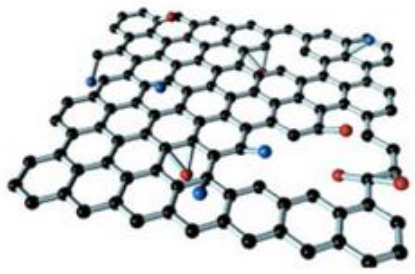
Tailored carbon nanomaterials for enhancements in mechanical properties of epoxy and polyurethane nanocomposites: scale up in the CTNano/UFMG.

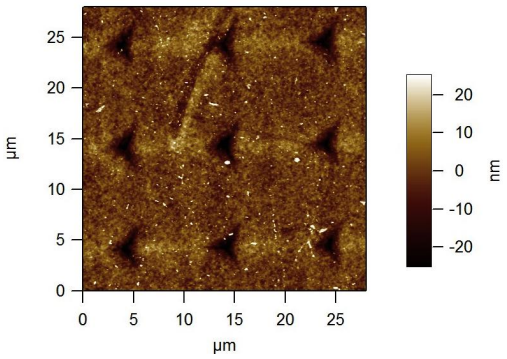
Glaura Goulart Silva

Chemistry Department - Federal University of Minas Gerais – Brazil
Technological Center for Nanomaterials - BHTec

Outline

- CTNano
- Scale up
- Tailored CNM
- Epoxy nanocomposites






Océano Atlántico
Boa Vista
Roraima
Amapá
Macapá
Belém
Manaos
Amazonas
Pará
São Luís
Maranhão
Fortaleza
Ceará
Rio Grande del Norte
Teresina
Paraíba
Piauí
Pernambuco
Recife
Alagoas
Sergipe
Maceió
Aracaju
Acre
Rio Branco
Porto Velho
Rondonia
Mato Grosso
Palmas
Tocantins
Bahía
Salvador
Cuiabá
Distrito Federal
Goiás
BRASÍLIA
Goiânia
Minas Gerais
Espírito Santo
Vitória
Mato Grosso del Sur
Campo Grande
Belo Horizonte
São Paulo
Río de Janeiro
Paraná
Curitiba
Santa Catarina
Florianópolis
Río Grande del Sur
Porto Alegre
0
500
1000 km


UFMG

PETROBRAS

BNDES

InterCement

UFMG

bh.tec Parque Tecnológico de Belo Horizonte

CTNANO

centro de tecnologia em nanomateriais

Finep 50 anos

FAPEMIG

CNPq

INCT

Instituto Nacional de Ciência e Tecnologia em Nanomateriais de Carbono

CTNANO

centro de tecnologia em nanomateriais









R$ 50 million raised

25 patents in nanomaterials

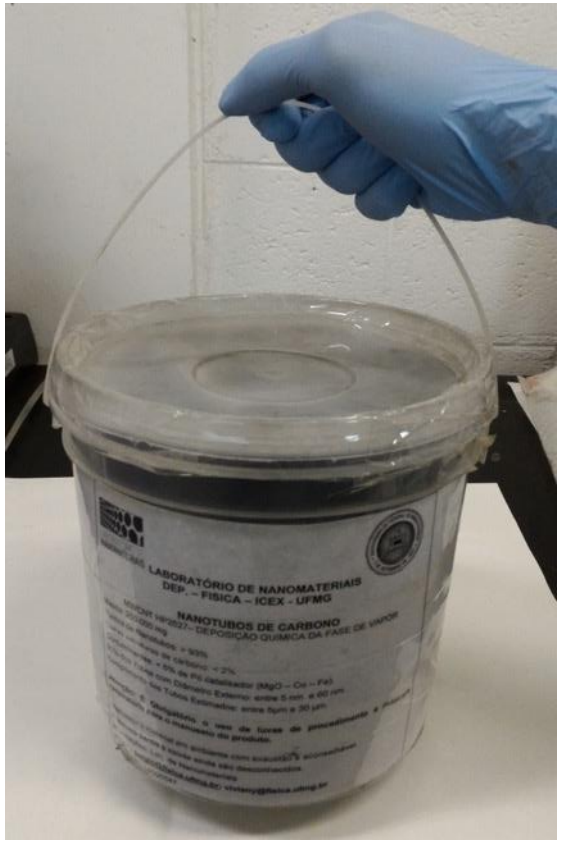
Team: 50+ members

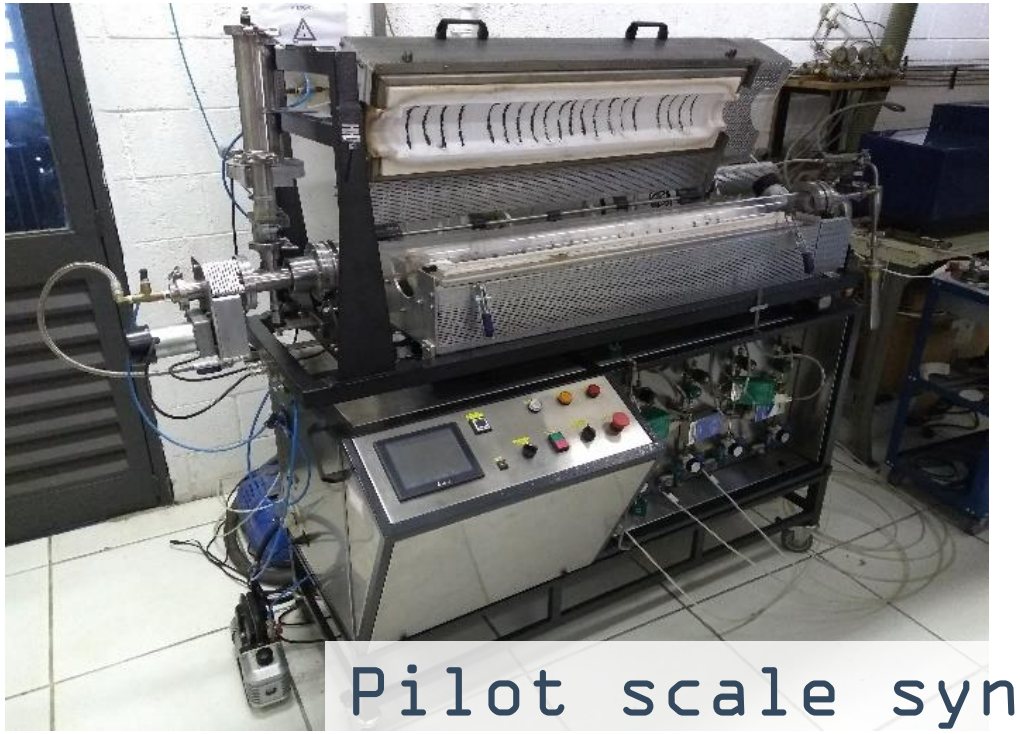
Formation of 200+ researches in the area

20 year experience in nanotubes and 10 in graphene

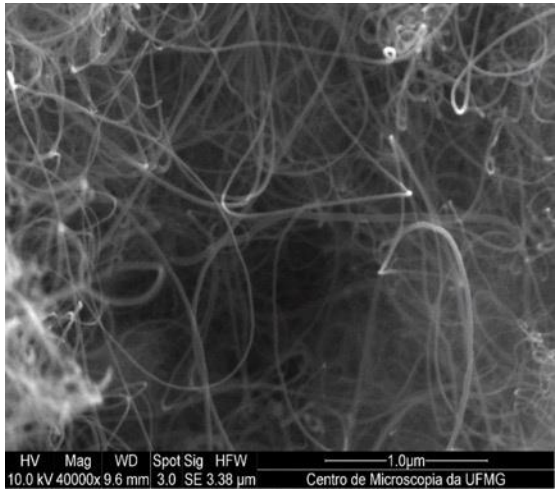

CTNANO
centro de tecnologia em nanomateriais
Carbon Nanotube synthesis (Pilot scale)
Nanostructured cement R&D
Characterization
HSE
Monitoring R&D
Polymeric Nanocomposites R&D
Graphene synthesis (Pilot scale)

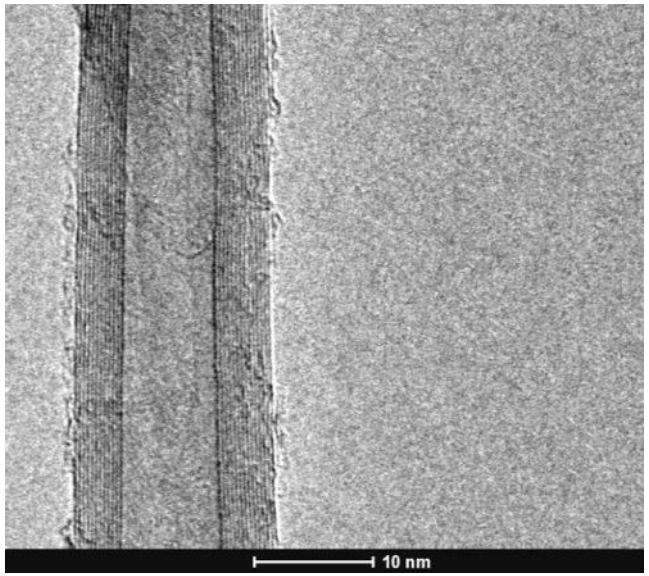

CTNANO
HEV-4647
NYG-5615
FABULOUS FUTURE





Pilot scale synthesis of MWCNT





MWCNT

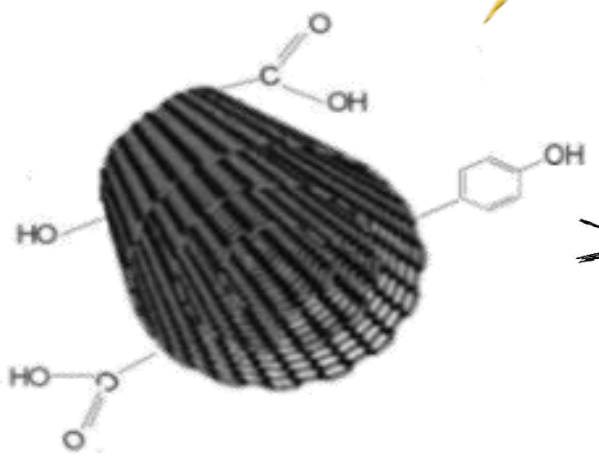
400g/day

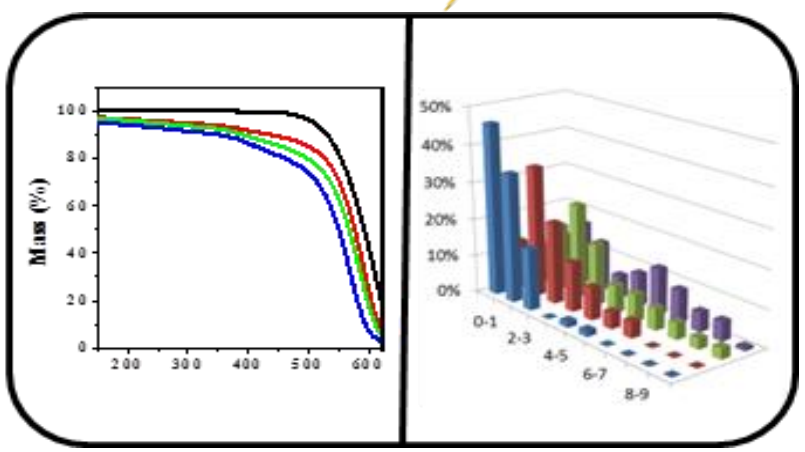
purity: ↖ 90%

Pilot scale synthesis of ox-MWCNT

Castro et al., *J. Braz. Chem. Soc.*, Vol. 28, No. 7, 1158-1166, 2017.

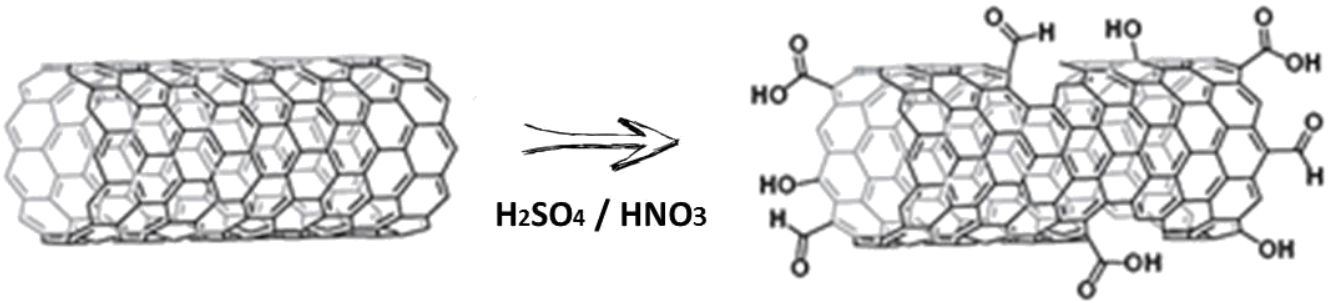
Acid treatment of MWCNTs → **Functionalization vs. length reduction** → **Statistical evaluation**





Tailored process → **Optimal conditions**

Acid treatment



Degree of functionalization and length reduction after acid treatment with different acid volumes

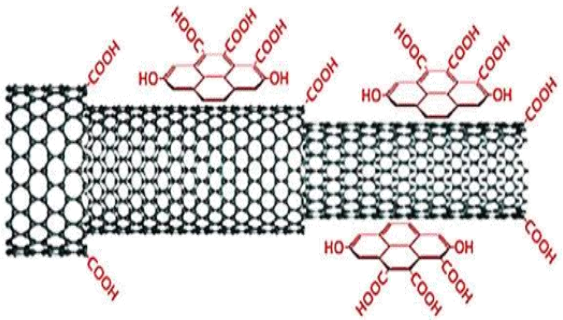
Acid volume/ mL	Degree of functionalization/ mass%	Arithmetic mean of CNTs length/ µm	Number of CNTs measured
176	5.5	2.9	230
88	5.7	3.6	136
44	5.9	4.5	140
20	4.6	4.6	137

Ox-MWCNT

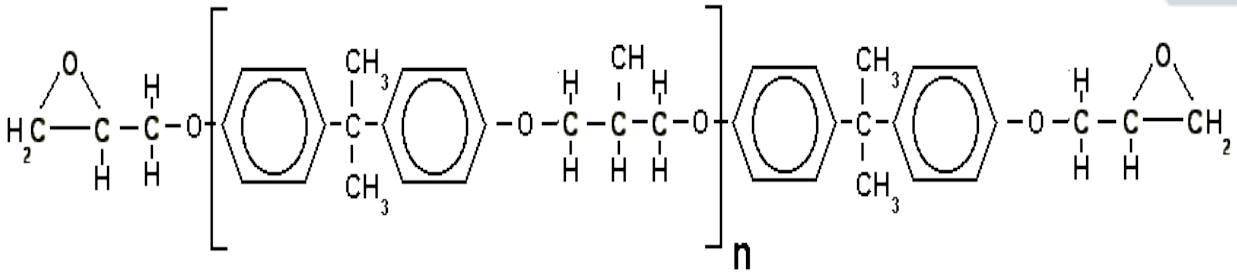
100 g/day

6%; 4,5 µm

Composite fabrication



0.1 mass%



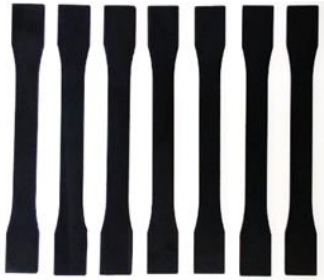
Epoxy resin: DGEBA

600 rpm
30 min

Different processing parameters

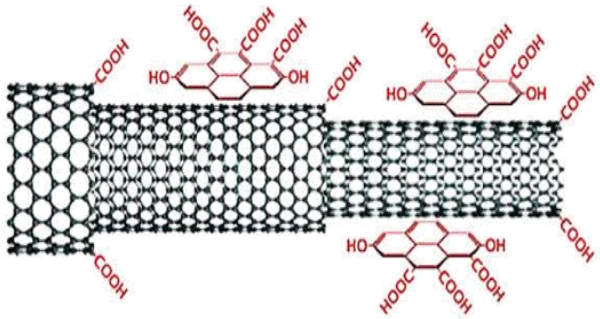
$H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$
Triethylenetetramine

phr: 15

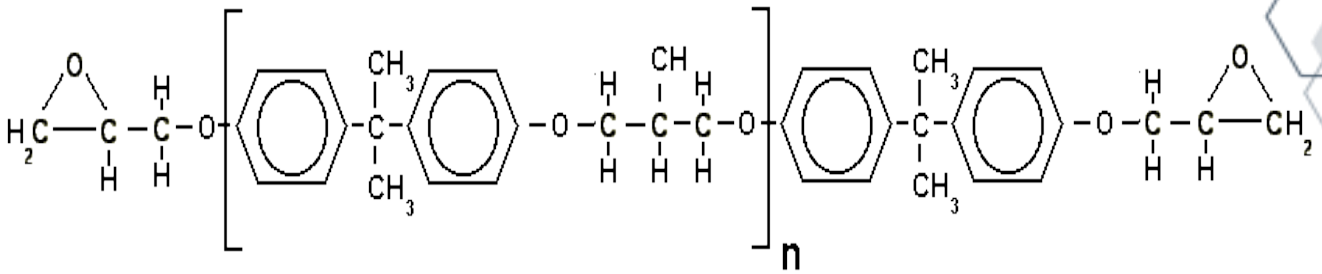


Composites characterization

Evaluation of length reduction after three-roll milling



0.5 mass%



Epoxy resin: DGEBA

600 rpm
30 min

100 or 300 rpm
5 passes of 10/5 µm

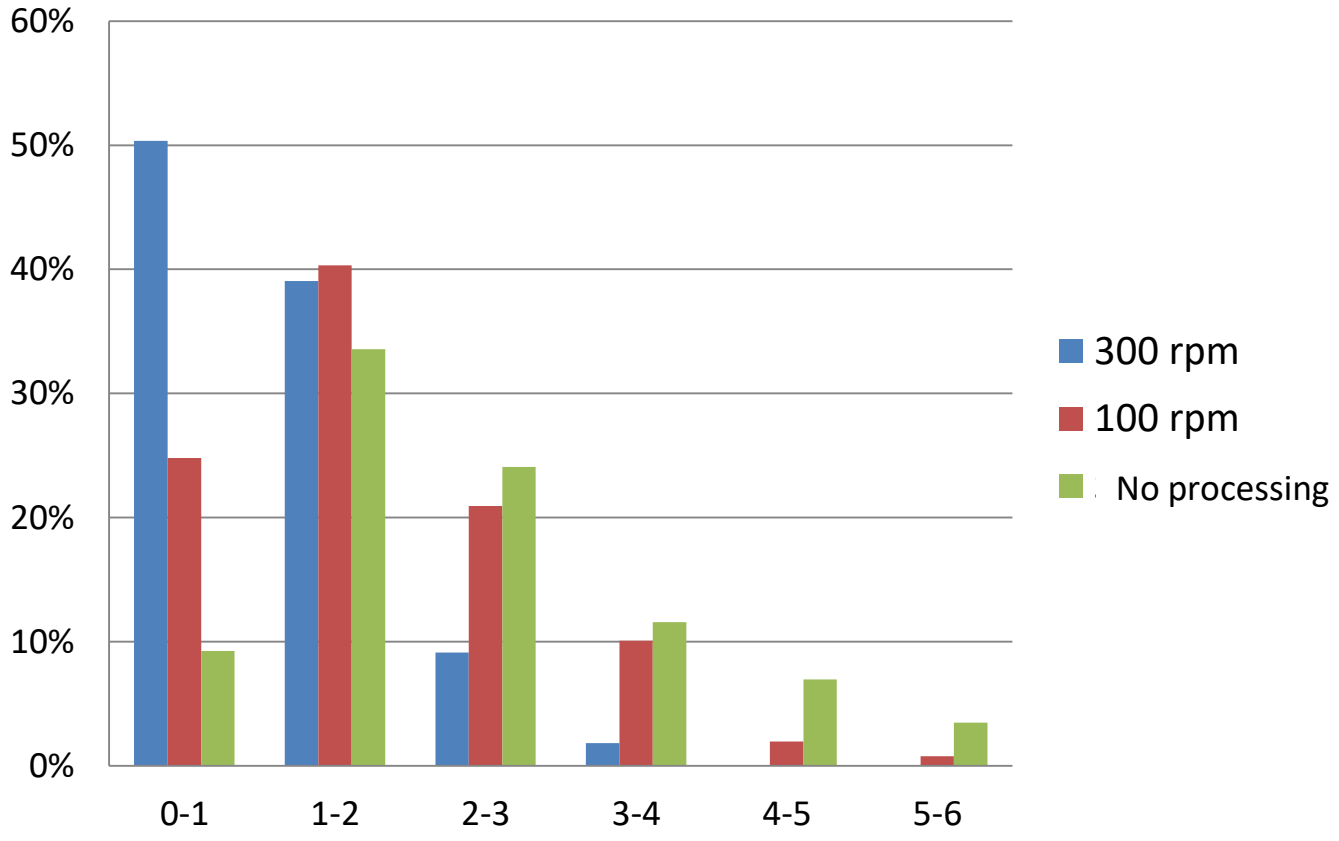
Filtration and
washing with acetone

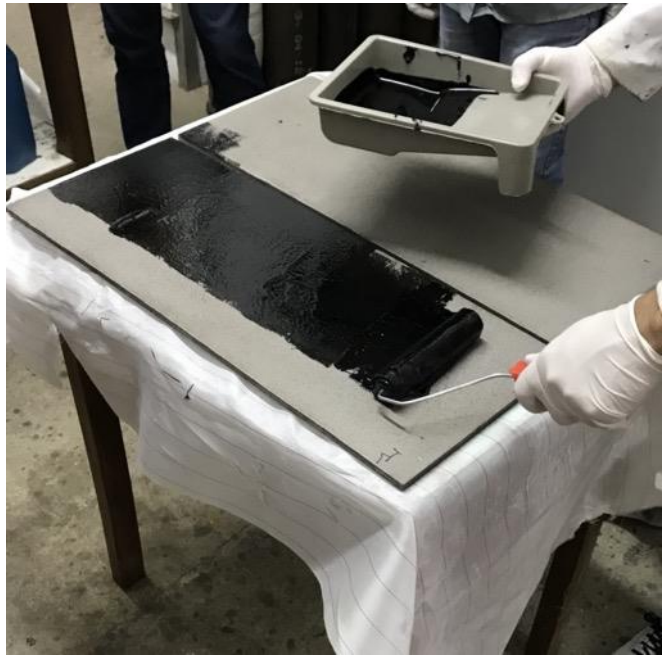
SEM characterization

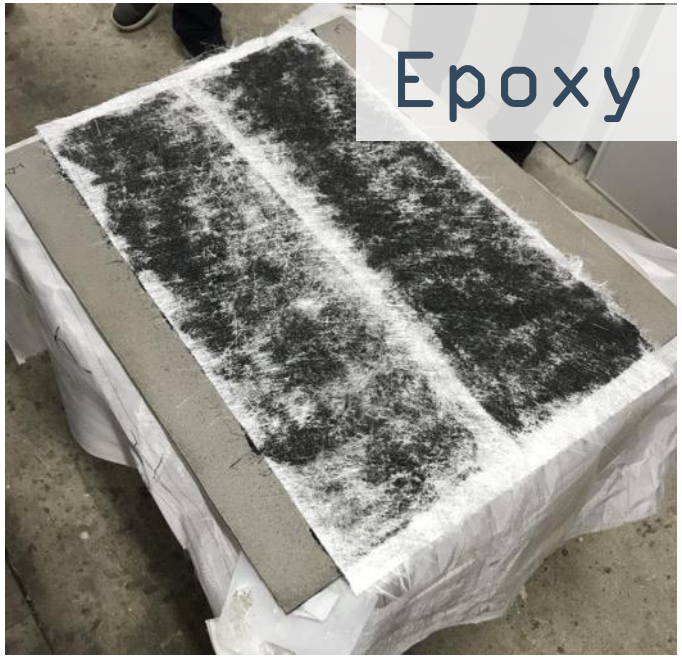
Evaluation of length reduction after three-roll

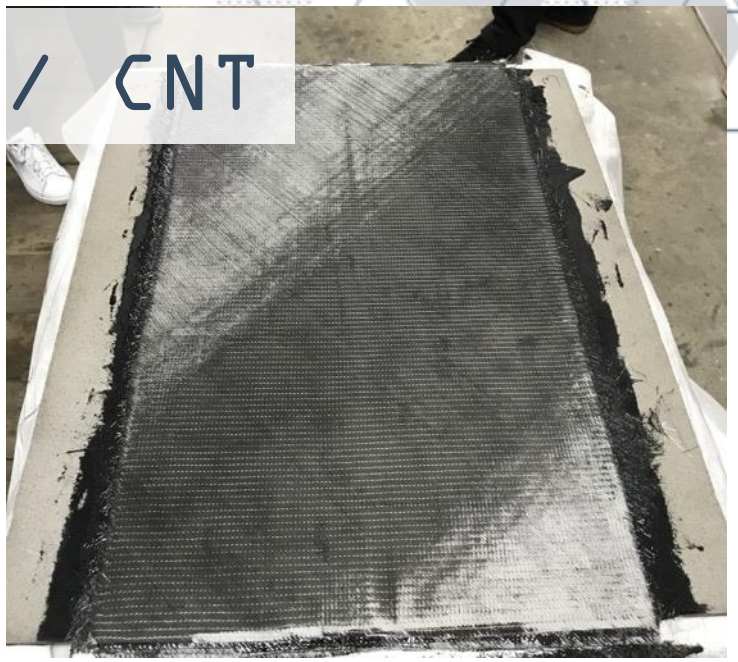
Length reduction after different processing parameters in the three-roll mill

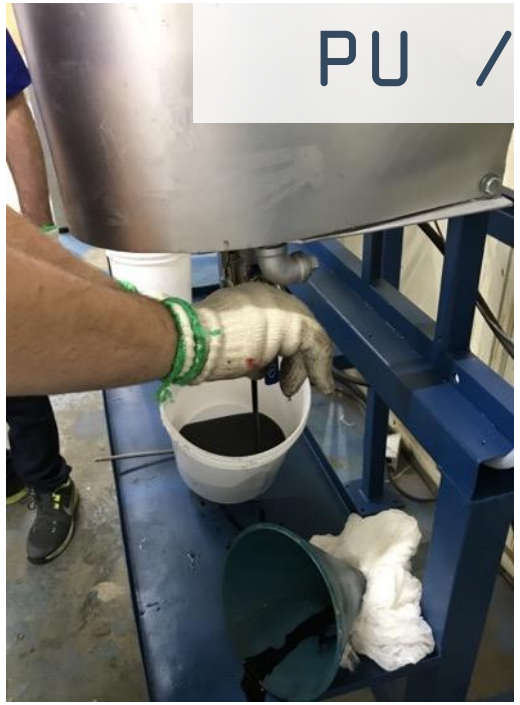
Roll speed/ rpm	Arithmetic mean of CNTs length/ µm	Number of CNTs measured
-	3.5	421
100	1.8	497
300	0.8	493






Epoxy / CNT




PU / CNT

Epoxy/CNT

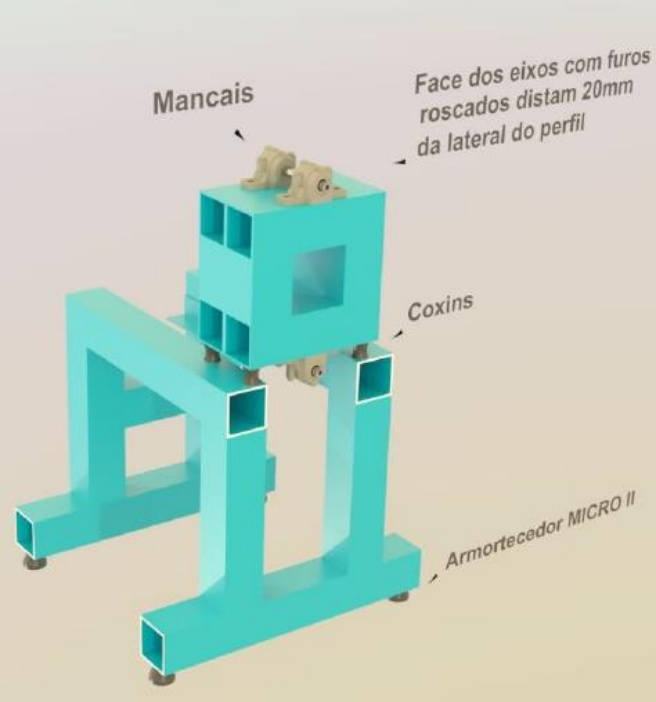
↖

~ 300% gain

On strain

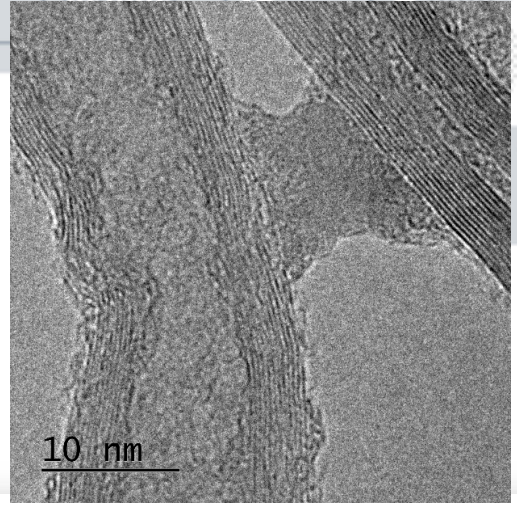
PU/CNT

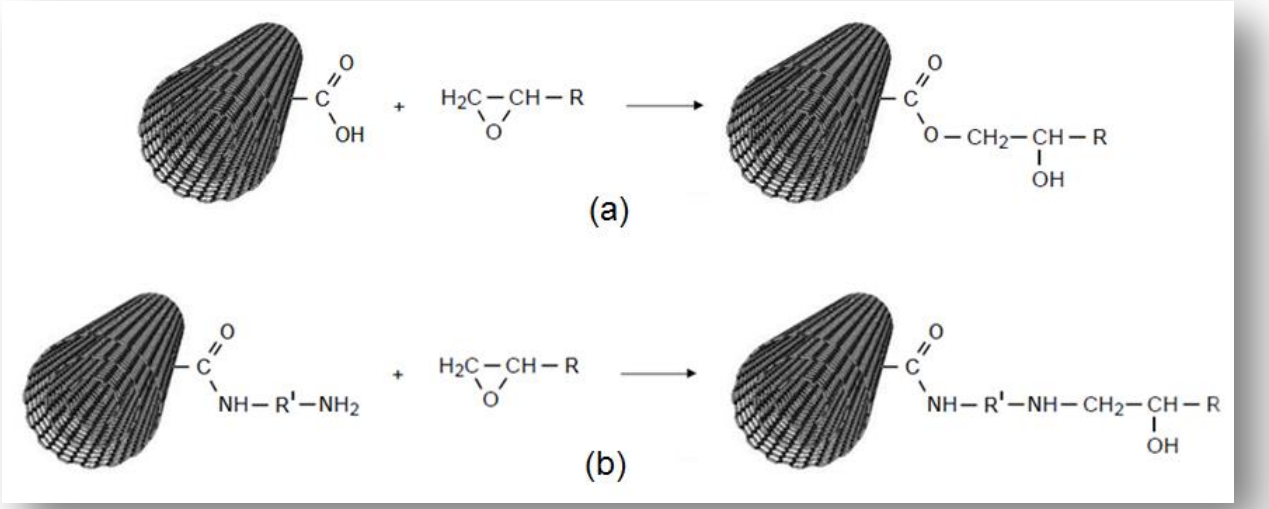
Design and construction of a Fatigue test machine

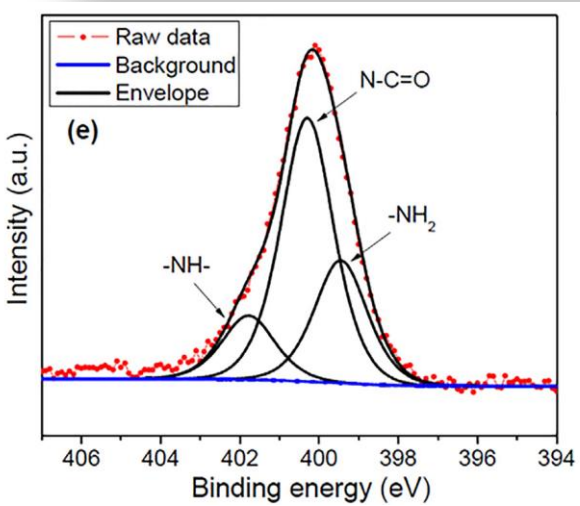


Characterization of covalent link between CNT and epoxy

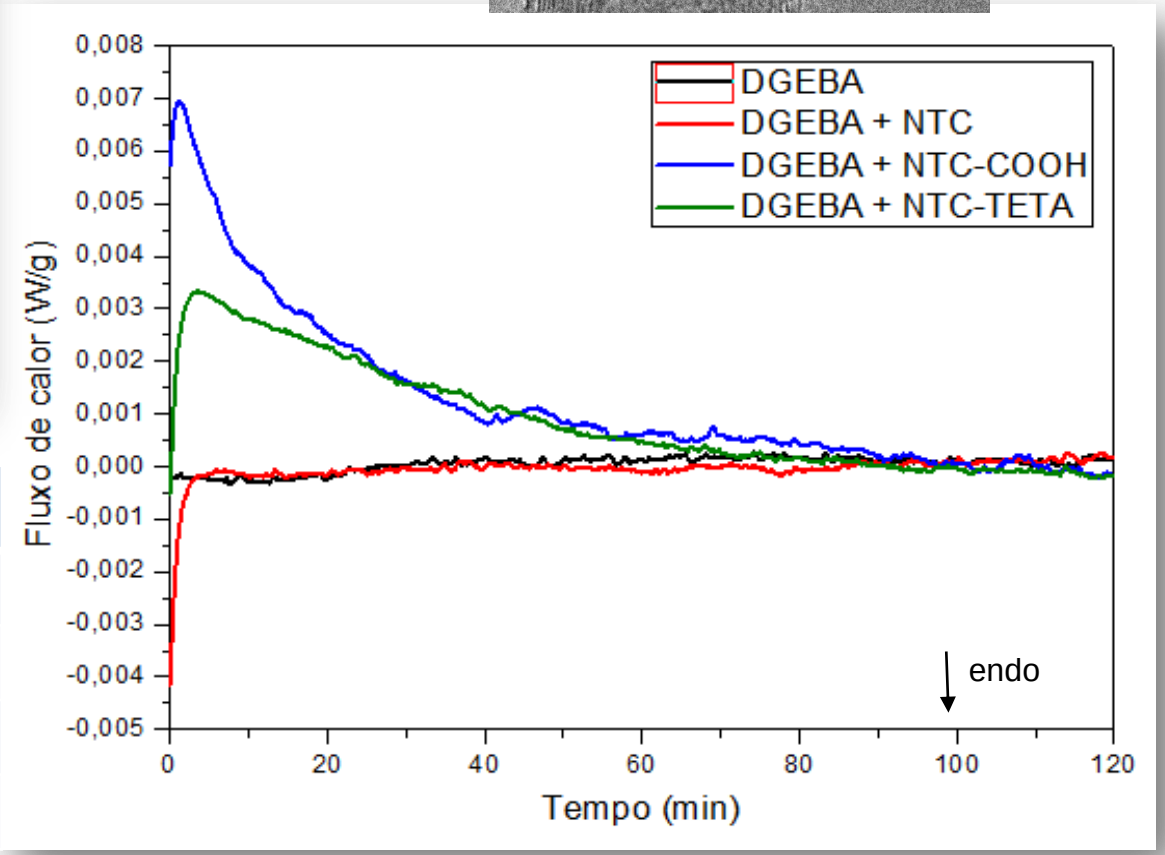
Neves et al, Applied Surface Science 436 (2018) 495–504



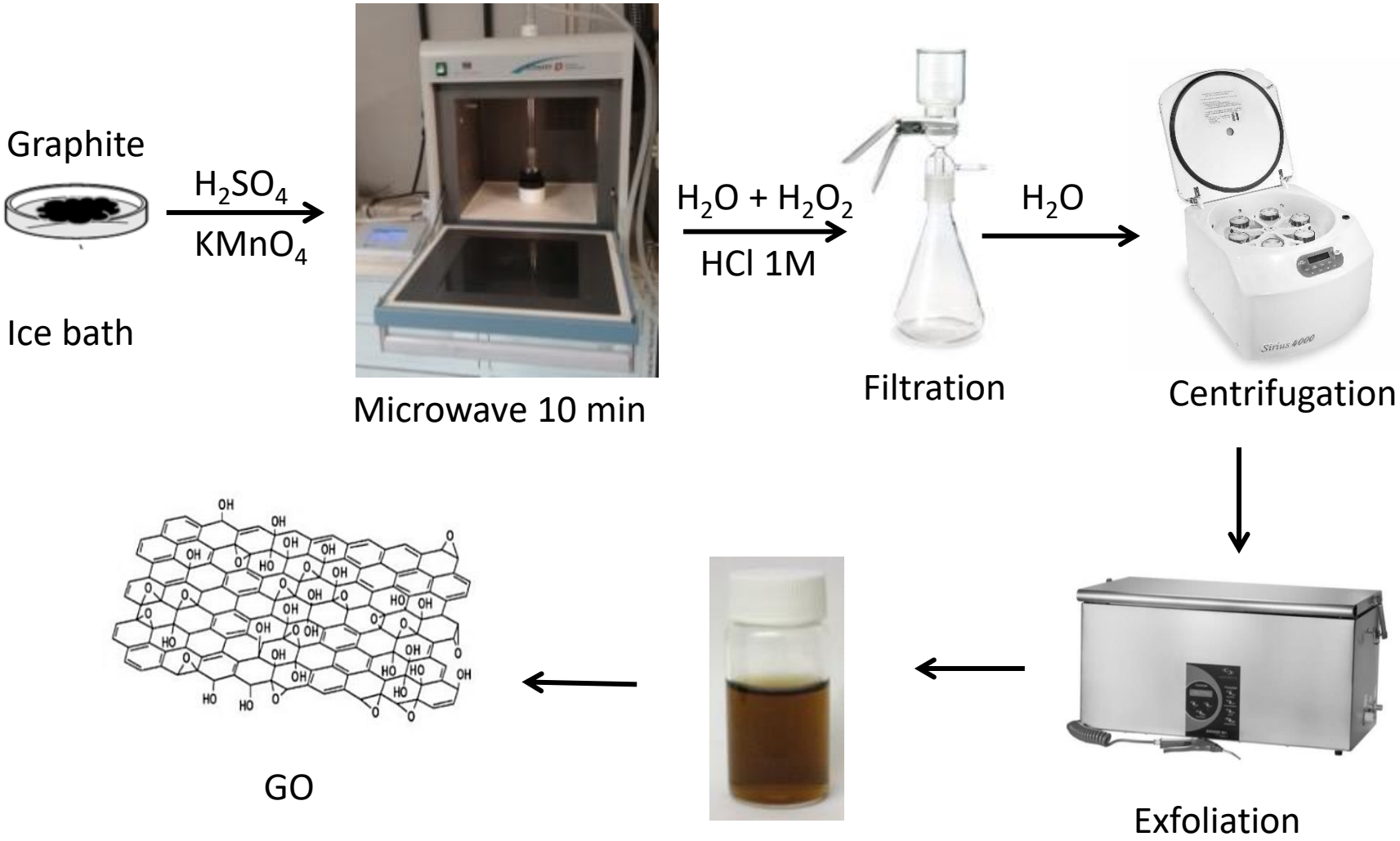




Sample	ΔH (J g^{-1})
DGEBA	-
DGEBA + CNT	-
DGEBA + CNT-COOH	8.7 ± 0.4
DGEBA + CNT-TETA	6.0 ± 0.6



Improved Hummers Method - Microwave Synthesis of GO



Viana M. M., et al., J. Braz. Chem. Soc., Vol. 26, No. 5, 978-984, 2015.

Graphene Oxide

Modified Hummers DQ-UFMG

15.03.2016

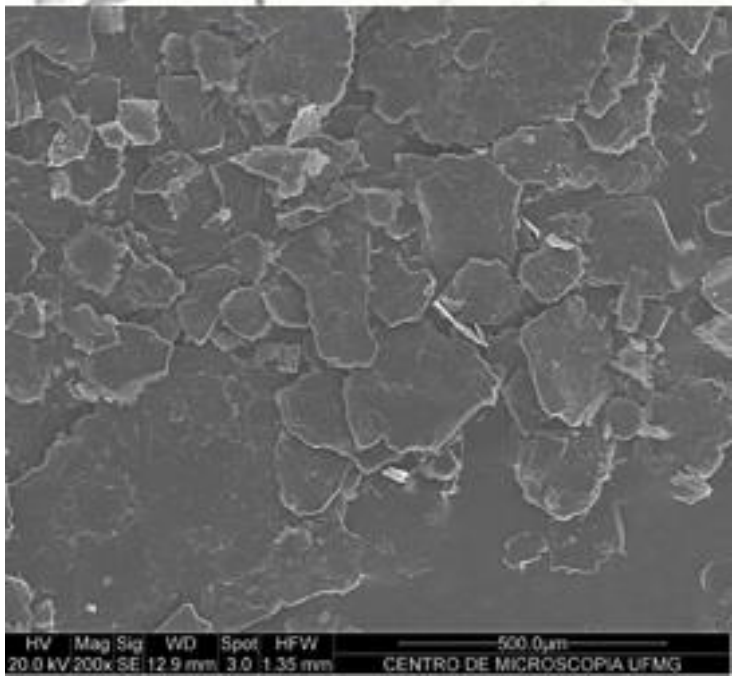
BR102016005632 2

"PROCESSO DE OBTENÇÃO DE ÓXIDO DE GRAFITE E DE ÓXIDO DE GRAFENO, PRODUTOS E USOS"

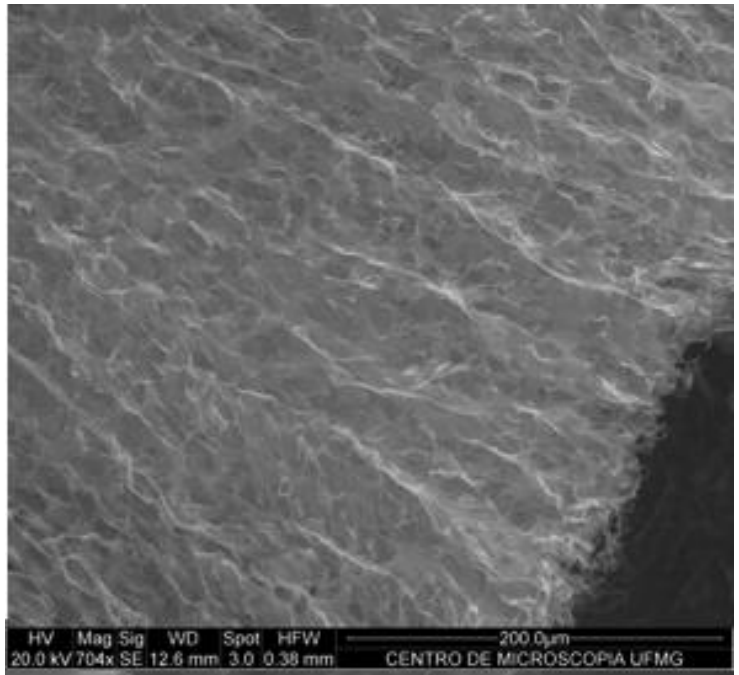
Vinicius Gomide de Castro / Juliana Cardoso Neves / Neuma das Mercês Pereira / Ana Luiza Silvestre Assis / Luciano Andrey Montoro / Glaura Goulart Silva

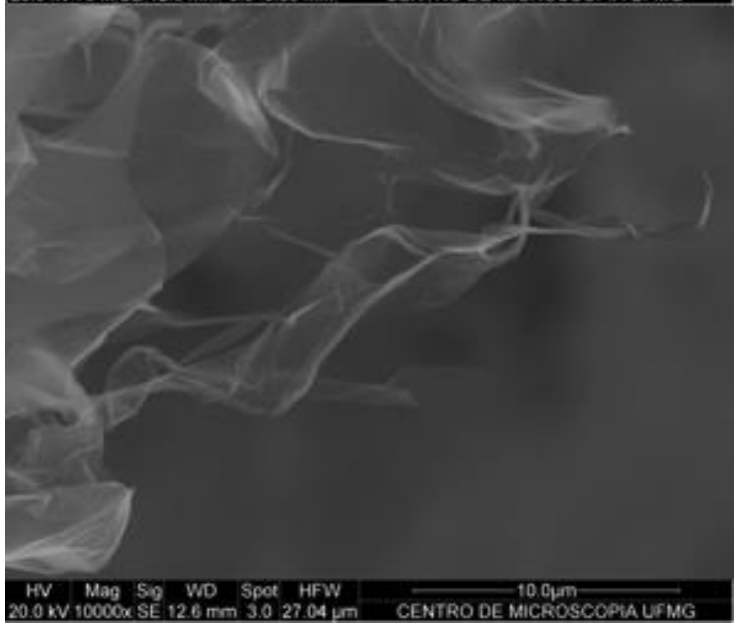
	Brodie	Staudenmaier	Hummers	Hummers Modified 1	Hummers Modified 2	Hummers Modified DQ-UFMG
Year	**1859**	**1898**	**1958**	**1999**	**2004**	**2016**
Oxidant agent	$KClO_3$, HNO_3	$KClO_3$, $NaClO_3$, HNO_3, H_2SO_4	$NaNO_3$, $KMnO_4$, H_2SO_4	$K_2S_2O_8$, P_2O_5, H_2SO_4, $KMnO_4$	$NaNO_3$, $KMnO_4$, H_2SO_4	$KMnO_4$, H_2SO_4, HCl - **MW**
Reaction time / hour	10 - 96	24 - 240	2 - 10	8	120	**0,3**
Interplanar spacement /nm	0,595	0,623	0,667	0,69	0,83	**1,1**

Graphite



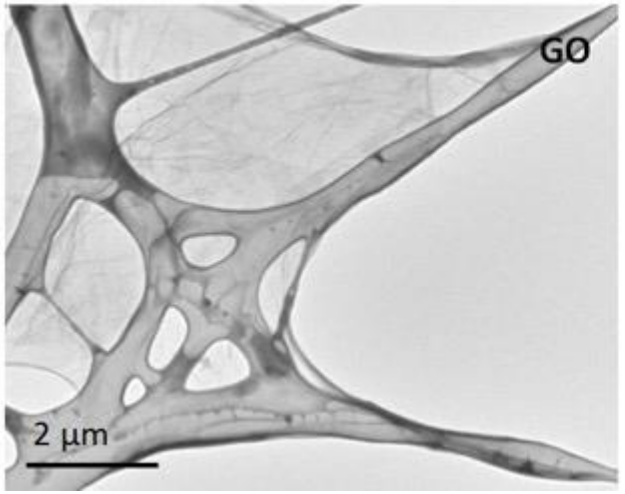
Graphene oxide

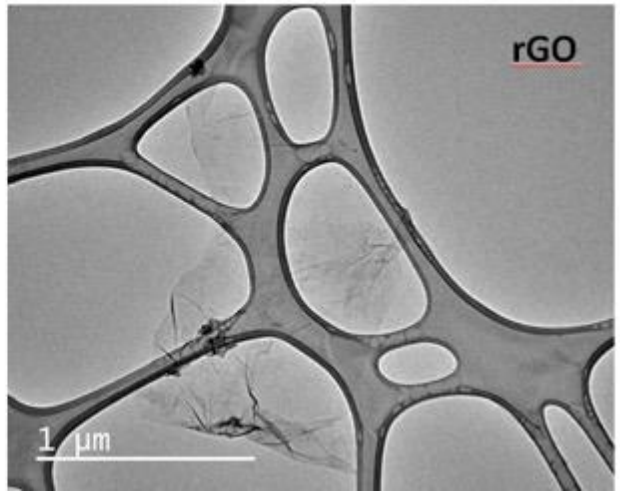




Characterization of GO and rGO

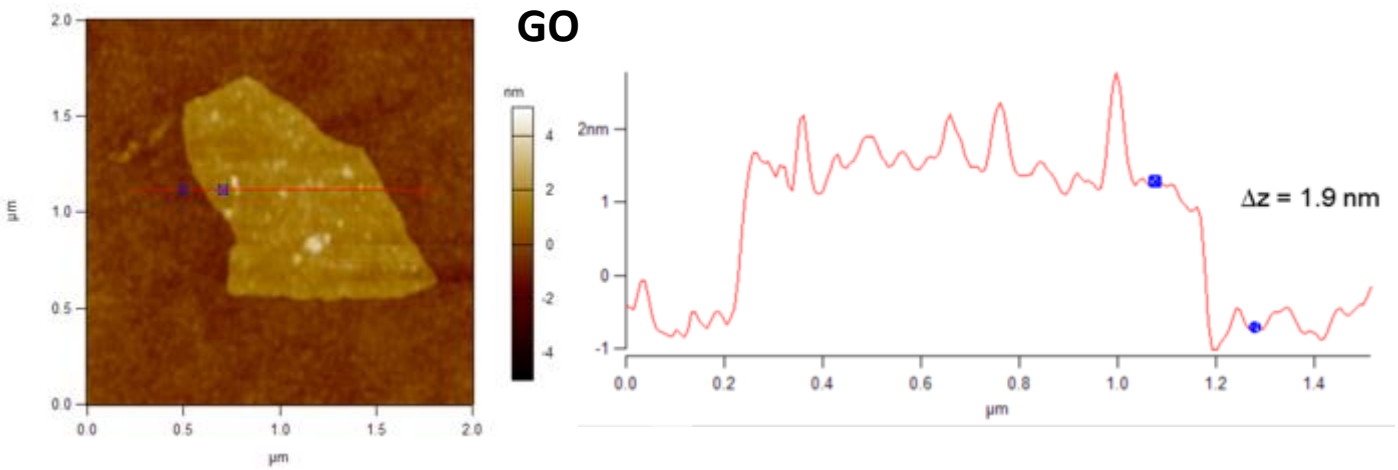
TEM



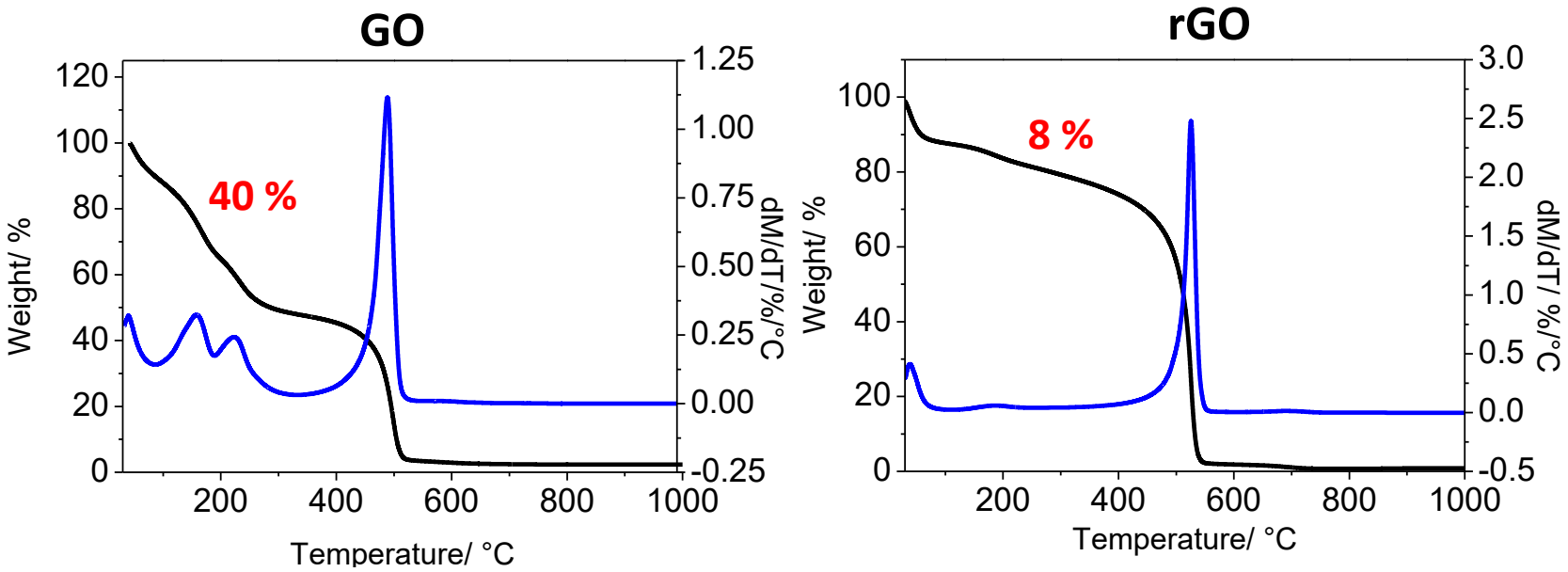


Border and center regions containing about 2 to 4 layers, and average width of the order of 2 to 5 µm.

AFM



TG

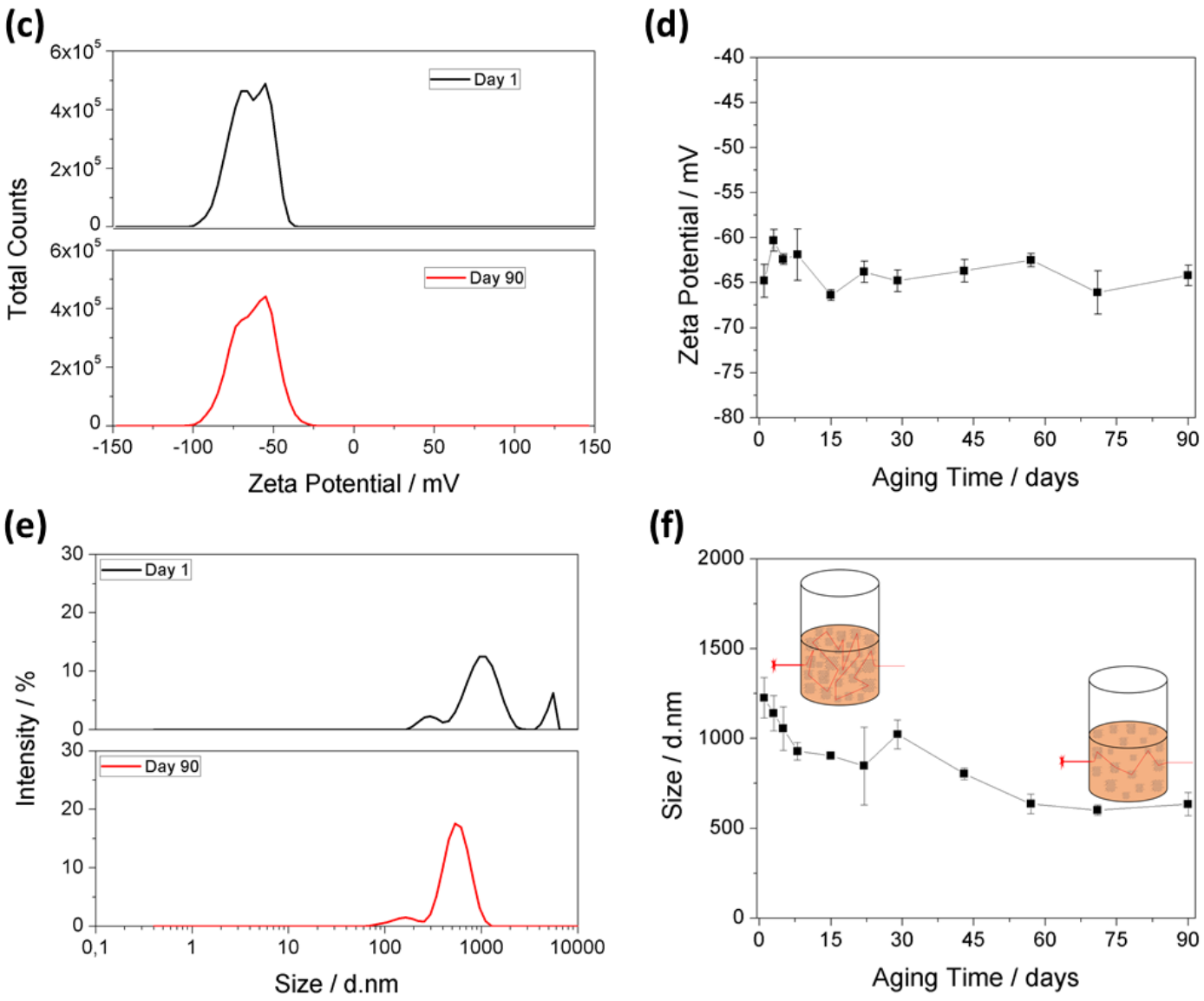


GO

10 g/day

>30%; 2-3 layers

DLS and zeta potential – GO stability



Nanocomposites Epoxy/GO

Polymer Testing 43 (2015) 182–192

Contents lists available at ScienceDirect

Polymer Testing

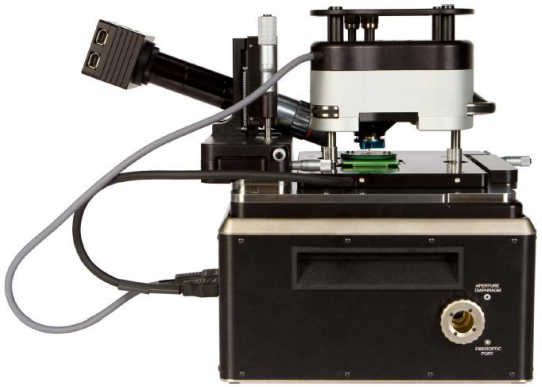
journal homepage: www.elsevier.com/locate/polytest

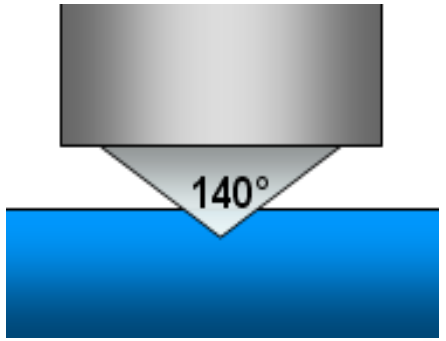
Material properties

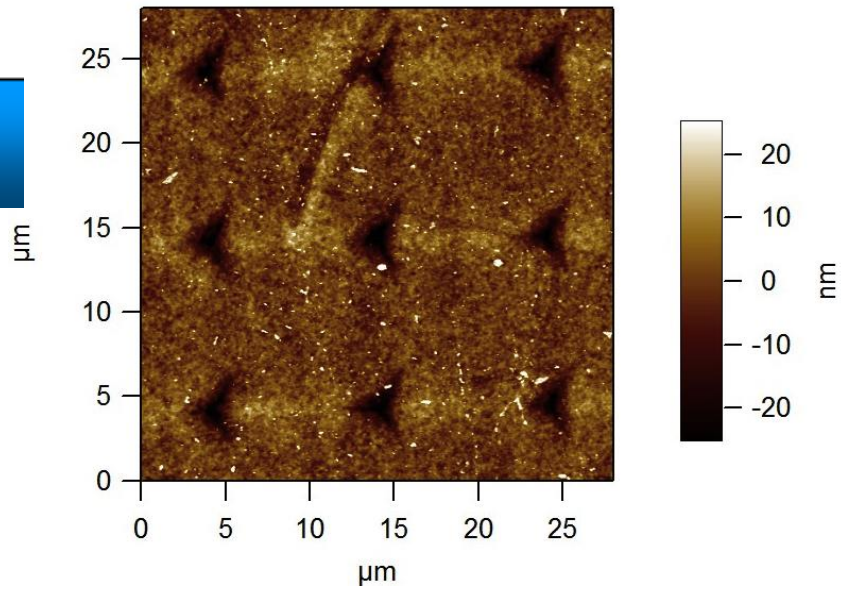
Multifunctional nanocomposites based on tetraethylenepentamine-modified graphene oxide/epoxy

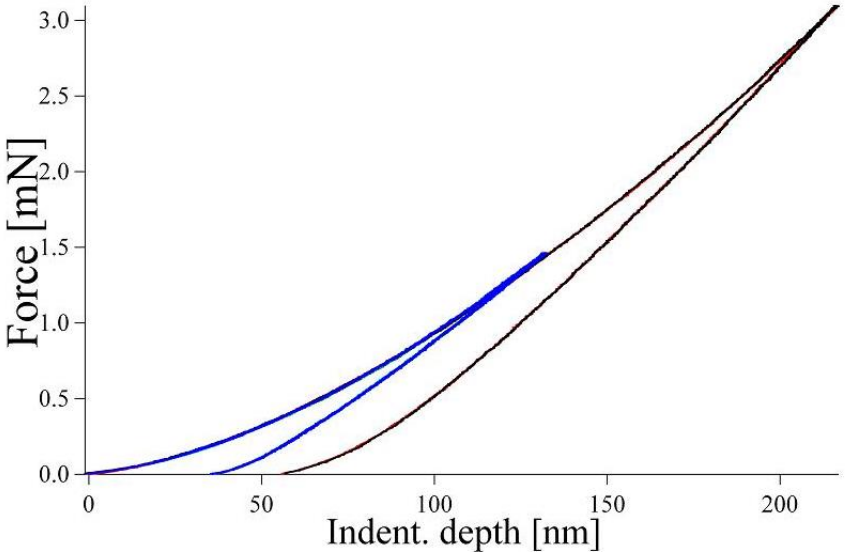
Hélio Ribeiro [a], Wellington Marcos da Silva [a], Juliana Cardoso Neves [a], Hállen Daniel Resende Calado [a], Roberto Paniago [b], Luciana Moreira Seara [c], Denise das Mercês Camarano [d], Glaura Goulart Silva [a, *]

Nanoindentation

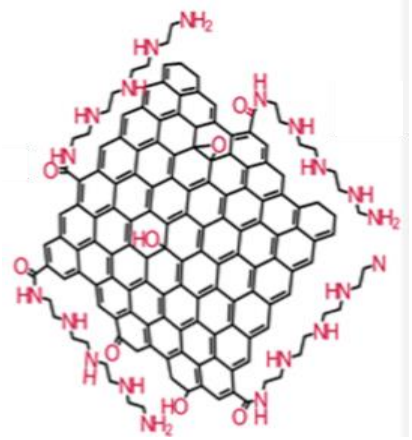


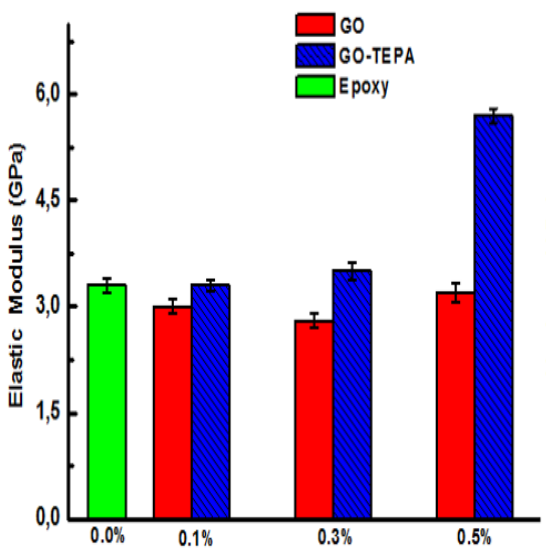


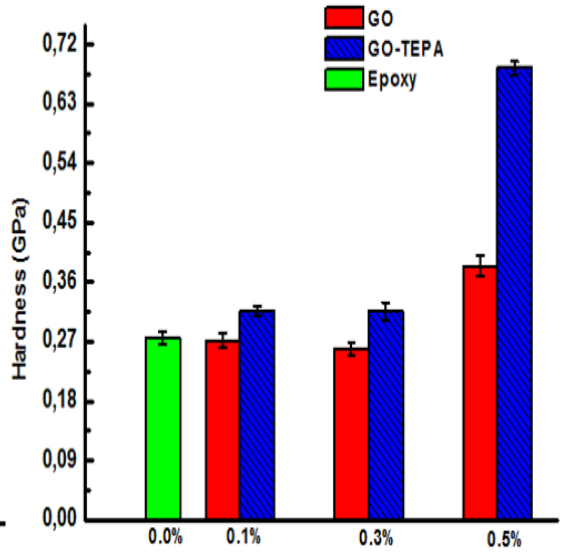


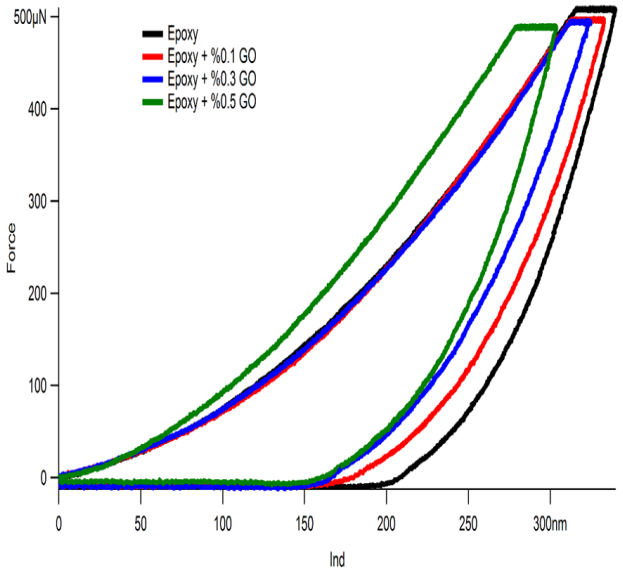


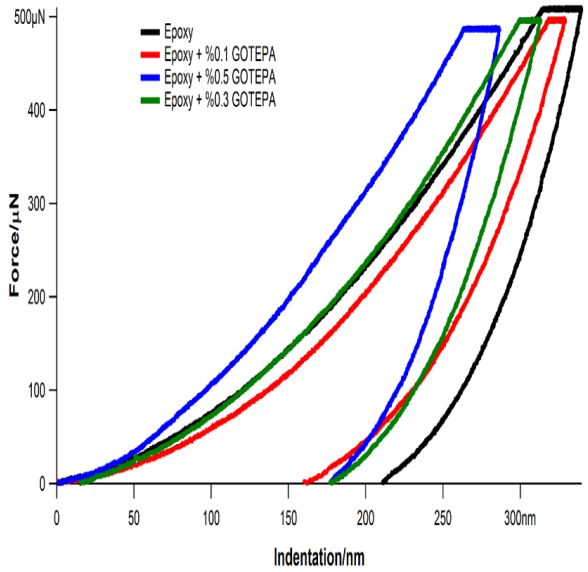
- Nanoindentation
- Epoxy/GO and GO-TEPA





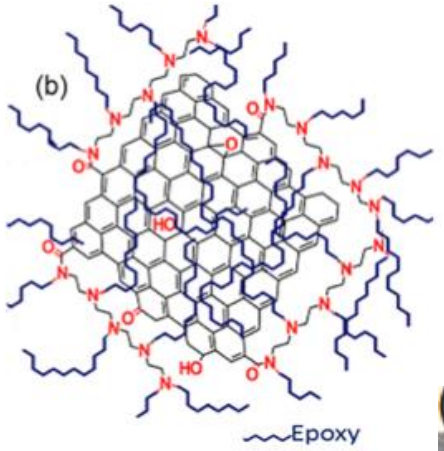


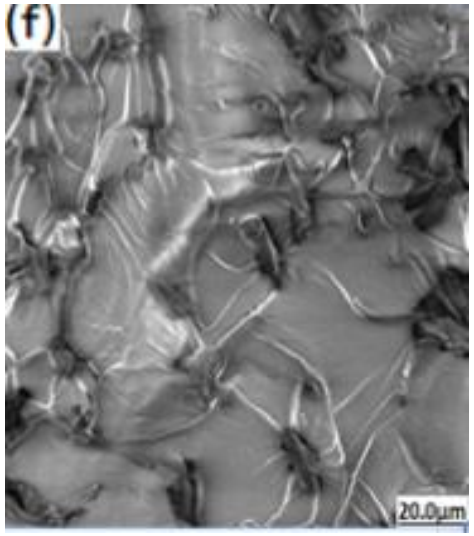


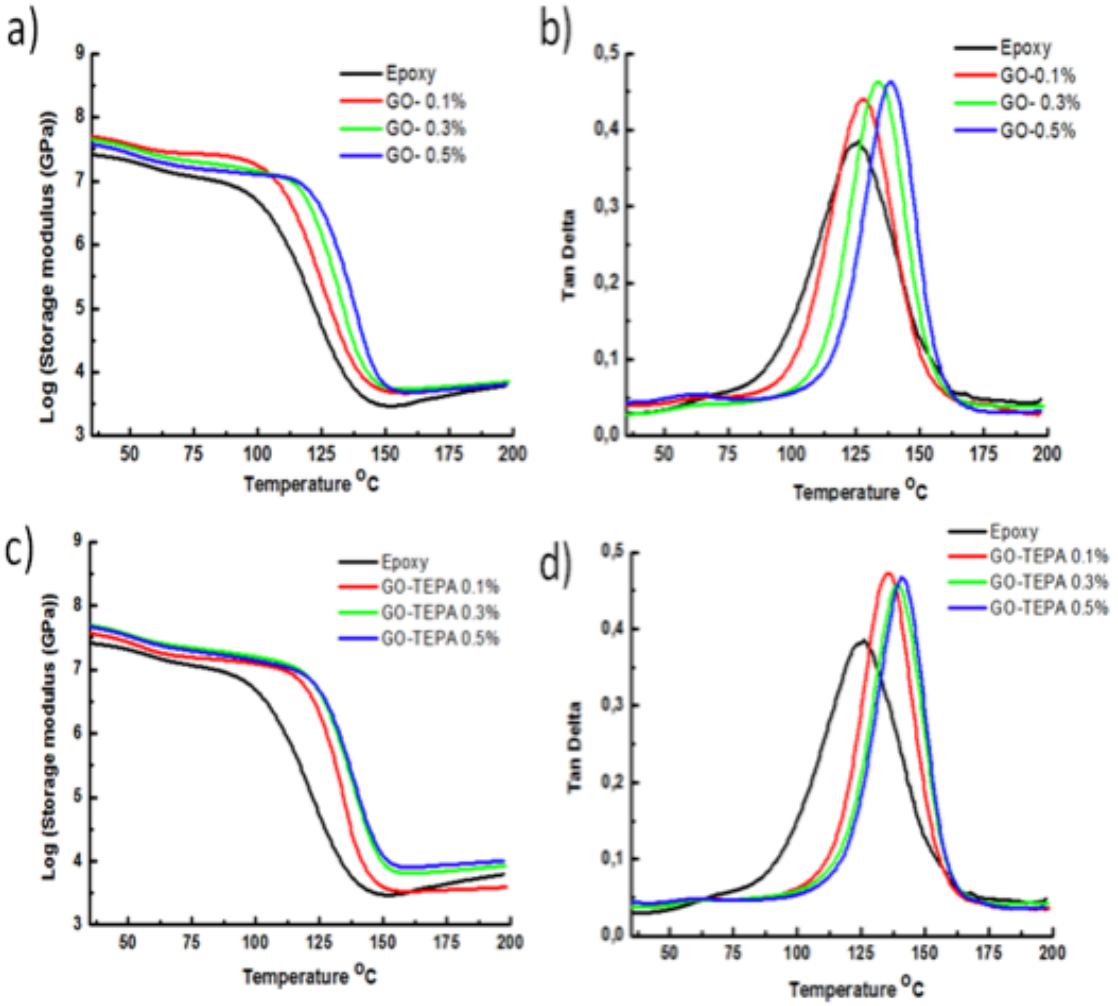


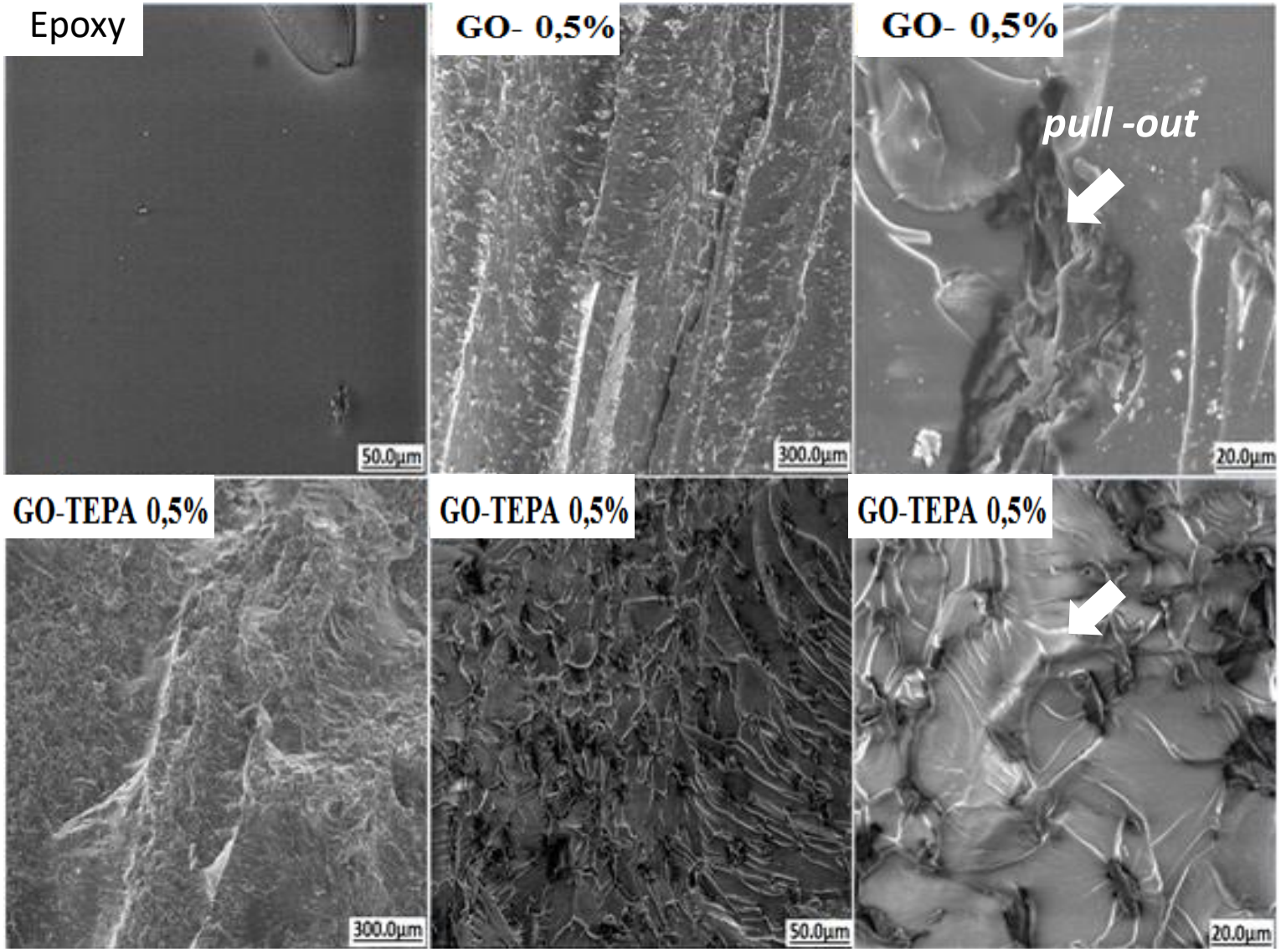
Increase of 72% in the elastic modulus and 143% in hardness for the composite containing 0.5 wt% of GO-TEPA

- DMA and SEM
- Epoxy/GO and GO-TEPA



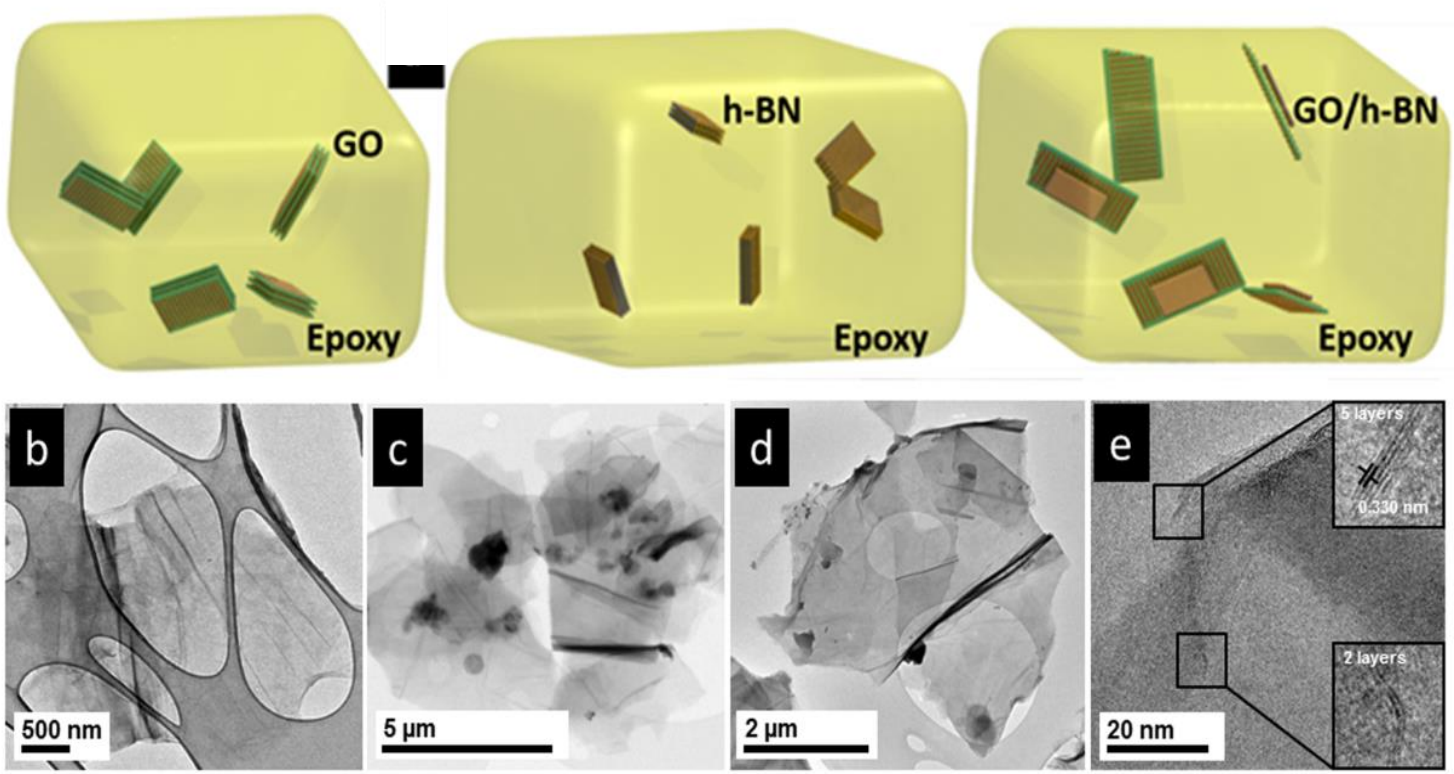


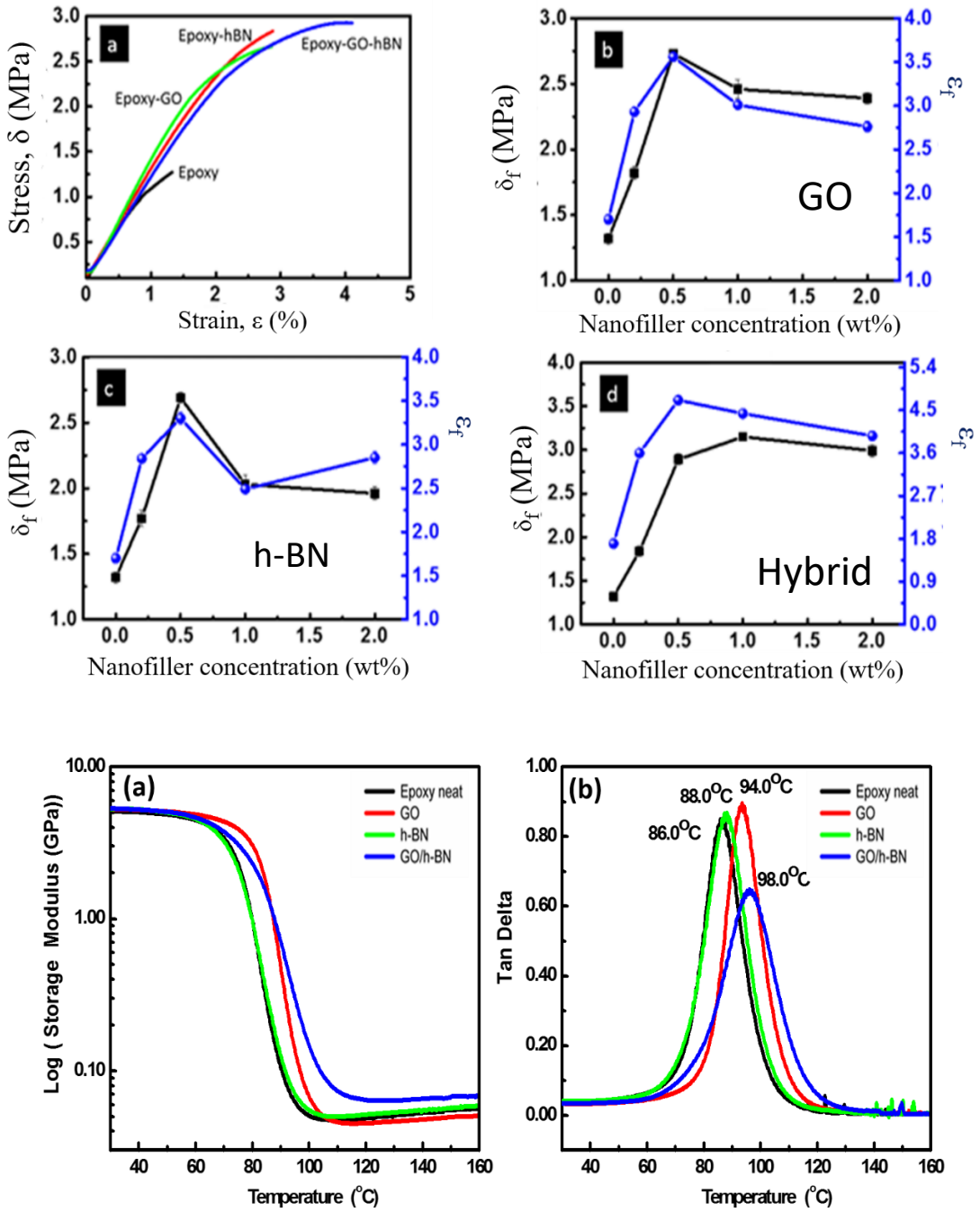



Epoxy
50.0µm
GO- 0,5%
300.0µm
GO- 0,5%
pull -out
20.0µm
GO-TEPA 0,5%
300.0µm
GO-TEPA 0,5%
50.0µm
GO-TEPA 0,5%
20.0µm

Hybrid 2D Nanostructures for Mechanical Reinforcement and Thermal Conductivity Enhancement in Polymer Composites

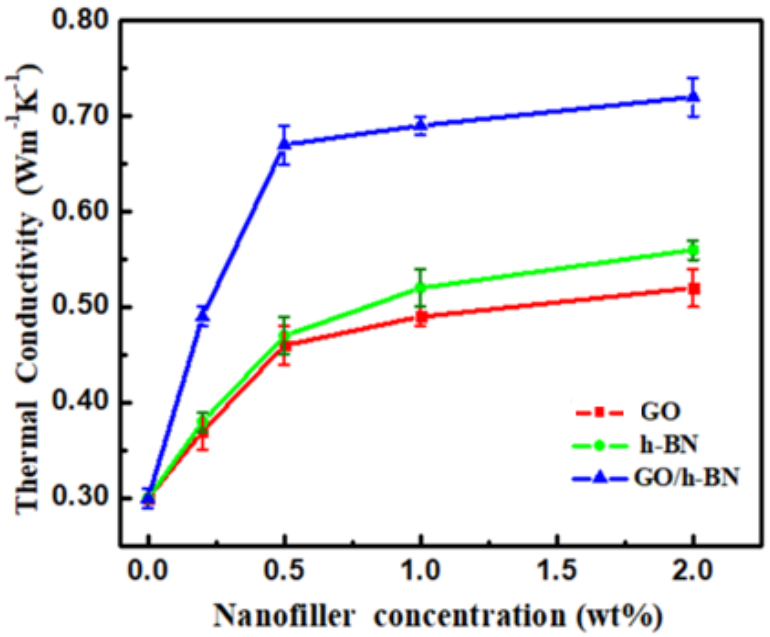
Ribeiro et al., Compos. Sci & Techn. 159 (2018) 103-

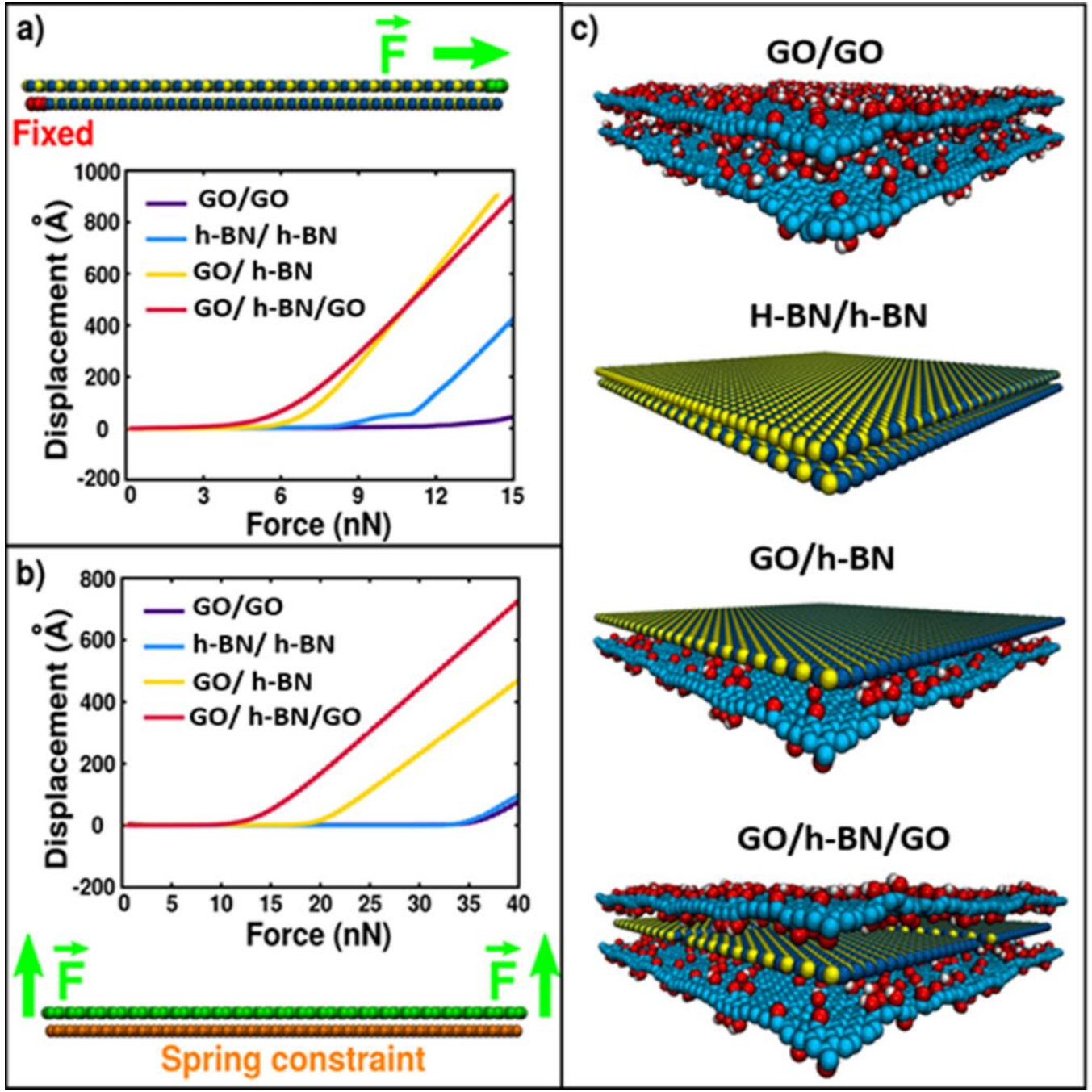




Results

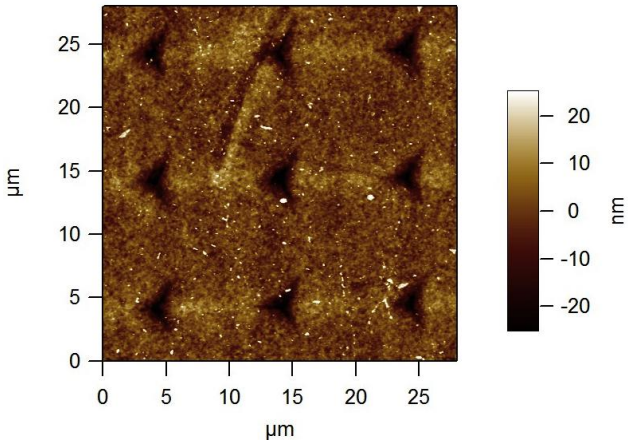
Increase of 142% on thermal conductivity with respect to the pure epoxy




a)
F
Fixed
Displacement (Å)
Force (nN)
GO/GO
h-BN/ h-BN
GO/ h-BN
GO/ h-BN/GO
b)
Displacement (Å)
Force (nN)
GO/GO
h-BN/ h-BN
GO/ h-BN
GO/ h-BN/GO
F
F
Spring constraint
c)
GO/GO
H-BN/h-BN
GO/h-BN
GO/h-BN/GO

Final comments

- CTNano
- Scale up
- Tailored CNM
- Epoxy nanocomposites



PETROBRAS

BNDES

InterCement

UFMG

bh.tec Parque Tecnológico de Belo Horizonte

CTNANO

centro de tecnologia em nanomateriais

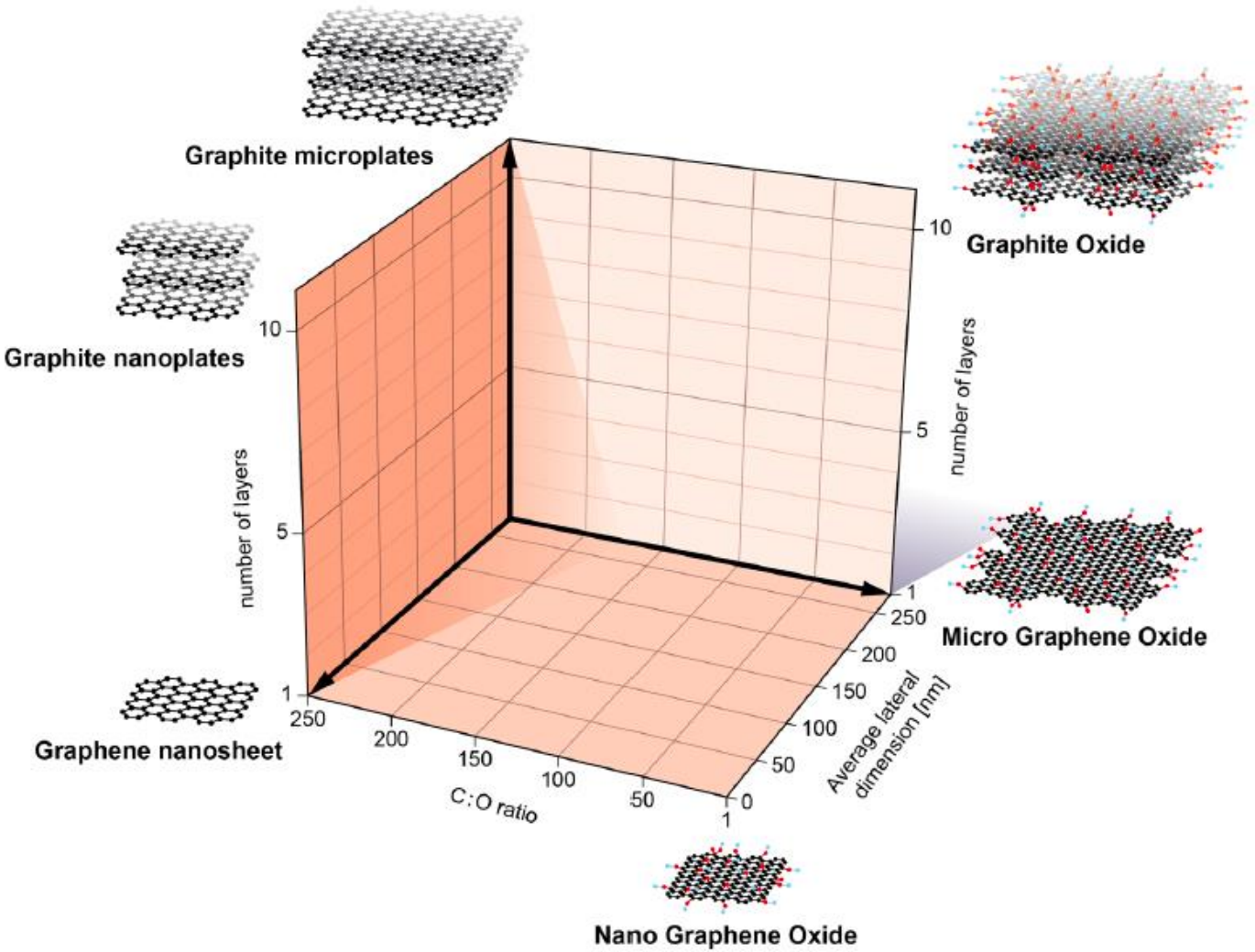
Finep 50 anos

FAPEMIG

centro de microscopia da UFMG

CNPq

INCT Instituto Nacional de Ciência e Tecnologia em Nanomateriais de Carbono



Classification Framework for Graphene-Based Materials.
Angew. Chem., Int. Ed. 2014, 53, 7714