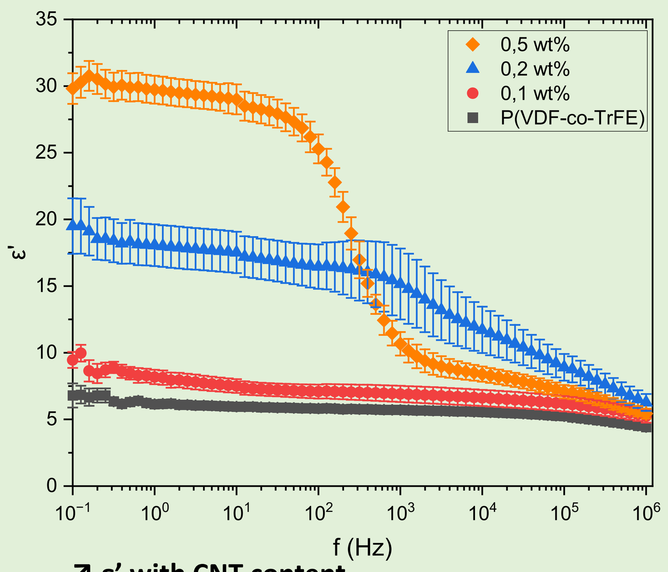
$$\mathbf{d_{ij}} = \left(\frac{\partial \mathrm{Pi}}{\partial \sigma_j}\right)_V$$

Quantify the ability to convert mechanical stress into electrical charge
"≈ Piezoelectric performance"



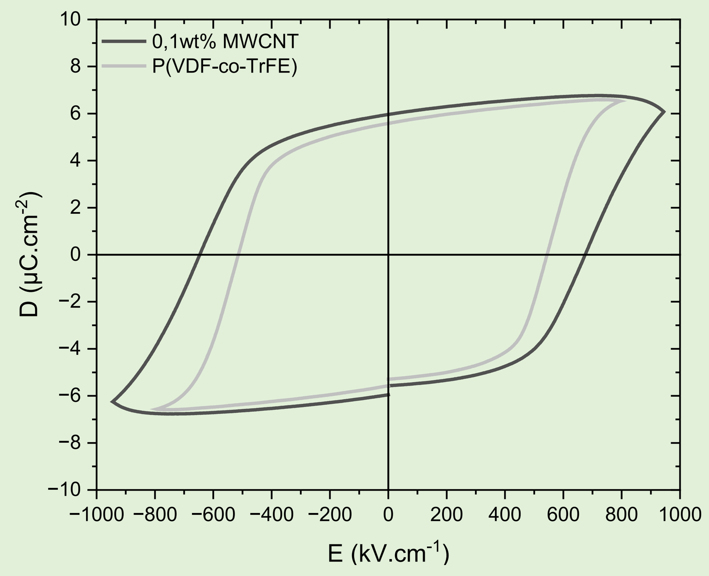
Direct measurements of piezoelectric coeffcient were not possible experimentally due to electrical breakdown phenomena due to the highly conductive carbon nanotubes during polarization

❖ Dielectric measurements



↗ ε' with CNT content
=> formation of microcapacitors : increase of interfacial polarization (≠ permittivities CNT/polymer)

❖ Ferroelectric measurements



- **Little to no reduction of P_r** : may be due to evolution crystalline structure and decreased of degree of crystallinity
$P_{r,(0,1wt\%)}$ = 5,4 µC.cm^{-2} / $P_{r,(P(VDF\text{-}co\text{-}TrFE))}$ = 5,6 µC.cm^{-2}

$$\boxed{d_{33} = 2\, Q_{33}\, \varepsilon_3\, P_r}\ ^{(4)}$$

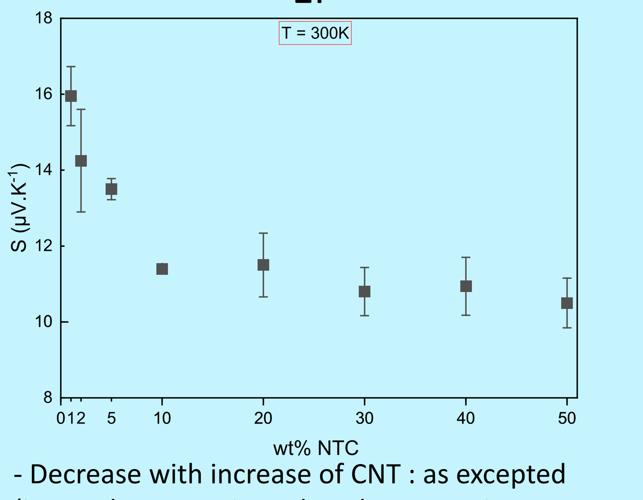
MWCNT enhance piezoelectric coefficient d_{33} :
Large increase of dielectric constant while P_r and Q_{33} (5) remain nearly unaffected

Thermoelectric properties

To quantify thermoelectric performmance we use the figure of merit at a given temperature (here, T = 300K)

❖ Seebeck coefficient

$$S = -\frac{\Delta V}{\Delta T}\ [\mu V.K^{-1}]$$



- Decrease with increase of CNT : as excepted (inversely proportionnal to charge carriers density)
- Values close to litterature for CNT/insulating polymer matrix (6-30 µV.K^{-1}) 2,3

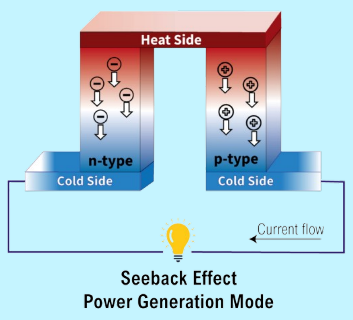
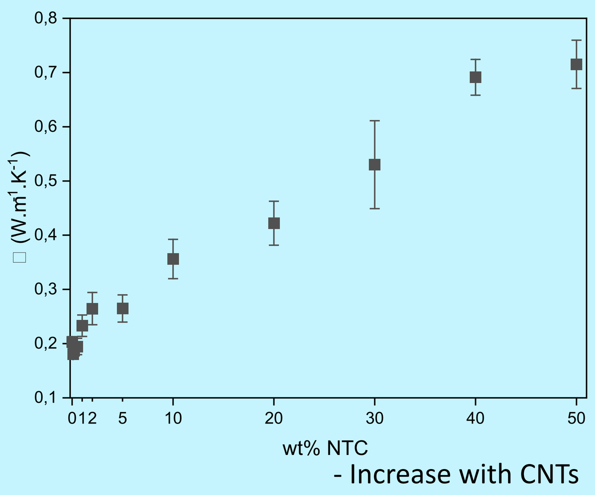


Figure of merit

$$\boxed{ZT = \frac{S^2 \times \sigma}{\kappa} \times T}$$

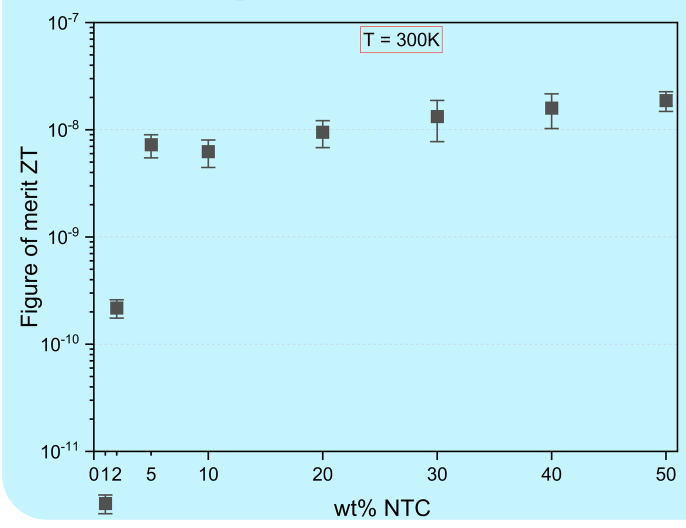
❖ Thermal conductivity

[W.m^{-1}.K^{-1}]



- Increase with CNTs
- Values **limited to below 0,8 W.m^{-1}.K^{-1}** (far from single CNT values which can be up to 3000 W.m^{-1}.K^{-1}) => thanks to matrix/fillers **interfaces** leading to **phonon diffusion**

❖ Figure of merit



❖ Electrical conductivity

[S.m^{-1}]
(see figure above)

- Values of ZT are around 10^{-8}
-> Low values but close to the values reported in the literature for insulating polymer/carbon nanotubes composites 2,3
- **Mainly controlled by electrical conductivity**
- A plateau observed at 5wt% CNT content : interesting because for **same TE performances, flexibility** from polymer matrix is retained

CONCLUSION & OUTLOOKS

- Above percolation threshold, MWCNT impart electrical conduction properties to the polymer matrix, **enabling thermoelectric properties**
- Below percolation threshold, MWCNT **enhance piezoelectric properties** of the polymer by increasing dielectric constants thanks to interfacial polarization
- PE samples and some TE samples (up to 5wt%) show better performances while retaining **flexibility**
- Outlooks : Functionalization of carbon nanotubes + measurements on thin films

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