

# Chemical Functionalisation of Carbon Nanotubes for the Dispersion in Polymer Matrices

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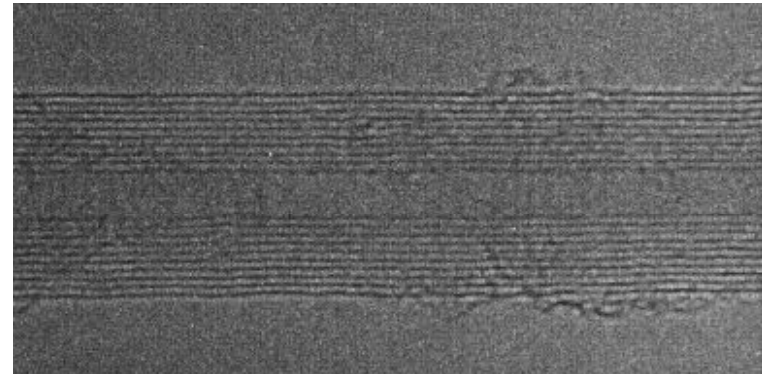
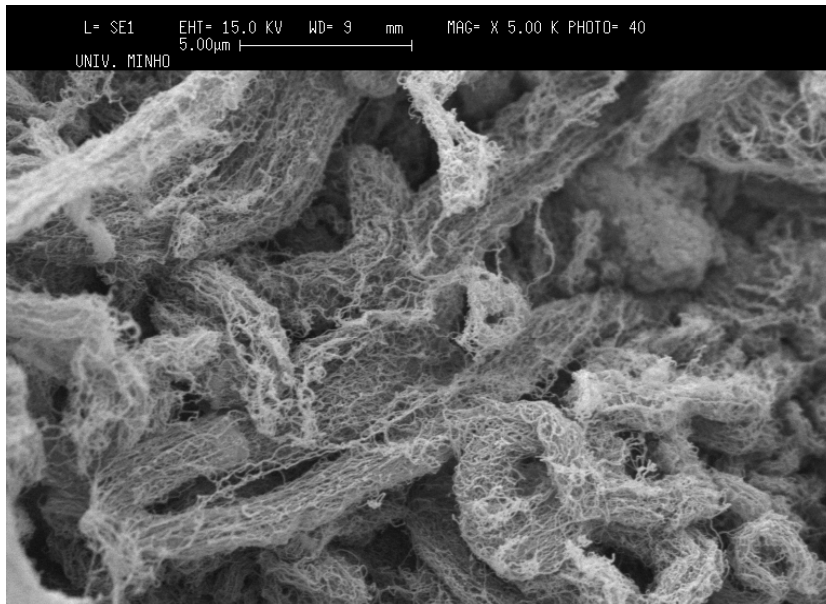
# Outline

- Carbon nanotubes, carbon nanofibres
- Functionalization reactions
- Polymer matrix composites



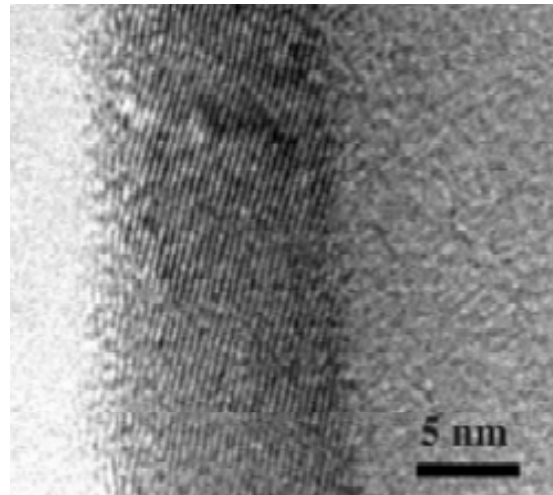
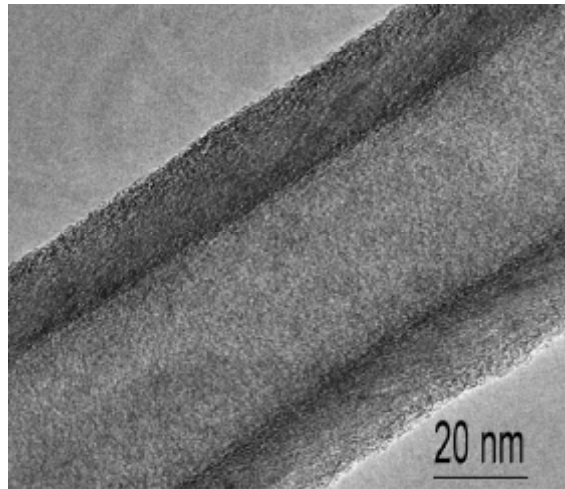
# Carbon Nanotubes

## Multiwall carbon nanotubes 7000 from Nanocyl

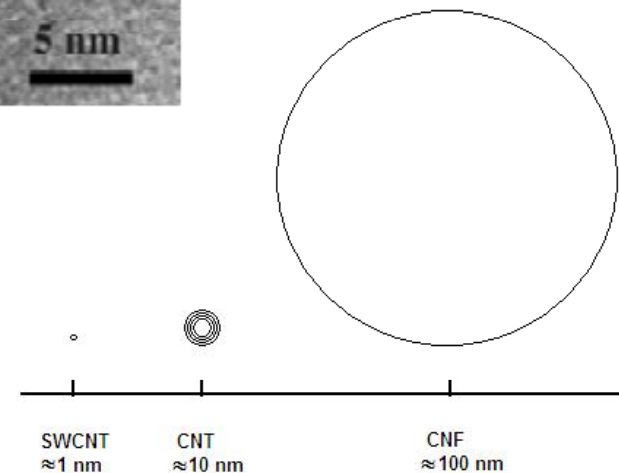
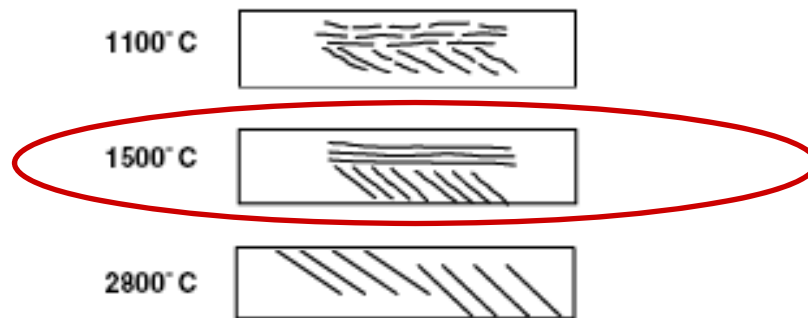


# Carbon Nanofibers

Pyrograf III CNF: P-24 PS, obtained from Applied Sciences Inc.



“Stacked cup” structure:



G. G. Tibbetts, M. L. Lake, K. L. Strong, B. P. Rice, *Comp. Sci. Technol.* **67**, p. 1709, 2007



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# Functionalization



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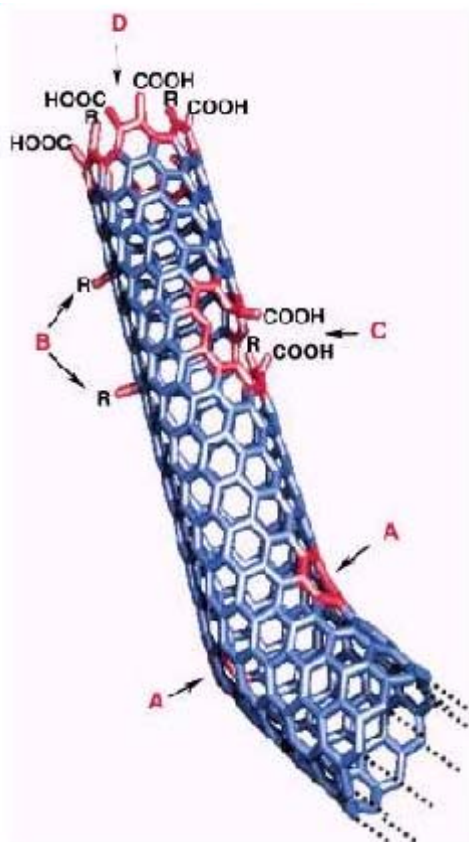
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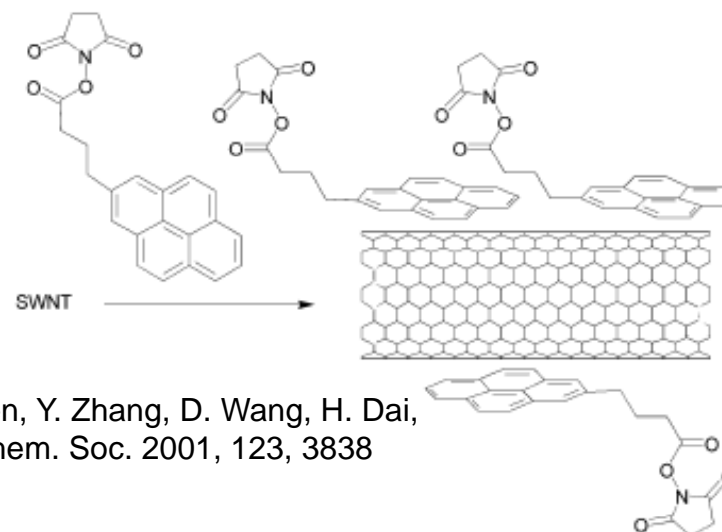
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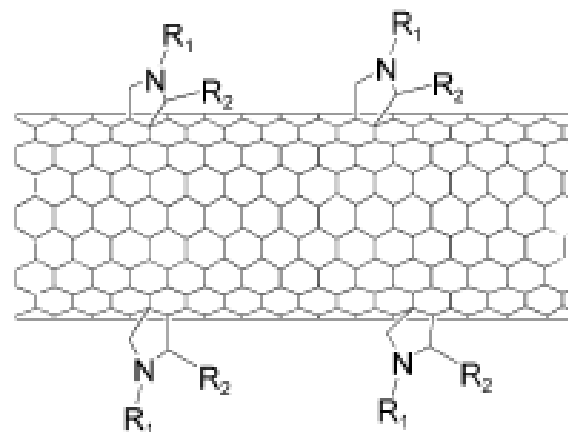
# Chemical functionalization



Holzinger, M.; Vostrowsky, O.; Hirsch, A.;  
Henrich, F.; Kappes, M.; Weiss, R.; Jellen, F.  
*Angew. Chem., Int. Ed.*, **2001**, 40, 4002–4005



R. J. Chen, Y. Zhang, D. Wang, H. Dai,  
*J. Am. Chem. Soc.* 2001, 123, 3838



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



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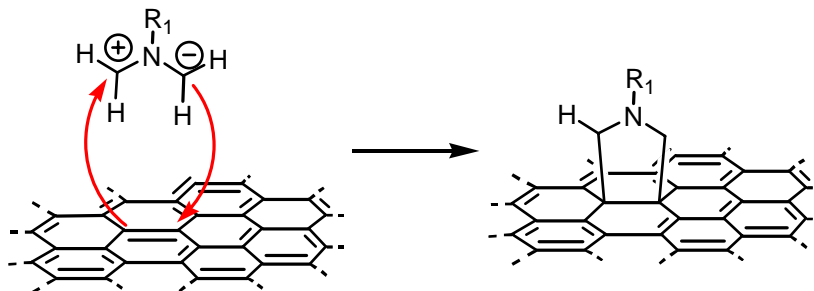
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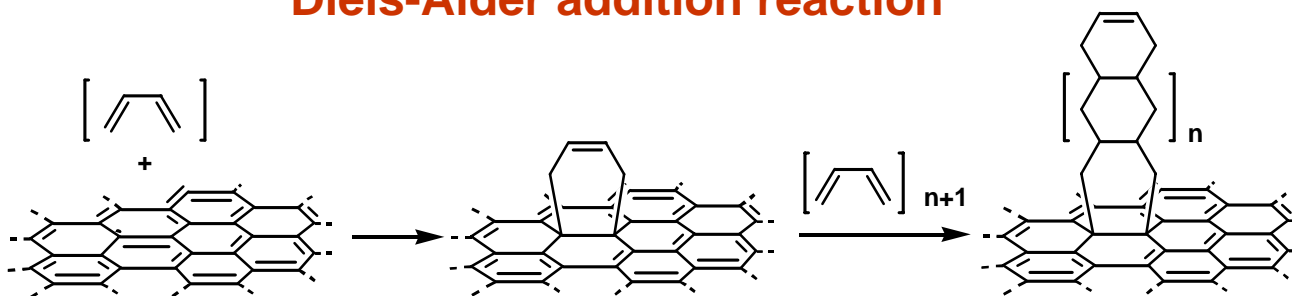
# Functionalization reactions

## 1,3-dipolar cycloaddition reaction



V. Georgakilas, K. Kordatos, M. Prato, D.M. Guldi, M. Holzinger, A. Hirsch, *J. Am. Chem. Soc.* **124**, 5, p.760, 2002

## Diels-Alder addition reaction

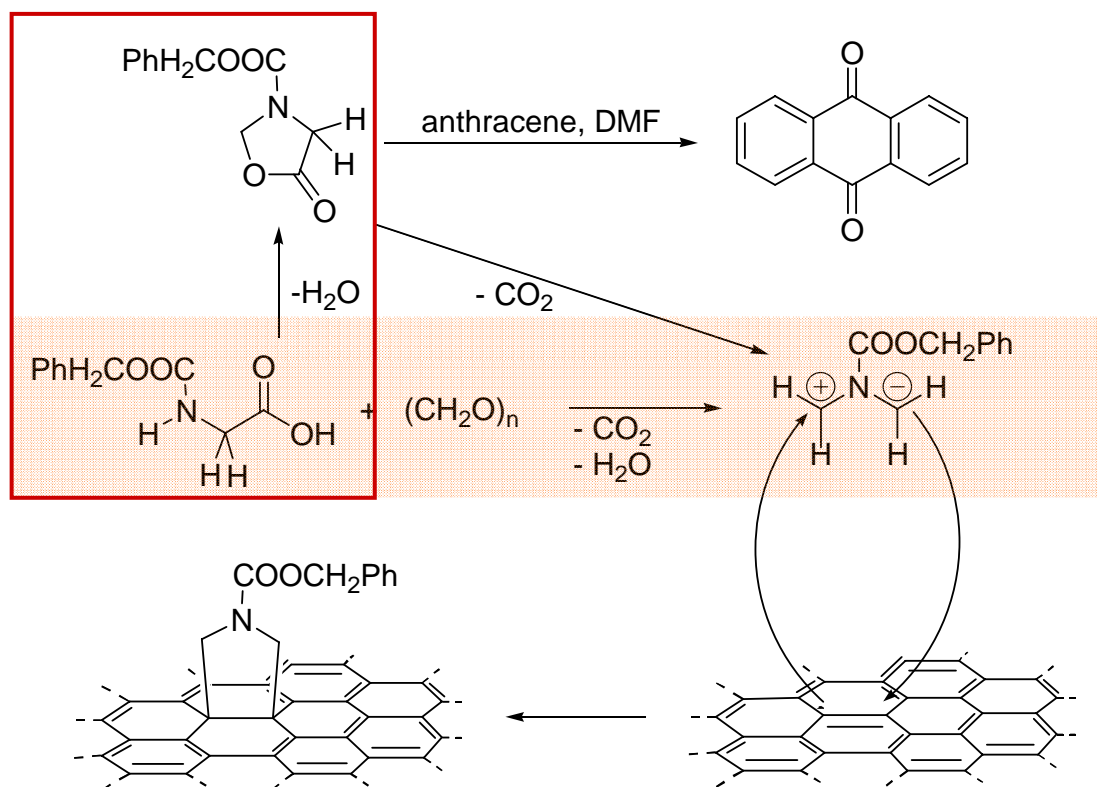
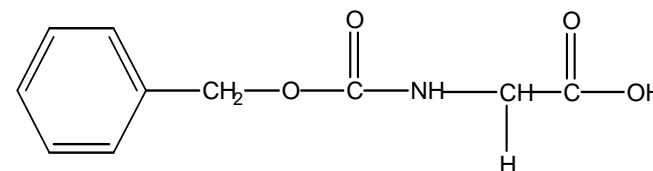


F. M. Fernandes, R. Araújo, M. F. Proença, C. J. R. Silva, M. C. Paiva, *J. of Nanosci. Nanotechnol.*, 2007, 7, 3514–3518.



# 1,3-dipolar cycloaddition

Amino acid: ***N*-carbonylbenzyloxyglycine**



R. Araújo, M. C. Paiva, M. F. Proença, C. J. R. Silva, *Composite Science and Technology*, 2007, 67, 806-810  
 R. Araújo, F. M. Fernandes, M. F. Proença, C. J. R. Silva, M. C. Paiva, *J. Nanosci. Nanotechnol.*, 2007, 7, 3441-3445



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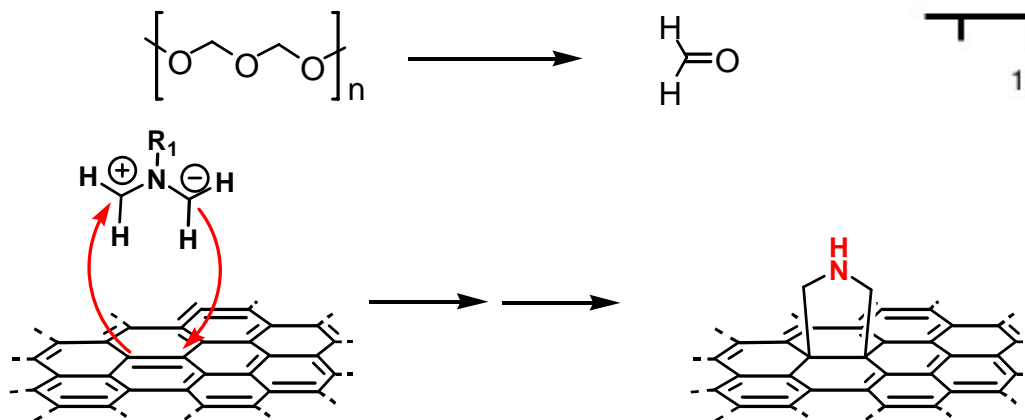
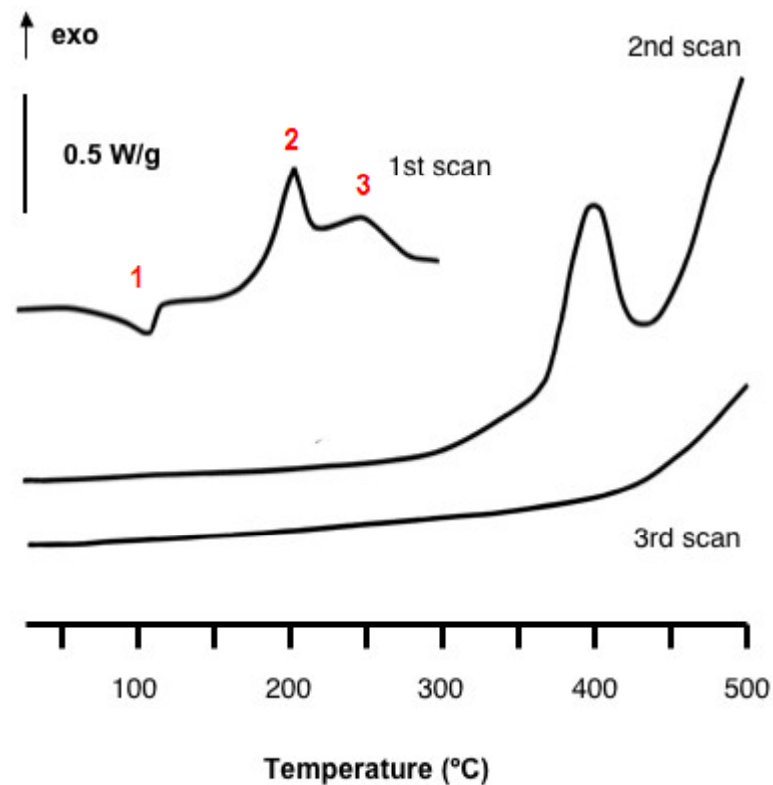
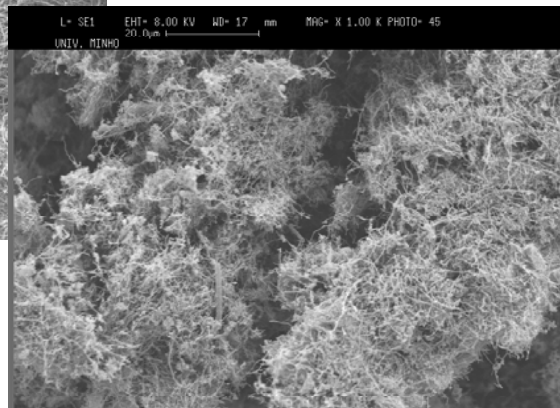
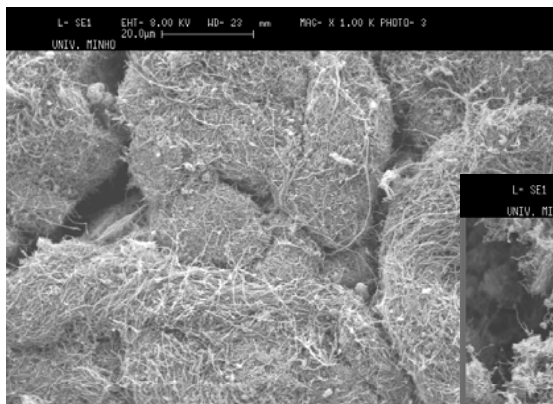
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# 1,3-dipolar cycloaddition - DSC

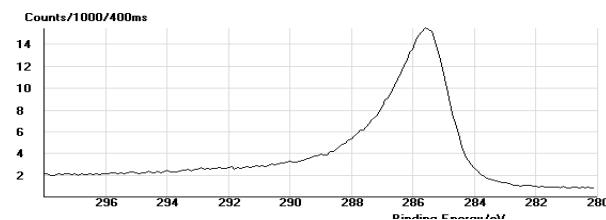


# 1,3-dipolar cycloaddition – XPS

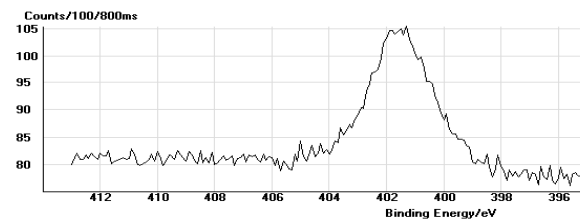
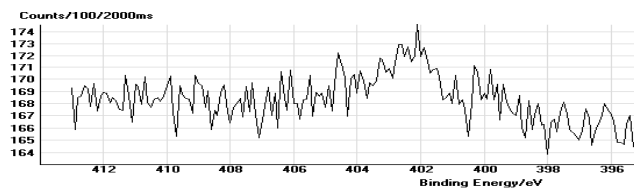
Non-functionalised

Functionalised by 1,3-dipolar cycloaddition

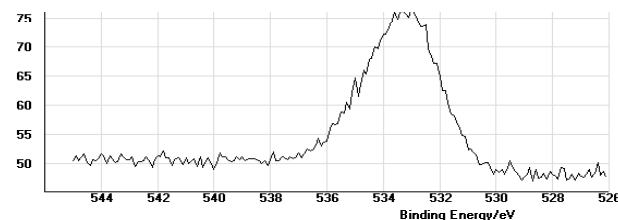
C1s



N1s



O1s



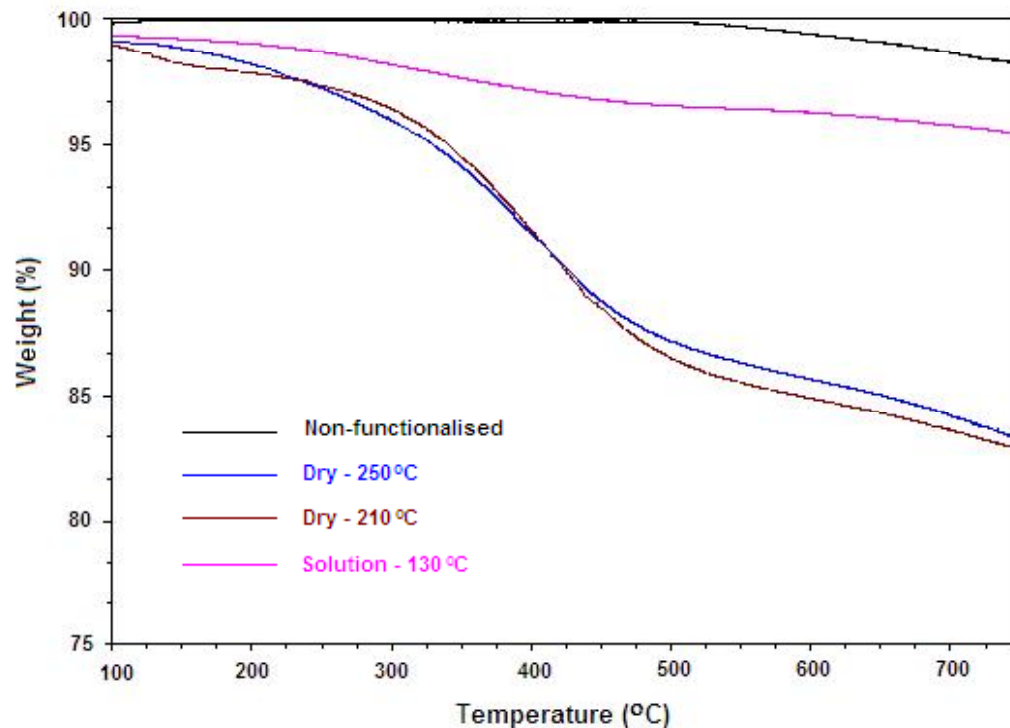
Sample	C (at%)	O (at%)	N (at%)
Non-functionalised	93.21	6.23	0.56
Dry – 250 °C	88.55	6.78	4.67



# 1,3-dipolar cycloaddition – TGA

Functionalisation of CNF under 3 different conditions:

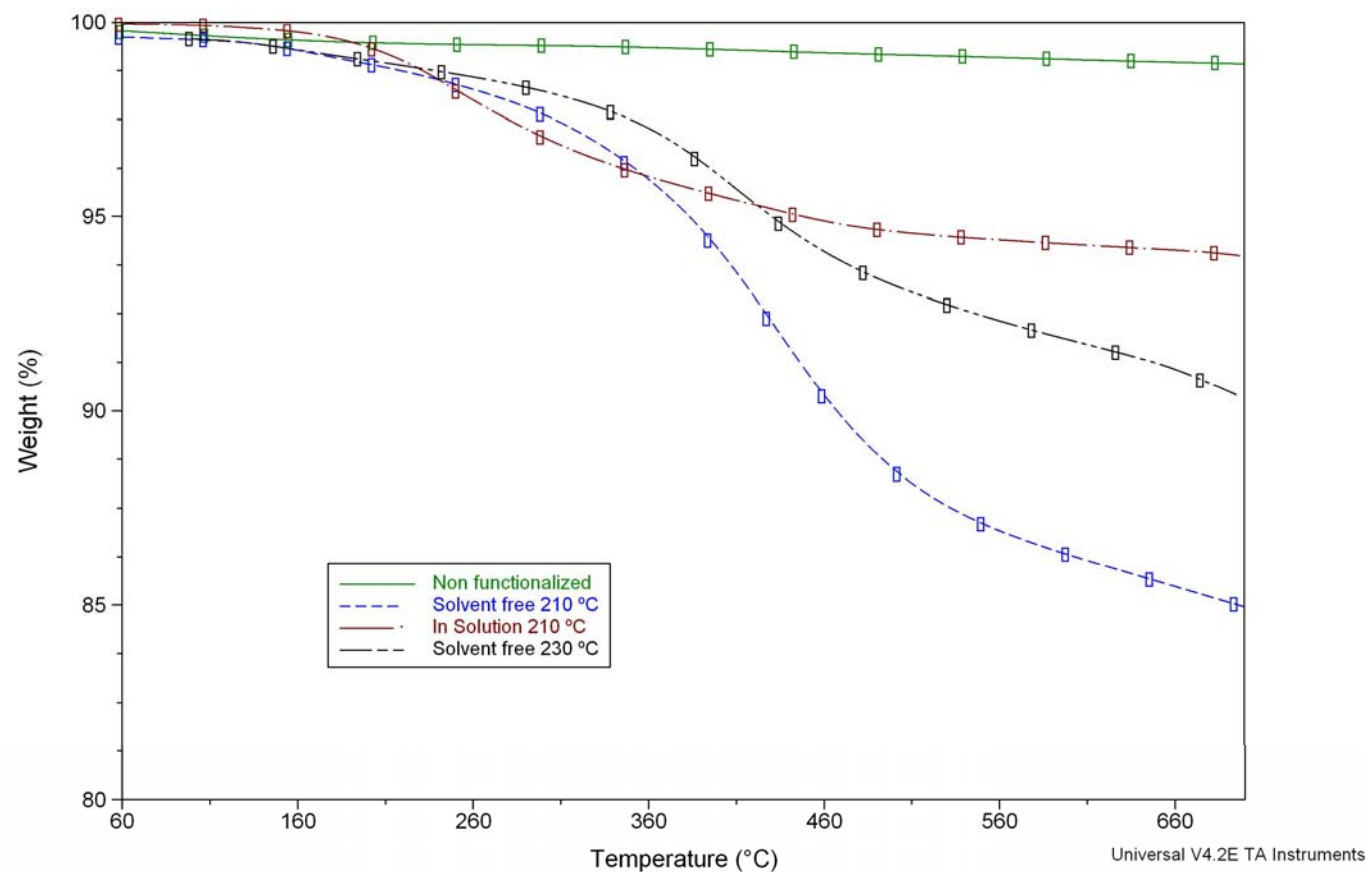
1. in solution (DMF), at 130 °C for 120 H
2. in dry conditions, heating the reagents and CNF at i) 210 °C for 30 H, and ii) 250 °C for 14 H.



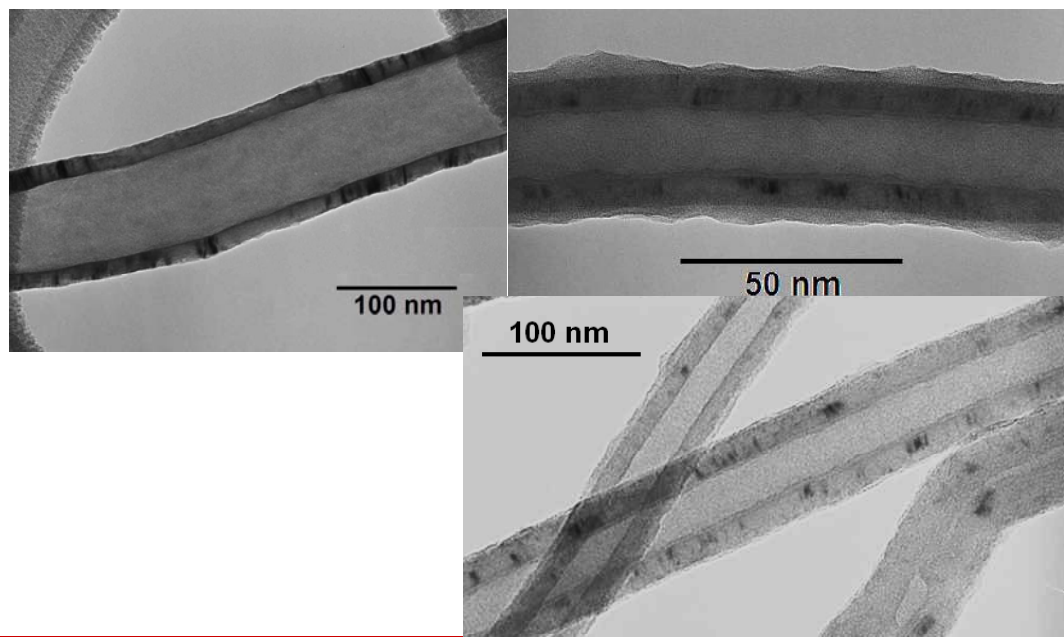
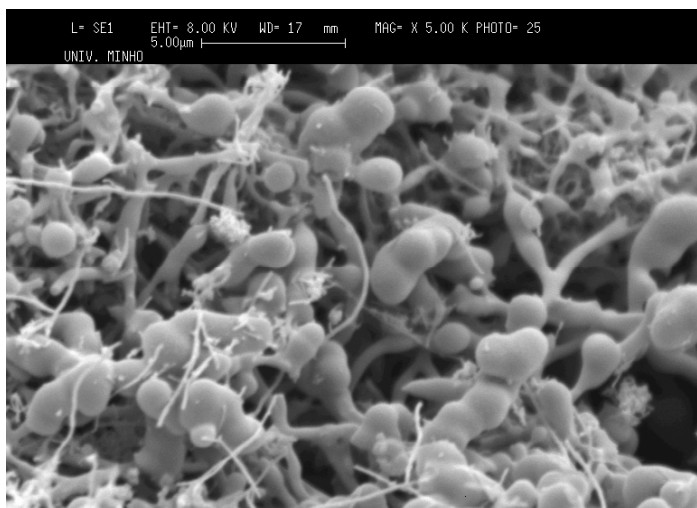
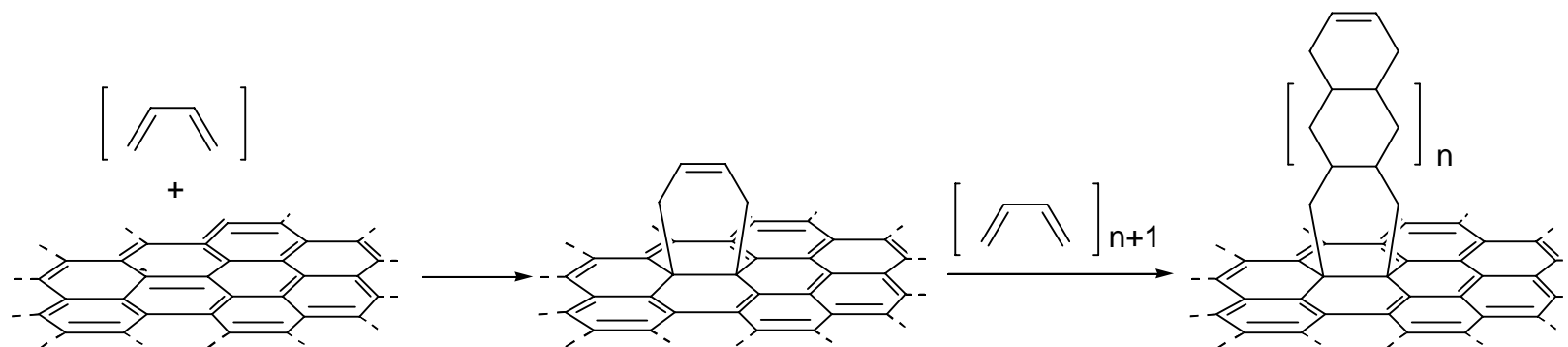
Sample	Weight loss (750°C) ± St. Dev.
Non-functionalised	1,5 ± 0,1
Dry – 250 °C	18 ± 3
Dry – 210 °C	17,7 ± 0,7
Solution -130 °C	7 ± 4



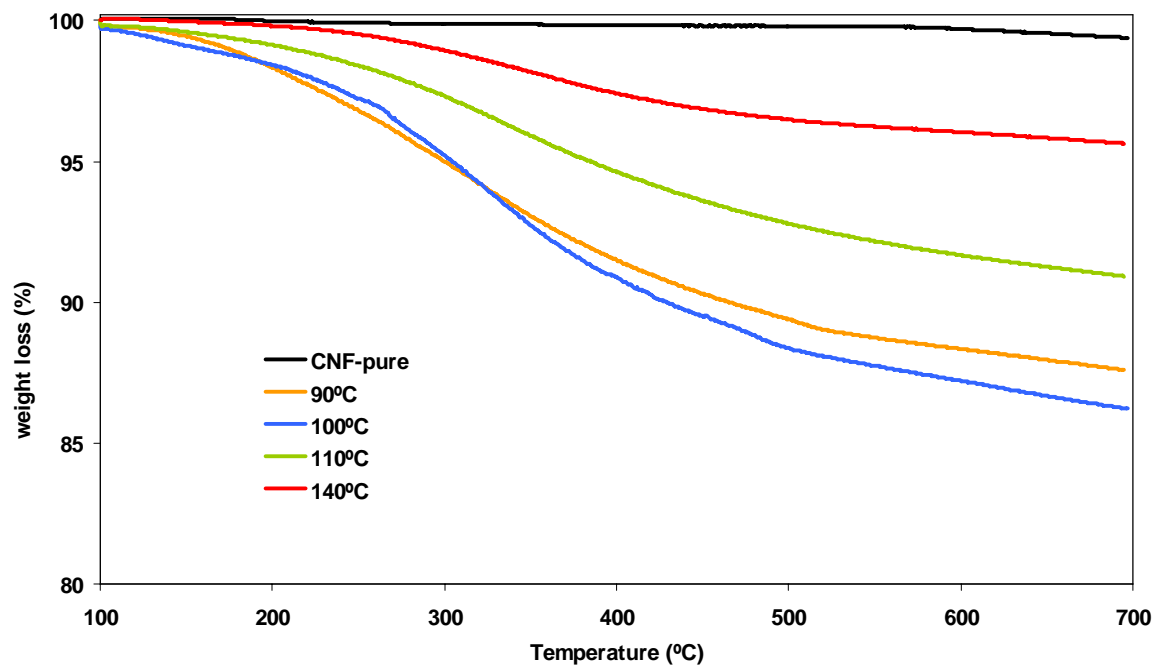
# 1,3-dipolar cycloaddition on MWNT – TGA



# Diels-Alder addition reaction



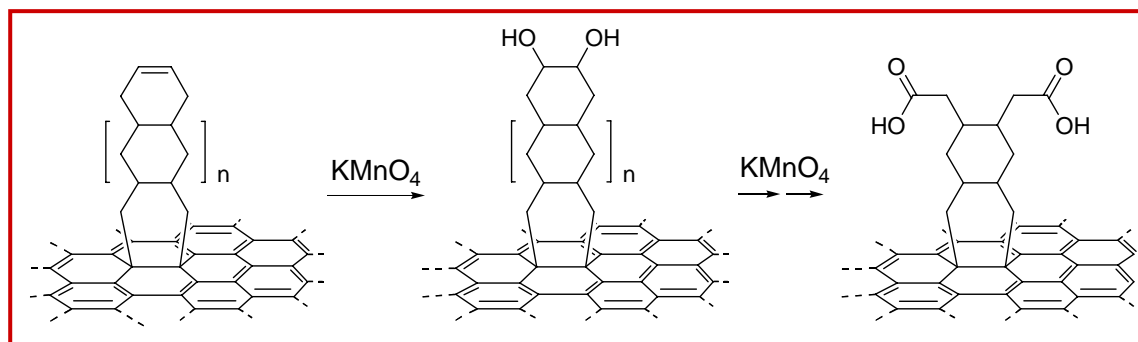
# Diels-Alder addition - TGA



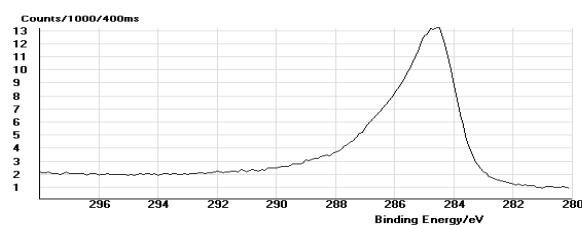
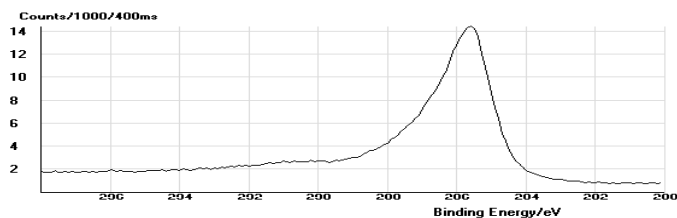
Reaction Temperature (°C)	Weight loss (750°C)
90 (diglyme)	15 ± 5
100 (diglyme)	15 ± 2
110 (diglyme)	8 ± 2
140 (diglyme)	5 ± 1
140 (dry, no solvent)	11 ± 3



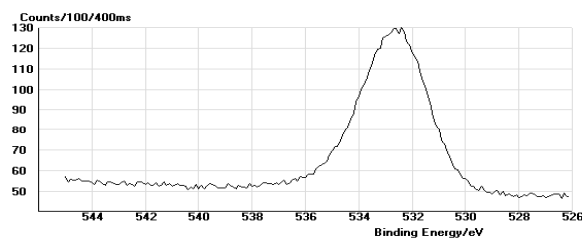
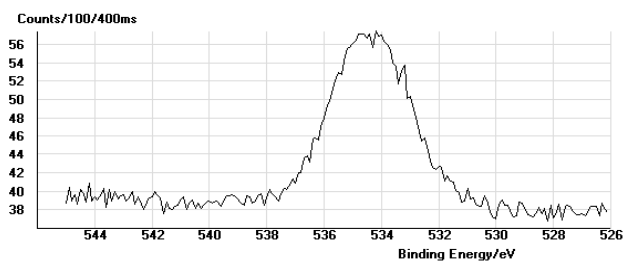
# Diels-Alder addition – XPS



**C1s**



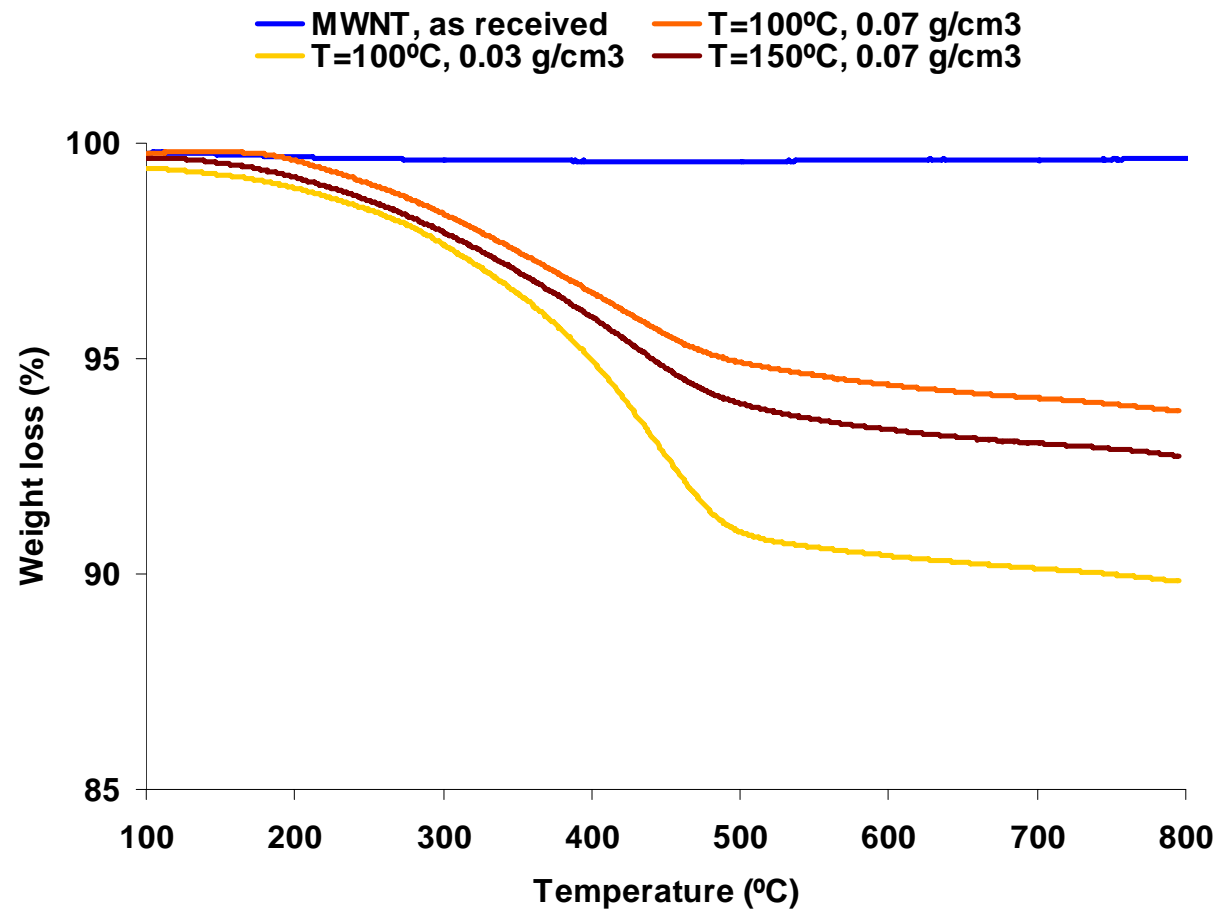
**O1s**



Sample	C (at%)	O (at%)
Non-functionalised	93	6
Functionalised at 100 °C	79	19



# Diels-Alder addition on MWNT - TGA





# Applications



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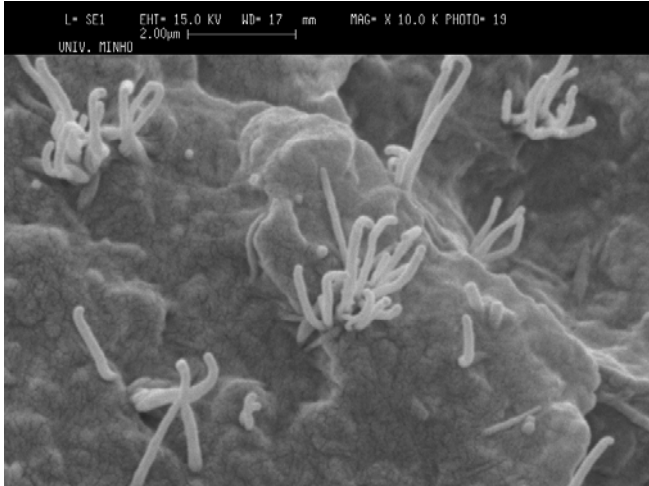
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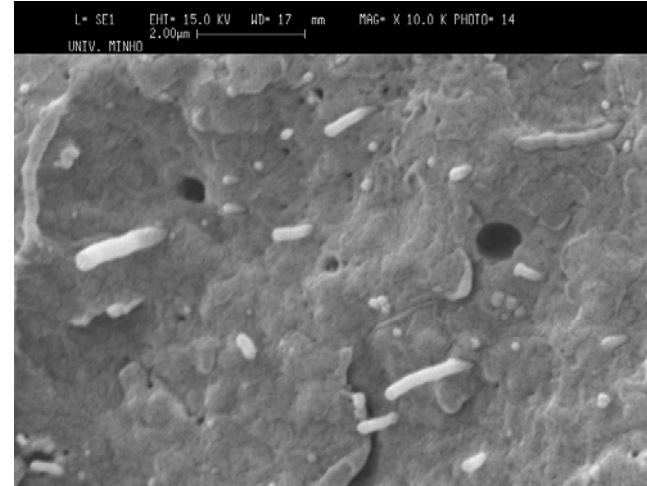
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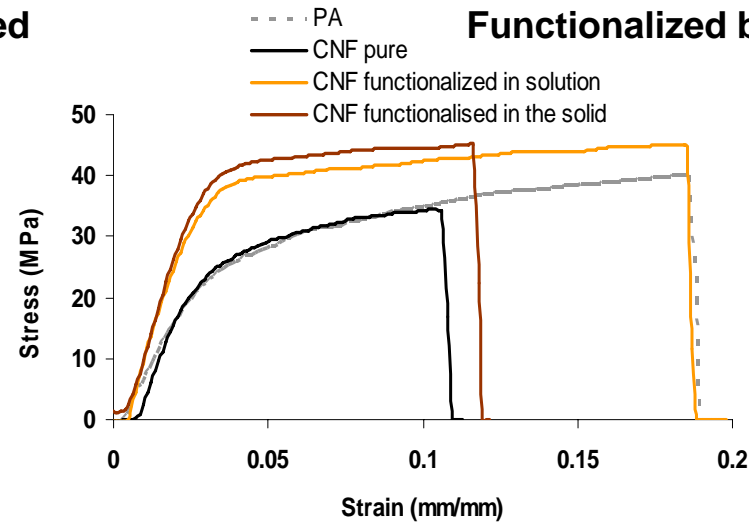
# Composites by solvent casting



**Non-functionalized**



**Functionalized by 1,3 dipolar cycloaddition**



# Composites by melt-mixing

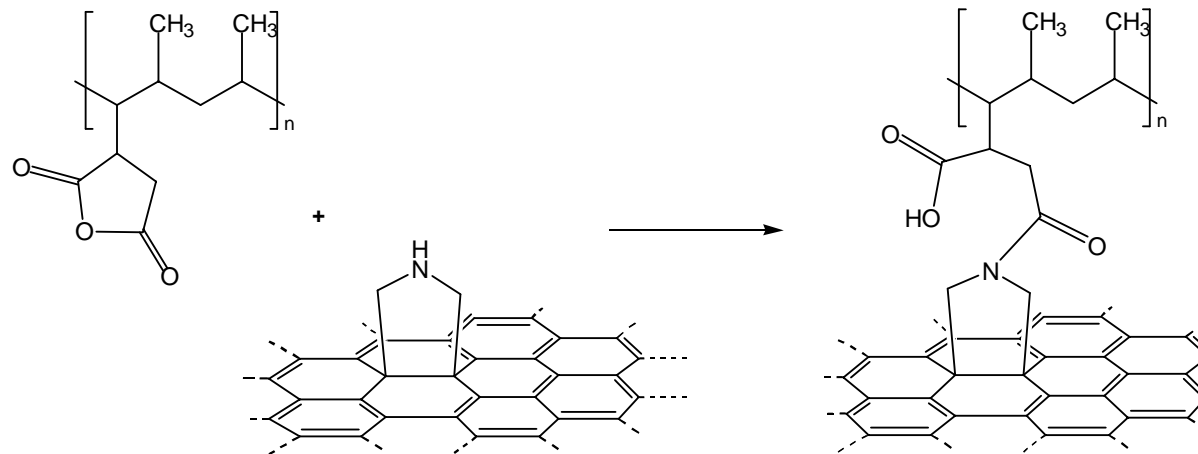
## Composites with:

Polypropylene (PP)

PP combined with PP modified with maleic anhydride (PP-g-MA)

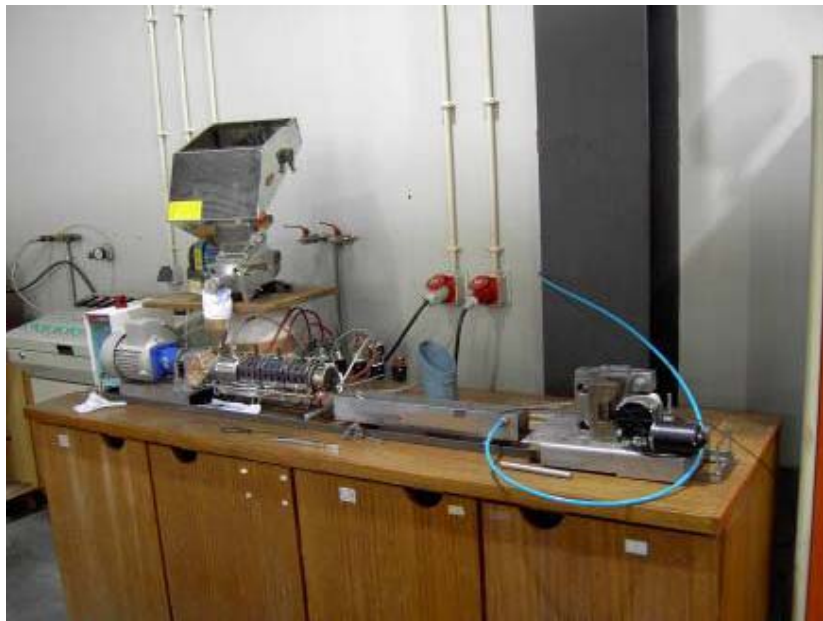
5% weight of CNF

- ✓ Non functionalised
- ✓ DA functionalised without solvent
- ✓ DA functionalised in diglyme
- ✓ 1,3-dipolar cycloaddition without solvent



# Extrusion

The different compositions of PP/CNF and PP/ PP-*g*-MA/CNF were mixed in the powder form and then melt mixed in a mini twin-screw extruder at a flow rate of 270 g/h and a temperature of 220°C.



Prototype mini twin-screw extruder, projected by J.A. Covas



# Extrusion: composite fracture surfaces

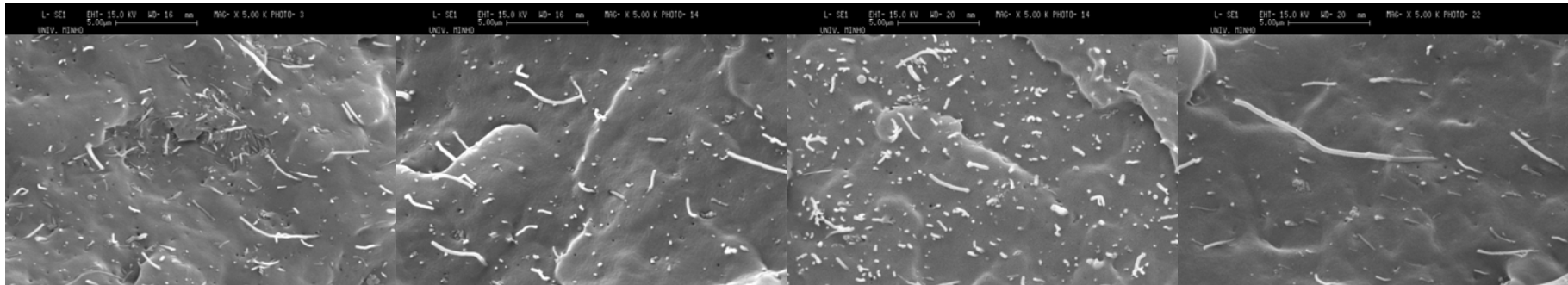
## PP matrix

Non-functionalised

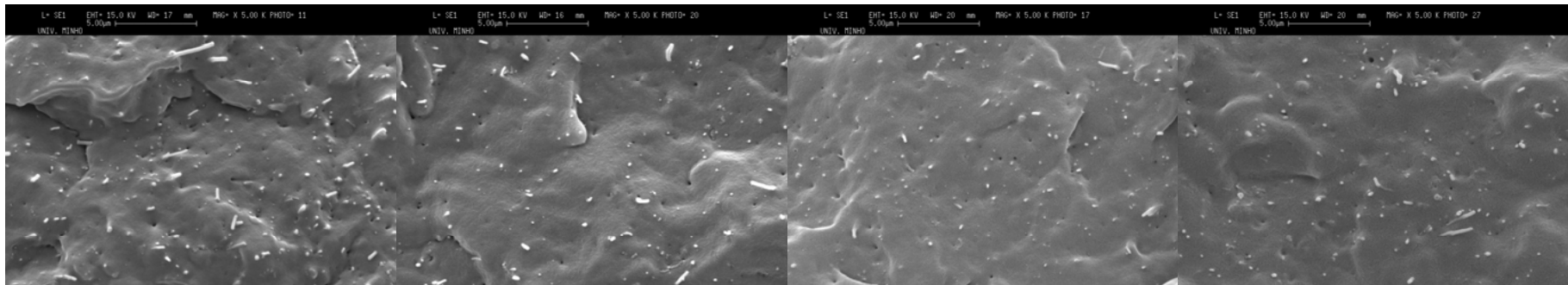
DA without solvent

DA in diglyme

1,3-dipolar cycloaddition

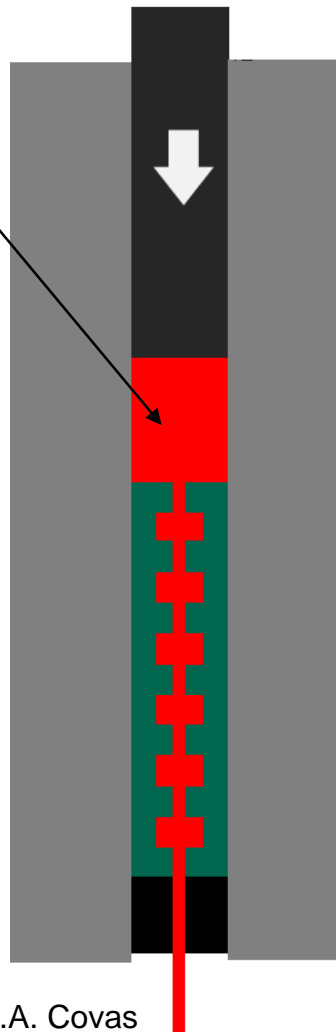


## (PP + PP-g-MA) matrix



# Extensional flow

Polymer powder  
+ CNF

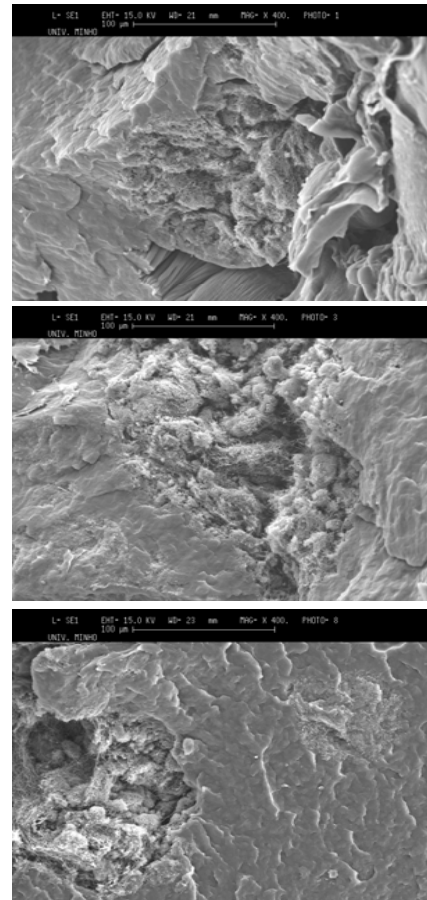


1<sup>st</sup>  
channel

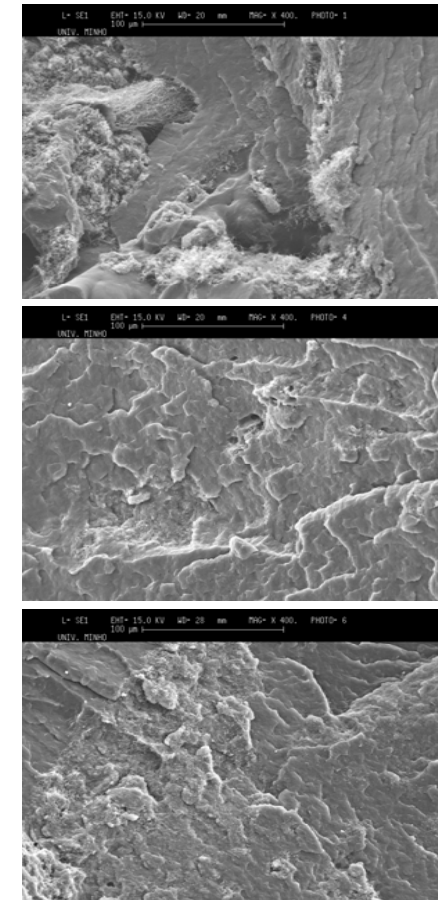
2<sup>nd</sup>  
channel

3<sup>rd</sup>  
channel

PP + Non functionalized  
CNF



PP + PP-g-MA +  
functionalized CNF



Prototype by J.A. Covas

M. Conceição Paiva, José A. Covas, Rui M. Novais, Vânia Andrade,  
*Proc. ChemOnTubes 2008*



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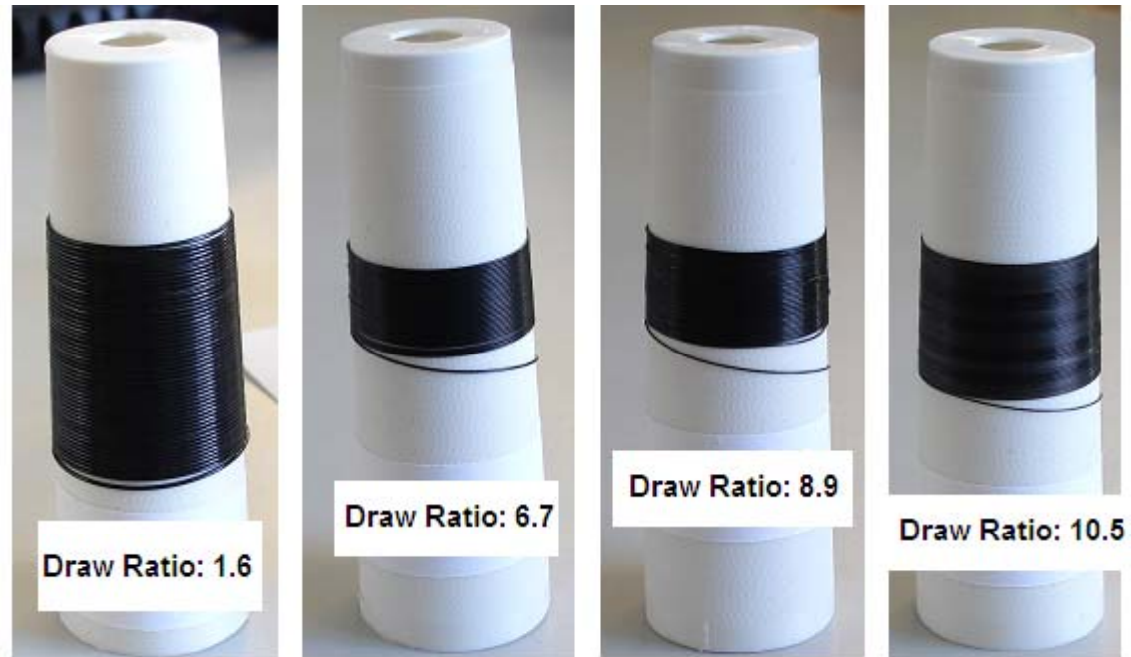
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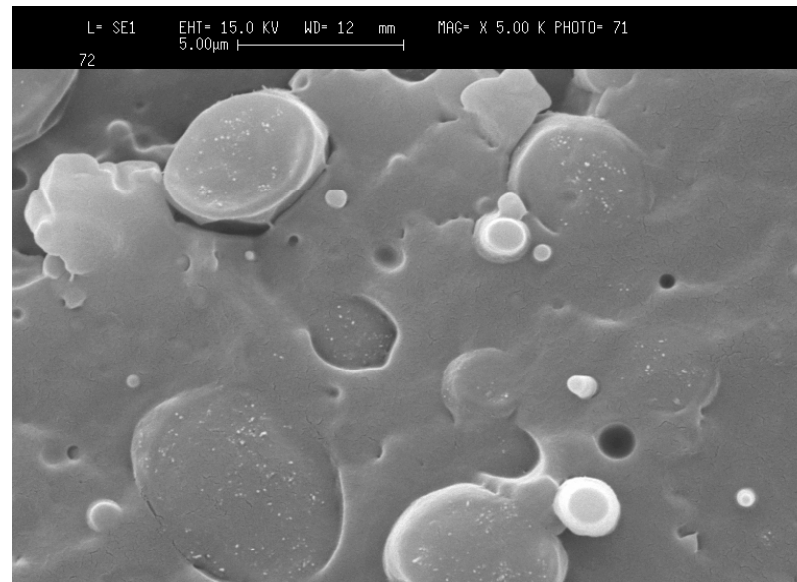
# Spinning of composite filaments



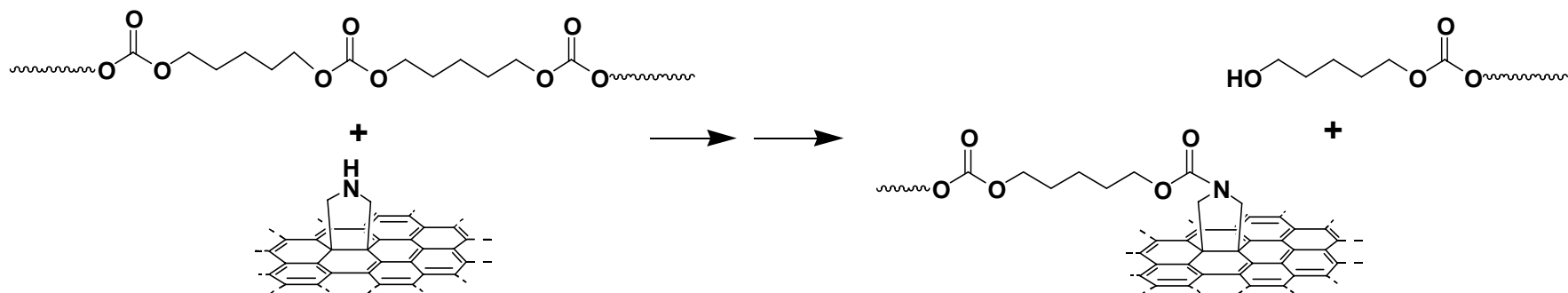
	Drawing Ratio	Elastic modulus (GPa)	Tensile strength (MPa)	Liquid sensing
<b>PCL/PP (50:50) + 3% CNT</b>	1.6	$0.85 \pm 0.15$	$32 \pm 1$	YES
	6.7	$3.6 \pm 0.7$	$298 \pm 43$	NO
	10.5	$8.3 \pm 1.5$	$405 \pm 135$	NO



# Spinning of composite filaments



Functionalization of CNT with polycaprolactone





## Conclusions

- ✓ Two organic functionalisation methods were implemented. Evidence of the functionalization of the CNF was obtained from TGA, XPS and TEM, SEM. CNT were also functionalized. The functionalization reactions were successful in solution and in solvent-free conditions.
- ✓ Composites were prepared by solvent casting and melt blending using different processes. Improved wetting of the functionalised CNF was observed.
- ✓ The CNT and CNF may be functionalized with the matrix polymer, for a number of polymers.



## Acknowledgements

- Financial support from FCT (Portuguese Foundation for Science and Technology), project POCI/QUI/59835/2004 and SFRH/BD/32189/2006
- INTELTEX - Integrated Project, Project no. NMP-CT-2006-026626
- I3N/IPC

Thank you for your attention!

