

Chemical Functionalization of Carbon Nanotubes for the Dispersion in Polymer Matrices

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Institute for Polymers and Composites



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The team:

- **Centro de Química U. Minho**

- Nanotube organic chemistry strategy: [M. Fernanda Proença](#)

- **I3N / IPC**

- Melt blending and extrusion: [José A. Covas](#)

- Micro-injection moulding / injection moulding: [António J. Pontes](#); [Carla Martins](#)

- *In situ* PU formation: [Fernando M. Duarte](#)

- **PhD students:**

[Rui M. Novais](#)

[Tânia Ferreira](#)

[Rui Araújo](#)

[Alexandre Ferreira](#)

- **MSc students:**

[Flora Barbosa](#)

[Cátia Cerqueira](#)

[M. Henrique Lopes](#)

[Vera Cruz](#)

- **Research Assistant:**

[Bruno Oliveira](#)

Collaborations:

- **Leibniz Institute of Polymer Research, Dresden (Germany)**

- CNT dispersion: [Petra Pötschke](#)

- XPS: [Frank Simon](#)

- **iNANO Research Center at Aarhus University (Denmark)**

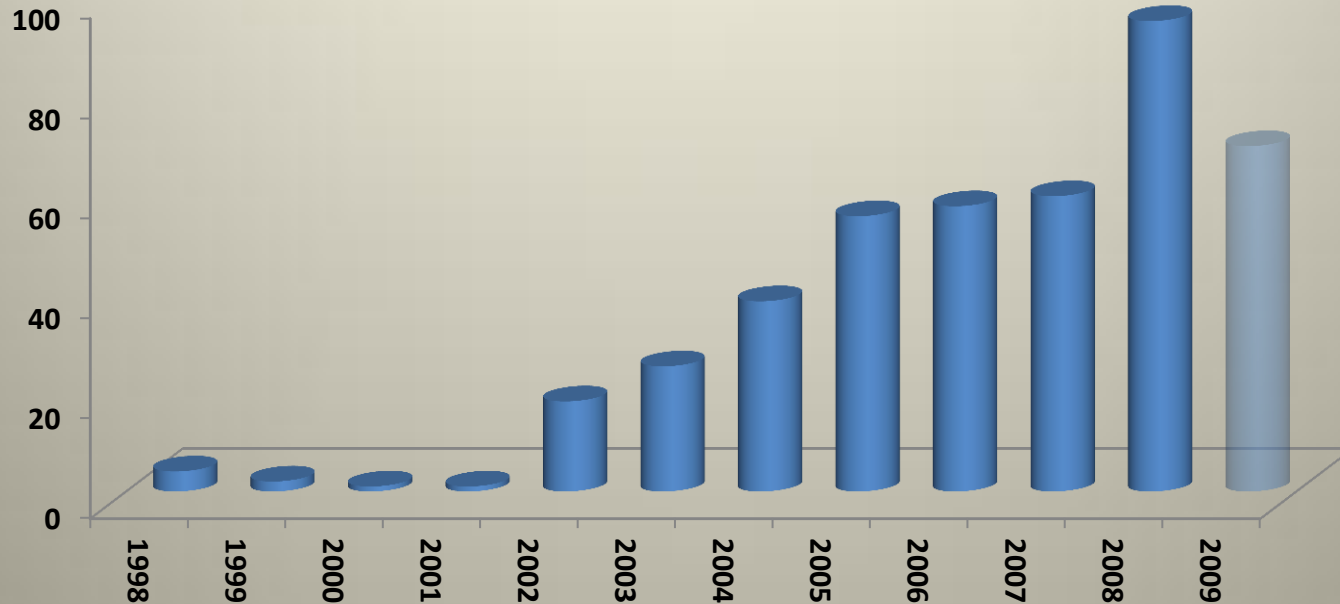
- STM analysis: [Flemming Besenbacher](#)

- **Applied Sciences Inc, Ohio, USA**



Chemical functionalization of carbon nanotubes

Search on *Web of Science*, entry: “carbon nanotube” and “chemical functionalization” in *topic*.



➤ Entangled form

➤ Surface chemical inertia

➤ Poor interface with other materials

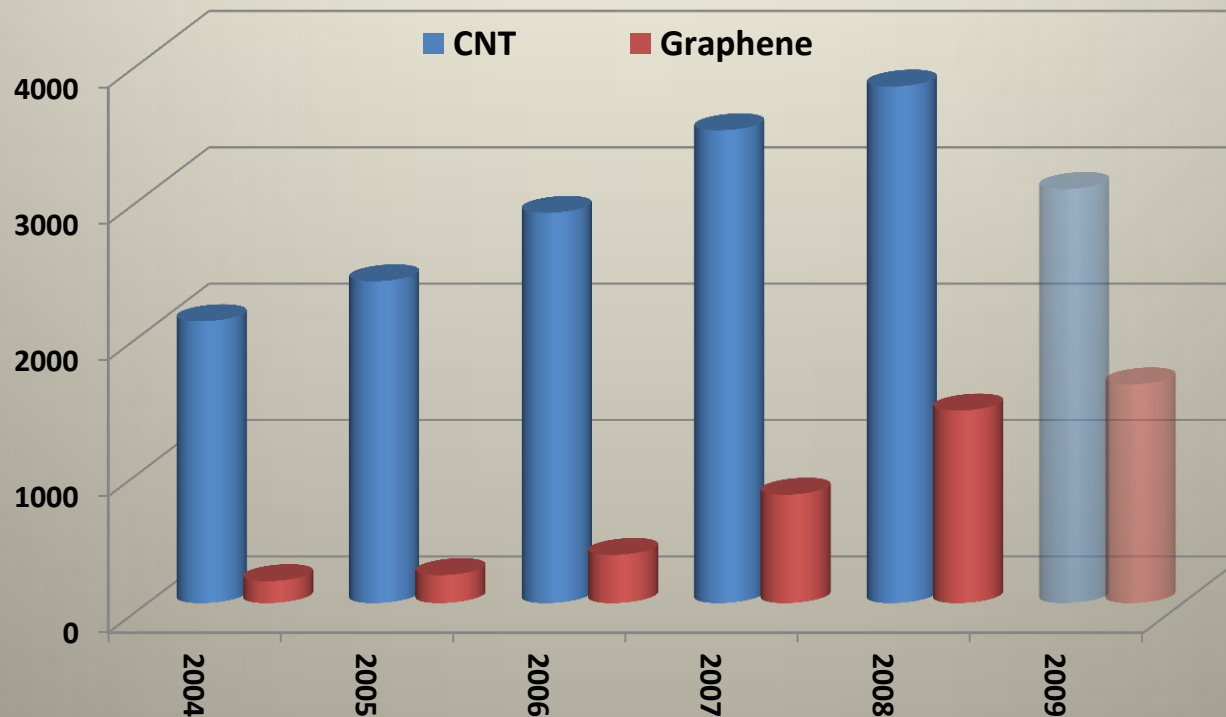
➤ Difficult to:

- distribute/disperse
- suspend/dissolve
- bond chemically

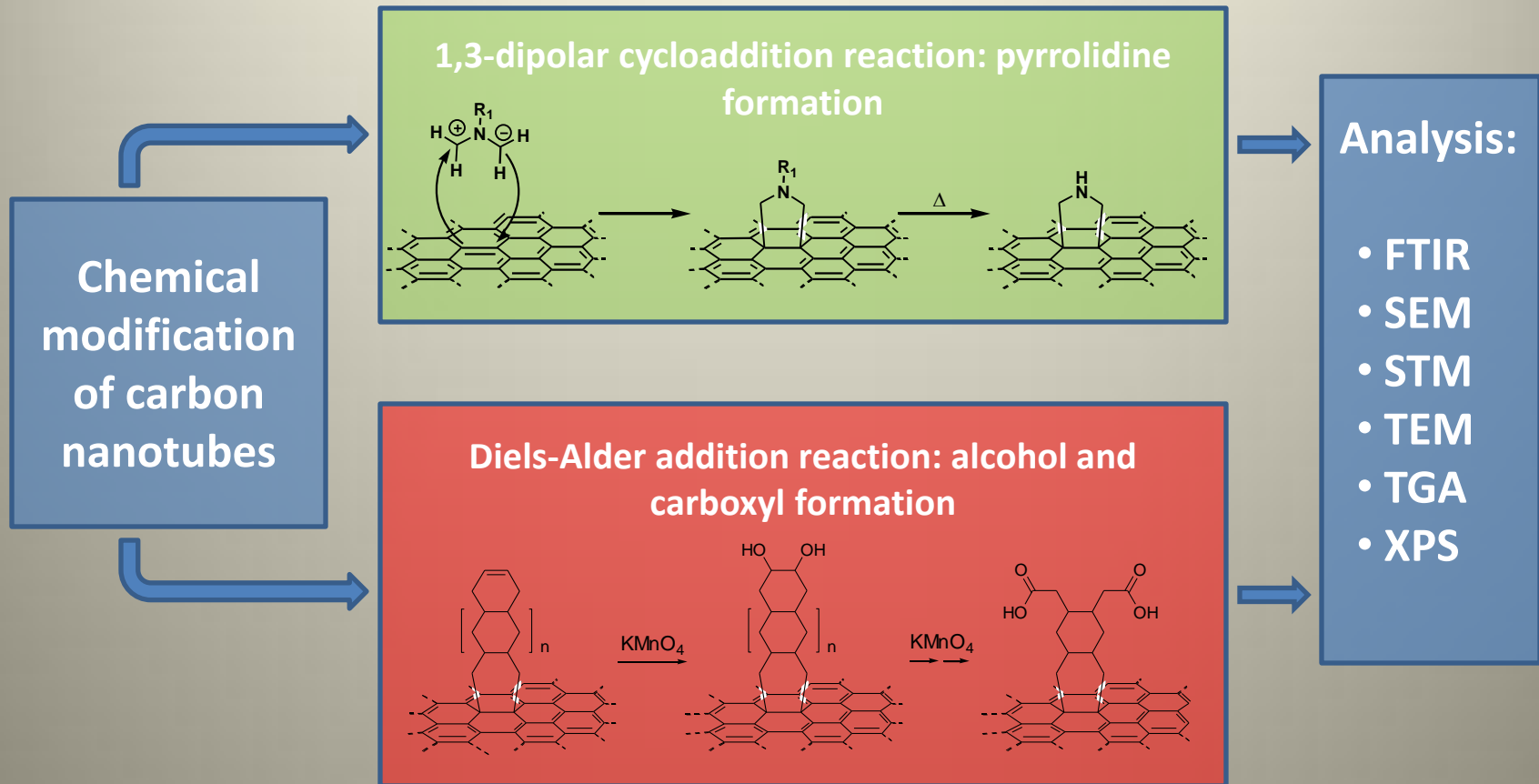


Chemical functionalization of carbon nanotubes

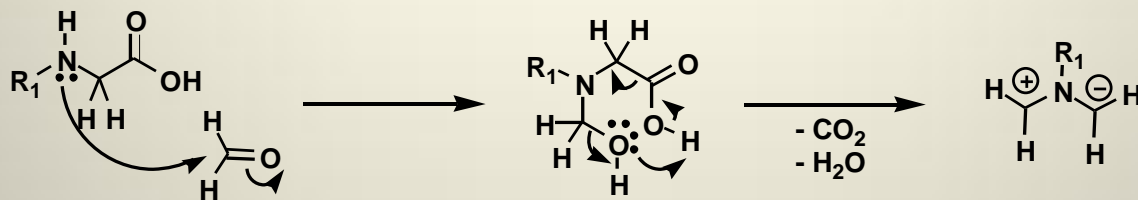
Search on *Web of Science*, entry: “carbon nanotube” or “graphene” in *topic*.



Chemical functionalization of carbon nanotubes



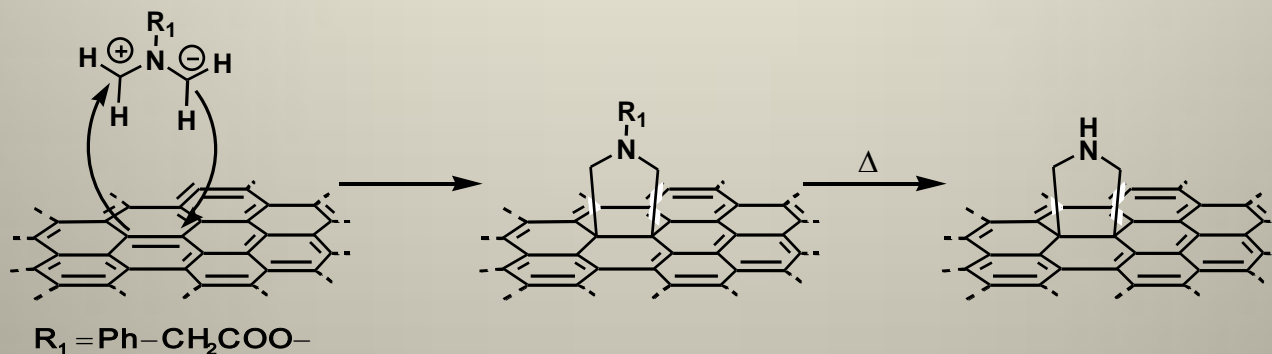
The 1,3-dipolar cycloaddition reaction



α -amino acid + aldehyde



dipolar species



V. Georgakilas, K. Kordatos, M. Prato, D. M. Guldi, M. Holzinger, A. Hirsch, *J. Am. Chem. Soc.* 2002, 124, 760

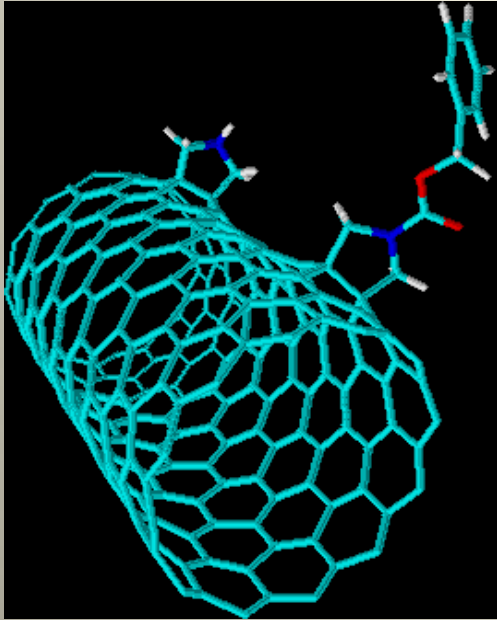
R. Araújo, M. C. Paiva, M. F. Proença, C. J. R. Silva, *Composite Science and Technology*, 2007, 67, 806-810

F. M. Fernandes, R. Araújo, M. F. Proença, C. J. R. Silva, M. C. Paiva, *J. Nanosci. Nanotechnol.*, 2007, 7, 3514–3518.

- In solution (DMF)
- Reaction time – 5 days
- In solvent-free conditions
- With heat: Reaction time – 2 to 7 hours
- With microwaves: a few seconds (under study)

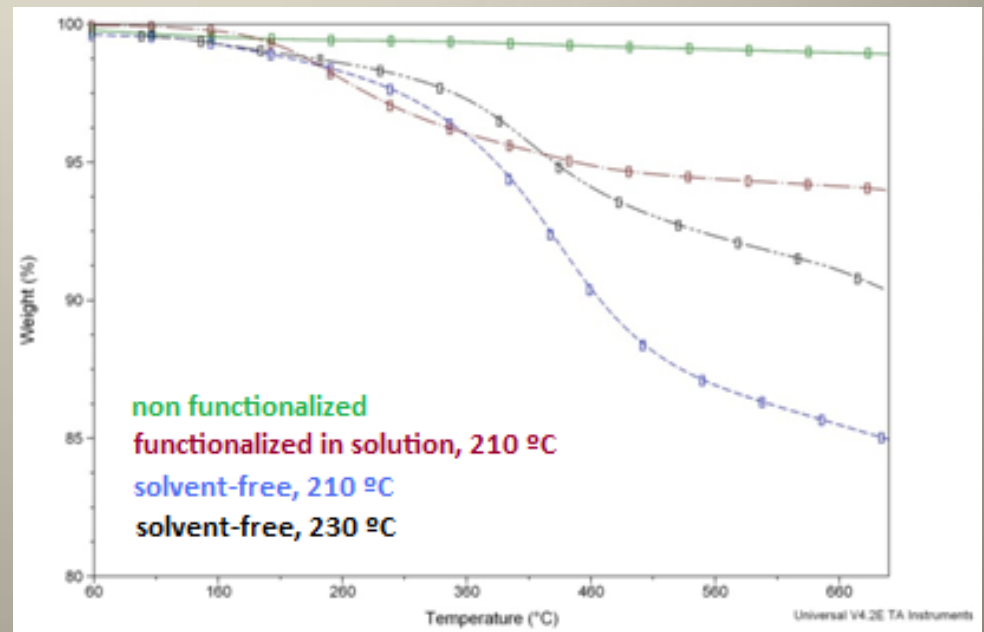
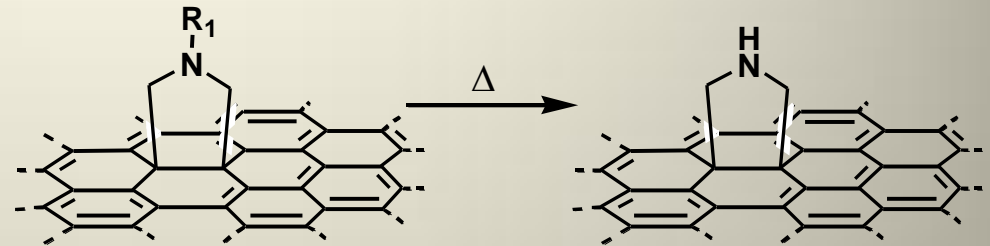


The 1,3-dipolar cycloaddition reaction - TGA

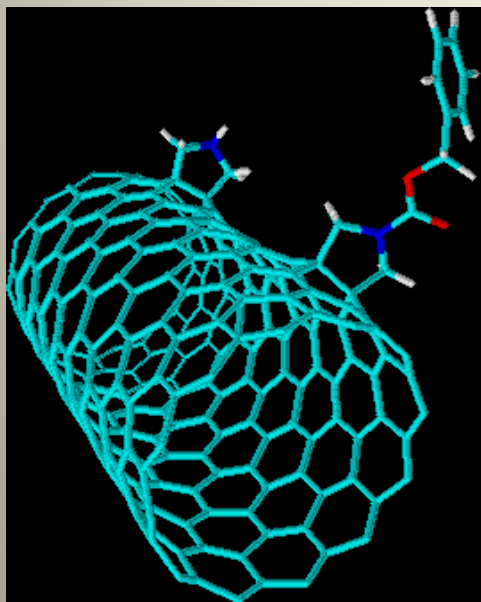


Aminoacid dispersed homogeneously at the CNT surface:

- Mixing the CNT in a solution/suspension of the AA and p-formaldehyde in diethyl eter
- Evaporation of the sovent
- Heating to the reaction temperature



The 1,3-dipolar cycloaddition reaction - XPS

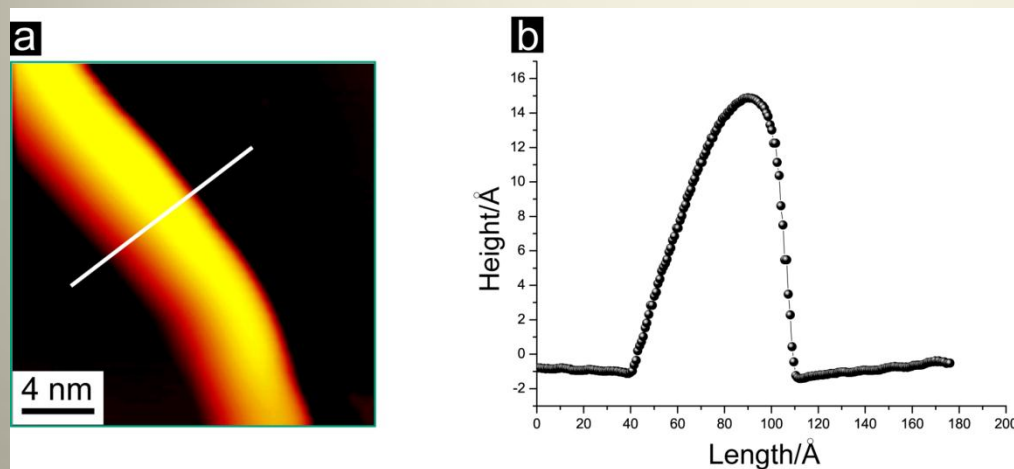


- Amount of **N** introduced by functionalization: constant at several T
- Amount of **O** introduced by functionalization: some variation with T and t

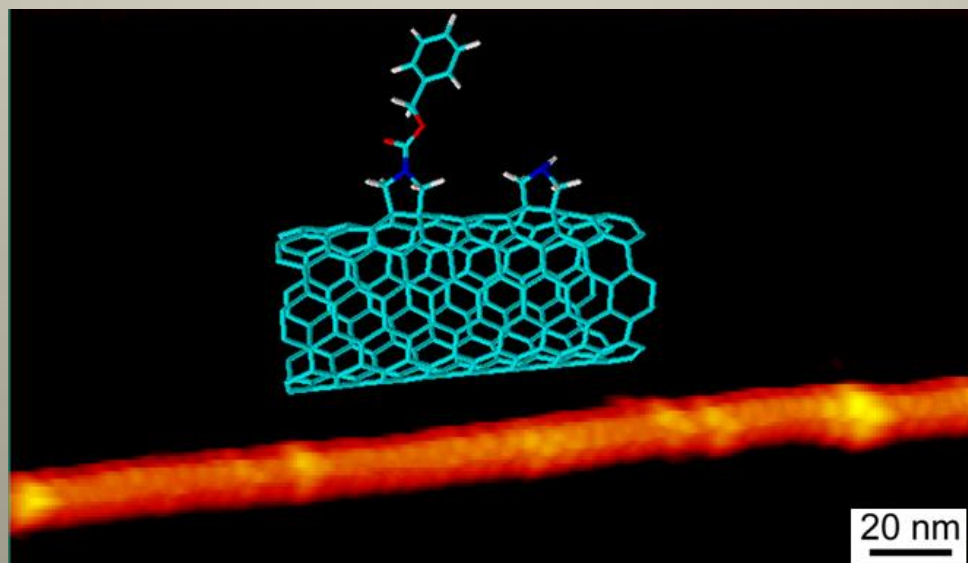
Sample	Time (h)	N:C	O:C	TGA wt %
CNT	0	0	0,008	1,6
CNT_180	1	0.021	0.036	21.2
	3	0.016	0.038	19.5
	6	0.018	0.042	19.4
CNT_210	2	0,02	0,053	25,8
	6	0,023	0,036	13,4
	7	0,028	0,036	22,0
	14	0,02	0,017	20,7
CNT_230	3	0.036	0.034	8.5
	9	0.028	0.021	12.5
	12	0.028	0.035	9.1
CNT_250	3	0.020	0.028	23.3
	5	0,019	0,016	19.9
	7	0,022	0,016	11,6
M W 60(1)		0.057	0.016	
M W 240(1)		0.022	0.026	
M 240 PF 10		0.021	0.022	



The 1,3-dipolar cycloaddition reaction - STM



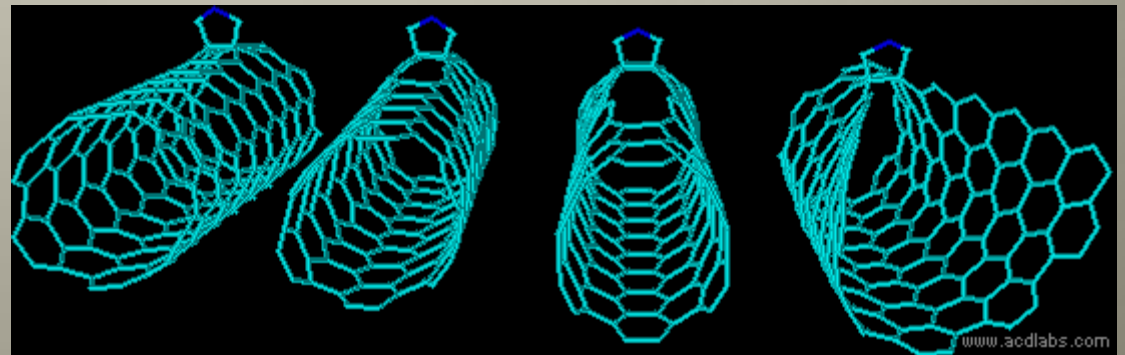
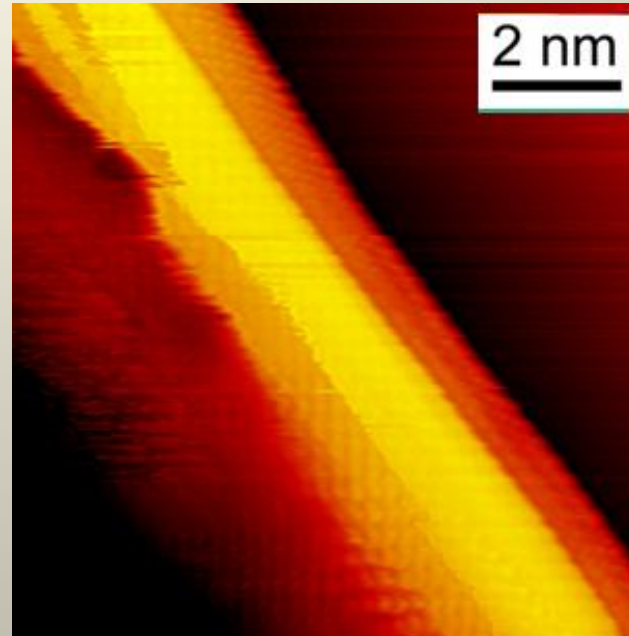
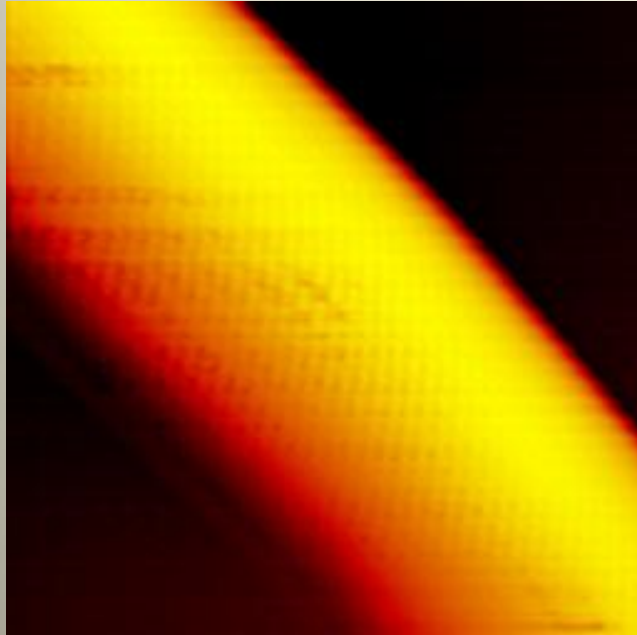
- UHV chamber (3×10^{-10} Torr), Pt/Ir tip
- constant current mode
- Typical bias voltage and tunneling current:
 - ✓ nanometer scale - 1000-2000 mV and 0.8-1.2 nA
 - ✓ Atomic scale - 30-100 mV and 1.5-2.0 nA



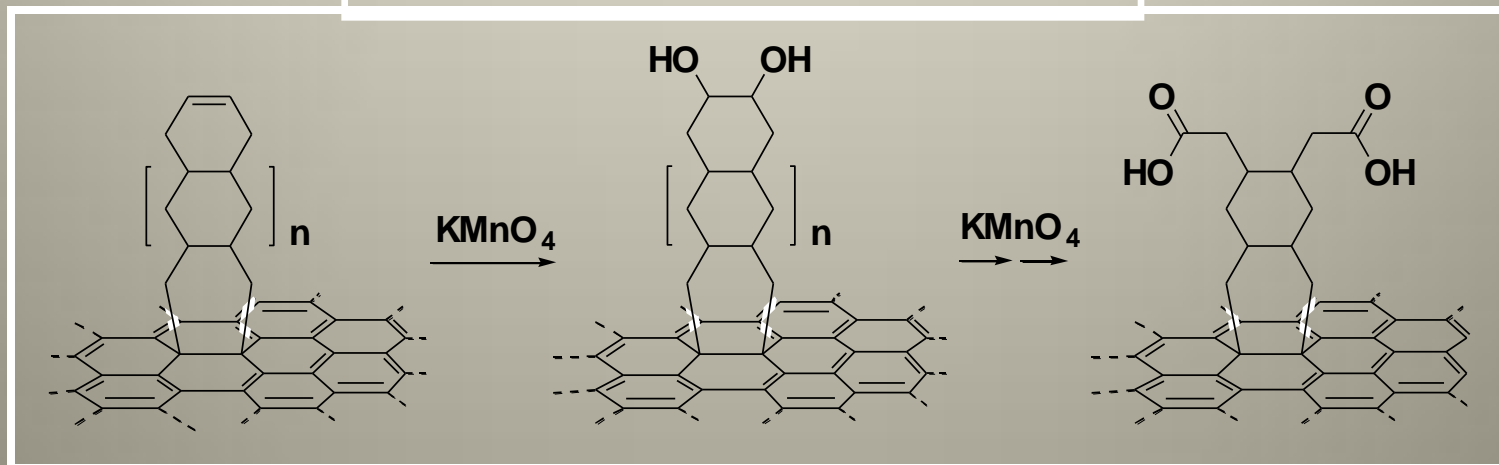
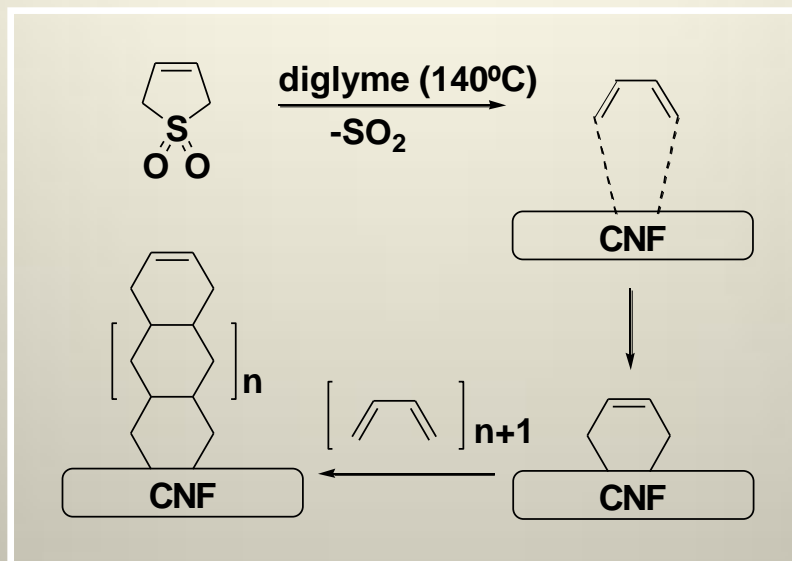
iNANO Research Center at Aarhus University



The 1,3-dipolar cycloaddition reaction - STM



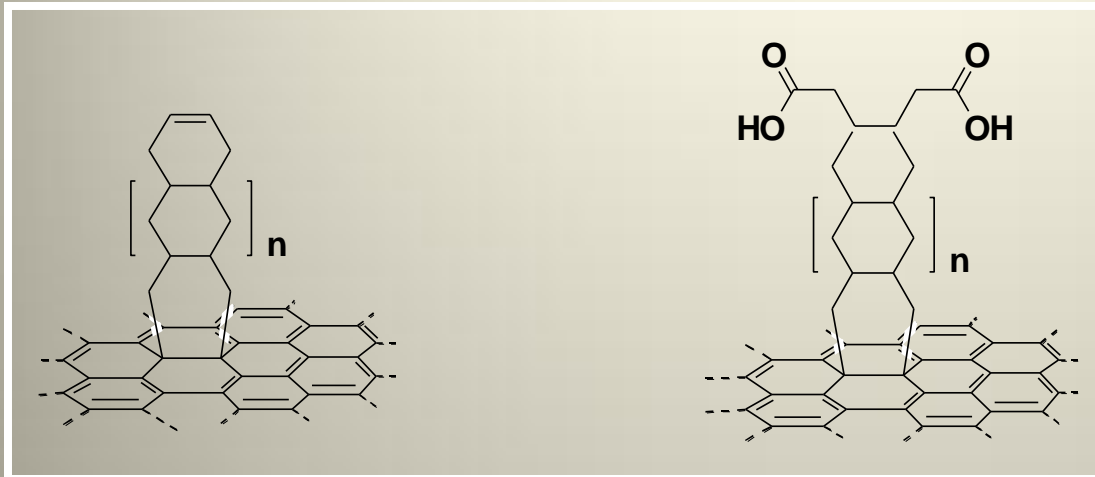
The Diels-Alder addition reaction



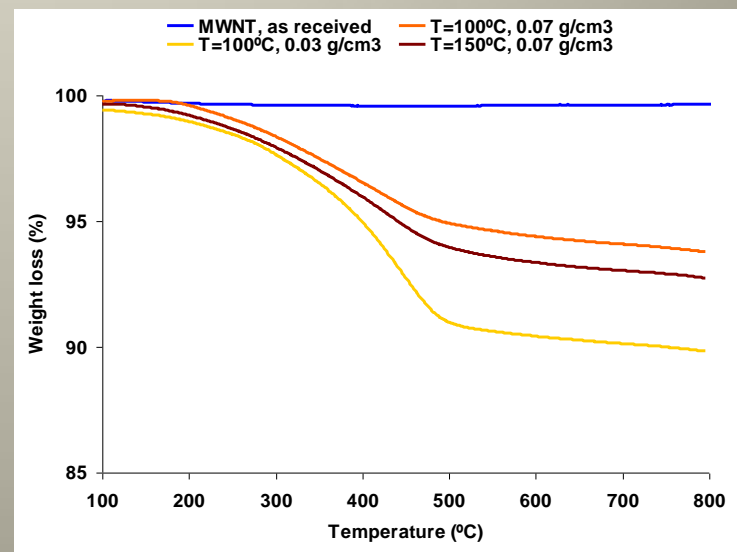
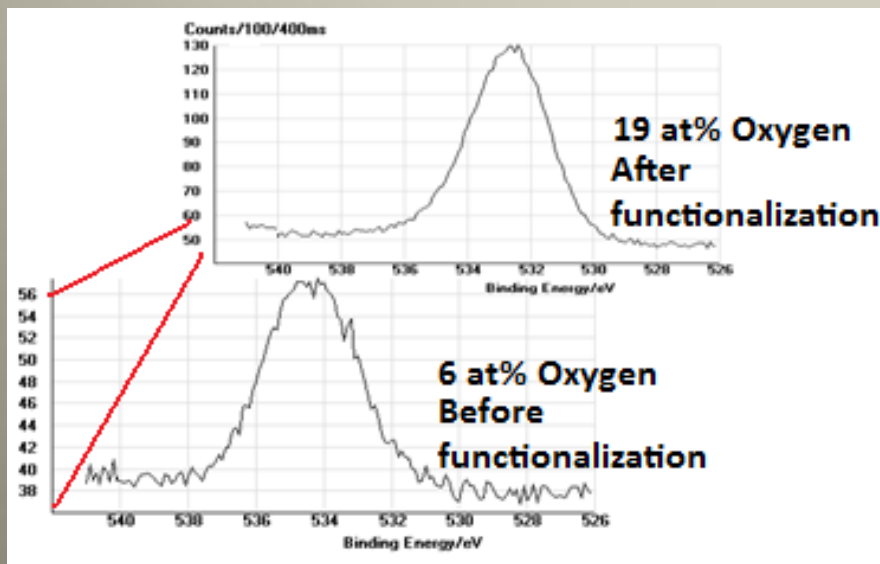
M. F. Proença, R. F. Araújo, M. C. Paiva, and C. J. R. Silva, *J. Nanosci. Nanotechnol.* 2009, 9, 6234-6238



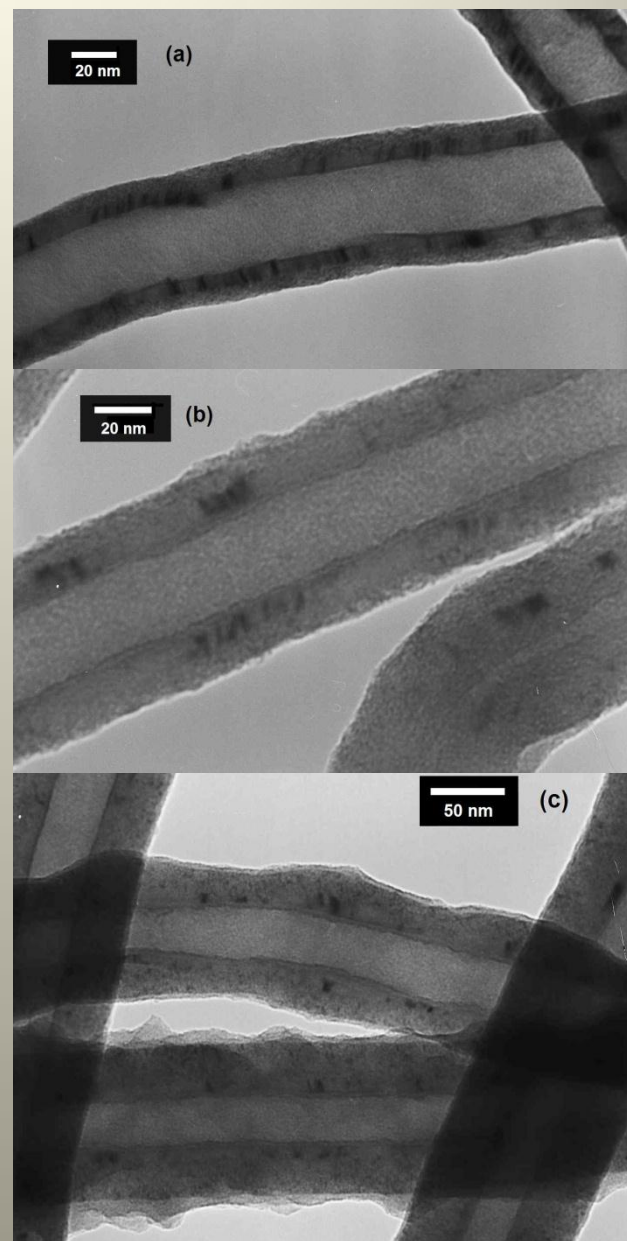
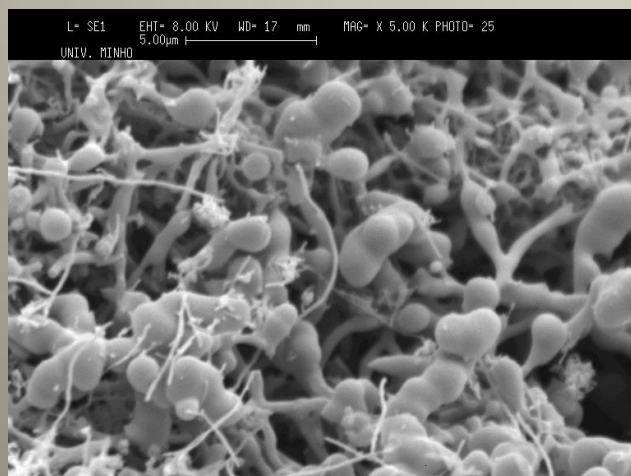
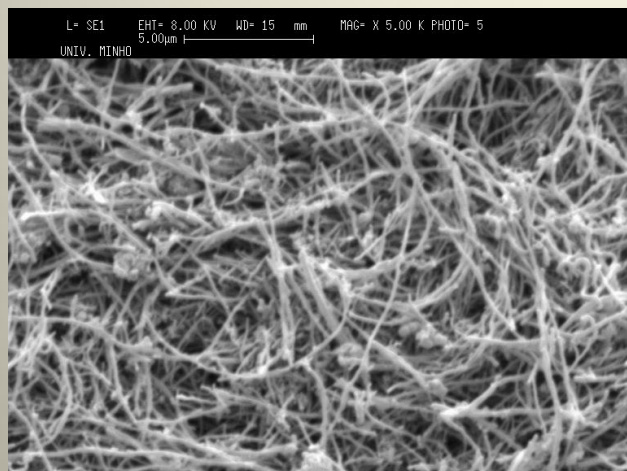
The Diels-Alder addition reaction



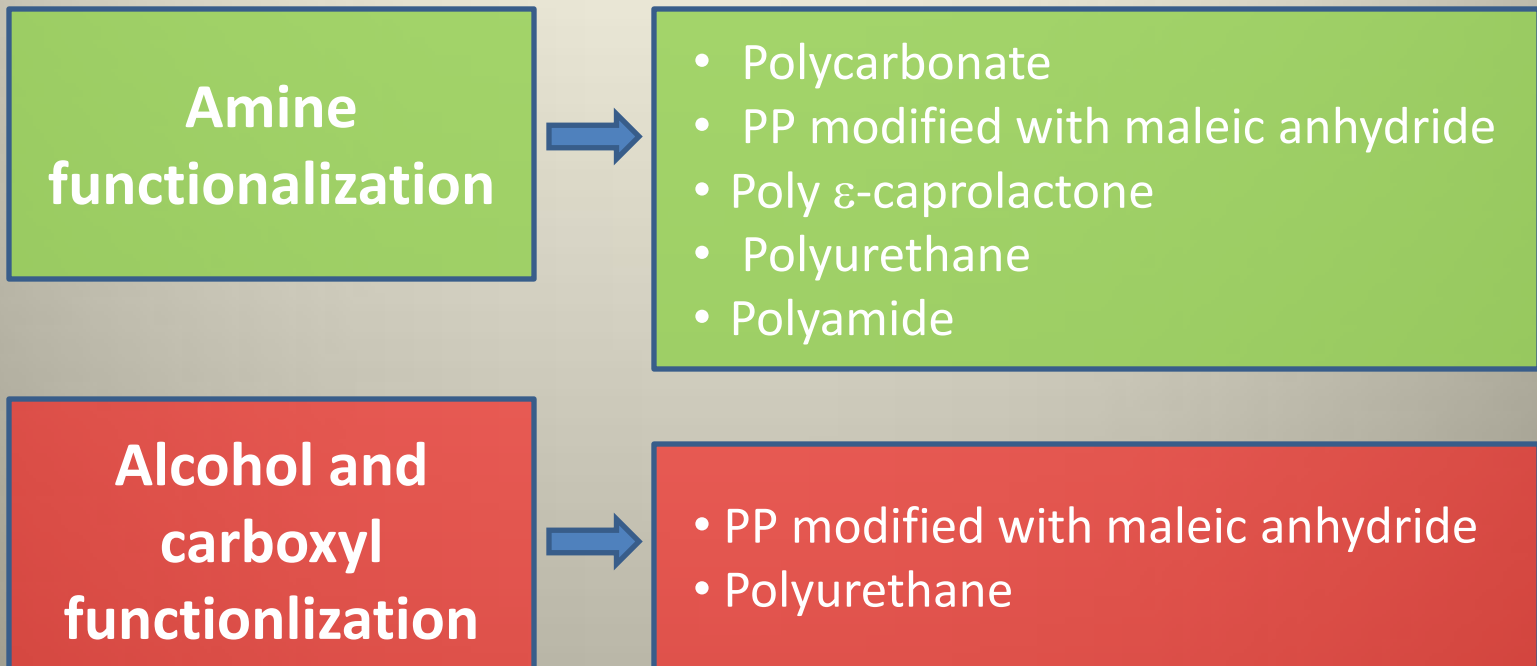
Temperature (°C)	Weight loss (750 °C)
90 (diglyme)	15 ± 5
100 (diglyme)	15 ± 2
110 (diglyme)	8 ± 2
140 (diglyme)	5 ± 1
140 (no solvent)	11 ± 3



The Diels-Alder addition reaction



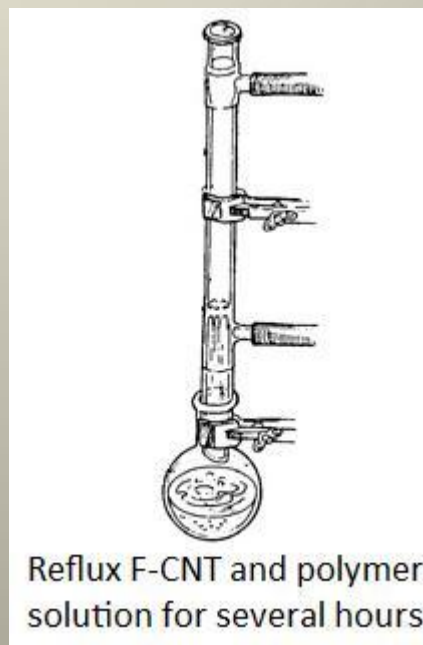
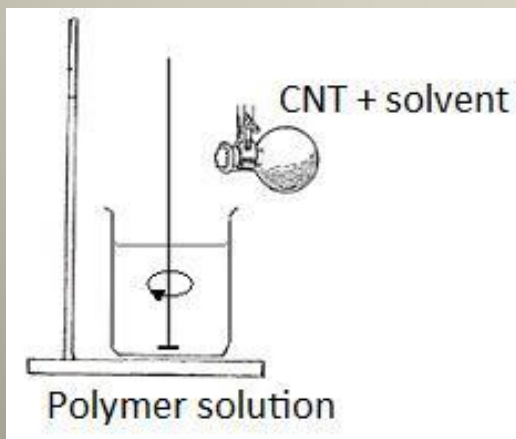
Functionalized CNT: reaction with polymers



Functionalized CNT: reaction with polymers

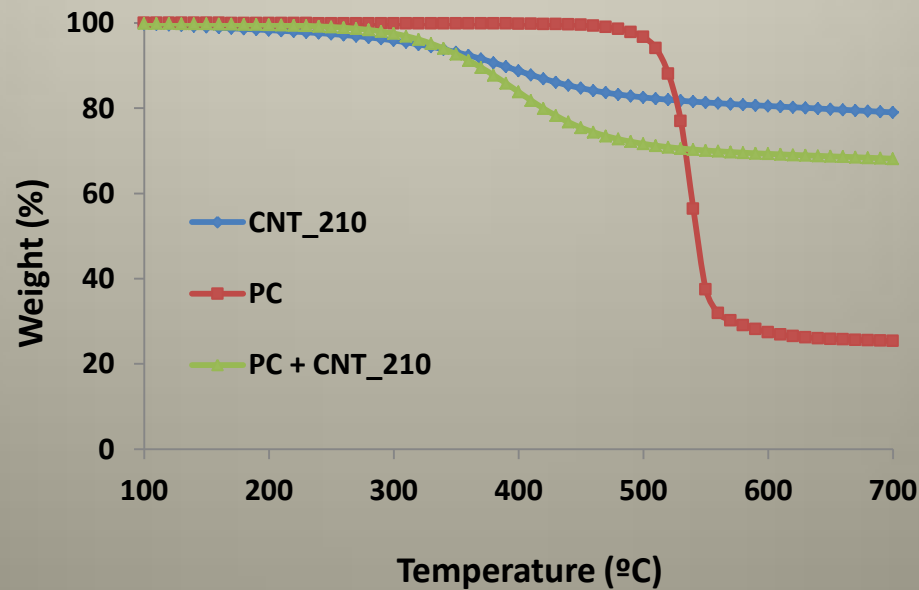
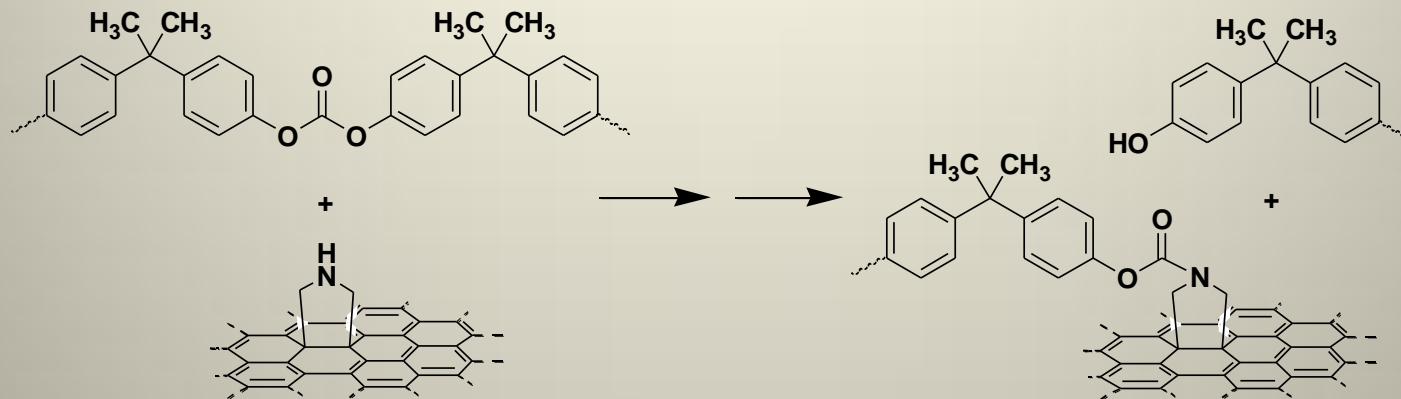
Reaction with polymers in solution:

- Prepare a suspension of the functionalized CNT in the polymer solution
- Reflux for several hours (depending on the polymer)
- Wash several times with solvent



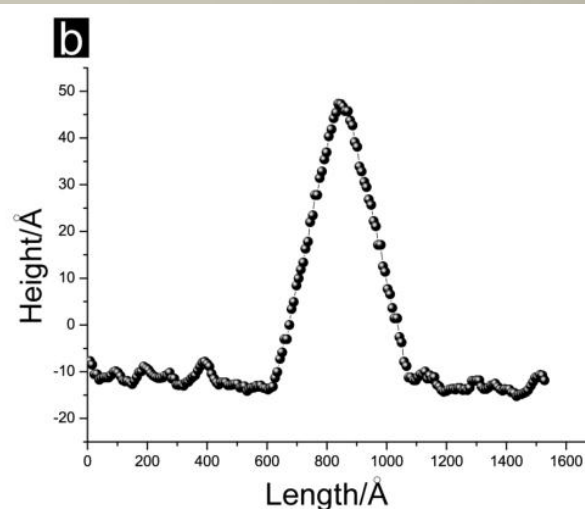
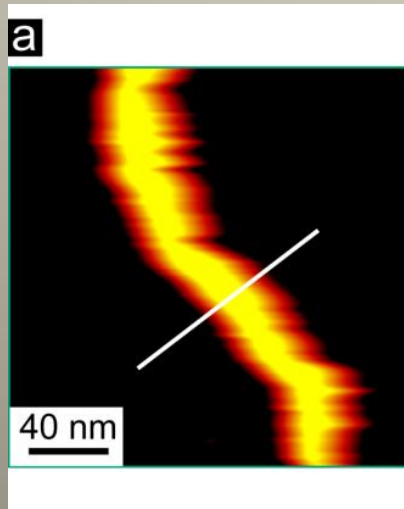
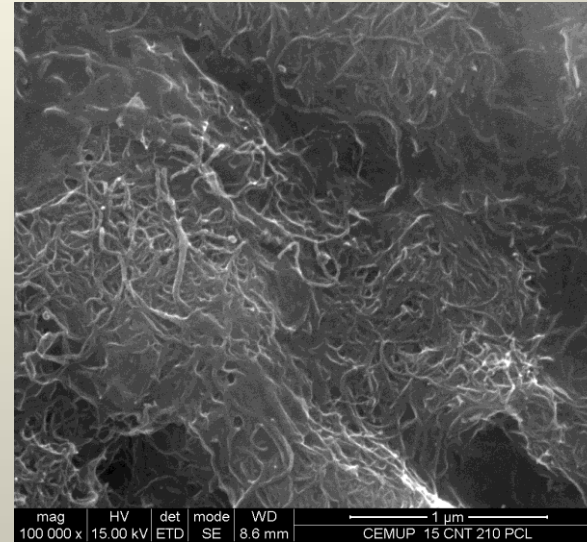
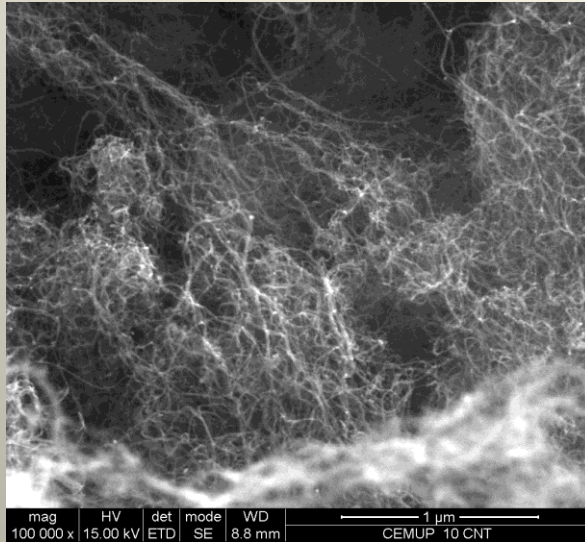
Functionalized CNT: reaction with polymers in solution

Reaction between pyrrolidine and carbonate group in PC



Functionalized CNT: reaction with polymers in solution

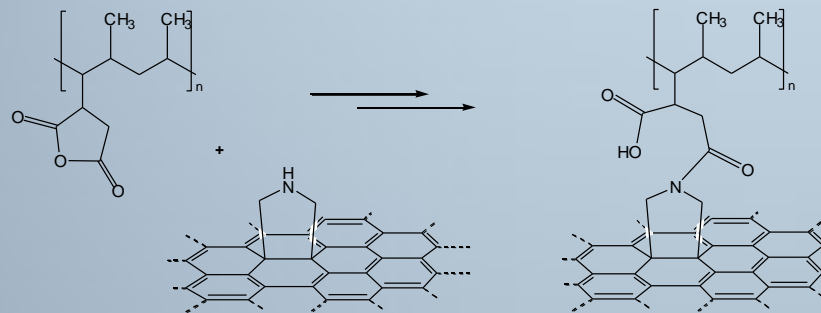
Reaction between pyrrolidine and carbonate group in PC



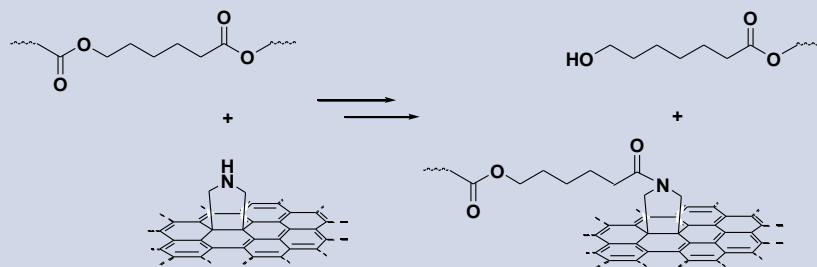
Functionalized CNT: reaction with polymers in solution

Reaction between pyrrolidine and:

Maleic anhydride grafted in PP

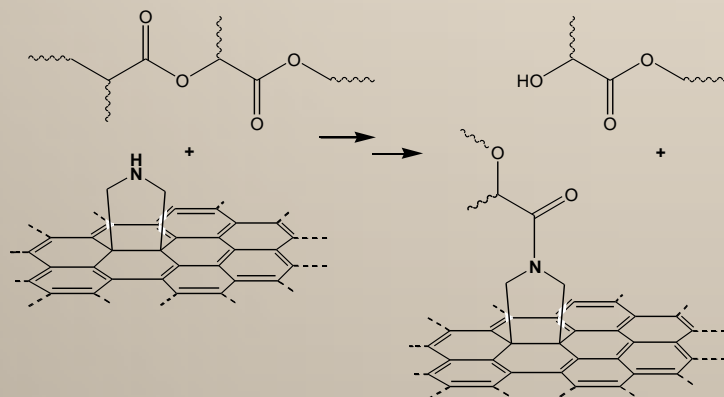


TGA (wt%)		
	F-CNT	Polymer-F-CNT
210 °C	22.2	33.2
250 °C	19.9	74.4



Esther group in PCL

TGA (wt%)		
	F-CNT	Polymer-F-CNT
210 °C	22.2	28.0
250 °C	19.9	26.5



Esther group in PLA

TGA (wt%)		
	F-CNT (210 °C)	Polymer-F-CNT
	22.2	65.2



Functionalized CNT: reaction with polymers in the melt

Composite	Type of CNT	Temperature (°C)	CNT composition (wt %)
PC	CNT pure CNT_210 CNT_250	280	20
PCL		180	
PP-g-MA		160	
PLA		220	

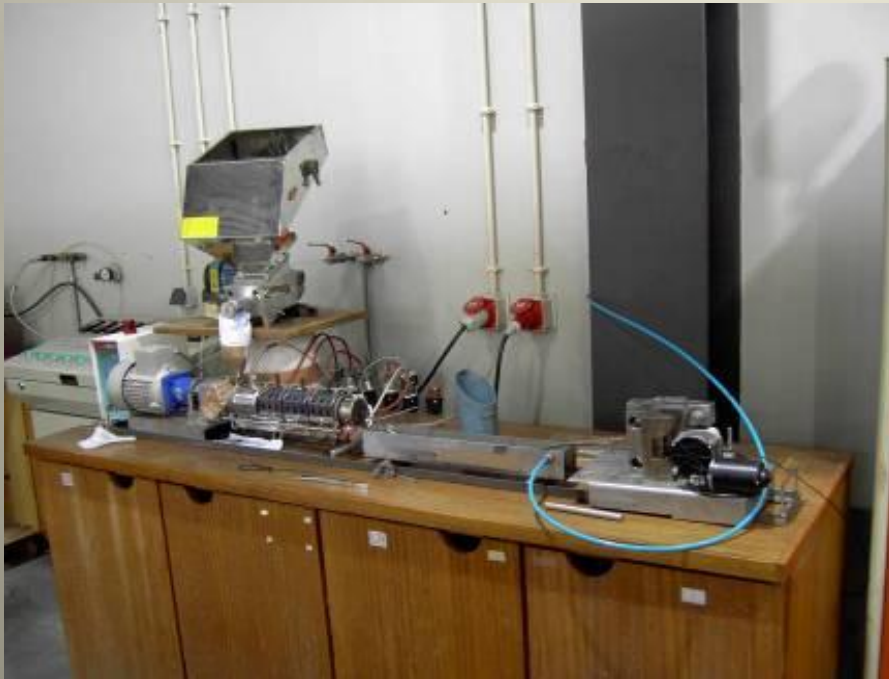
- Do the CNT react with the melted polymer during mixing?
- Is the CNT functionalization stable at processing temperature?
- If a low M_w polymer fraction is formed by reaction with the F-CNT, is it large enough to affect the interface properties?

DACA micro compounder, Petra Pötschke, IPFDD



CNT dispersion in polymers

Twin-screw extrusion: predominantly shear flow



José A. Covas, IPC, U. Minho



CNT dispersion in polymers: twin-screw extrusion

Study of dispersion in composites formed by:

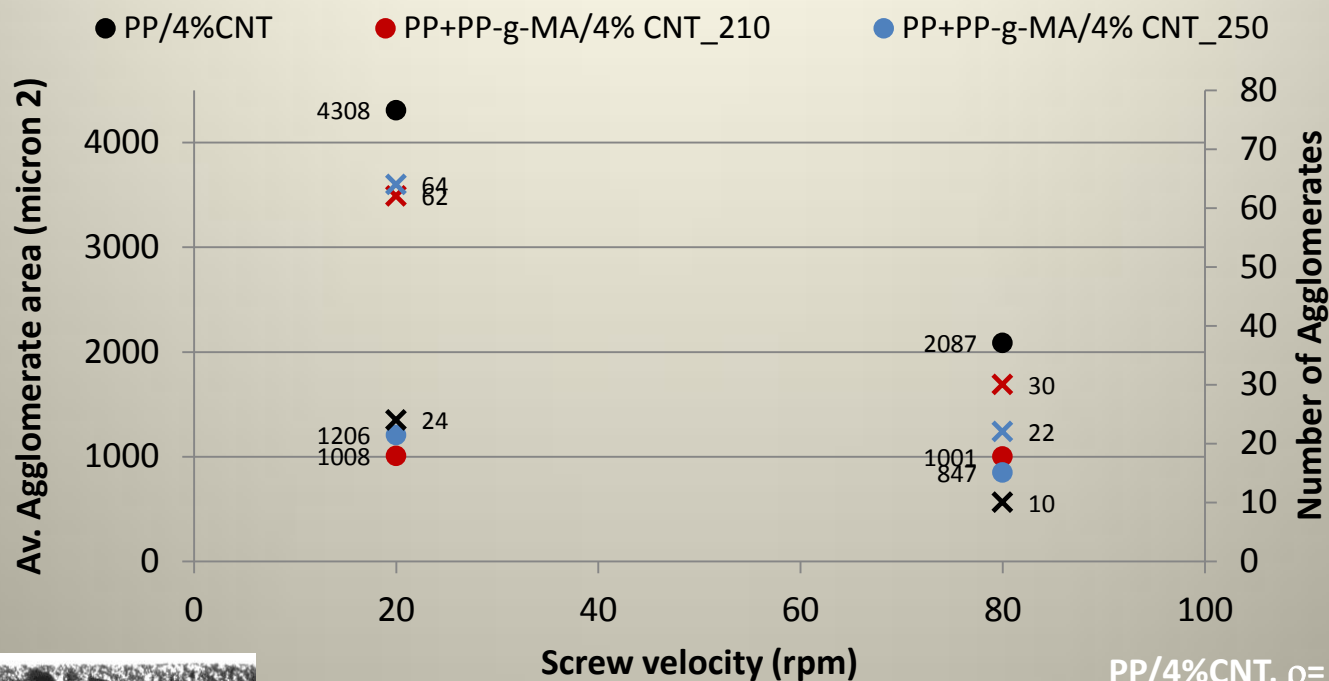
- PP + 4% CNT
- PP + PP-g-MA + 4% FCNT_210
- PP + PP-g-MA + 4% FCNT_250

Experiment	Flow Rate (g/h)	Screw velocity (rpm)
1	130	80
2	130	20
3	40	80
4	40	20

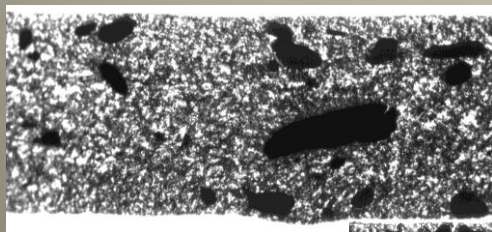


CNT dispersion in polymers: twin-screw extrusion

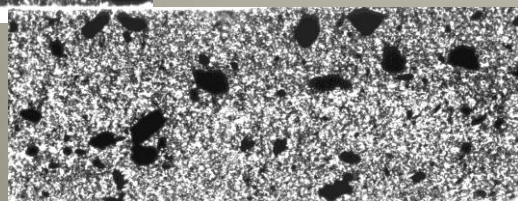
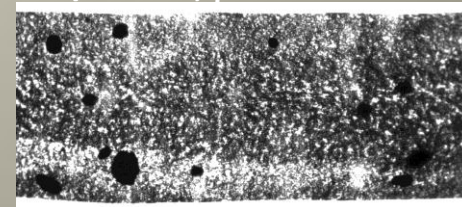
40 g/h Flow rate



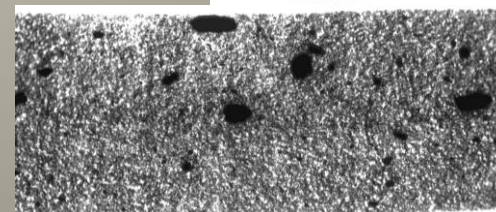
PP/4%CNT



PP/4%CNT, $\rho = 1.2 \pm 0.5 \Omega\text{m}$



PP+PP-g-MA/4%CNT_210, $\rho = (6.5 \pm 4) \times 10^7 \Omega\text{m}$

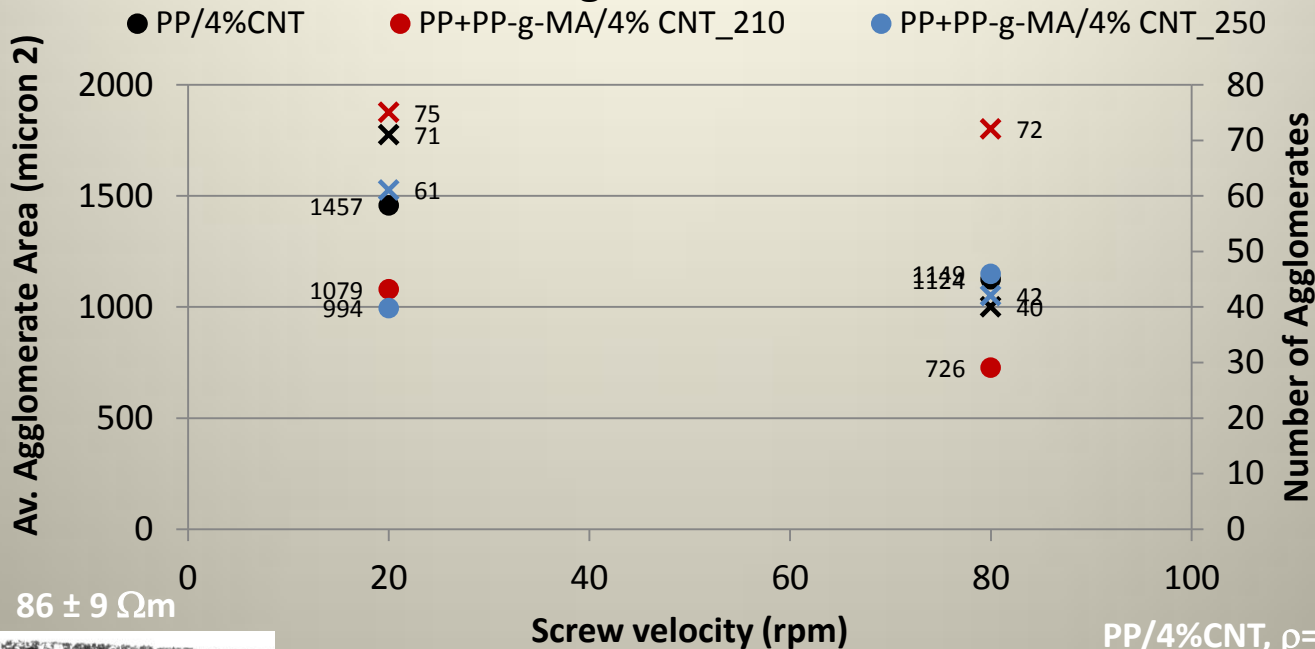


PP+PP-g-MA/4%CNT_210, $\rho = (2.4 \pm 0.3) \times 10^2 \Omega\text{m}$

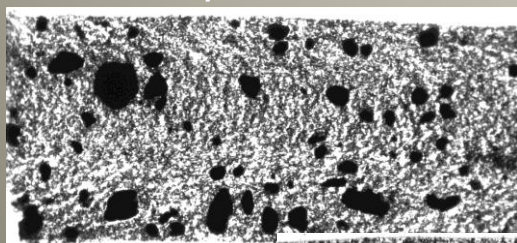


CNT dispersion in polymers: twin-screw extrusion

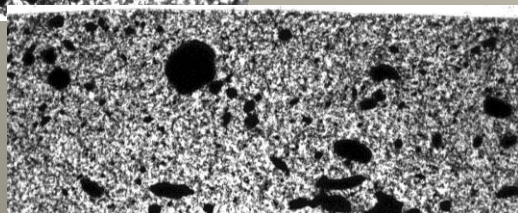
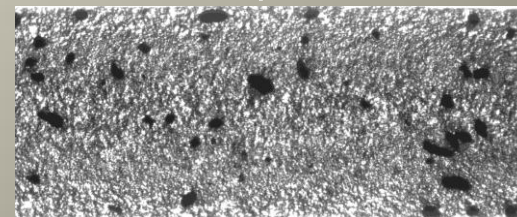
130 g/h Flow rate



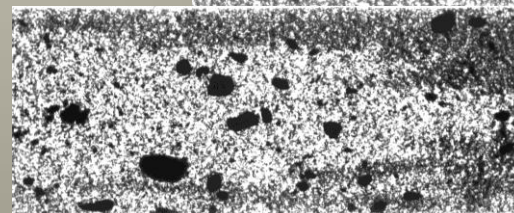
PP/4%CNT, $\rho = 86 \pm 9 \Omega\text{m}$



PP/4%CNT, $\rho = 0.7 \pm 0.1 \Omega\text{m}$



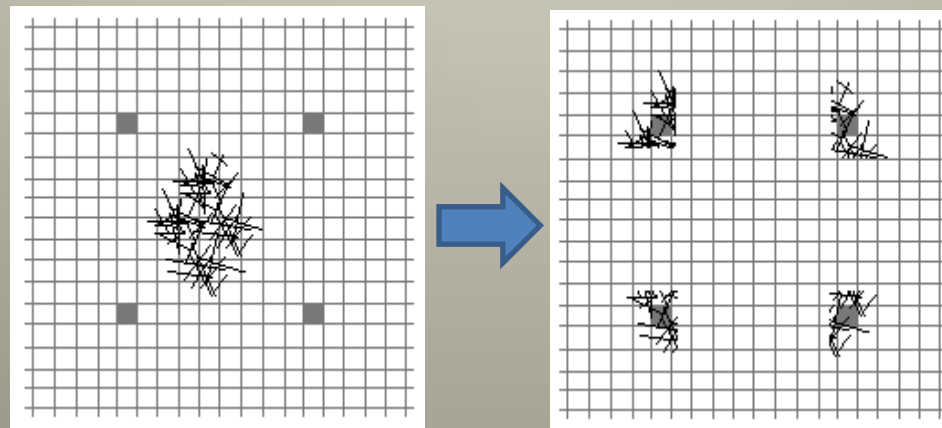
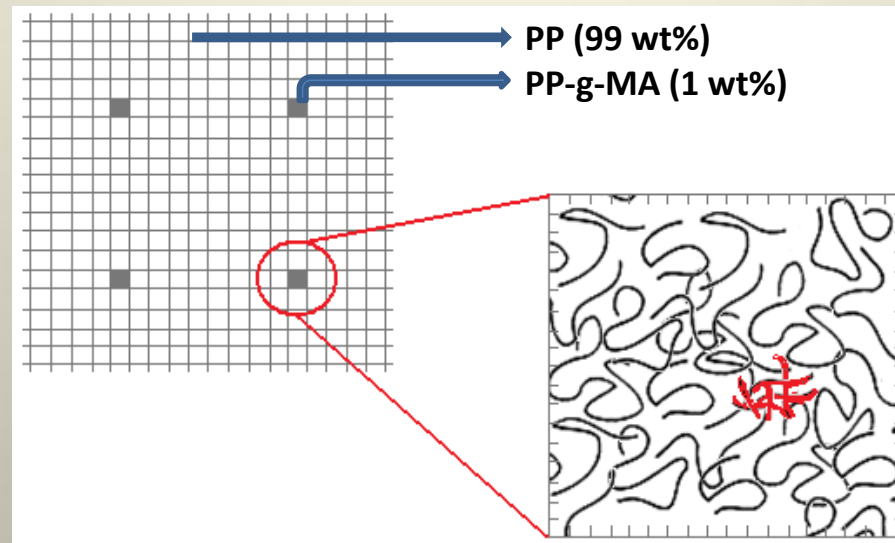
PP+PP-g-MA/4% CNT_210, $\rho = (6 \pm 5) \times 10^8 \Omega\text{m}$



PP+PP-g-MA/4% CNT_210, $\rho = (1.4 \pm 0.2) \times 10^5 \Omega\text{m}$

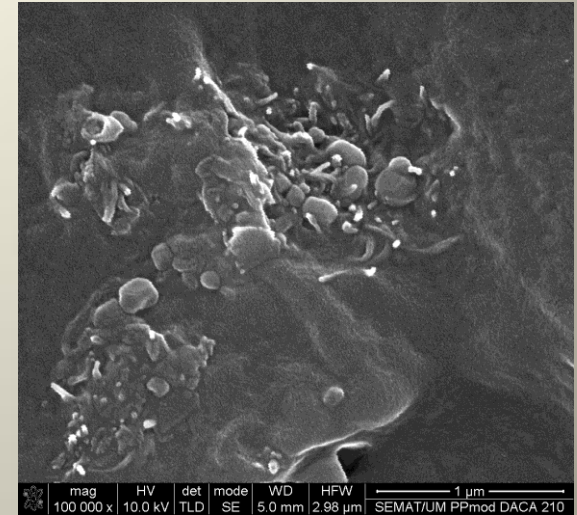
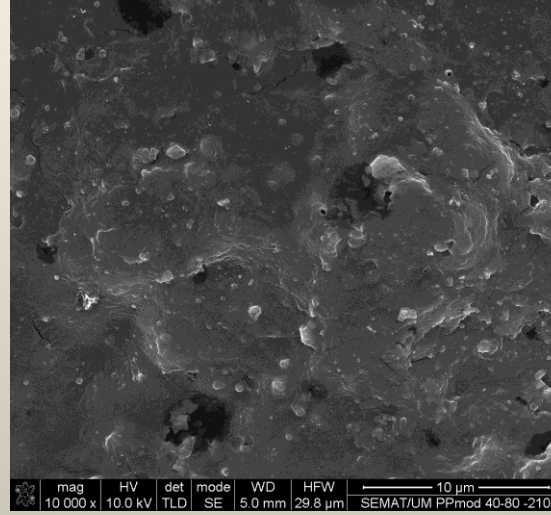
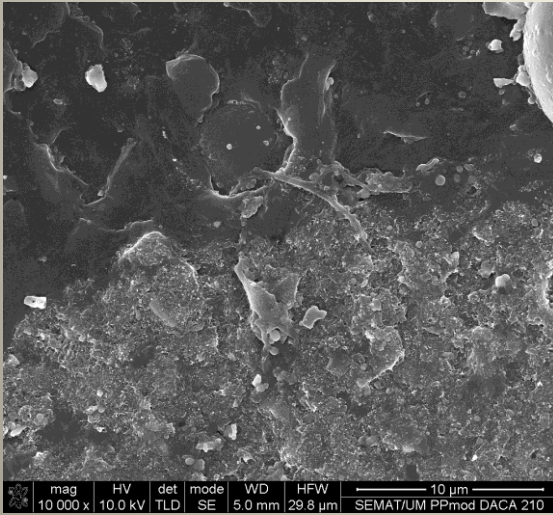


CNT dispersion in polymers: twin-screw extrusion

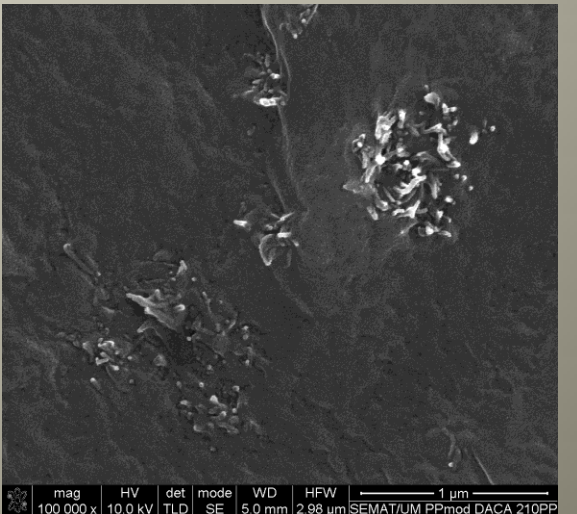
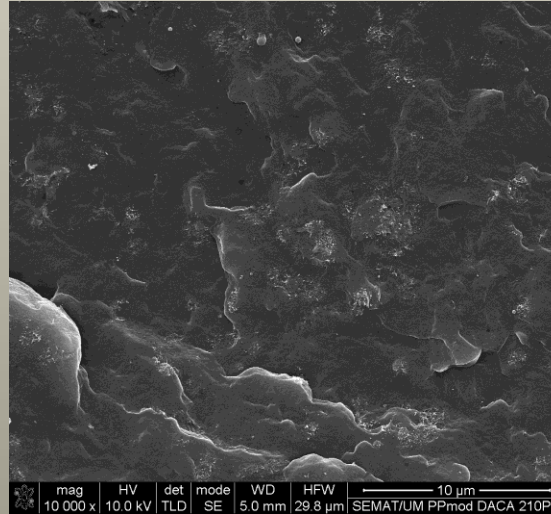
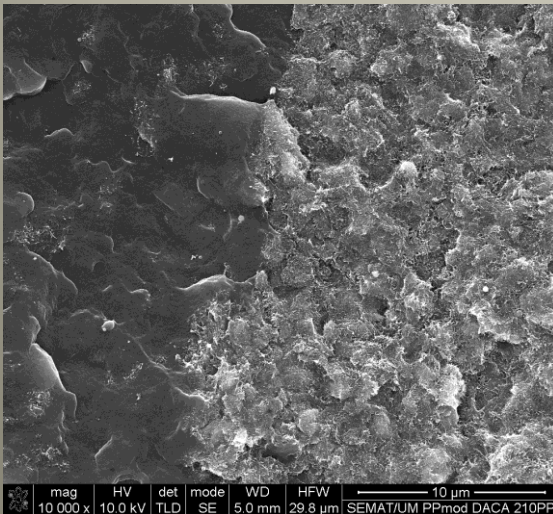


CNT dispersion in polymers : DACA micro compounder

PP+PP-g-MA/4% FCNT_210

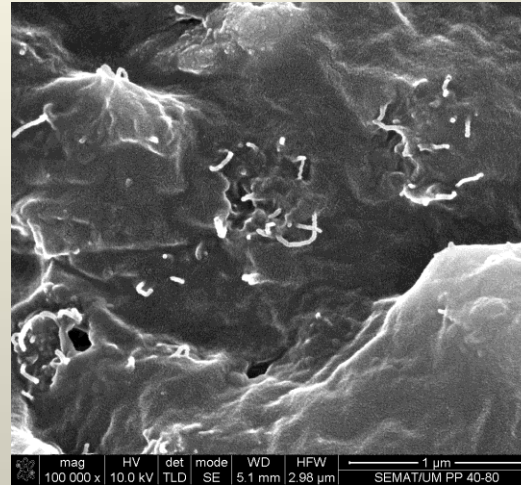
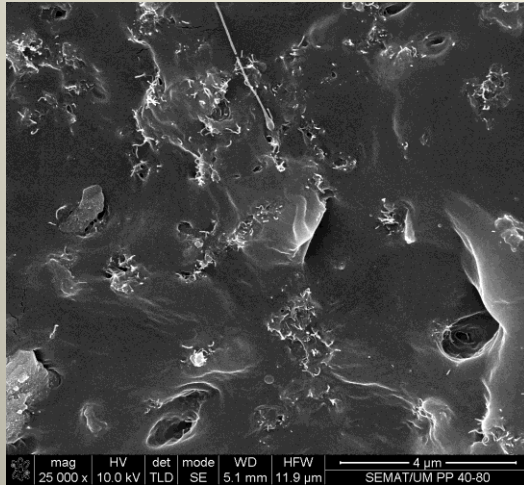


PP+PP-g-MA/(4% FCNT_210/PP-g-MA)

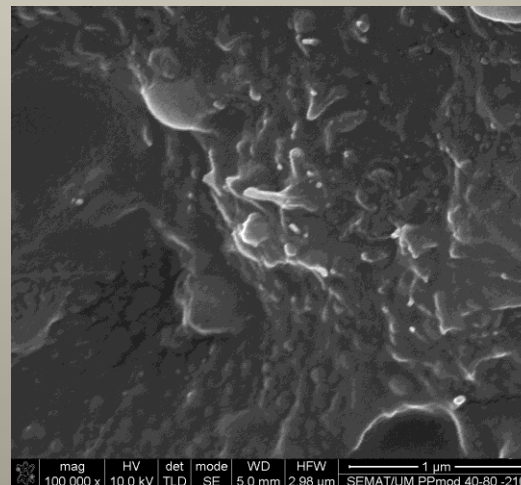
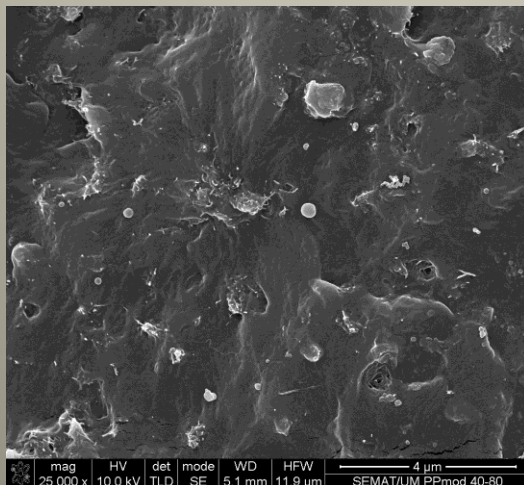


CNT dispersion in polymers: twin-screw extrusion

PP with non-functionalized CNT



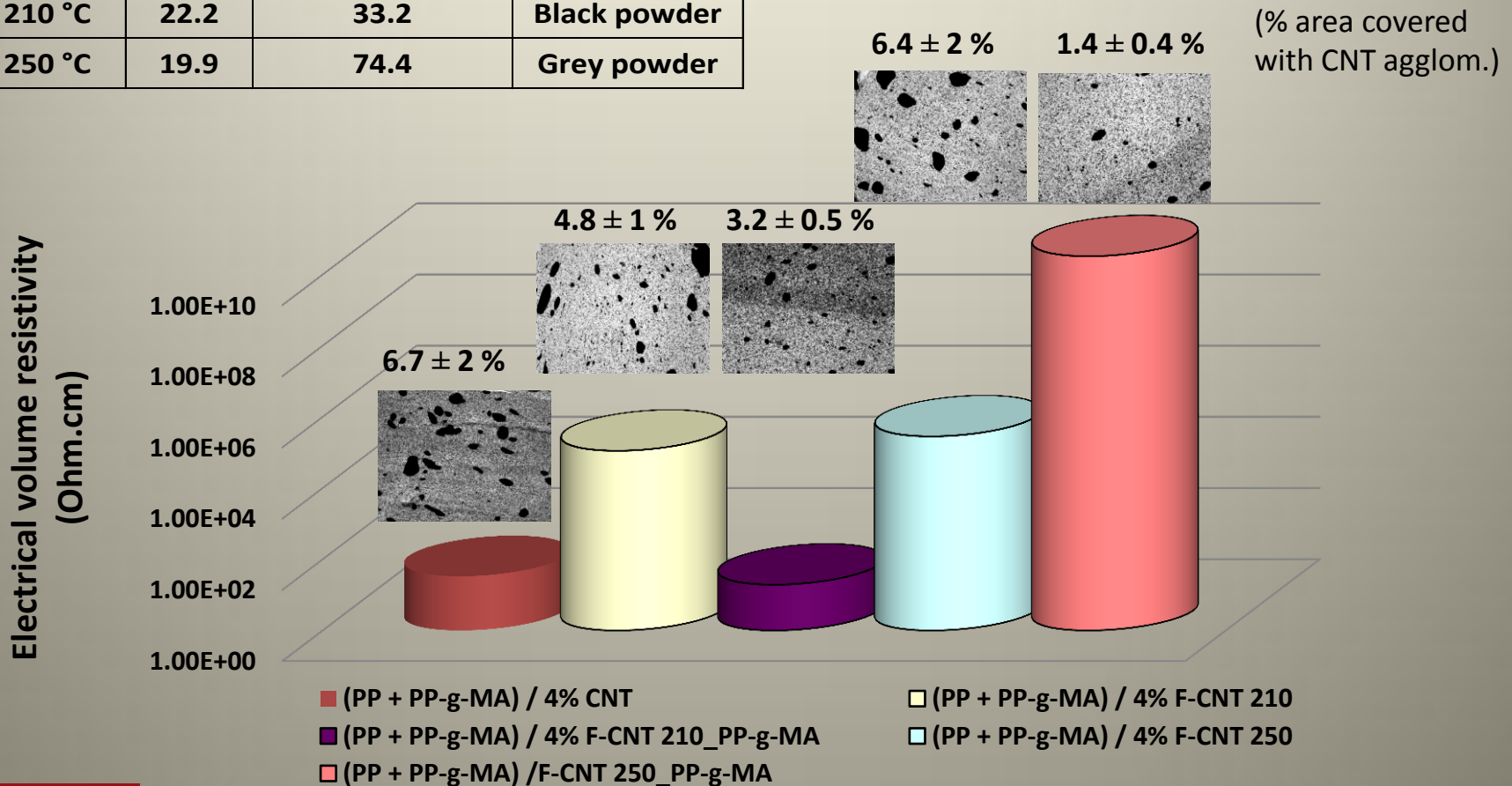
PP with functionalized CNT (210 °C)



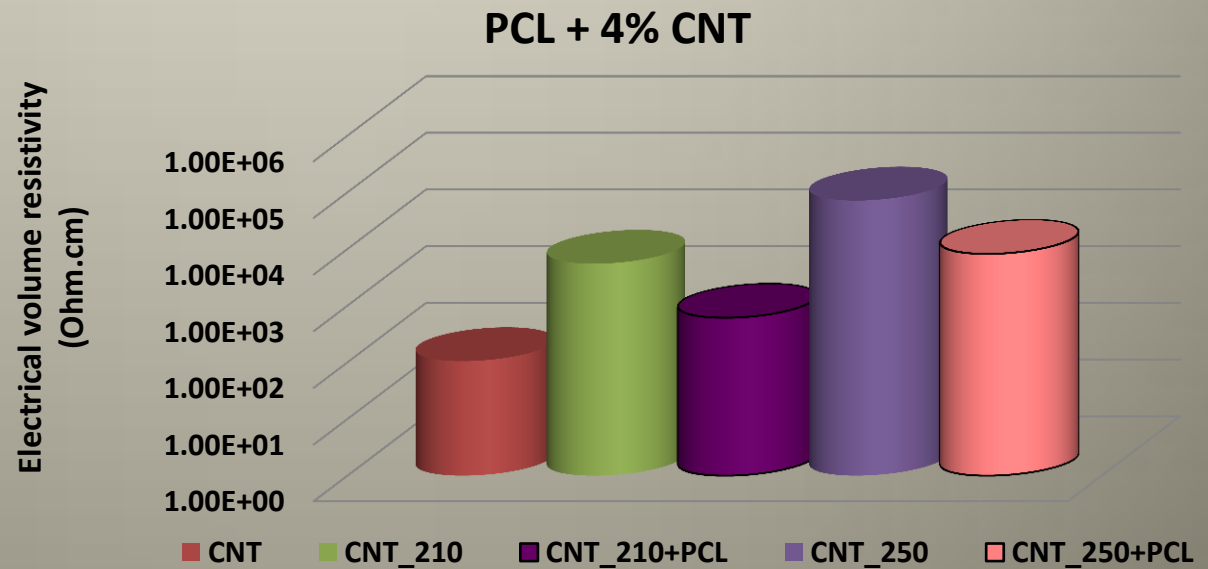
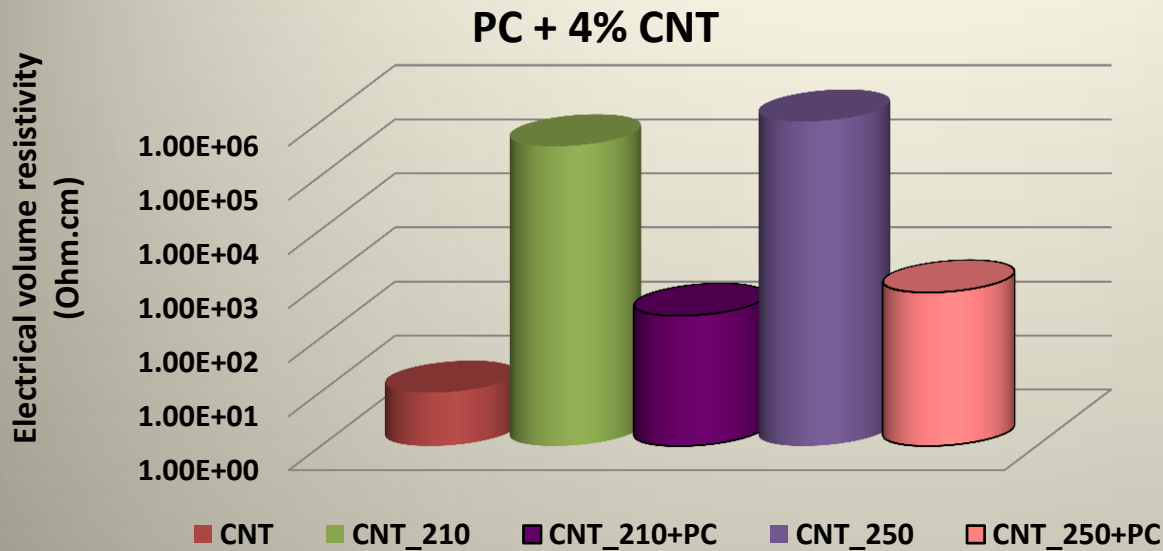
CNT dispersion in polymers: DACA compounder

Composites with F-CNT that reacted with PP-g-MA in solution (PP-modified FCNT)

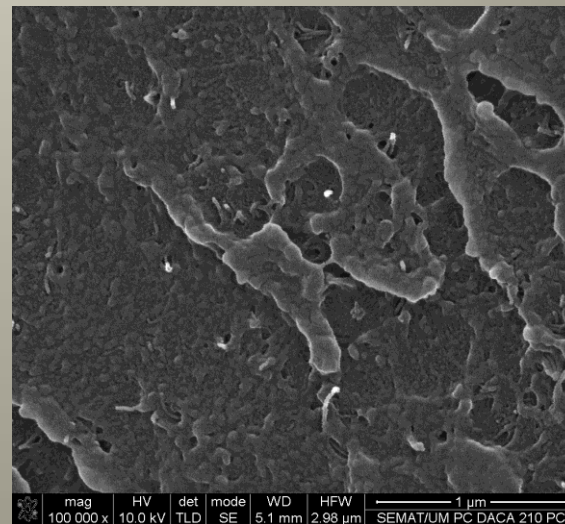
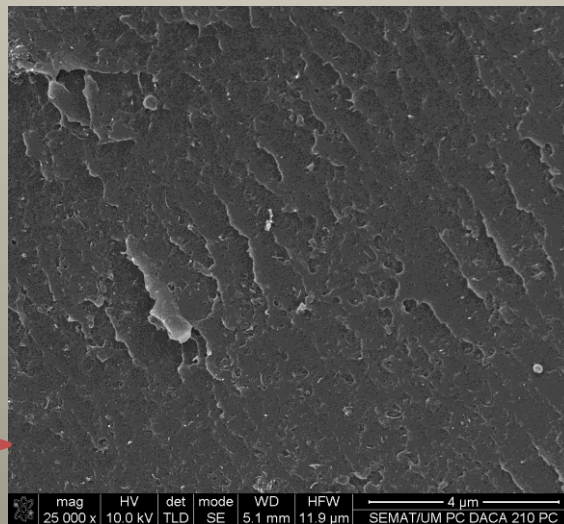
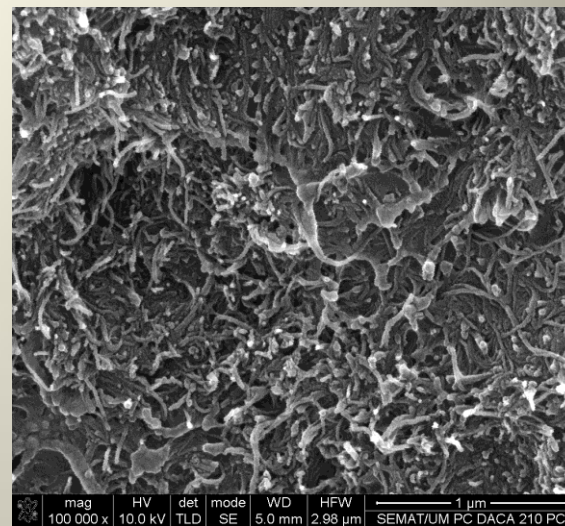
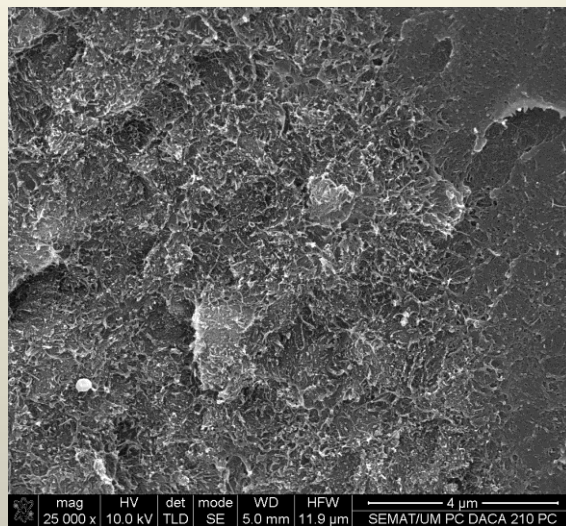
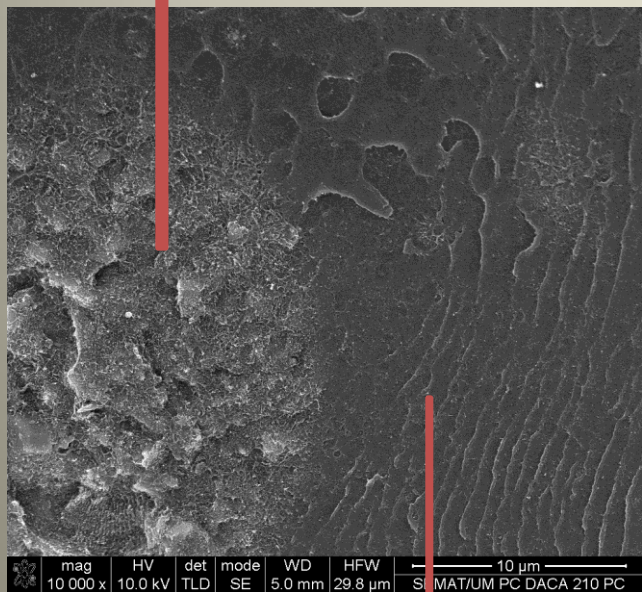
		TGA (wt%)	
F-CNT		Polymer-F-CNT	CNT aspect
210 °C	22.2	33.2	Black powder
250 °C	19.9	74.4	Grey powder



CNT dispersion in polymers: DACA compounder



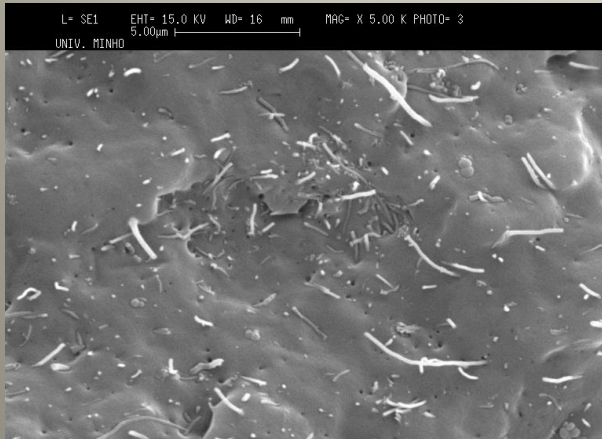
CNT dispersion in polymers: PC/4% FCNT_210



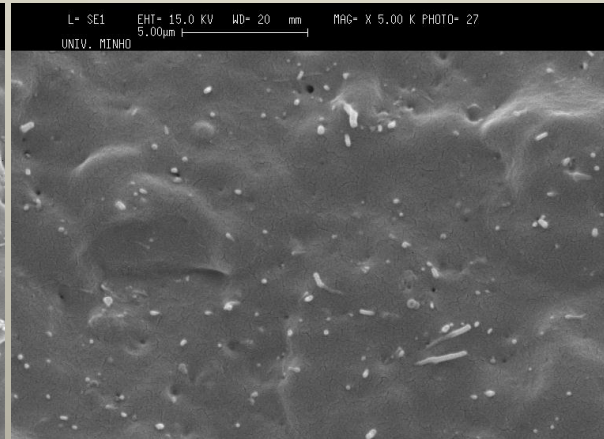
Functionalized CNF: interface with polymers

CNF (Pyrograf III) dispersed in a blend of PP and modified PP

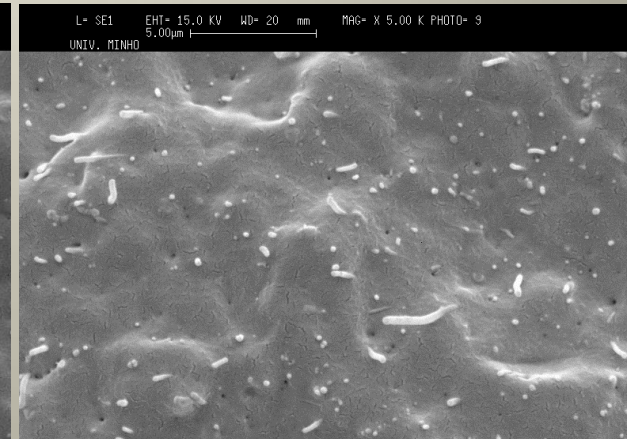
Non functionalized CNF



CNF functionalized by 1,3-dipolar cycloaddition



CNF functionalized by Diels-Alder cycloaddition

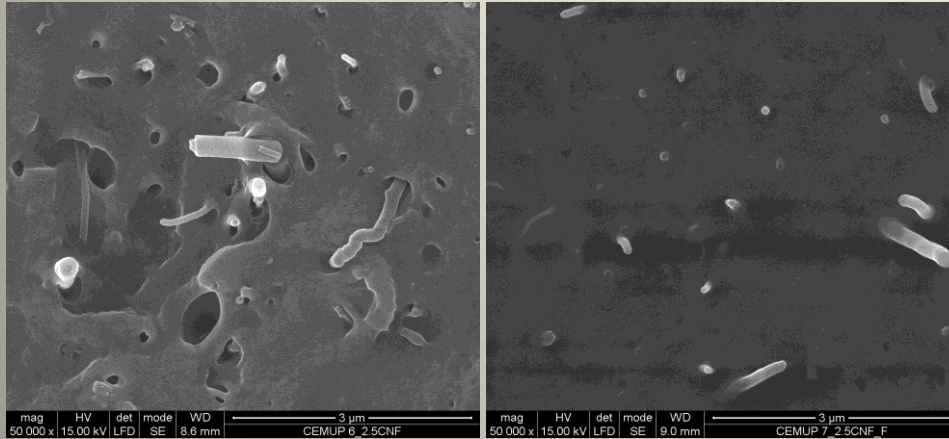


M. C. Paiva, R. M. Novais, R. F. Araújo, K. K. Pederson, M. F. Proença, C. J. R. Silva, C. M. Costa, S. Lanceros-Méndez, *Polymer Composites*, DOI 10.1002/pc.20813



Functionalized CNF and CF: interface with polymers

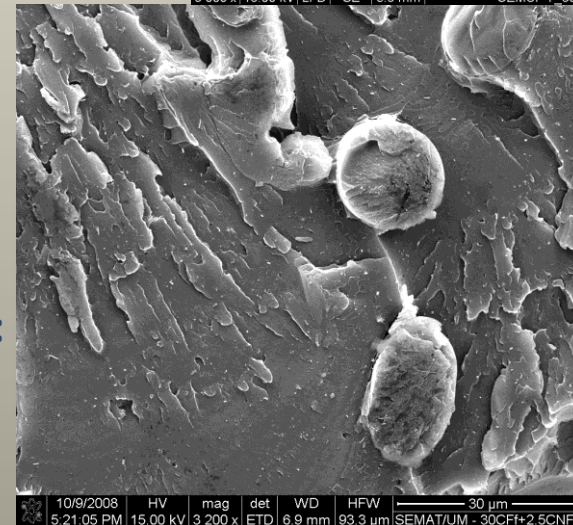
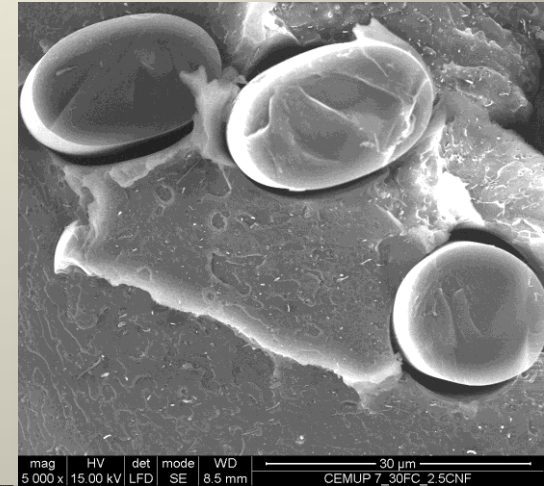
CNF (Pyrograf III) dispersed in PC



Non functionalized CNF

CNF functionalized by
1,3-dipolar cycloaddition

CF and CNF non functionalized:



CF and CNF functionalized:

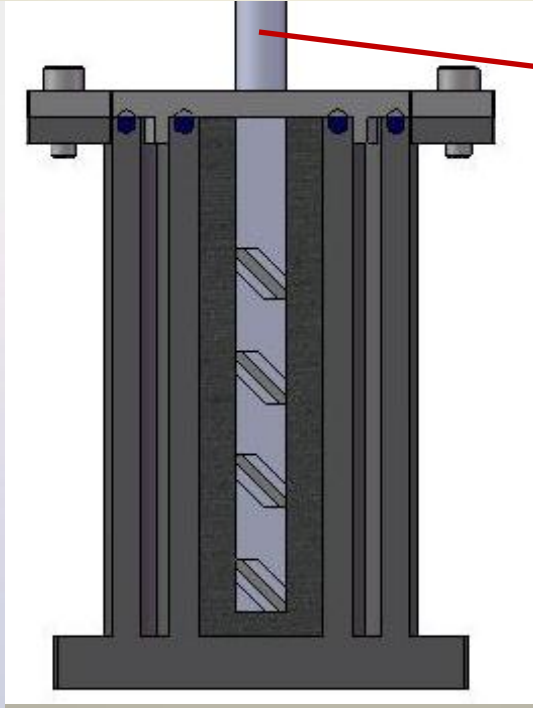
M.H. Lopes, P. Pereira, C. Pereira, Rui M. Novais, M.C. Paiva, C.I. Martins, S. Lanceros-Mendes, P. Cardoso, *Proceedings of PPS 24*, 2008, 15-19 June, Salerno, Italy



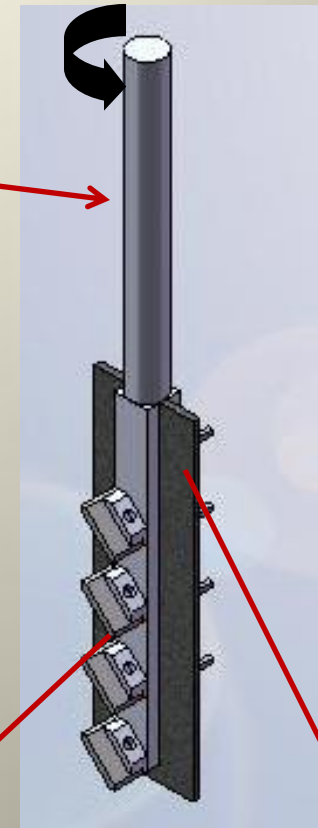
CNT dispersion in high viscosity liquids



Fernando M. Duarte, IPC, U. Minho



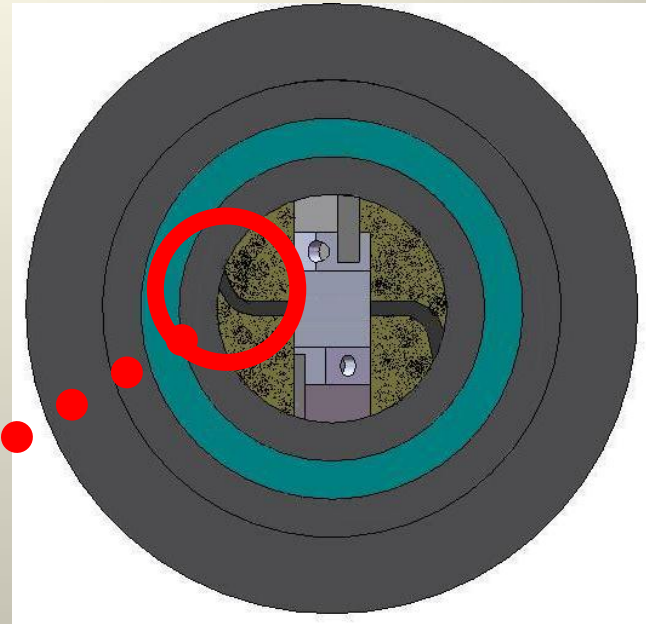
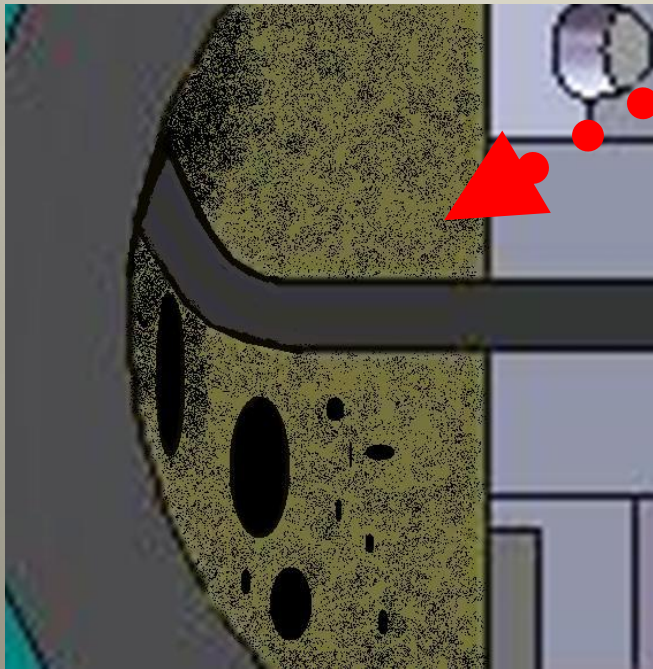
Oblique silicon scraper
(minimize
the Weissenberg effect)



Vertical silicon
scraper (induce
shear and
extensional stress)

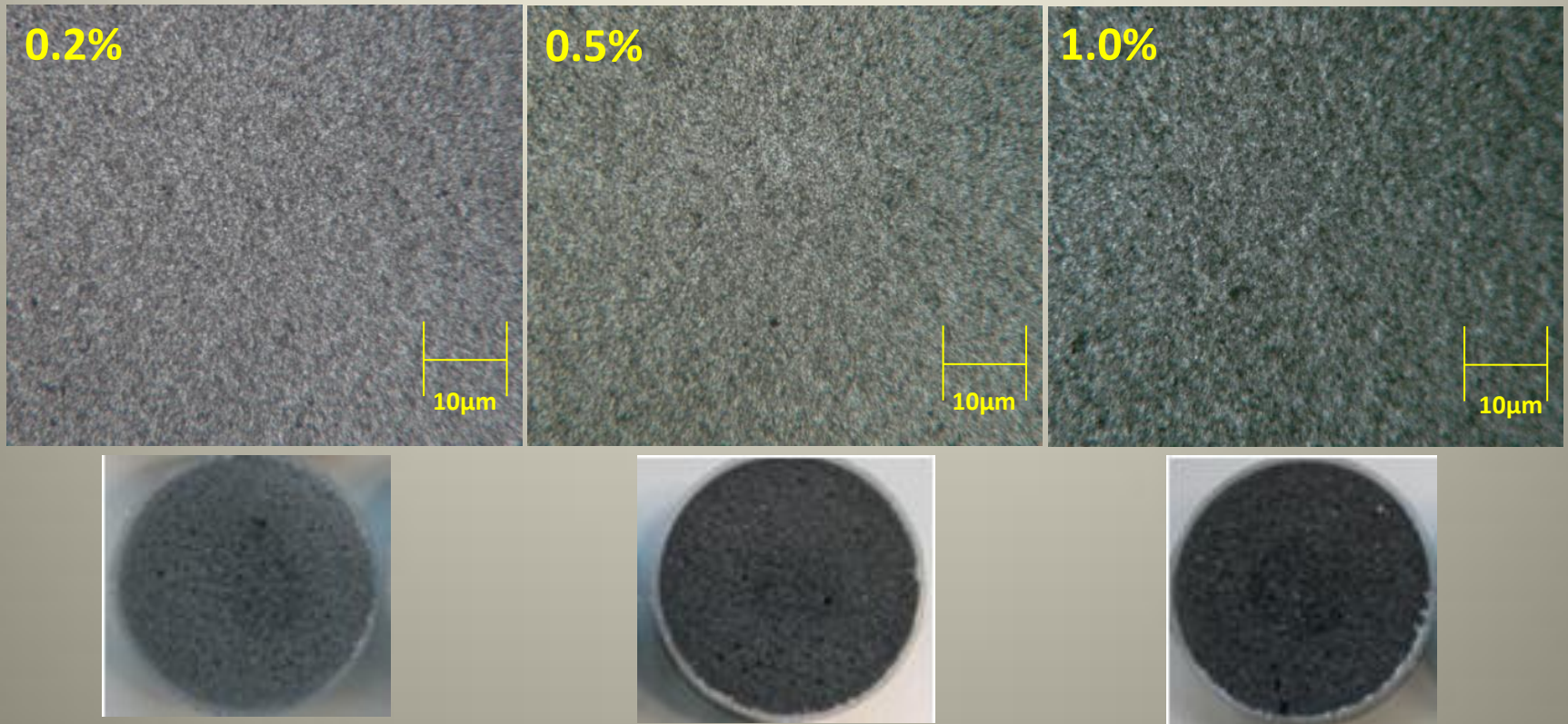


CNT dispersion in polyol



CNT dispersion in polyol

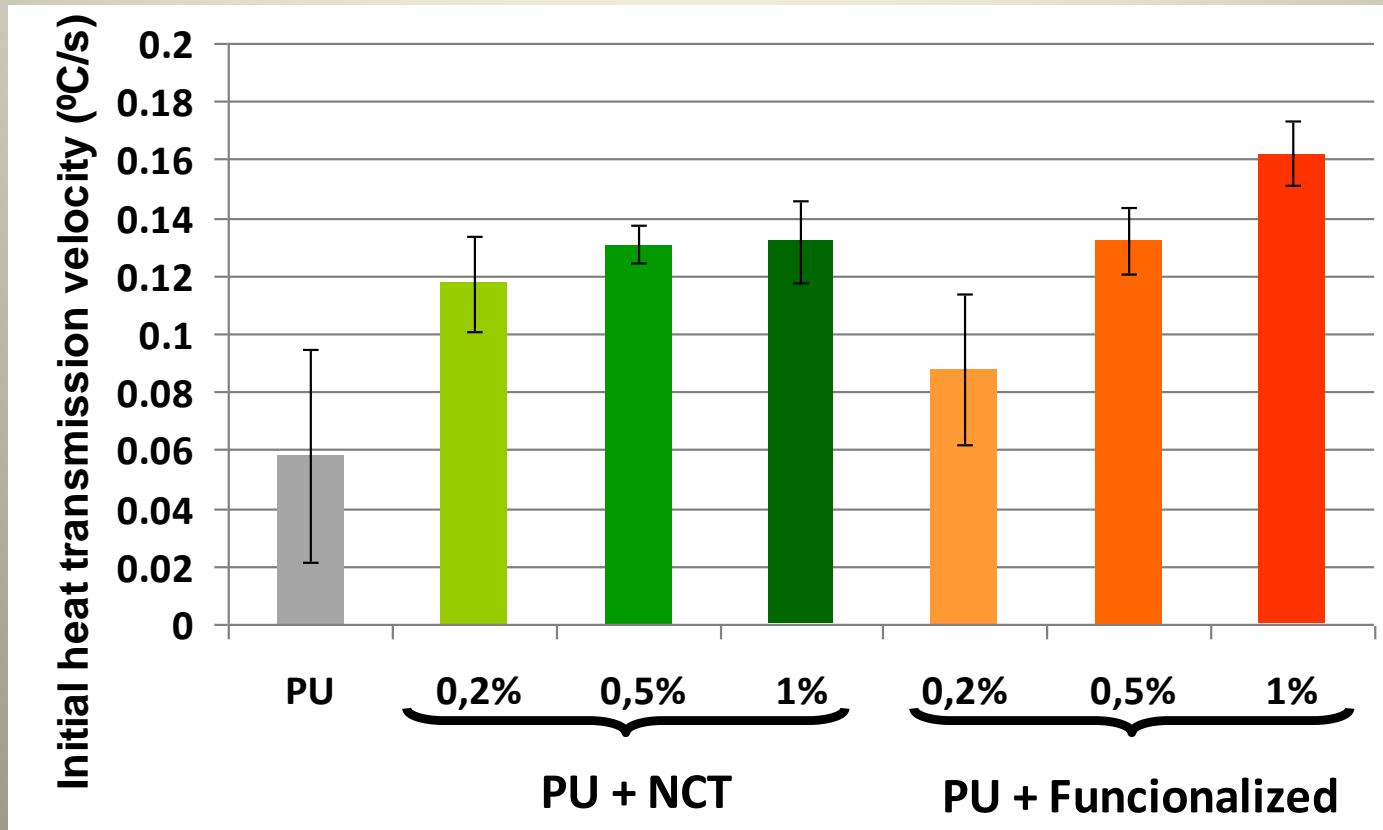
Dispersion of the non-functionlized CNT in the polyol after 30 minutes of mixing



F. Barbosa, C. Cerqueira, F. M. Duarte, M. C. Paiva , *CARBON 2009*, 14-19 June 2009, Biarritz, France



Heat transmission: Initial heat transmission velocity



F. Barbosa, H. Vilas Boas, A. G. Araujo, H. O. Louro, F. M. Duarte, M. C. Paiva, PPS, Cyprus

October 2009



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