From master curves for the mechanical reinforcement of rubber based nanocomposites to lightweight materials for automotive

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RUBBERCON
RUBBER PRODUCTS FOR AUTOMOTIVE
PRAGUE – CZECH REPUBLIC
23.–25. 5. 2017

Department of Chemistry, Materials and Chemical Engineering G. Natta

Department of Mechanical Engineering

Department of Civil and Environmental Engineering

LiDuP
Lightweight Construction and Durability Performance

Objectives of the work

- ☞ To develop lightweight elastomeric materials
  for automotive application

- ☞ To prepare elastomer composites based on sp^2 carbon allotropes

- ☞ To identify a common correlation between
  features of sp^2 carbon allotropes
  and properties of elastomer composites

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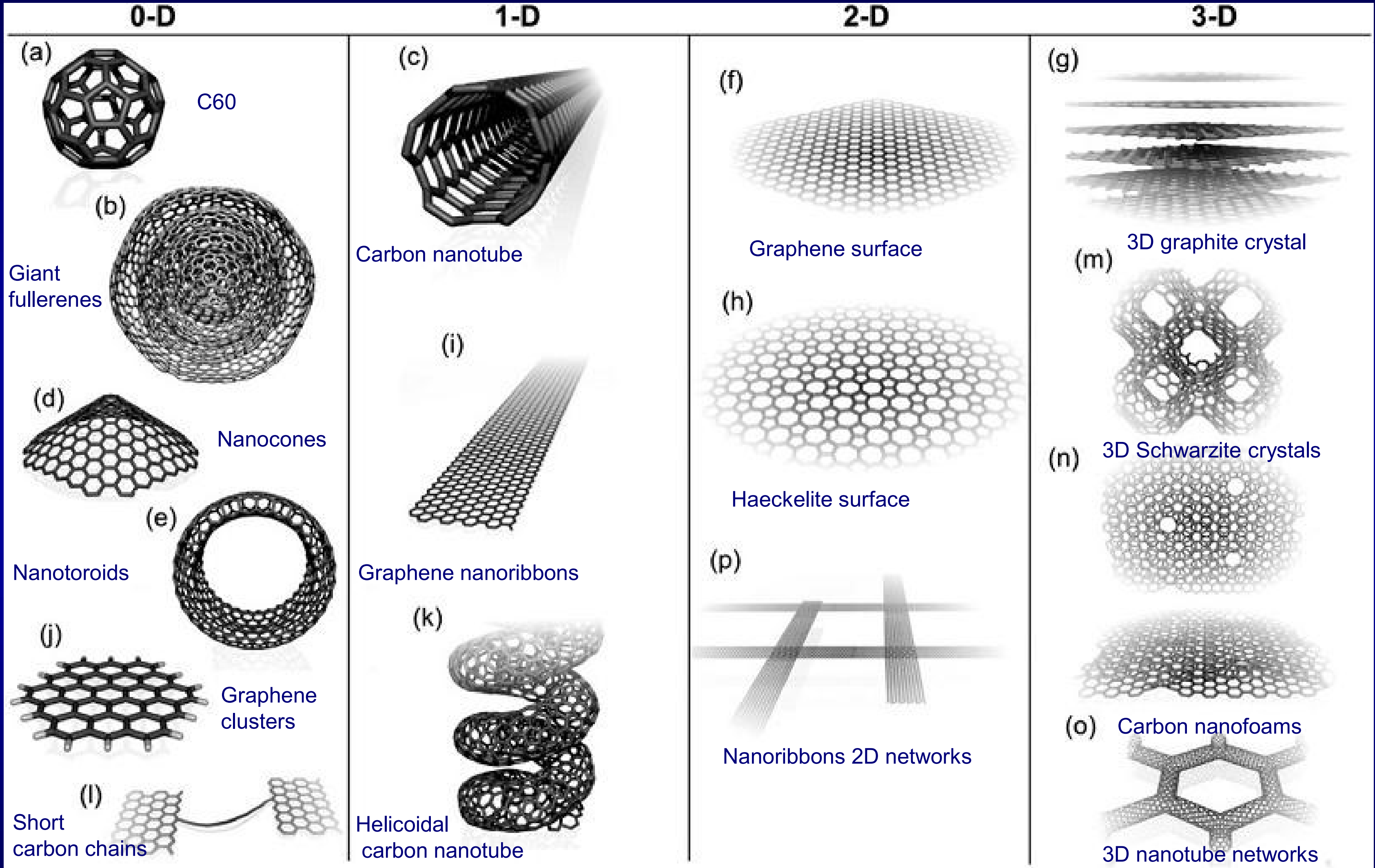
  features of sp^2 carbon allotropes
  and properties of elastomer composites

  - ☞ To design composites suitable for automotive application
    on the basis of this correlation

Outline of the presentation

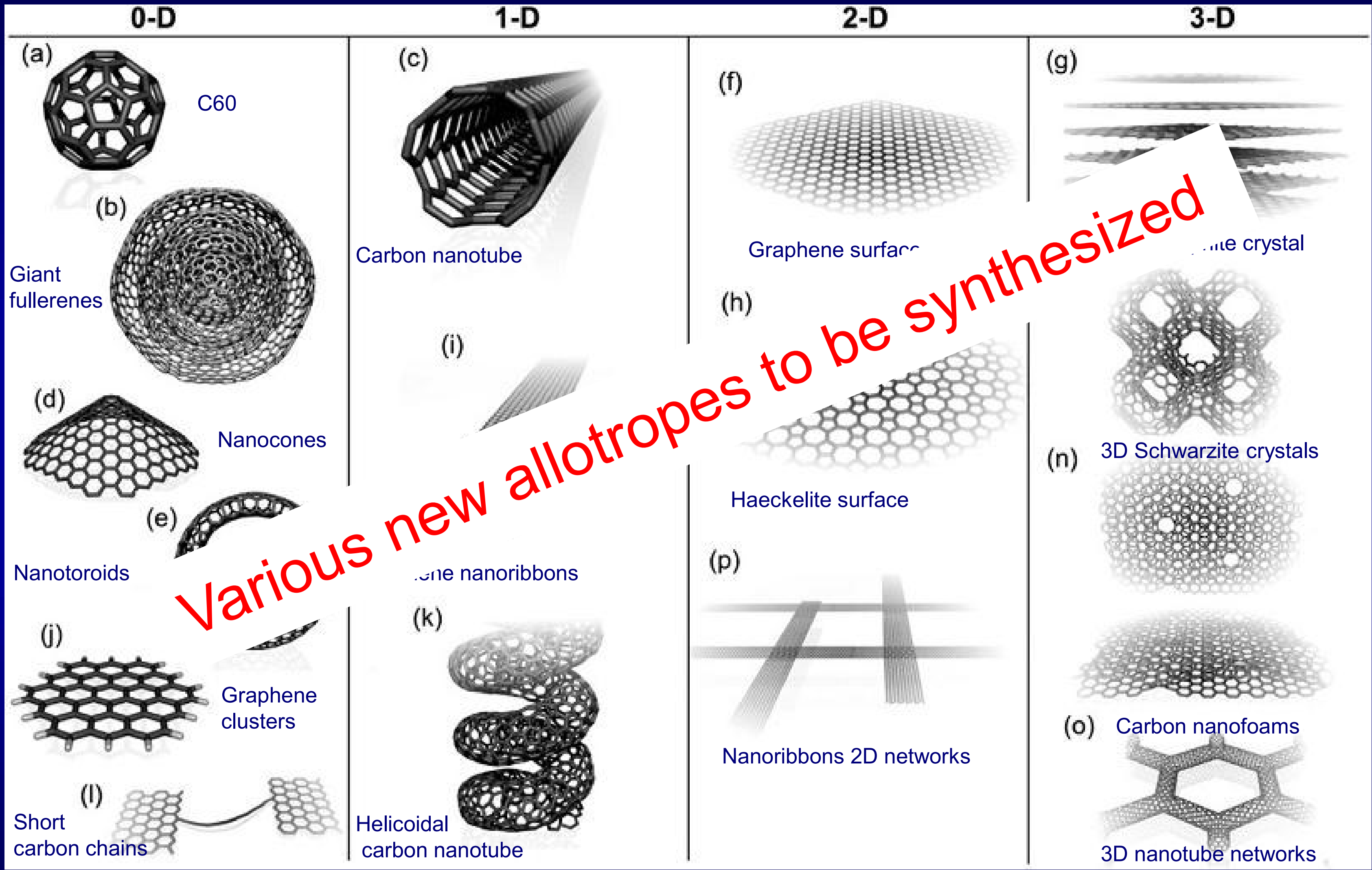
- Characterization of sp^2 carbon allotropes
- Master curves for the mechanical reinforcement of elastomer composites based on sp^2 carbon allotropes
- Anisotropic properties of composites
- Design and preparation of lightweight materials
- Impact on CO_2 emission

Carbon allotropes



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

Carbon allotropes



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

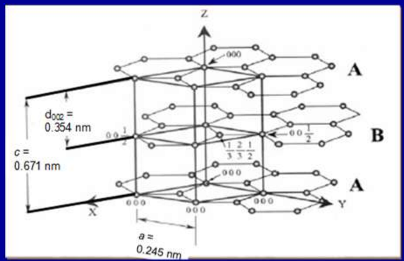
Jin Zhang et al, Carbon 98 (2016) 708e732

Carbon fillers from a layer of sp^2-bonded carbon atoms

graphene

stacked

wrapped



few stacked layers

few layers graphene

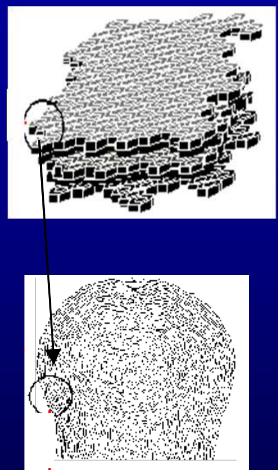
grades with different
shape anisotropy

many stacked layers

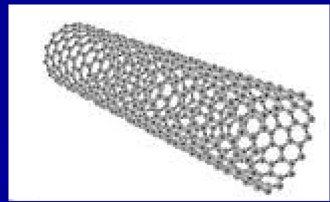
graphite

carbon black

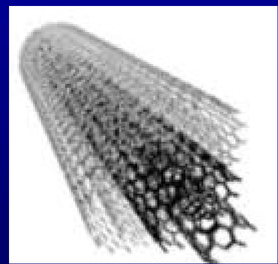
few stacked layers
randomly arranged
in spheres



CNT



single walled



multi walled

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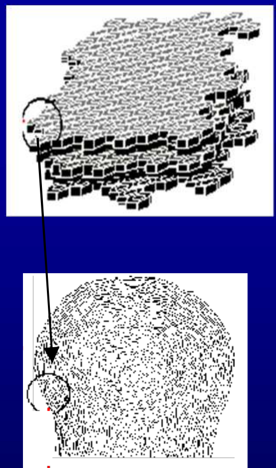
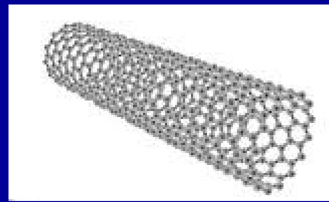
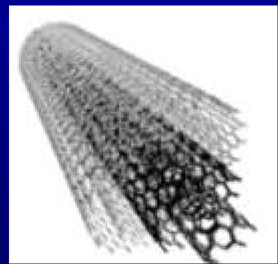


CNT



single walled

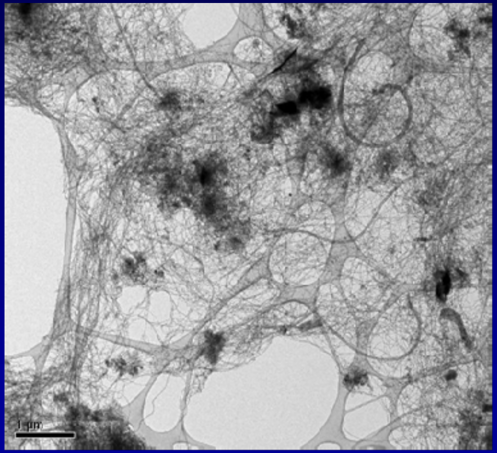


multi walled

Analysis of mechanical reinforcement

CNT and CB as the sp^2 carbon allotropes

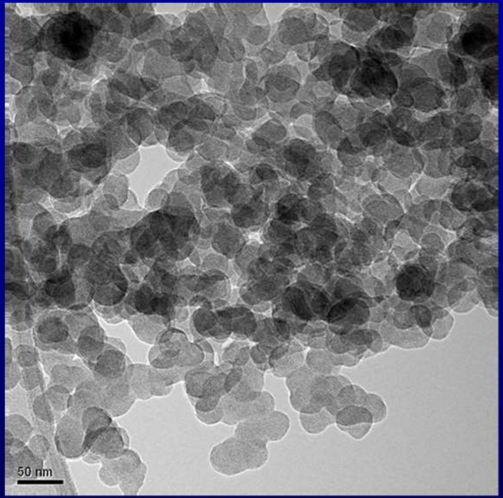
CNT

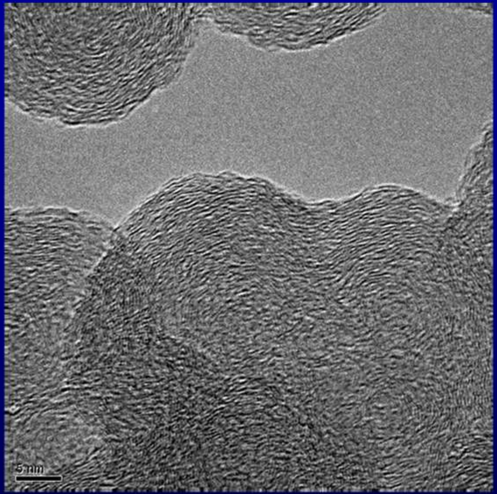


NANOCYL® NC7000™
from Nanocyl

Carbon purity ≈ 90% (TGA)

CB

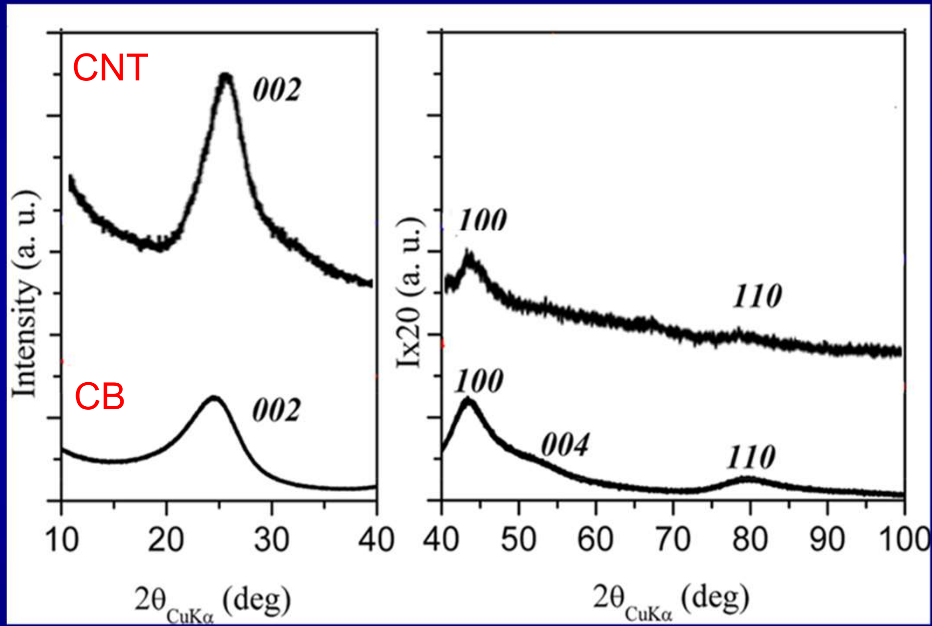




CBN326
from Cabot

Carbon purity ≈ 98% (TGA)

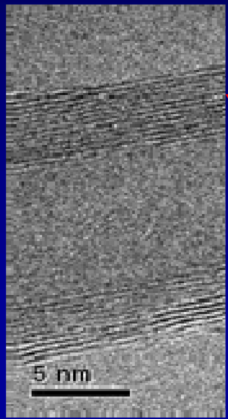
WAXD patterns of CNT and CB



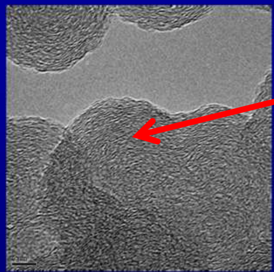
☞ Turbostratic structure

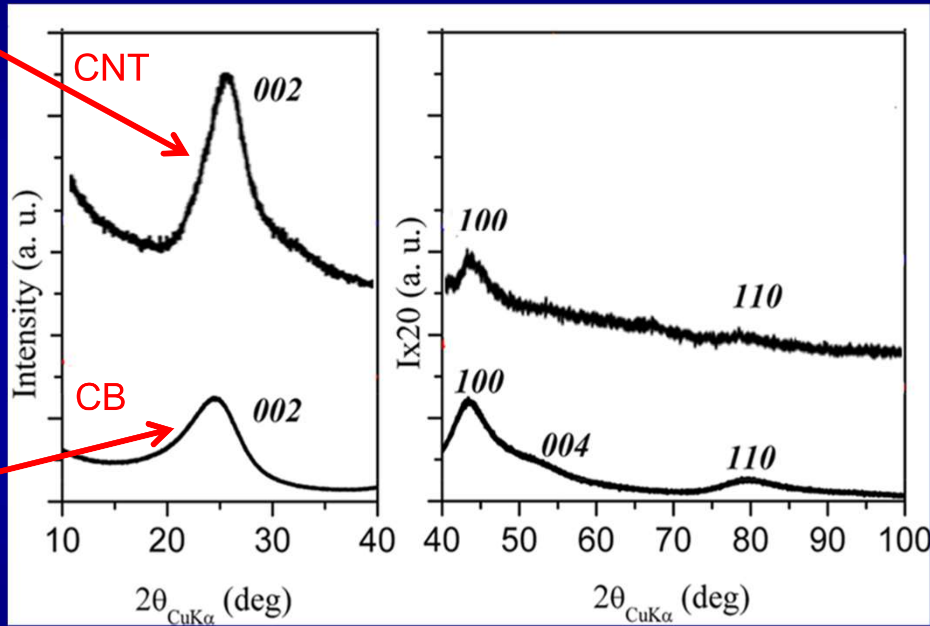
WAXD patterns of CNT and CB

10 - 8



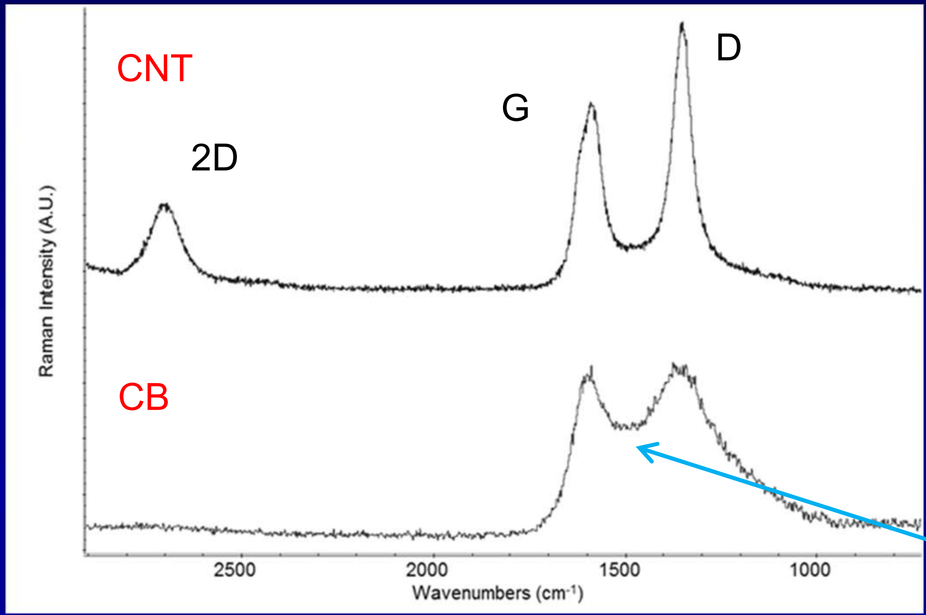
≈ 5





☞ Turbostratic structure

Raman spectra of CNT and CB

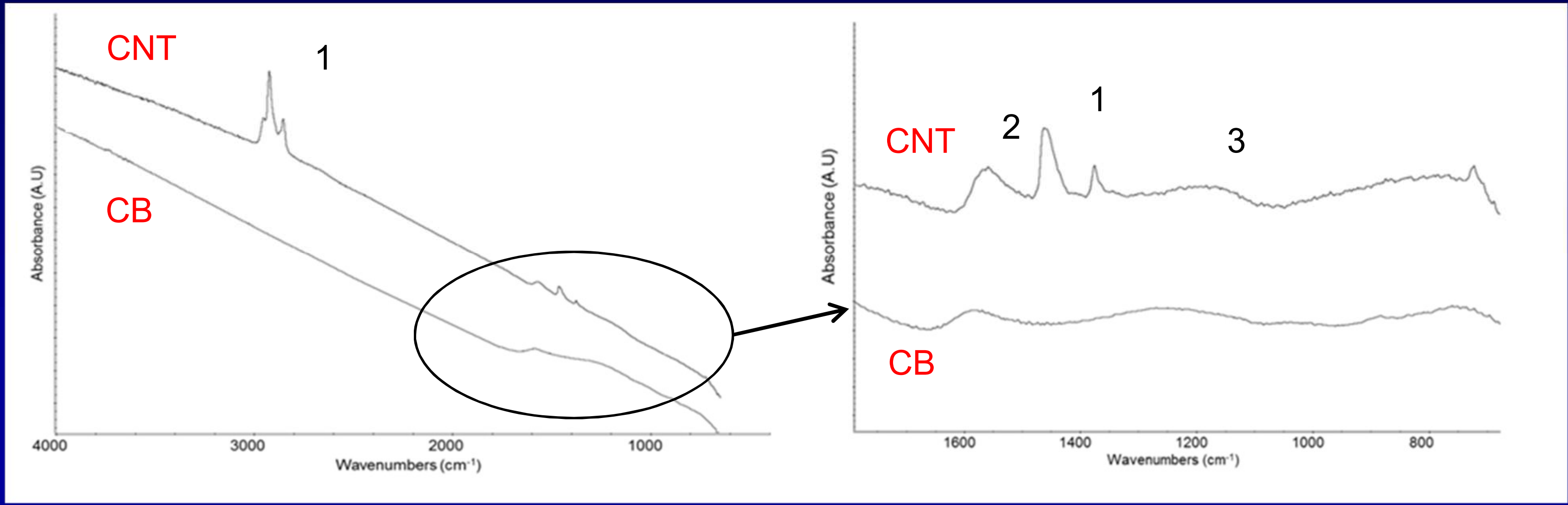


disordered

sp^3 carbon structures

☞ much higher degree of disorder in CB

Infrared spectra of CNT and CB



1 vibrations of CH_2 and CH_3 groups

2 E_{1u} IR active mode of the collective C=C stretching vibration

3 vibration of OH groups, bending of epoxy or ether groups

☞ Functional groups in CNT

Carbon nanofillers: main features

Carbon filler	BET surface area (m^2/g)	Acidic groups (mmol/g)[a]	pH
CB N326	77	1.3	7.6
CNT	275	2	8.7

[a] by Boehm titration: carboxy, epoxy, hydroxy groups

Analysis of mechanical reinforcement

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

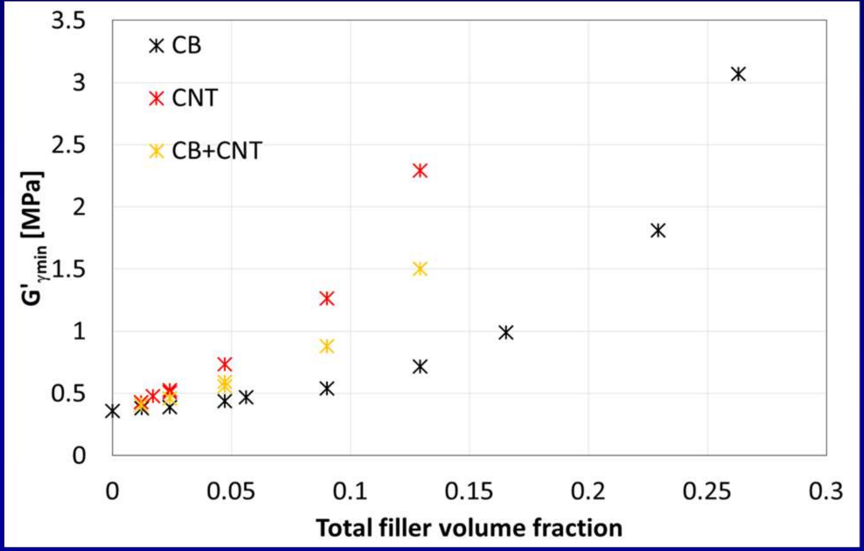
CNT	0; 1; 2; 3; 4; 5; 6; 6.5; 7.5; 10; 11; 14; 18; 20	
CB N326	0; 10; 15; 20; 22; 30; 35; 45; 50; 60	
CB N326	10	+ CNT: 0 ÷ 14
CB N326	22	+ CNT: 0 ÷ 14
CB N326	35	+ CNT: 0 ÷ 14

Fillers with the same volume fraction

Composites crosslinked with dicumyl peroxide: 1.40 phr

Initial Modulus as a function of the total filler content

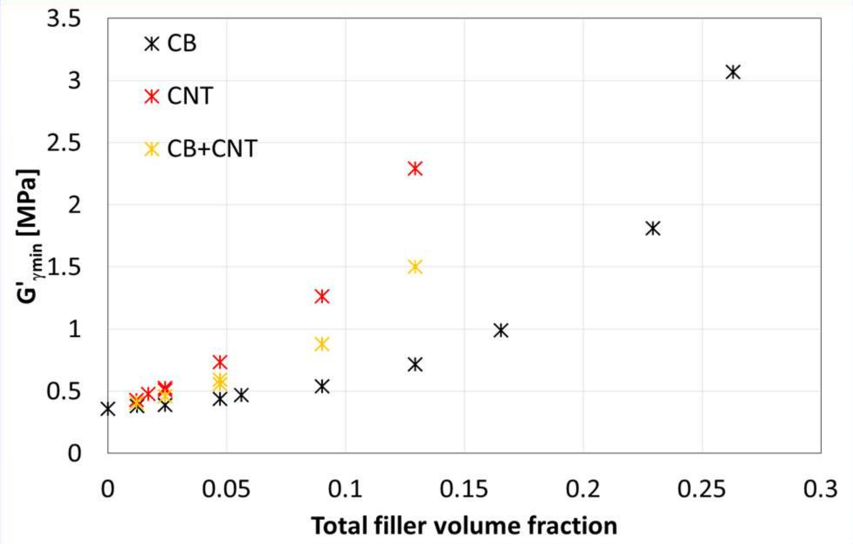
IR



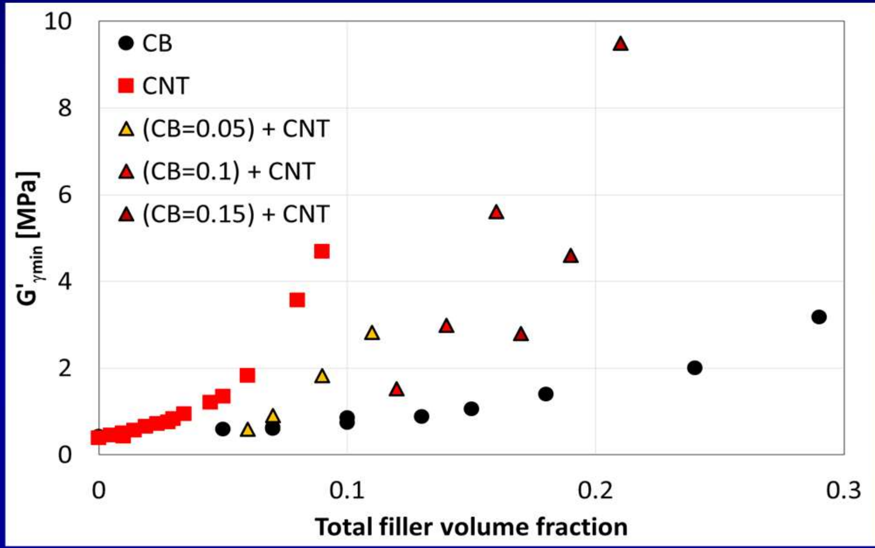
Data from shear stress tests, 50°C

Initial Modulus as a function of the total filler content

IR



SBR

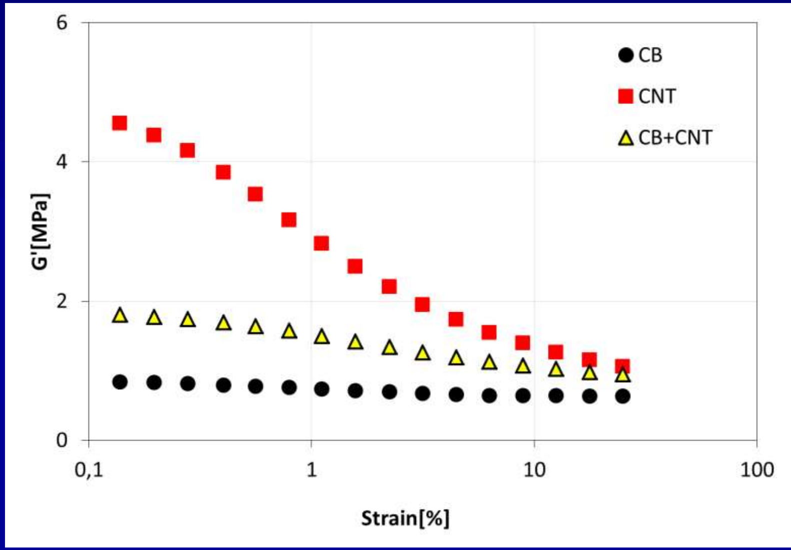


☞ Composites with CNT have larger modulus than composites with only CB

Data from shear stress tests, 50°C

Initial Modulus as a function of the strain amplitude

SBR

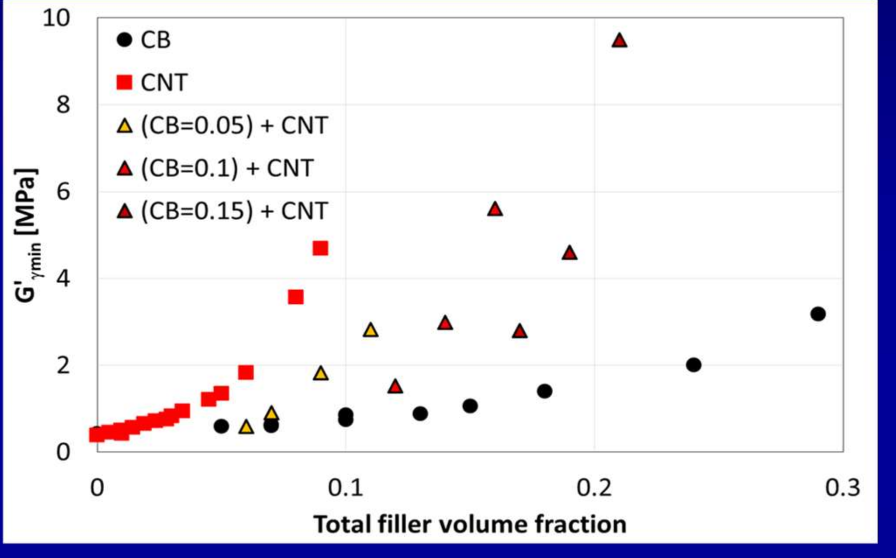


0.09 - 0.1 as total filler volume fraction

☞ Composites with CNT have larger Payne effect than composites with only CB

Data from shear stress tests, 50°C

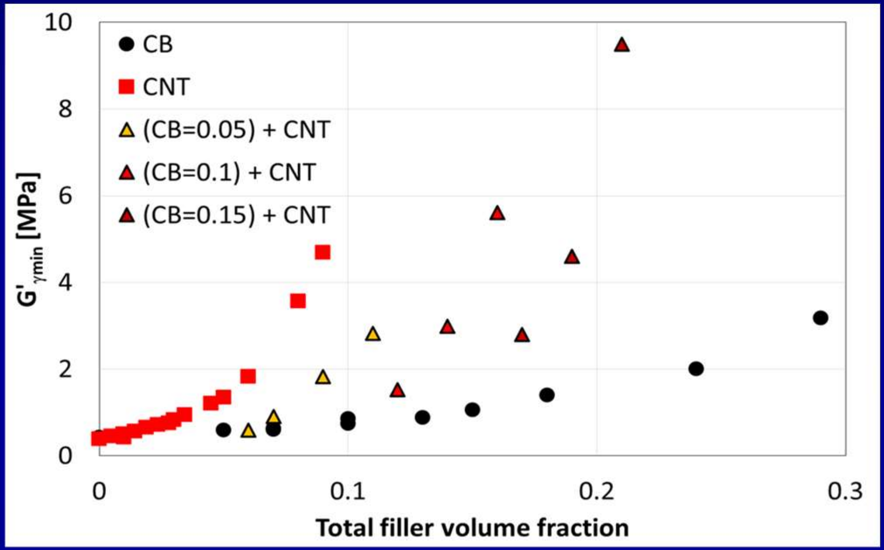
Initial Modulus and Payne effect as a function of the total filler content

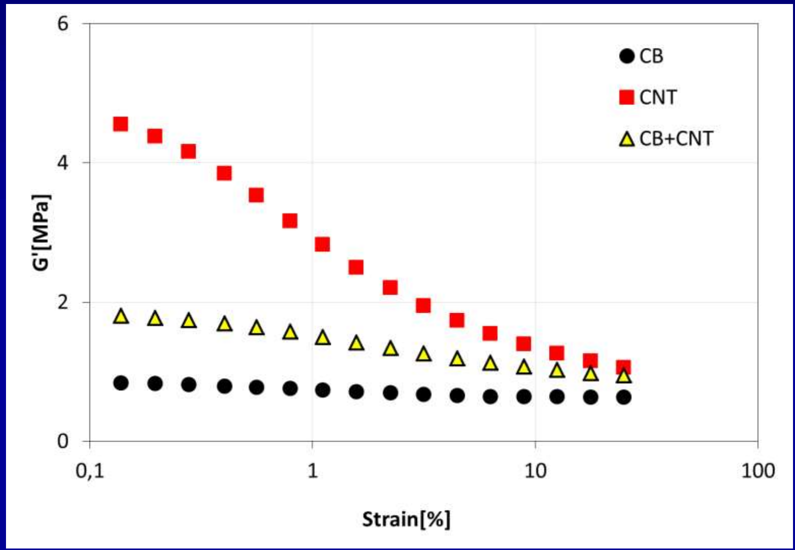


SBR as the elastomer

Data from shear stress tests, 50°C

Initial Modulus and Payne effect as a function of the total filler content





SBR as the elastomer

Data from shear stress tests, 50°C

Back to the objectives

- ☞ To identify a common correlation between features of sp^2 carbon allotropes and properties of elastomer composites

- ☞ To design composites suitable for automotive application on the basis of this correlation

Specific interfacial area as the parameter to correlate mechanical reinforcement

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

filler properties

A = BET surface area

ρ = density

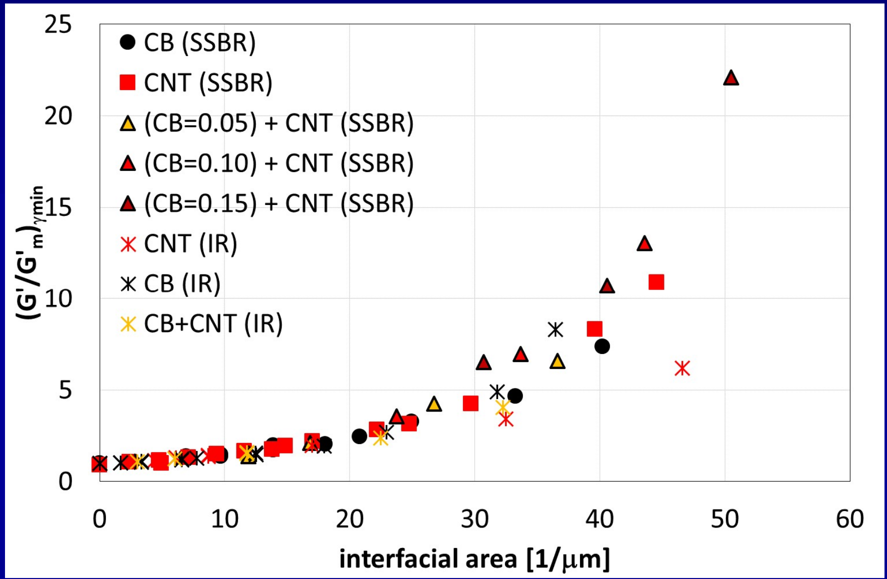
Φ = volume fraction

measure unit: m^2 / m^3

Surface / volume in the composite

Master curve for the initial modulus of elastomers composites

with sp^2 carbon allotropes

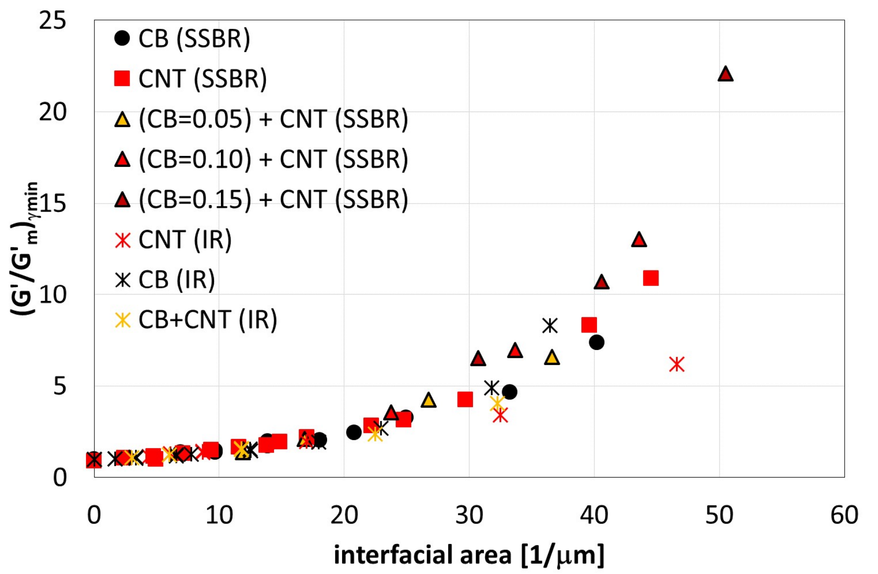


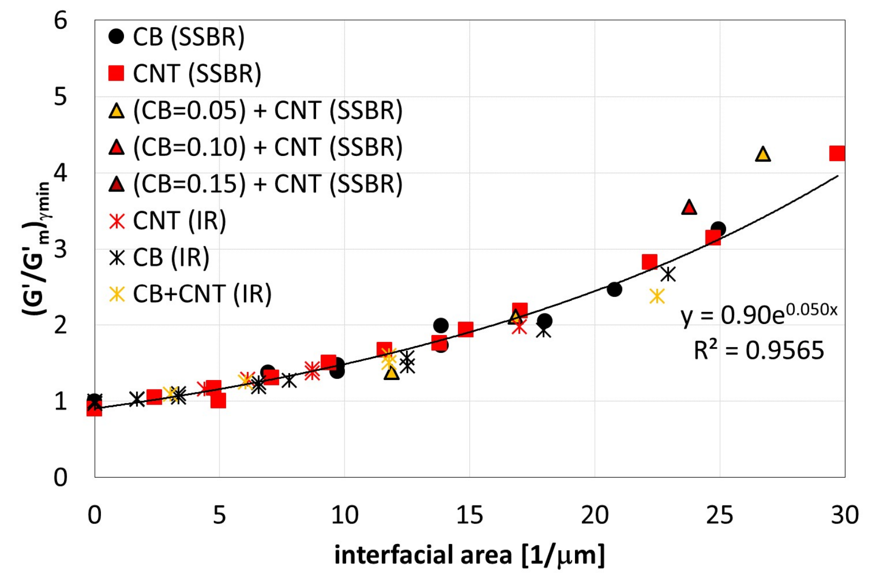
Elastomers: IR, SBR

Data from shear stress tests, 50°C

Master curve for the initial modulus of elastomers composites

with sp^2 carbon allotropes



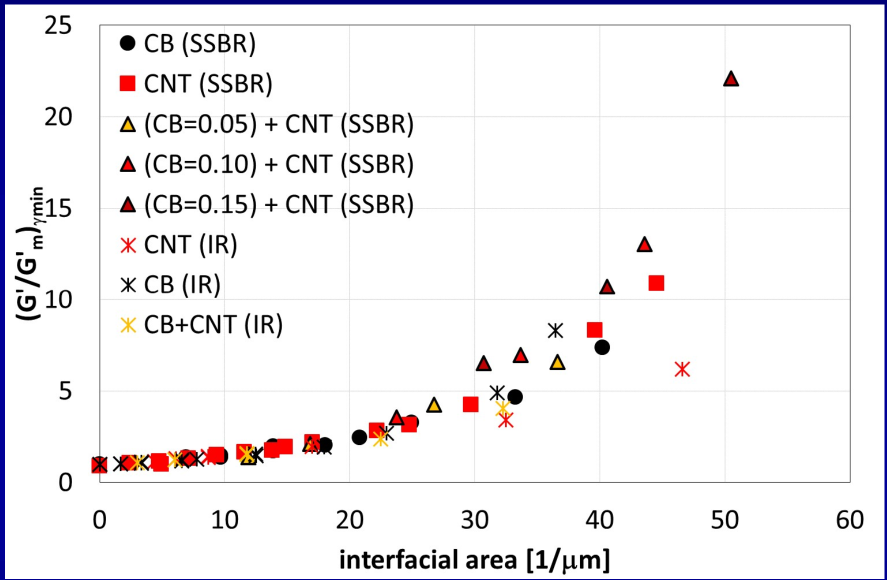


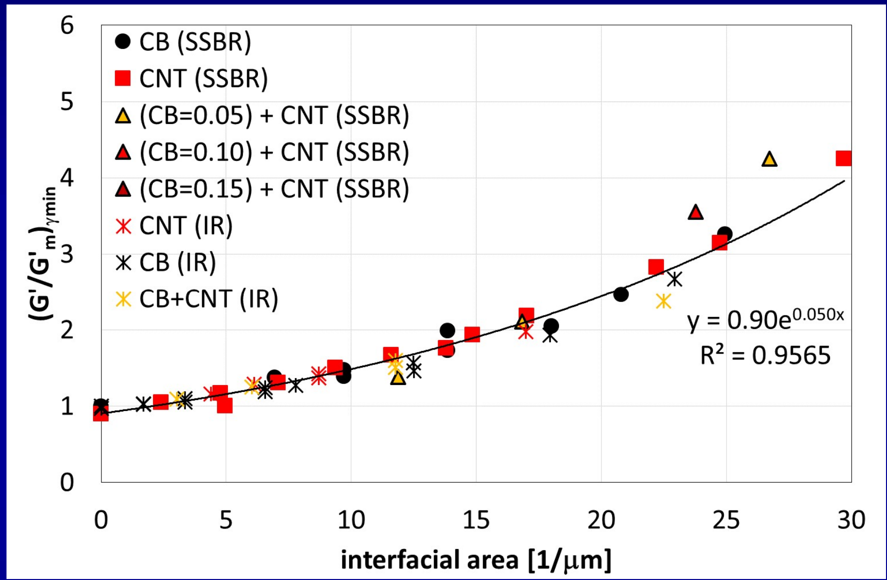
Elastomers: IR, SBR

Data from shear stress tests, 50°C

Master curve for the initial modulus of elastomers composites

with sp^2 carbon allotropes





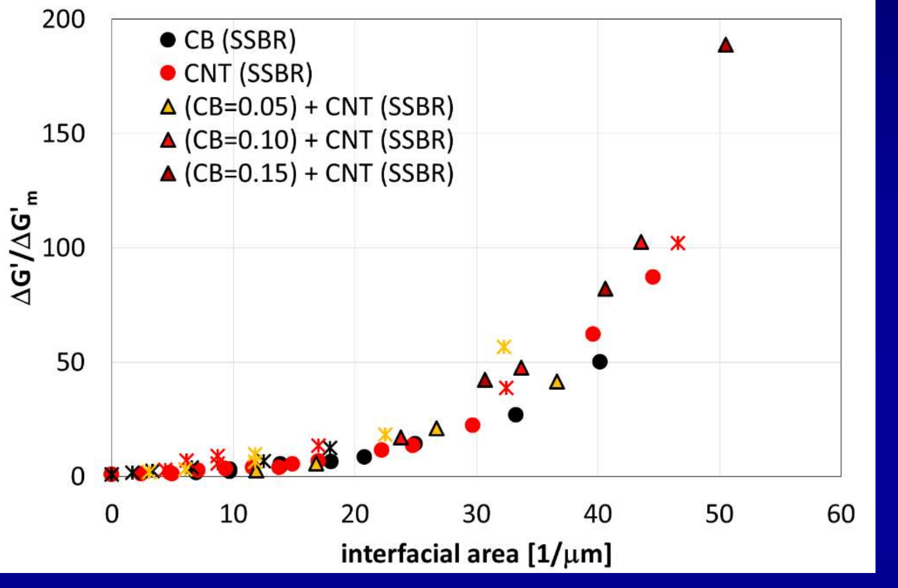
Elastomers: IR, SBR

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



Elastomers: IR, SBR

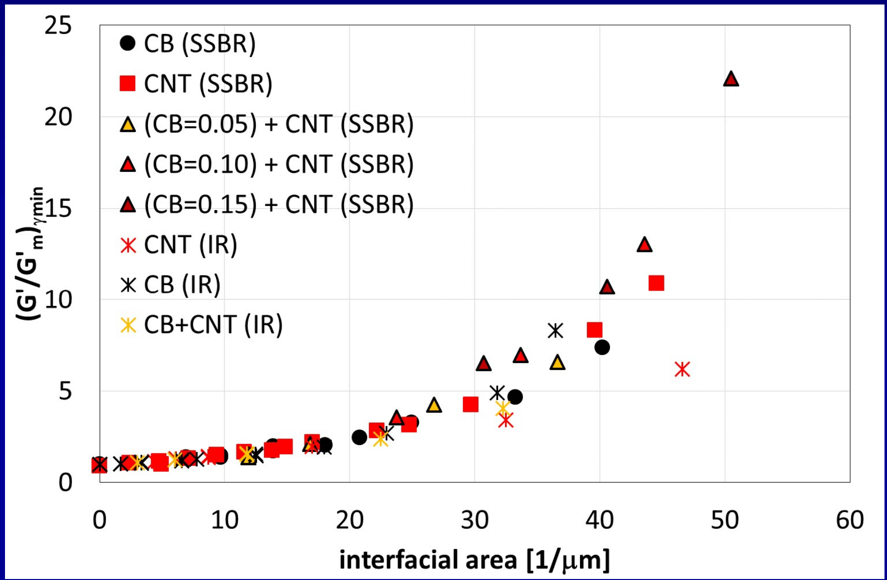
Data from shear stress tests, 50°C

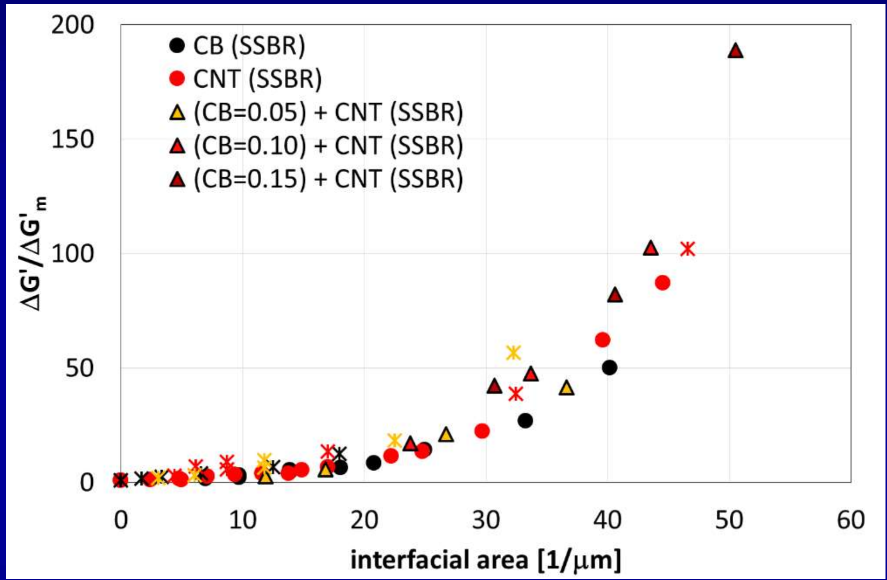
Master curves for the mechanical reinforcement of elastomer composites

with sp^2 carbon allotropes

G'

ΔG'





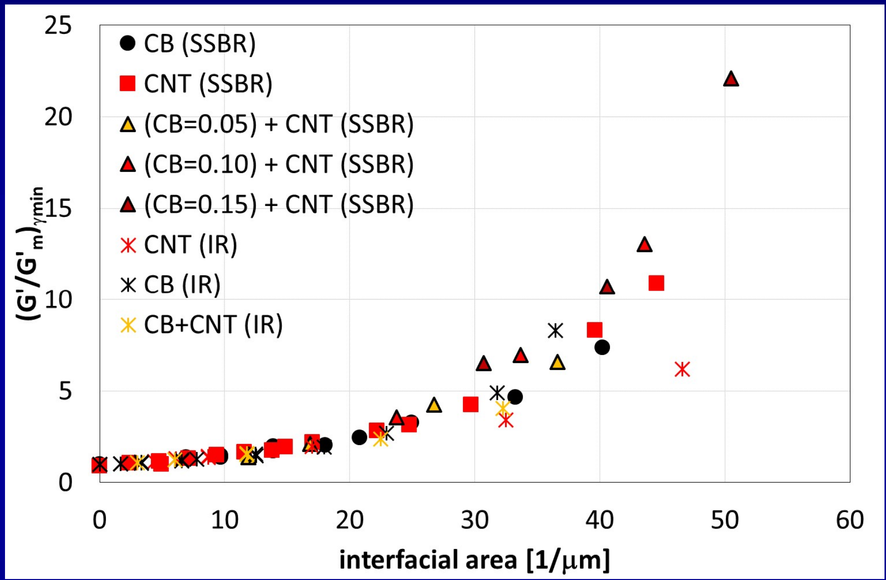
IR, SBR as the elastomers

Data from shear stress tests, 50°C

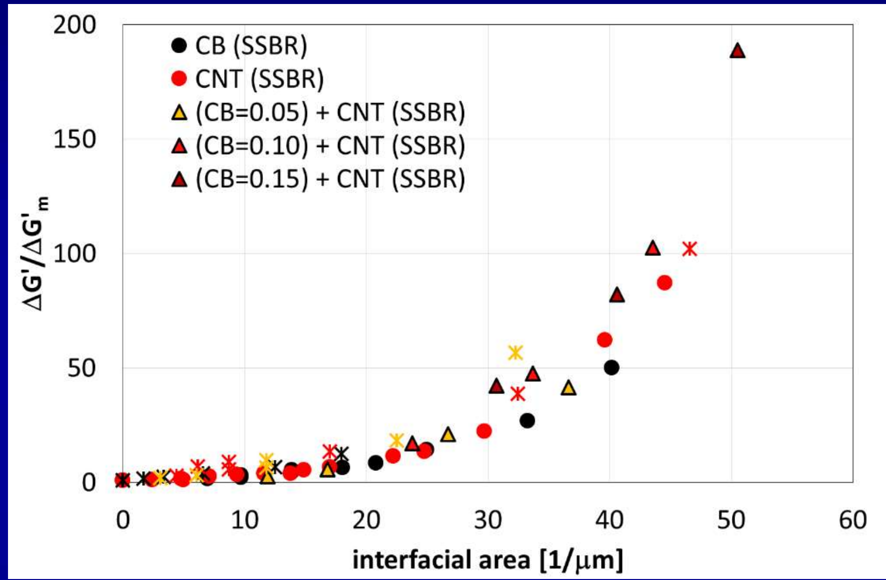
Master curves for the mechanical reinforcement of elastomer composites

with sp[2] carbon allotropes

G’



ΔG’

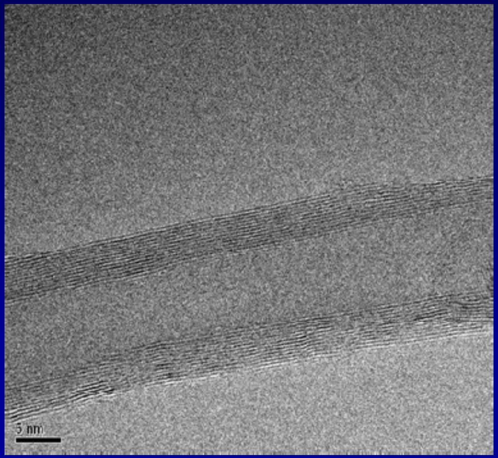


IR, SBR as the elastomers

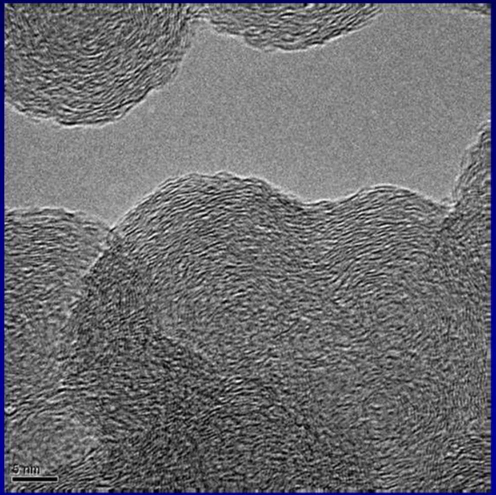
Data from shear stress tests, 50°C

CNT and CB as the sp^2 carbon allotropes

CNT

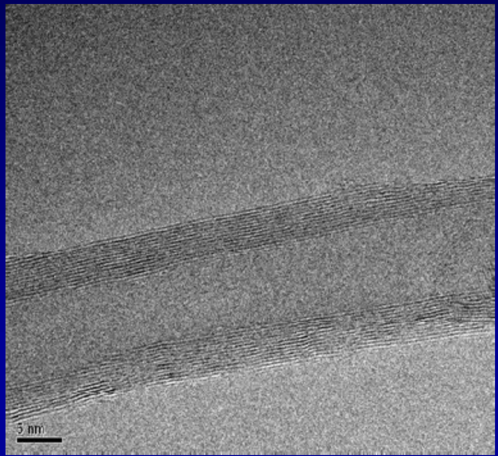


CB

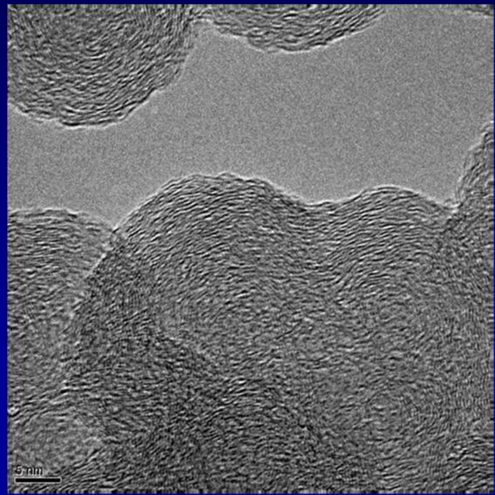


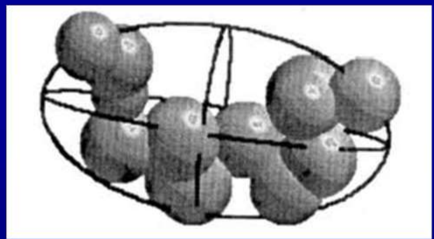
CNT and CB lead to anisotropic properties of composites?

CNT



CB



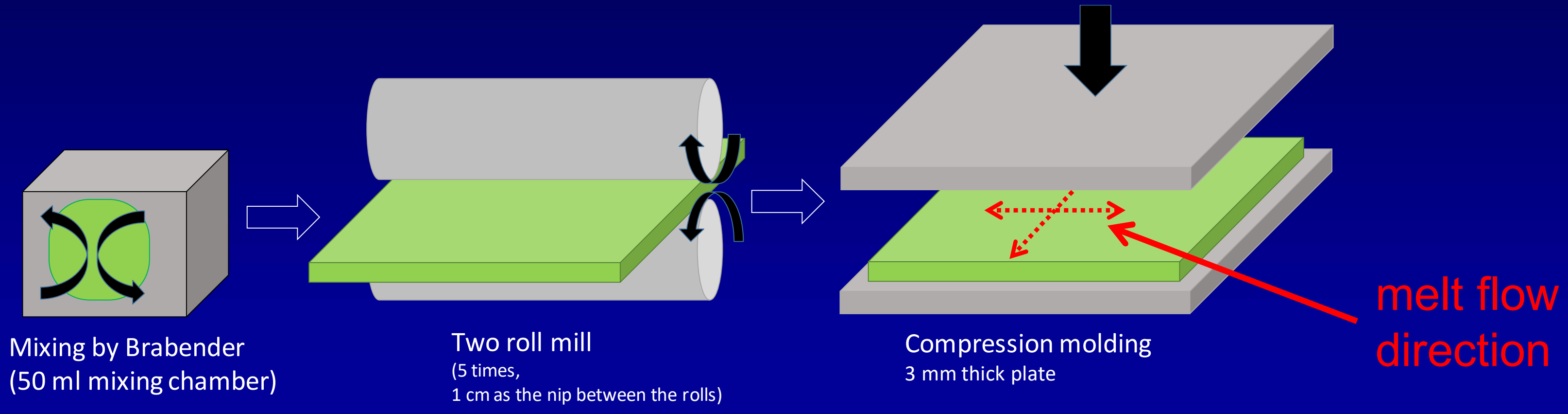


N220 aggregate

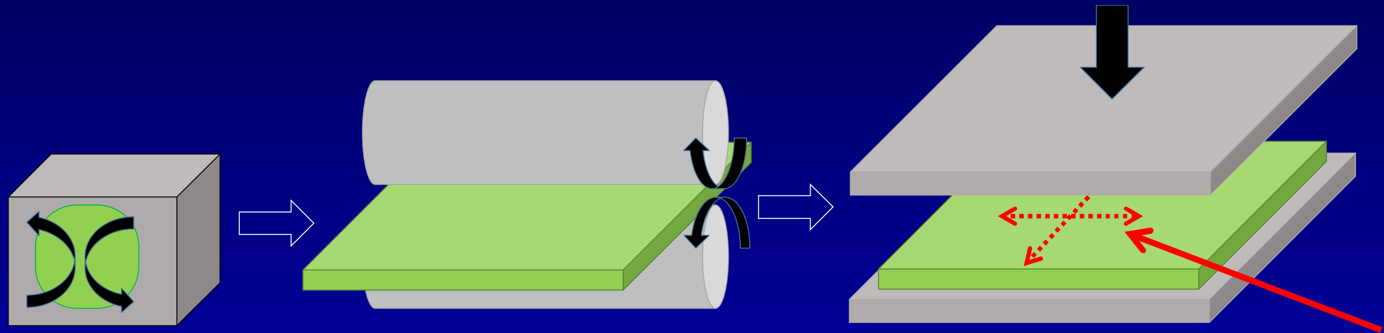
''Aggregates generally exhibit anisotropy,
in the form of a reduction of aggregate breadth, or ''flatness'', in one direction''
…but even perfectly spherical particles can give anisotropy, if not homogeneously dispersed!

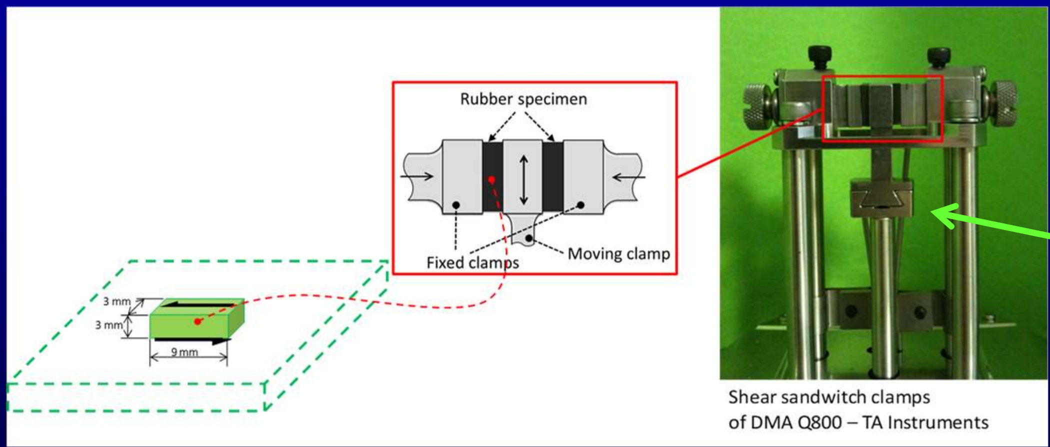
Grueber et al., Rubber Chemistry and Technology 67(2):280-287, 1994

Samples preparation

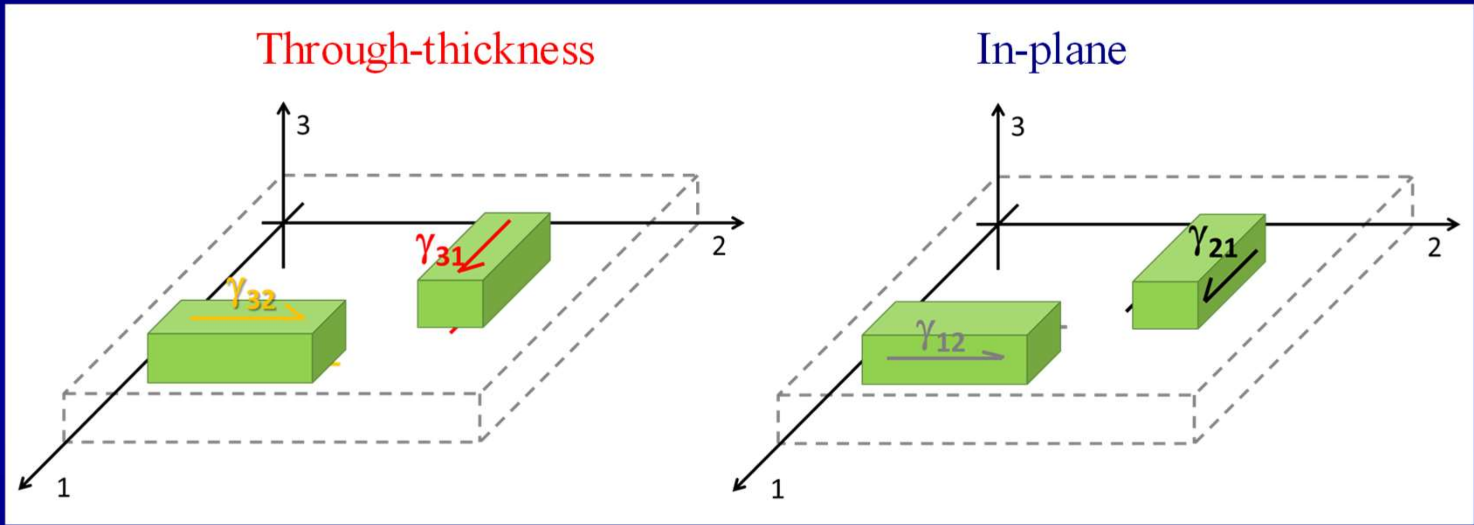


Samples preparation and device for shear stress tests





Shear stress tests: through thickness and in plane

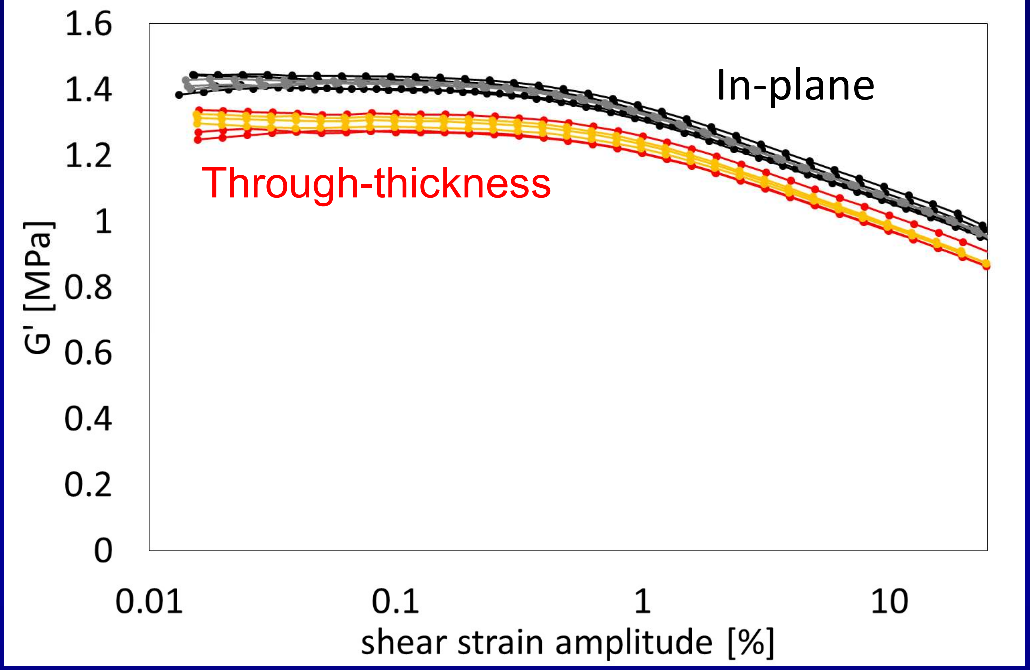


Stress on faces perpendicular to axis 3

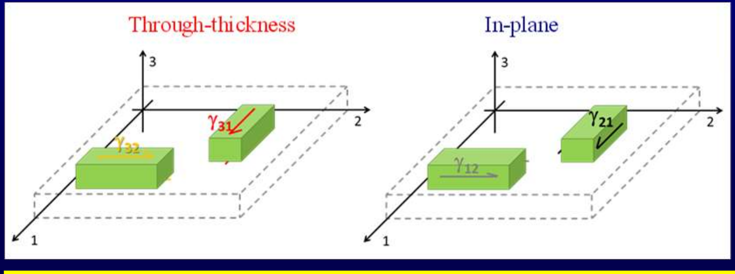
Stress on faces perpendicular to axis 1

Shear modulus vs shear strain amplitude

NR + 35 phr CB N326



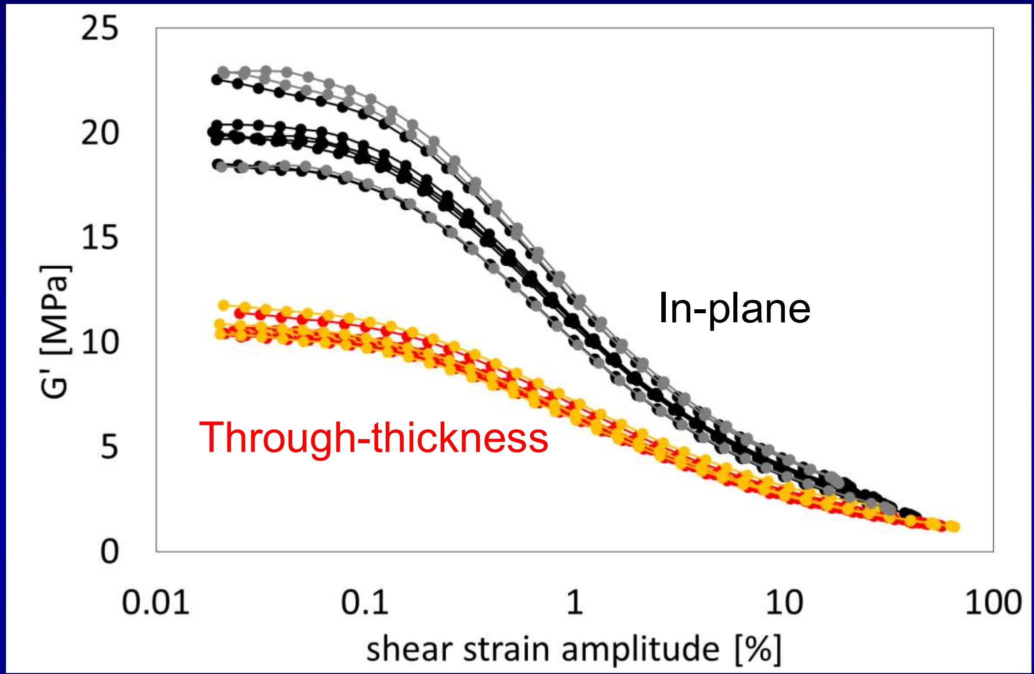
Slight anisotropic behaviour



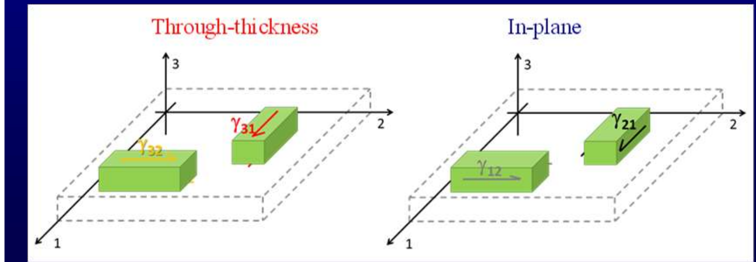
Peroxide crosslinked

Shear modulus vs shear strain amplitude

NR + 35 phr CNT



Transversal isotropic behavior

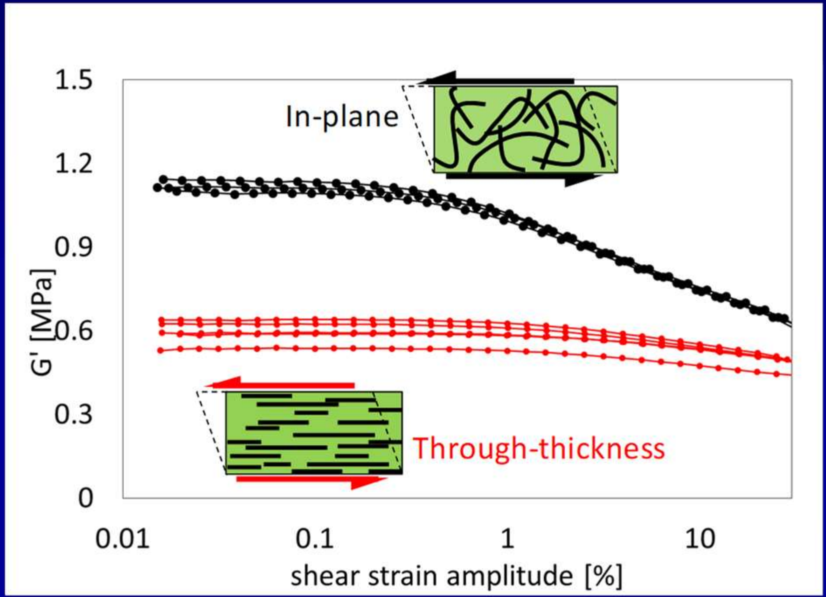


Anisotropic

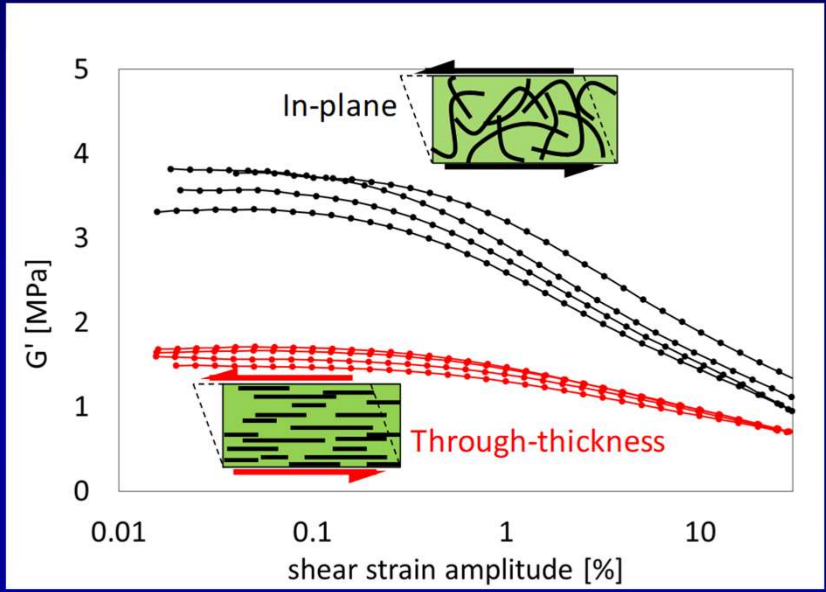
Payne Effect

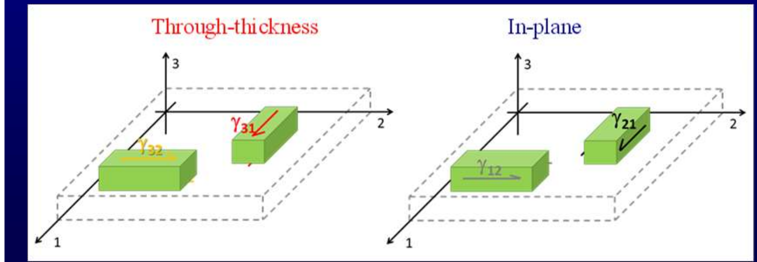
Shear modulus vs shear strain amplitude

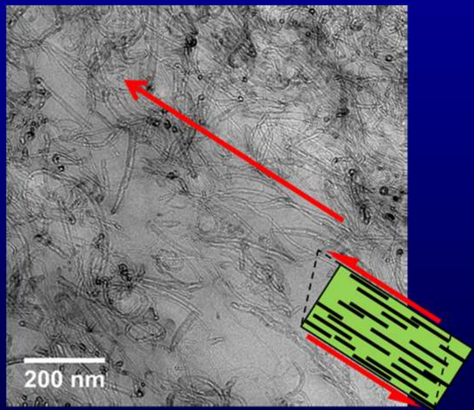
NR + 4 phr CNT



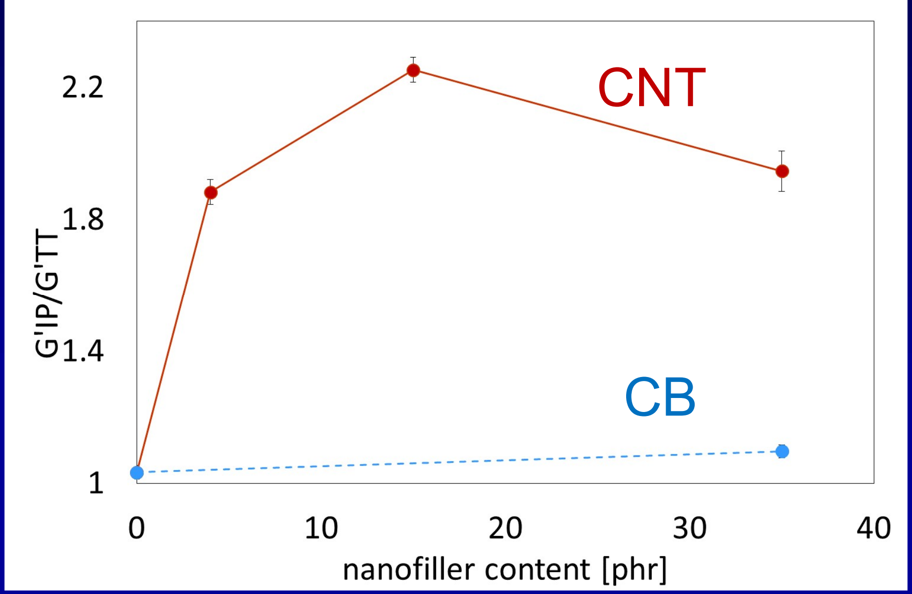
NR + 15 phr CNT

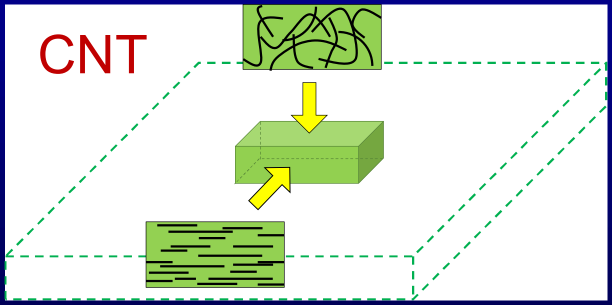


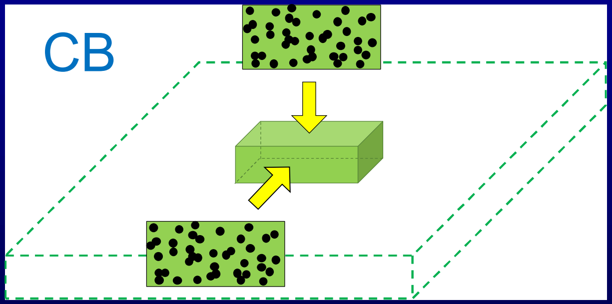




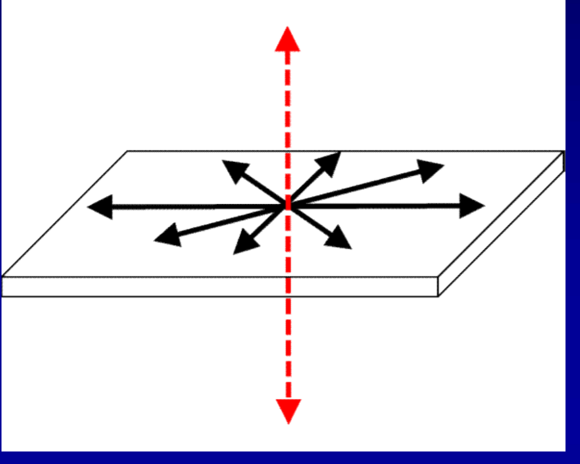
CNT leads to anisotropic properties of the composites







Transversal isotropic behaviour …



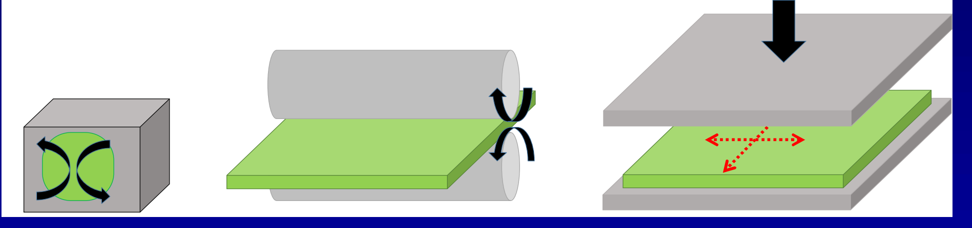
NR composites
with CNT, nano graphite

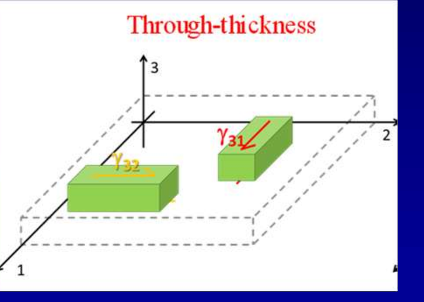
Grand Canyon

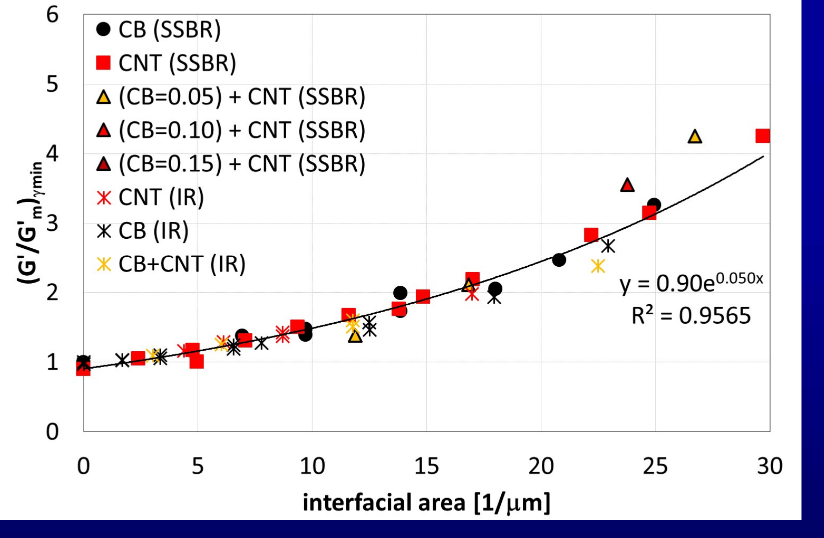
… for carbon fillers with high aspect ratio

Master curve for the initial modulus of elastomers composites

with sp^2 carbon allotropes







Elastomers: IR, SBR

Data from shear stress tests, 50°C

Lightweight materials from the master curve of mechanical reinforcement

To define the target dynamic rigidity of an elastomer composite

↓

To achieve such rigidity with the best combination of sp^2 carbon allotropes

↓

Objective:
lightweight materials

What to do?

Master curve based on interfacial area

↓

To solve the equation of the master curve:

equation to correlate modulus and interfacial area

↓

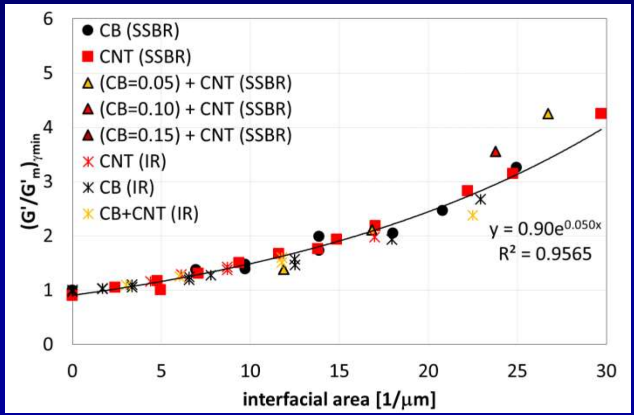
To define target modulus and density

↓

Best combination of sp^2 carbon allotropes

Lightweight materials from the master curve of mechanical reinforcement

☞ To solve the equation of the master curve

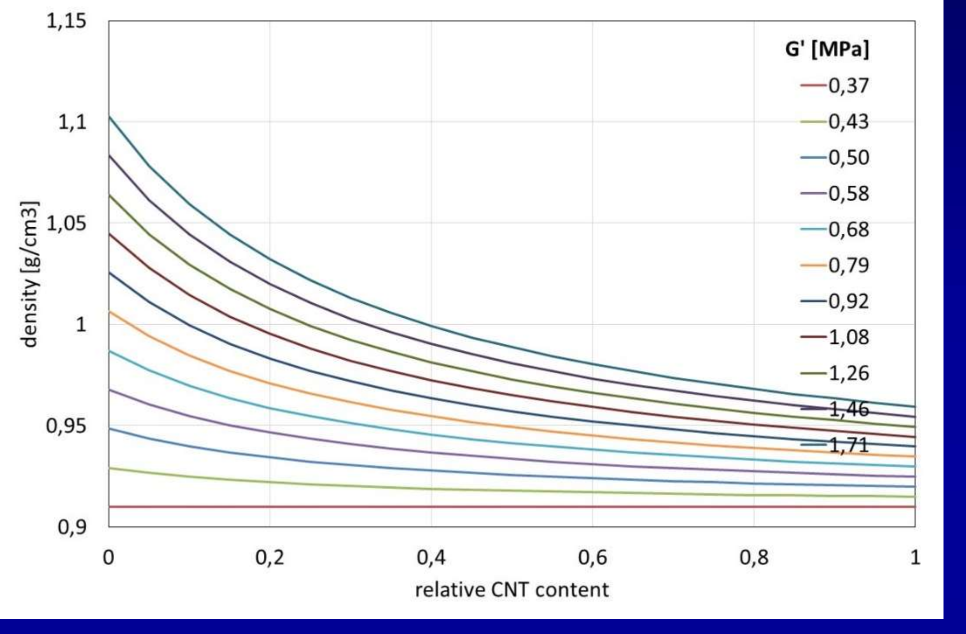


$$G'_{\gamma min}/G'_{m} = 0.90e^{0.050\ i.a.}$$

☞ Target density

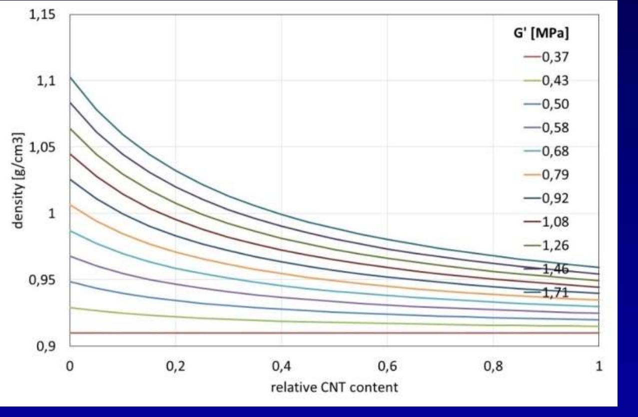
$$\rho_C = \rho_{CB} * \phi_{CB} + \rho_{CNT} * \phi_{CNT} + \rho_m * (1 - \phi_{CB} - \phi_{CNT})$$

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

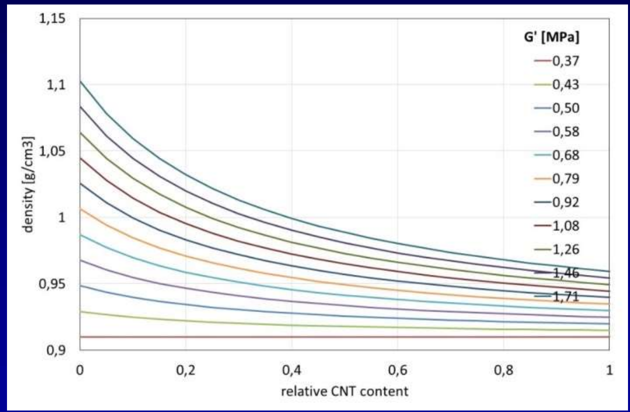
↓

% 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	Target G' = 1,46 Mpa
↓	↓
% CNT in CB/CNT = 0	Target density = 1
↓	↓
density = 1.08	% CNT in CB/CNT = 30

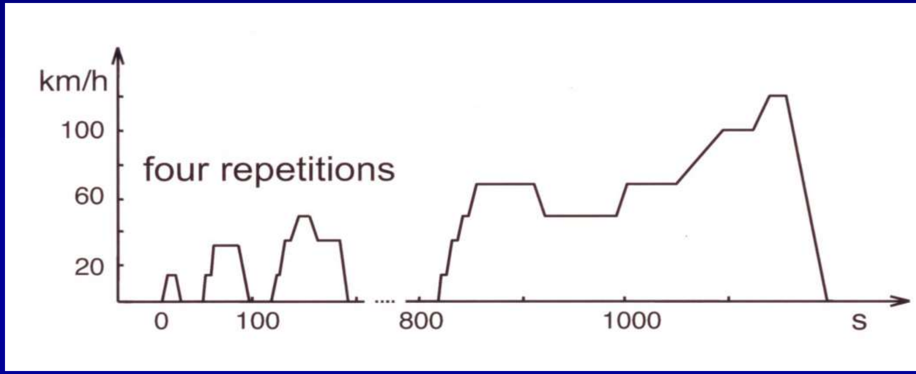
Reduction of the tyre mass
and benefits in terms of CO_2 emission of vehicles

Definition of driving cycle - New European Driving Cycle (NEDC)

4 repetitions of ECE 15 driving cycle

+

1 repetition of Extra Urban Driving Cycle (EUDC)



	Unit		ECE 15	EUDC
Distance	[km]		4×1.013 = 4.052	6.955
Duration	[s]		4×195 = 780	400
Average Speed	[km/h]		18.7 (with idling)	62.6
Maximum speed	[km/h]		50	120

Mastinu, G, Ploechl, M. Road and off-road vehicle system dynamics handbook, CRC Pres, Bora Raton ; USA 2014

NEDC - Energy E required to travel 100 km

$$E = A \cdot C_x \cdot 1.9 \cdot 10^4 + m \cdot f_R \cdot 8.4 \cdot 10^2 + m \cdot 10$$

(kJ/100km)

A cross section area of the vehicle

C_x is the drag coefficient

m is the vehicle mass

f_R is the rolling resistance of tyres

☞ all of the three terms of the sum are of the same order of magnitude

Sensitivity of E

with respect to

- aerodynamic drag coefficient $p_1 = C_x$,
- tyre rolling resistance $p_2 = f_R$
- vehicle mass $p_3 = m$

$$\lim_{\delta p_i \to 0} \frac{[E(p_i + \delta p_i) - E(p_i)] / E(p_i)}{\delta p_i / p_i} = \frac{\partial E}{\delta p_i} \frac{p_i}{E}$$

$$\frac{\partial E}{\delta p_1} = \frac{\partial E}{\partial C_x} = A \cdot 1.9 \cdot 10^4$$

$$\frac{\partial E}{\delta p_2} = \frac{\partial E}{\partial f_R} = m \cdot 8.4 \cdot 10^2$$

$$\frac{\partial E}{\delta p_3} = \frac{\partial E}{\partial m} = a \cdot C_x \cdot 1.9 \cdot 10^4 + f_R \cdot 8.4 \cdot 10^2 + 10$$

E percent variations for 10% variation of p_i

Vehicle type	Data					% variation of E due to 10% variation of		
	Rated Power kW	A m^2	C_x	f_R	m kg	C_x	f_R	m
Mid-range	140	2.2	0.26	$12 \cdot 10^{-3}$	1560	2	4	9
Compact	55	2.0	0.29	$10 \cdot 10^{-3}$	1120	4	3	8
Sports	310	1.95	0.29	$12 \cdot 10^{-3}$	1650	2	4	9
SUV	200	2.3	0.41	$14 \cdot 10^{-3}$	2640	2	4	9

aerodynamic drag coefficient $p_1 = C_x$,

tyre rolling resistance $p_2 = f_R$

vehicle mass $p_3 = m$

☞ *Vehicle mass reduction* is the more effective way to reduce the energy required to travel

Mass of tyres

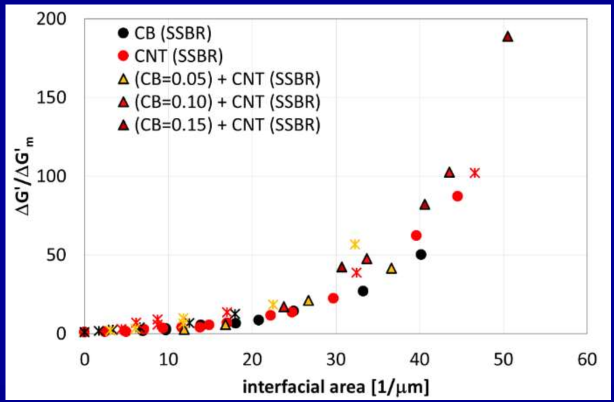
Tyre size	Tyre mass
155/70 R13	6.5 kg
185/70 R13	7.0 - 7.2 kg
175/65 R14	6.5 - 7.2 kg
195/65 R15	8.2 - 9 kg
>R20	>15 kg

Reducing the mass of tyres

Reducing the mass of a tyre means reducing

- the energy consumption E (for travelling 100 km)

- the rolling resistance f_R



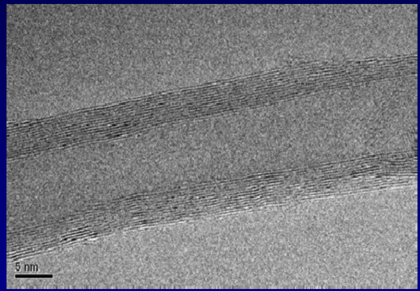
Assumption

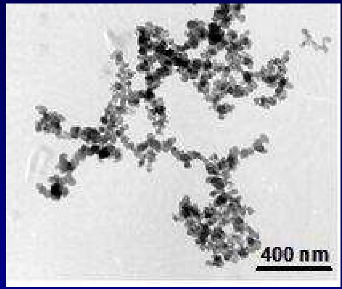
During normal rolling of the tyre
the rolling resistance is related only to hysteresis losses.
Since hysteresis losses are related and proportional to the tyre mass,
the percentage rolling resistance reduction
is equal to the percentage tyre mass reduction.

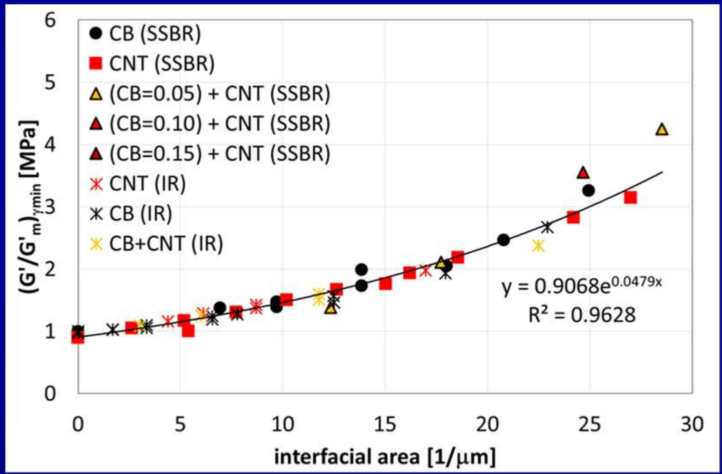
Energy saved due to mass reduction

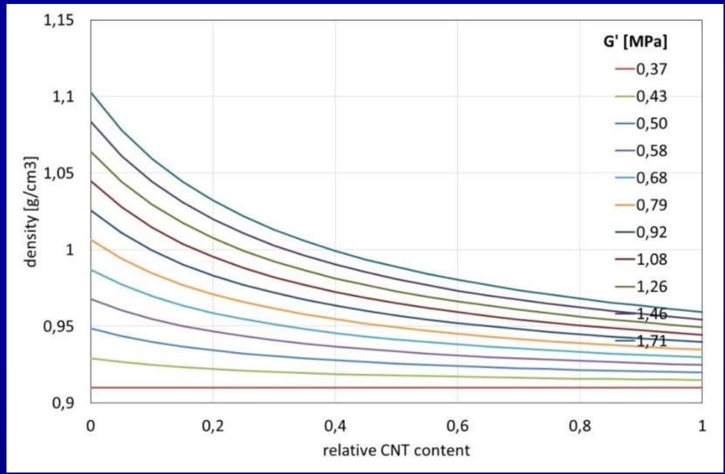
Vehicle type	Tyre	Vehicle mass reduction	% Energy saved due to mass reduction only	% Energy saved due to RR reduction	Total % Energy saved due to mass reduction
Mid-range	195/70 R15	4 kg	0.1	4	4.1
Compact	155/70 R13	3 kg	0.2	3	3.1
Sports	245/45 R19	>5	<0.5	4	4.5
SUV	>R20	>6	<0.2	4	4.2

Conclusions









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Thanks
for the attention!