Anisotropic effects and master curves for rubbers with sp^2 carbon allotropes: towards light weight materials

Maurizio Galimberti[1]

Silvia Guerra[1], Giuseppe Infortuna[1], Vincenzina Barbera[1], Andrea Bernardi[1], Giuseppe Mastinu[1], Silvia Agnelli[2], Stefano Pandini[2]

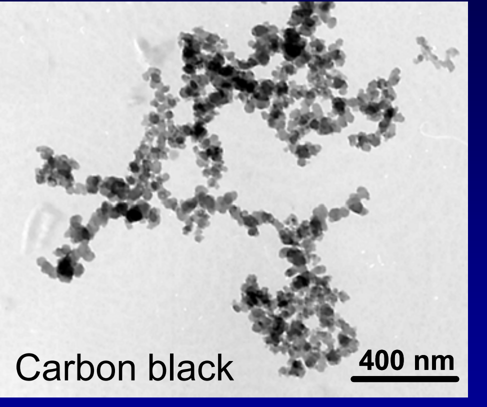
[1]Politecnico di Milano [2]Università di Brescia

International Elastomer Conference

192nd Technical Meeting ACS Rubber Division

Cleveland (OH) October 9 - 12, 2017

sp^2 Carbon allotropes



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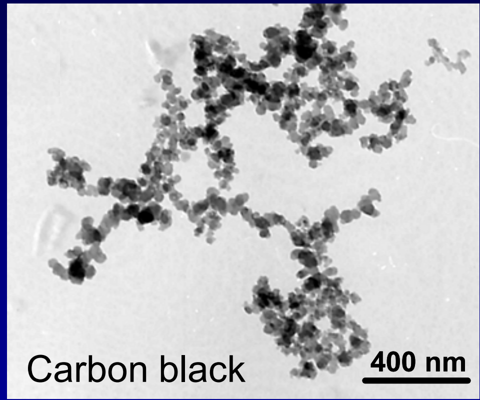
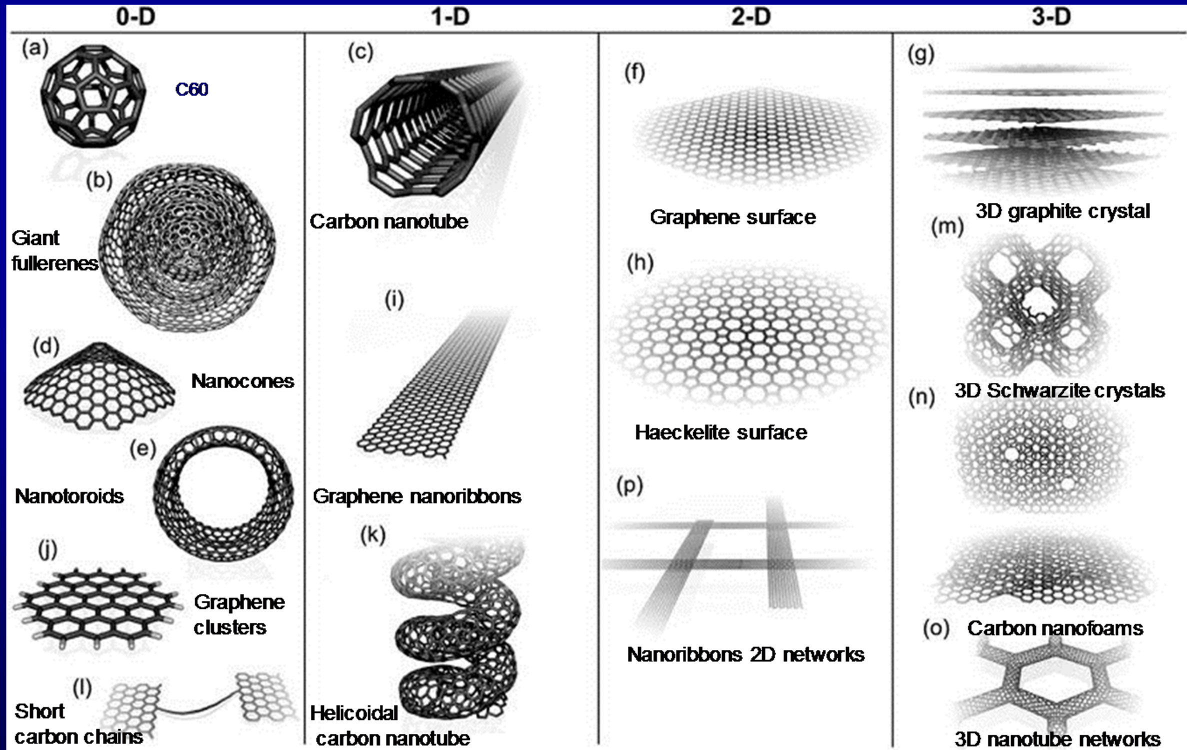
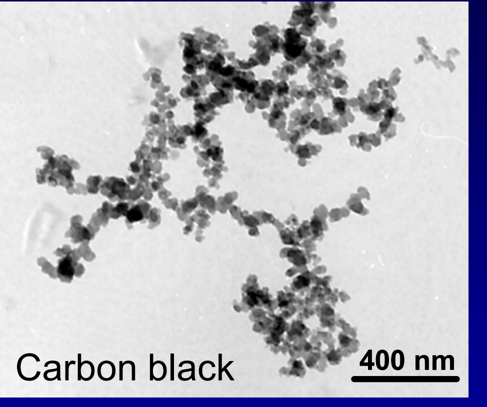
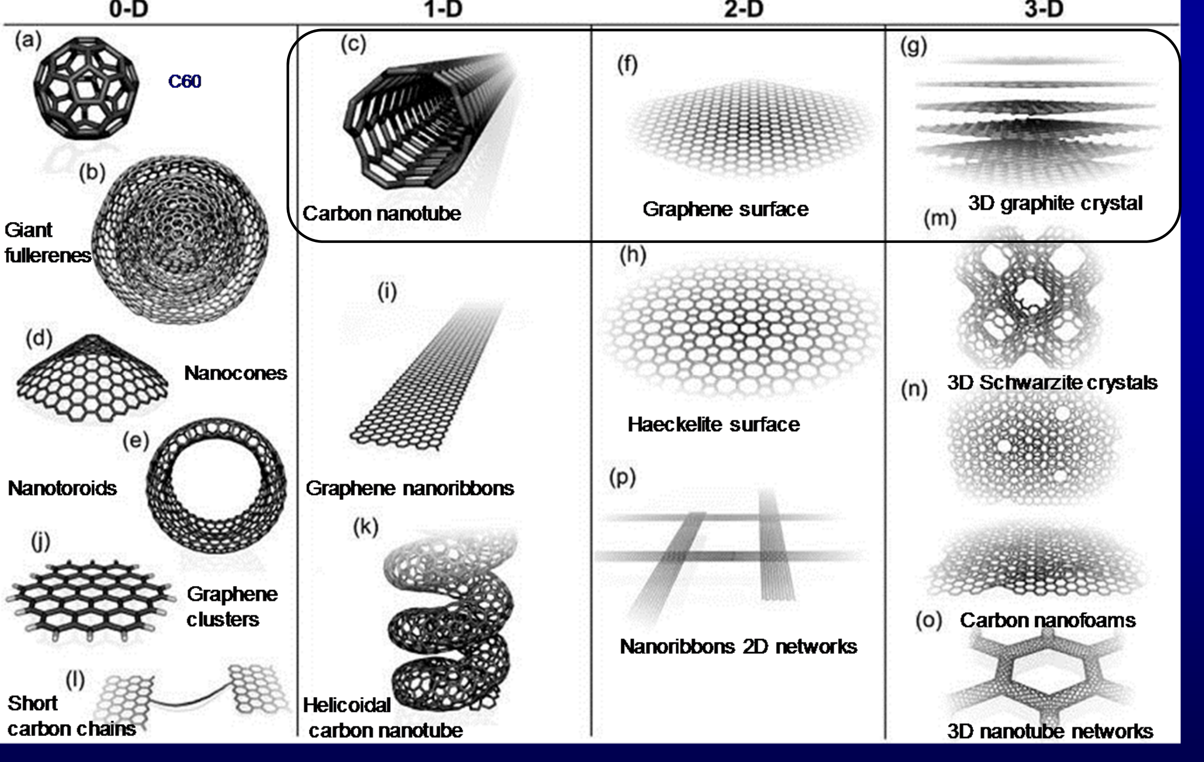




M. Terrones, et al. Nano Today 5 (4) (2010) 351e372.

sp^2 Carbon allotropes





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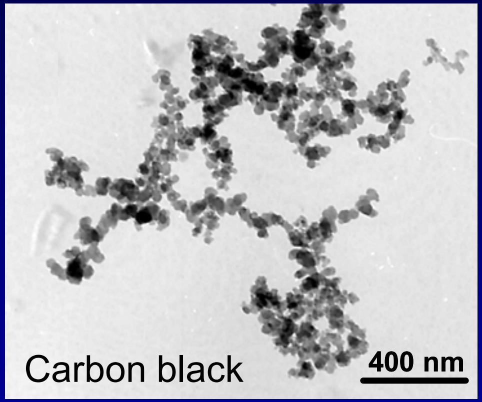
sp^2 Carbon allotropes



M. Terrones, et al. Nano Today 5 (4) (2010) 351e372. Jin Zhang et al, Carbon 98 (2016) 708e732

Objectives of the contribution to the Rubber Division Meeting

☞ Rationalization of sp^2 carbon allotropes, nano and nanostructured,
behaviour
in rubber compounds:
mechanical and electrical properties.

↓

Common correlations?

Prediction of properties and behaviour?

☞ Design of rubber materials

Characterization of sp^2 carbon allotropes

Carbon black

CBN326, N110: from Cabot

CNT

1 - Baytubes C150 P: from Bayer Material Science

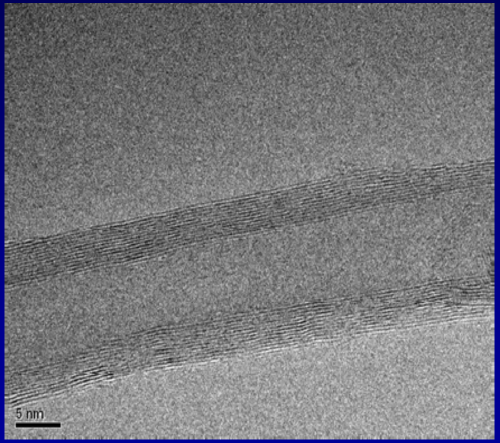
2 - NC7000: from Nanocyl

High surface area graphite (HSAG)

Asbury Synthetic Graphite 8427

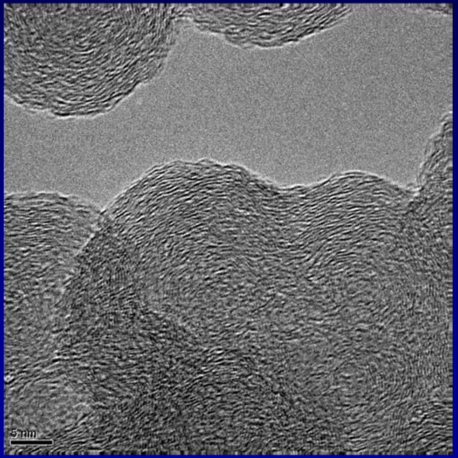
CNT and CB as the sp^2 carbon allotropes. How they look like?

CNT



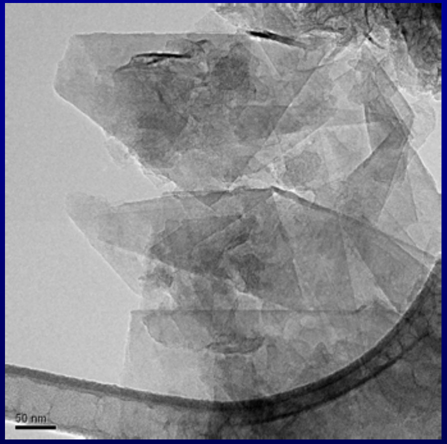
NANOCYL NC7000
from Nanocyl

CB



CBN326
from Cabot

HSAG



Asbury Synthetic Graphite 8427

Carbon nanofillers: main features

Carbon filler	Carbon Purity (%) (TGA)	Surface area (m^2/g) (BET)	DBP absorption number (ml/100g)	Number of stacked layers (XRD)	Acidic groups (mmol/g)[a] (Boehm titration)	pH
CB N326	98	77	85	5	1.3	5.7 – 9.7
CB N 110	98	137	113	n.d.	n.d.	6.9 – 9.5
CNT - 1	n.d.	200	316	10	n.d.	n.d.
CNT - 2	90	275	n.d.	8	2.0	n.d.
HSAG	99.5	330	162	35	1.1	4.6

[a]carboxy, epoxy, hydroxy groups

M. Galimberti, G. Infortuna, S. Guerra, V. Barbera, S. Agnelli, S. Pandini eXPRESS Polymer Letters, 2017, accepted for publication

S. Agnelli, V. Cipolletti, S. Musto, M. Coombs, L. Conzatti, S. Pandini, T. Riccò, M. Galimberti, eXPRESS Polymer Letters 8(6) (2014) 436

S. Musto, V. Barbera, V. Cipolletti, A. Citterio, M. Galimberti, eXPRESS Polymer Letters Vol.11, No.6 (2017) 435–448

Analysis of mechanical reinforcement

Rubber

IR: SKI3, Nizhnekamskneftekhim Export

S-SBR: Nipol NS 522, Zeon Corporation

Composites with carbon allotropes, based on IR

Composites with only one filler (phr)

IR = 100

CNT	0	1.25	2.50	5.00	10.00	15.00	30.00
G	0	1.39	2.78	5.56	11.11	16.67	33.30
CB N326	0	1.25	2.50	5.00	10.00	15.00	30.00

Fillers with the same volume fraction

Composites crosslinked with dicumyl peroxide: 1.40 phr

M. Galimberti, S. Agnelli, V. Cipolletti, "Progress in Rubber Nanocomposites 1st Edition" ISBN: 9780081004098, Elsevier
S. Agnelli, V. Cipolletti, S. Musto, M. Coombs, L. Conzatti, S. Pandini, T. Riccò, M. Galimberti, eXPRESS Polymer Letters 8(6) (2014) 436

Composites with carbon allotropes, based on IR

Composites with hybrid filler systems (phr)

IR = 100

CNT	0	1.25	2.50	5.00	10.00	15.00	30.00
CNT/CB			1.25/ 1.25	2.50/ 2.50	5.00/ 5.00	7.50/ 7.50	15.00/ 15.00
G	0	1.39	2.78	5.56	11.11	16.67	33.30
G/CB	0		1.39/ 1.25	2.78/ 2.50	5.55/ 5.00	8.34/ 7.70	16.65/ 15.00
CB N326	0	1.25	2.50	5.00	10.00	15.00	30.00

Fillers with the same volume fraction

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Composites with carbon allotropes, based on S-SBR

Composites with hybrid filler systems (phr)

SBR = 100

CNT	0; 1; 2; 3; 4; 5; 6; 6.5; 7.5; 10; 11; 14; 18; 20	
CB N326	0; 10; 15; 20; 22; 30; 35; 45; 50; 60	
CB N326	10	+ CNT: 0 ÷ 14
CB N326	22	+ CNT: 0 ÷ 14
CB N326	35	+ CNT: 0 ÷ 14

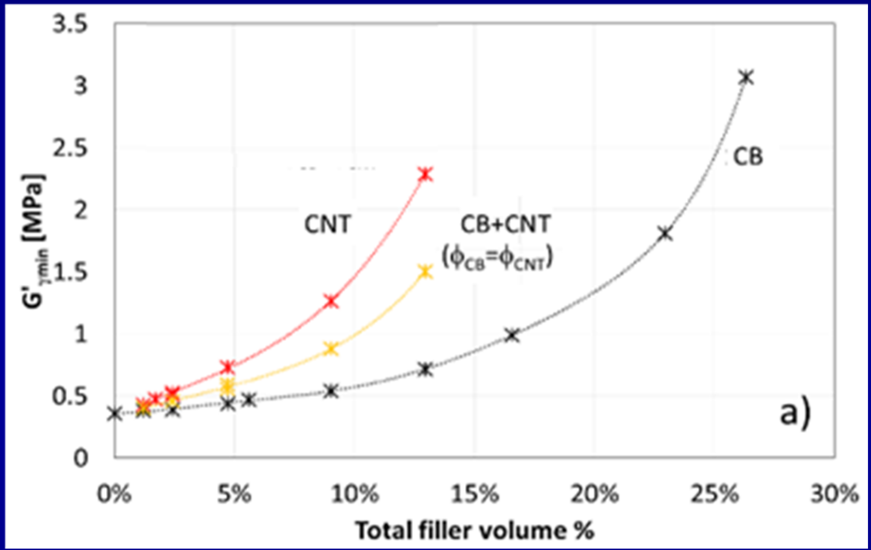
Fillers with the same volume fraction

Composites crosslinked with dicumyl peroxide: 1.40 phr

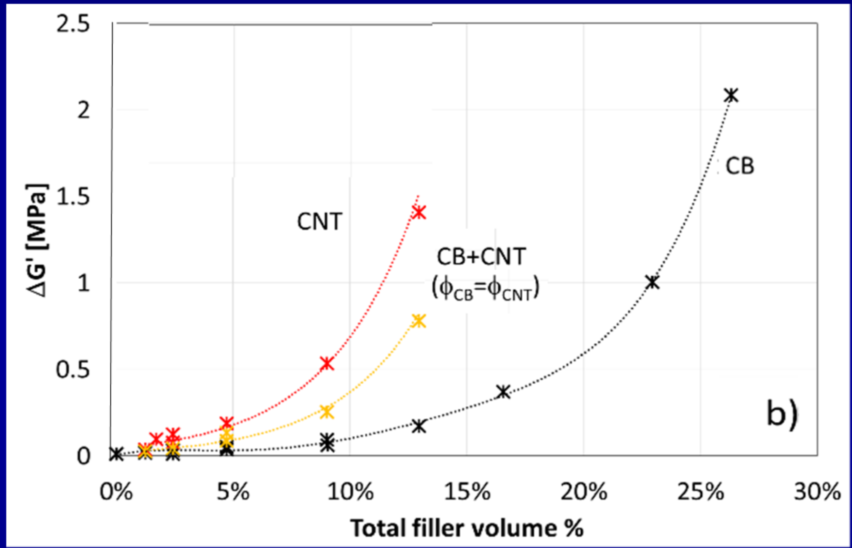
IR based compounds. $G'_{\gamma min}$ and ΔG' vs total filler vol%

Carbon allotropes: CB and CNT

G'



ΔG'



☞ CNT leads to higher values of both $G'_{\gamma min}$ and ΔG'

Data from shear stress tests, 50°C

SBR based compounds. $G'_{\gamma min}$ and ΔG' vs total filler vol%

Carbon allotropes: CB and CNT

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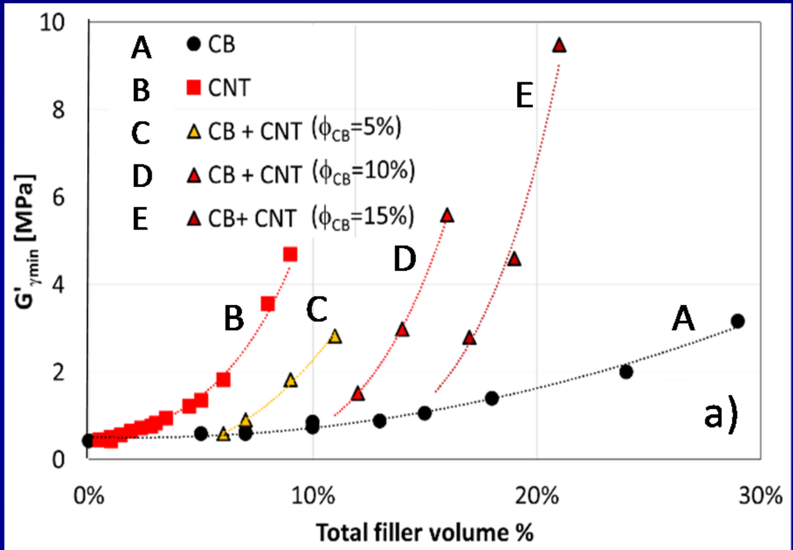
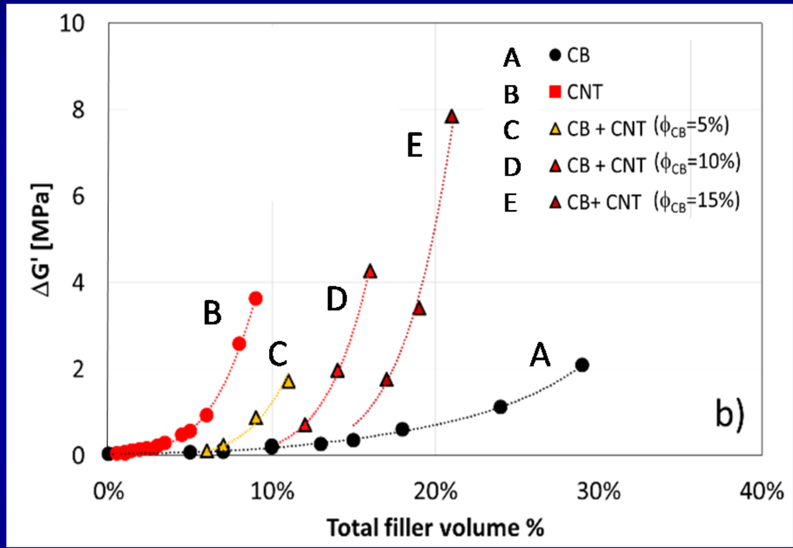


ΔG'



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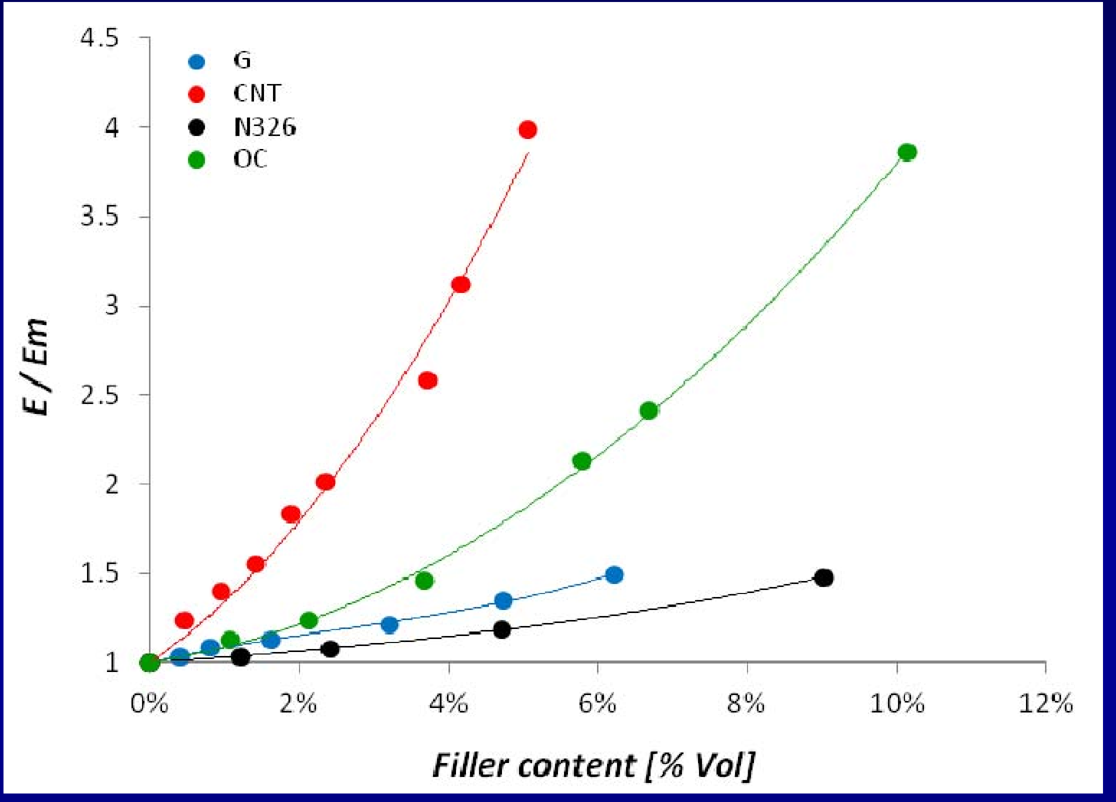
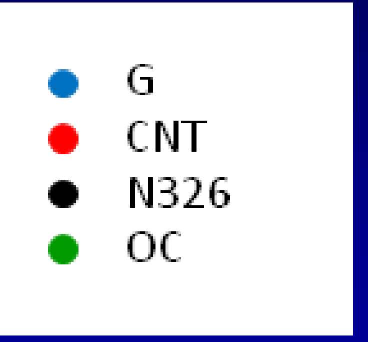
Data from shear stress tests, 50°C

IR based compounds. $G'_{\gamma min}$ vs total filler vol%





dry melt blending, internal mixers

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

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

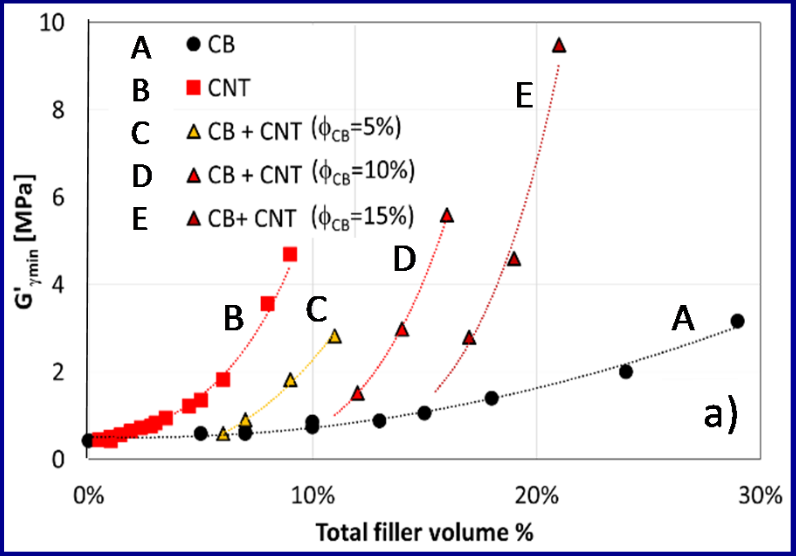
Galimberti M., Coombs M., Cipolletti V., Riccò T., Agnelli S., Pandini S., KGK 7-8 (2013) 31-36

Galimberti M., V. Kumar, M. Coombs, V. Cipolletti, S. Agnelli, S. Pandini, L. Conzatti, RCT 87(2) (2014) 197-218

SBR based compounds. $G'_{\gamma min}$ and ΔG' vs total filler vol%

Carbon allotropes: CB and CNT

G'



Data from shear stress tests, 50°C

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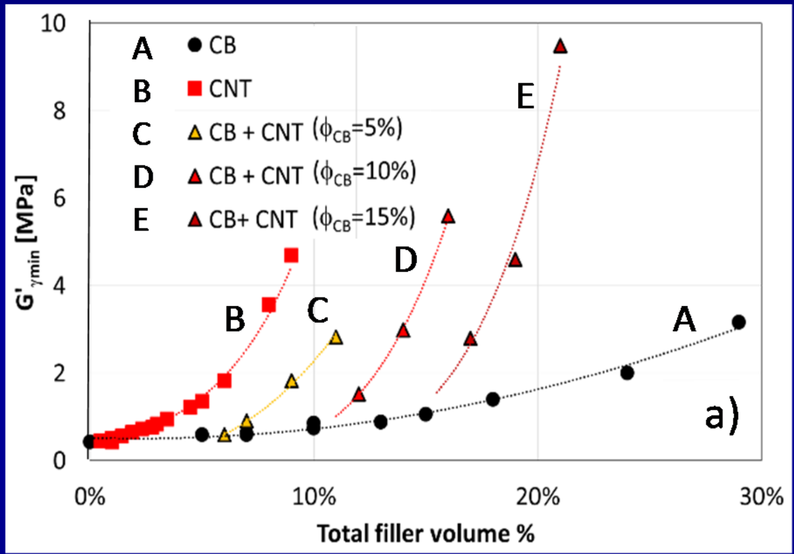
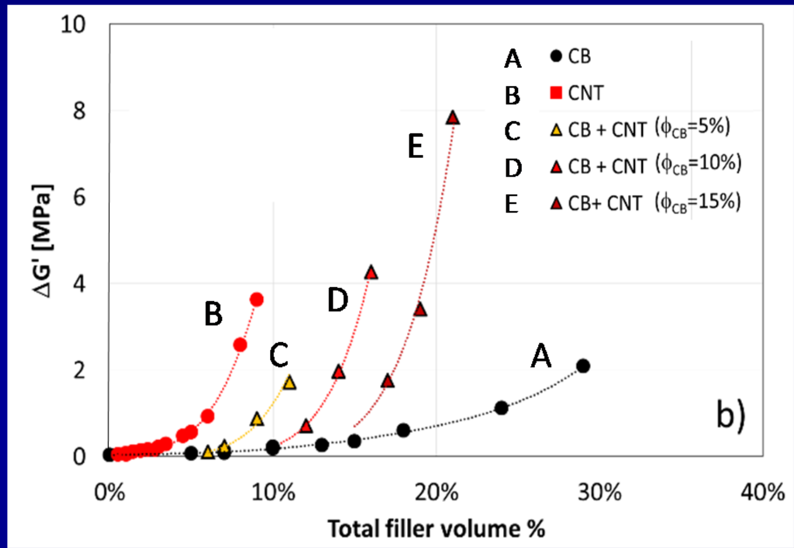


ΔG'



Data from shear stress tests, 50°C

Specific interfacial area

«for composites with the same chemical nature of the fillers,

the reinforcement changes with filler-polymer interfacial area,

at the same filler volume fraction»

Kalfus J., Jancar J., *Polymer Composites*, 28, (2007) 365-371

Specific interfacial area

Specific interfacial area = $A \cdot \rho \cdot \Phi$

filler properties

A = BET surface area

ρ = density

Φ = volume fraction

measure unit: m^2 / m^3

Surface / volume in the composite

«for composites with the same chemical nature of the fillers,

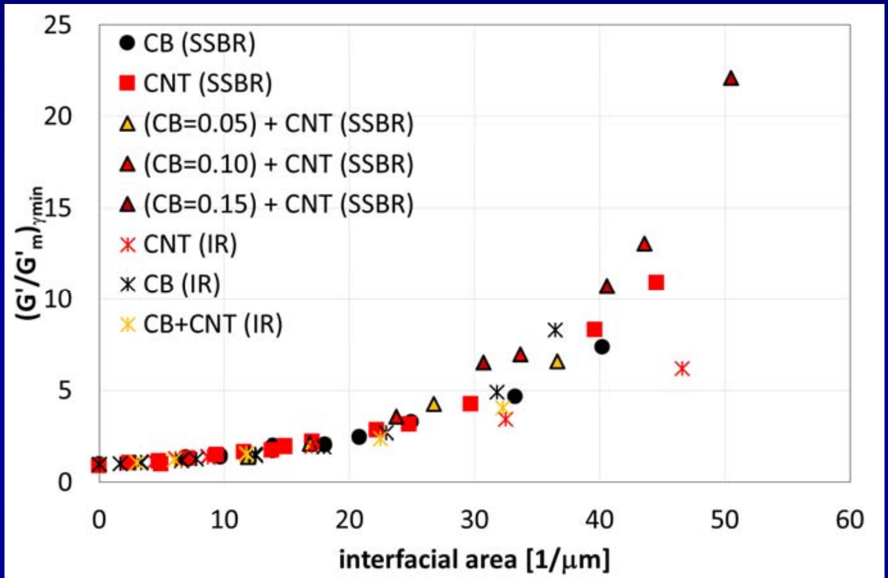
the reinforcement changes with filler-polymer interfacial area,

at the same filler volume fraction»

Kalfus J., Jancar J., *Polymer Composites*, 28, (2007) 365-371

Master curve for the initial modulus of elastomers composites

with sp[2] carbon allotropes

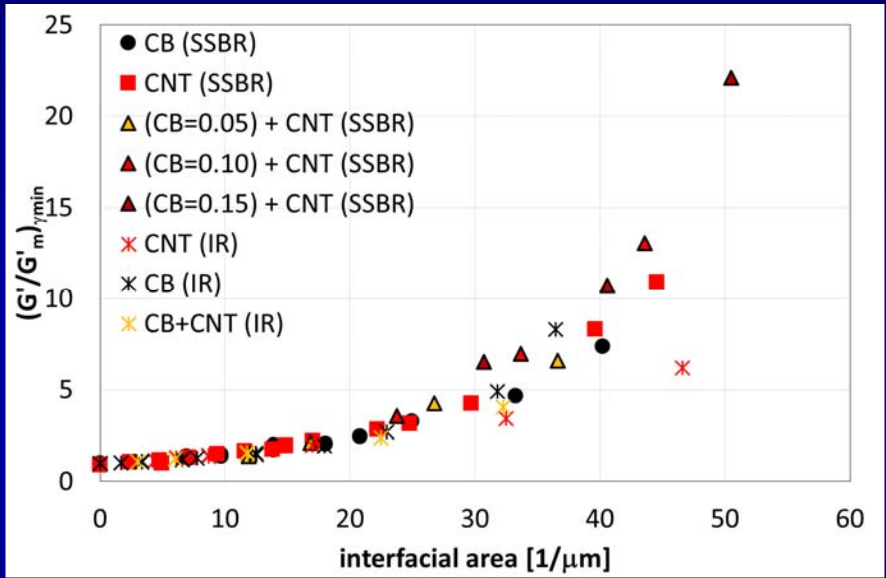


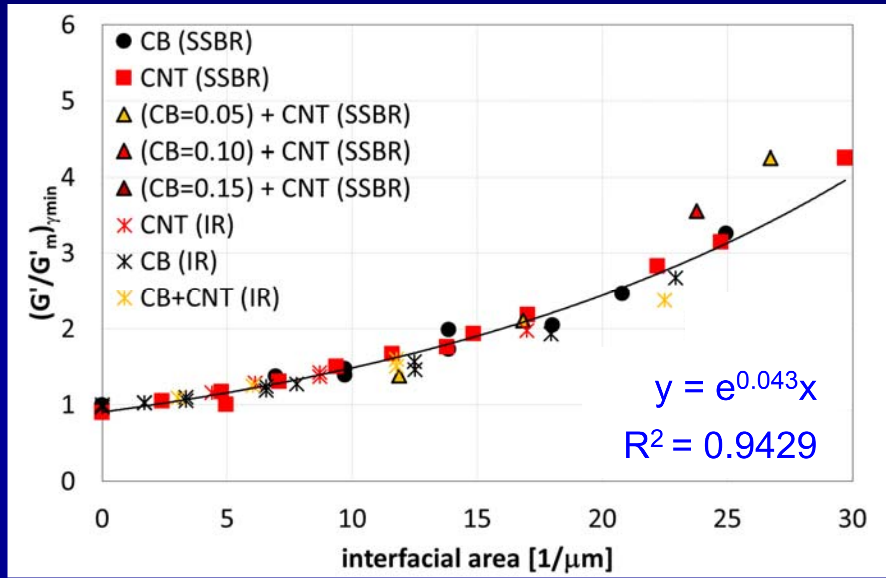
Rubber: IR, SBR

Data from shear stress tests, 50°C

Master curve for the initial modulus of elastomers composites

with sp^2 carbon allotropes





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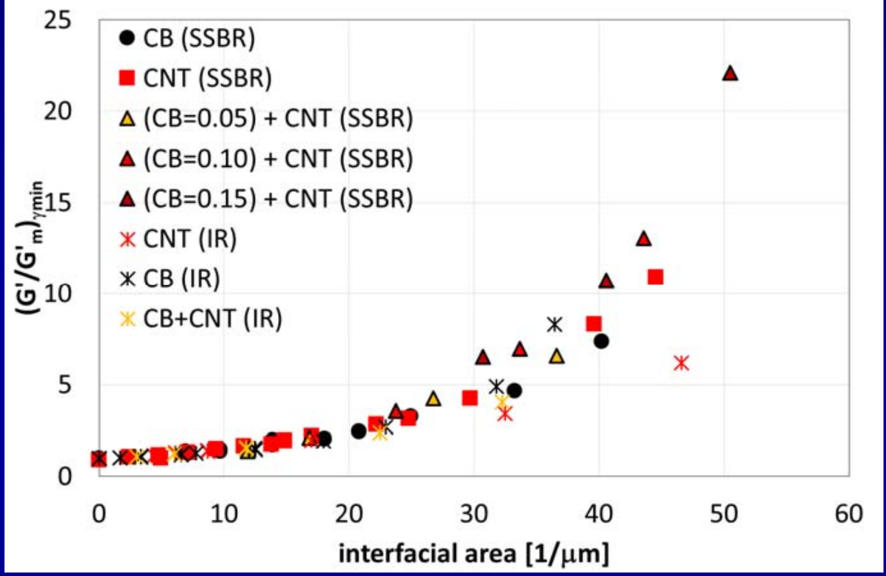
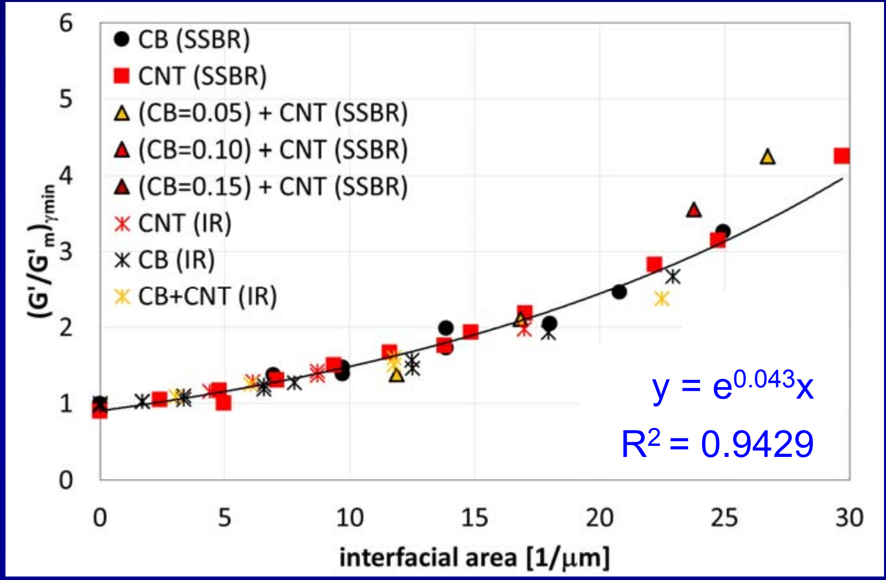




Rubber: IR, SBR

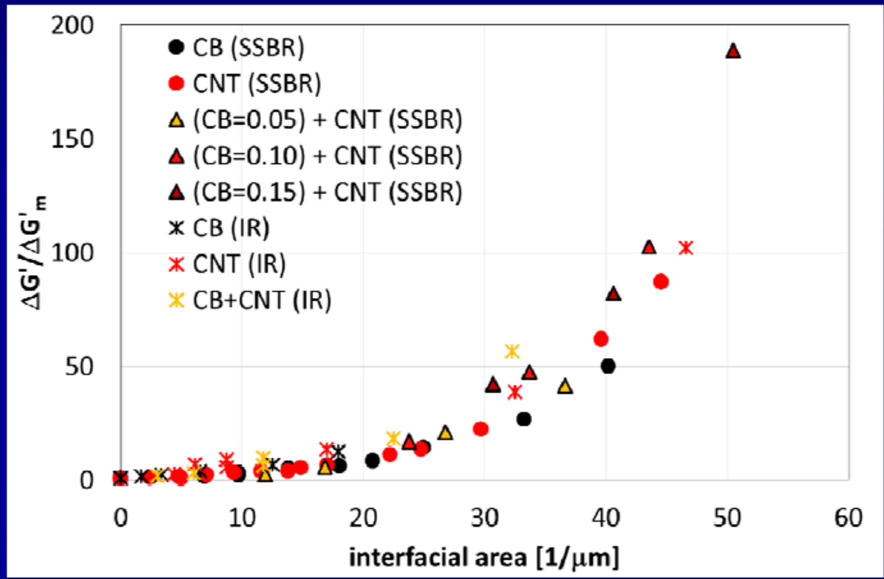
Up to

40 phr CB, 12 phr CNT

Data from shear stress tests, 50°C

Master curve for the Payne effect of elastomers composites

with sp^2 carbon allotropes



$y = e^{0.043x}$

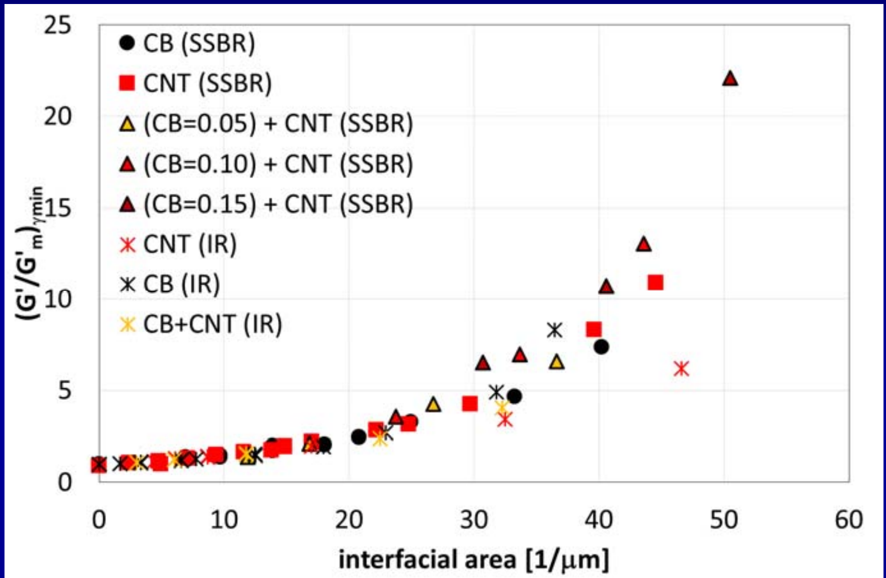
Rubber: IR, SBR

Data from shear stress tests, 50°C

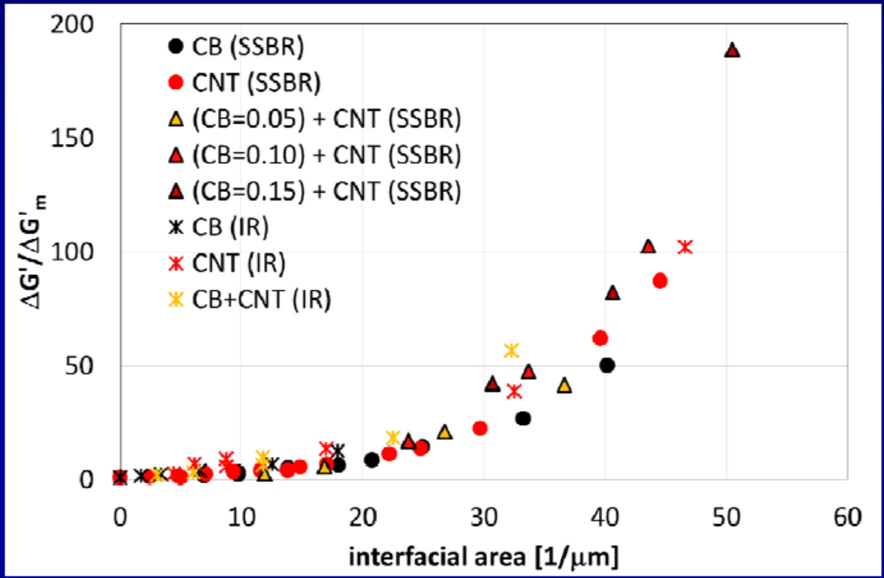
Master curves for the mechanical reinforcement of elastomer composites

with sp^2 carbon allotropes

G’



ΔG’



IR, SBR as the rubbers   Data from shear stress tests, 50°C

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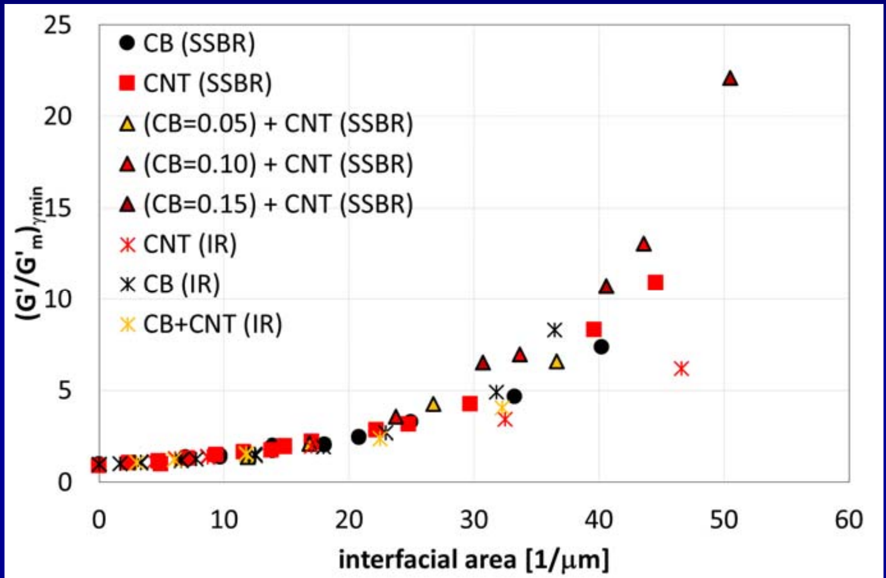
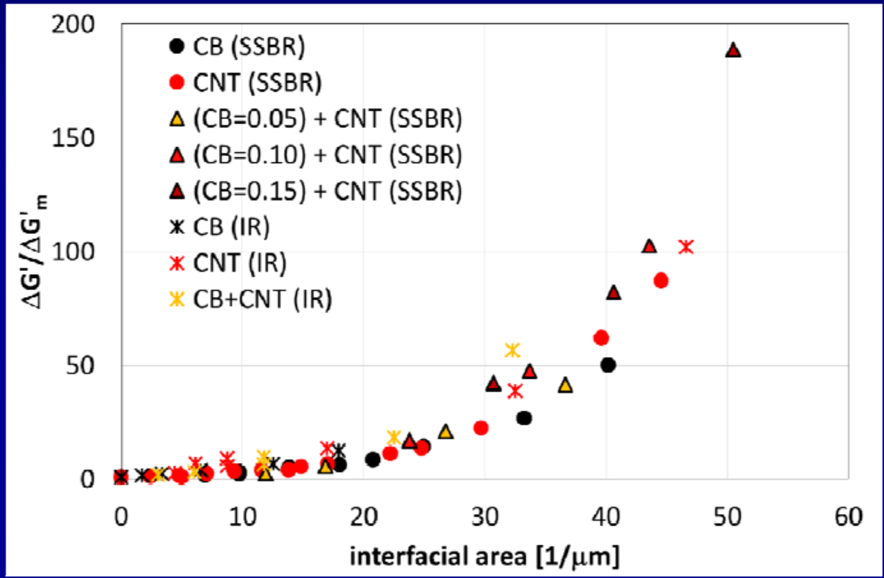


ΔG'



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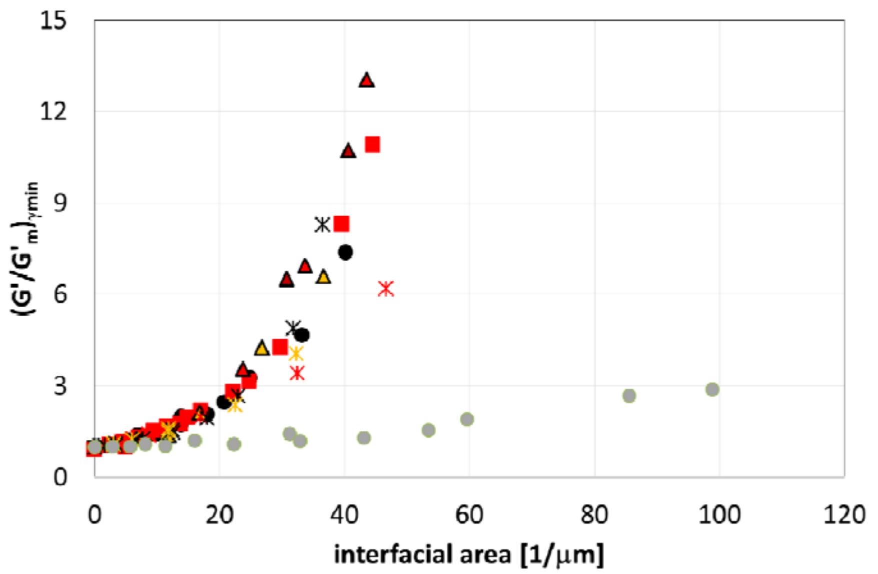
Master curves for the mechanical reinforcement of elastomer composites

with sp^2 carbon allotropes

What about nanosized graphite?



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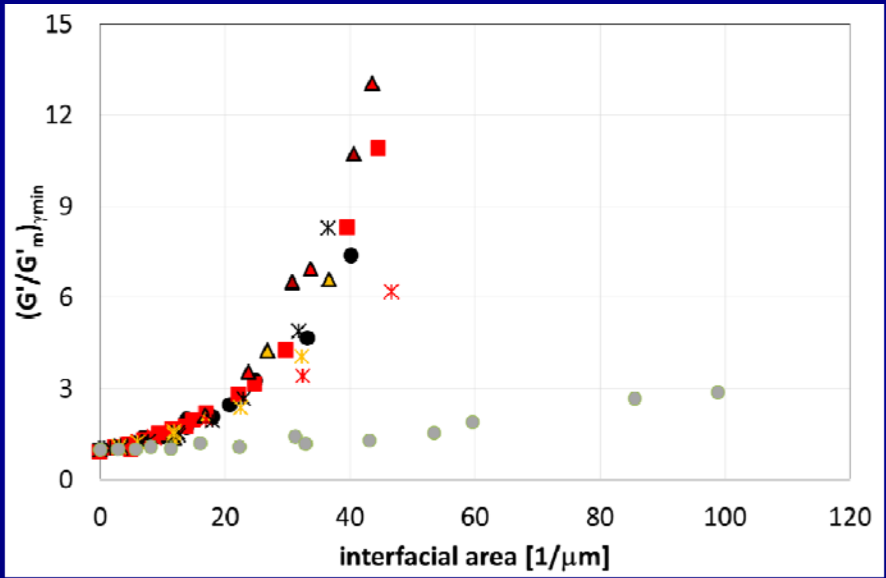

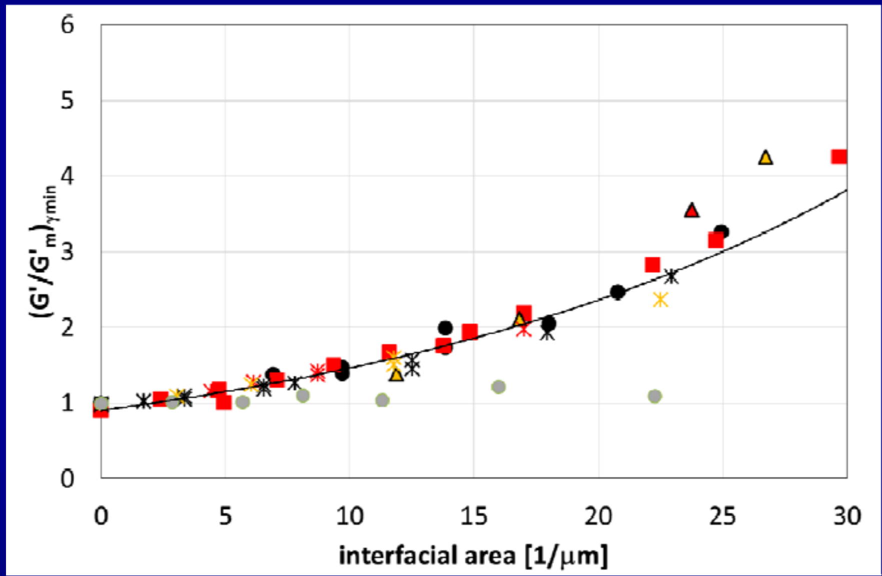

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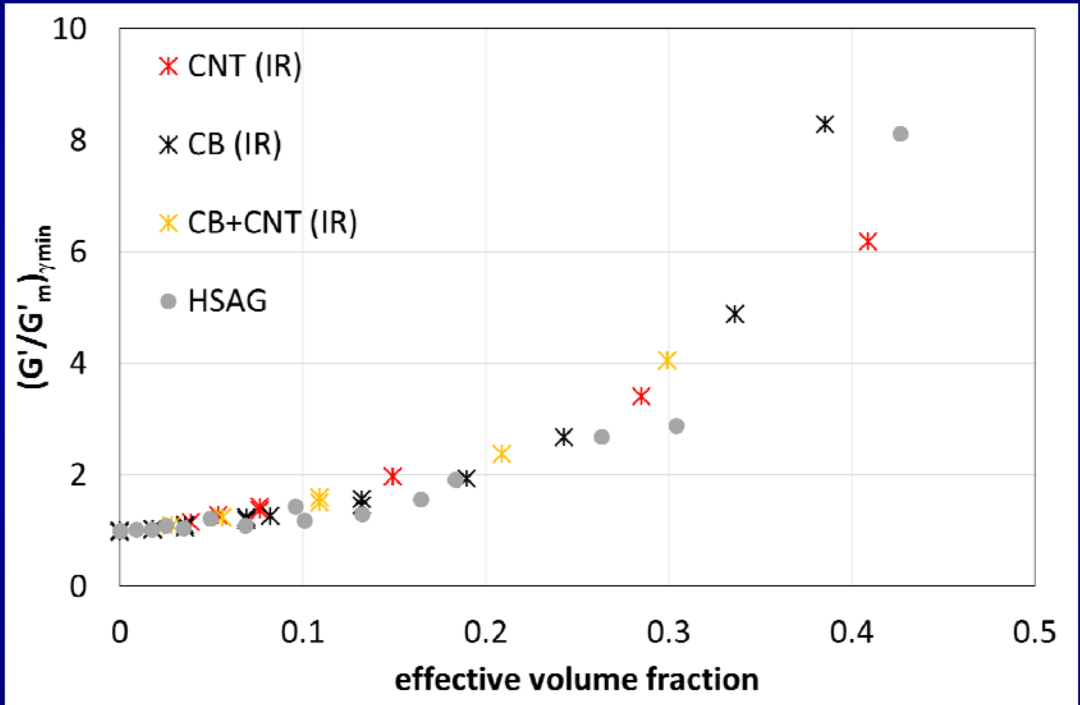
Master curves for the mechanical reinforcement of elastomer composites

with sp^2 carbon allotropes

With DBP absorption - IR as the rubber



Allotrope	DBP [mL/100g]
CB	85
CNT	316
HSAG	162

$$\phi_c = \frac{\phi}{2} \cdot \left[1 + \frac{1 + 0.02139 \cdot DBP}{1.46}\right]$$

S. Musto, V. Barbera, V. Cipolletti, A. Citterio, M. Galimberti, eXPRESS Polymer Letters Vol.11, No.6 (2017) 435–448

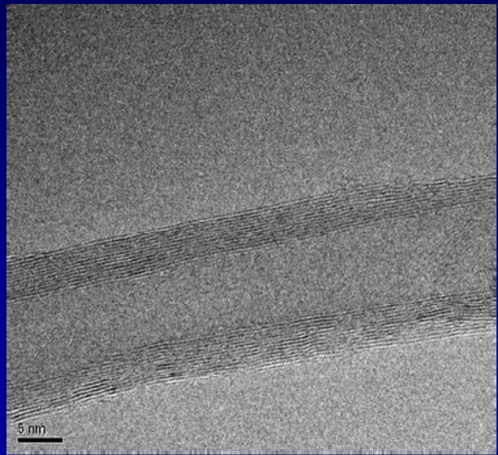
S. Agnelli, V. Cipolletti, S. Musto, M. Coombs, L. Conzatti, S. Pandini, T. Riccò, M. Galimberti, eXPRESS Polymer Letters 8(6) (2014) 436

Analysis of mechanical reinforcement

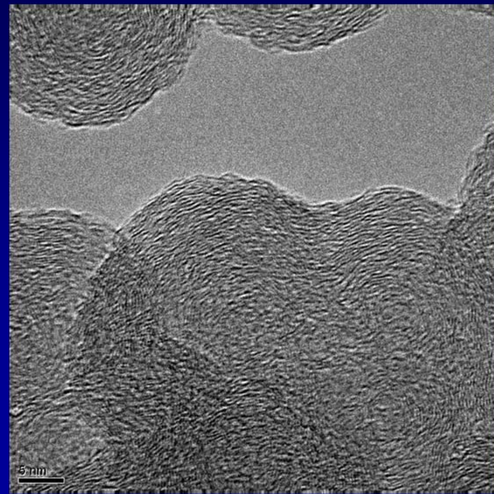
Anisotropic properties

Carbon allotropes lead to anisotropic properties of rubber compounds?

CNT



CB



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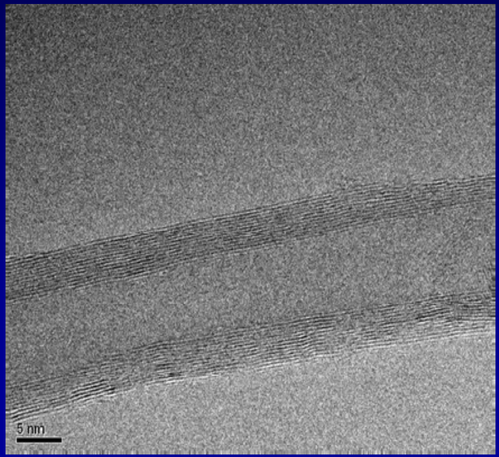
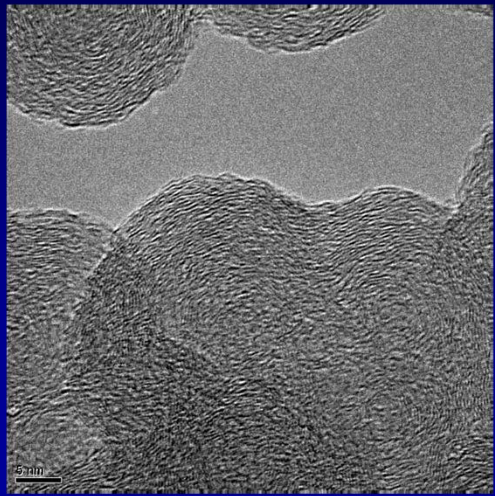
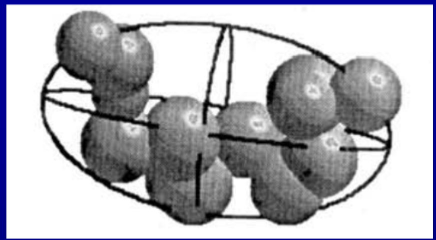


CB





N220 aggregate

''Aggregates generally exhibit anisotropy,
in the form of a reduction of aggregate breadth, or ''flatness'', in one direction''
…but even perfectly spherical particles can give anisotropy, if not homogeneously dispersed!

Grueber et al., Rubber Chemistry and Technology 67(2):280-287, 1994

Recipes and preparation

Ingredient	Amount [phr (volume fraction)]			
NR	100	100	100	100
Filler	0	4 (0.02)	15 (0.07)	35 (0.15)
DCUP	1.4	1.4	1.4	1.4

Fillers

HSAG, CNT, CB: N326

Internal mixer: 50 mLmixing chamber.

50 g NR masticated at 80°C, 1 min, rotors 60 rpm.

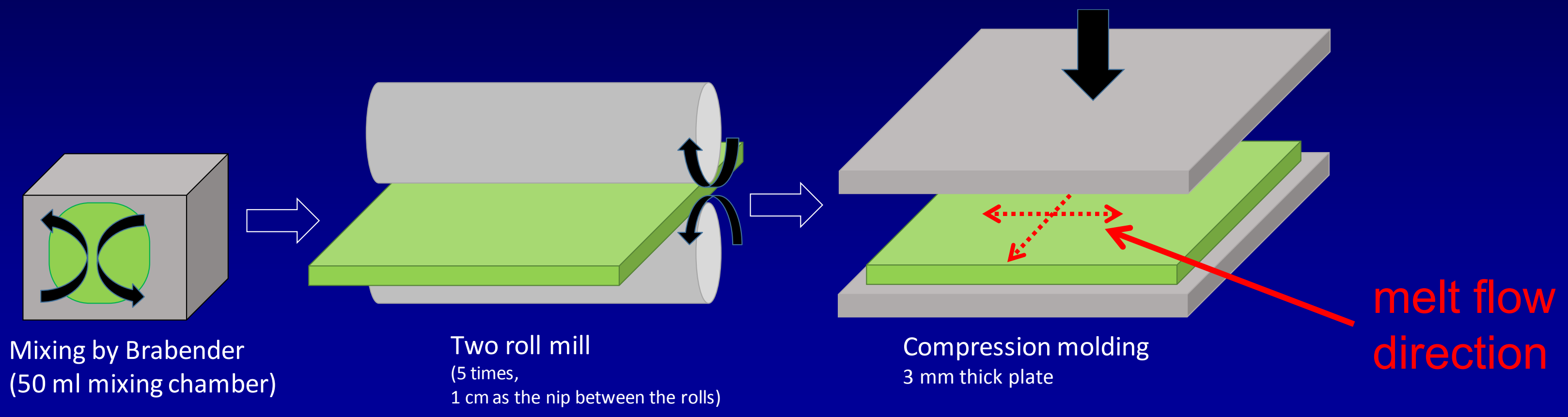
Filler then added.

Mixing performed for further 4 minutes.

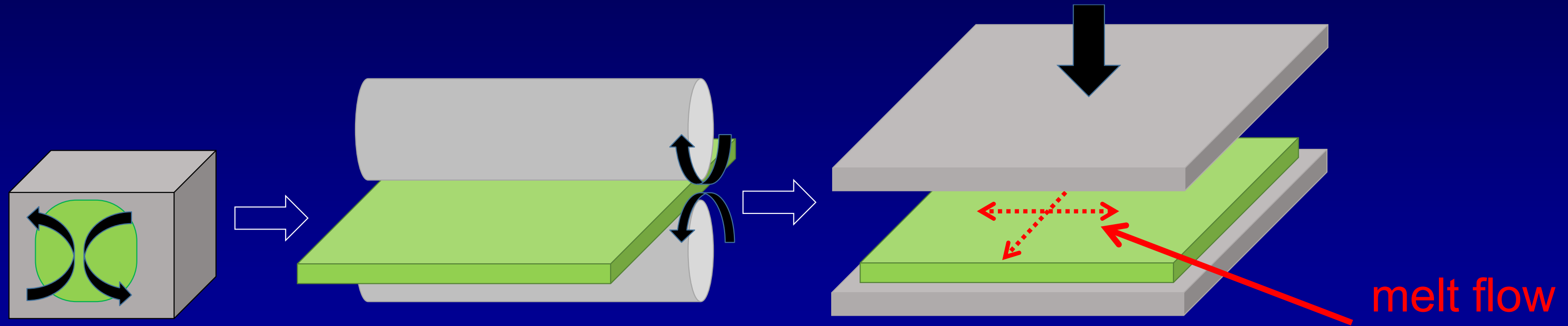
Peroxide added, composite discharged after 2 minutes.

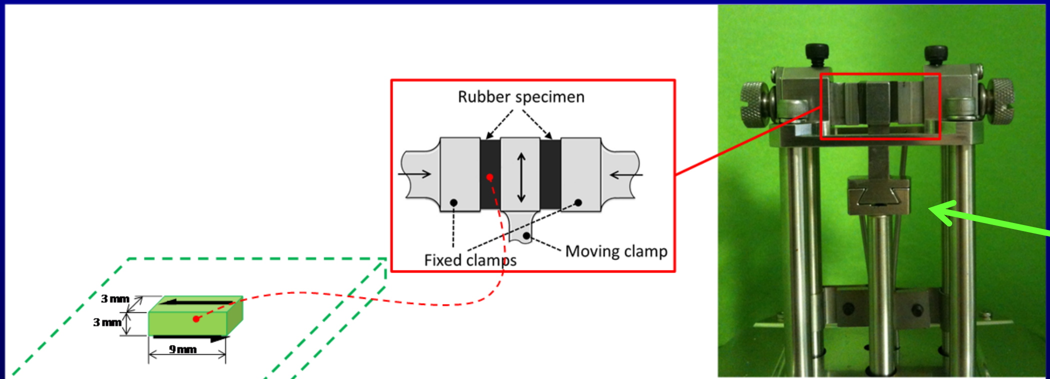
S. Agnelli, S. Pandini, A. Serafini, S. Musto, M. Galimberti *Macromolecules 2016, 49(22), 8686–8696*

Samples preparation



Samples preparation and device for shear stress tests

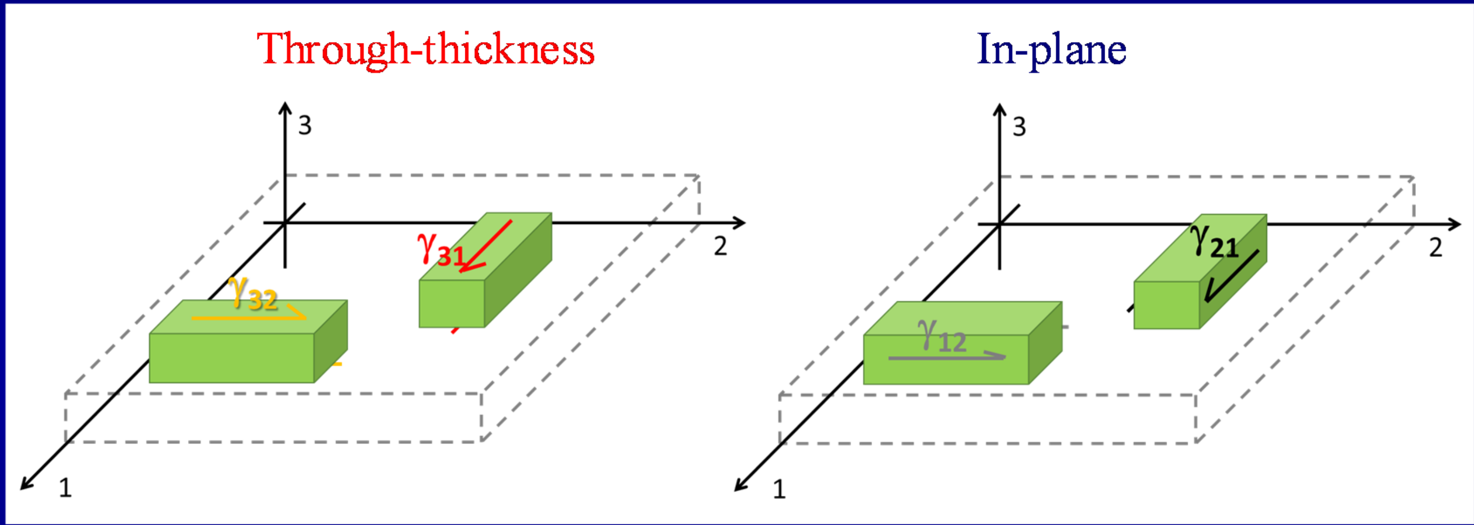




Shear sandwitch clamps
of DMA Q800 – TA Instruments

Device for shear stress tests

Shear stress tests: through thickness and in plane

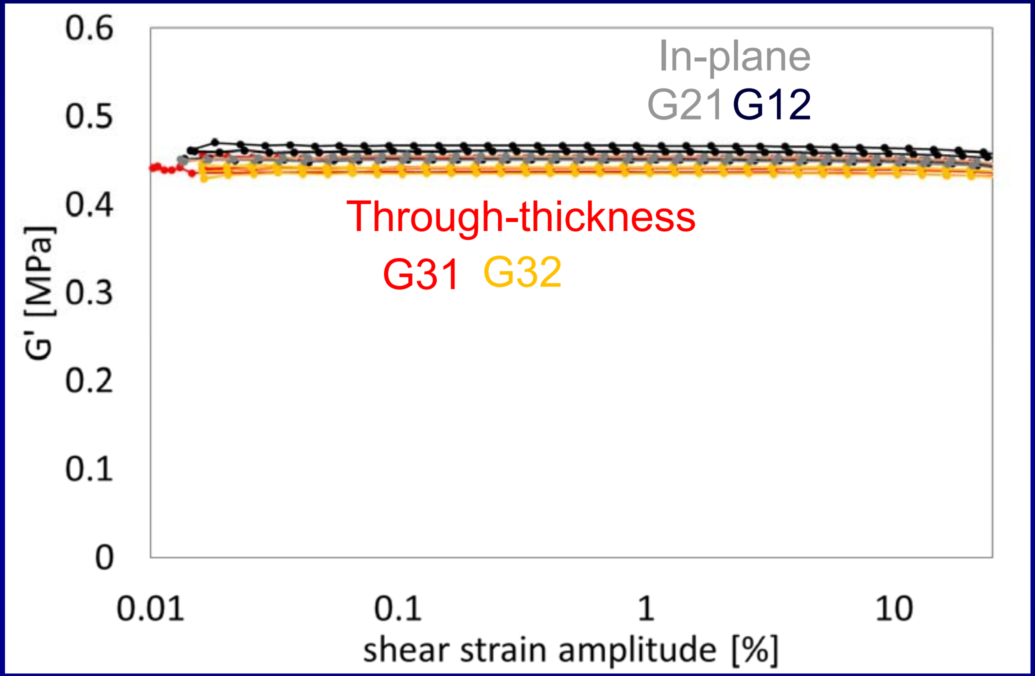


Stress on faces perpendicular to axis 3

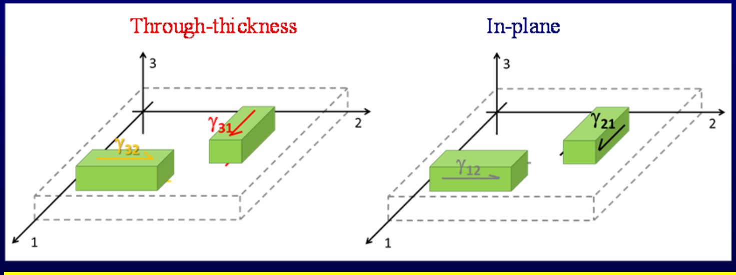
Stress on faces perpendicular to axis 1 or 2

Shear modulus vs shear strain amplitude

NR



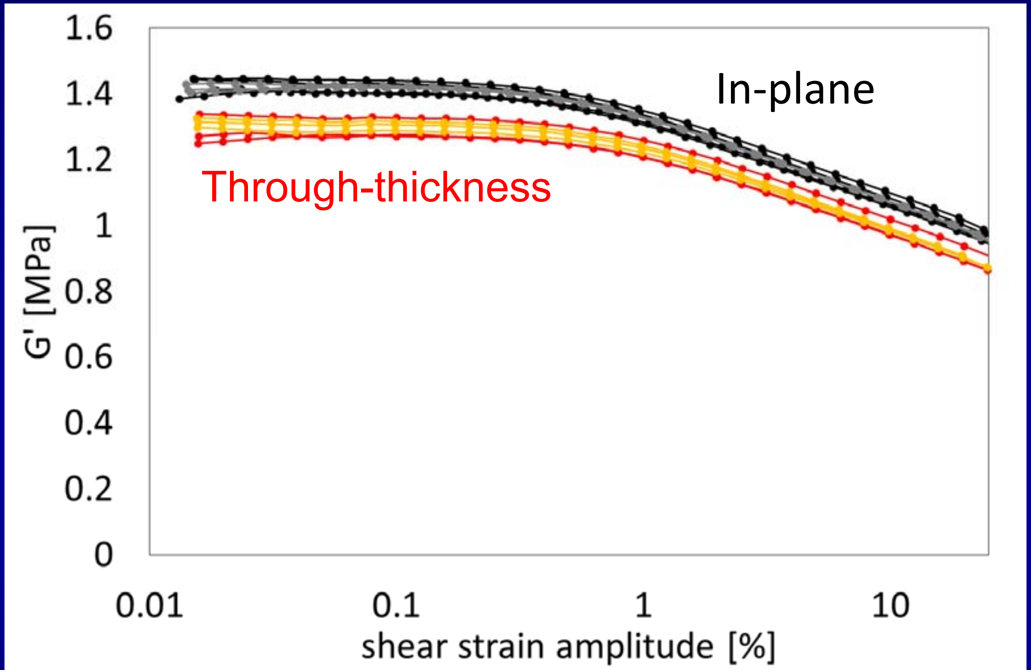
Isotropic behaviour
No Payne effect



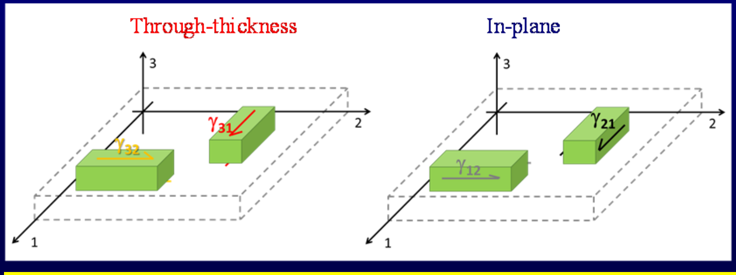
Peroxide crosslinked

Shear modulus vs shear strain amplitude

NR + 35 phr CB N326



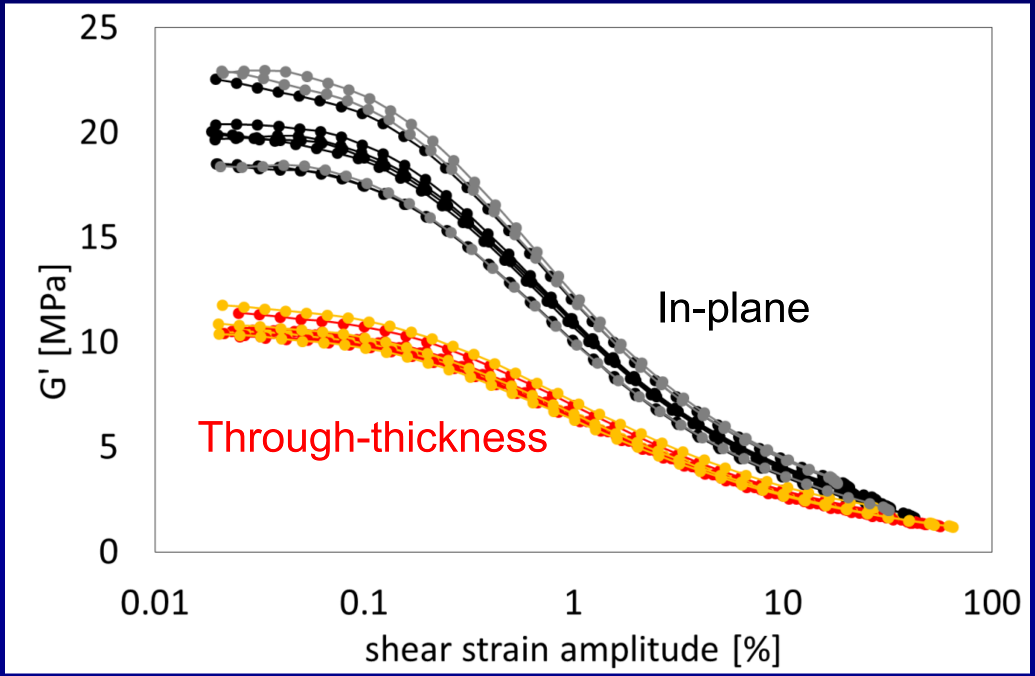
(slight) anisotropic behaviour



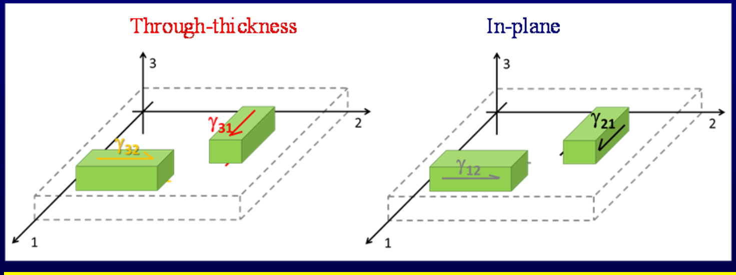
Peroxide crosslinked

Shear modulus vs shear strain amplitude

NR + 35 phr CNT



Transversal isotropic behavior



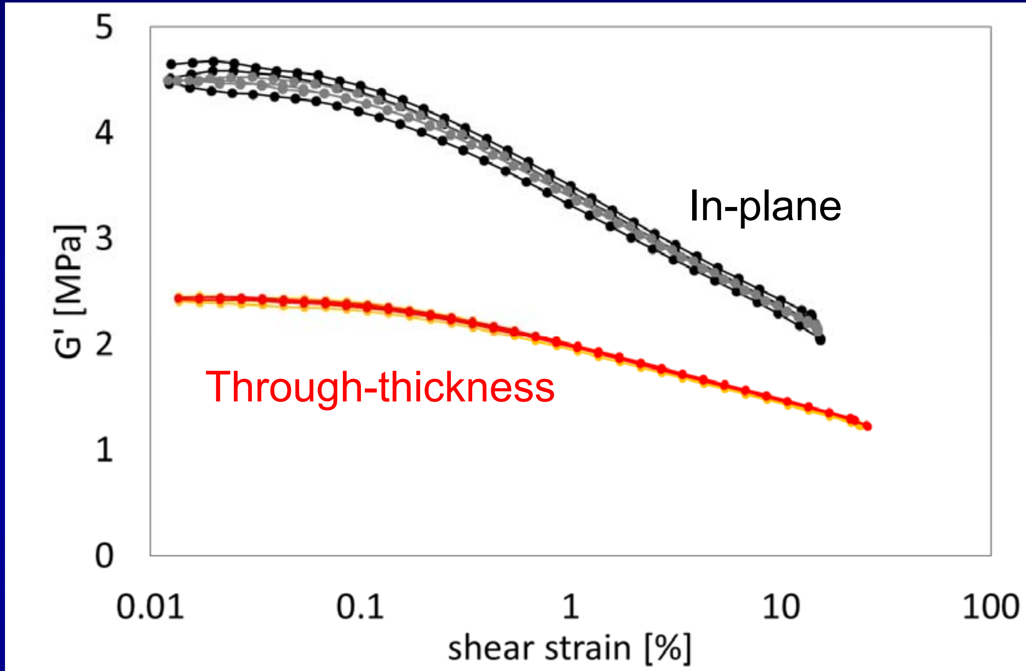
Anisotropic

Payne Effect

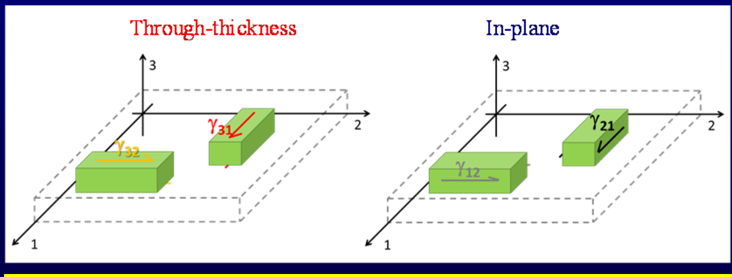
Peroxide crosslinked

Shear modulus vs shear strain amplitude

NR + 35 phr HSAG



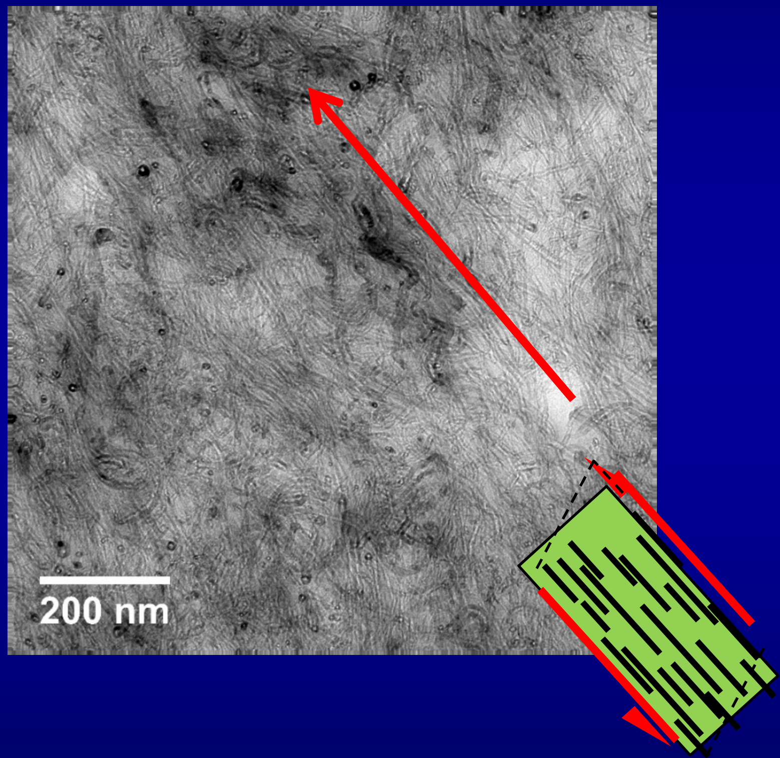
Transversal isotropic behavior



Peroxide crosslinked

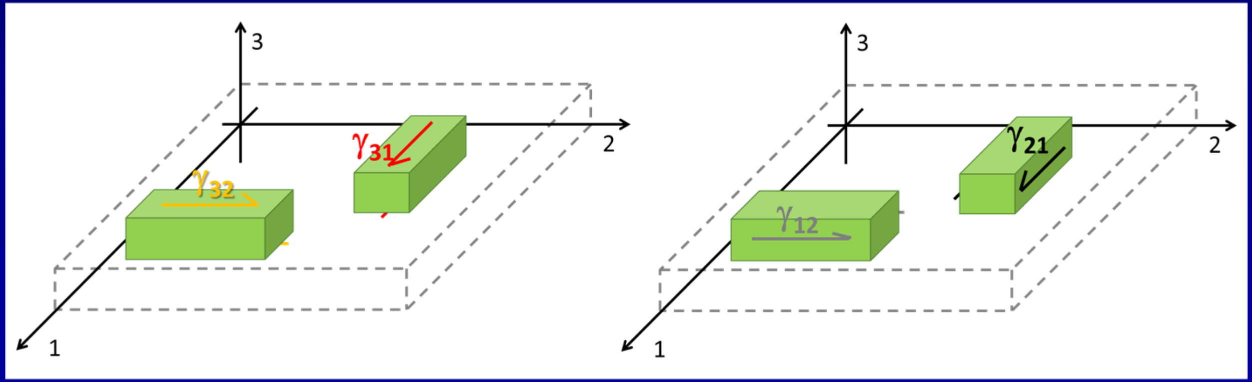
Transmission electron microscopy

NR + 35 phr CNT

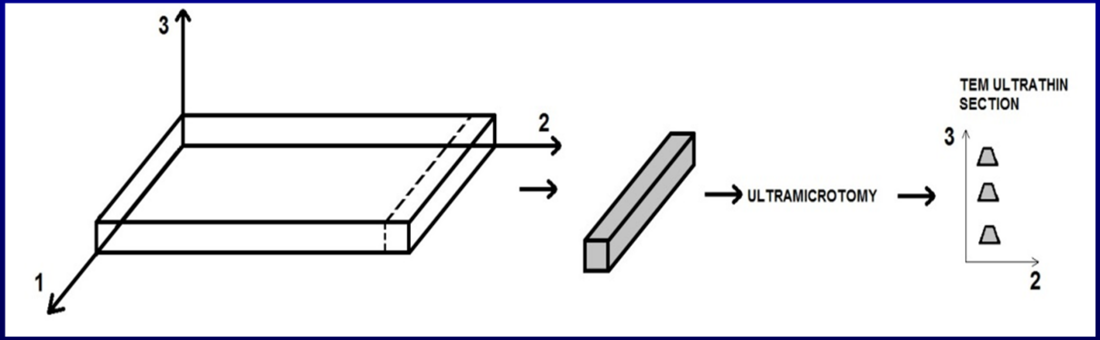


Electron diffraction measurements

by Selected Area Electron Diffraction Patterns



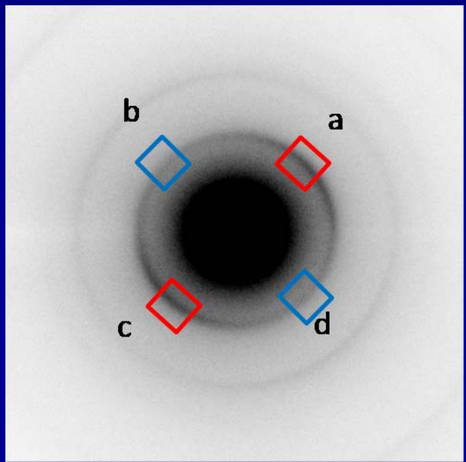
Ultrathin sections (70 – 100 nm) obtained perpendicular to the reference axis 1



Electron diffraction measurements

by Selected Area Electron Diffraction Patterns

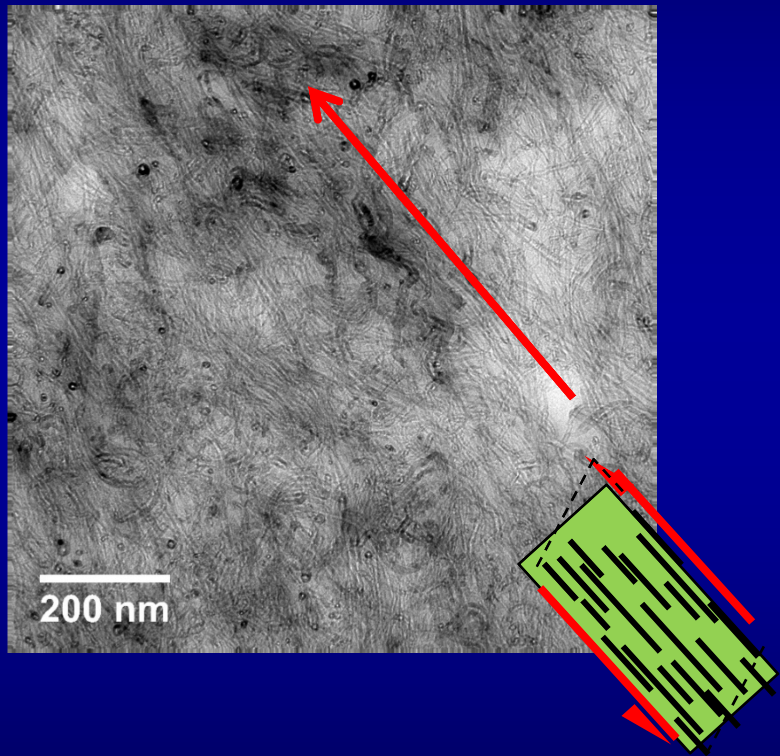
NR + 35 phr CNT



(002) Debye-Scherrer ring

Lower intensity sectors

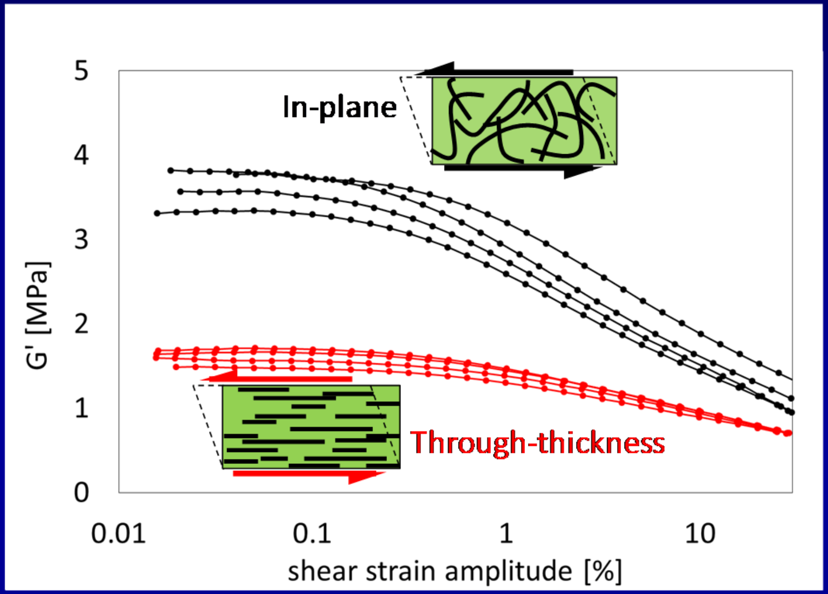
Higher intensity sectors

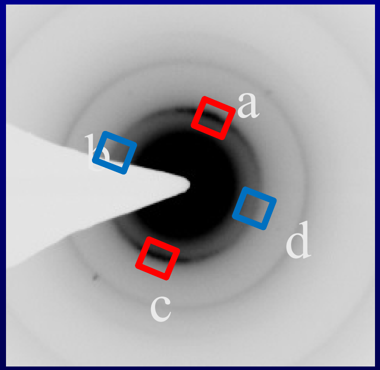


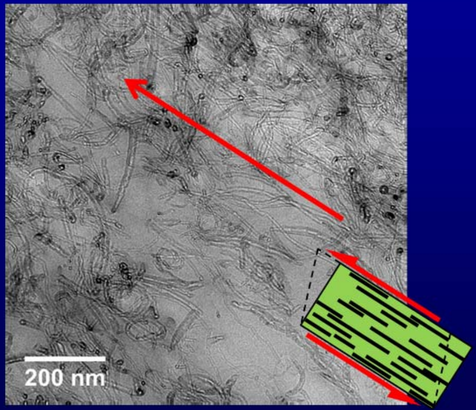
☞ CNT preferential orientation

NR based composites with carbon nanofillers

NR + 15 phr CNT

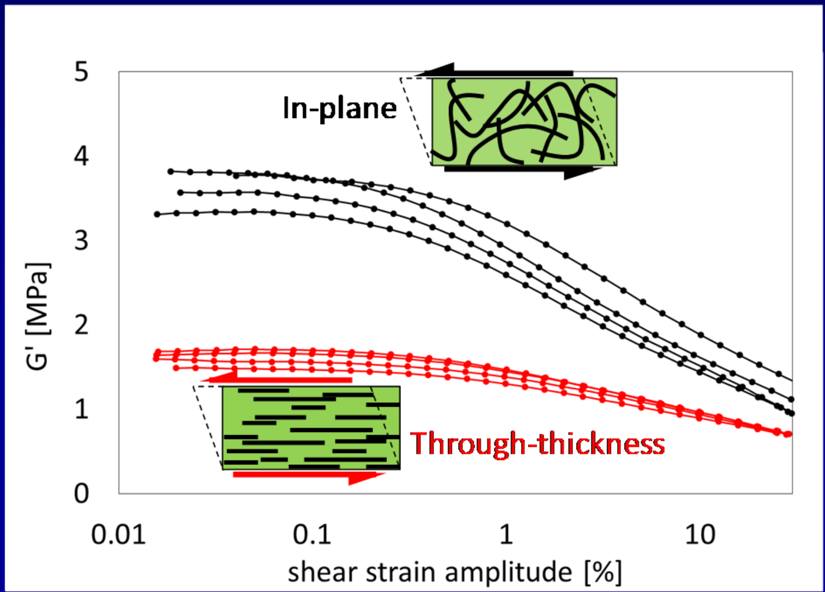




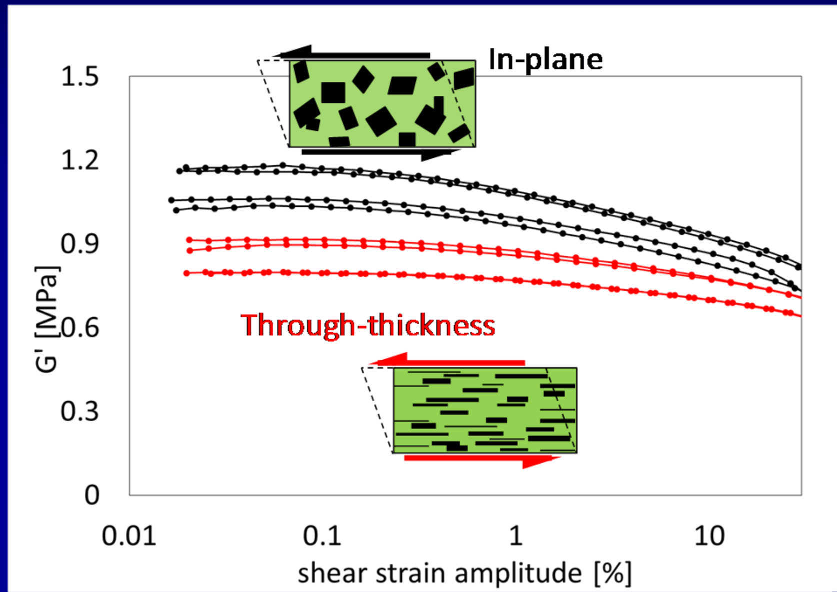


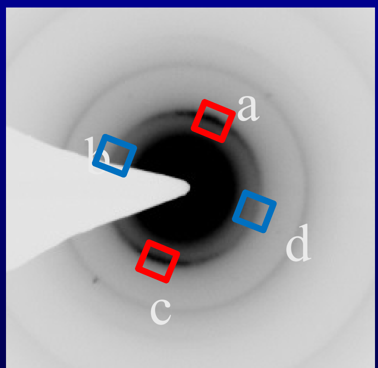
NR based composites with carbon nanofillers

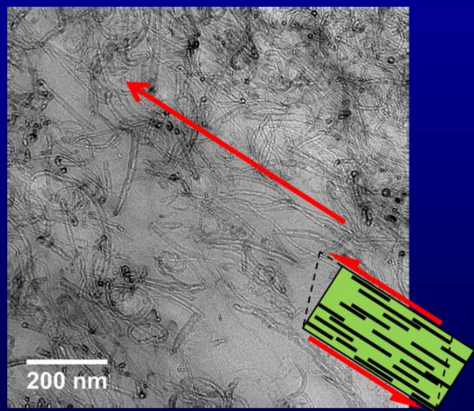
NR + 15 phr CNT

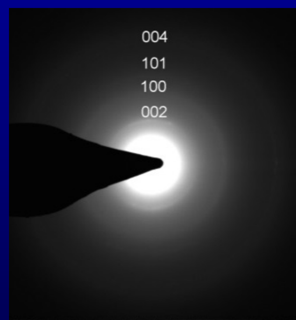


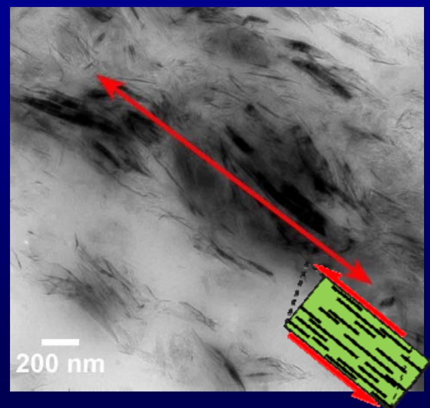
NR + 15 phr HSAG





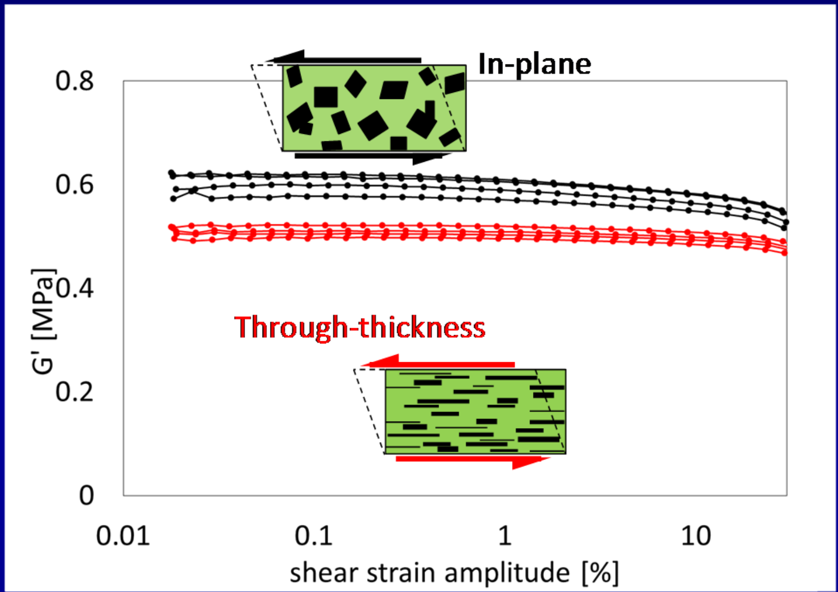




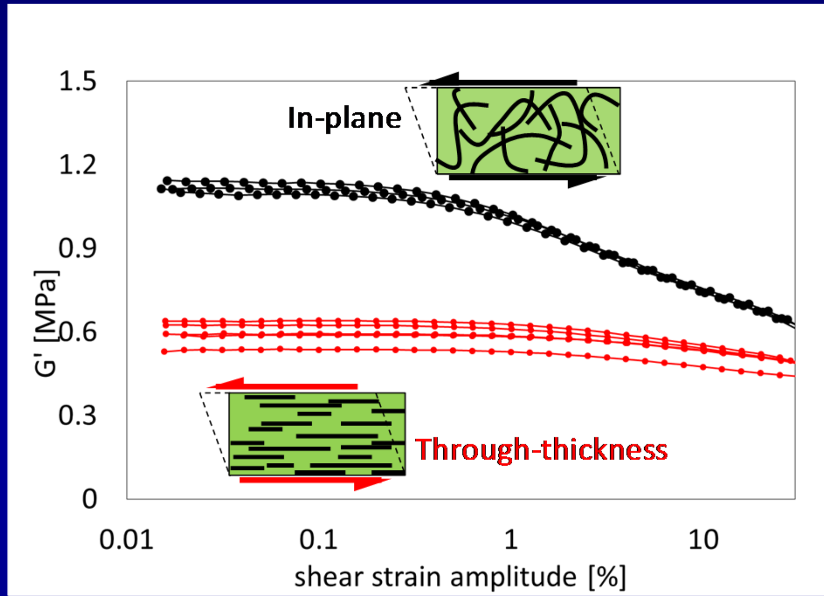


NR based composites with carbon nanofillers

NR + 4 phr HSAG

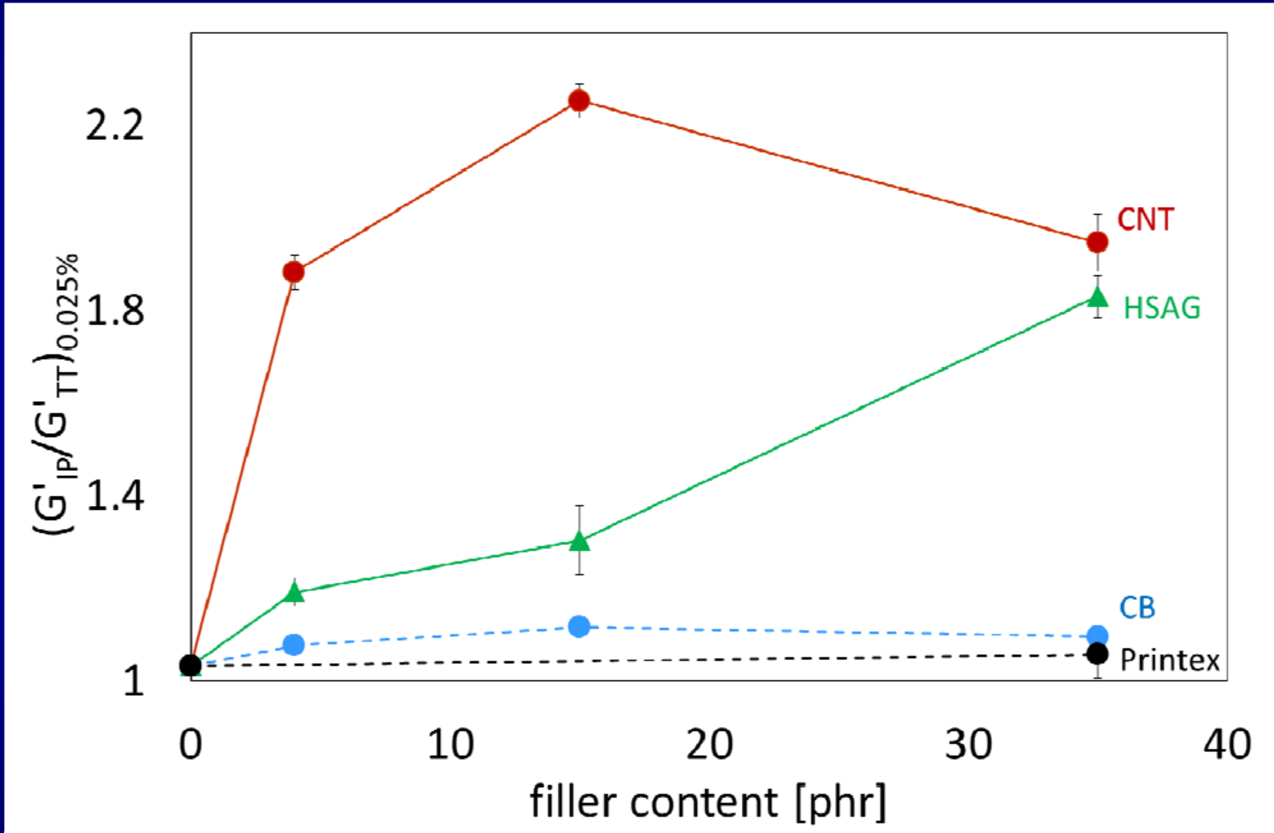


NR + 4 phr CNT



Anisotropy index as a function of carbon filler content

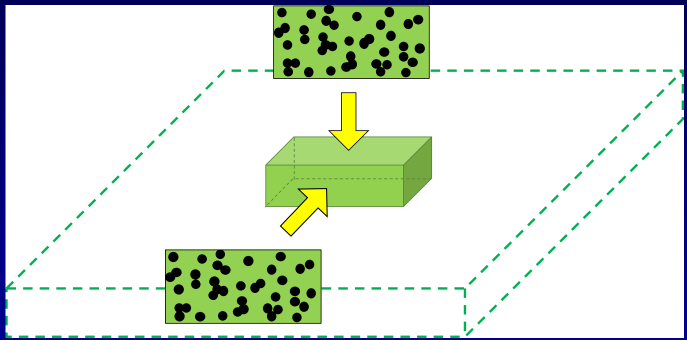
Anisotropy index = G'_{IP}/G'_{TT}



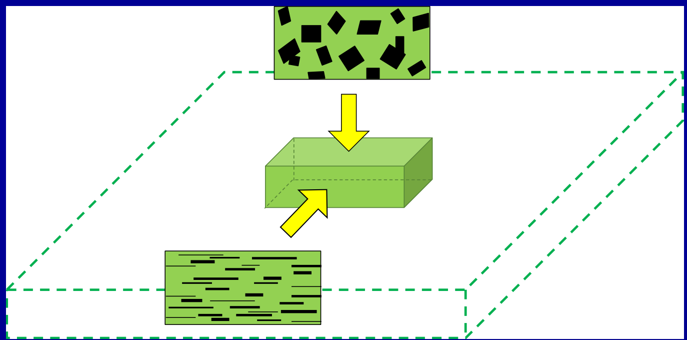
S. Agnelli, S. Pandini, F. Torricelli, P. Romele, A. Serafini, V. Barbera, M. Galimberti *submitted*

S. Agnelli, S. Pandini, A. Serafini, S. Musto, M. Galimberti *Macromolecules 2016, 49(22), 8686–8696*

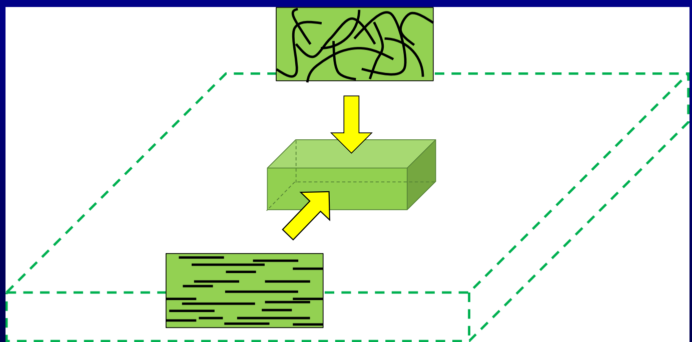
NR based composites with carbon nanofillers



NR + CB

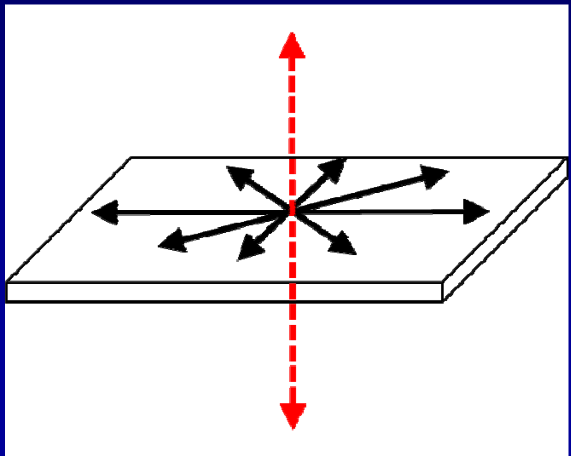


NR + HSAG



NR + CNT

Transversal isotropic behaviour …



NR composites
with CNT, nano graphite

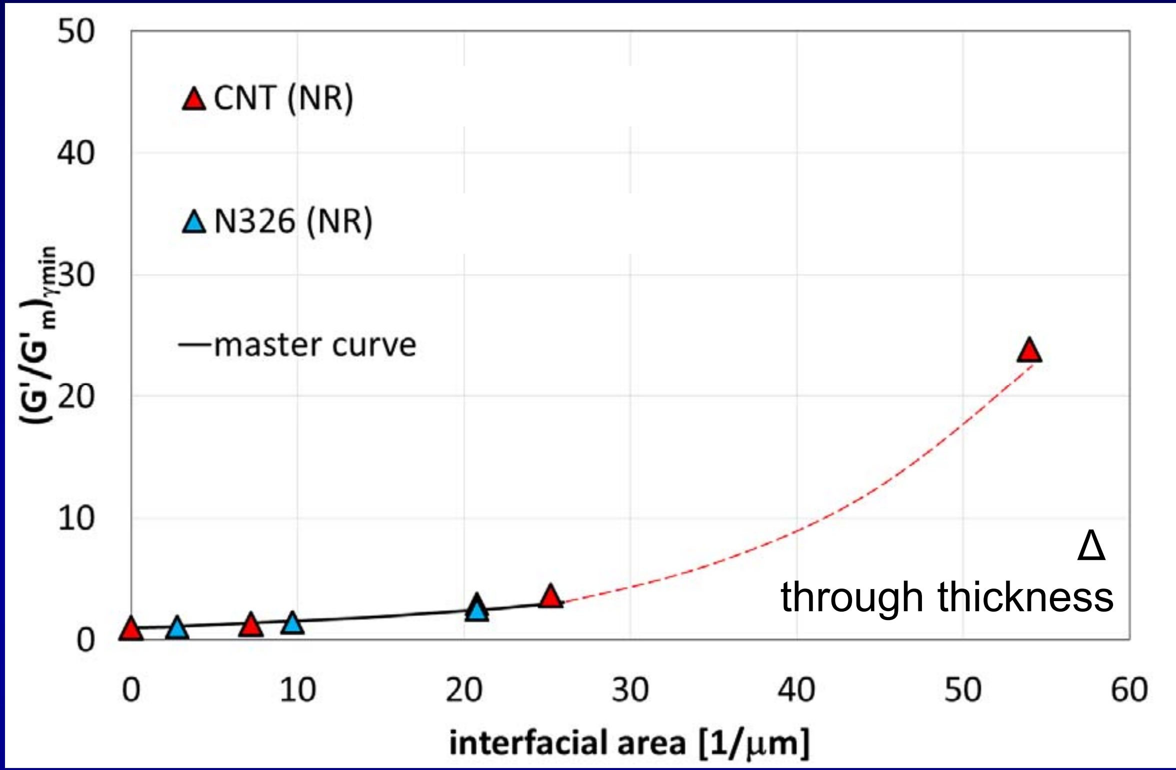
Grand Canyon

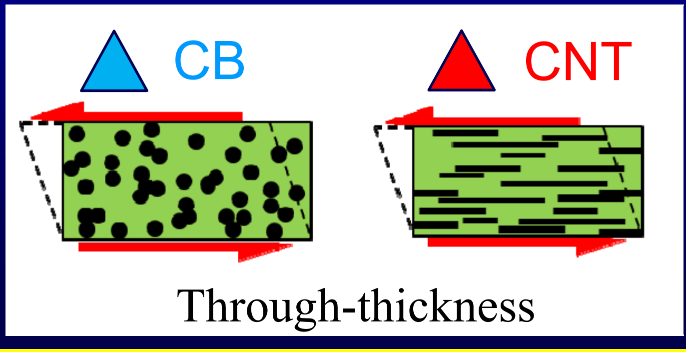
… for carbon fillers with high aspect ratio

Analysis of mechanical reinforcement

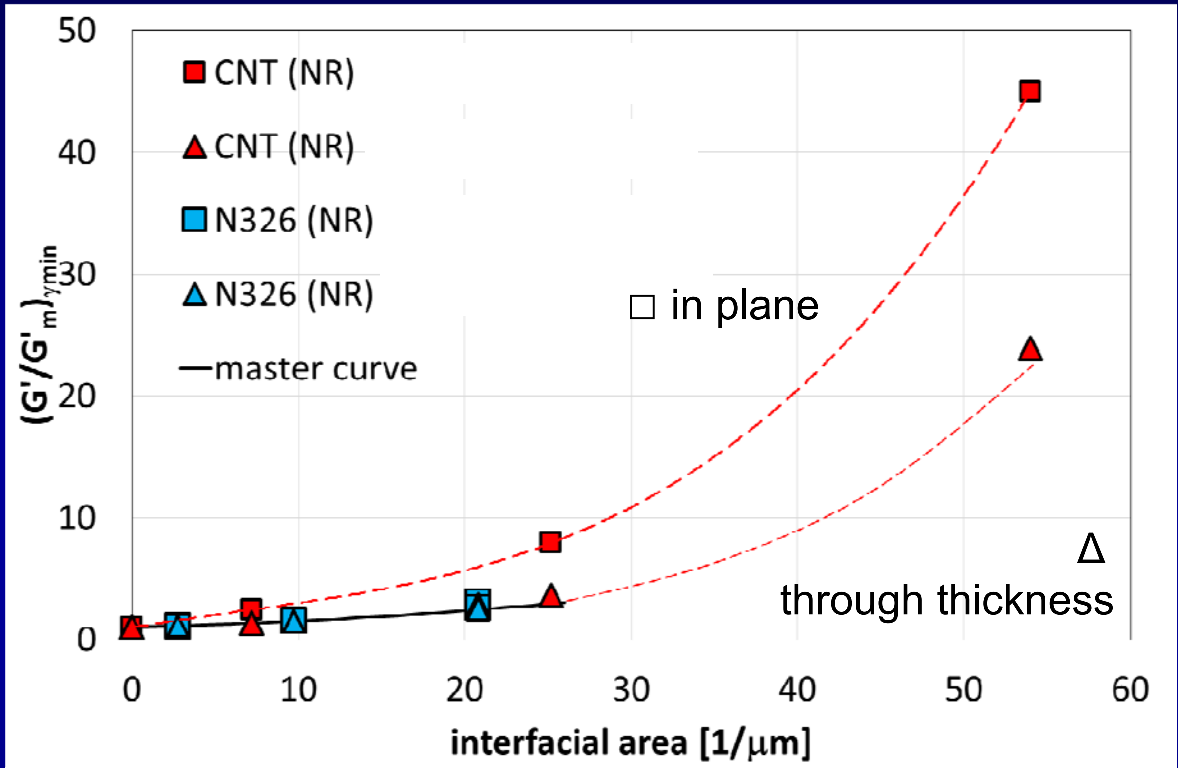
Mastercurve and anisotropy

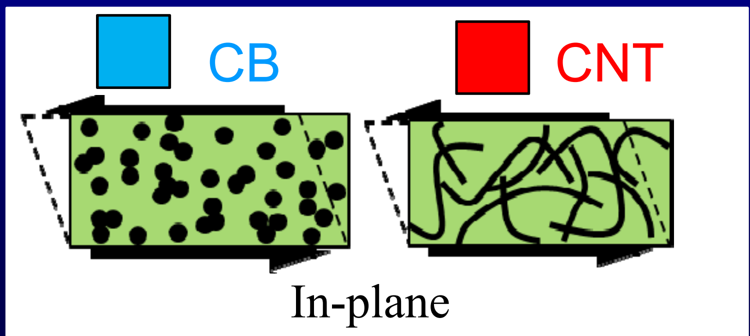
Mastercurve and anisotropy

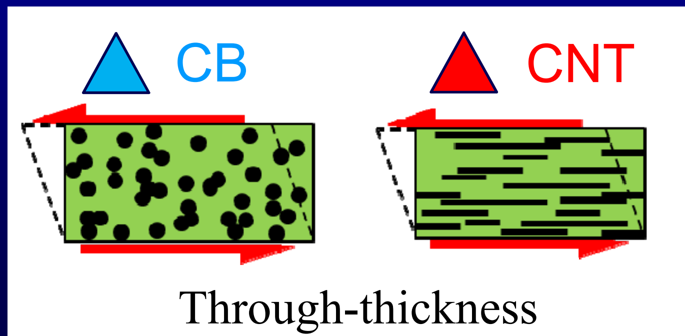




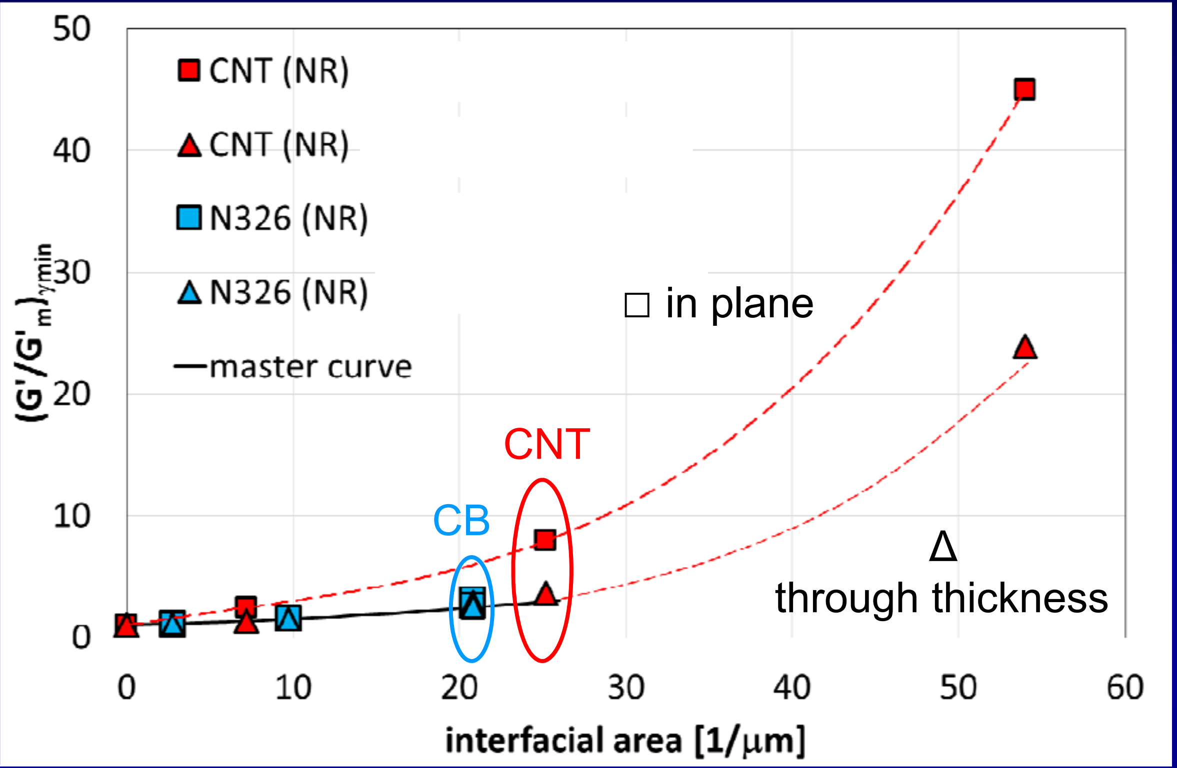
Mastercurve and anisotropy

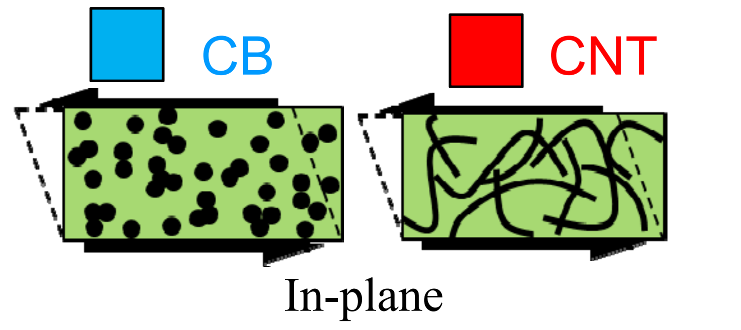


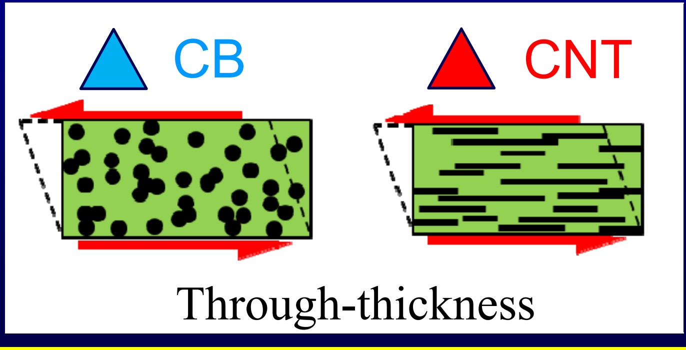




Mastercurve and anisotropy





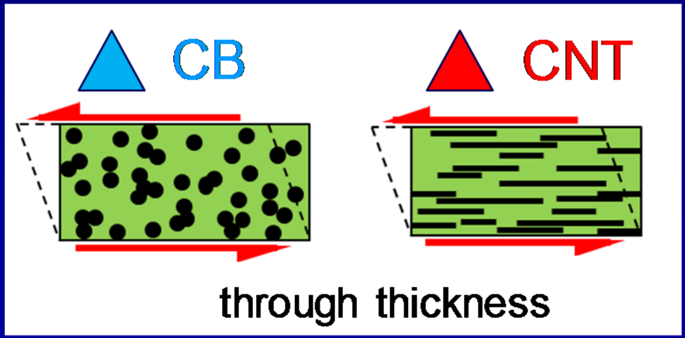


Anisotropic (nano)fillers and composites' modulus

☞ *Warning*

Use of Guth model. It should be used for fillers randomly distributed

☞

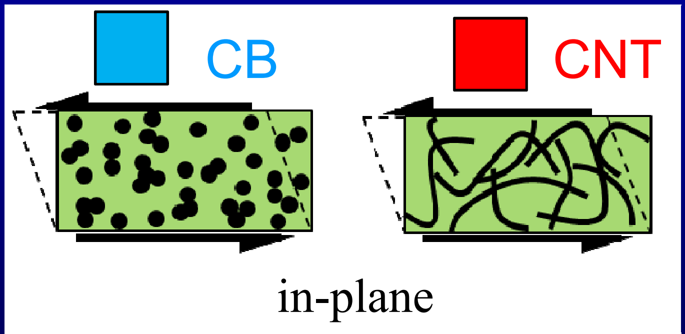


Load is parallel to fibers' direction

Modulus depends on:

volume fraction and surface area

☞



Load is perpendicular to fibers' direction

Modulus depends on:

volume fraction and surface area

and filler aspect ratio

Design of materials

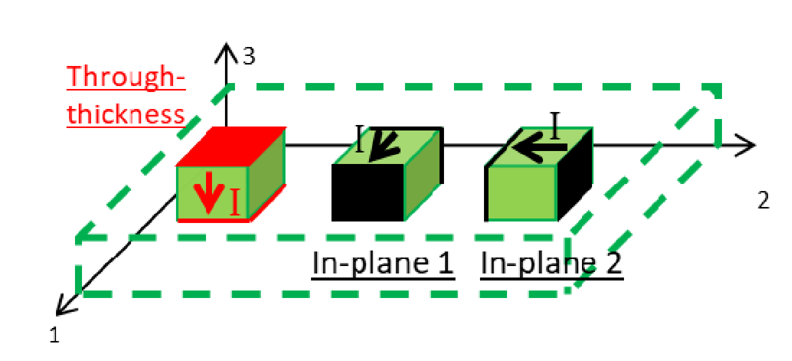
Anisotropic electrical properties

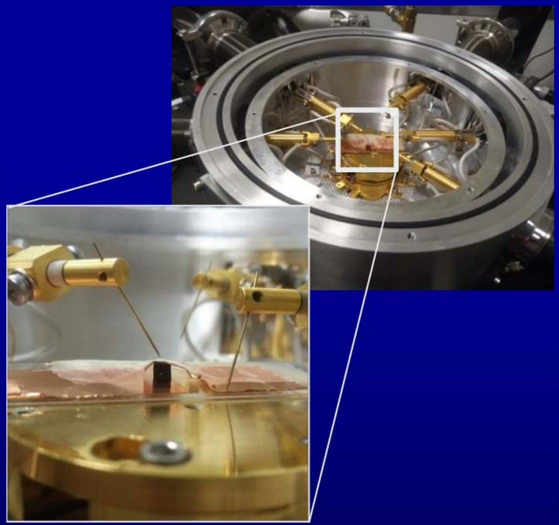
Lightweight materials

Design of materials

Anisotropic electrical properties

Electrical resistivity measurements

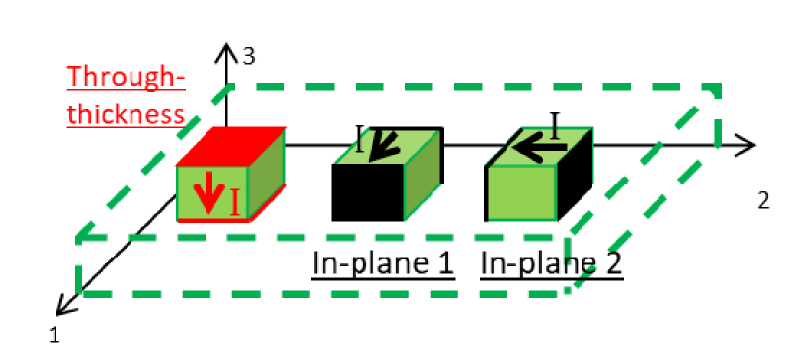


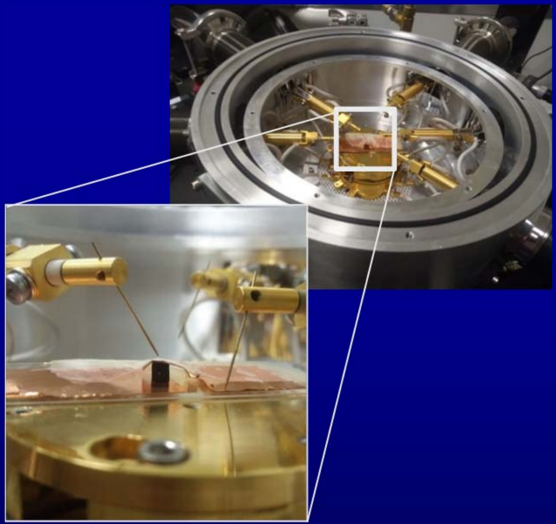


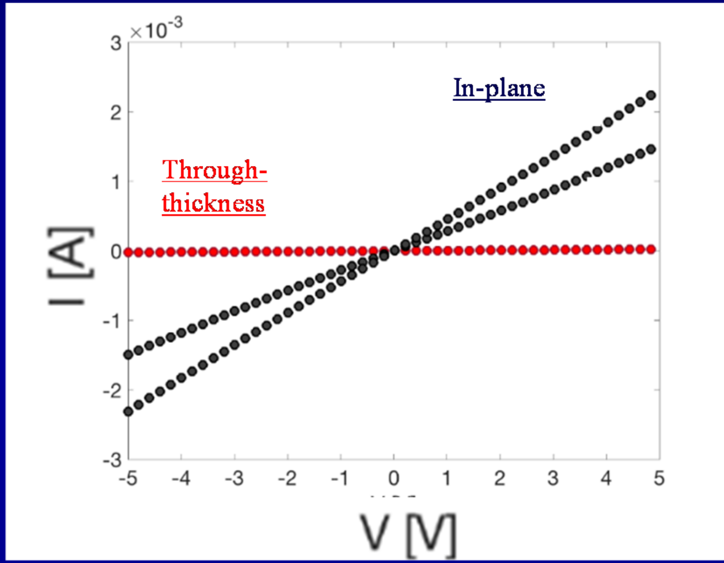
Measurement setup

Specimens: 3x3x3 mm^3. KEITHLEY 2636A System Sourcemeter. Contacts: Copper+silver paste

Electrical resistivity measurements







$$\rho = R\,(S/h)$$

Measurement setup

Specimens: 3x3x3 mm^3. KEITHLEY 2636A System Sourcemeter. Contacts: Copper+silver paste

In-plane

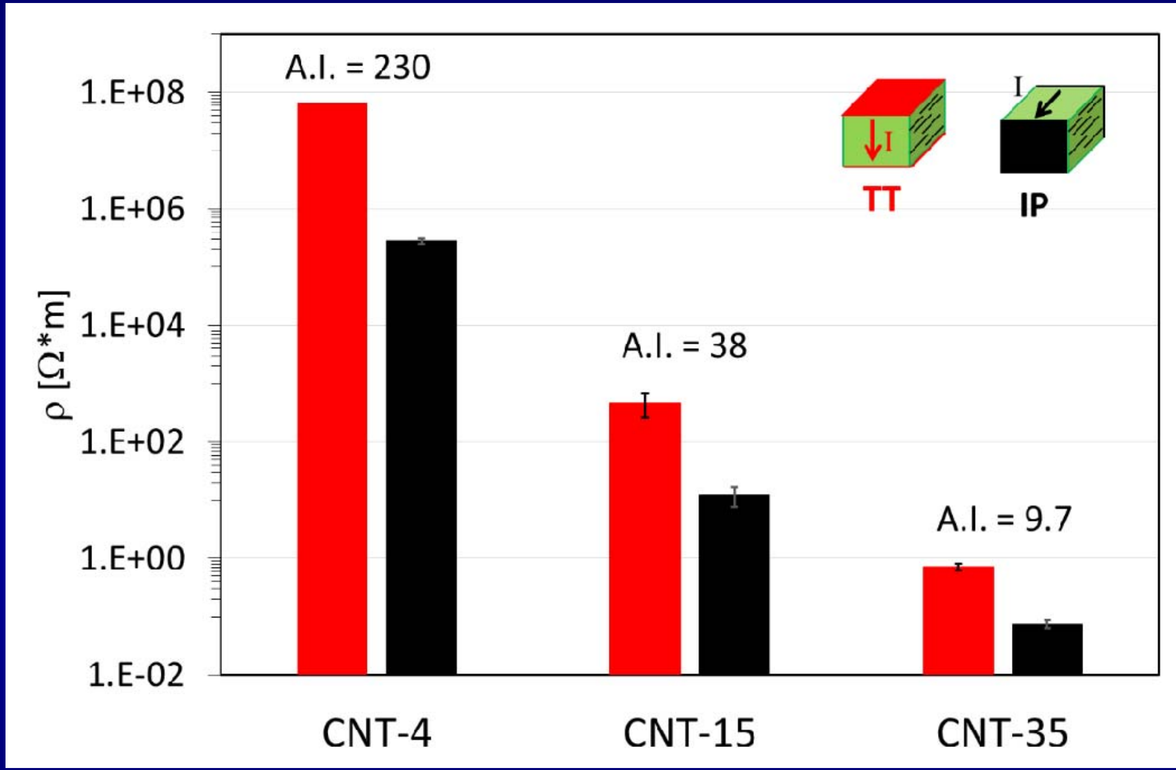
Through-thickness

I [A]

V [V]

Electrical resistivity measurements - Anisotropy Index

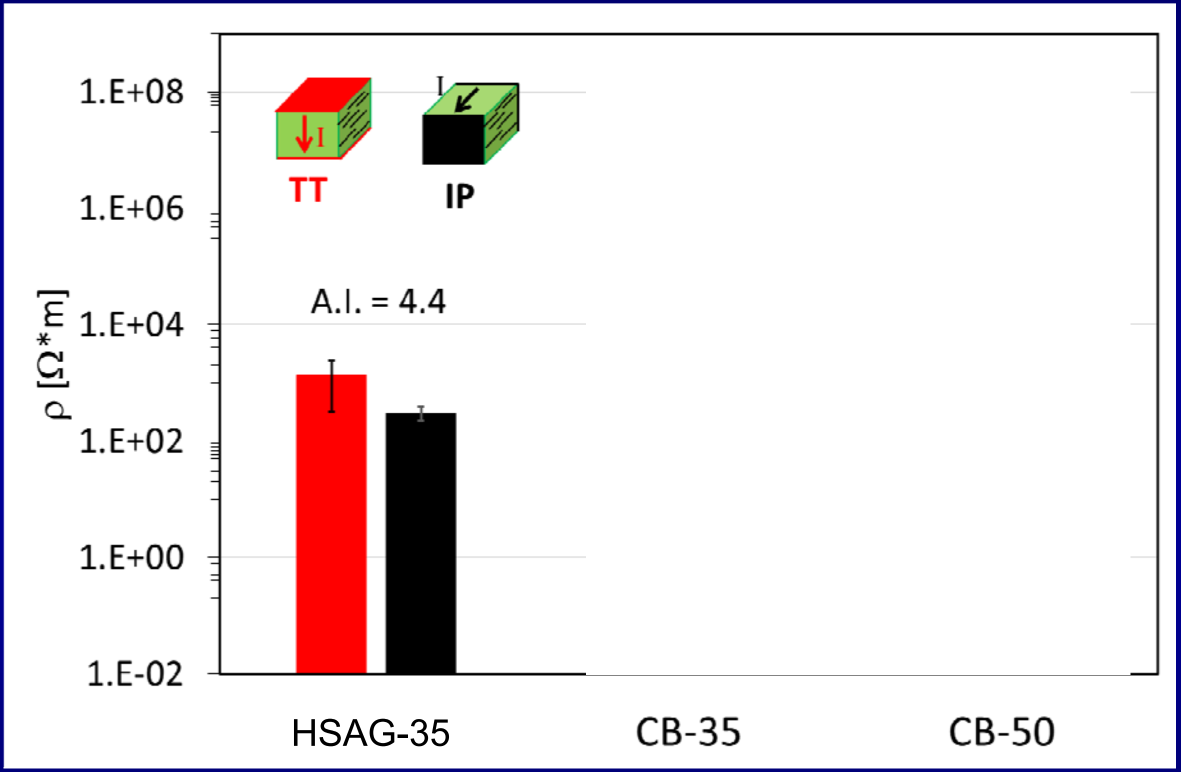
CNT in NR



A.I. = Anisotropy Index = $\rho_{TT}/\ \rho_{IP}$

Electrical resistivity measurements - Anisotropy Index

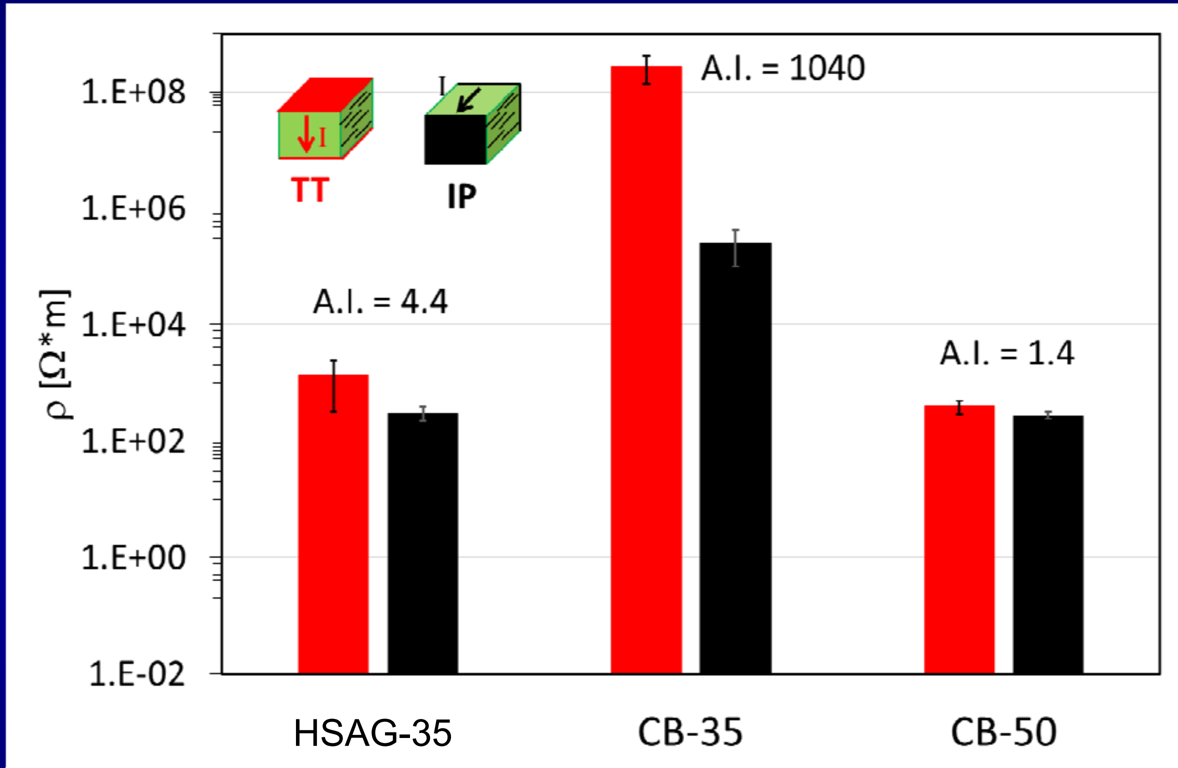
HSAG, in NR



A.I. = Anisotropy Index = ρ_{TT} / ρ_{IP}

Electrical resistivity measurements - Anisotropy Index

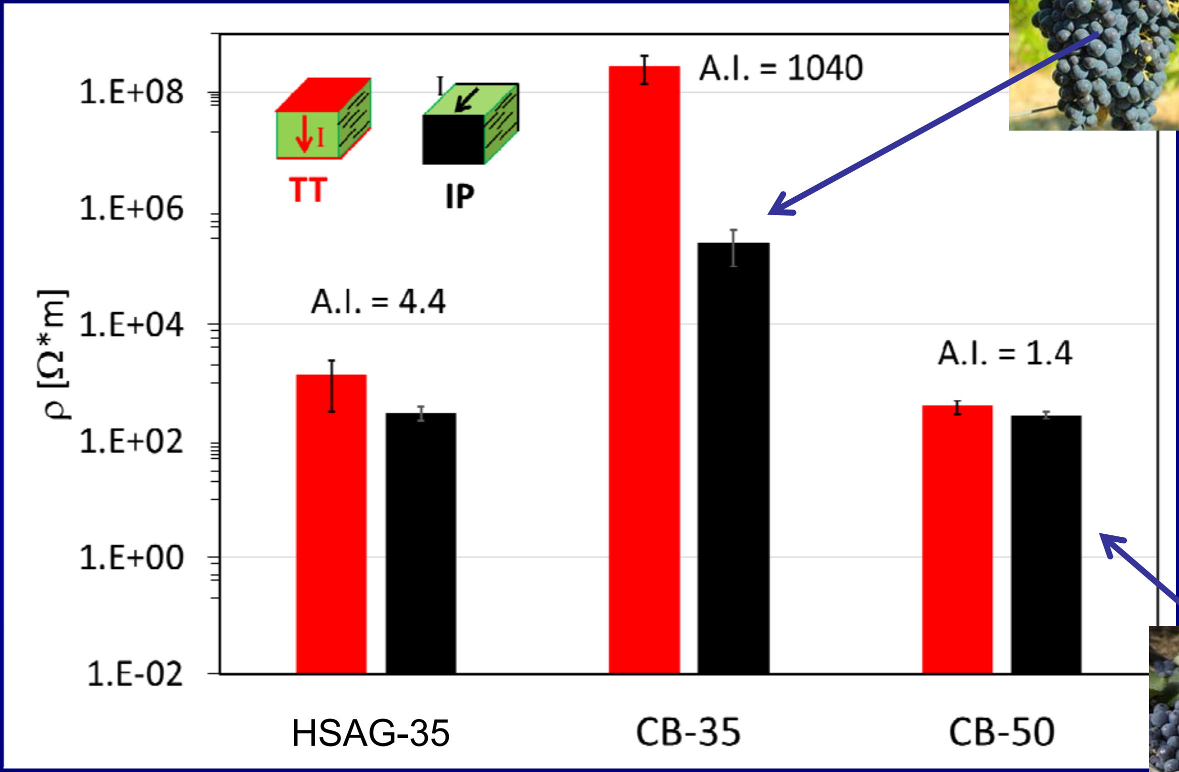
HSAG, CB in NR



A.I. = Anisotropy Index = ρ_{TT} / ρ_{IP}

Electrical resistivity measurements - Anisotropy Index

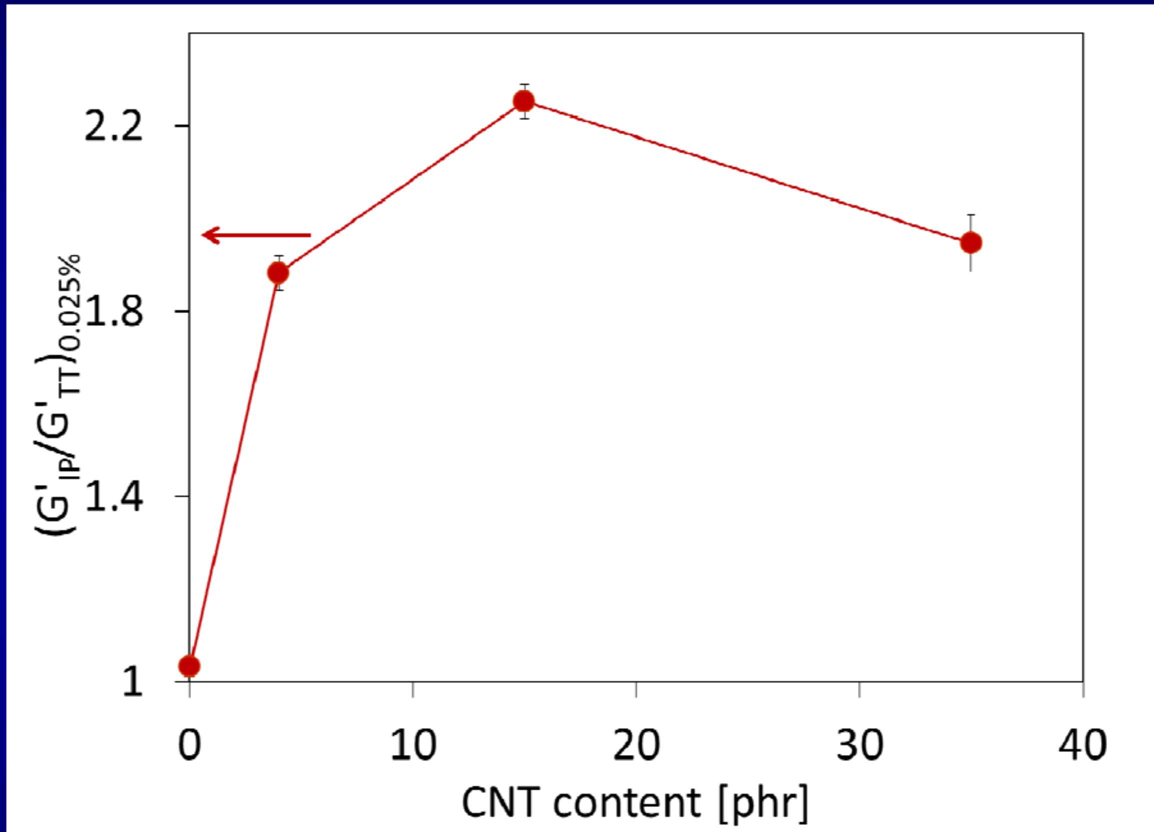
HSAG, CB in NR



A.I. = Anisotropy Index = ρ_{TT} / ρ_{IP}

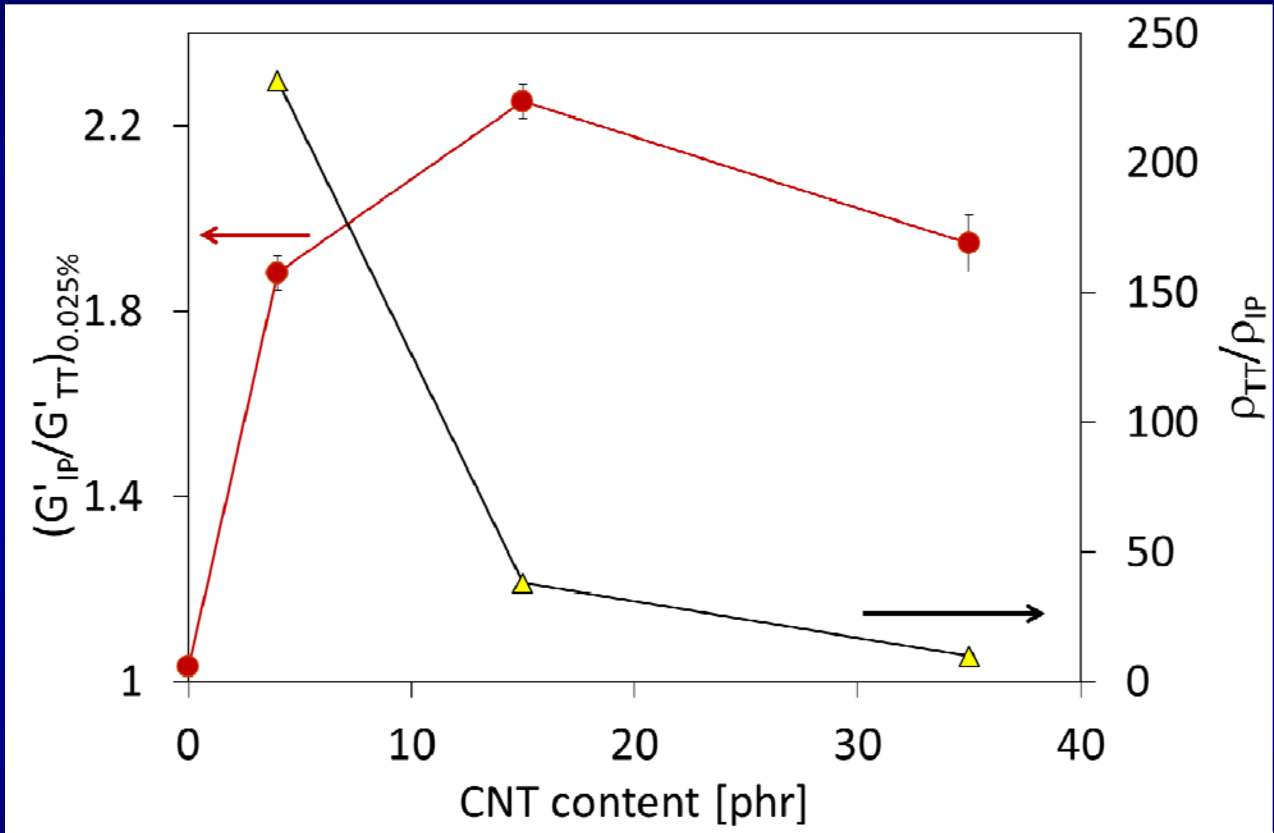
Mechanical and electrical anisotropy indexes

Mechanical anisotropy index



CNT based compounds. Mechanical and electrical anisotropy indexes

Mechanical anisotropy index



Electrical anisotropy index

Design of materials

Lightweight materials

Lightweight materials from the master curve of mechanical reinforcement

Equation of the master curve

to correlate modulus and interfacial area

↓

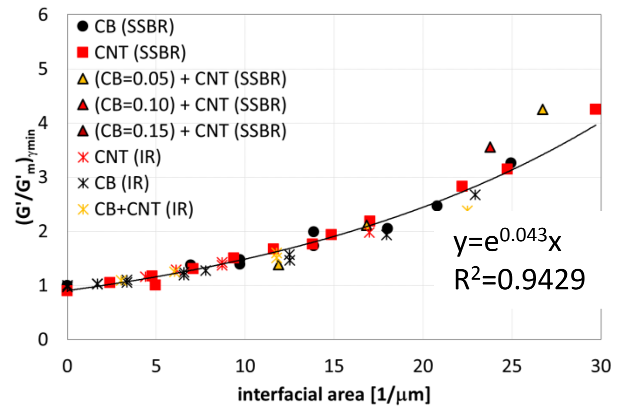
Target modulus and density

↓

Best combination of sp^2 carbon allotropes: lighweight materials

Lightweight materials from the master curve of mechanical reinforcement

☞ To solve the equation of the master curve

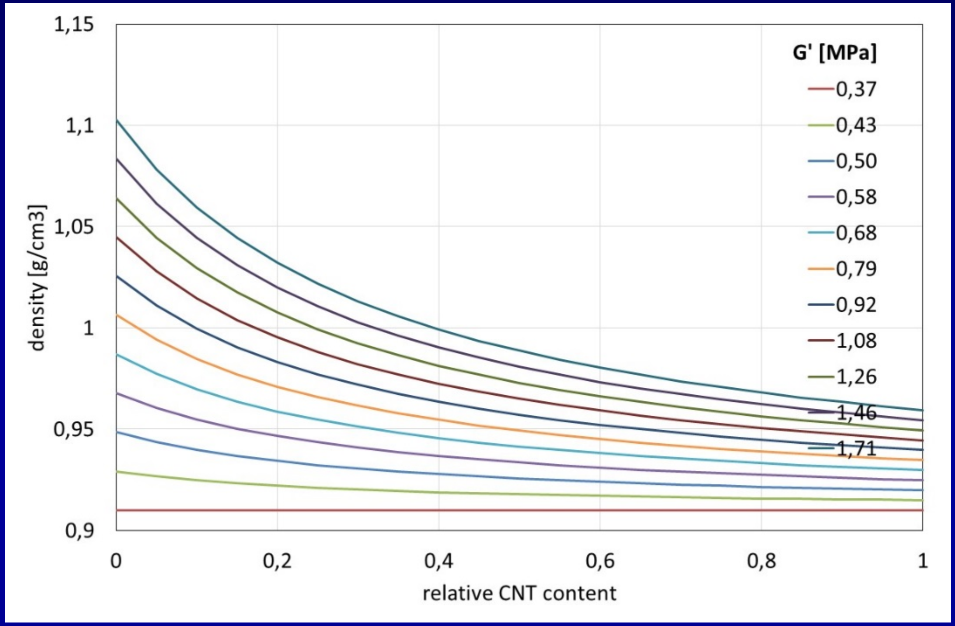


$$G'_{\gamma min}/G'_{m} = e^{0.043\ i.a.}$$

☞ Target density

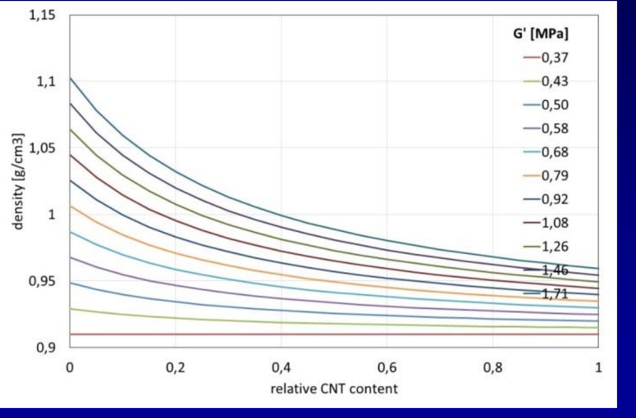
$$\rho_{C} = \rho_{CB} * \phi_{CB} + \rho_{CNT} * \phi_{CNT} + \rho_{m} * (1 - \phi_{CB} - \phi_{CNT})$$

Target modulus and density as a function of relative CNT content



Relative CNT content $= \phi_{CNT}/(\phi_{CB}+\phi_{CNT})$

Target modulus and density as a function of relative CNT content



Relative CNT content = $\phi_{CNT}/(\phi_{CB}+\phi_{CNT})$

Target G' = 1,46 MPa

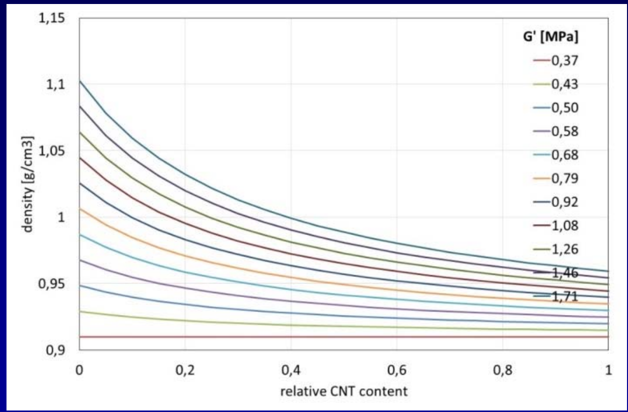
↓

% CNT in CB/CNT = 0

↓

density = 1.08

Target modulus and density as a function of relative CNT content

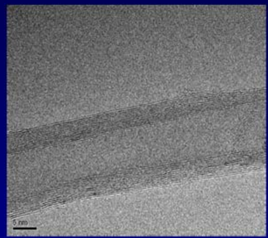


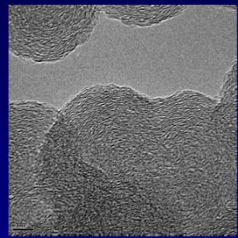
Relative CNT content = $\phi_{CNT}/(\phi_{CB}+\phi_{CNT})$

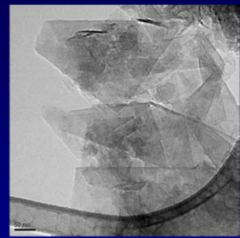
Target G' = 1,46 MPa → % CNT in CB/CNT = 0 → density = 1.08

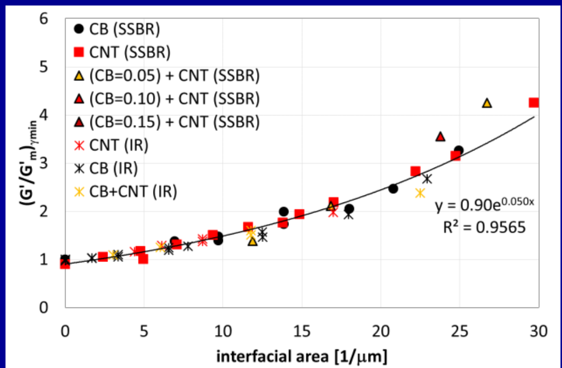
Target G' = 1,46 MPa → Target density = 1 → % CNT in CB/CNT = 30

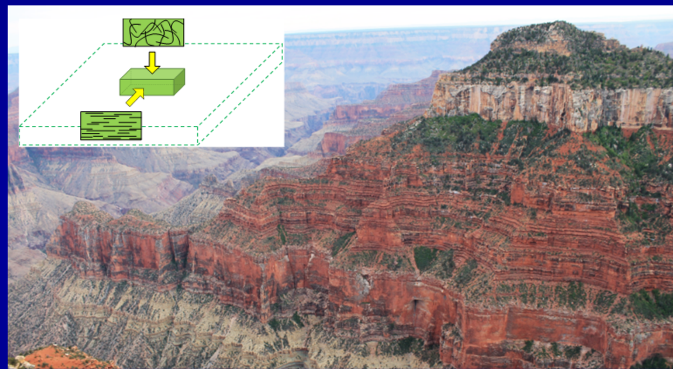
Conclusions

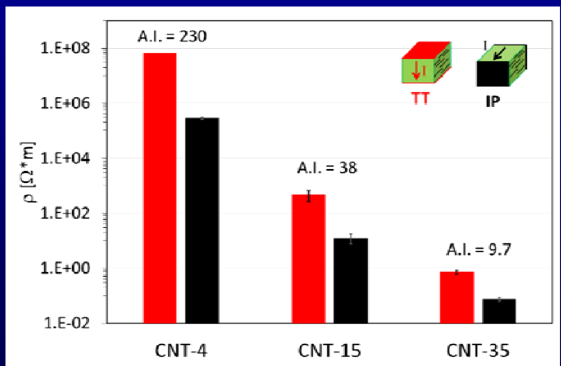


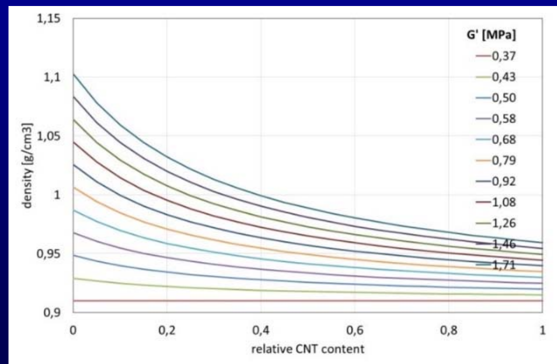












Acknowledgments

- www.lidup.polimi.it

- Fabrizio Torricelli, Paolo Romele — University of Brescia

- Pirelli Tyre

Rubber Division
American Chemical Society

Enhancing science, technology and business across the ***evolving elastomeric community****.*

Thanks
for the attention!