Carbon nanotubes and silver flakes filled epoxy resin for new conductive hybrid adhesives

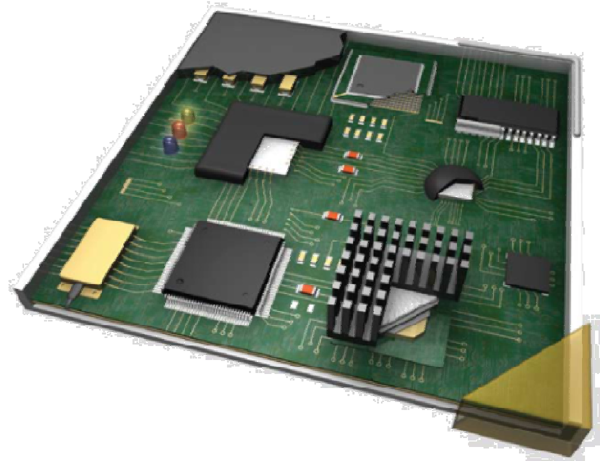
F. Marcq*, P. Demont, P. Monfraix, A. Peigney, C. Laurent, F. Courtade, T. Jamin

*marcq@cict.fr

Current solutions for electrical and thermal management

- Electrical and thermal management for electronic devices based on bare dice

→ **silver filled epoxy adhesives**

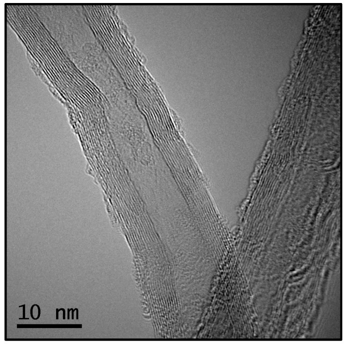


- <u>Main issues :</u>
  – Poor thermal conductivity (≈ 0.5 - 3 W/(m.K))
  – Small surface's devices because of the high rigidity of the adhesives (75 wt% Ag)

Silver vs. CNTs

- <u>Silver :</u>
  - Electrical conductivity : **6.10^7 S/m**
  - Thermal conductivity : **426 W/(m.K)**

- <u>CNTs :</u>
  - Electrical conductivity : **≈ 10^5 S/m**
  - Thermal conductivity : **≈ 400 W/(m.K)**



- <u>High aspect ratio of CNTs implicates :</u>
  - Electrical percolation at **low loading**
  - **Mechanical reinforcement** of the matrix

→ **CNTs good candidates to replace silver**

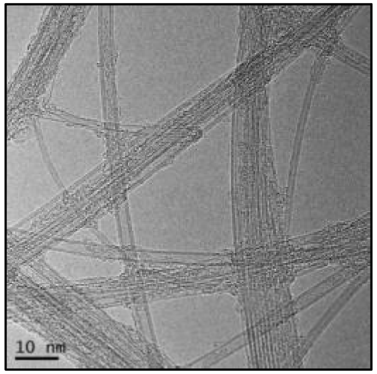
INSTITUT CARNOT CIRIMAT

Comparative study between CNTs and µAg

CNTs

→ **DWCNTs from Cirimat ***

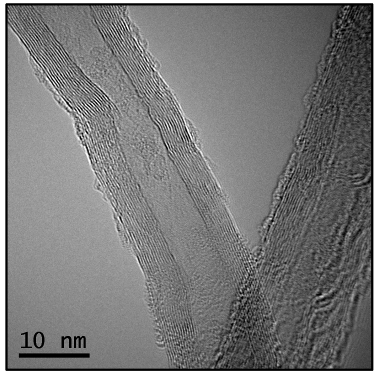
Ø = 2.80 nm
length ≈ 10 µm
→ aspect ratio ≈ 3500



HR-TEM characterization done at Cirimat

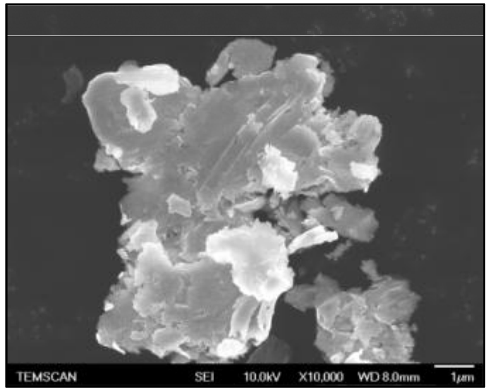
→ **Commercial MWCNTs**

Ø = 11.66 nm
length ≈ 2 µm
→ aspect ratio ≈ 170



µAg → **Silver flakes from Amepox**

Average particle size : 2 – 3 µm

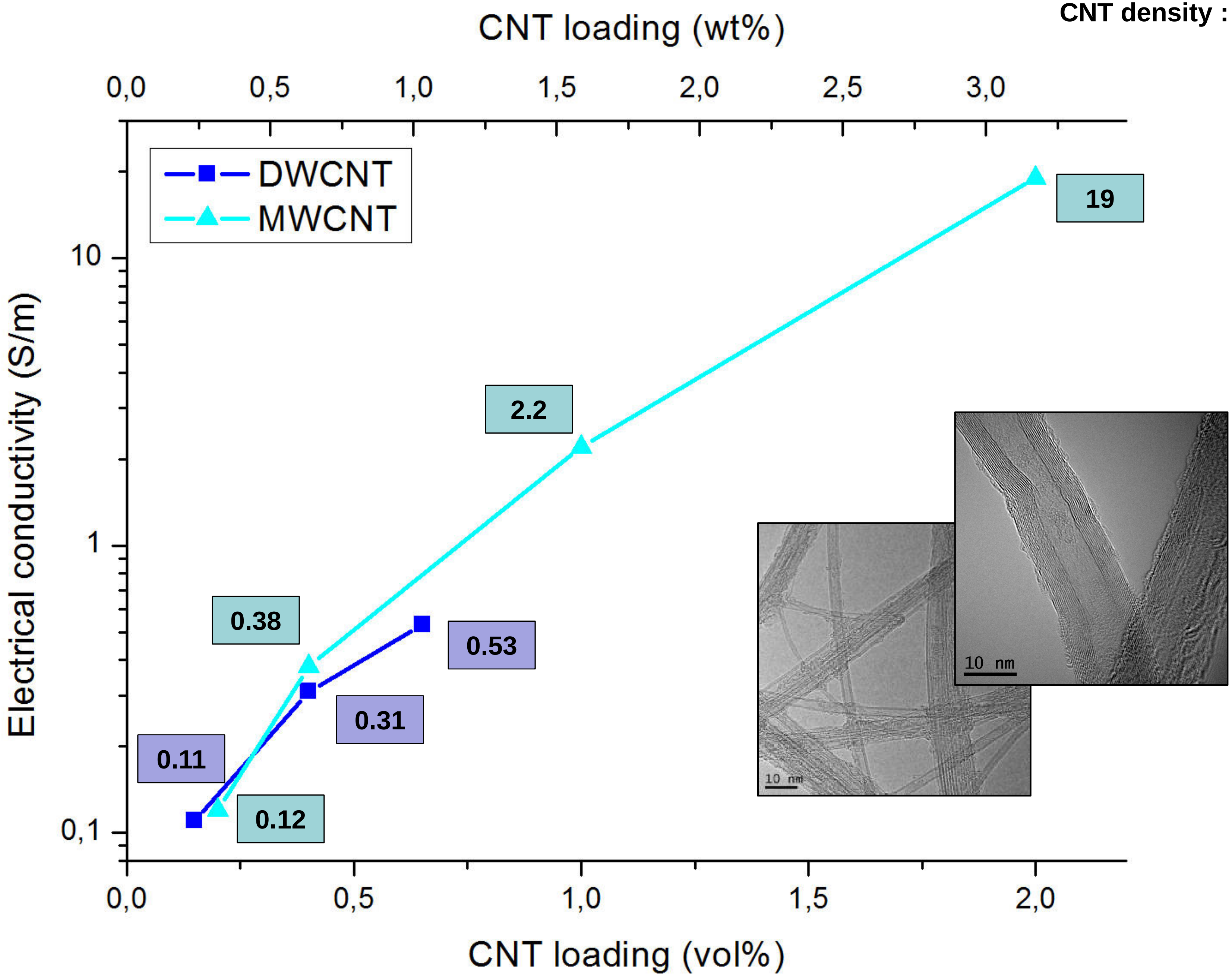


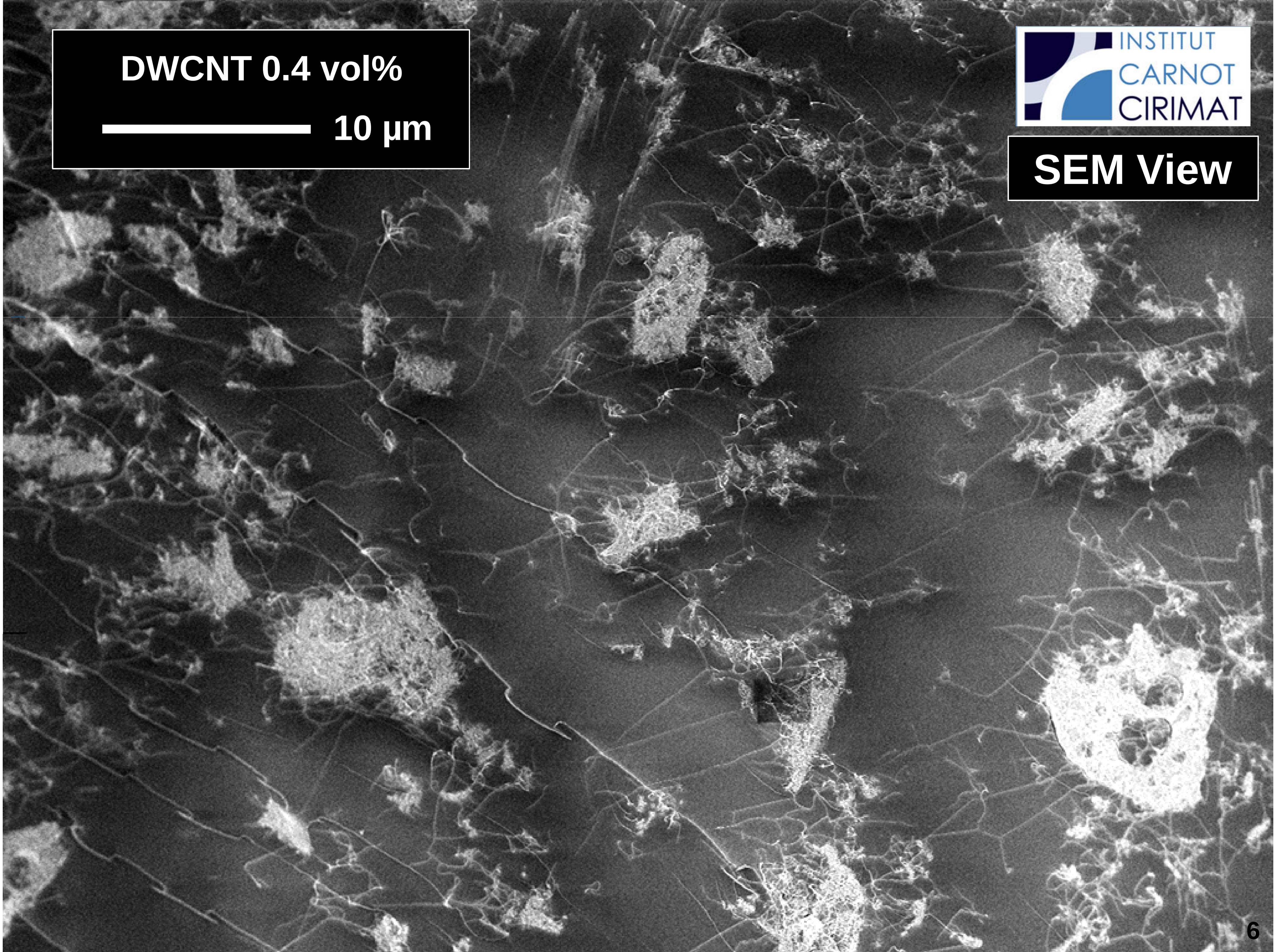
SEM characterization done at Cirimat

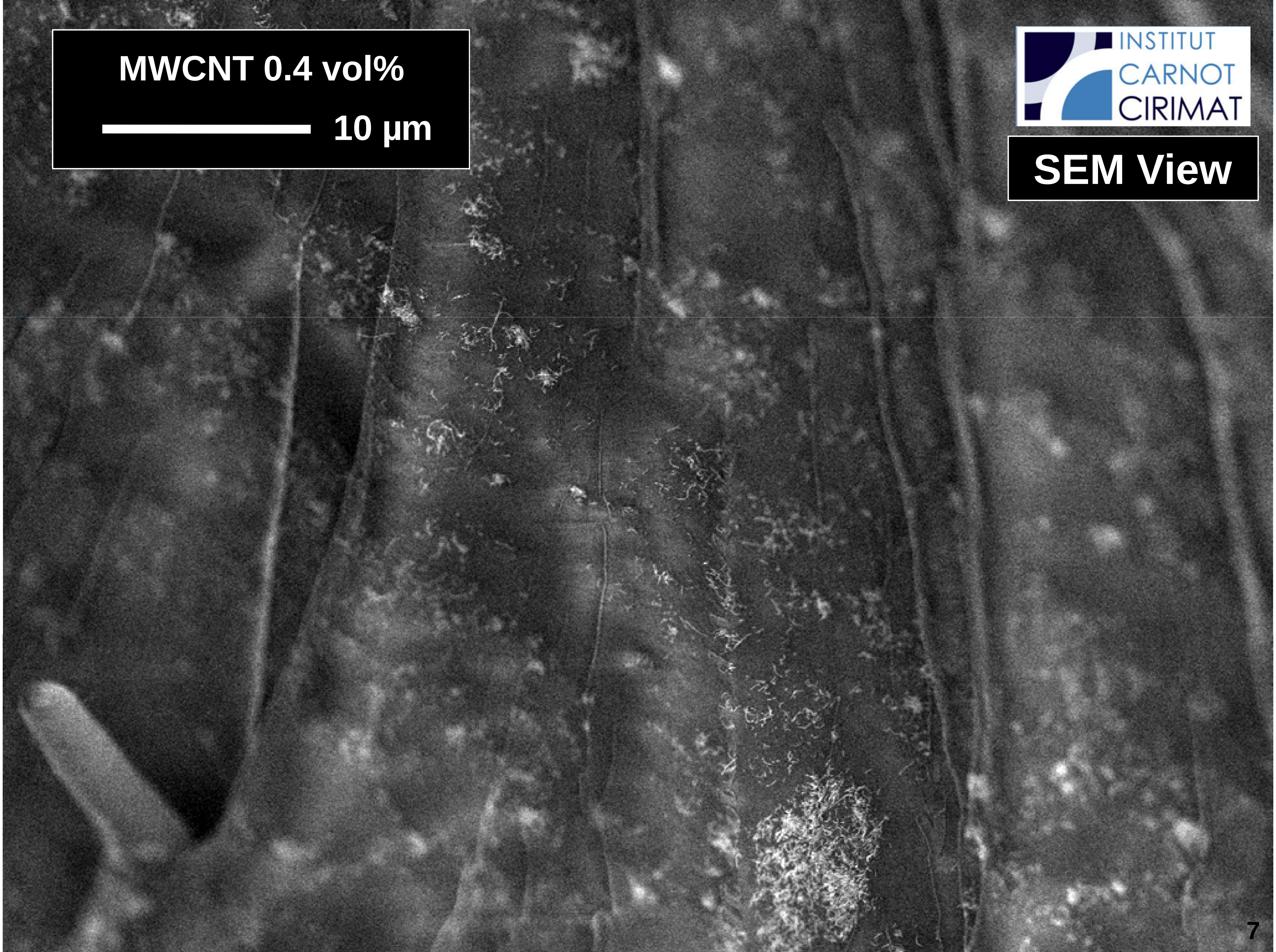
* Flahaut et al., Gram-scale CCVD synthesis of double-walled carbon nanotubes, Chem. Commun., 2003, 1442–1443

Electrical conductivity of CNTs filled composites

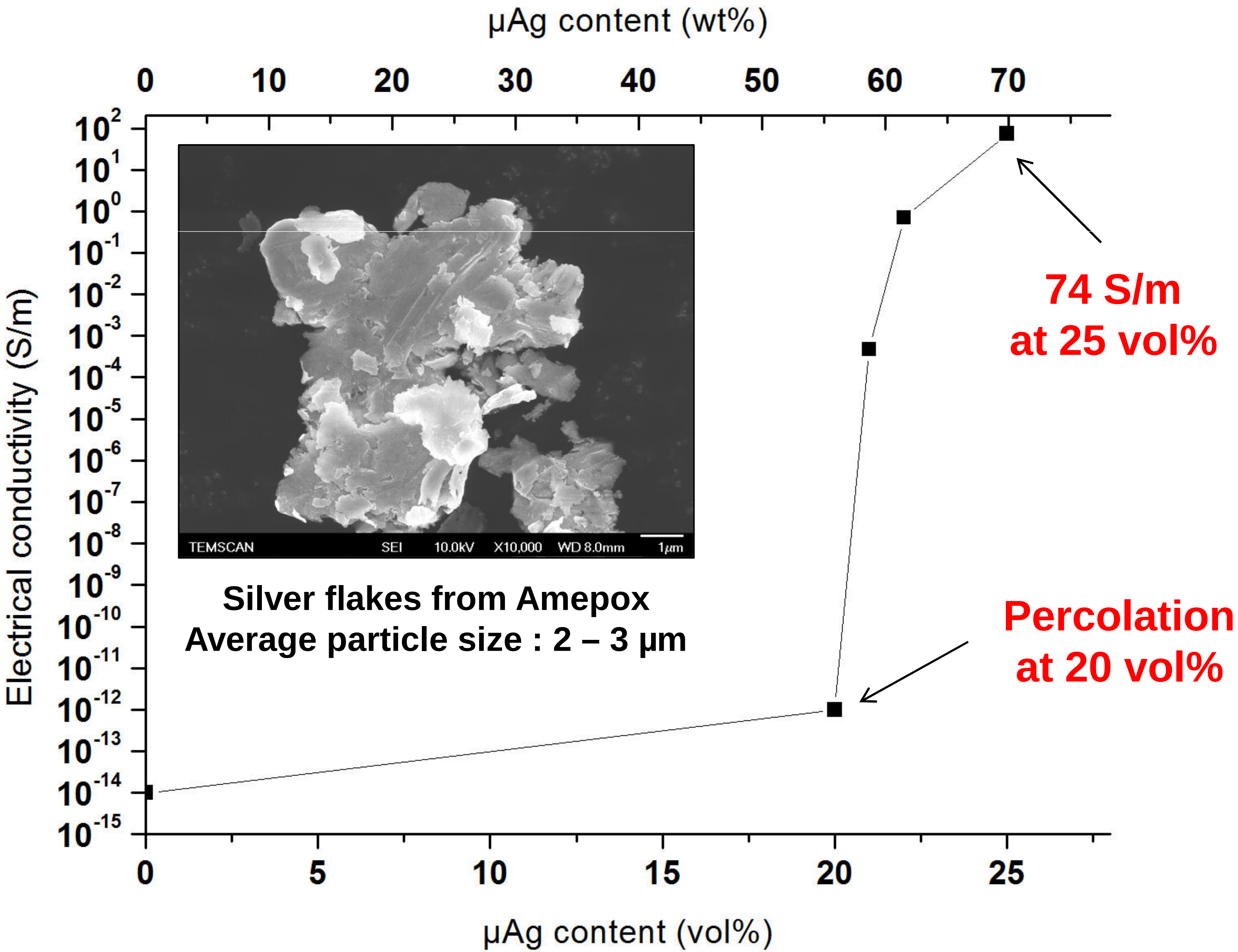
CNT density : 2.1 g/cm^3

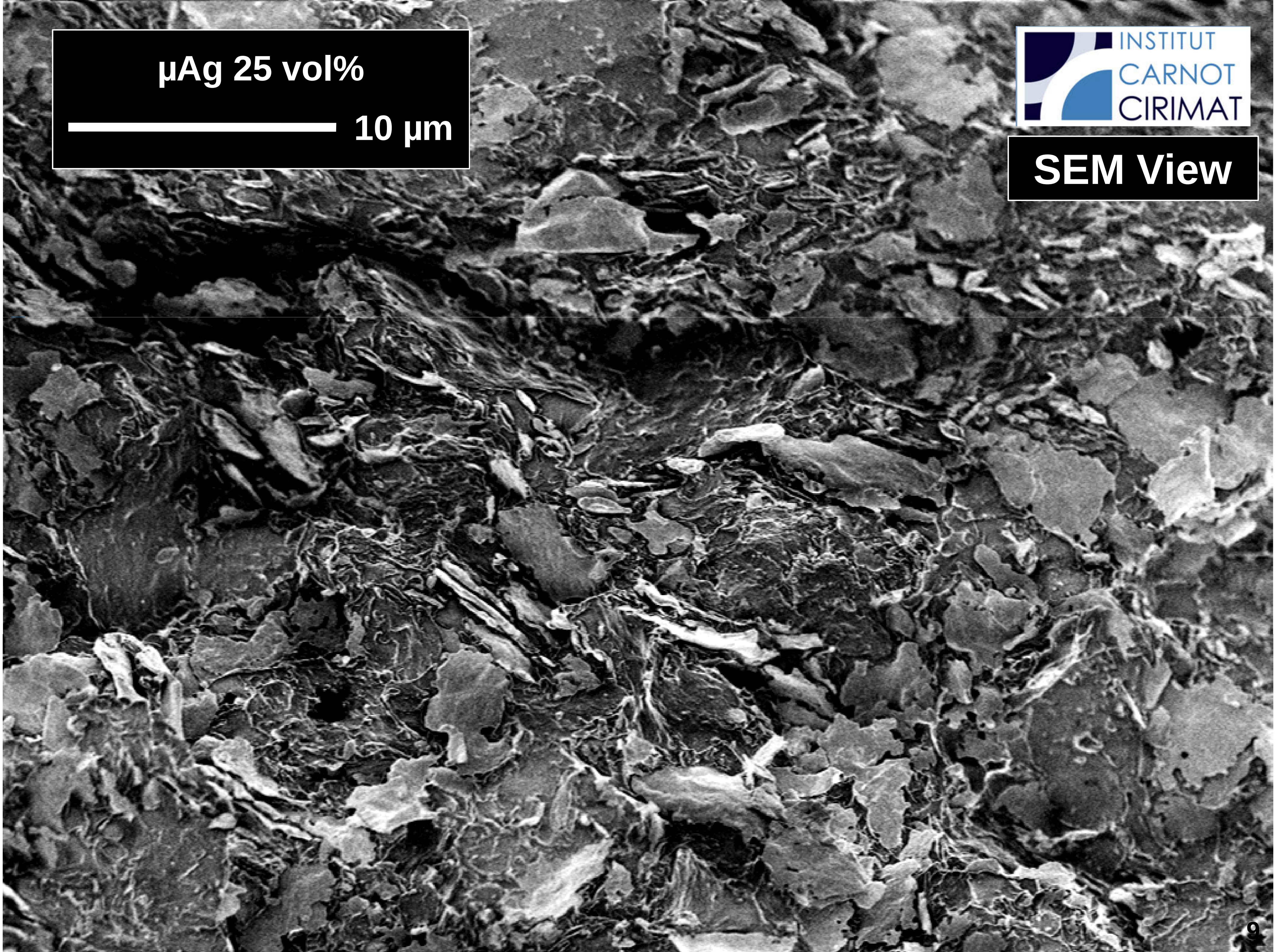



DWCNT 0.4 vol%
10 µm
INSTITUT CARNOT CIRIMAT
SEM View


MWCNT 0.4 vol%
10 µm
SEM View

Electrical conductivity of silver flakes filled composites




µAg 25 vol%
10 µm
INSTITUT CARNOT CIRIMAT
SEM View

Thermal conductivities

Composition	Thermal conductivity [W/(m.K)]
Pure epoxy matrix	**0.20** ± 0.03
DWCNT 0.4 vol%	**0.27** ± 0.04
MWCNT 0.4 vol%	**0.26** ± 0.04
MWCNT 2 vol%	**0.30** ± 0.04
µAg 25 vol%	**0.62** ± 0.09

Measuring method 1

CNTs vs. µAg

	CNTs	µAg
Max electrical conductivity	19 S/m	74 S/m
Max thermal conductivity	0,30 W/(m.K)	0,62 W/(m.K)

→ **CNTs : comparable to best results in literature**

→ **µAg : commercial adhesives claim even higher electrical and thermal conductivities**

⇒ **CNT filled adhesives have electrical and thermal conductivities too low to replace silver filled adhesives**

Hybrid solutions

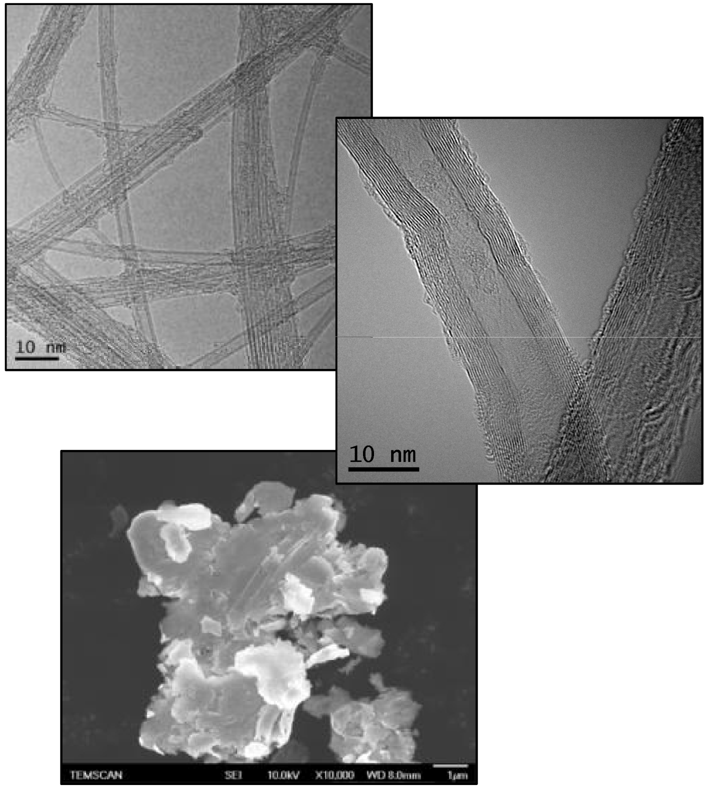
- Patent, literature and commercial reviews show the increasing interest for hybrid solutions such as micro + nano – fillers
- They are mainly micrometric flakes + nano-powders

→ **CNTs have a high aspect ratio, thermal and electrical conductivities**

→ **Hybrid composites µAg + CNTs have potentialities in electrical and thermal conductivities and mechanical properties**

Particles used for preliminary tests

- DWCNTs from Cirimat
- Commercial MWCNTs
- Silver flakes from Amepox



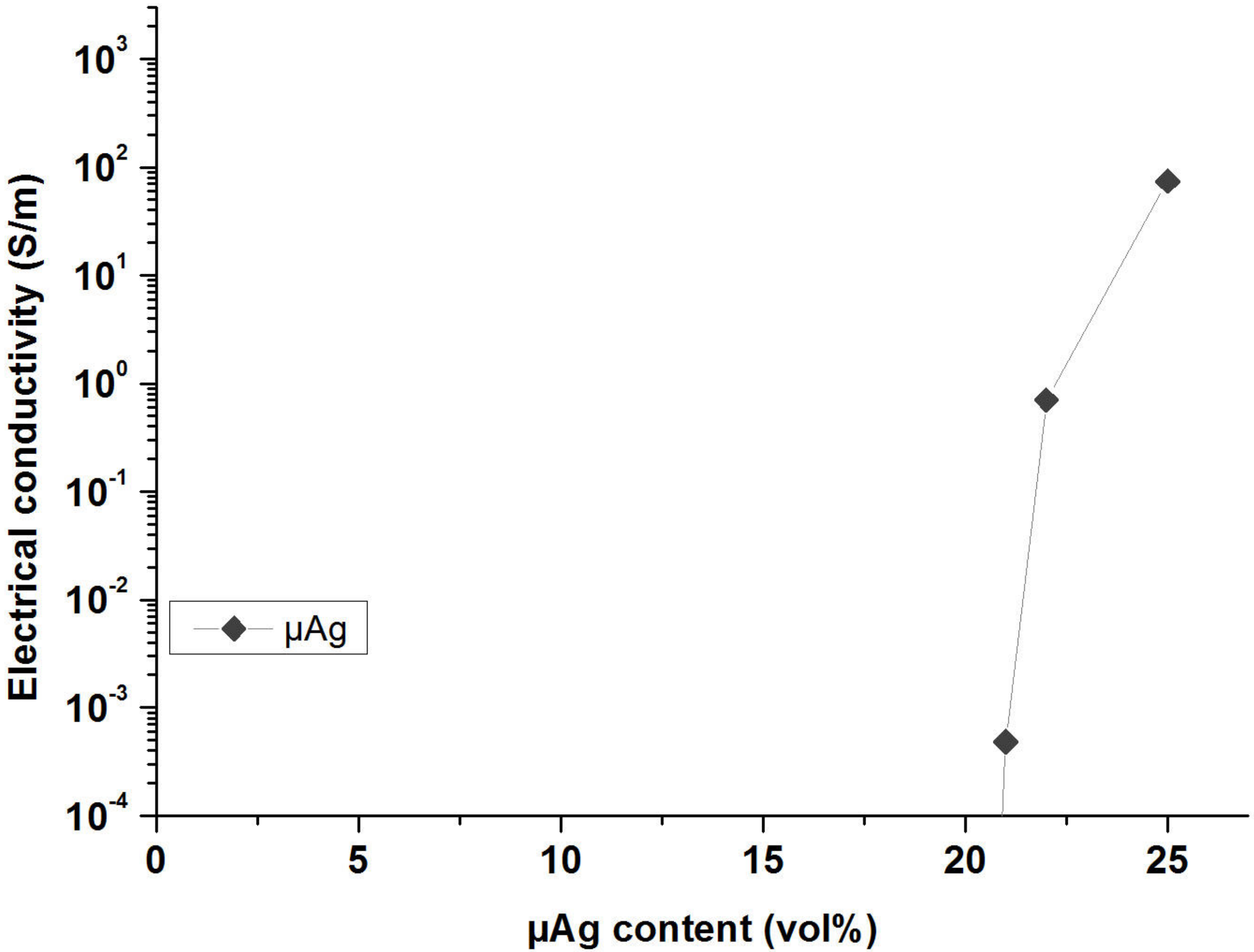
↓

2 types of hybrid fillers

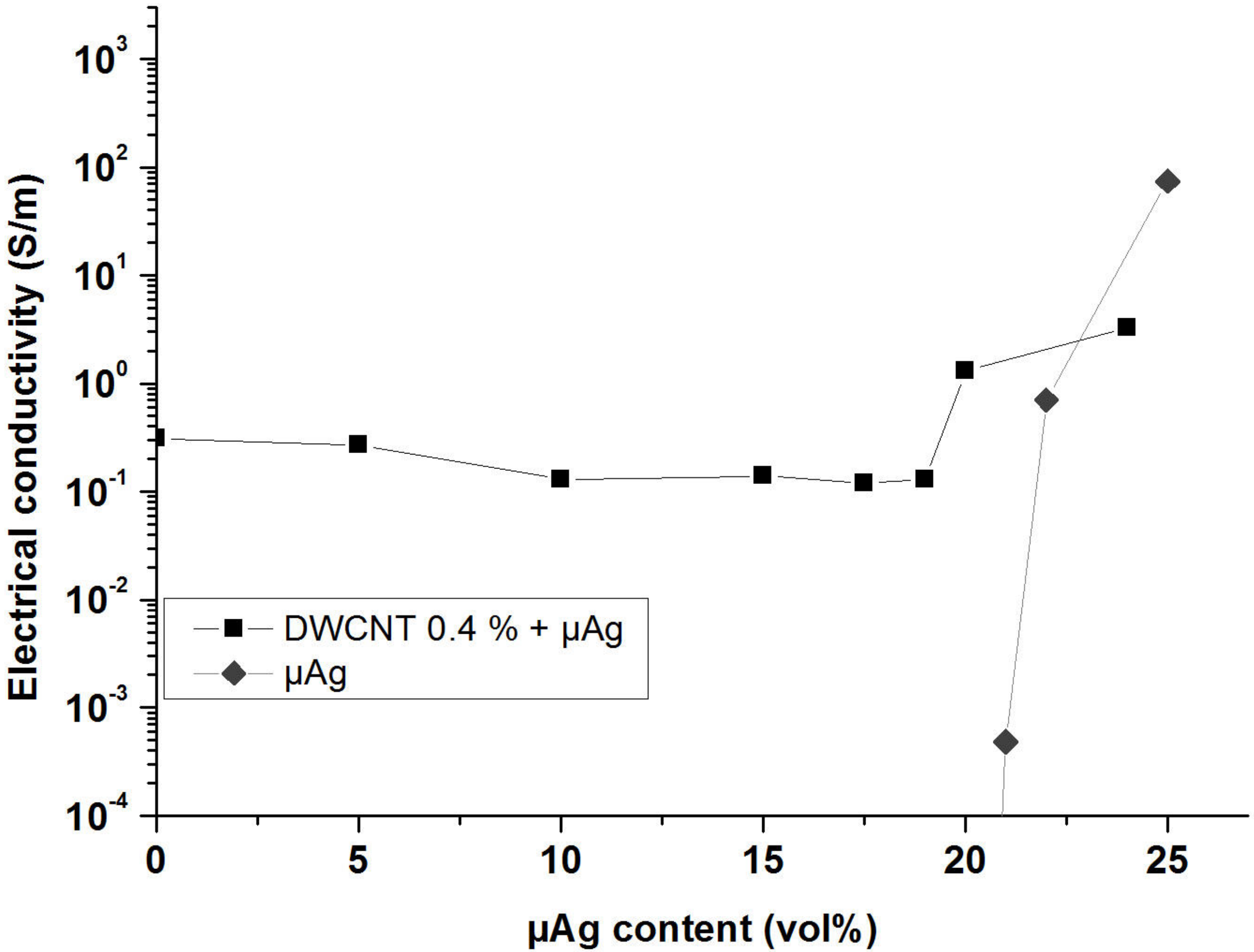
µAg + DWCNTs **µAg + MWCNTs**

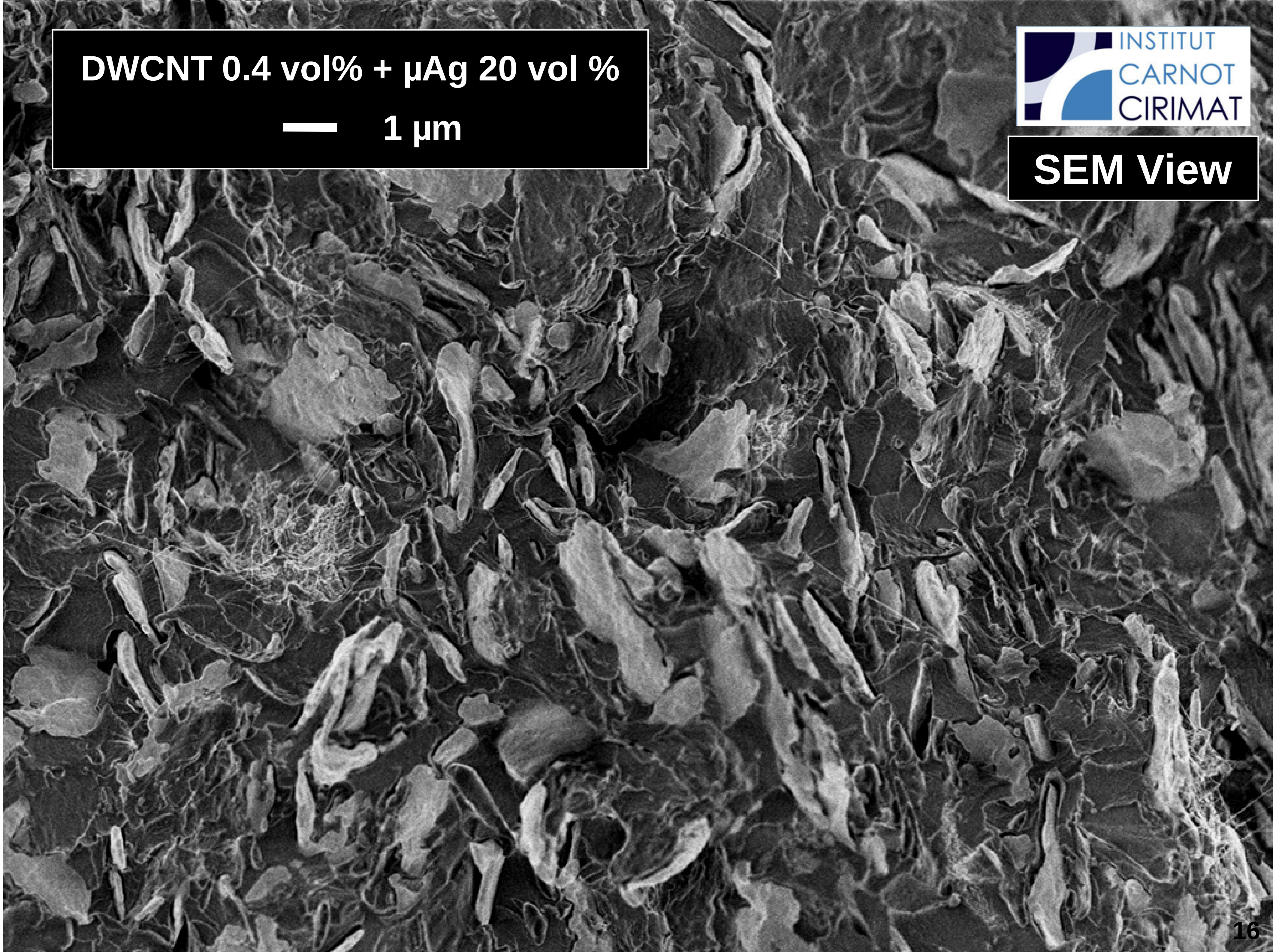
INSTITUT CARNOT CIRIMAT

Electrical conductivities



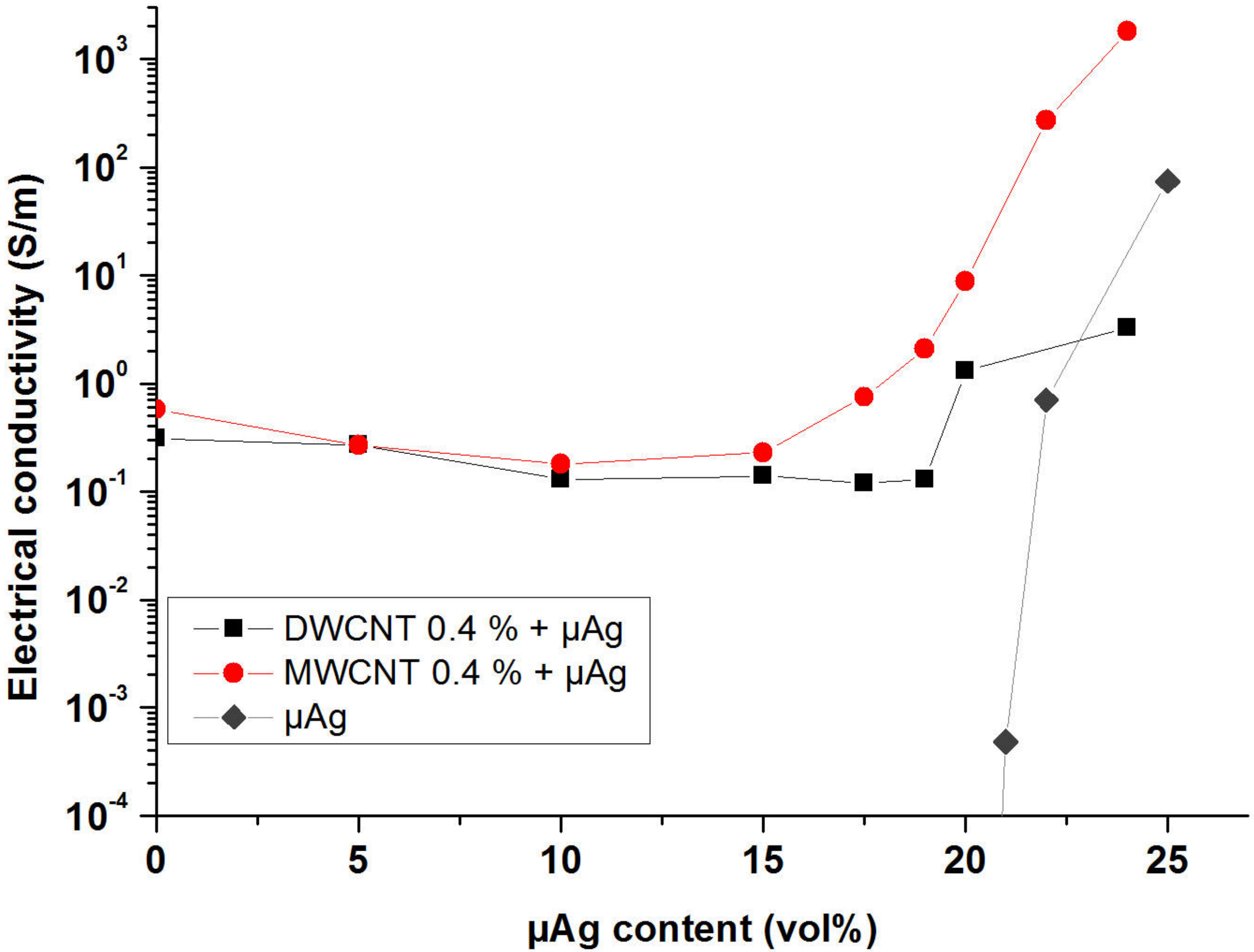
Electrical conductivities



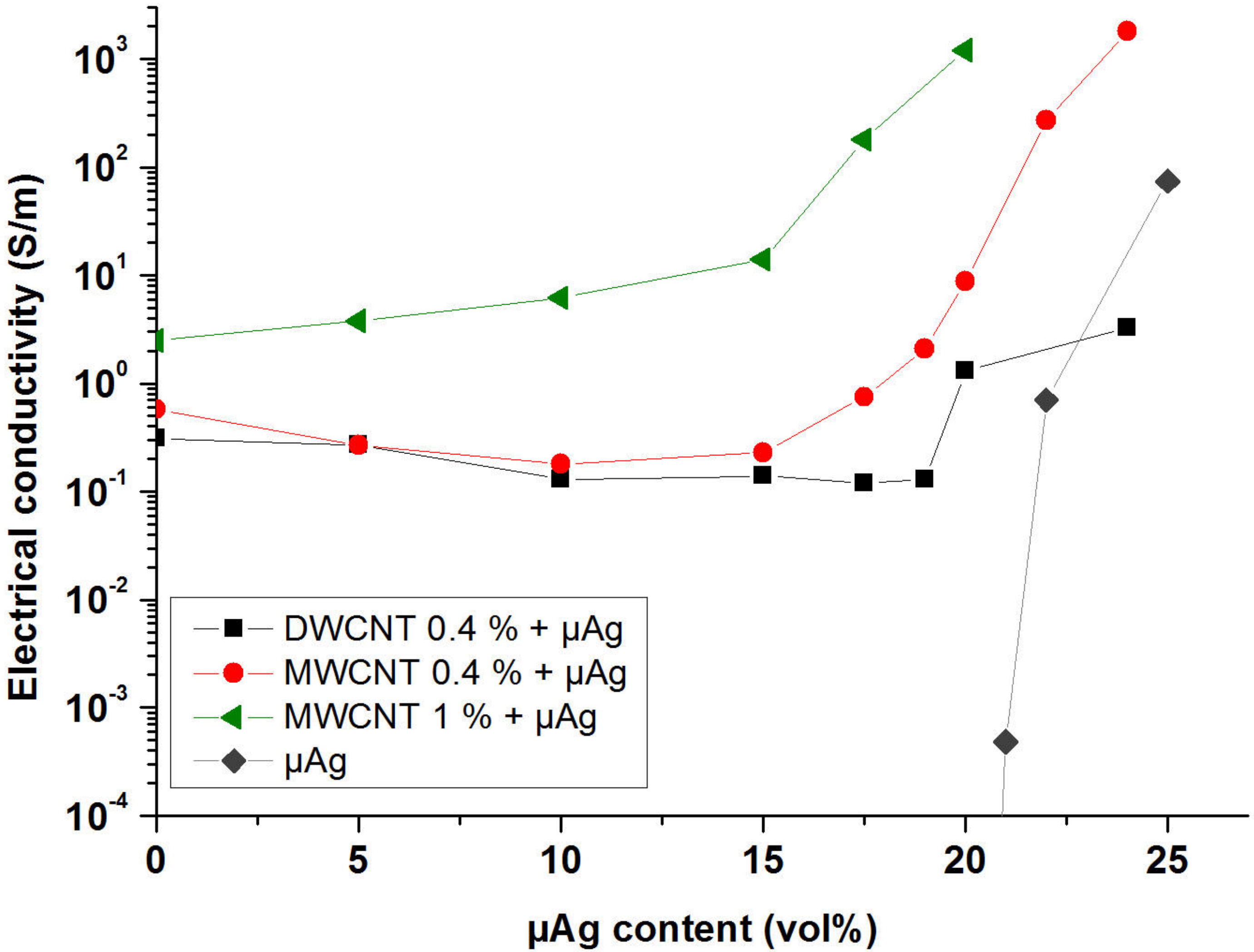

DWCNT 0.4 vol% + µAg 20 vol %
1 µm
INSTITUT CARNOT CIRIMAT
SEM View

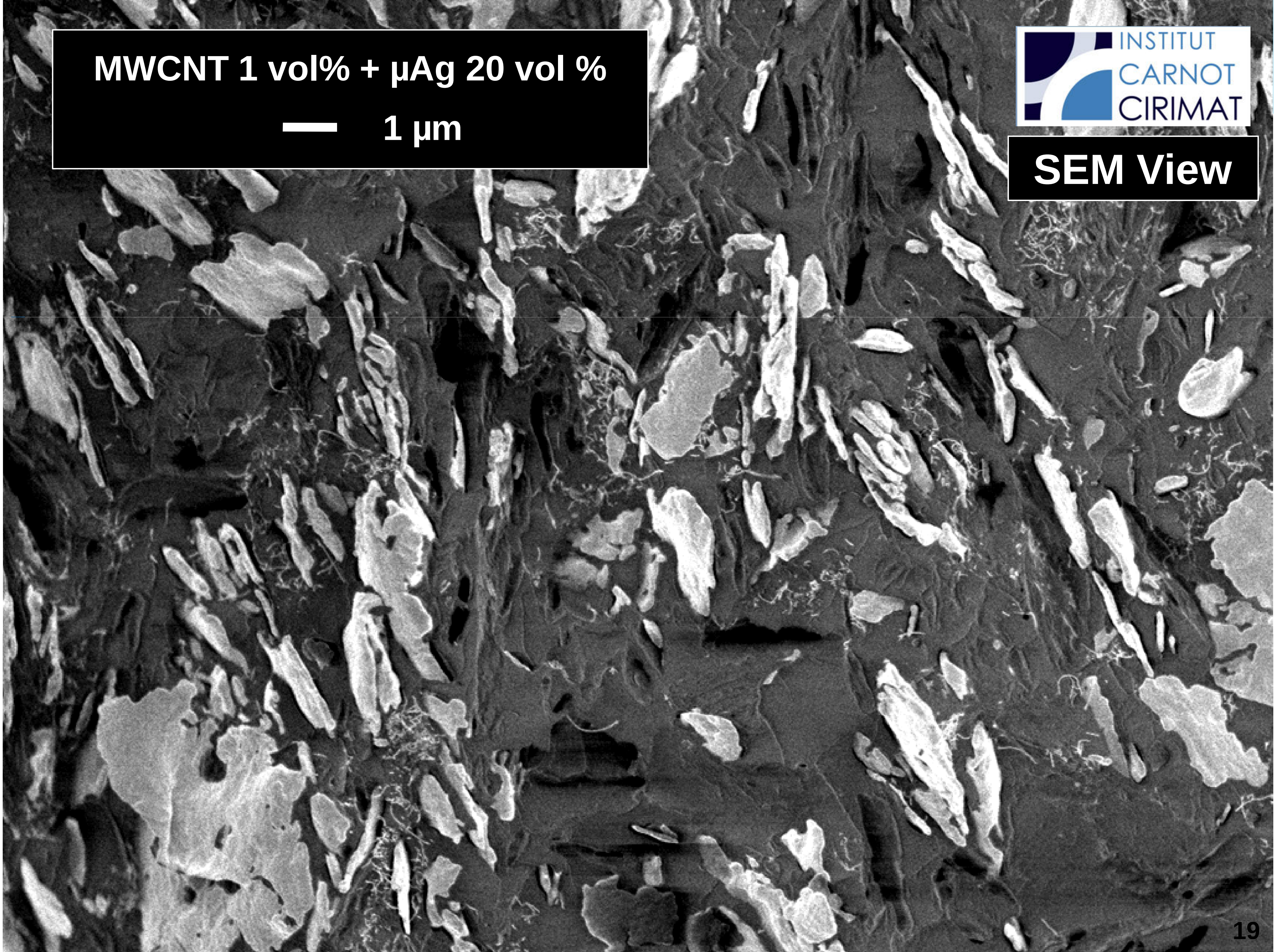
INSTITUT CARNOT CIRIMAT

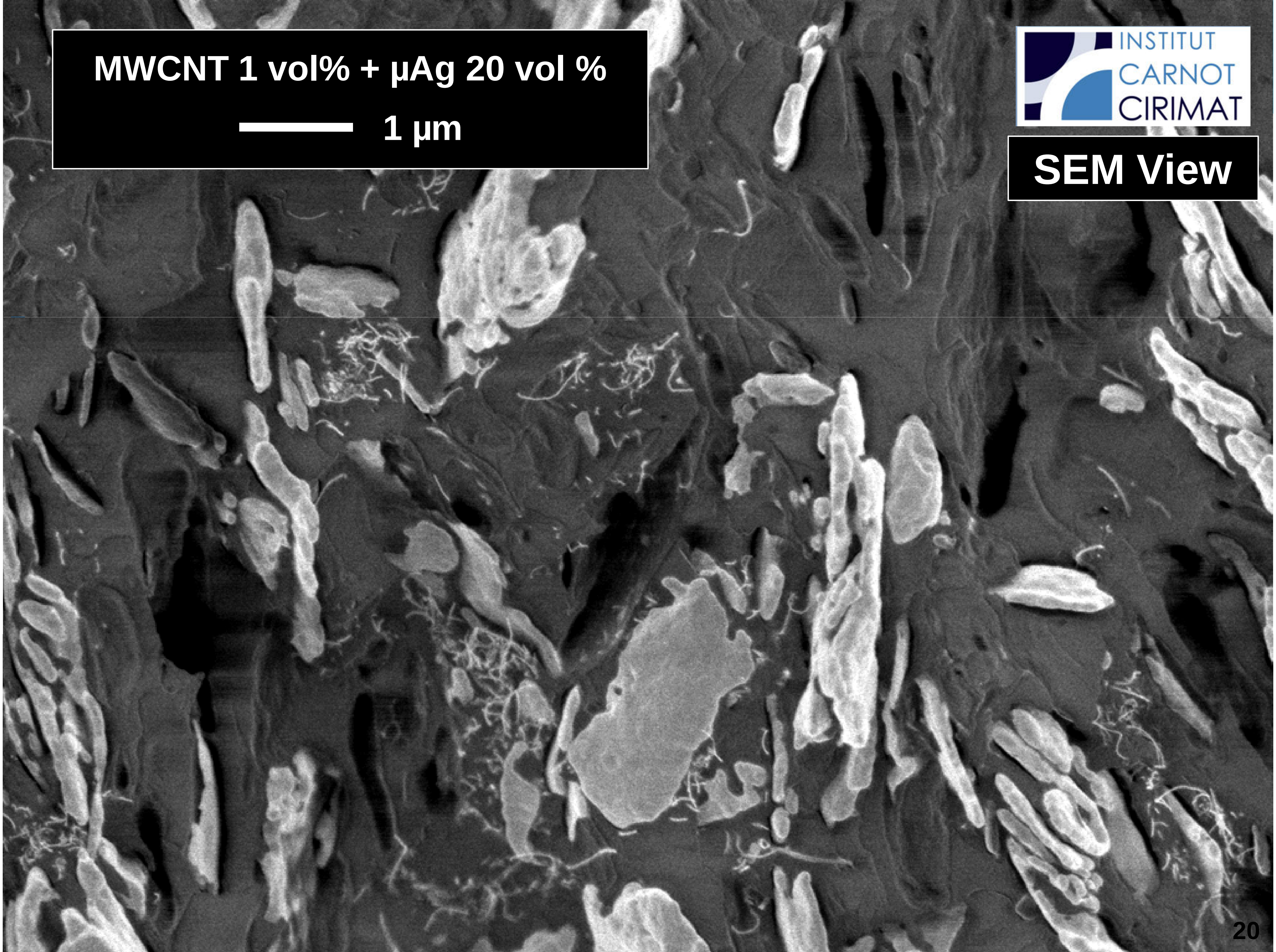
Electrical conductivities



Electrical conductivities




MWCNT 1 vol% + µAg 20 vol %
1 µm
INSTITUT CARNOT CIRIMAT
SEM View


MWCNT 1 vol% + µAg 20 vol %
1 µm
INSTITUT CARNOT CIRIMAT
SEM View

Thermal conductivities

Composition	Thermal conductivity [W/(m.K)]
Pure epoxy matrix	**0.12** ± 0.02
µAg 20 vol%	**0.47** ± 0.07
µAg 25 vol%	**0.48** ± 0.07
DWCNT 0.4 vol% + µAg 20 vol%	**0.45** ± 0.07
MWCNT 0.4 vol% + µAg 20 vol%	**0.43** ± 0.07

Measuring method 2

INSTITUT CARNOT CIRIMAT

Conclusion on hybrid composites

- **Synergetic effect** between MWCNTs and µAg above 15 vol% of µAg
- Electrical conductivities **higher than** silver filled adhesives
- **No improvement** in thermal conductivity

	µAg	µAg + MWCNTs
Max electrical conductivity	74 S/m	2000 S/m
Max thermal conductivity	0.48 W/(m.K)	0.43 W/(m.K)

INSTITUT CARNOT CIRIMAT

Main conclusion

- **CNTs** as only filler **can not replace** silver flakes in adhesives for thermal and electrical management
- **Hybrid filler µAg + MWCNTs** show very good results in **electrical conductivity** :
  - High conductivity with **less silver** → can be a interesting way to obtain better **mechanical properties** from adhesives
- Thermal conductivity of hybrid composites is **comparable** to silver filled composite

INSTITUT CARNOT CIRIMAT

Perspectives

- **Interface**
  - Impact on electrical and thermal conductivities

- **Mechanical properties** : evaluate properties of the assembly of components on substrates through :
  - Thermal cycles
  - Long term storage at high temperature

INSTITUT CARNOT CIRIMAT

Acknowledgment

- The authors would like to thank :
  - **Euripides** frame program through CANOPY project n° EUR -06-103
  - The french space agency **CNES** through contract R&T n°81582/00
  - The **Polish Canopy partners** from Wroclaw University and Amepox