Applicazione di CNT in matrici termoplastiche e termoindurenti

Domenico Acierno, Giovanni Filippone, Pietro Russo

Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale
Università di Napoli Federico II
Centro Regionale di Competenza Nuove Tecnologie per le Attività Produttive

Nanotubi di Carbonio. Sintesi, Applicazioni, Opportunità.
16 Maggio 2013.

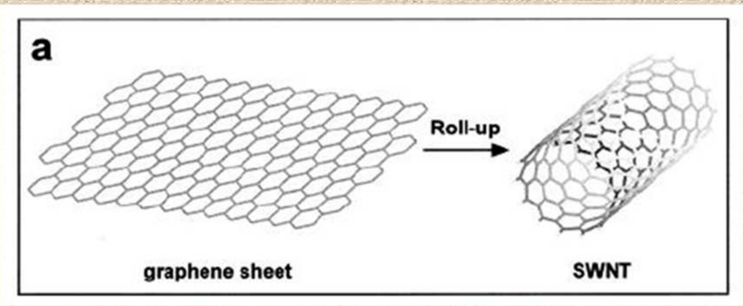
Discovery

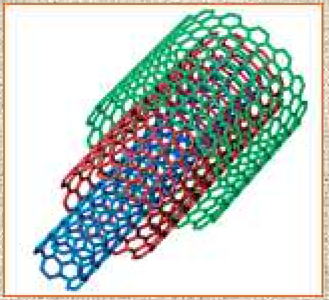
They were discovered in 1991 by the Japanese electron microscopist Sumio Iijima who was studying the material deposited on the cathode during the arc-evaporation synthesis of fullerenes. He found that the central core of the cathodic deposit contained a variety of closed graphitic structures including nanoparticles and nanotubes, of a type which had never previously been observed

Carbon nanotubes (CNTs): properties

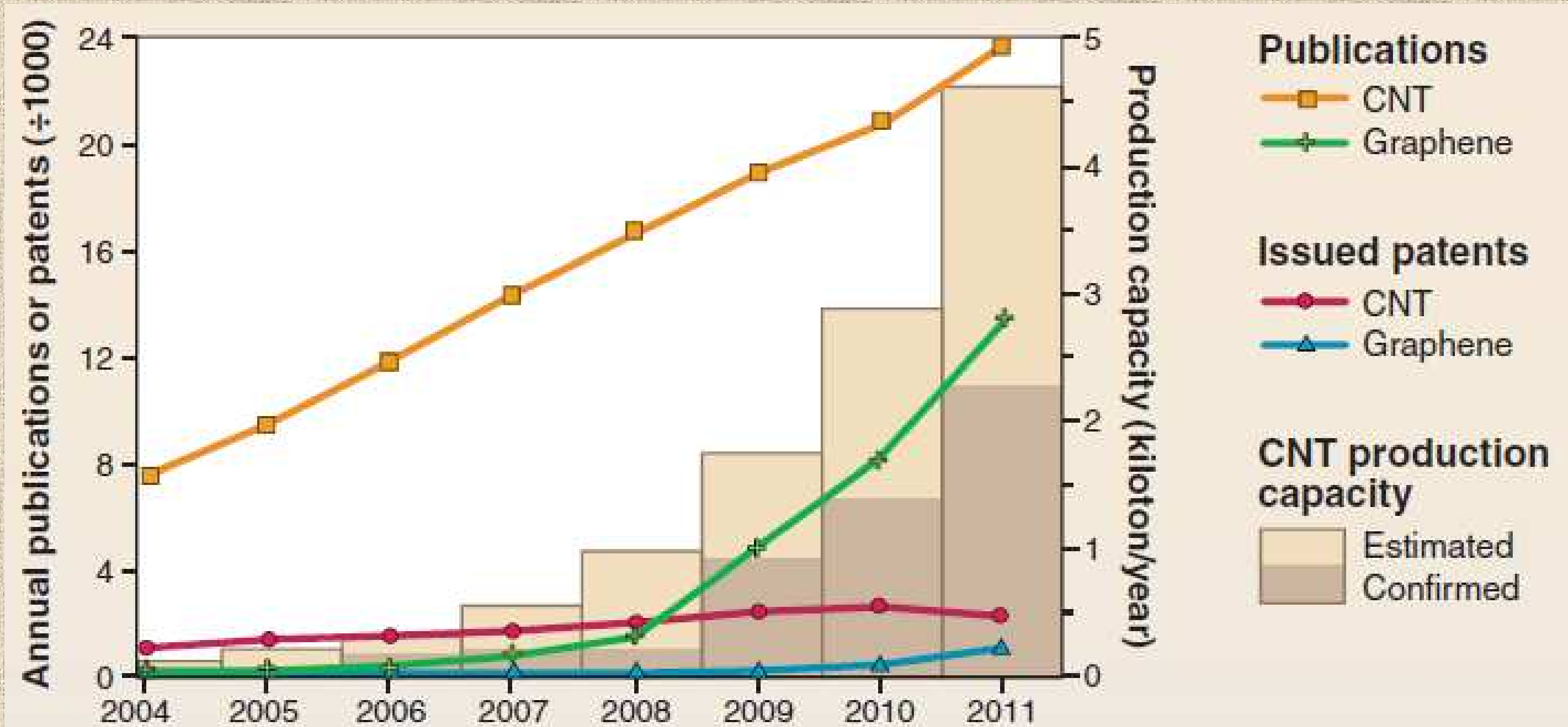
Carbon nanotubes exhibit outstanding properties such as:

- low density (within the range of 1.3-1.4 g/mL)
- excellent electronic properties
- high mechanical strength (*tensile strength approximately of 20 GPa*)
- high electrical and thermal conductivity, and
- thermal stability





MWNT



De Volder M.F.L., Tawfick S.H., Baughman R.H., Hart A.J. *Carbon Nanotubes: Present and Future Commercial Applications*. Science 339, 535-539 (Feb 2013)

Motivations

To build composites with superior properties, nanoscale reinforcements have natural advantages than their micrometer-sized counterparts because of their high specific surface.

However, a huge challenge still lies in the manufacturing of a high performance nanocomposite because of the agglomeration tendency of the nanometer-sized fillers and poor load transfer efficiency between the matrix and reinforcements.

A good example is carbon nanotube (CNT) reinforced composites: even in the cases where CNTs are optimally dispersed at high volume fraction, their moduli and strengths are at least 2 orders of magnitude lower than what was theoretically predicted by composite theory.

↓

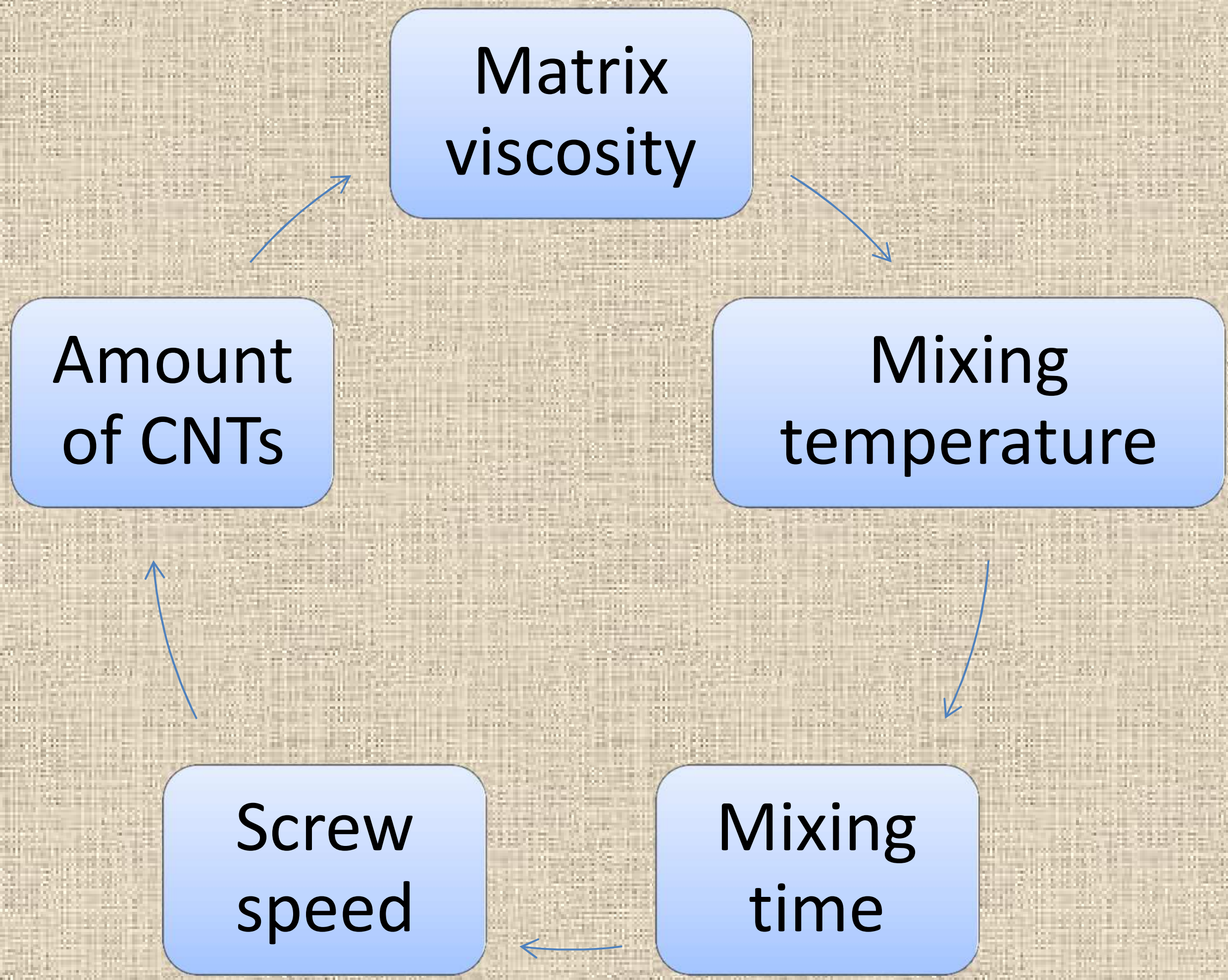
Increase of nanofiller content

(costs, physical properties, processability, and so on)

Chemical functionalization at the filler-matrix interface

(costs, not always easy, and so on)

INFLUENCE OF PROCESSING CONDITIONS



Approach 1

Confining nanofiller along specific directions or within specific regions of a polymer matrix

Maximazing benefits **Reducing filler amounts**

The material can be structured by controlling:
-location of fibers
-fibers draw ratio
-amount of filler

To achieve the maximun effect avoiding waste of nanofillers and without compromising economical aspects

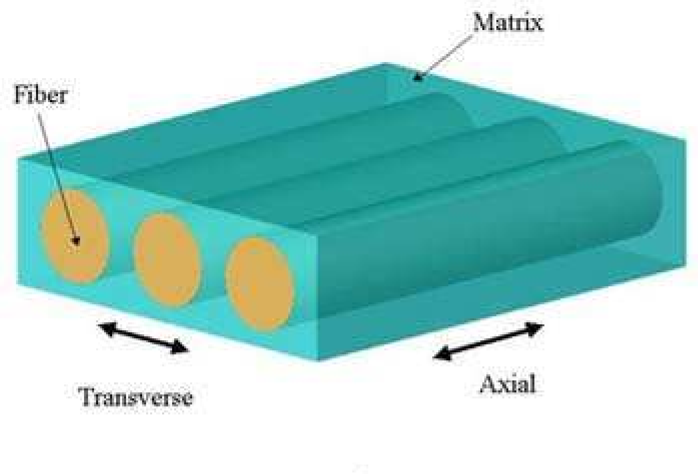
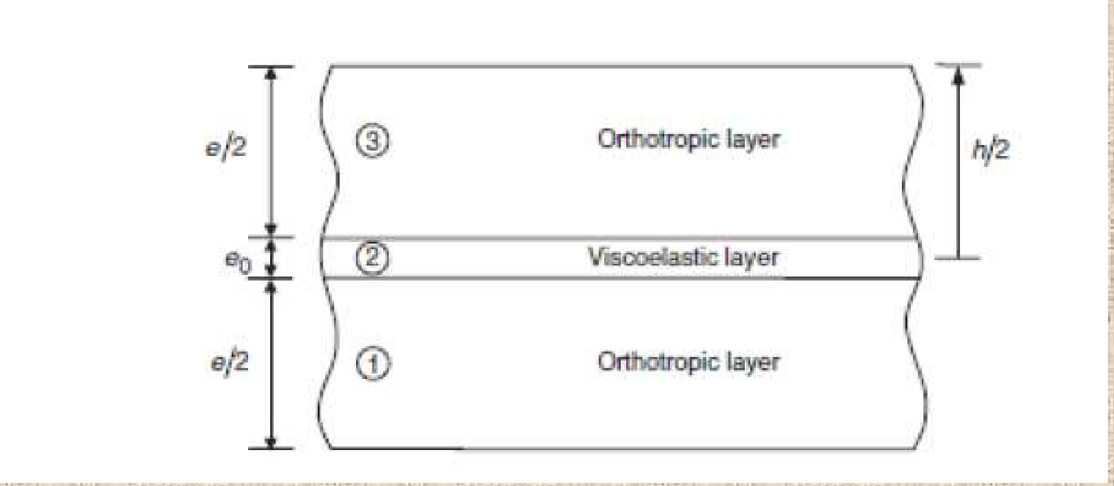


Figure 1

P. Russo, D. Acierno, S. Acierno *Thermoplastic PolyUrethane fibers filled with multi-walled carbon nanotubes: relationships among fiber draw ratio, filler content and performances of epoxy based items* Proceeding of the 15th European Conference on Composite Materials, June 24-28th, 2012 – Venice (I)

Approach 2

Composite films containing carbon nanotubes



Materials

Composite fibers

Poly (Butylen Terephthalate)

POCAN B 1505 MFI =20g/10min

Thermoplastic PolyUrethane

Film grade Elastollan 1185 A (Polyether Type) (ELASTOGRAN GmbH) (ρ=1.12 g/cm^3)

Polystyrene

STYRON™ 634 General Purpose Polystyrene Resin (ρ=1.05 g/cm^3; $MFR_{200℃/5.0\ Kg}$=3.5 g/10 min)

Multiwalled Carbon Nanotubes

(Shenzen Nanotechport Co. Ltd)

L= 5-15 µm, Surface area=40-300 m^2/g, purity>95%

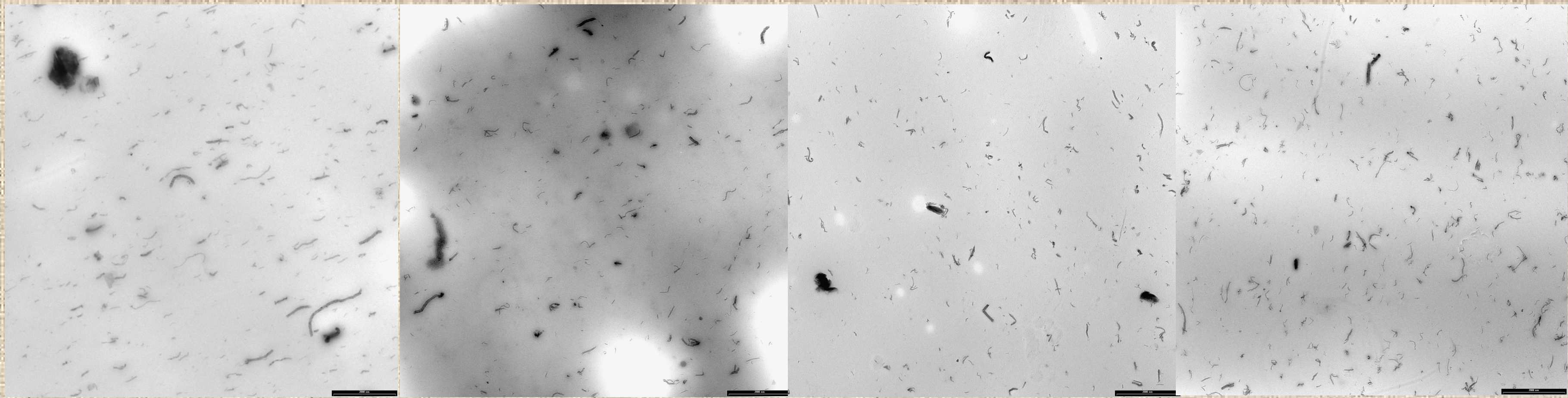
Four types: D= 10-30, 20-40, 40-60 and 60-100 nm (double wall)

Fiber production at DICMAPI

DSM *Xplore* spinning line

Samples of PBT composite fibres containing 0.5 wt% of MWCNTs:

60100 **4060** **2040** **1030**



AR increase

MWCNTs appear to be dispersed homogeneously within the polymer matrix although some aggregates are formed.
As expected (DR=30) no alignment of dispersed CNTs is evident.

D. Acierno, M. Lavorgna, F. Piscitelli, P. Russo, P. Spena *Polyester based nano composite fibers: a preliminary investigation on structure, morphology and mechanical properties* Advances in Polymer Technology **30**(1), 41-50 (2011)

Aspect ratio effect on tensile properties of PBT fibers

MWCNTs diameter (nms)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Neat PBT	2427	62	662
0.5 wt% MWNT			
10-30	2525	61	1300
20-40	2968	68	1186
40-60	2858	65	1075
60-100	2731	74	1040

D. Acierno, P. Russo, P. Spena *Poly(butylene terephthalate) and polystyrene composite fibers containing nanotubes: preliminary process-structure-property relationships* Proceeding ICCE 17 – International Conference on Composites or Nano Engineering – July 26th-August 1st, 2009, Honolulu, USA

Filler content effect on tensile properties of PBT fibers

MWCNTs content (wt%)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Neat PBT	2427	62	662
MWNT 1030			
0.2	2459	69	1127
0.5	2525	65	1300
1	2802	74	991
MWNT 60100			
0.2	2594	62	937
0.5	2731	74	1040
1	2637	67	866

P. Russo, D. Acierno, P. Spena *Polyester based nanocomposite fibres: morphological and mechanical investigations* 4th Edition of International Workshop on Thermoplastic Matrix Composites 27-31st July 2009, Edimburgh UK

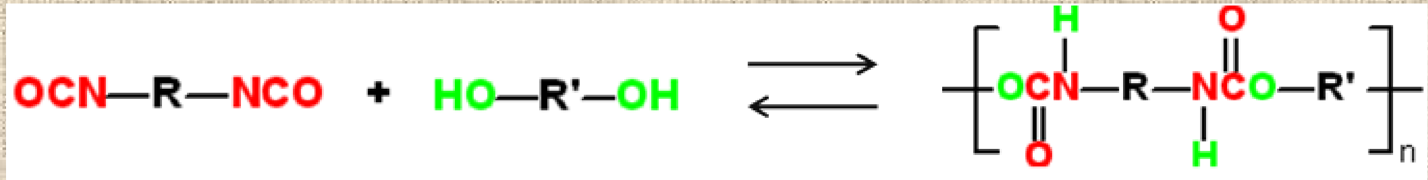
Aspect ratio effect on tensile properties of PS fibers

MWNTs diameter (nm)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Neat PS	3827	98	5
0.5 wt% MWNT			
10-30	4534	101	5
20-40	4559	83	5
40-60	4678	95	4
60-100	4532	101	4

Filler content effect on tensile properties of PS fibers

MWNTs content (wt%)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Neat PS	3827	98	5
MWNT 1030			
0.2	3874	121	4
0.5	4534	101	5
1	4111	108	5
MWNT 60100			
0.2	4245	128	4
0.5	4532	101	4
1	4230	131	4

Thermoplastic PolyUrethanes



Linear segment block copolymers

soft segments

hard segments

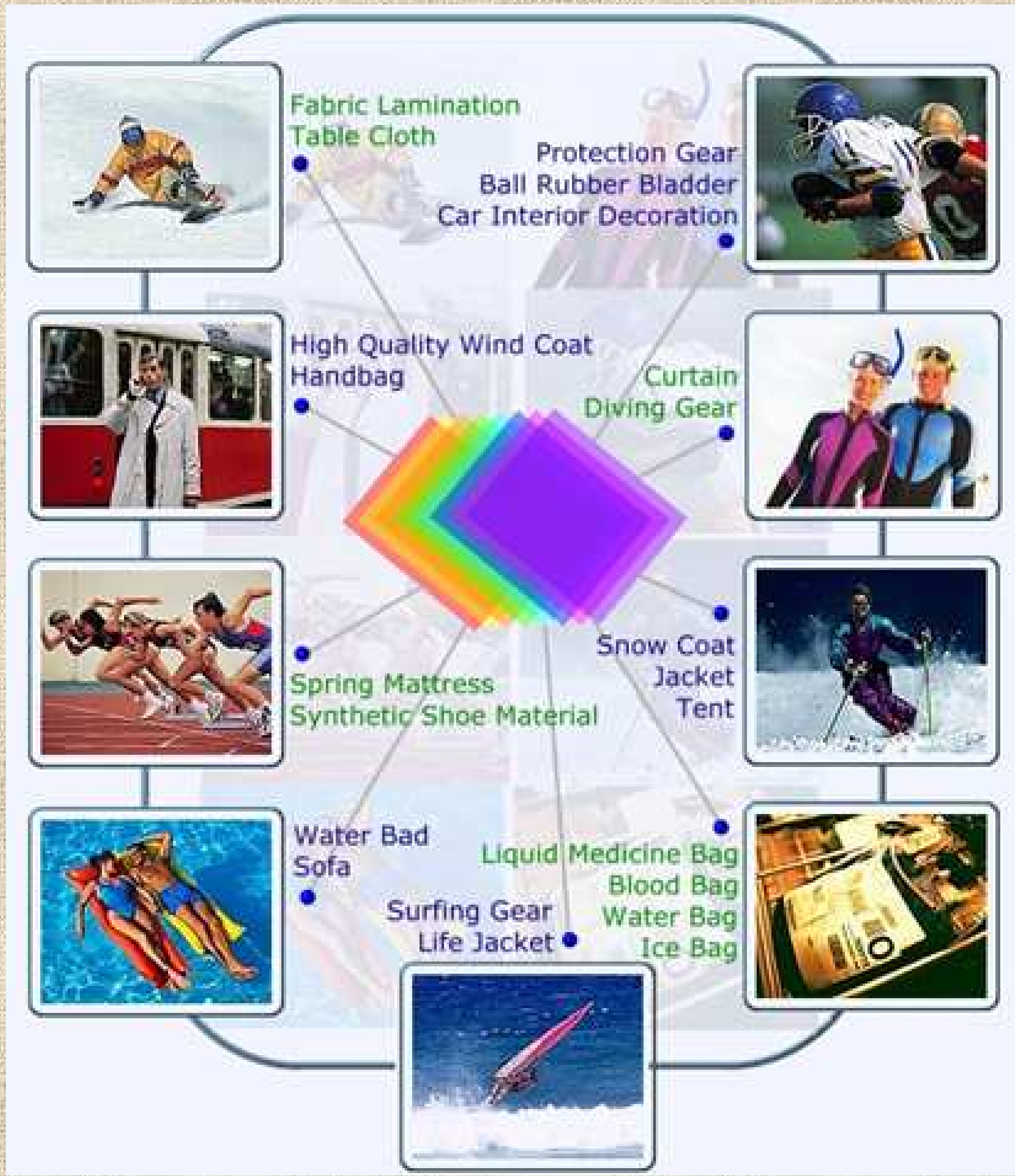
Segments formed by long and flexible randomly arranged polyether or polyester chains

Segments consisting of short chains based on diisocyanate and acting as physical crosslinks as well as reinforcing filler

TPUs properties

- Wide range of service temperatures
- Wide range of harness options
- Excellent tear resistance
- Excellent compression strength
- Excellent resistance to non polar solvents
- Excellent abrasion resistance
- High tensile strength

TPUs applications



Thermoplastic PolyUrethane

Elastollan 1185 A (ELASTOGRAN GmbH)

Property	Unit	Value	Normative
Hardness	Shore A	**85**	DIN 53505
Density	g/cm³	**1.21**	DIN EN ISO 1183-1-A
Stress Maximum	MPa	**50**	DIN 53504-S2
Strain at break	%	**600**	DIN 53504-S2
Melting Temperature T_m	°C	**150**	—
Processing Temperature	°C	**175 ÷ 205**	—

Multiwalled Carbon Nanotubes

(Shenzen Nanotechport Co. Ltd)

Length 5-15 µm

External diameter (nm): 60-100

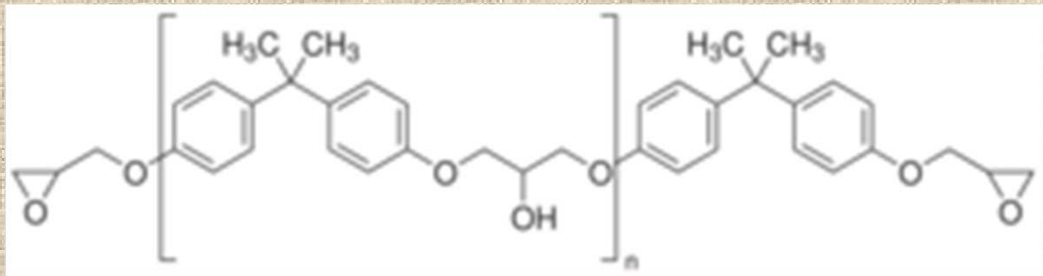
Specific Surface Area (m^2/g): 55-65

Experimental: Preparation of epoxy coupons

Epoxy resin constituents:

The prepolymer:

Poly (Bisphenol-A-co-epichlorohydrin), glycidyl end-capped $\rho = 1.169$ g cm^{-3}.
(Sigma Aldrich)

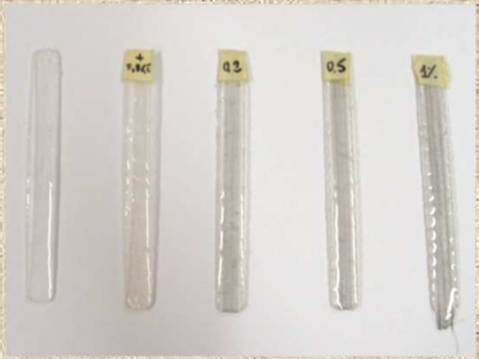


The hardener:

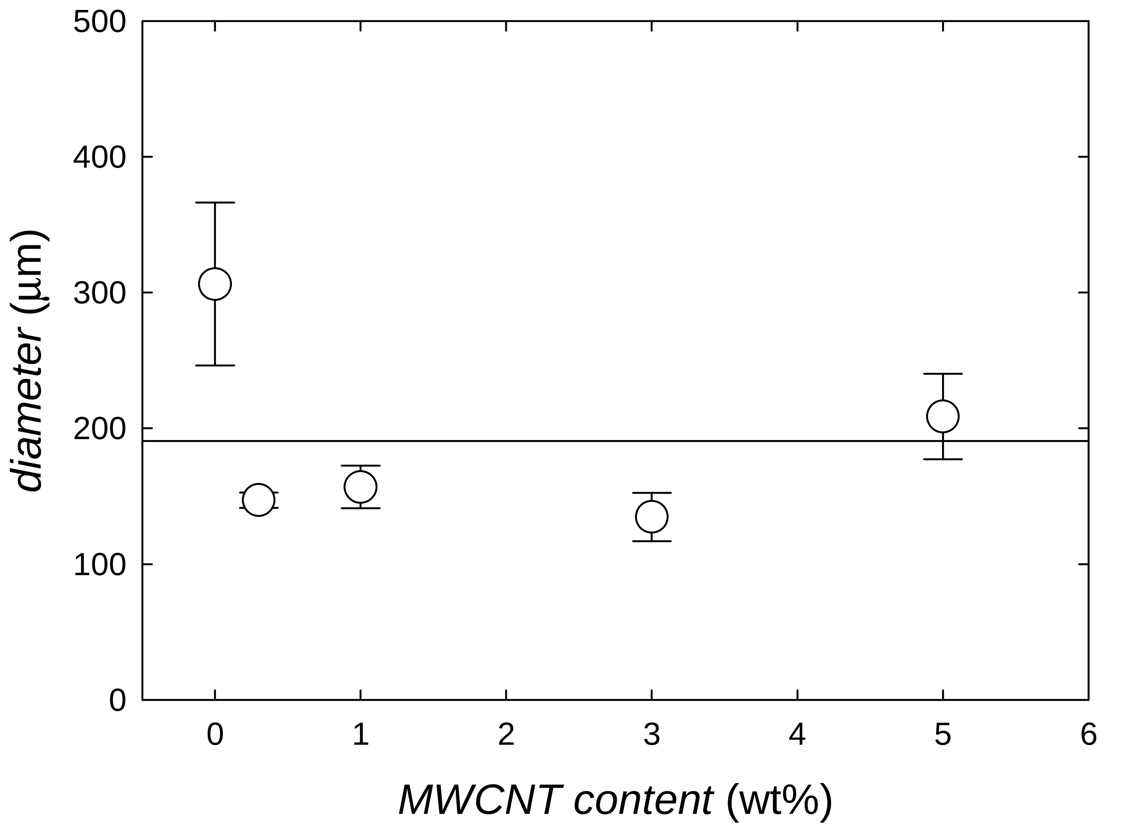
Diethyltoluenediamine (DETDA 80) $\rho = 1.019$ g cm^{-3}.
(Lonza)

Experimental: *Preparation of epoxy coupons*

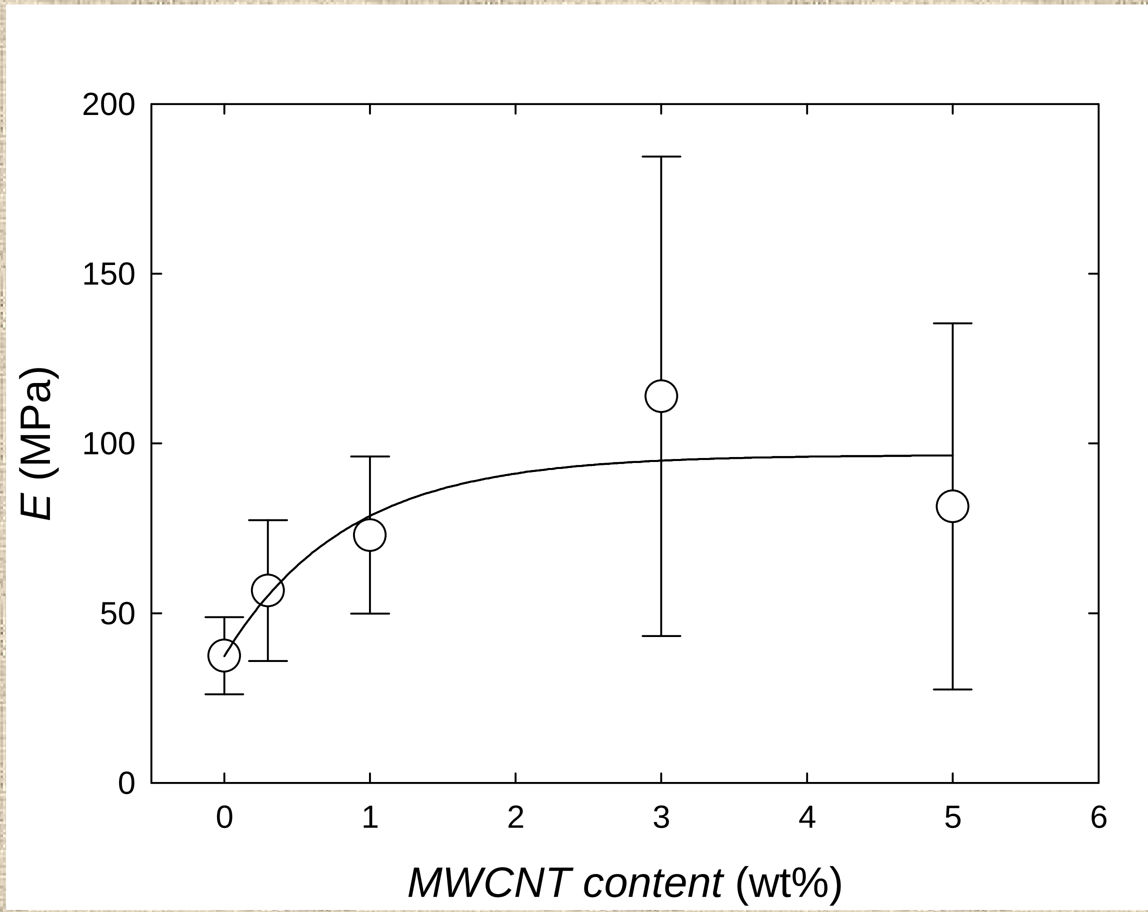
Preliminary epoxy based coupons were obtained by placing parallel composite fibers (**so far with a content of filler up to 1wt%**) in a specific mold cavity in which the thermosetting resin / hardener (mix ratio 86/14) formulation was subsequently poured, degassed for 15 min at 100 °C and then cured applying the following protocol: 3 h isothermal step at 135 °C followed by 3 h at 180 °C.



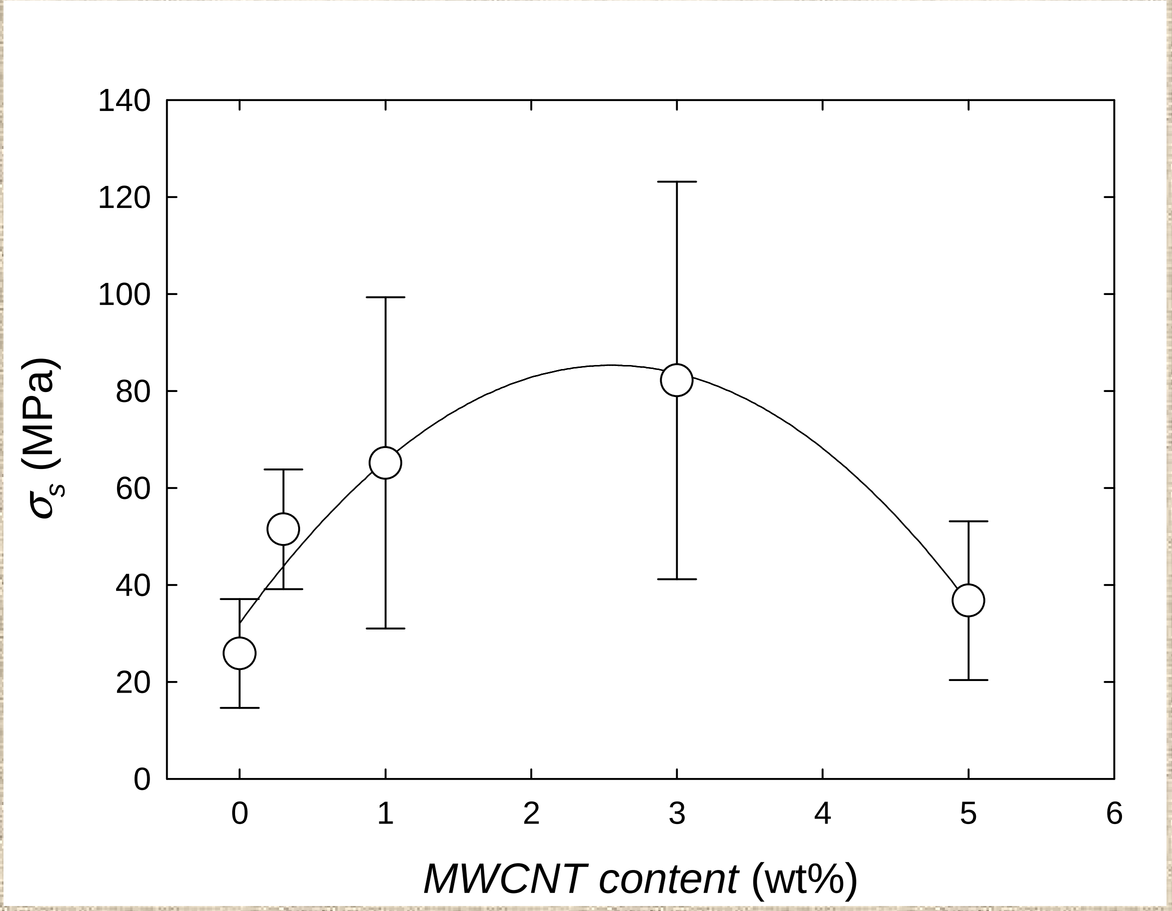
Results and discussion: *fiber diameters*



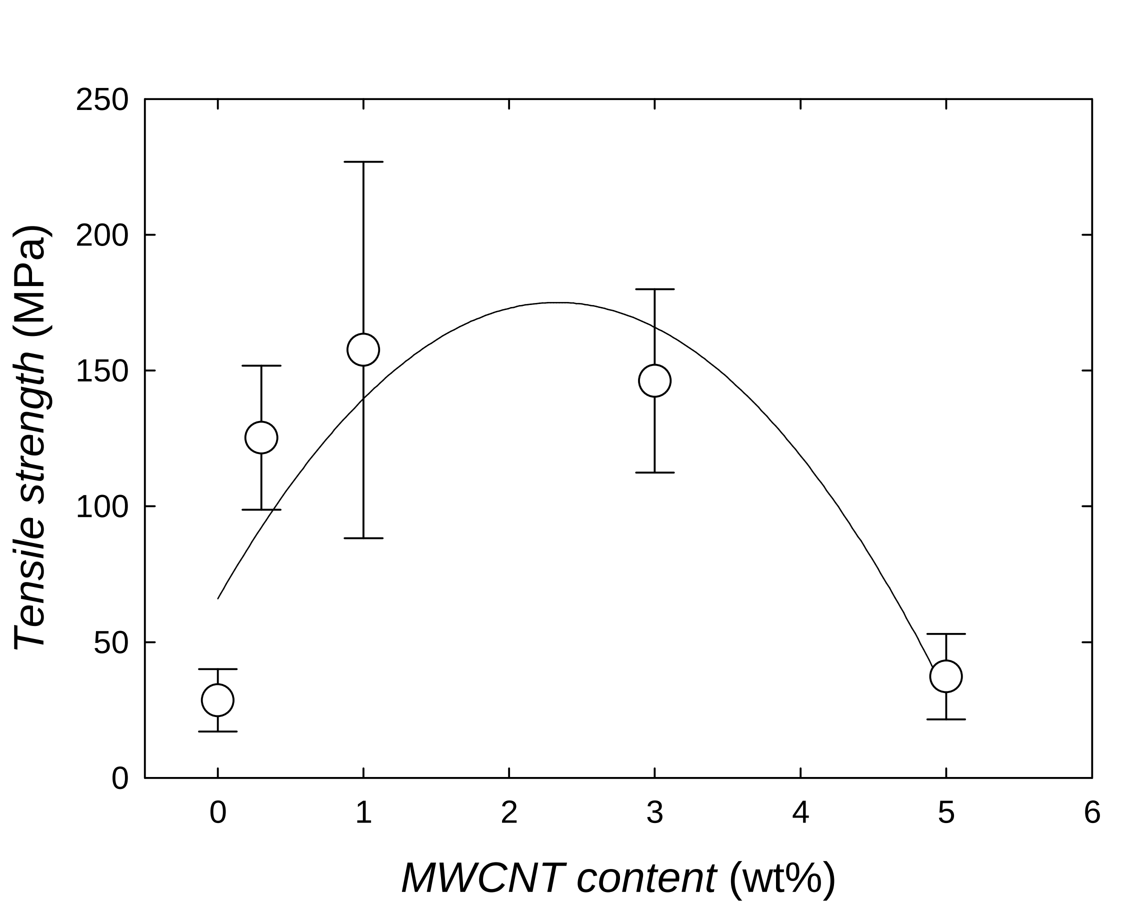
Results and discussion: fiber modulus



Results and discussion: strenght at yield



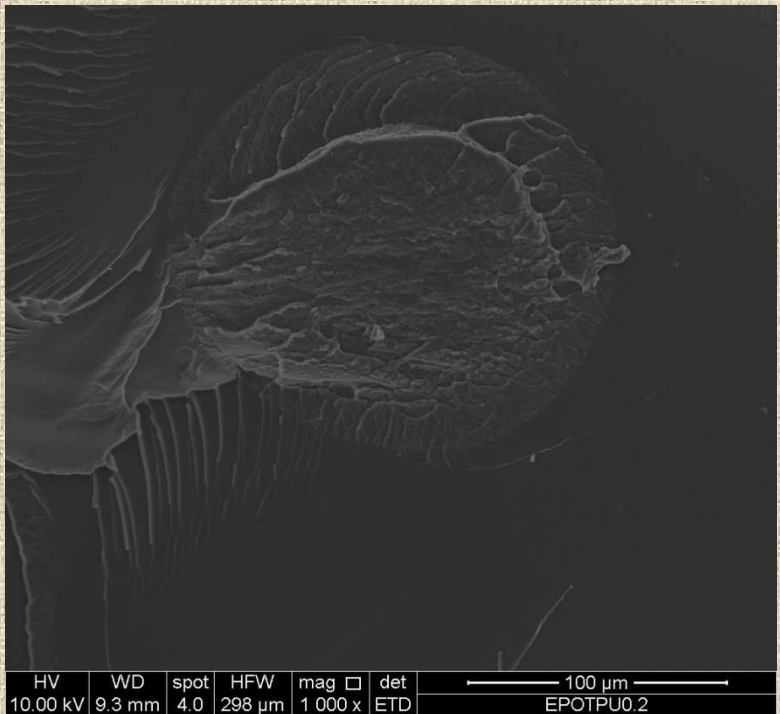
Results and discussion: tensile strenght of fibers



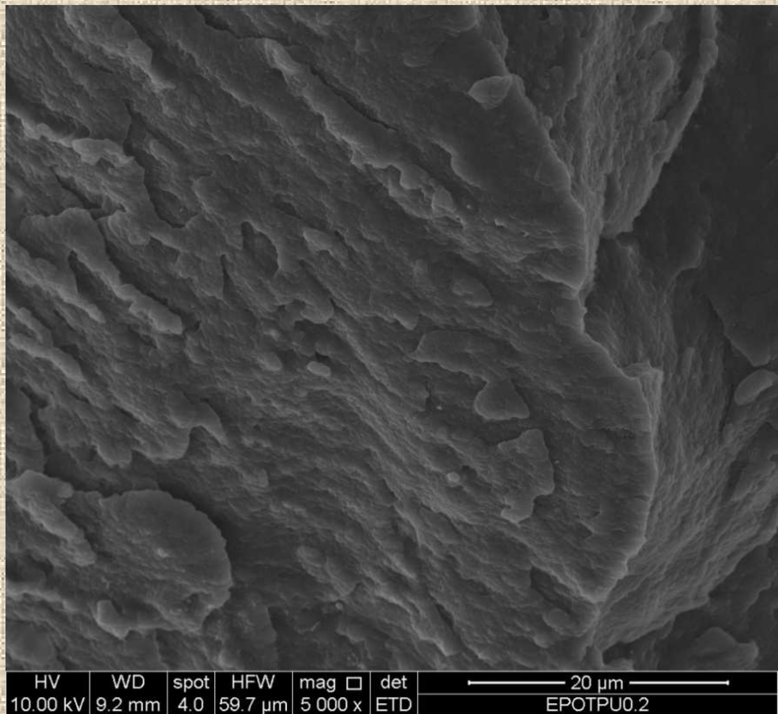
Results and discussion: epoxy coupons

The morphology

TPU fiber embedded in the epoxy resin
Magnification 1000x

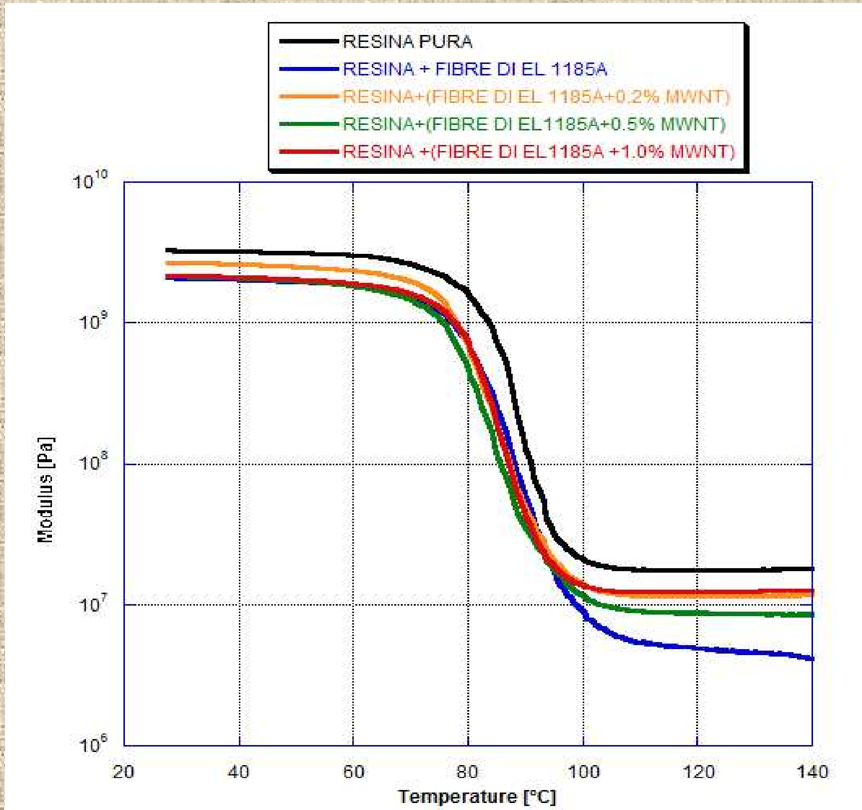


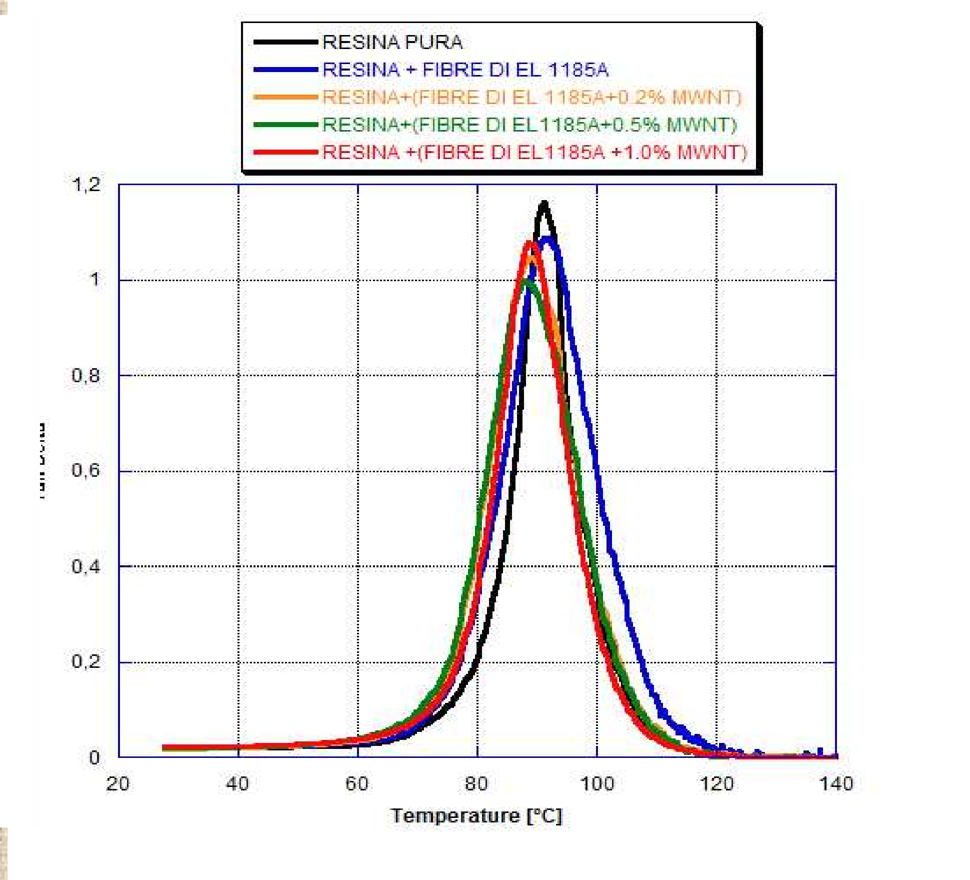
Detail of TPU matrix
Magnification 5000x



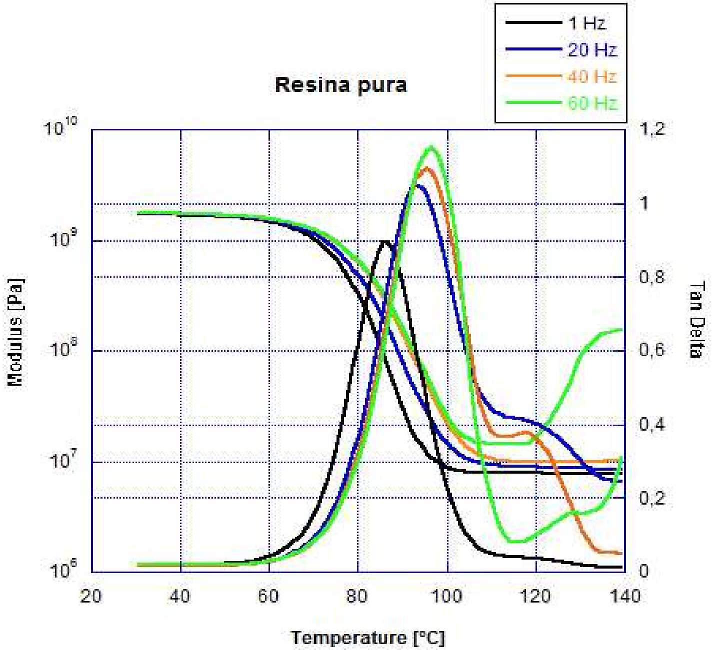
Results and discussion: epoxy coupons

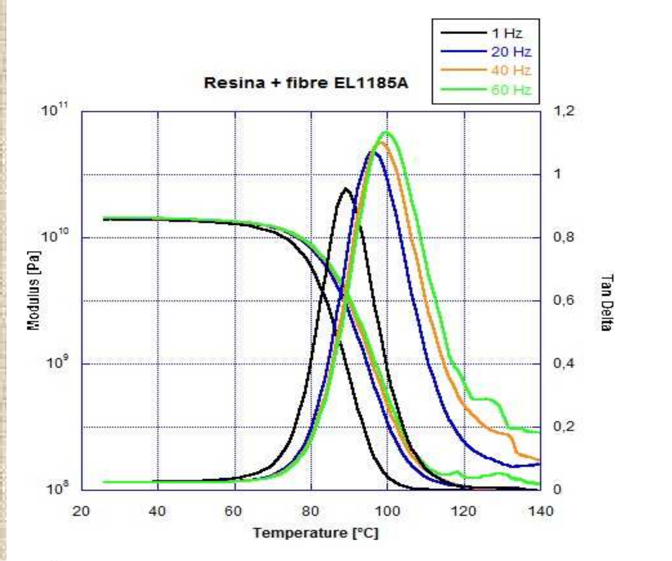
Dynamic-mechanical properties



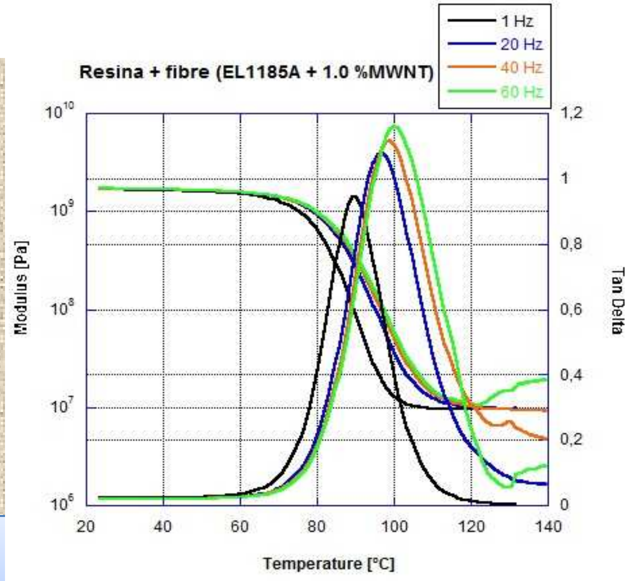


Results and discussion: DMA at various frequencies





As expected, the increase of the frequency shifts the transition zone and the damping signal at higher temperatures, as well as giving a greater intensity of the signal tan δ.



Further increases recorded in terms of E 'and tan δ which appear beyond the zone of the glass transition can be attributed to the application of a non-optimal treatment process of the resin.

Results and discussion: *Flexural properties epoxy coupons*

Coupon	Modu... (Mpa...		...tr... (...
Neat Epoxy Resin (Epo)	1101		
Epo + EL1185A fibers	3369	71,98	0,032
Epo + (EL1185A fibers + 0.3% MWNT)	388		
Epo + (EL1185A fibers + 0,5% MWNT)	432		
Epo + (EL1185A fibers + 1.0 % MWNT)	603		

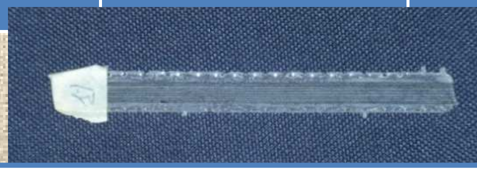
Neat Epoxy Resin (Epo)


Epo + EL1185A


Epo + (EL1185A + 0,2% MWNT)


Epo + (EL1185A + 0,5% MWNT)


Epo + (EL1185A + 1,0% MWNT)




It is evident a reduction of the module with the introduction of the rubber phase and an evident recovery of the same with increasing the content of nanotubes.

Conclusive remarks on composite epoxy coupons

Melt spun Thermoplastic PolyUrethane based fibers containing up to 1% by weight of multiwalled carbon nanotubes have been used to reinforce an epoxy formulation.

Composite fibers show improved tensile parameter at least for contents of filler up to 3% by weight.

Epoxy items containing composite fibers, so far aligned just in one direction, show a bending modulus, relevantly reduced in presence of neat TPU reinforcing elements, but increasing with the filler content of the same.

Reported benefits may be significantly enhanced.

Work is in progress with aim, among others:

1) to optimize the curing process so far considered for the thermosetting resin,

2) to estimate the effects definitely related to:

•higher content of nanotubes in the fibers as they are confined;

•greater number of fibers and different arrangement of the same;

•draw ratio of the fibers;

•disposal of the same.

Approach 2: Film production

The comparison of two different processing techniques was made by performing film extrusion on:

a) **cast film** apparatus with flat die geometry and chill roll cooling system;

b) **film blowing** technique by making use of a tubular die geometry with air cooling and draw up nip rolls.

In both cases, the material was dried in vacuum at 70 °C for 12 hours prior to any use.

To overcome the relevant stickiness of TPU based films the winding up of cast filming was performed by coupling in line a continuous paper ribbon whereas the problem of film blowing production has been approached by making use of a co-extrusion system where PU layers were separated by low density polyethylene (LDPE) ones.

P. Russo, M. Lavorgna, F. Piscitelli, D. Acierno, L. Di Maio *Thermoplastic polyurethane films reinforced with carbon nanotubes: the effect of processing on the structure and mechanical properties* European Polymer Journal **49**, 379-388 (2013)

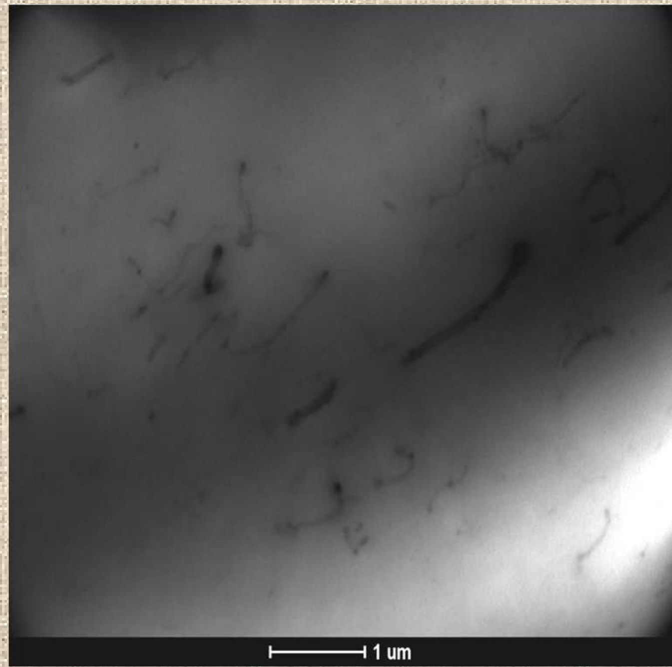
P. Russo, L. Di Maio, D. Acierno *Process-properties relationships of thermoplastic polyurethane based materials filled with carbon nanotubes* Proceedings 18th International Conference on Composite Materials. Jeju, Korea. August 21-26, 2011

P. Russo, L. Di Maio, D. Acierno *Preparation and characterization of thermoplastic polyurethane/carbon nanotubes cast films* Proceedings of the EUROMAT 2011, Montpellier (Fr), 12-15 settembre 2011

Film blowing lab equipment

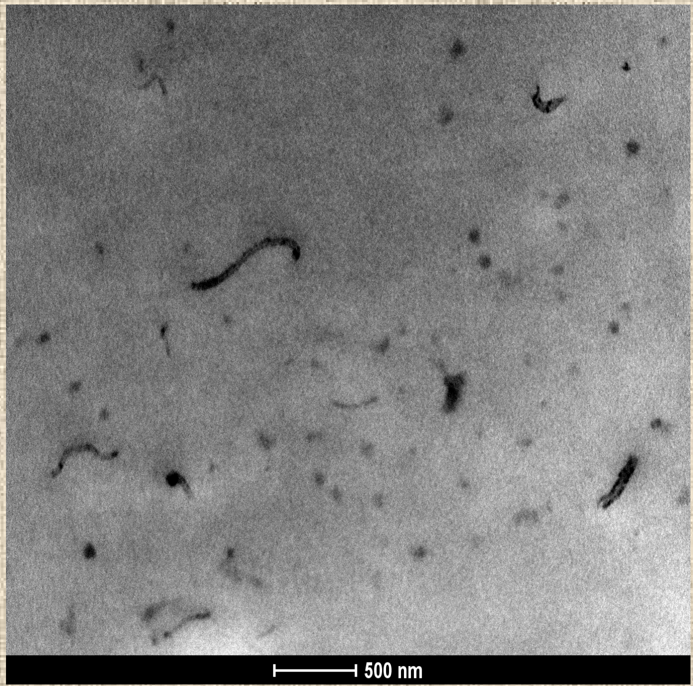
Morphological aspects

Cast film (1 wt%)

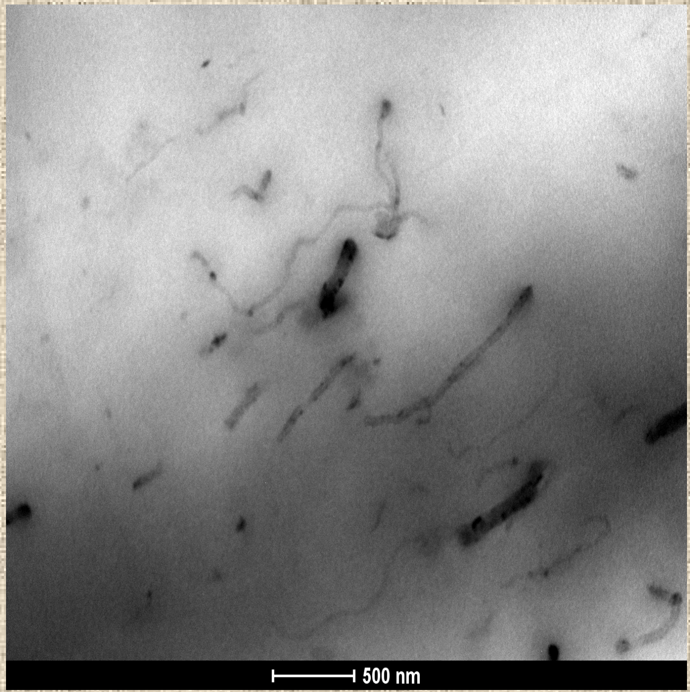


Blown film (1 wt%)

Morphological aspects



Cast film (1 wt%)



Blown film (1 wt%)

Tensile parameters: Longitudinal direction

SAMPLES (NTC content)	E [MPa]	ε_{br}[%]	σ_{max}[MPa]
Film casting			
EL 1185A	**7.2±1.1**	**791±22**	**24.4±2.2**
0.2 wt%	11.6±0.6	502±43	32.3±1.9
0.5 wt%	13.7±1.4	491±27	34.7±1.2
1 wt%	14.6±0.4	461±31	26.6±1.5
Film blowing			
EL 1185A	**10.1 ± 1.0**	**730 ± 23**	**24.3 ± 3.8**
0.2 wt%	12.6 ± 2.8	574 ± 57	9.7 ± 2.1
0.5 wt%	13 .2± 4.1	627 ± 56	10.4 ± 1.7
1 wt%	11.1± 1.7	608 ± 21	11.9 ± 1.1

Dynamic mechanical properties

The storage modulus

Samples	E' -80°C (MPa)	E' 40°C (MPa)	E' -80°C (MPa)	E' 40°C (MPa)
EL 1185A	974	14.8	1294	12.7
0.2 wt% MWNTs	1787	21.3	1170	19.8
0.5 wt% MWNTs	1887	22.4	1172	22.1
1 wt% MWNTs	2156	20.6	1722	24.3
	Cast film		Blown film	

Dynamic mechanical properties
Loss factor

Samples	H_{MAX}	WMH	H_{MAX}	WMH
EL 1185A	0.37	46	0.40	43
0.2 wt% MWNTs	0.33	43	0.32	41
0.5 wt% MWNTs	0.34	43	0.29	40
1 wt% MWNTs	0.34	39	0.30	40
	Cast film		**Blown film**	

Conclusions : composite films

TPU based films, containing multi-wall carbon nanotubes were prepared using two typical technologies of filming: film casting and film blowing.

From morphological analysis it seems that the conditions of film casting are able to provide better dispersion of nanotubes with respect to film blowing ones, at the same filler loading.

This latter consideration justifies, without doubts, the best mechanical performances founds for flat films with respect to blown ones all over the investigated thermal range.

RAW MATERIALS

Polymer: **Polystyrene (PS, by Polimeri Europa)**

Filler:

- ***Commercial*** **multi-walled carbon nanotubes (MWCNTs) (Baytubes® C150P by Bayer)**
- ***Experimental*** **MWCNTs:**

Fluidized bed chemical vapor deposition technique

γ-alumina substrate impregnated with iron as bed material, ethylene as carbon source and nitrogen as fluidizing agent. *

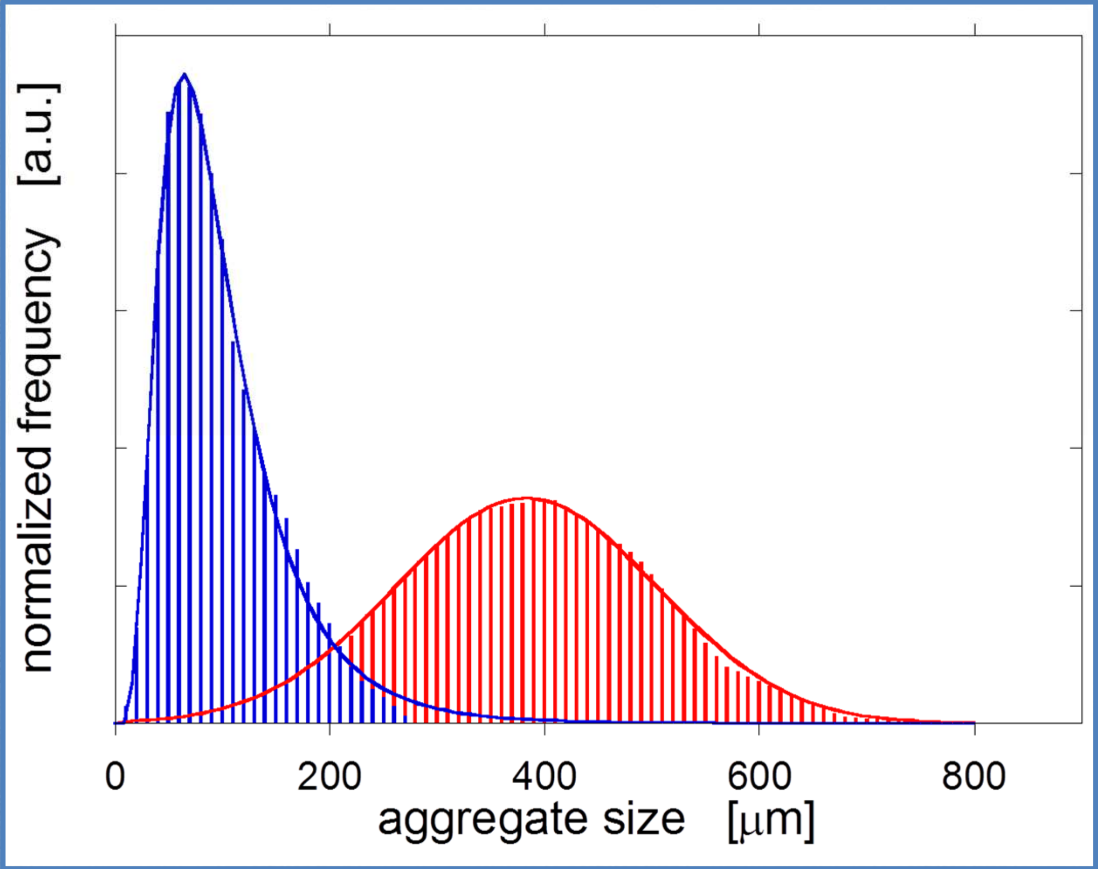
Three-step purification process

1. refluxing sulphuric acid solution to dissolve catalyst particles;
2. washing with water to remove the residual amount of acid;
3. drying to remove the remaining water adsorbed.

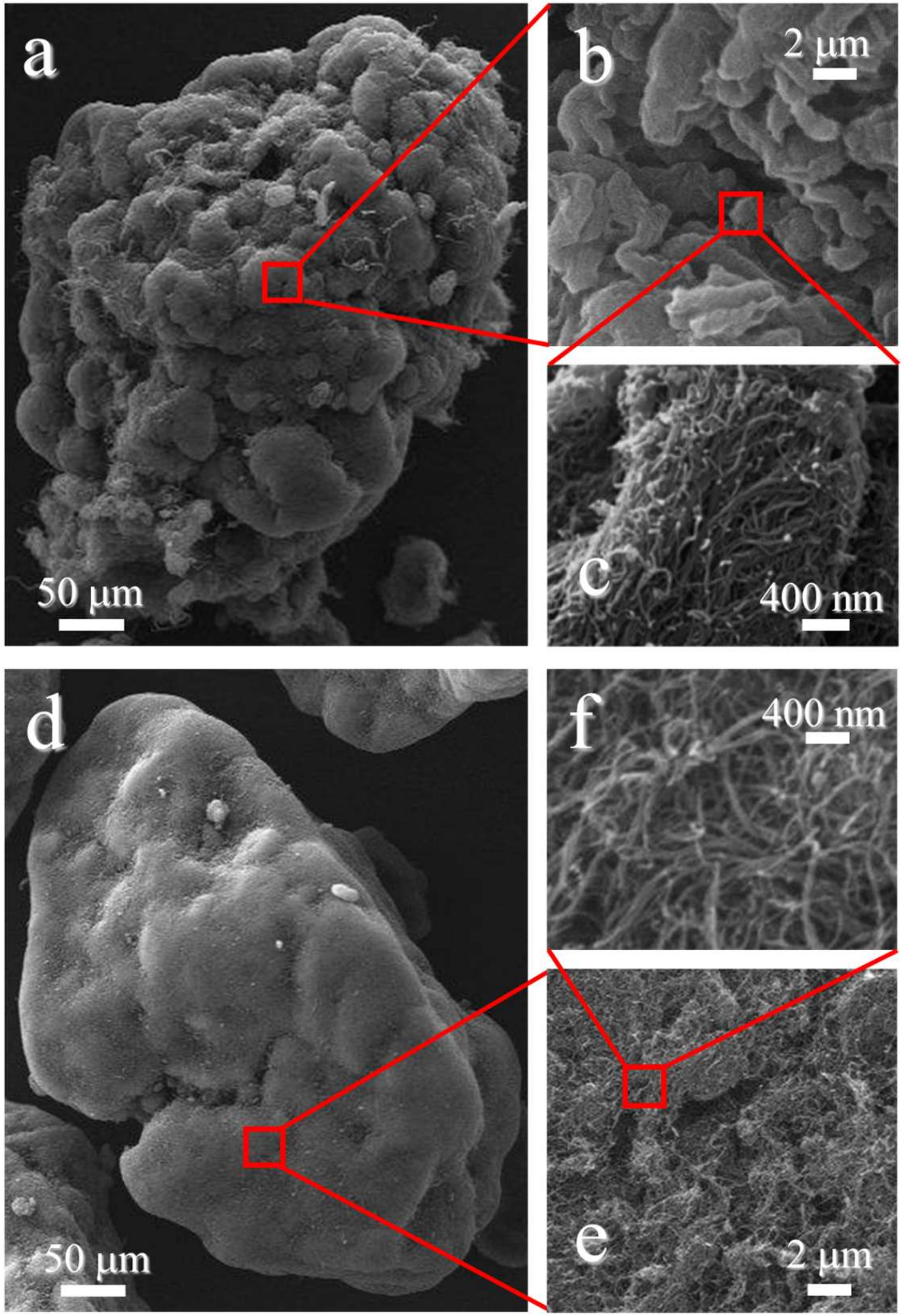
* Mazzocchia C. V., Bestetti M., Acierno D., Tito A., A process for the preparation of a catalyst, a catalyst obtained thereby, and its use in the production, European patent 2213369 (A1), 2010-08-04

Main features of the two kinds of MWCNTs

Property	Synthesized MWCNTs	Commercial MWCNTs
Carbon purity	>99%	≥95%
Outer mean diameter	~10 nm	~10.5 nm
Mean length	~720 nm	~770 nm
Aggregates average size	103±63 μm	382±122 μm
Aggregates bulk density	90÷120 Kg m^{-3}	130÷150 Kg m^{-3}

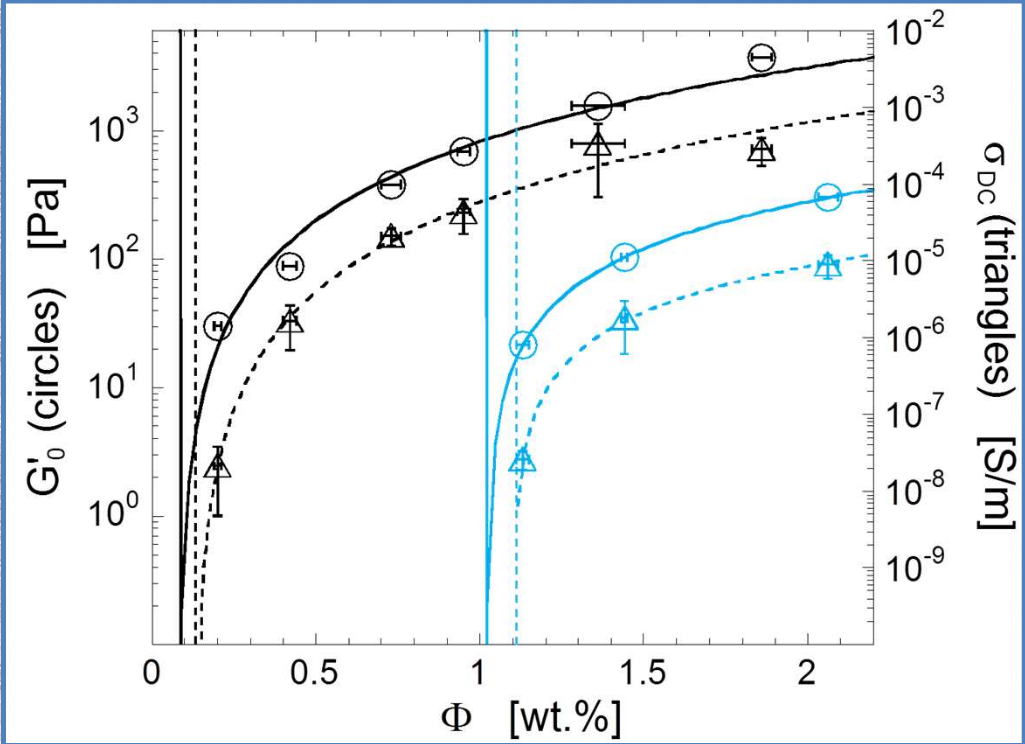


Normalized size distribution functions of synthesized (blue) and commercial (red) CNT aggregates.
Solid lines are Lognormal and Gaussian fittings, respectively



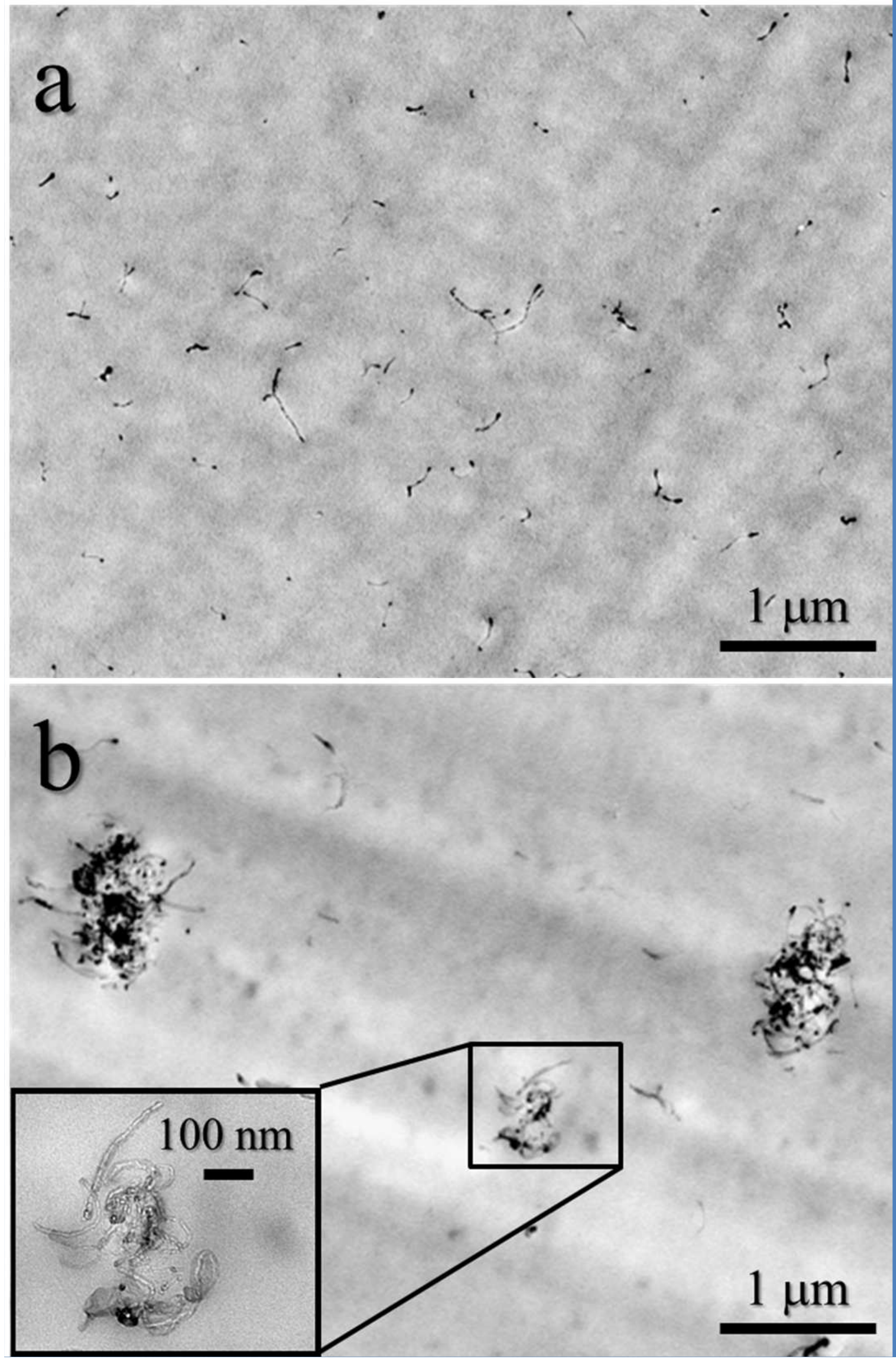
SEM micrographs of the primary aggregates of the (a-c) synthesized and (d-f) commercial CNTs on different length scales.

Percolation thresholds



Φ-dependence of the network elasticity (circles) and the DC electrical conductivity (triangles) for the nanocomposites filled with synthesized (black) and commercial (blue) nanotubes. Lines are power law fittings.

Salzano de Luna M., Pellegrino L., Daghetta M., Mazzocchia C.V., Acierno D., Filippone G. *Importance of the morphology ad structure of the primary aggregates for the dispersibility of carbon nanotubes in polymer melts*. Comp. Sci. Techn. In press.



TEM micrographs of nanocomposites at (a) Φ=0.07 wt.% of synthesized nanotubes and (b) at Φ=0.32 wt.% of commercial ones

Last conclusive remarks

The dispersibility of experimental MWCNTs has been investigated focusing on the role of the morphology and structure of the primary CNT aggregates, taking commercially available nanotubes with the same features but differently arranged in the aggregates as reference.

Specifically, the synthesized particles are in the form of small and loosely packed clusters made by interwoven bundles of combed yarns of nanotubes. Differently, the aggregates of the commercial particles appear as bigger blocks, whose fine-textured surface is the result of a random arrangement of highly entangled nanotubes.

The peculiar hierarchical structure of the synthesized particles results in a superior dispersibility in the host polymer matrix, as confirmed by both rheological measurements and dielectric spectroscopy.


Thank you very much for your kind attention