Applicazione di CNT in matrici elastomeriche

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Valeria Cipolletti, Sara Musto, Giulia Peli, Serena Cioppa

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Dipartimento di Chimica, Materiali, Ingegneria Chimica "G. Natta"

Nanotubi di carbonio:

sintesi, applicazioni ed opportunità

16 maggio 2013

Politecnico di Milano

Piazza Leonardo da Vinci 32, Aula Giulio Natta

Items of the presentation

- ☞ Processing methods for the preparation of nanocomposites
- ☞ CNT organization in the polymer matrix
  - distribution and dispersion
  - structure and aspect ratio
- ☞ CNT – polymer interface
- ☞ Properties of CNT based nanocomposites
  - vulcanization behaviour
  - electrical conductivity
  - thermal conductivity
  - mechanical reinforcement
- ☞ Hybrid filler systems based on CNT

Processing methods for the preparation

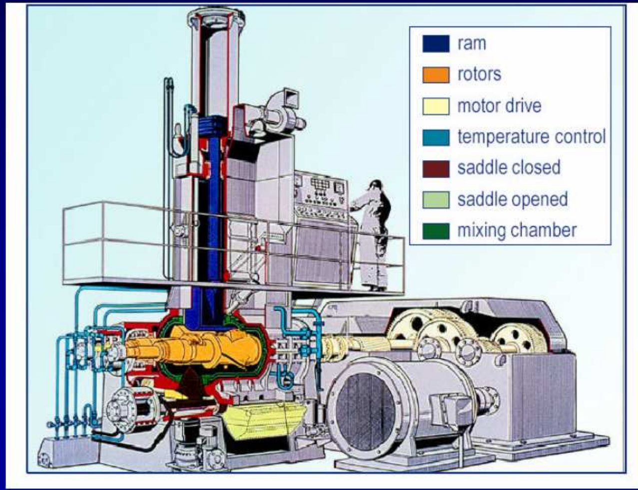
of CNT based nanocomposites

Processing methods for the preparation of nanocomposites

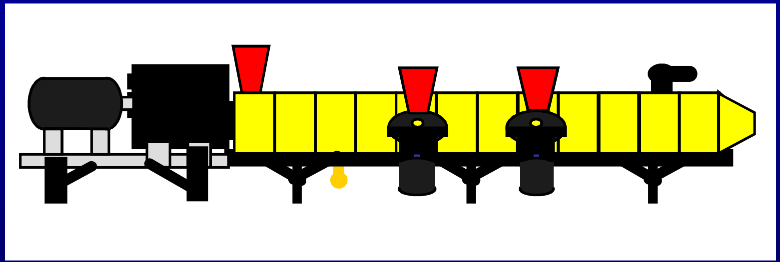
- *Dry* melt blending
- *Wet* melt blending
- Solution blending

Melt blending

two roll mill



Banbury®



Twin screw extruder

Brabender®

Dry melt blending

PI introduced in the internal mixer and masticated
90 – 100℃, 1 min, rotors: 30 rpm

CNT added - mixing: 100℃, 4 min

Composite discharged

Addition of activators and curatives
mixing: 60℃, 4 min

Composite discharged

Composite homogeneized at two roll mill.
5 times, rotors: 38 and 30 rpm

Successive steps

Galimberti M., Coombs M., Riccio P., Ricco` T., Passera S., Pandini S., Conzatti L., Ravasio A., Tritto I. *Macromol. Mater. Eng.* 2012, 298(2), 241-251

Wet melt blending

☞

CNT in EtOH = 1:10 wt + non-ionic surfactant

Ultrasonication: 200W$_{effective}$, 25kHz, 2h

S-SBR / BR = 50 / 50 on a two-roll mill and masticated

80℃ , 5min

Addiition of CNT / EtOH - mixing 15min

Composite discharged

Addition of activators and curatives at two roll mill:

mixing at RT

Composite homogeneized at two roll mill

25 min

Successive steps

A. Das, K.W. Stockelhuber, R. Jurk, M. Saphiannikova, J. Fritzsche, H. Lorenz, M. Kuppler, G. Heinrich
Polymer 2008, 49, 5276 - 5283

Latex blending

☞ Aqueous dispersion of NR (latex)

☞
- CNT + H_2O + surfactant (SDS), reflux for 6h
- Insoluble powder separated by centrifugation, washed with deionized water, dried under air at 40°C
- CNT in deionized H_2O , ultrasonication for 2h

CNT/SDS + NR latex,
magnetically stirred for 3h at 2000 rpm

Composite dispersion:
Ultrasonication, 1h

Thick slurries cast on a flat plastic mold, dried under air at 50℃ for 24h

Successive steps

C. F. Matos, F. Galembeck, A. J. G. Zarbin
Carbon 2012, 50, 4685-4695

Solution blending

☞ NR dissolved in toluene

☞ CNT sonicated in toluene

30 min

Addition of CNT/toluene to NR/toluene:

mechanically stirred for 20min, then dried in open air at RT

Addition of activators and curatives

at two roll mill, 80℃, 15min

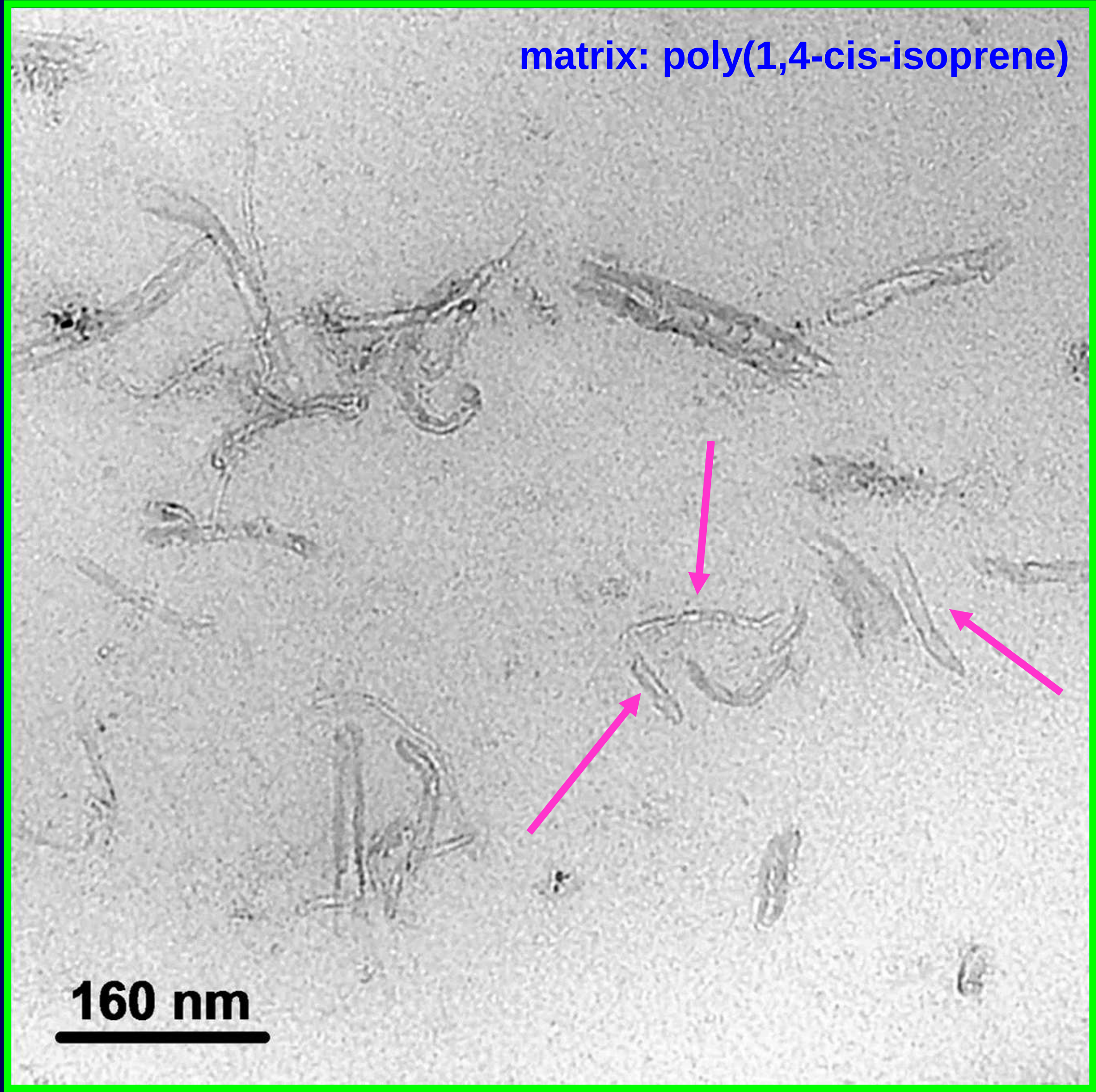
Successive steps

A.A. Abdullateef, S.P. Thomas, M. A. Al-Harthi, S.K. De, S. Bandyopadhyay, A.A. Basfar, M. A. Atieh; *Journal of Applied Polymer Science* 2012, 125, E76 – E84

CNT organization in the polymer matrix

Composites from dry melt blending

IR	100
CNT	5



Well dispersed CNT

CNT broken
by mixing

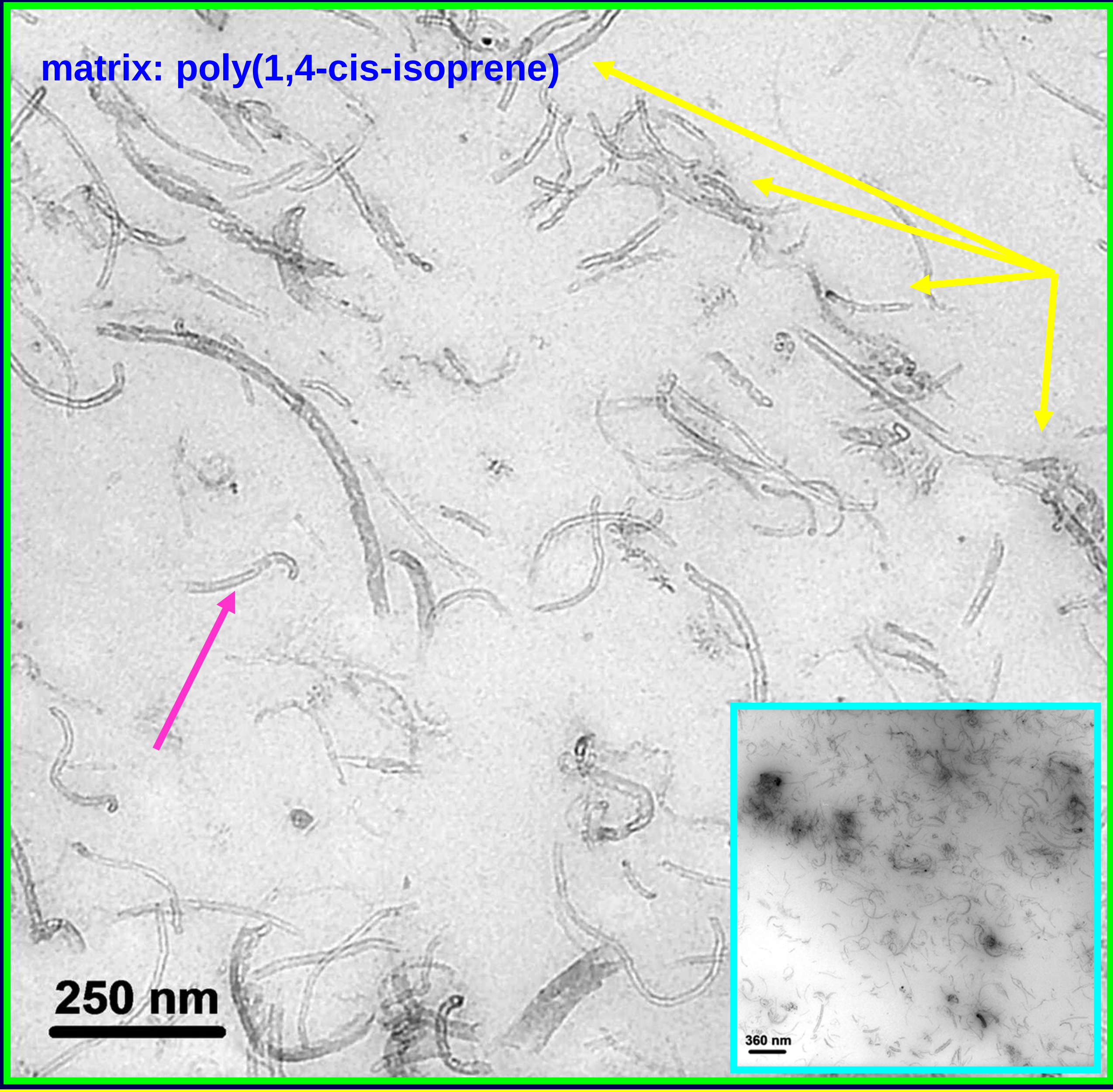
Galimberti M. et al
Macromol. Mater. Eng. 2012, 298(2), 241-251

Composites from dry melt blending

IR	100
CNT	11

CNT broken
by mixing

CNT percolation
at 7 phr



Galimberti M. et al
Macromol. Mater. Eng. 2012, 298(2), 241-251

Composites from *wet* melt blending

CNT/EtOH

Improvement of CNT dispersion

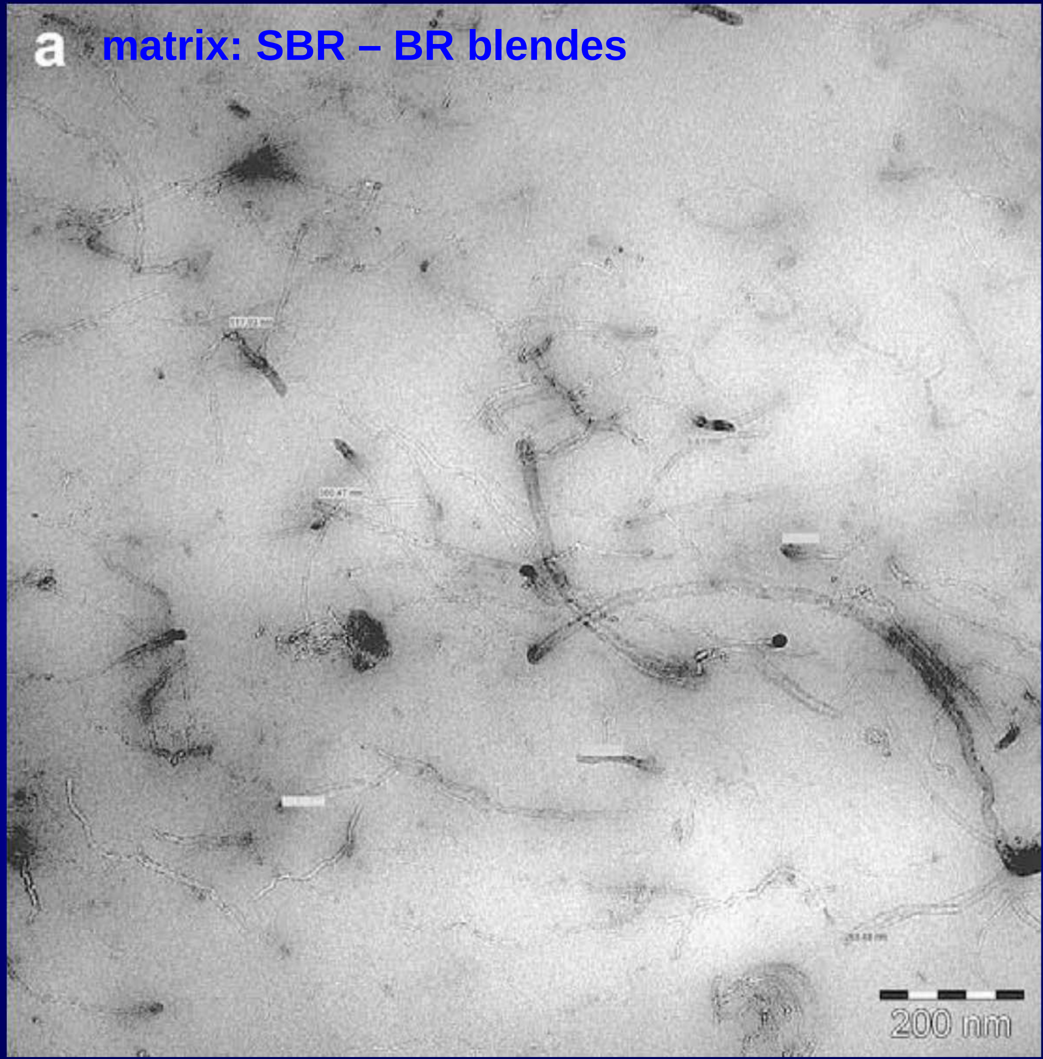
Diameter of tube: 6 – 27nm

Lenght of tubes:

from a few to several hundred nm

CNT percolation

at 5 phr

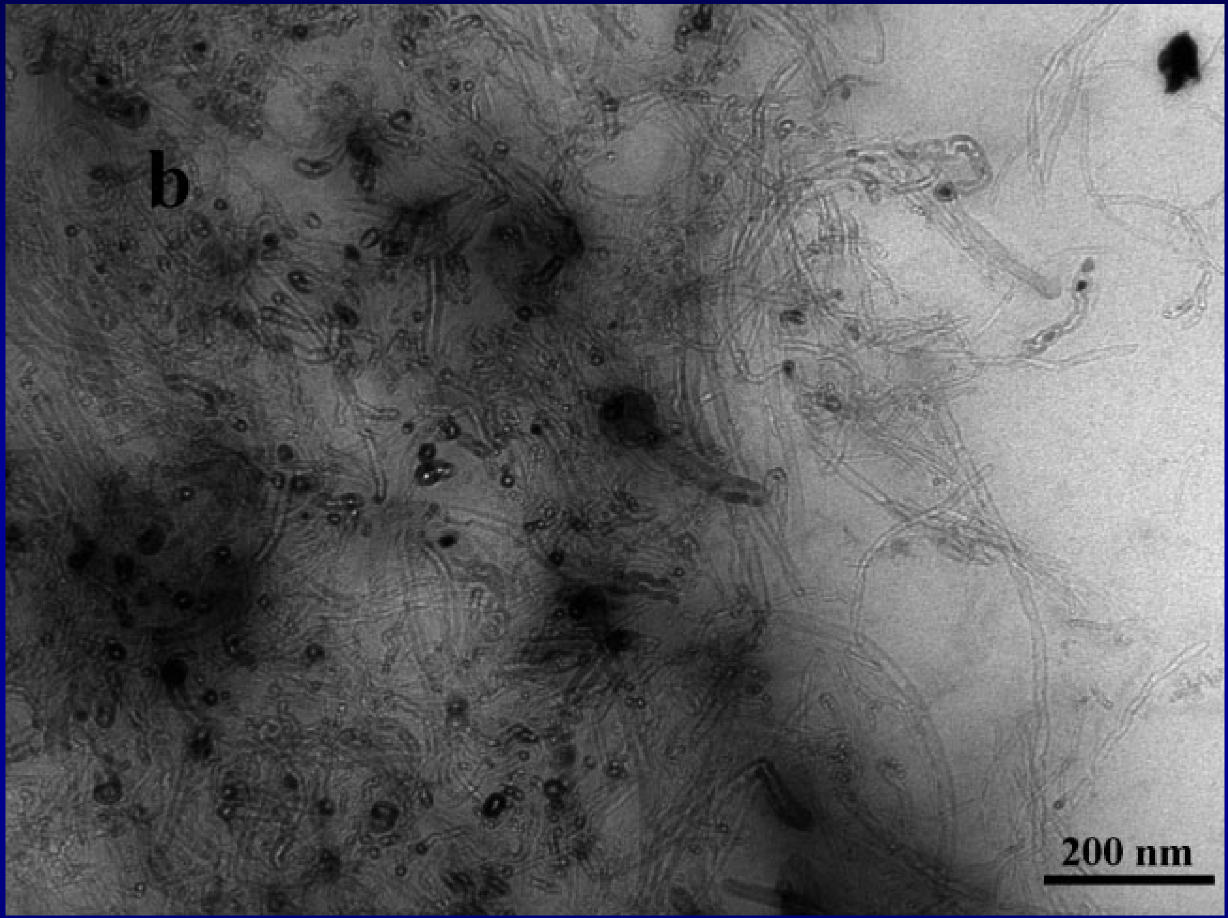


A. Das, K.W. Stockelhuber, R. Jurk, M. Saphiannikova, J. Fritzsche, H. Lorenz, M. Kuppler, G. Heinrich *Polymer* 2008, 49, 5276 - 5283

Composites from solution blending

Improvement
of CNT dispersion

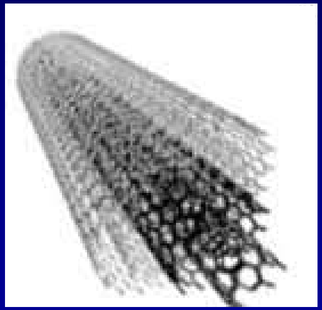
Presence of both individual and agglomerates of CNT

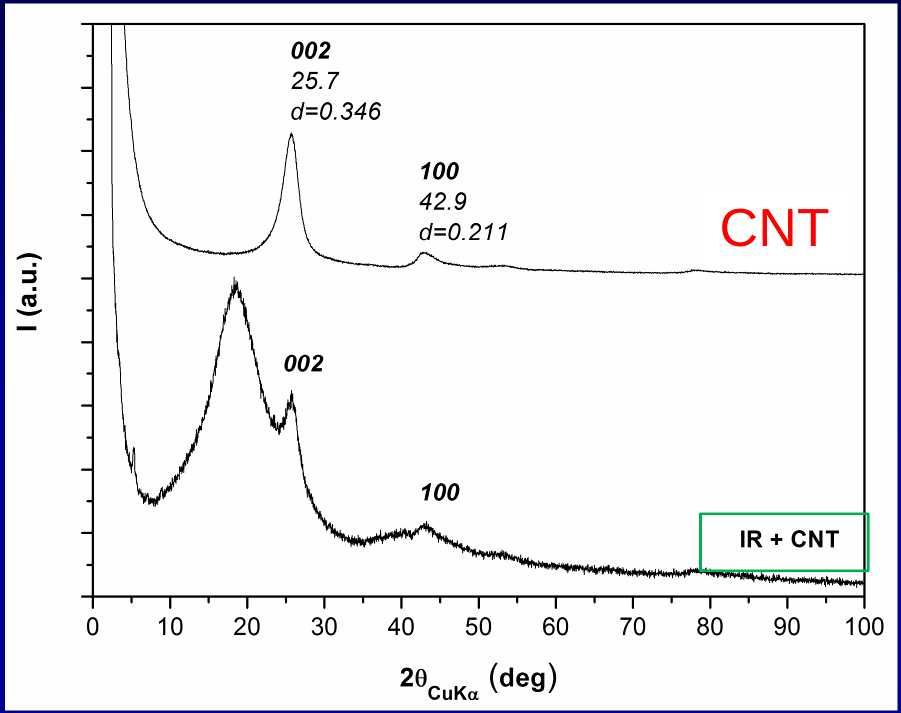


NR / CNT 3.8 wt%

L. Bokobza, and M. Kolodziej
Polym Int 2006, 55, 1090 - 1098

Crystalline structure of CNT





XRD analysis

IR 100, CNT 11

Scherrer equation: $D_{hk\ell} = 0.9\ \lambda / \beta_{hk\ell} \cos\theta_{hk\ell}$

Sample	d_{002} (nm)	D_{002} (nm)	N° piled layer
IR + CNT	0.346	~ 5	~ 15
CNT	**0.346**	**3.7**	**10**

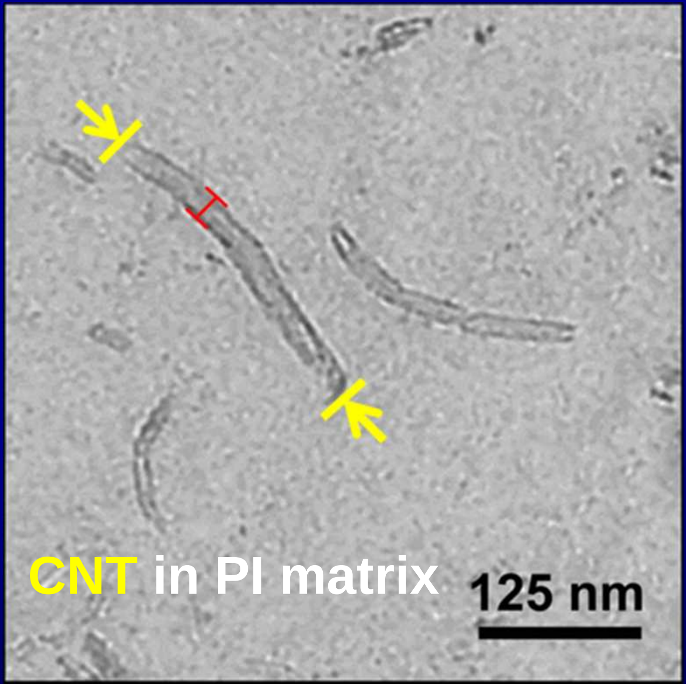
M. Galimberti, M. Coombs, V. Cipolletti, L. Giannini, T. Riccò, S. Pandini, L. Conzatti, M. Mauro, G. Guerra
Presented at 181th Technical Meeting of the Rubber Division of ACS, San Antonio (TX), April 22-25, 2012

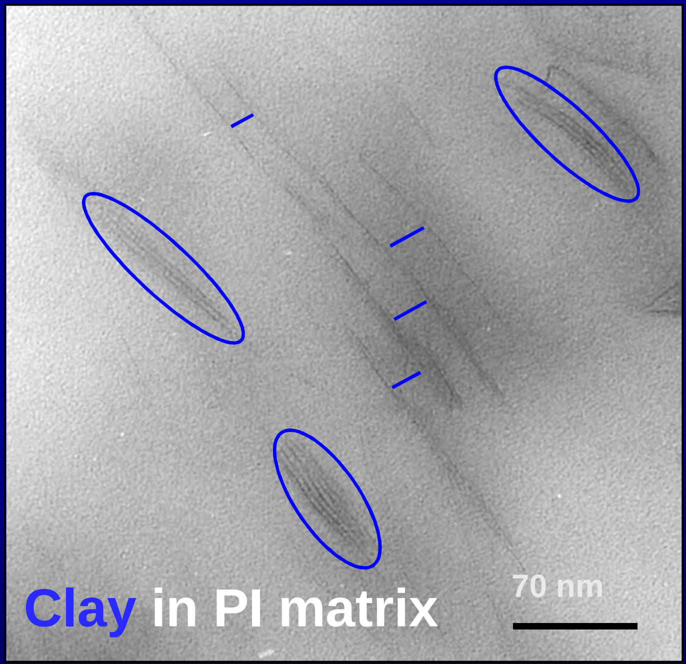
Aspect ratio of CNT

Aspect ratio

defined as the ratio of length to diameter for a fiber, such as CNT

or the ratio of diameter to thickness for platelets, such as clay.





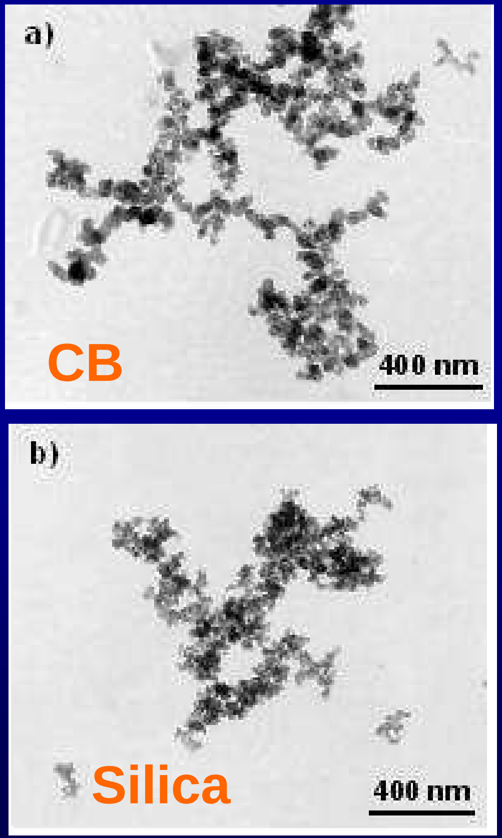
TEM micrographs taken at ISMAC-CNR Genova, L. Conzatti

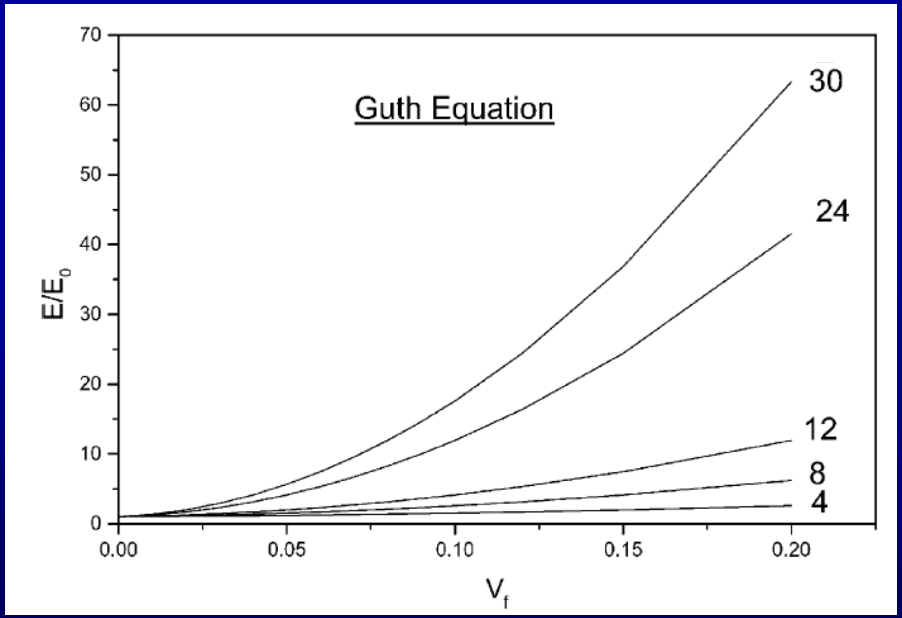
Aspect ratio of CNT in polymer composites

Why is important?

The Guth equation

$$E = E_m\,(1 + 0.67\,f\,\Phi + 1.62\,f^2\,\Phi^2)$$





Aspect ratio of CNT in polymer composites

CNT aspect ratio from Guth equation

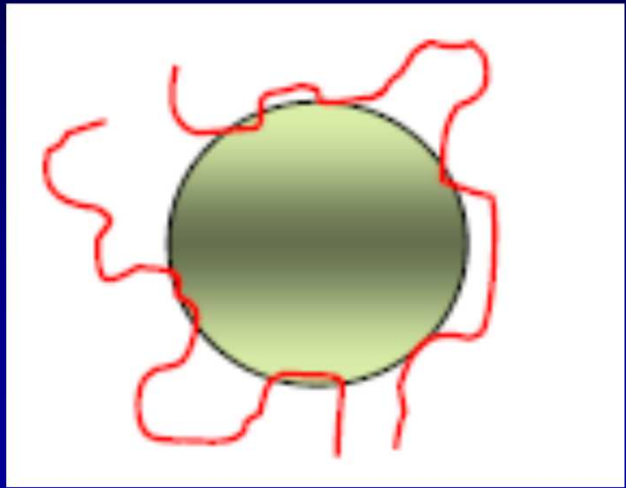
The Guth equation

$$E = E_m (1 + 0.67 f \Phi + 1.62 f^2 \Phi^2)$$

Polymer	f value	ref.
blend poly(1,4-cis-butadiene) / poly(styrene-co-butadiene)	15 - 20	A. Das, K. W. Stöckelhuber, R. Jurk, M. Grenzer, J. Fritzsche, H. Lorenz, M. Klüppel, G. Heinrich, *Polymer* **2008**, *49(24)*, 5276-83
poly(styrene-co-butadiene)	40 - 45	L. Bokobza, *Polymer*. **2007**, *48,* 4907-20
poly(isoprene)	22	Galimberti M., Coombs M., Riccio P., Ricco` T., Passera S., Pandini S., Conzatti L., Ravasio A., Tritto I. Macromol. Mater. Eng. 2012, 298(2), 241-251

CNT – polymer interface

CNT – polymer interface

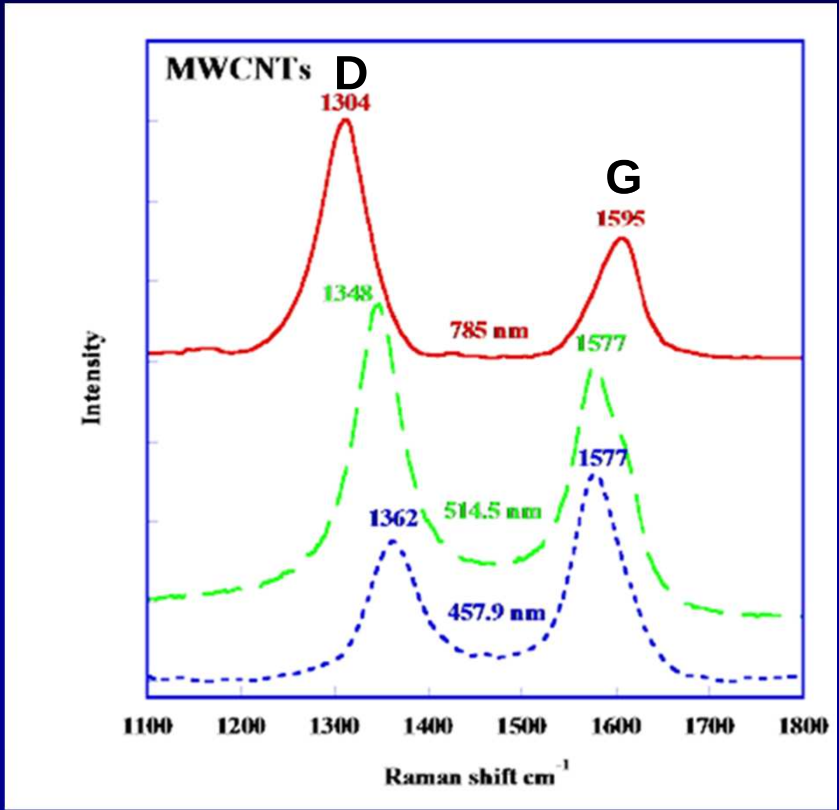


Filler-rubber interaction

Techniques used to study filler-polymer interface

- Solid-state NMR Spectroscopy
- Bound Rubber
- DSC: Tg
- Raman Spectroscopy

CNT – polymer interface

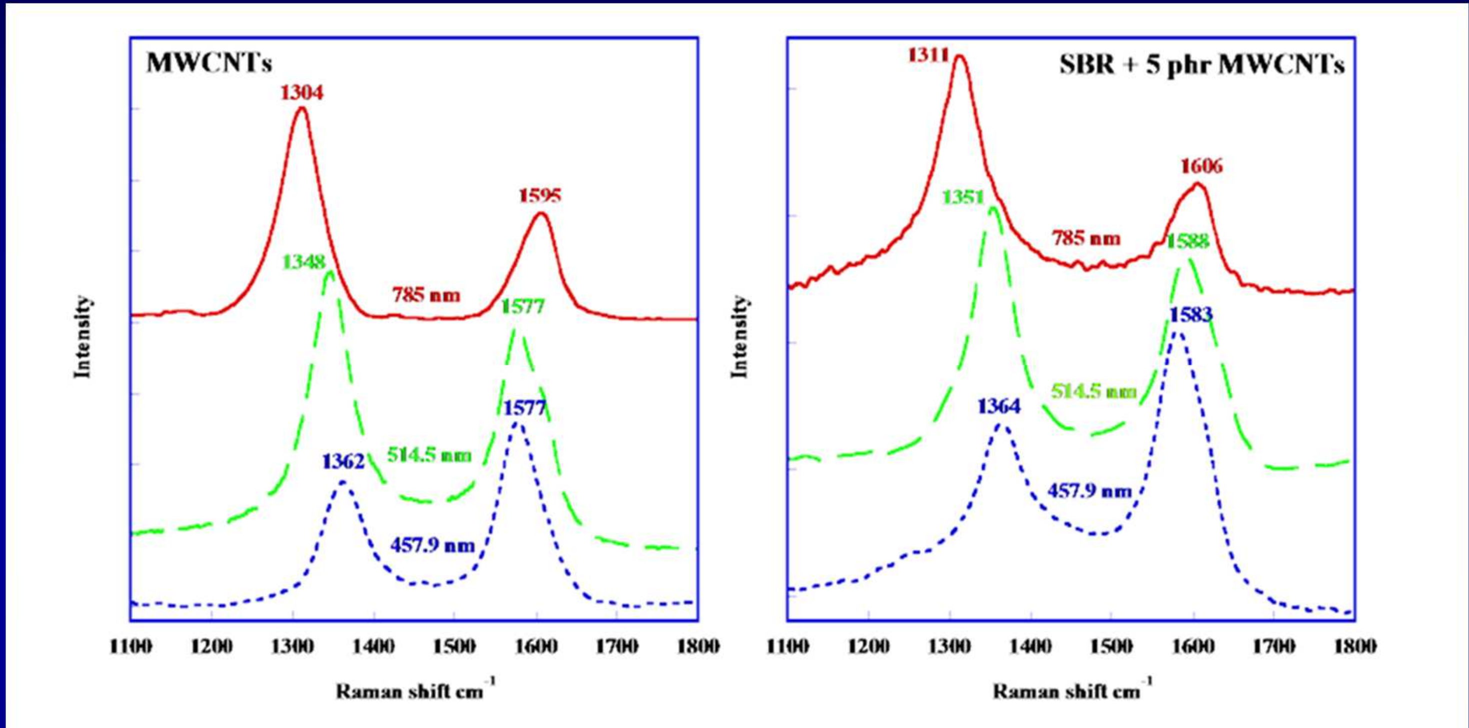


- G band
  in-plane vibration of C–C bond
- D band
  activated by the presence
  of disorder in carbon systems.

Raman spectra of CNT obtained with laser wavelengths 457.9, 514.5 and 785 nm

L. Bokobza
Presented at 181th Technical Meeting of the Rubber Division of ACS, San Antonio (TX)
April 22-25, 2012

CNT – polymer interface



upshifting

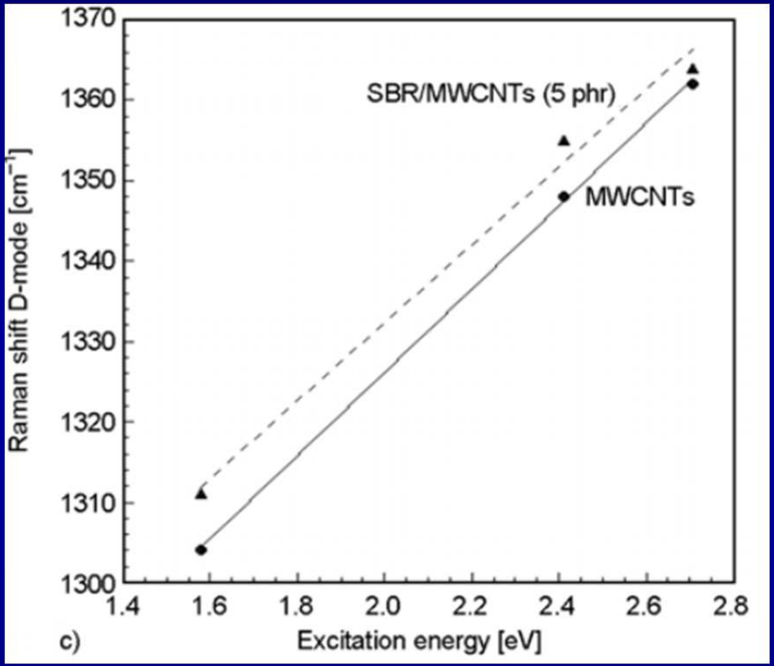
disentanglement and subsequent dispersion

in the polymeric medium

L. Bokobza
Presented at 181th Technical Meeting of the Rubber Division of ACS, San Antonio (TX)
April 22-25, 2012

CNT – polymer interface

Dependence of the wavenumber of the D band on laser energy

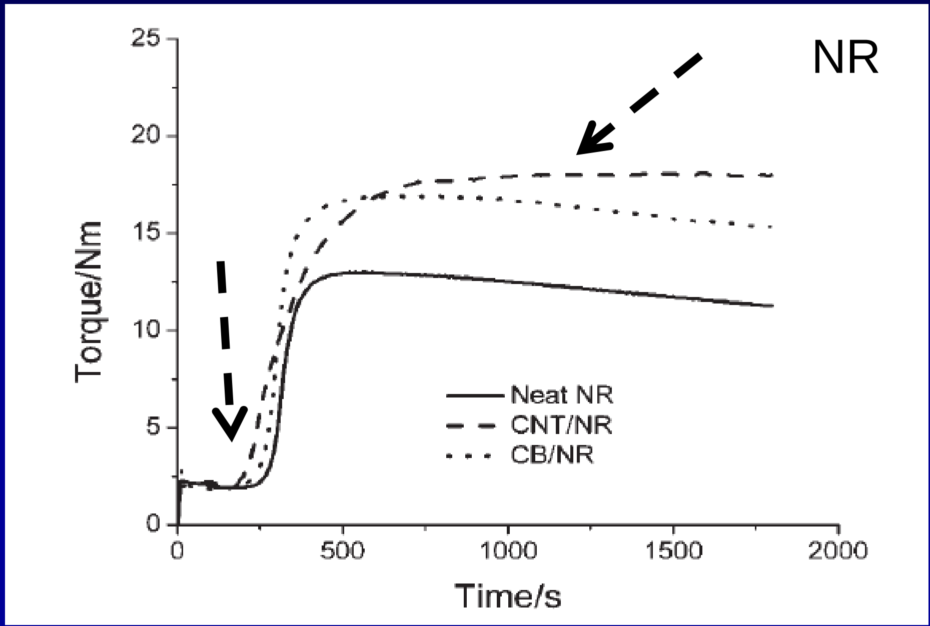


The wavenumber of the D band increases with increasing laser energy

L. Bokobza*, J. Zhang *eXPRESS Polymer Letters Vol.6, No.7 (2012) 601–608*

Properties of CNT based nanocomposites

Vulcanization behaviour



CB, CNT = 25 phr

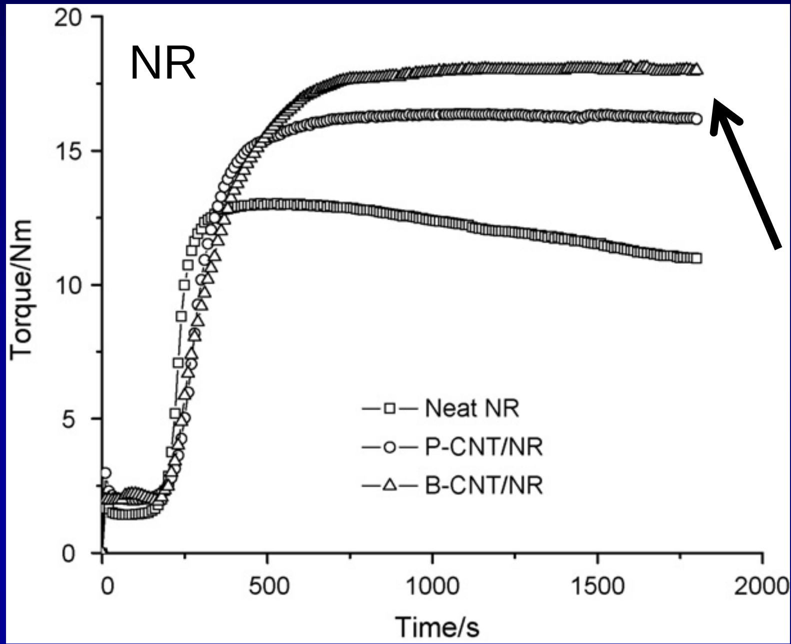
Reduction of scorch time
due to enhanced thermal conductivity

Higher Modulus

	Neat NR	CNT/NR	CB/NR
	phr	*phr*	*phr*
NR	100	100	100
Zinc Oxide	5	5	5
Stearic Acid	3	3	3
Sulfur	2,8	2,8	2,8
N-Cyclohexyl-2-benzothiazole-sulfenamide	1,3	1,3	1,3
2-Mercaptobenzothiazole	0,1	0,1	0,1
Ball-milled CNTs	0	25	0
CB	0	0	25

Sui, G.; Zhong, W. H.; Yang, X. P.; Yu, Y. H.; Zhao, S. H.
Polymers for Advanced Technologies (2008),19(11), 1543-1549

Vulcanization behaviour



CB, CNT = 25 phr

P-CNT = Purified CNT

B–CNT = Ball-milled CNT

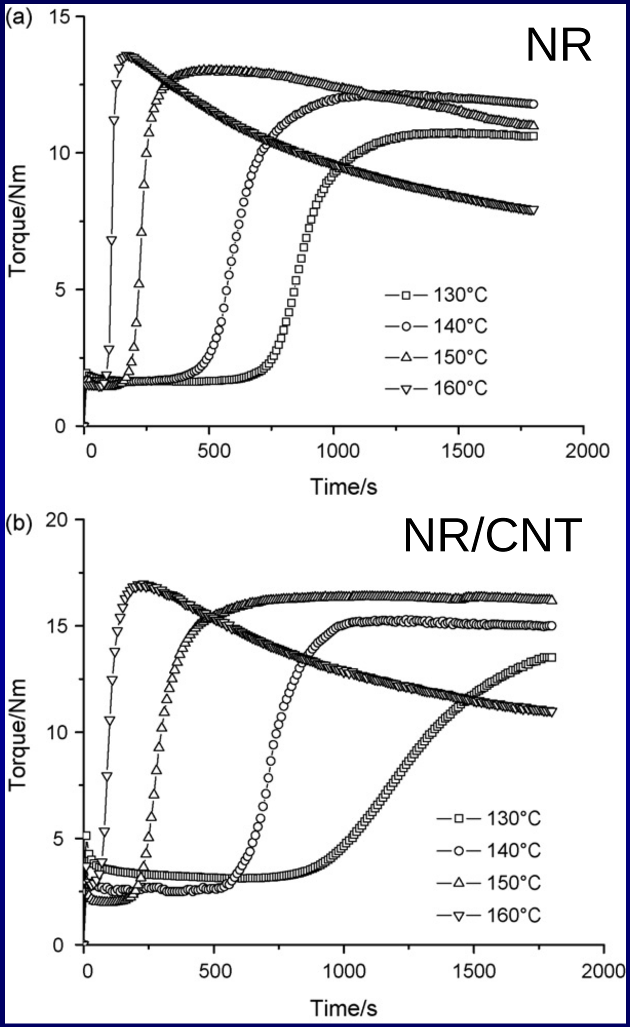
Slight increase in scorch time

Higher modulus

	Neat NR	P-CNT/NR	P-CNT/NR
	phr	*phr*	*phr*
NR	100	100	100
Zinc Oxide	5	5	5
Stearic Acid	3	3	3
Sulfur	2,8	2,8	2,8
N-Cyclohexyl-2-benzothiazole-sulfenamide	1,3	1,3	1,3
2-Mercaptobenzothiazole	0,1	0,1	0,1
Purified CNTs	0	25	0
Ball-Milled CNTs	0	0	25

G. Sui, W. H. Zhong, X. P. Yang, Y. H. Yu, S. H. Zhao
Mater. Sci. Eng.: A 485, 524 (2008).

Vulcanization behaviour



Sample	Activation energy (kJ/mol)
Neat NR	58.51
P-CNT/NR	90.96

Higher activation energy

due to absorption of accelerators

on CNT

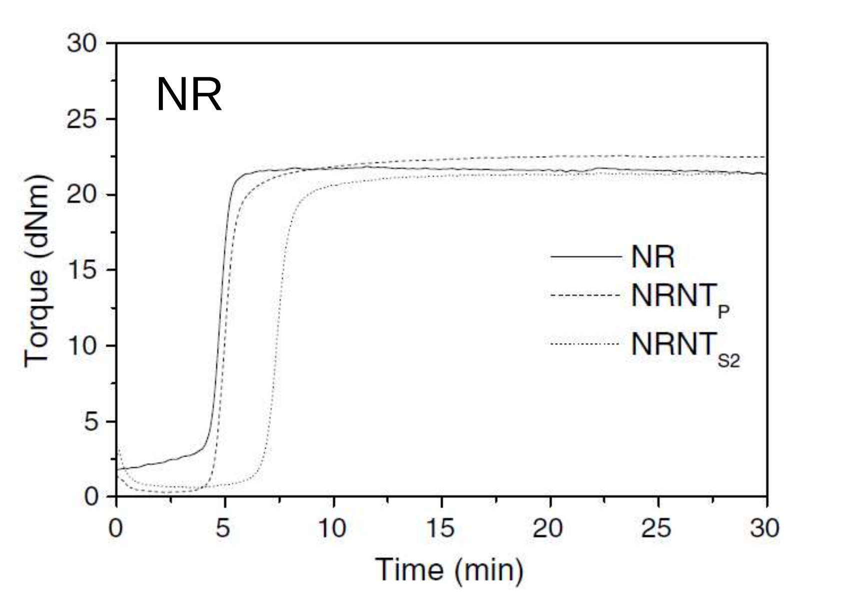
Higher modulus

CNT = 25 phr

	Neat NR	P-CNT/NR	P-CNT/NR
	phr	*phr*	*phr*
NR	100	100	100
Zinc Oxide	5	5	5
Stearic Acid	3	3	3
Sulfur	2,8	2,8	2,8
N-Cyclohexyl-2-benzothiazole-sulfenamide	1,3	1,3	1,3
2-Mercaptobenzothiazole	0,1	0,1	0,1
Purified CNTs	0	25	0
Ball-Milled CNTs	0	0	25

G. Sui, W. H. Zhong, X. P. Yang, Y. H. Yu, S. H. Zhao
Mater. Sci. Eng.: A 485, 524 (2008).

Vulcanization behaviour



CNT = 1 phr

Rubber: NR,
$NRNT_P$ = with pristine CNT
$NRNT_{S2}$ = with functionalized CNT

Scorch time increase for $NRNT_P$ or $NRNT_{S2}$

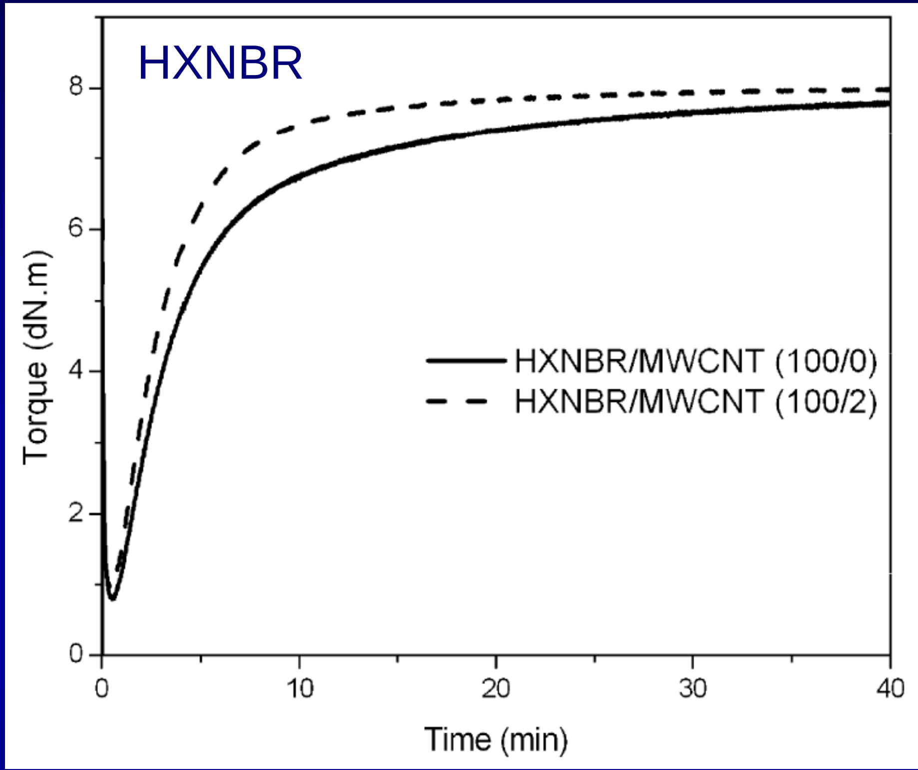
Further scorch time increase for CNT with COOH groups

Higher Modulus

	Amounts
	phr
NR	100
Zinc Oxide	5
Stearic Acid	2
Antioxidant (Polymerized trimethyl quinoline)	1
Multiwall carbon nanotube	1
MBTS	1,2
TMT	0,6
Sulfur	2,5

M. Shanmugharaj, J. H. Bae, K. Y. Lee, W. H. Noh, S. H. Lee, S. H. Ryu, *Compos. Sci. Technol.* 67, 1813 (2007).

Vulcanization behaviour



HXNBR
33% AN,
5% COOH
3.5% residual double bonds

CNT = 0, 1, 2 and 4 phr

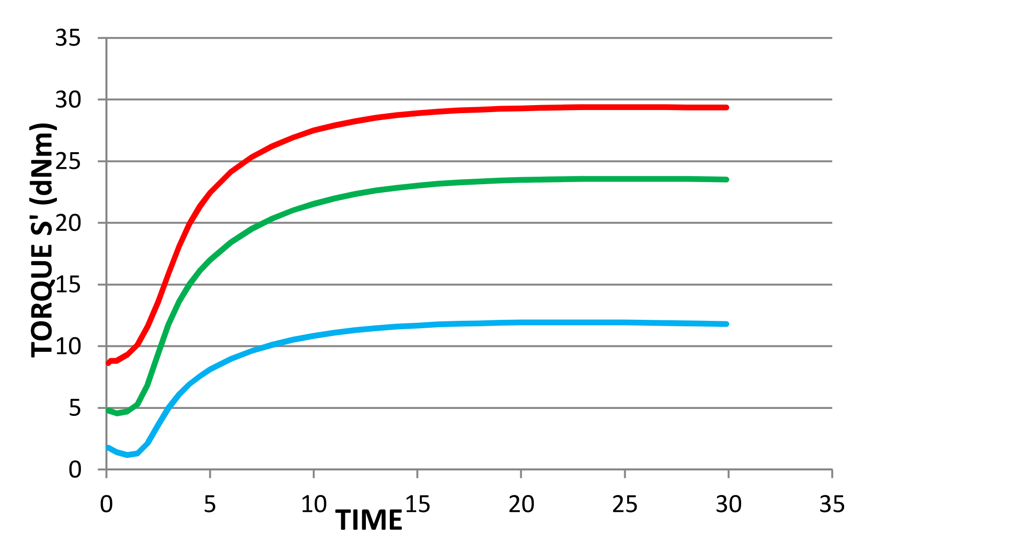
DCP = 3 phr

Shorter scorch due to the increase of thermal conductivity

Higher Modulus

L. Lu, Y. Zhai, Y. Zhang, C. Ong, S. Guo
Appl. Surf. Sci. **255**, 2162 (2008).

Vulcanization behaviour



	GR ' RAW' + CB	GR ' RAW' + CNT	GR ' RAW' + 50CNT/50CB
	phr	phr	phr
NR	100	100	100
CB – N 326	35	0	17,5
CNT	0	35	17,5
Zinc Oxide	6	6	6
Stearic Acid	0,5	0,5	0,5
Sulfur	3,5	3,5	3,5
TBBS	0,7	0,7	0,7

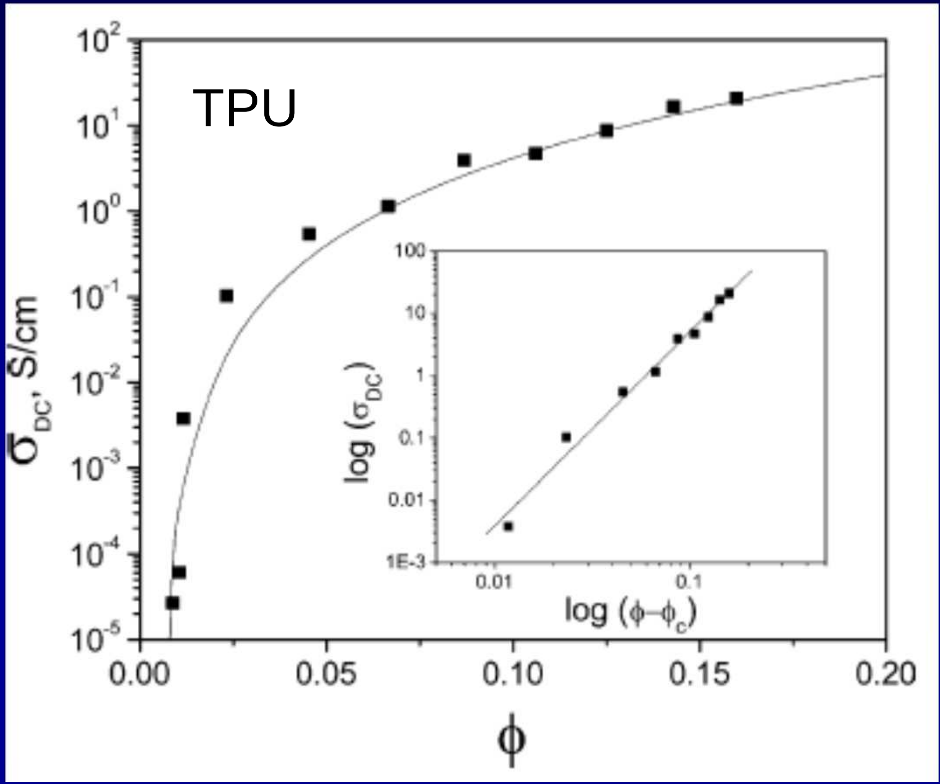
Shorter scorch

Higher Modulus

	NR + CB	NR + CNT	NR + $CNT_{50\%}/CB_{50\%}$
MAXIMUM TORQUE (dNm)	11,94	29,4	23,61
t (1) min	**2,01**	**1,25**	**1,67**
t (90) min	**7,27**	**3,65**	**4,9**

S. Musto, M. Galimberti
Unpublished results

Electrical Conductivity



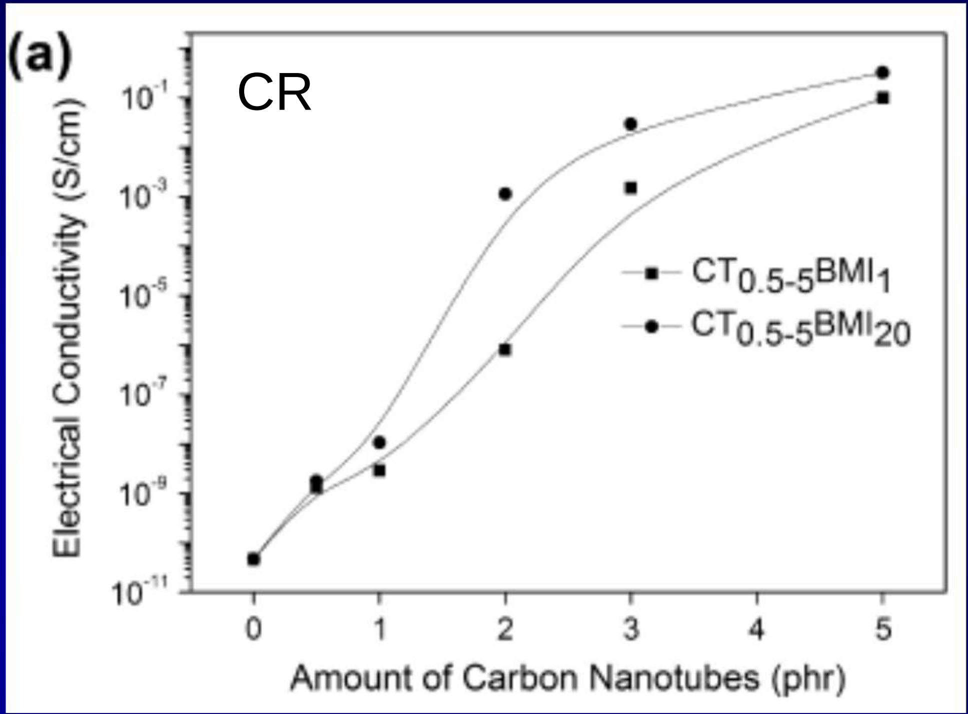
MWCNT ≈ 0.5 – 10 Vol%

Low electrical Percolation
φ (volume fraction) ~ 0.005

Conductivity
σ ~ 1-10 S/cm

Hilmar Koerner, Weidong Liu, Max Alexander, Peter Mirau, Heather Dowty, Richard A. Vaia
Polymer (2005), 46, 4405 -4420

Electrical Conductivity



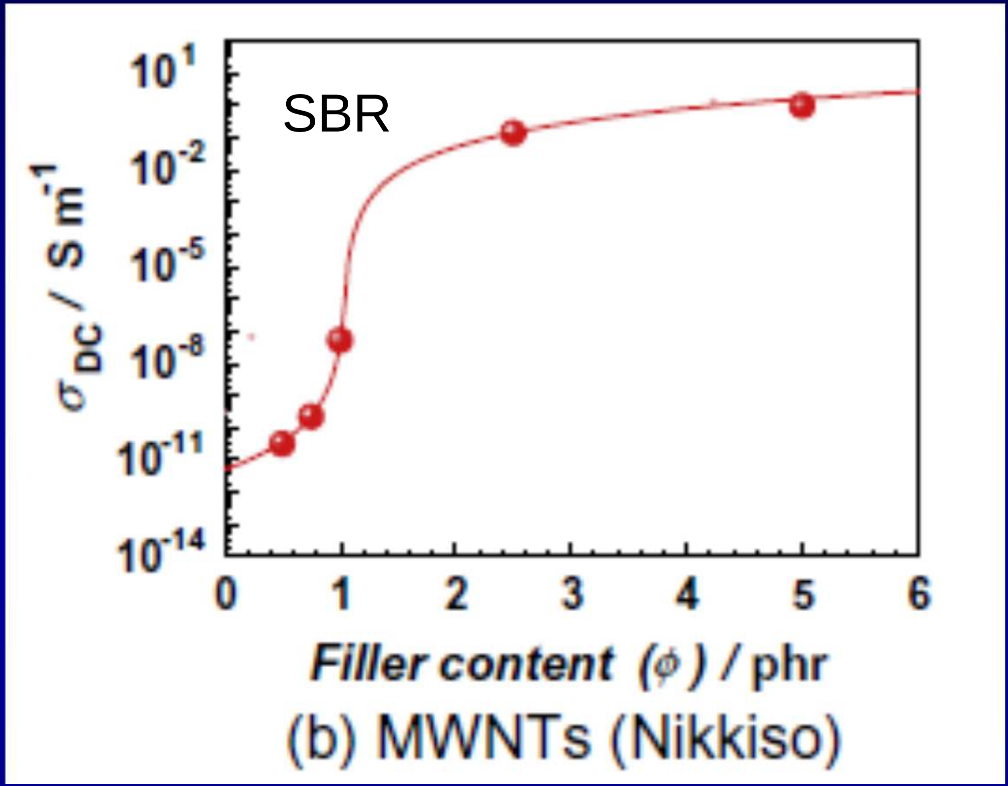
BMI = ionic liquid

Percolation Threshold
1 - 3 phr

Conductivity
$\sigma_{DC} \sim 10^{-1}$ S/cm

Kalaivani Subramaniam, Amit Das, Gert Heinrich
Composites Science and Technology (2011), 71, 1441 - 1449

Electrical Conductivity



Percolation Threshold

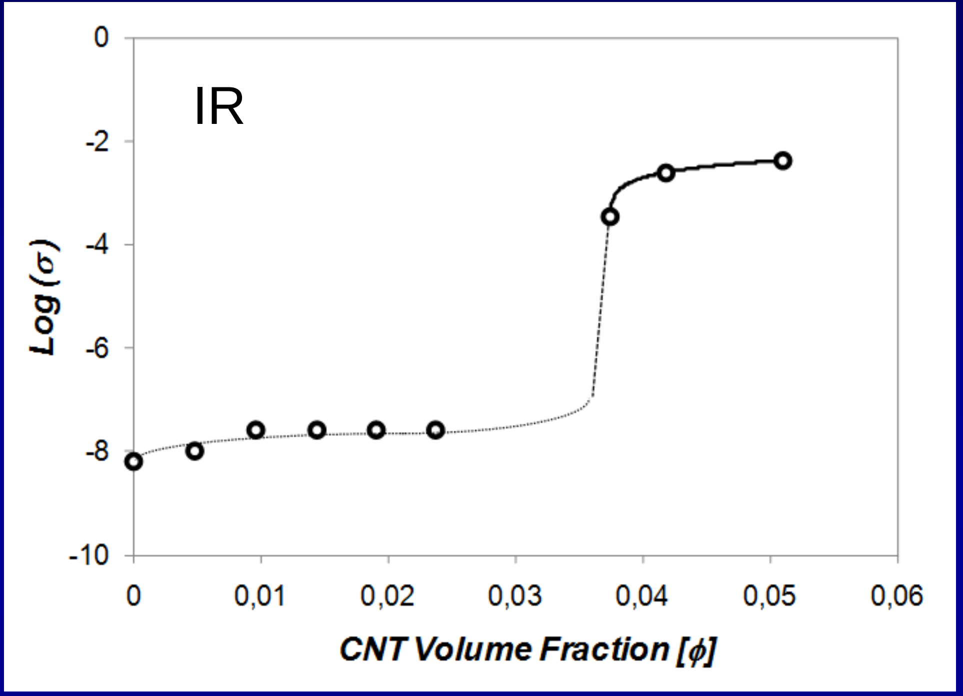
$\varphi c \approx 0.95$ phr

Conductivity

$\sigma_{DC} \sim 5 \cdot 10^{-2}$ S/cm

Koji Tsuchiya, Ayumu Sakai, Tomoya Nagaoka, Katsumi Uchida, Takeo Futukawa, Hirofumi Yajima
Composites Science and Technology (2011), 71, 1098 - 1104

Electrical Conductivity

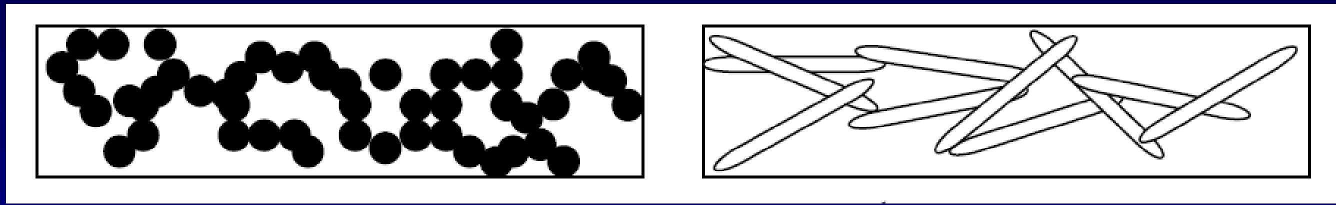


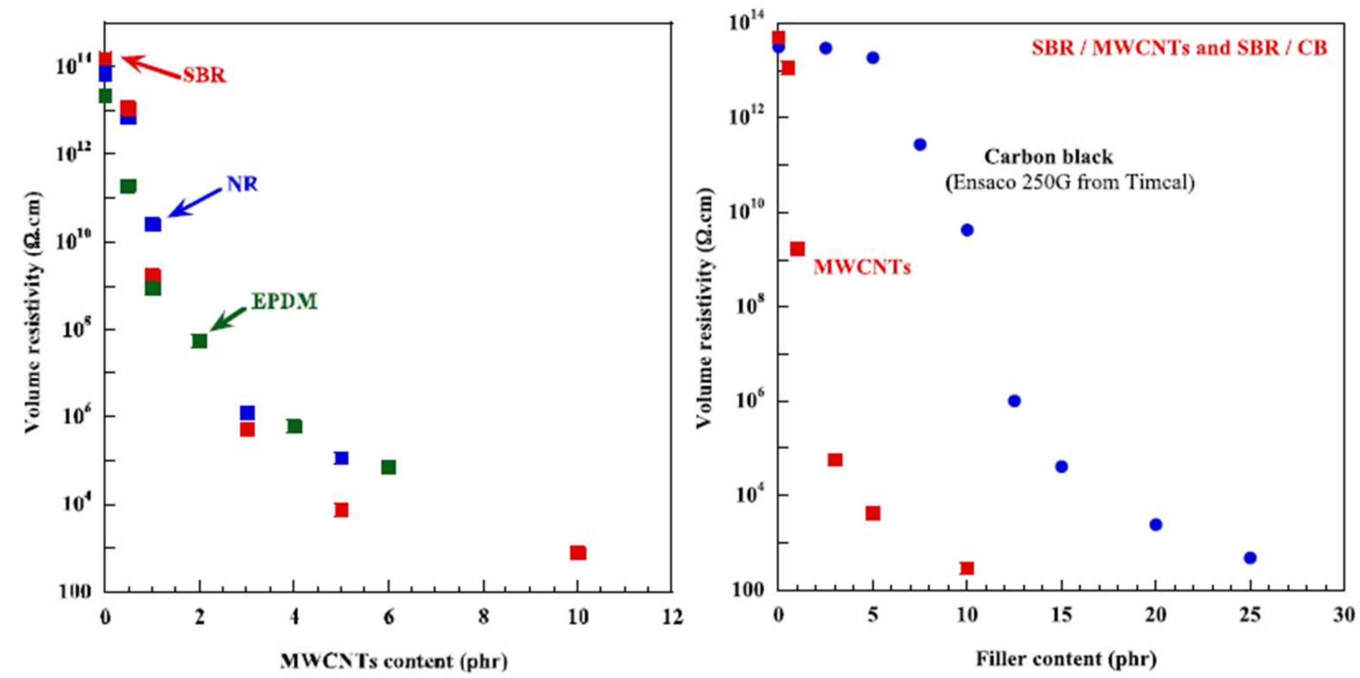
Percolation Threshold
φ_c (volume fraction) $\approx$ 0.037

Conductivity
$\sigma_{DC} \approx 10^{-2}$ S/m

Galimberti M., Coombs M., Riccio P., Ricco` T., Passera S., Pandini S., Conzatti L., Ravasio A., Tritto I.
Macromol. Mater. Eng. 2012, 298(2), 241-251

Electrical conductivity



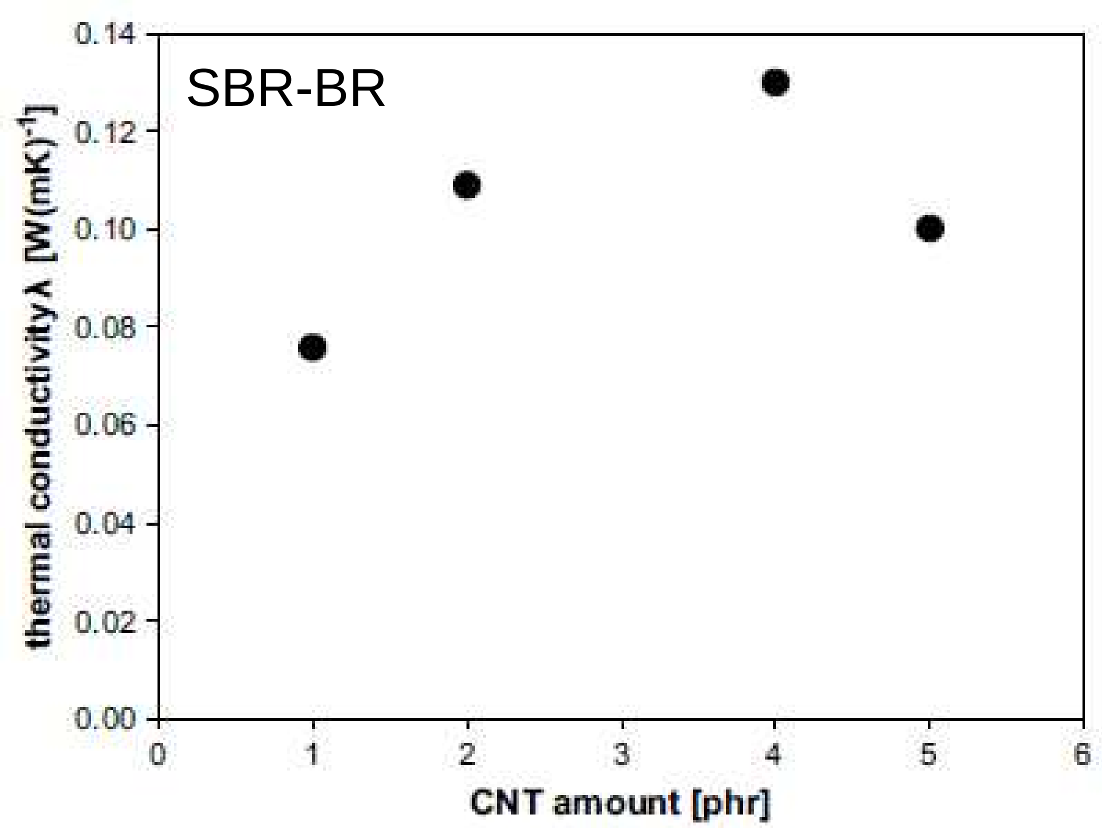


Percolation threshold at ~ 0. 5 phr (vol. fraction ~ 0.002)

L. Bokobza
Presented at 181th Technical Meeting of the Rubber Division of ACS, San Antonio (TX)
April 22-25, 2012

Thermal Conductivity

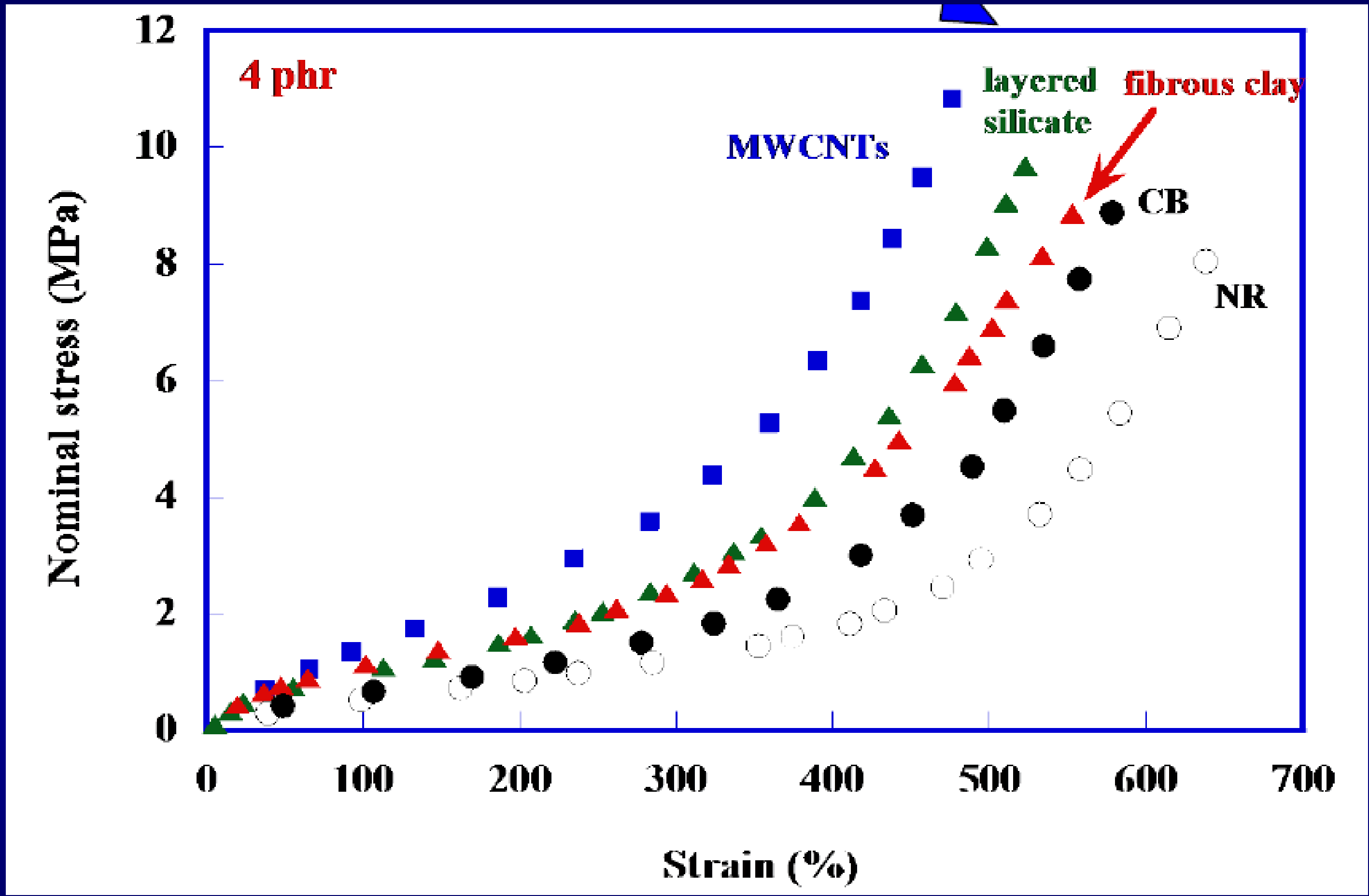
CNT (*Wet* melt blending)



Slight enhancement

A. Das, K.W. Stockelhuber, R. Jurk, M. Saphiannikova, J. Fritzsche, H. Lorenz, M. Kuppler, G. Heinrich
Polymer 2008, 49, 5276 - 5283

Mechanical Properties



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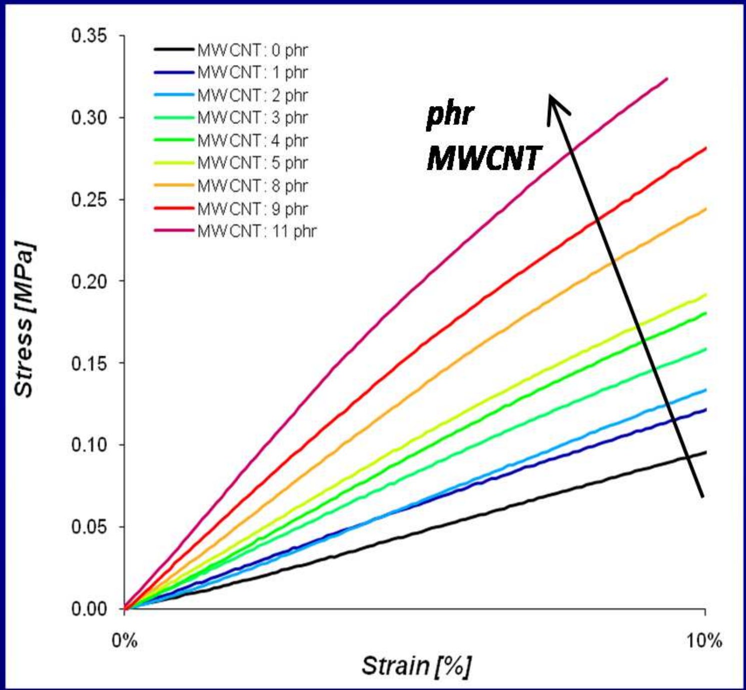
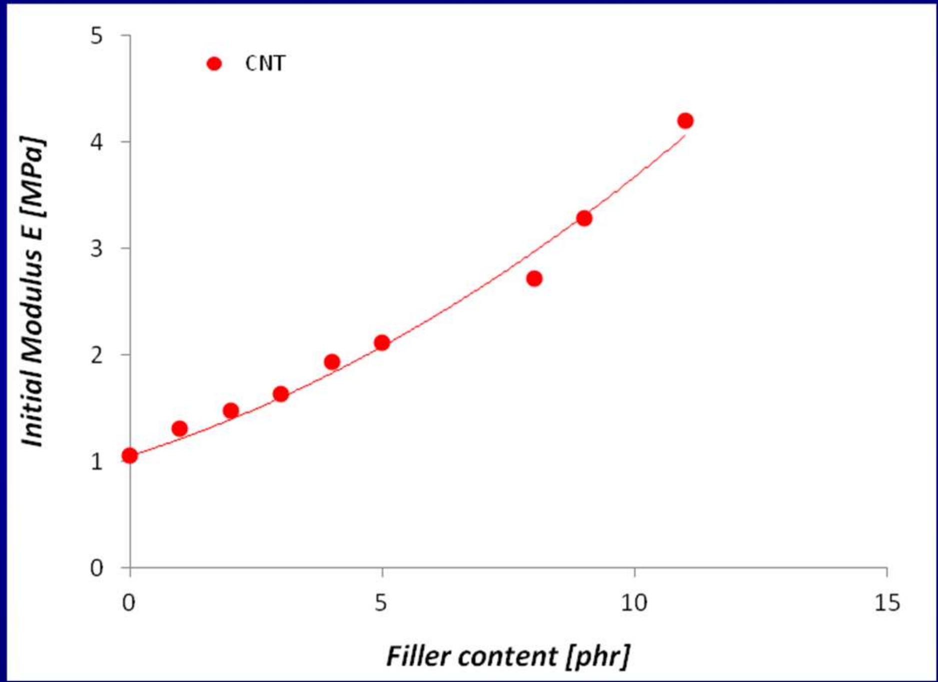
Presented at 181th Technical Meeting of the Rubber Division of ACS, San Antonio (TX)
April 22-25, 2012

Mechanical Properties

Stress strain curves

E Initial modulus
from stress strain curves



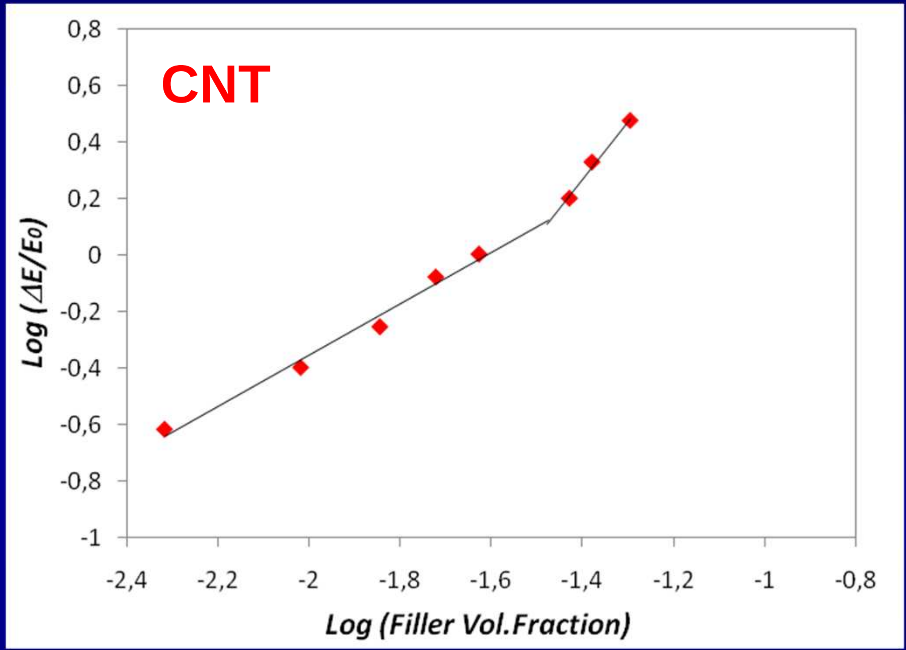


Galimberti M., Coombs M., Riccio P., Ricco` T., Passera S., Pandini S., Conzatti L., Ravasio A., Tritto I.
Macromol. Mater. Eng. 2012, 298(2), 241-251

Mechanical Properties

Filler percolation threshold

Hüber – Vilgis plots*



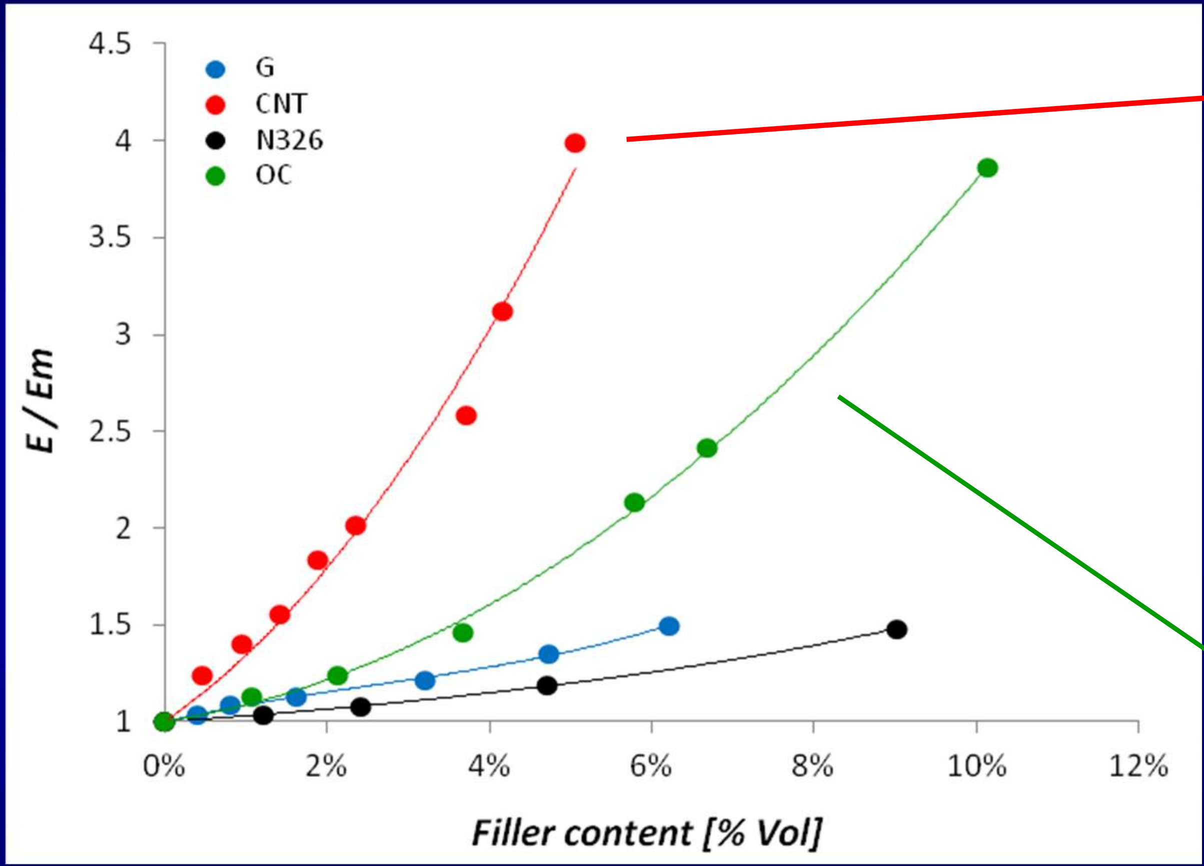
ϕ = 0.034 phr = 7.2

Galimberti M. et al.
Macromol. Mater. Eng. 2012, 298(2), 241-251

* Huber G., Vilgis T.A.,
Kaut Gummi Kunstst 52(2) (1999) 102-7

Mechanical Properties

E initial modulus vs. Filler content



From Guth Equation:
$f_{CNT} = 22$

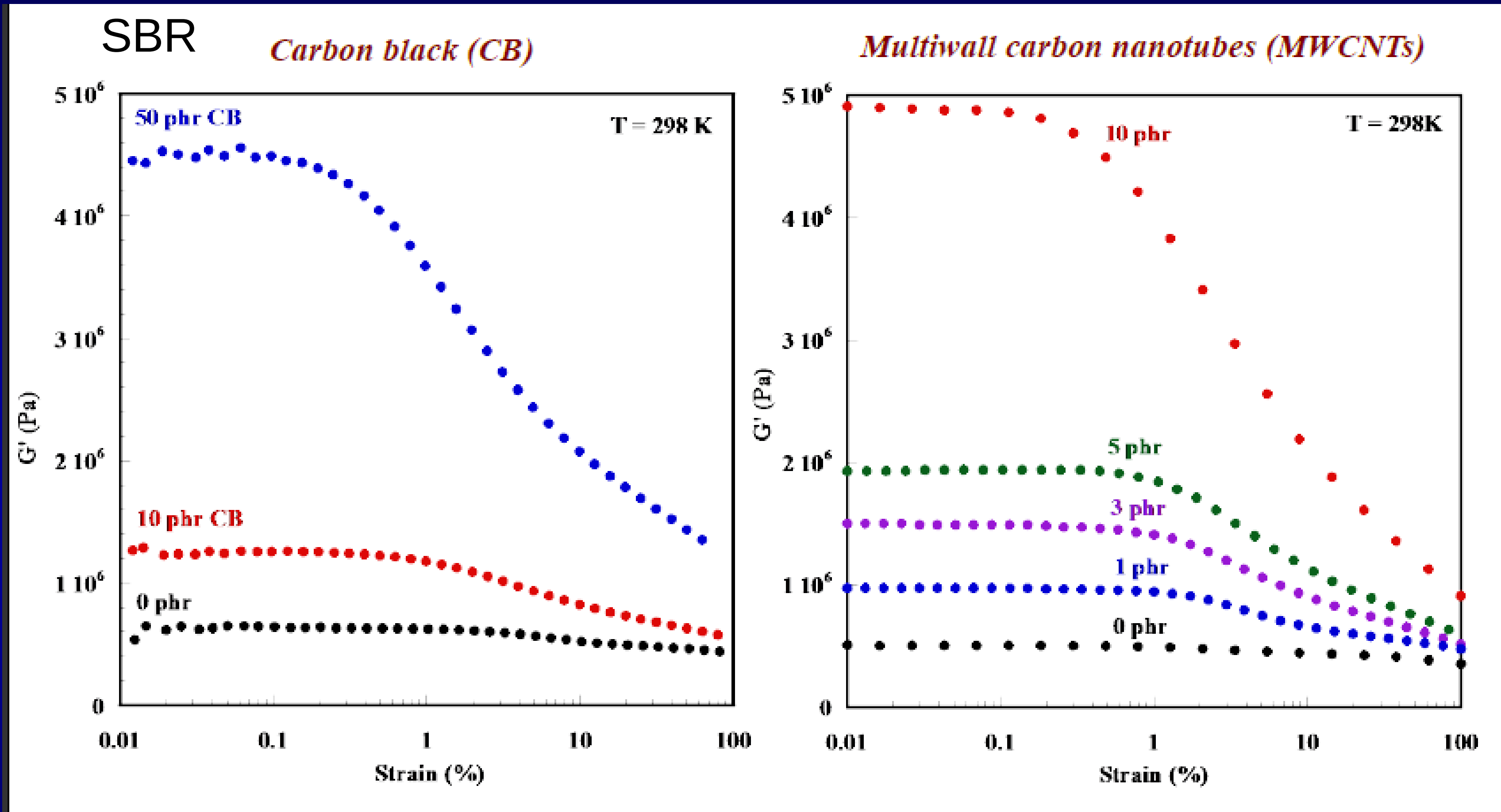
From Guth Equation:
$f_{OC} = 11.5$

Galimberti M., Coombs M., Cipolletti V., Riccio P., Ricco` T., Pandini S., Conzatti L., *Applied Clay Science* 65–66 (2012) 57–66

Galimberti M., Coombs M., Riccio P., Ricco` T., Passera S., Pandini S., Conzatti L., Ravasio A., Tritto I. *Macromol. Mater. Eng.* 2012, 298(2), 241-251

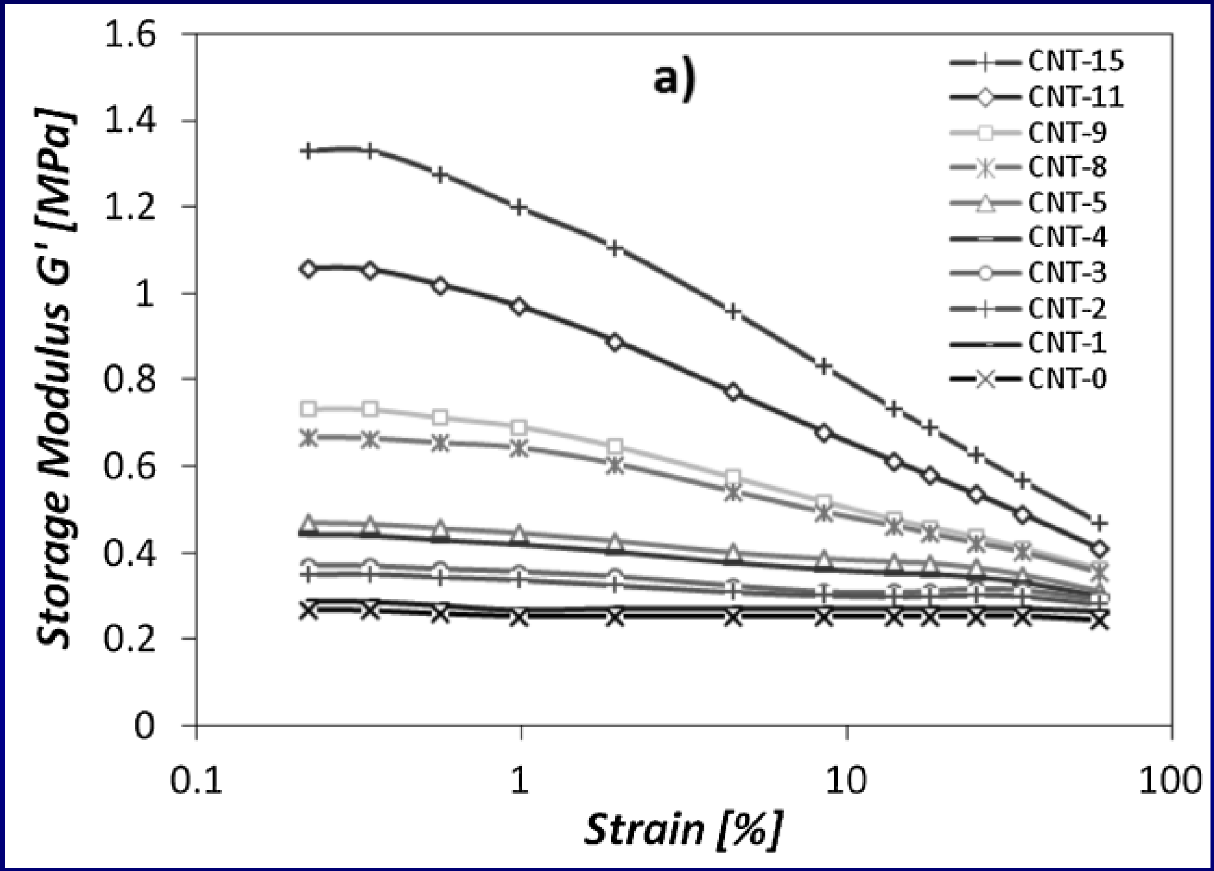
M. Galimberti, V. Kumar, M. Coombs, V. Cipolletti, S. Agnelli, S. Pandini, L. Conzatti, *Rubber Chem. Technol*. in press

Non linearity of dynamic mechanical behaviour



L. Bokobza
Presented at 181th Technical Meeting of the Rubber Division of ACS, San Antonio (TX)
April 22-25, 2012

Non linearity of dynamic mechanical behaviour



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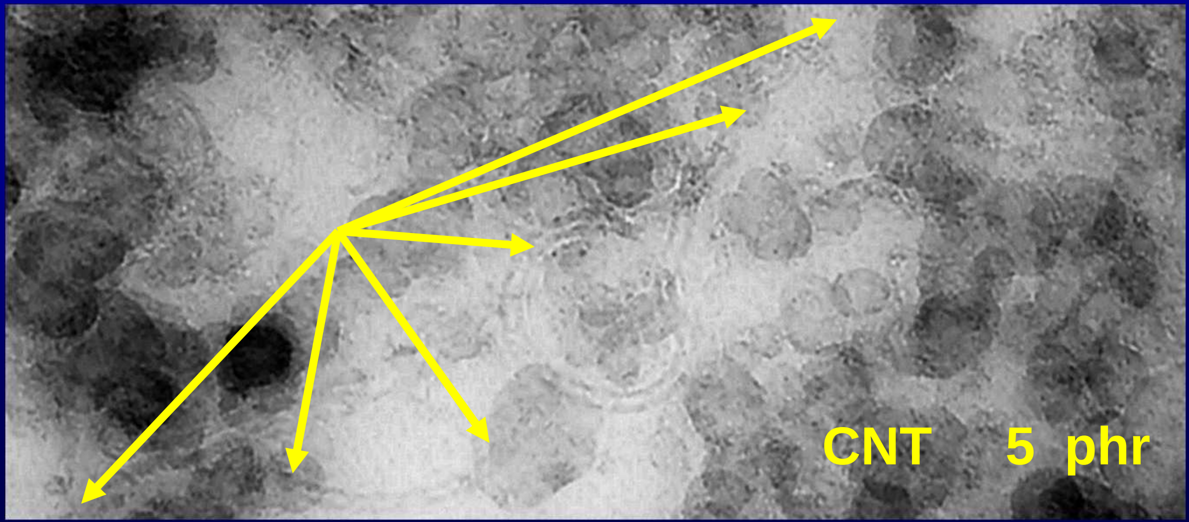
Hybrid filler systems based on CNT

IR + CB + CNT nanocomposites - TEM micrographs

CNT	0	1.1	2.3	3.4	4.6	5.7	8	11.3
Other ingredients: ZnO 4 , Stearic acid 2 , Sulphur 2 , CBS 1 , Phtalic Anhydride 1								

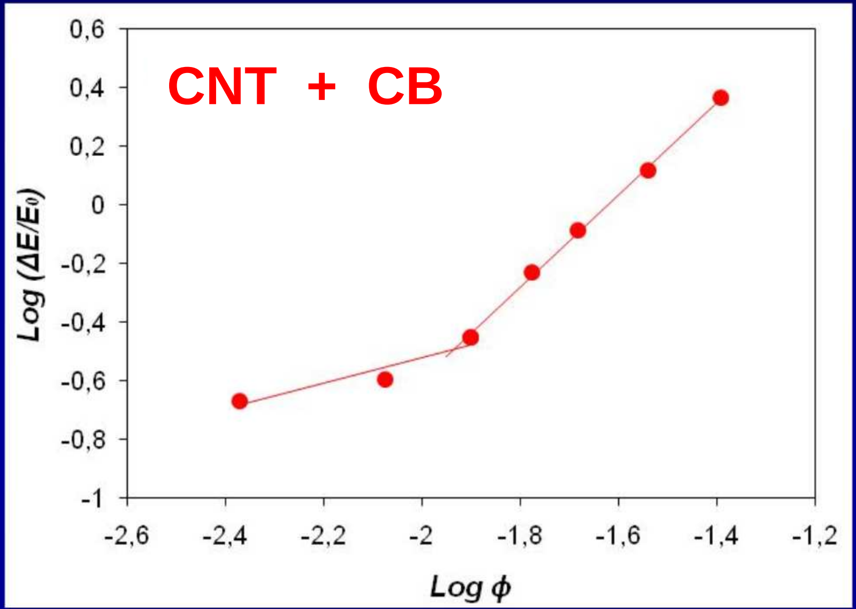
IR = 100 CB = 60

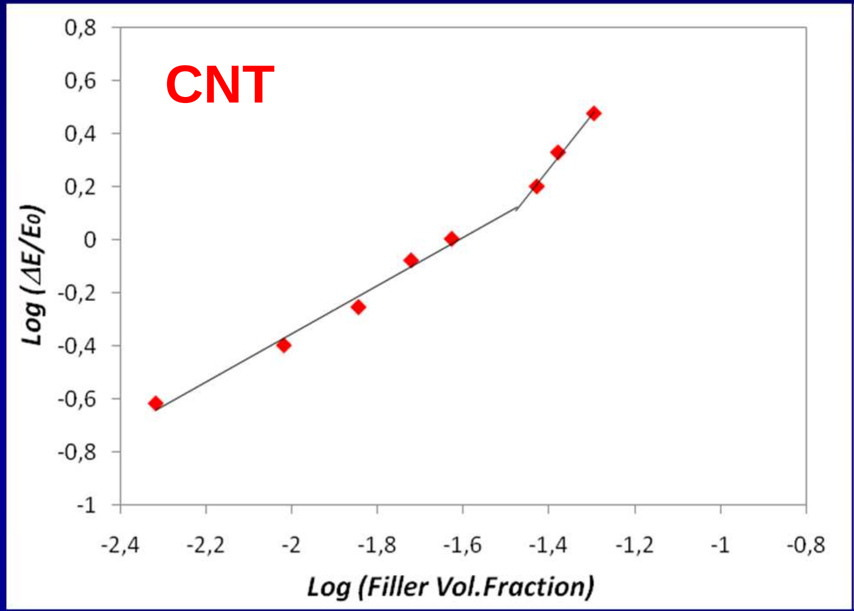


☞ High affinity of CNT for Carbon Black

IR + CB + CNT nanocomposites - Filler network

Filler percolation threshold





phr = 2.8

phr = 7.2

G. Huber, T. A. Vilgis,
Kaut Gummi Kunstst. 1999, 52(2), 102-7

Galimberti M., Coombs M., Riccio P., Ricco` T., Passera S., Pandini S., Conzatti L., Ravasio A., Tritto I.
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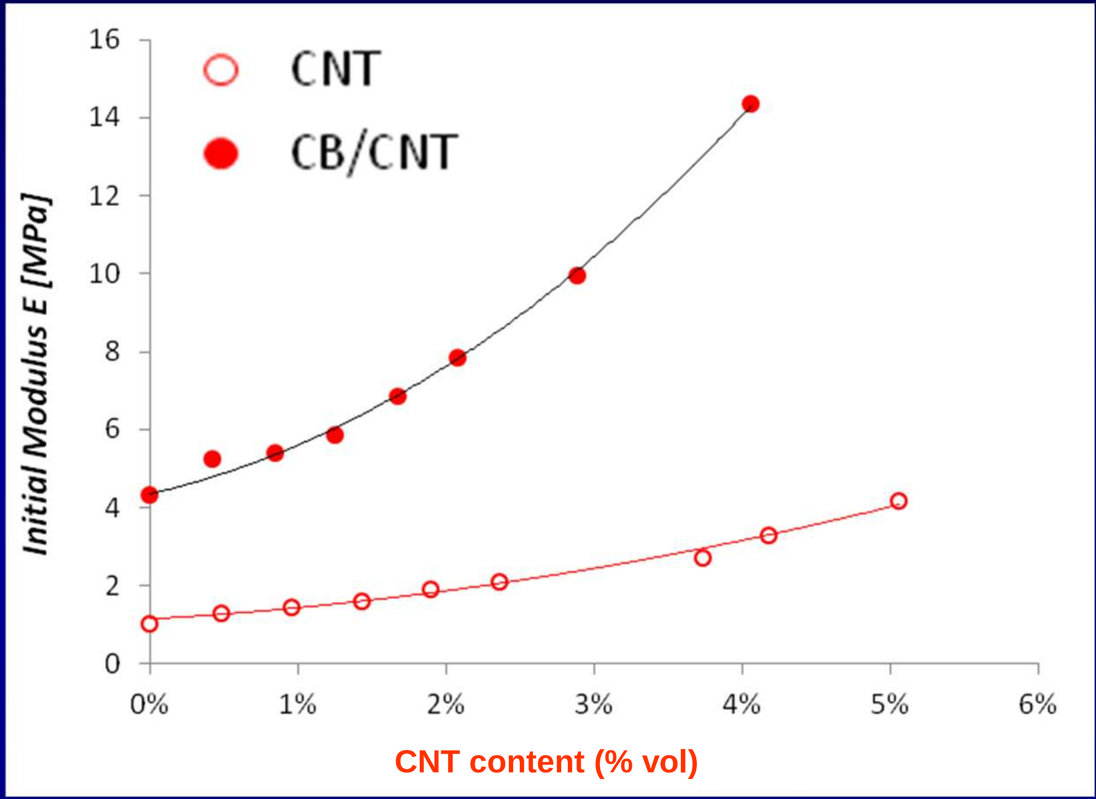
IR + CB + CNT nanocomposites - Initial modulus



Galimberti M., Coombs M., Cipolletti V., Riccò T., Agnelli S.,Pandini S., KGK 2013 in press

Interactions between CB and nano-fillers

First approach:

Prediction of E modulus from simple additive model

↓

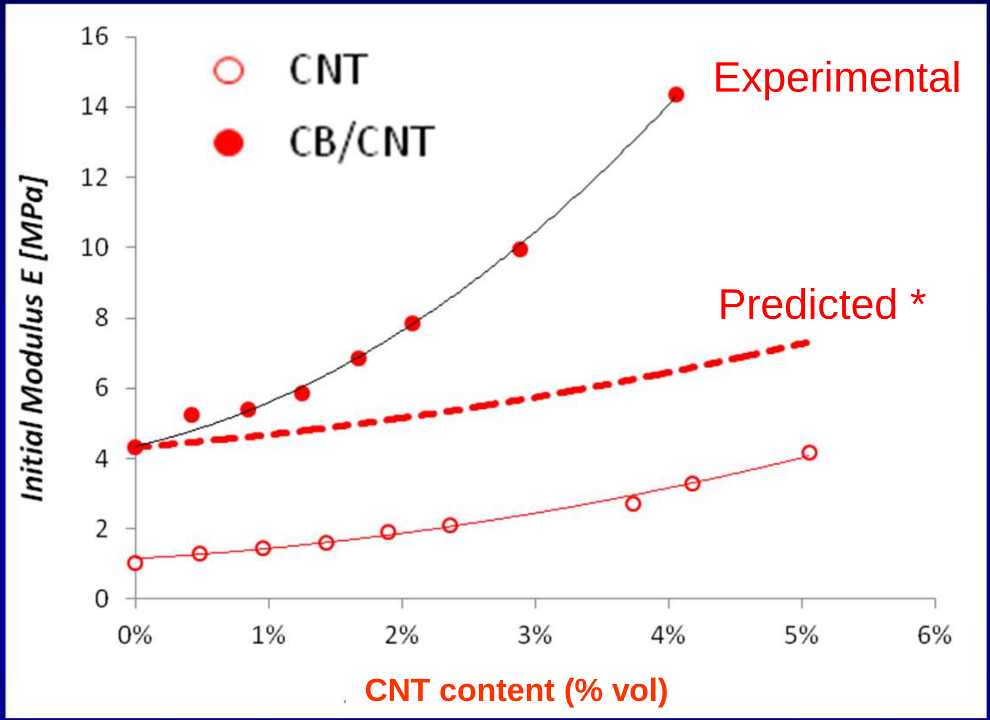
$$E_{(CB + nanofiller)} = E_{(CB)} + E_{(nanofiller)} - E_{(IR)}$$

For interacting mixtures

there should be an interactive term

S.S. Sternstein, G. Ramorino, B. Jang, Ai-Jun Zhu. RCT vol. 78 (2), 258-270, (2005)

IR + CB + CNT nanocomposites



* E (CB+CNT) = E (CB) + E (CNT) - E (IR)

Galimberti M., Coombs M., Cipolletti V., Riccò T., Agnelli S.,Pandini S., KGK 2013 in press

Interactions between CB and nano-fillers

E (CB + nanofiller) = E (CB) + E (nanofiller) - E (IR) + ΔE

Interactive term

Caveat!

☞ Δ is due to non linearity of reinforcement

☞ Different relative amount of fillers

S.S. Sternstein, G. Ramorino, B. Jang, Ai-Jun Zhu. RCT vol. 78 (2), 258-270, (2005)

Composites based on CB and CNT

IR = 100

☞

CB	0	2.50	5.00	10.00	15.00	30.0

☞

CNT	0	2.50	5.00	10.00	20.00

☞

CB	0	1.25	2.50	5.00	10.00
CNT	0	1.25	2.50	5.00	10.00

Recipes in phr, Fillers with the same volume fraction

Composites crosslinked with dicumyl peroxide: 1.40 phr

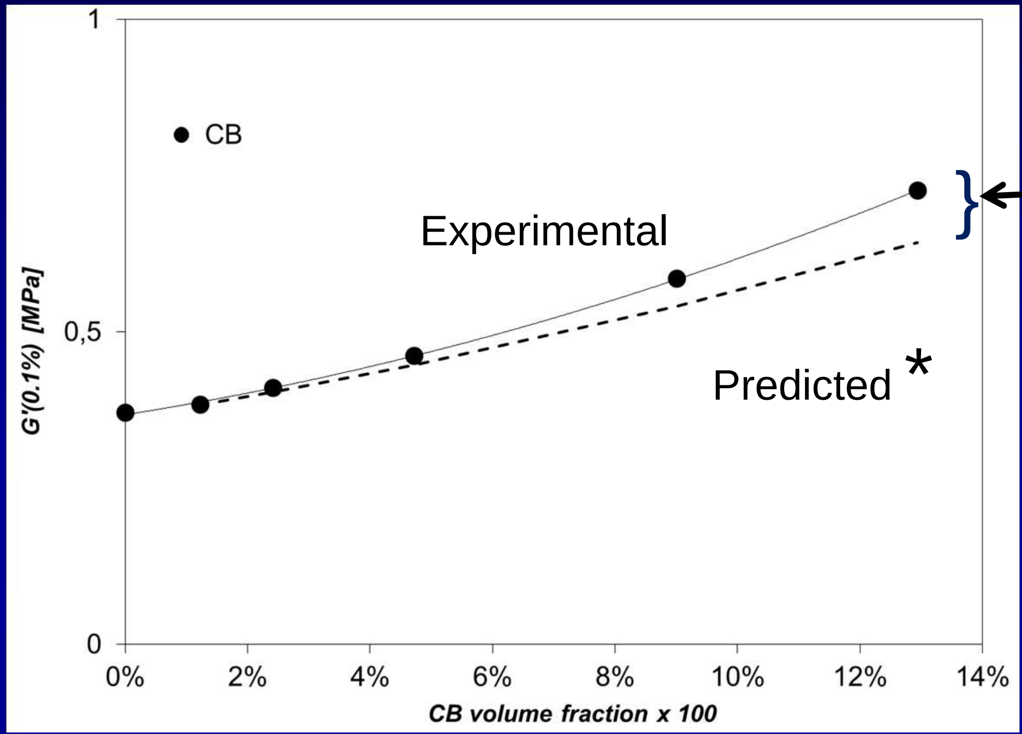
Interactions between CB and nano-fillers

$$G' (CB + filler) = G' (CB) + G' (filler) - G' (IR) + \Delta G'$$

Interactive term

$$\Delta G' = G' (CB + filler) - G' (CB) - G' (filler) + G' (IR)$$

Composites based on CB

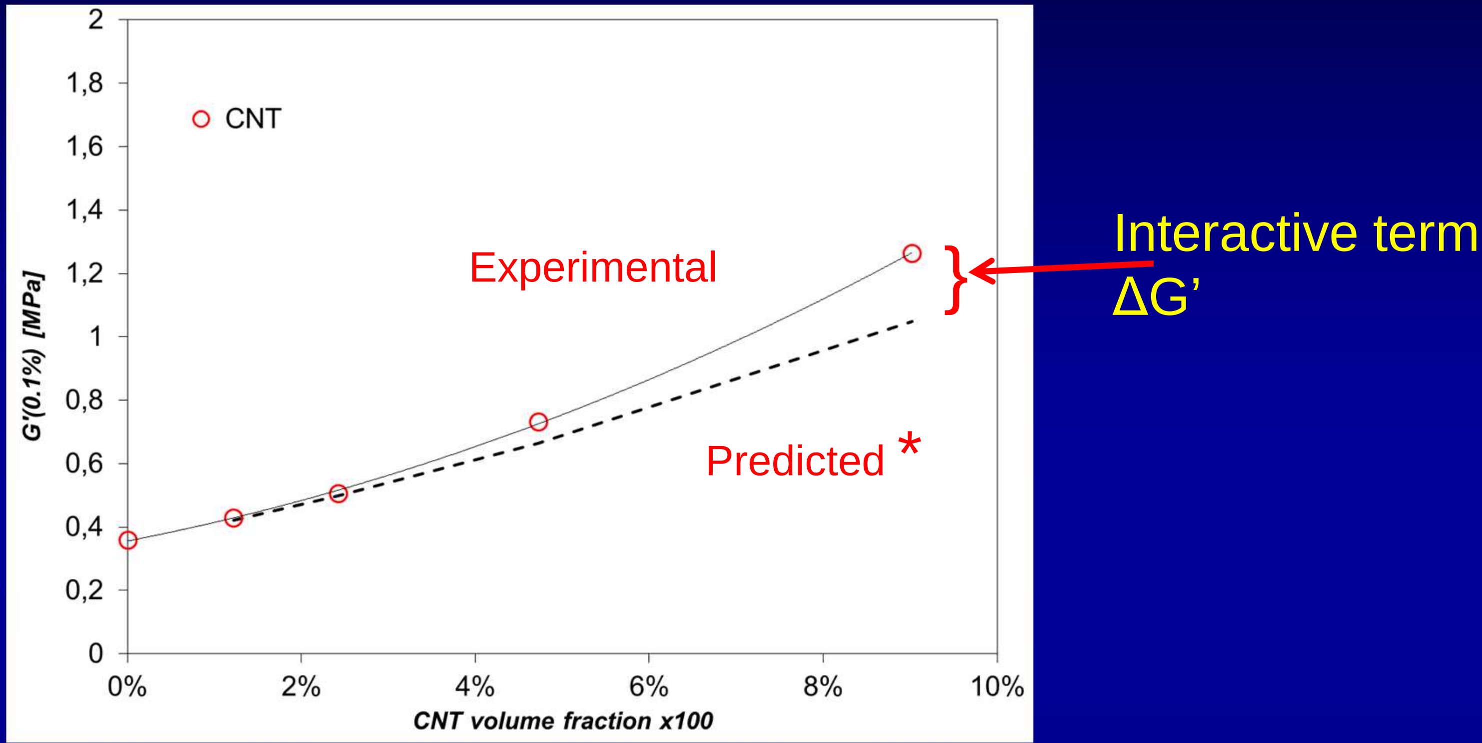


Interactive term $\Delta G'$

For a given volume fraction χ_i

$$* \quad [G'_{predicted}(CB + CB)]_{\chi_i} = G'(CB)_{\chi_i/2} + G'(CB)_{\chi_i/2} - G'(IR)$$

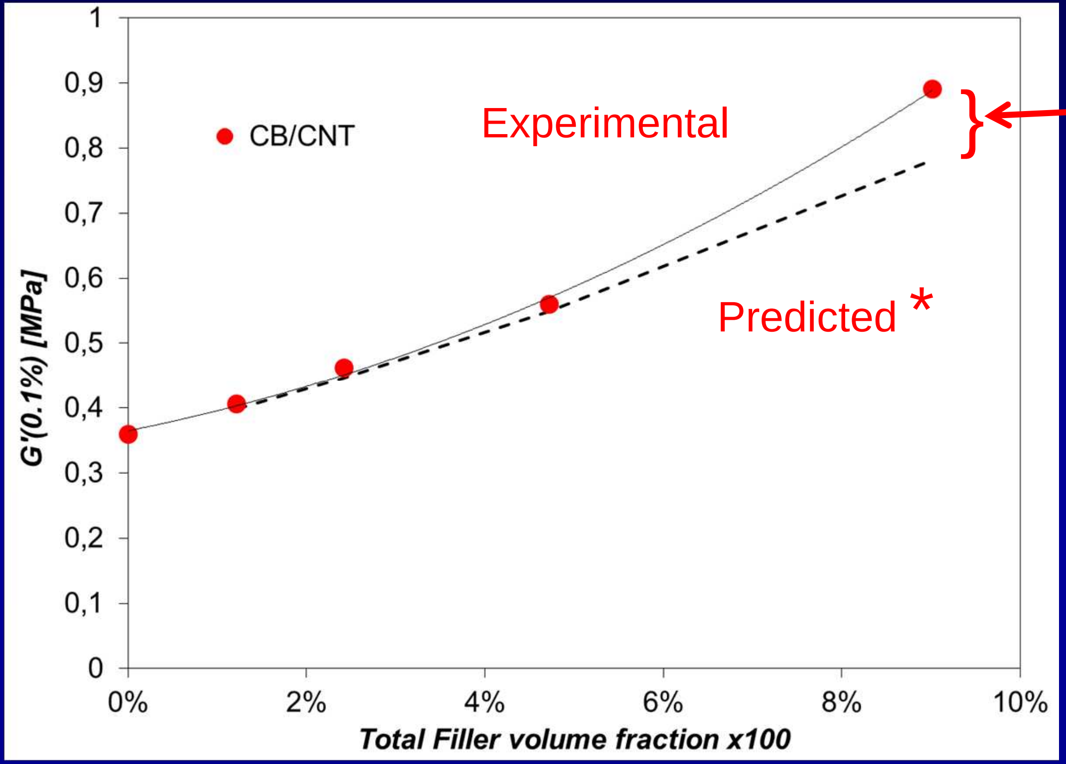
Composites based on CNT



For a given volume fraction χ_i

$$* \quad [G'_{predicted}(CNT + CNT)]_{\chi_i} = G'(CNT)_{\chi_i/2} + G'(CNT)_{\chi_i/2} - G'(IR)$$

Composites based on CB and CNT



Interactive term
ΔG'

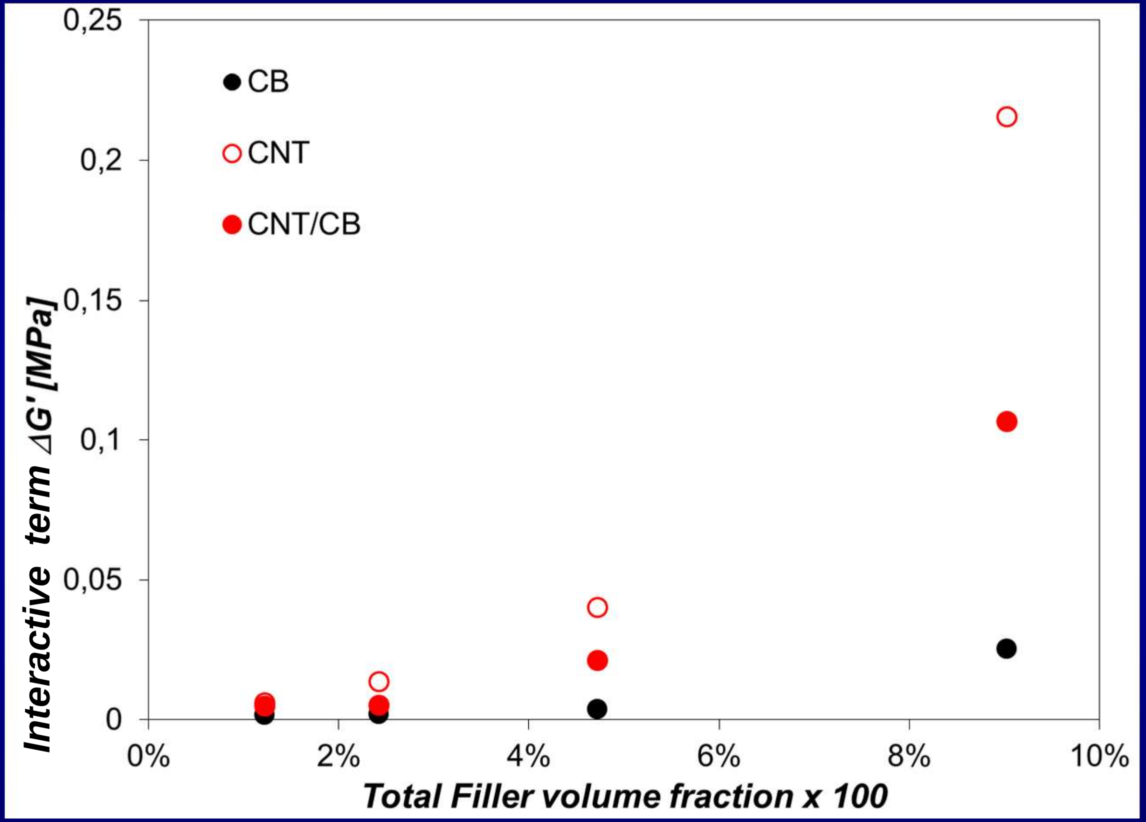
For a given volume fraction χ_i

*

$$[G'_{predicted}(CB + CNT)]_{\chi_i} = G'(CB)_{\chi_i/2} + G'(CNT)_{\chi_i/2} - G'(IR)$$

Composites based on CB and CNT

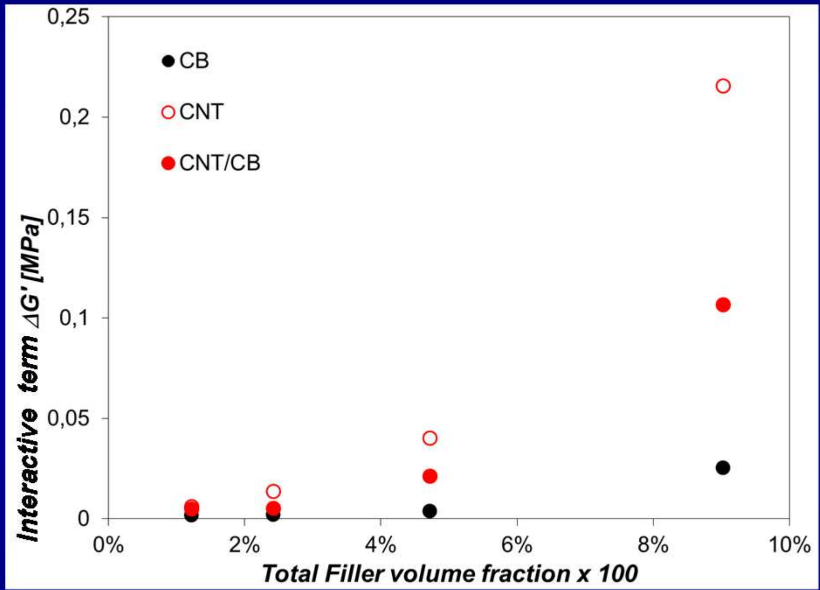
Interactive term ΔG' vs total filler volume fraction

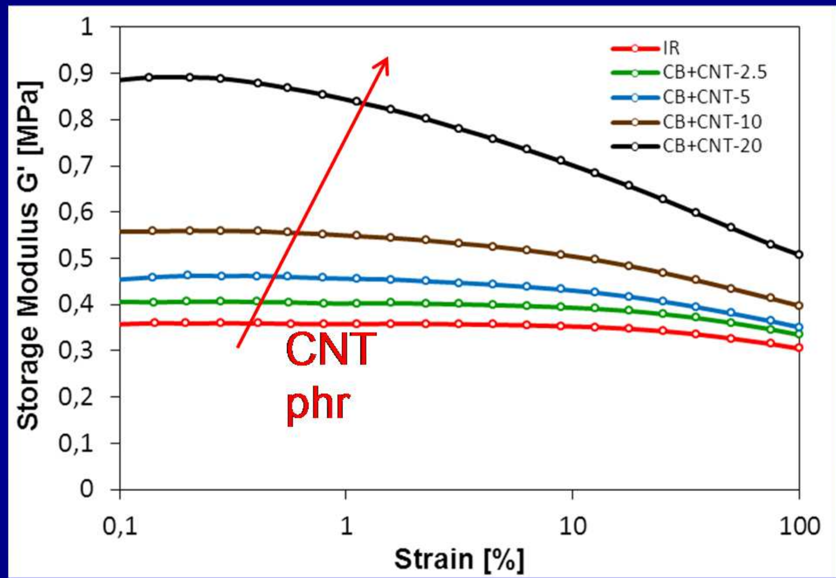


M. Galimberti, M. Coombs, V. Cipolletti, T. Riccò, S.Agnelli, S. Pandini,
Presentation at "KHK 10th Fall Rubber Colloquium, Hannover (D), November, 7th - 9th 2012"

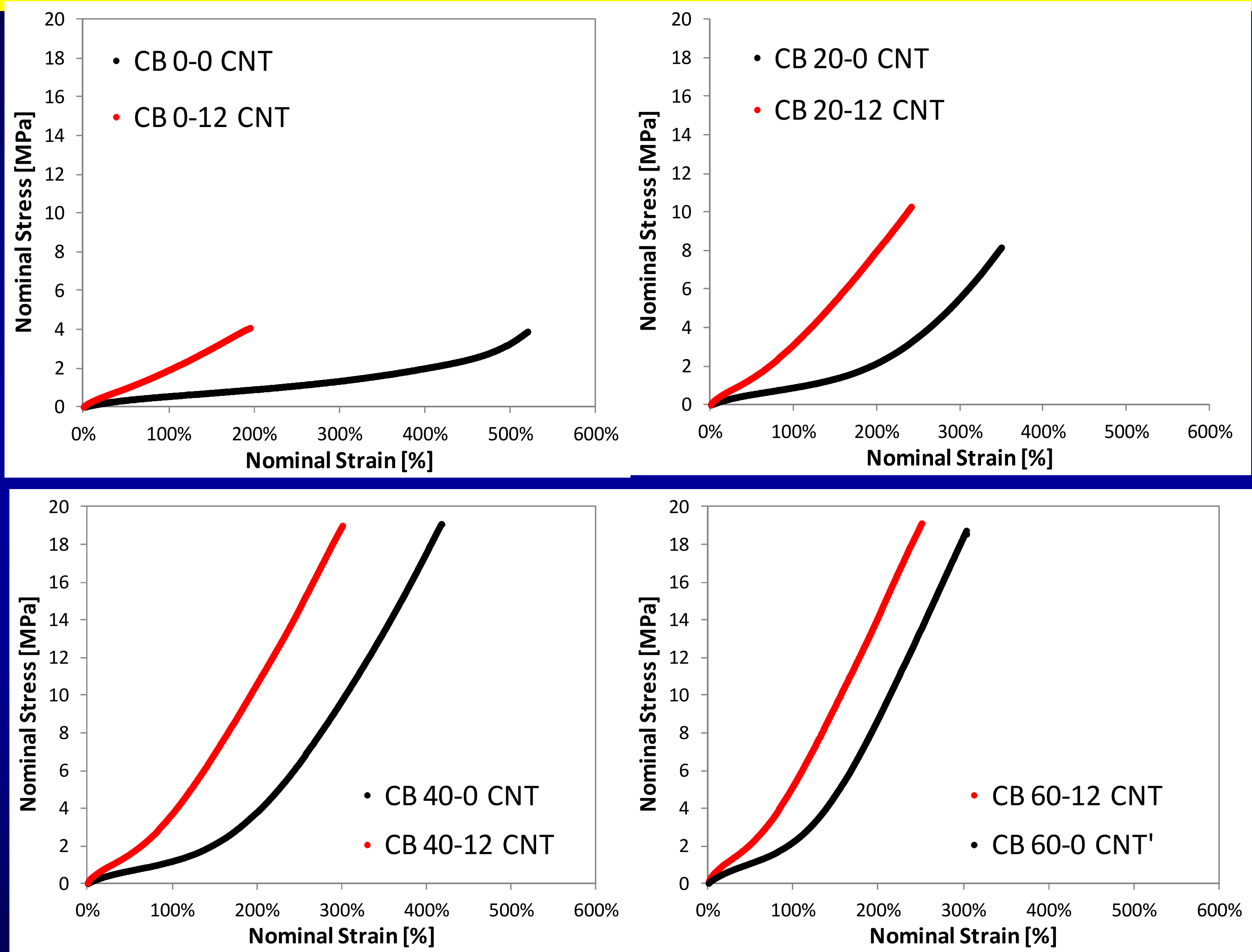
Non linearity of dynamic mechanical behaviour

Shear storage modulus vs strain amplitude





Hybrid filler systems: CNT + CB – Stress strain curves



M. Galimberti et al Presented at 181th Technical Meeting of the Rubber Division of ACS, San Antonio (TX) April 22-25, 2012

Conclusions: CNT .....

- ☞ Enhance
  - electrical conductivity
  - thermal conductivity
  - mechanical properties
  - vulcanization efficiency
- ☞ Can be evenly distributed and dispersed through "drop in" processing technologies
- ☞ Can be used in a much lower amount with respect to traditional fillers
- ☞ Establish hybrid filler networks