XIV Convegno Nazionale AIMAT 2017
XI CONVEGNO NAZIONALE INSTM

Anisotropic properties of natural rubber nanocomposites with sp^2 carbon allotropes

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Rubber reinforcement: carbon fillers vs nanofillers

Particle geometry:

Examples:
TEM images of isoprene rubber + 30 phr filler*

Primary particles
dimension scale:
dispersion:

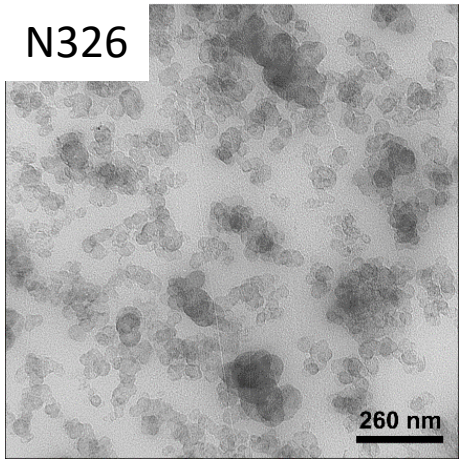
Surface area:

Conventional fillers

Carbon black (CB)

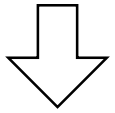
3D-like

N326



~10 nm
particles aggregated

low



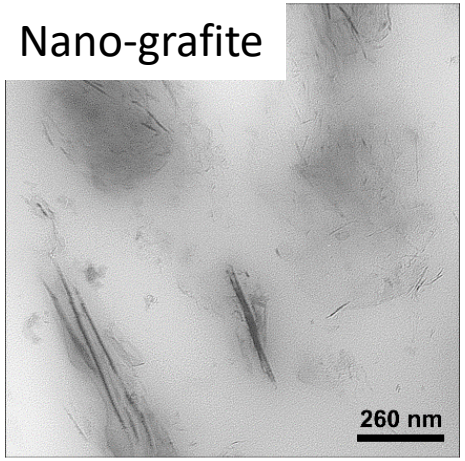
vs

Nanofillers

Graphene nanoparticles

2D-like

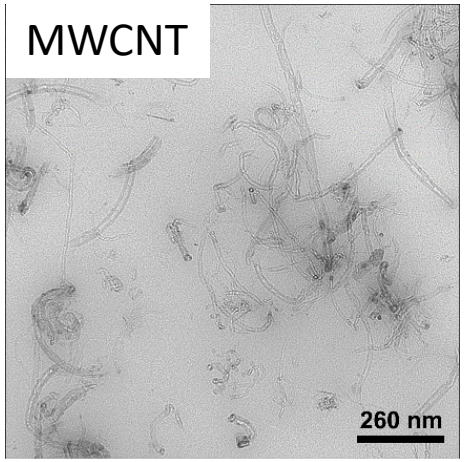
Nano-grafite



Carbon nanotubes

1D-like

MWCNT



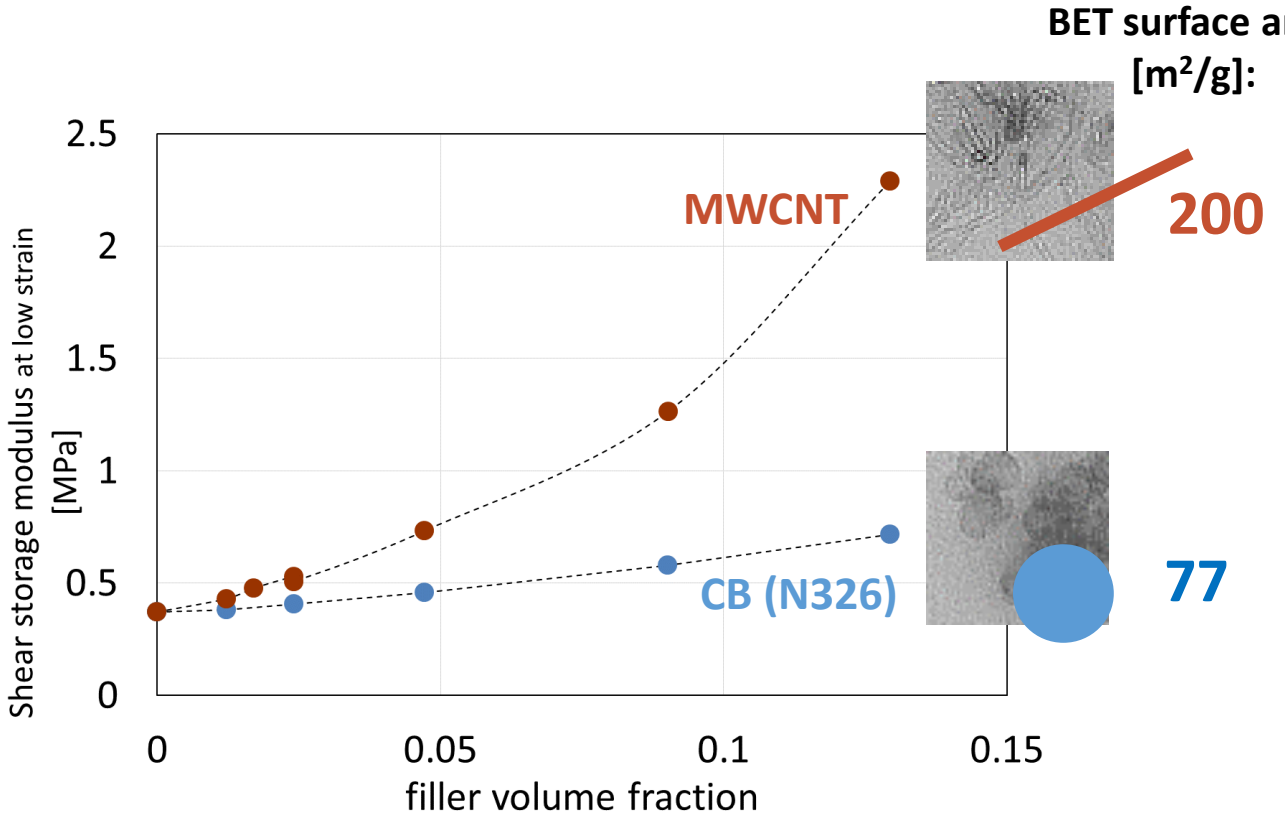
~1 nm
particles singularly dispersed

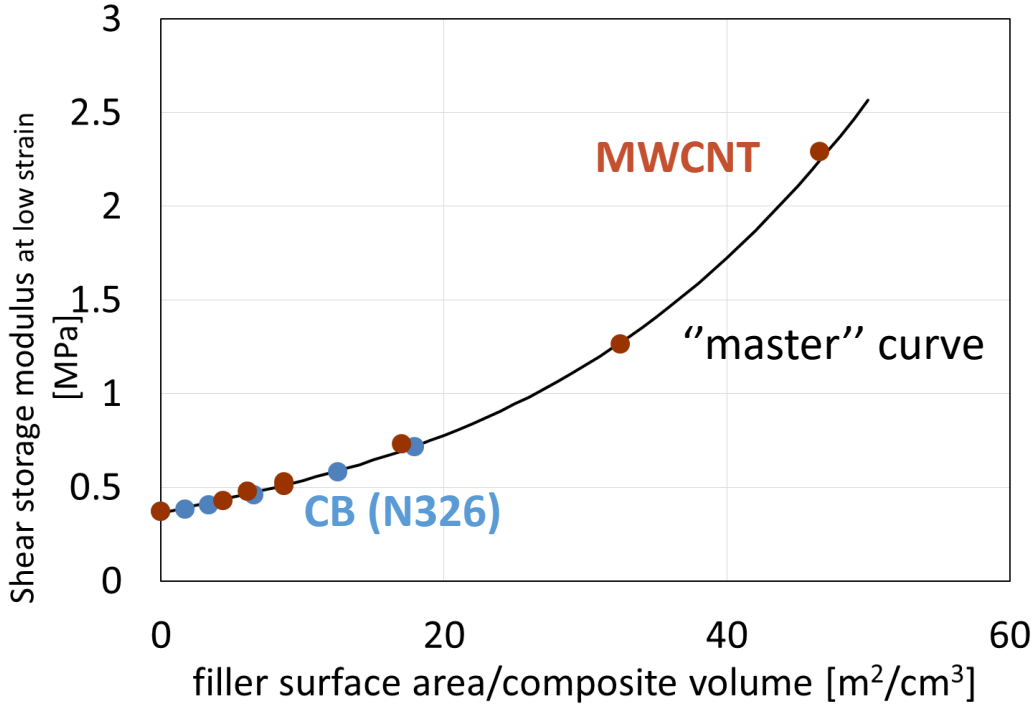
high

*Agnelli et al.,eXPRESS Polymer Letters Vol.8, No.6 (2014) 436–449

Rubber reinforcement: carbon fillers vs nanofillers

High surface area = high reinforcement efficiency





Agnelli et al.,eXPRESS Polymer Letters Vol.8, No.6 (2014) 436–449

Rubber reinforcement: carbon fillers vs nanofillers

Particle geometry:

Conventional fillers

Carbon black (CB)

3D-like 

Nanofillers

Graphene nanoparticles

2D-like 

Carbon nanotubes

1D-like 

Aspect ratio: max dimension/min dimension of the particle

High aspect ratio → possible preferential orientation → ANISOTROPIC properties

Anisotropy in rubbers filled with CNT

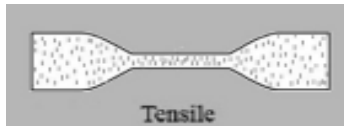
Orientation and alignment of CNT is seeked to fully exploite their properties along specific directions,
particularly for electronical applications (field emission displays and sensors, data storage, and light-emitters)

Methods for the alignment of CNTs
(Ponnamma et al., Mater. Chem. C, 2014, 2, 8446):

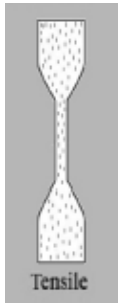
- extrusion or injection molding. Alignment degree can be tuned by the shear rate as well as the pressure applied
- In situ polymerization
- mechanical stretching
- electrospinning
- filtration
- plasma-enhanced chemical vapor deposition (PECVD)
- template
- force field-induced alignment
- magnetic field-induced alignment
- liquid crystalline phase-induced alignment

"The alignment of MWCNTs in the 50/50 NR/NBR blends can be controlled by milling the compounds at a tight nip gap."
(Kueseng et al., Polymer Testing 32 (2013) 1229–1236)

TD = Transverse direction



MD = Machine direction



Milling direction

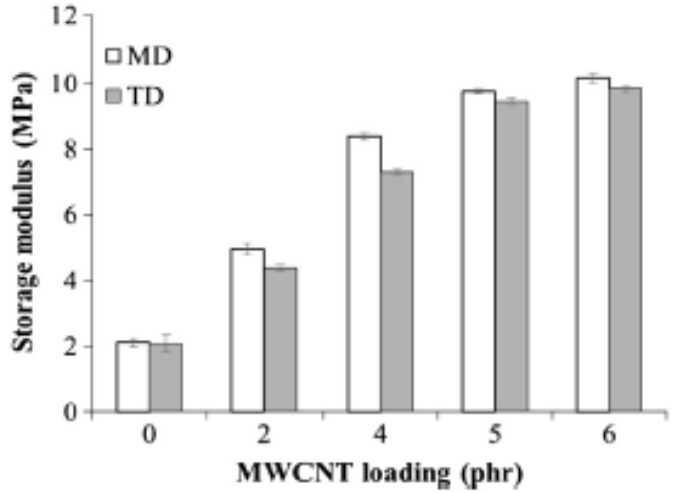


Fig. 13. Storage modulus at 30 °C of the blends in MD and TD at various MWCNT loadings.

Most attention is given to unidirectional alignment and longitudinal properties.

Aim of the work

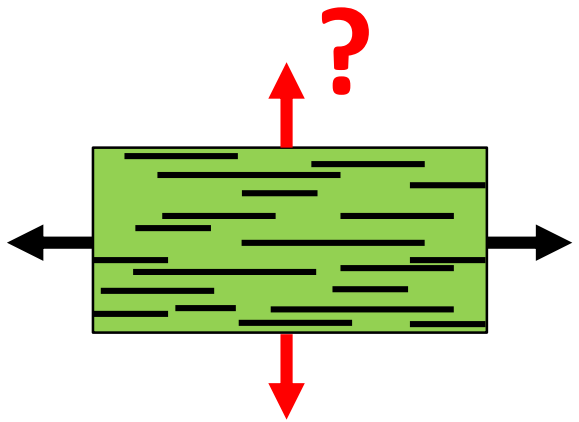
Describe anisotropic properties

of a nanofilled homogeneous elastomeric material

along three main spatial directions

in a very common rubber product:

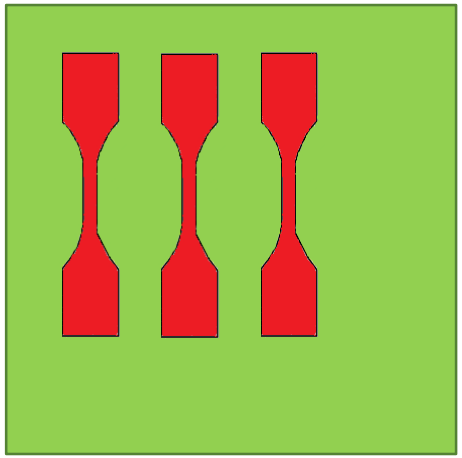
a rubber plate.



Evaluation also of the properties along transversal directions, usually neglected.

WHY?

Proper material characterization



The plate is a typical product for quality tests and material standard characterization neglects transversal direction.

Advanced design

Plate is produced by a common base production technique, at low shar rate. Other processes can allow to tune anisotropy levels.

Rubber bellows

Experimental details

- Material: NR filled with different fillers (CB) and nanofillers (nanoG and CNT)
- A base production process is used: compression molding
- Tests along different directions, also through the thickness → shear tests
- Property considered: dynamic moduli and Payne effect

Materials

- Matrix: peroxide cured natural rubber (**NR**)
- Fillers and nanofillers:
  - **nanoG**: Synthetic Graphite 8427® from Asbury Graphite Mills Inc (BET surface area=330 m^2/g)
  - **CNT**: Baytubes® C150 P from Bayer Material Science (BET surface area =200 m^2/g)
  - CB: **N326** from Cabot (BET surface area =77 m^2/g)
  - CB: **Printex** XE2 from Degussa (BET surface area =1000 m^2/g)

Ingredient	Amount [phr (volume fraction)]			
NR	100	100	100	100
Filler	0	4 (0.02)	15 (0.07)	35 (0.15)
DCUP	3.5	3.5	3.5	3.5

NR=SMR GP, from Lee Rubber
DCUP=dicumyl peroxide.

phr = weight parts per hundred rubber

Experimental details

- Material: NR filled with different fillers (CB) and nanofillers (nanoG and CNT)
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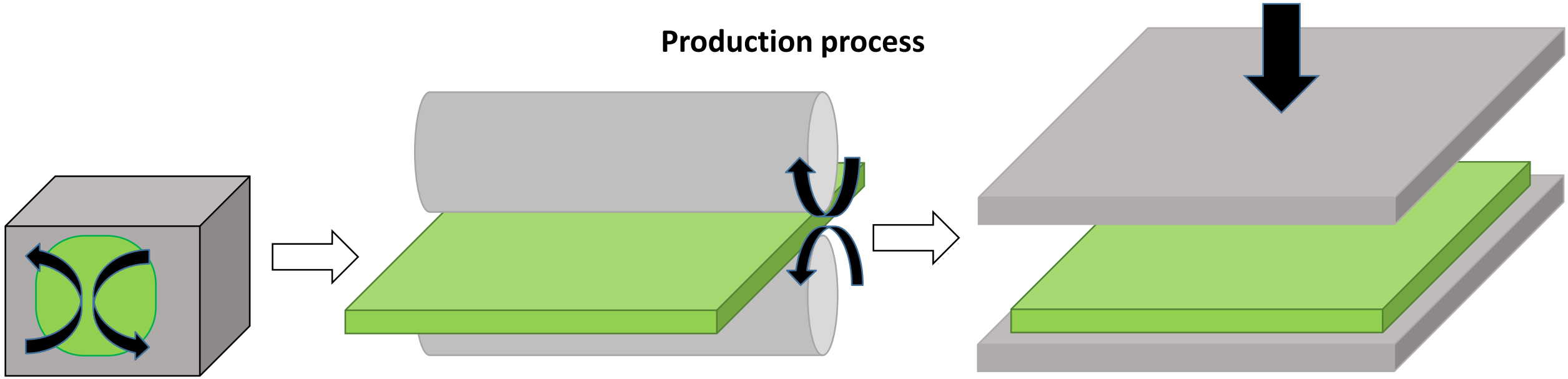
Production process



Mixing by Brabender
(50 ml mixing chamber)

Two roll mill
(5 times,
1 cm as the nip between the rolls)

Compression molding
3 mm thick plate

Experimental details

- Material: NR filled with different fillers (CB) and nanofillers (nanoG and CNT)
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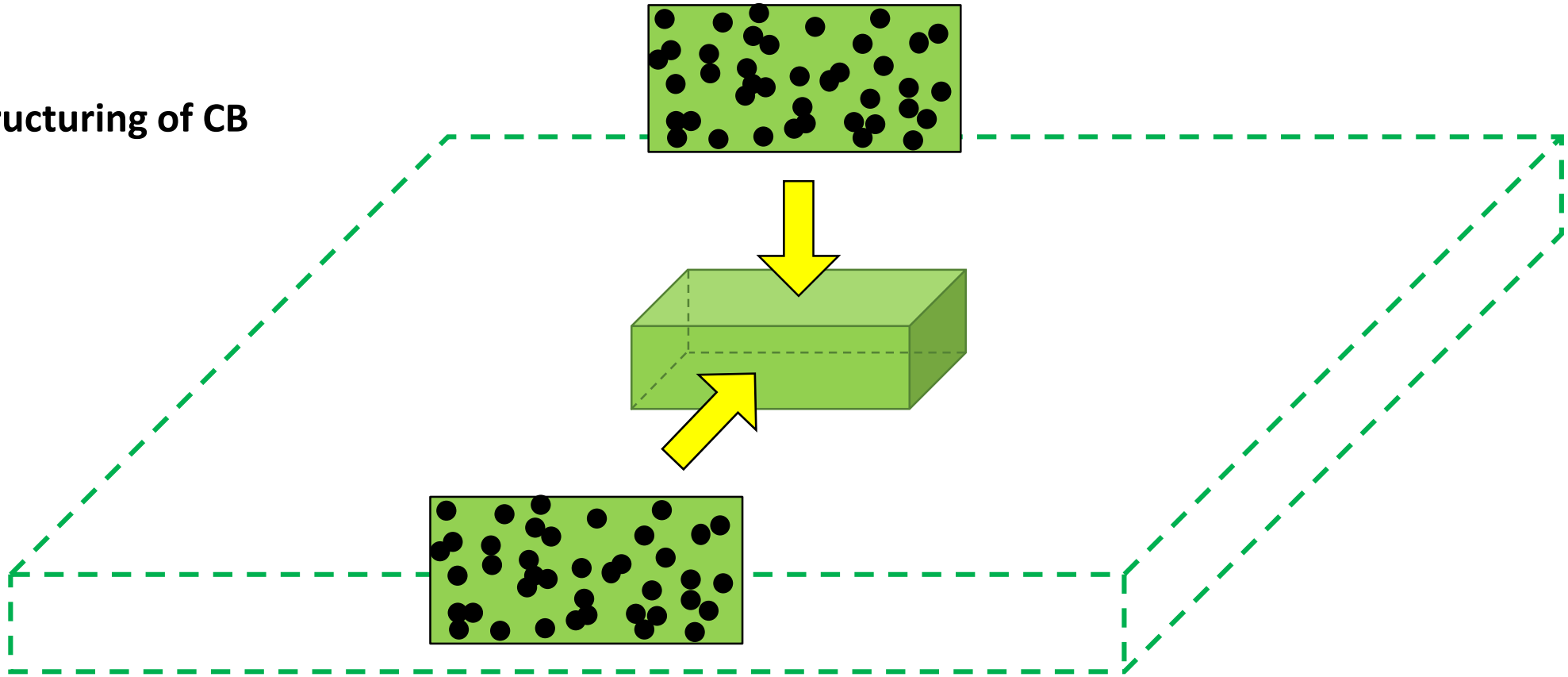
- Property considered: dynamic moduli and Payne effect

Expected structuring of CB



Experimental details

- Material: NR filled with different fillers (CB) and nanofillers (nanoG and CNT)
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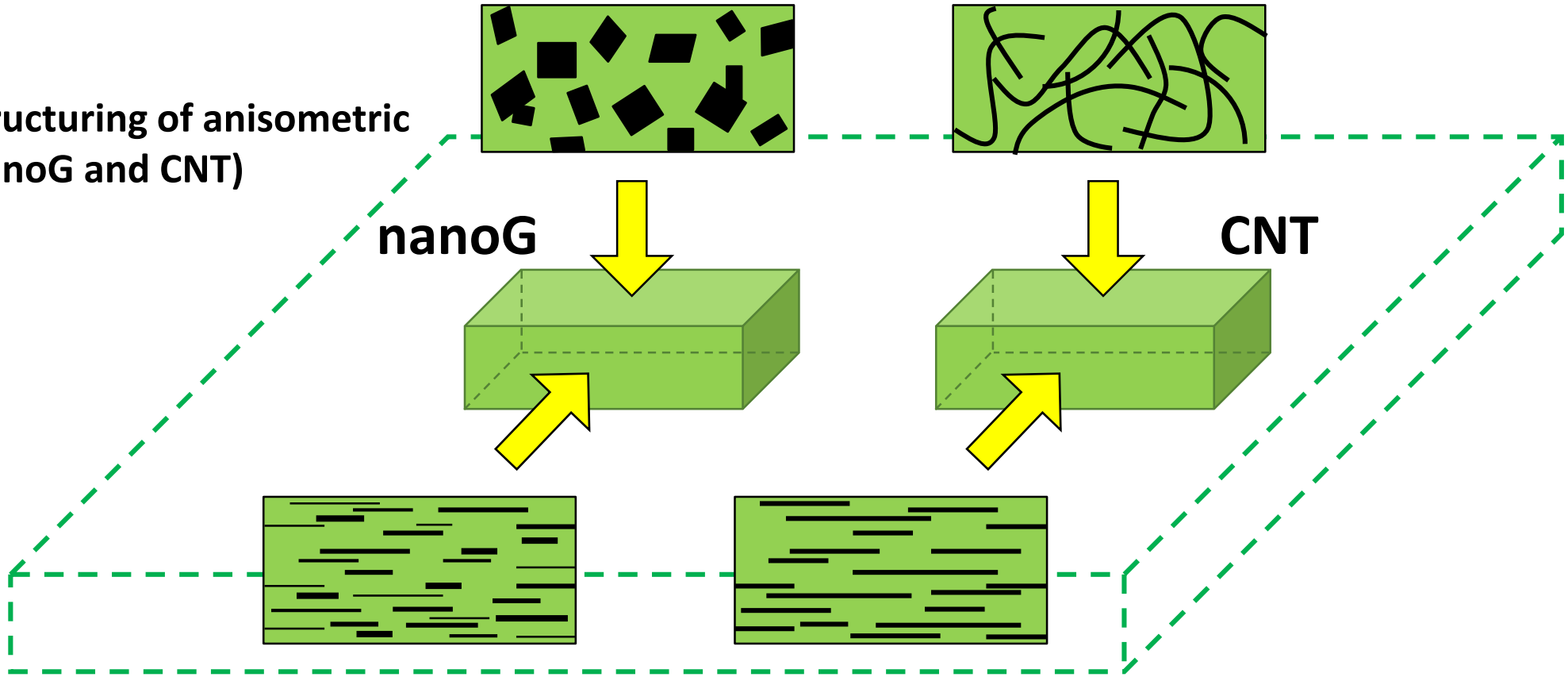
- Property considered: dynamic moduli and Payne effect

Expected structuring of anisometric particles (nanoG and CNT)



Experimental details

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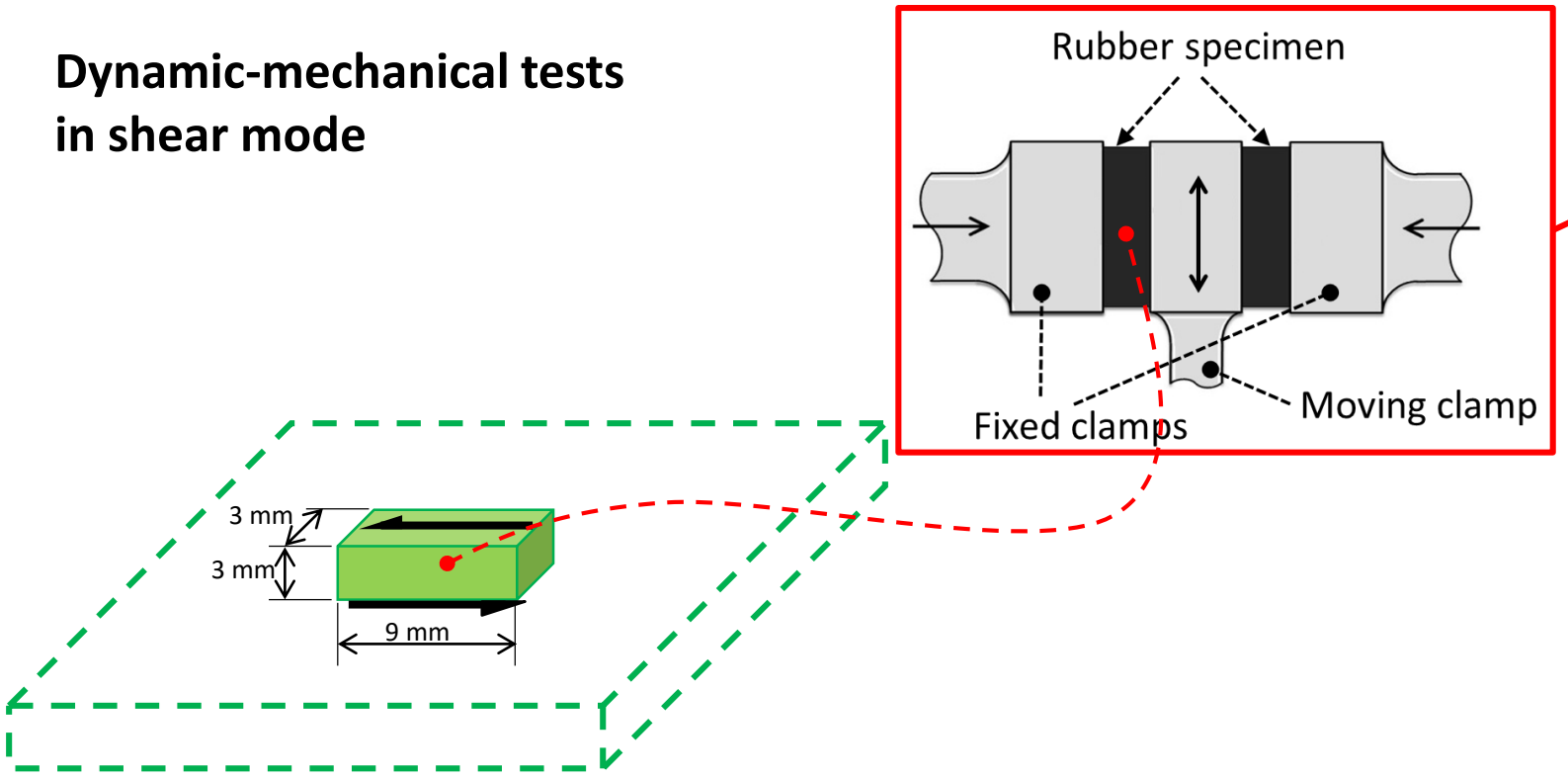
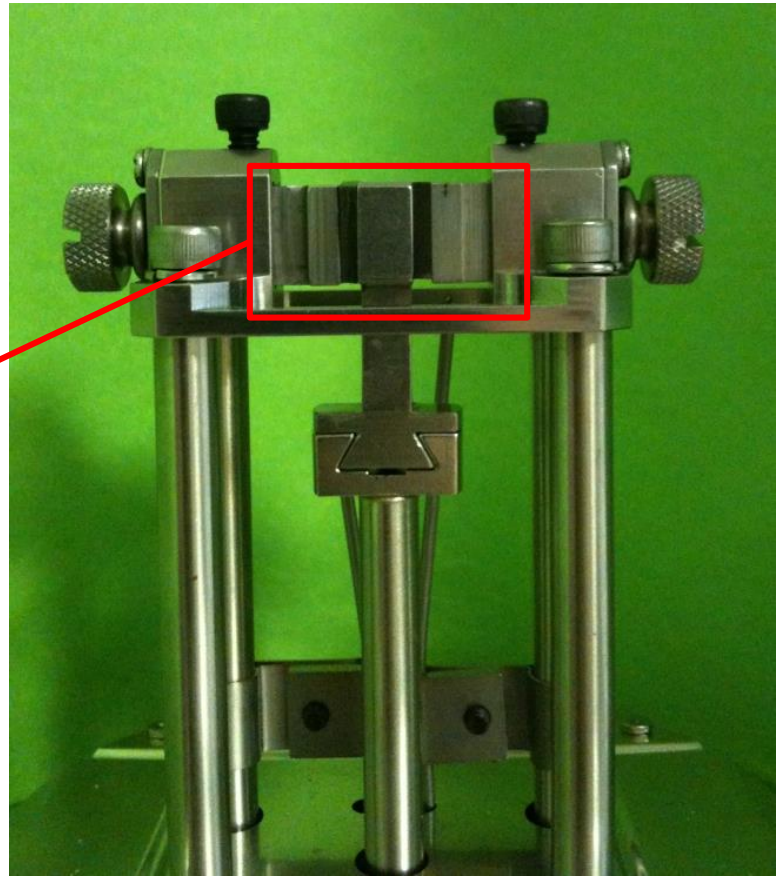
- Property considered: dynamic moduli and Payne effect

Dynamic-mechanical tests in shear mode





Shear sandwitch clamps
of DMA Q800 – TA Instruments

Experimental details

- Material: NR filled with different fillers (CB) and nanofillers (nanoG and CNT)
- A base production process is used: compression molding
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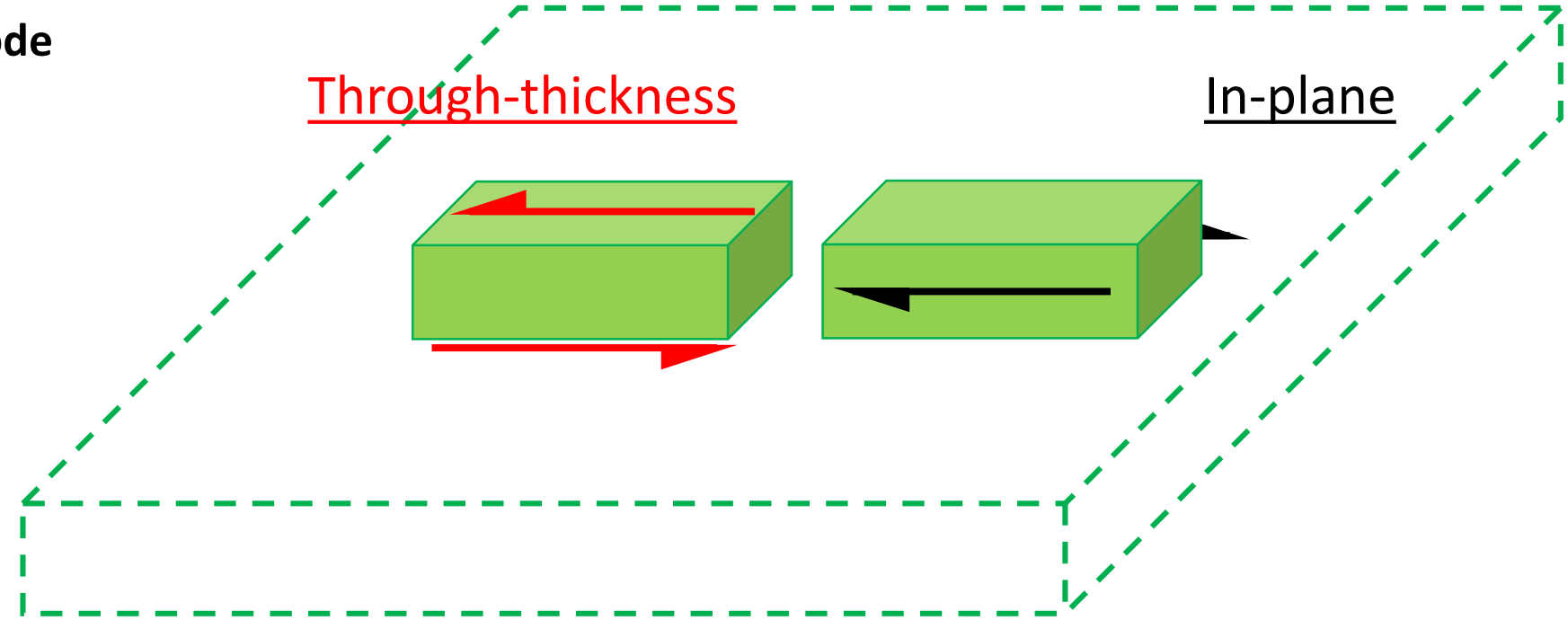
- Property considered: dynamic moduli and Payne effect

Dynamic-mechanical tests in shear mode



Experimental details

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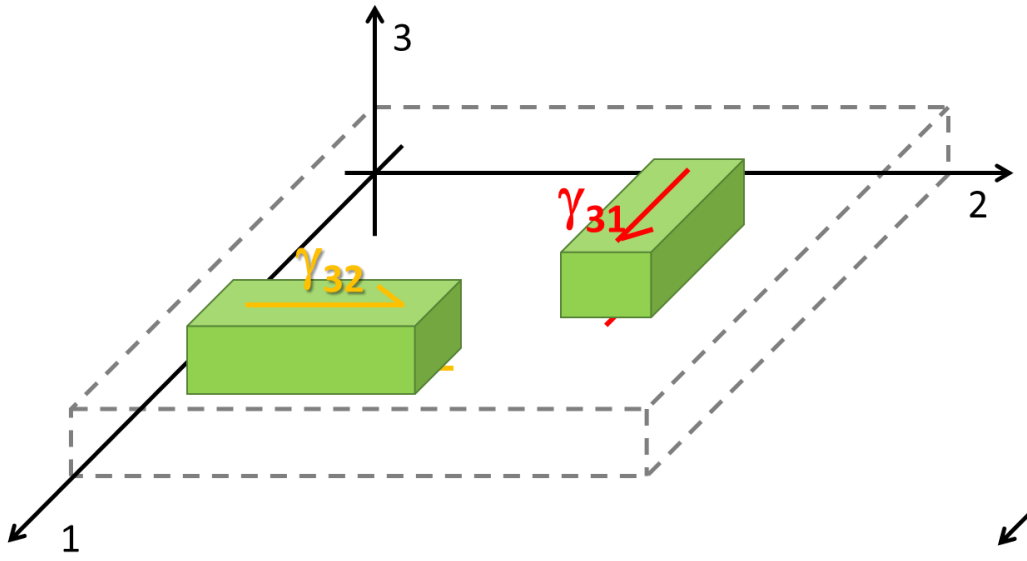
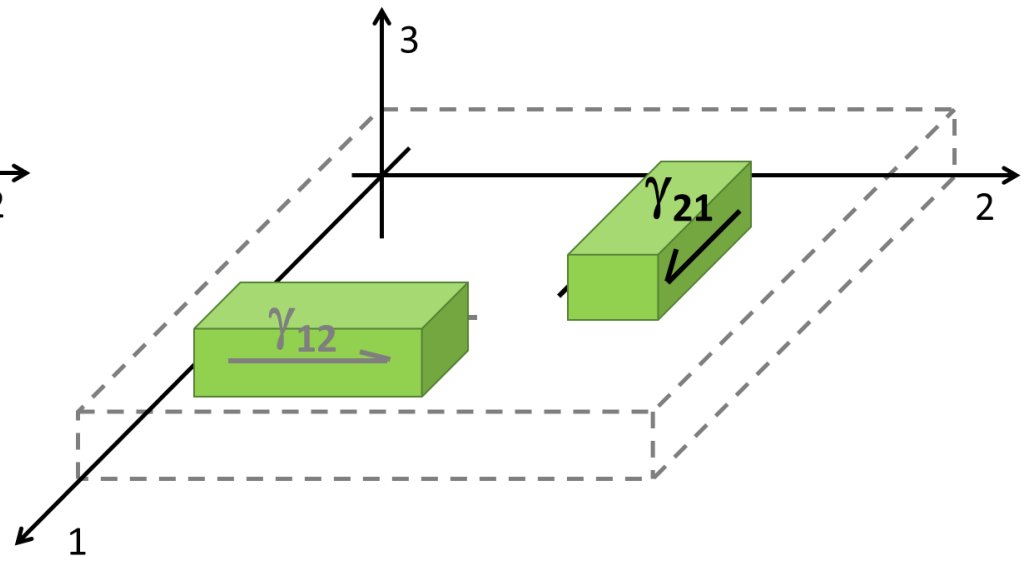
- A base production process is used: compression molding
- Tests along different directions, also through the thickness → shear tests
- Property considered: dynamic moduli and Payne effect

Dynamic-mechanical tests in shear mode

Through-thickness



In-plane



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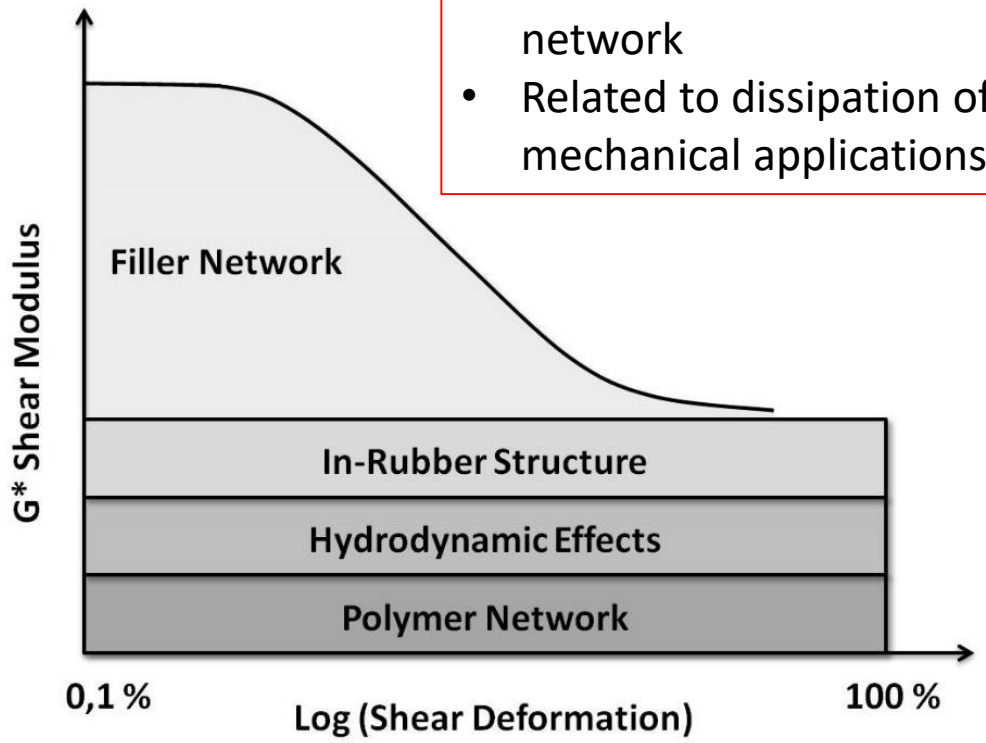
- A base production process is used: compression molding
- Tests along different directions, also through the thickness → shear tests
- Property considered: dynamic moduli and Payne effect

Dynamic-mechanical tests in shear mode

Test conditions:
Room temperature (23÷26°C)
Frequency: 1 Hz
Shear strain amplitude range: 0.013%÷30%

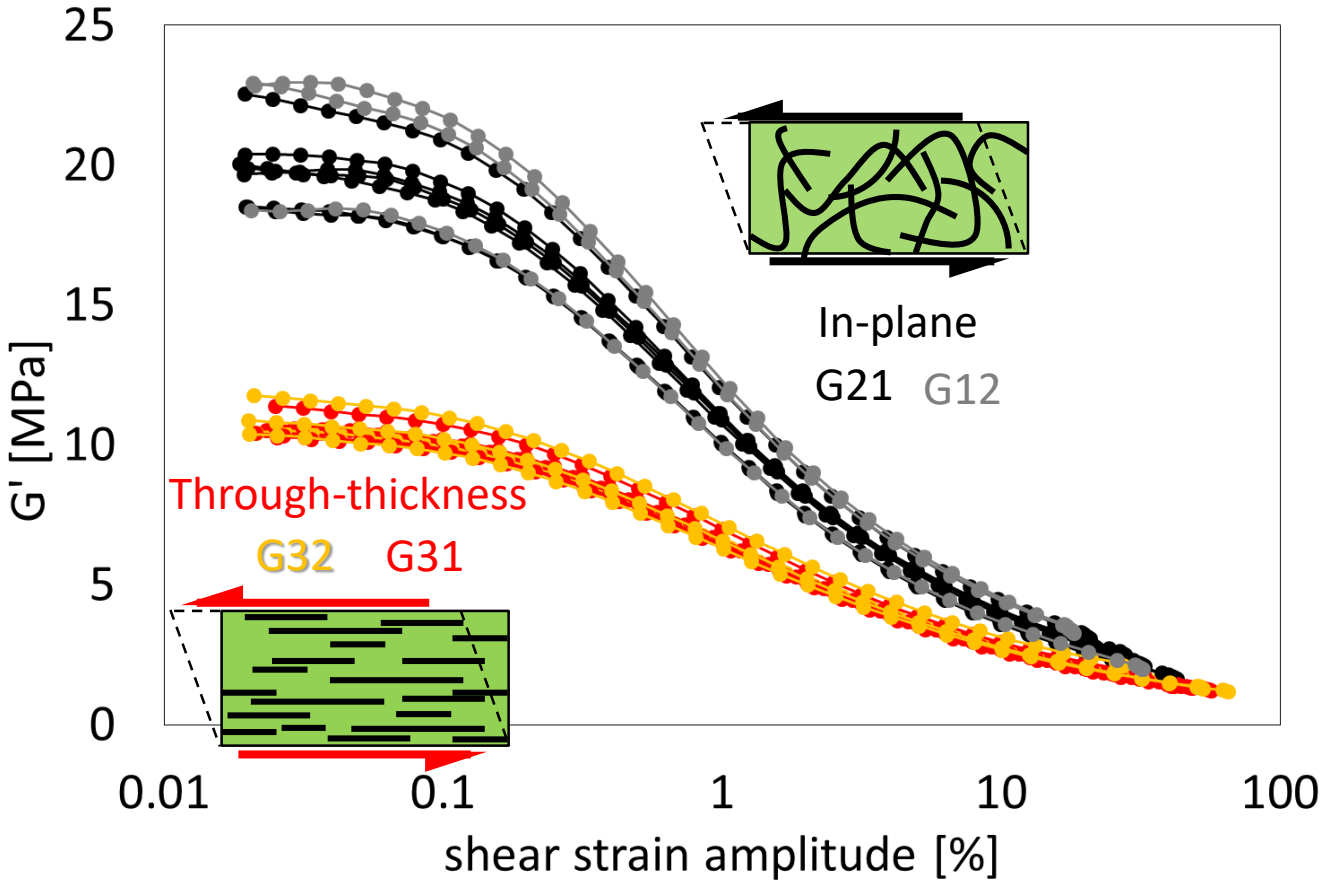
Payne effect

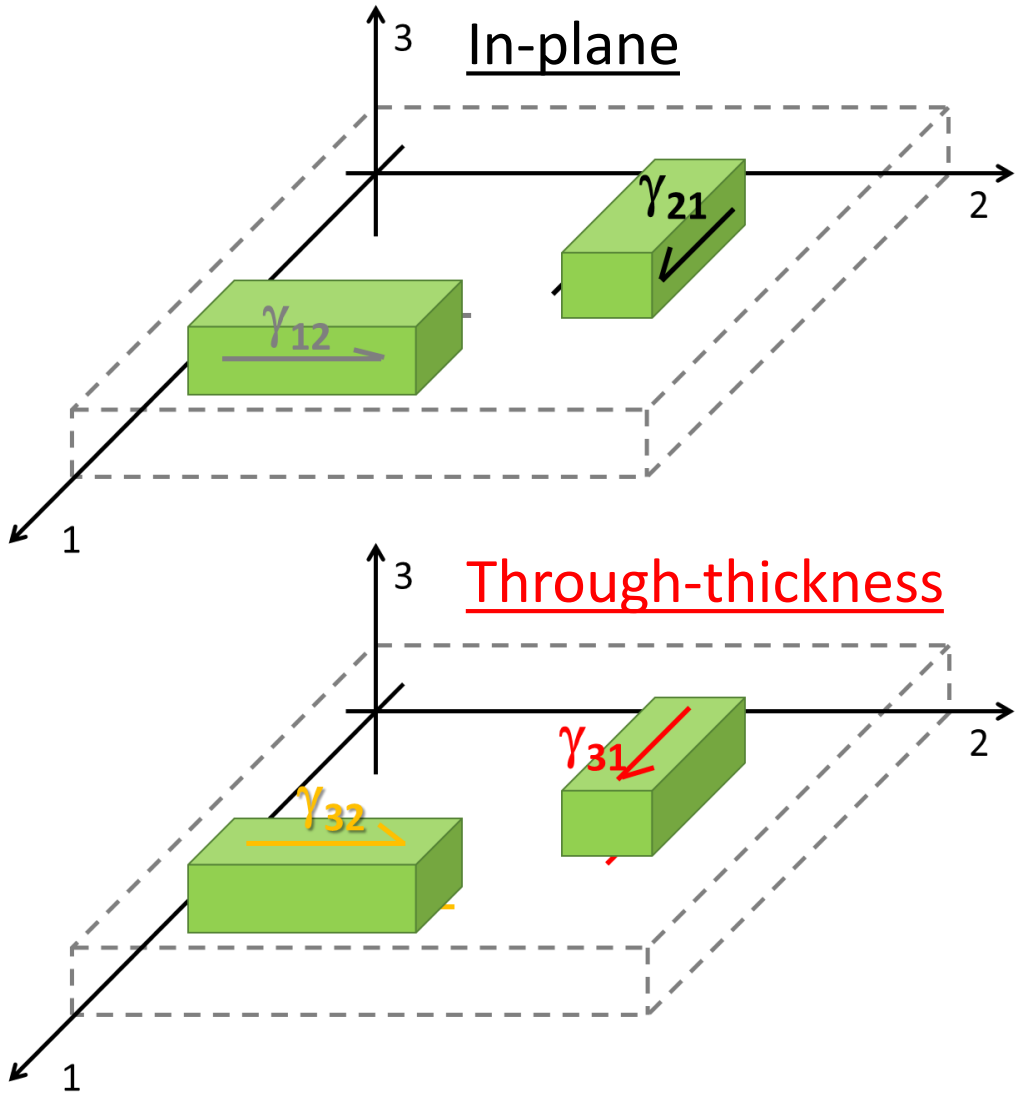
- Provides information about the strength of filler network
- Related to dissipation of energy in dynamic-mechanical applications of elastomeric materials



Results

NR + 35 phr CNT

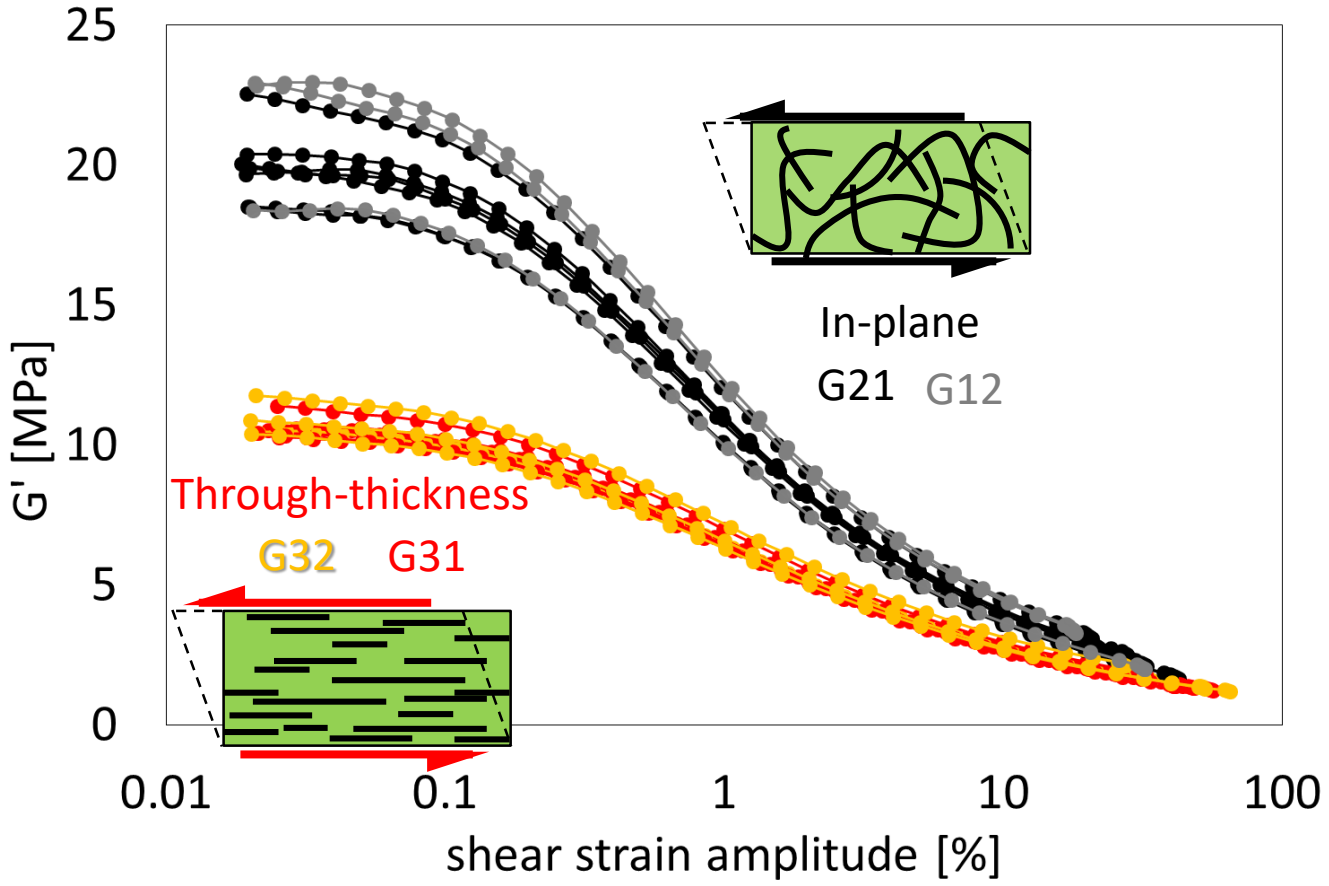




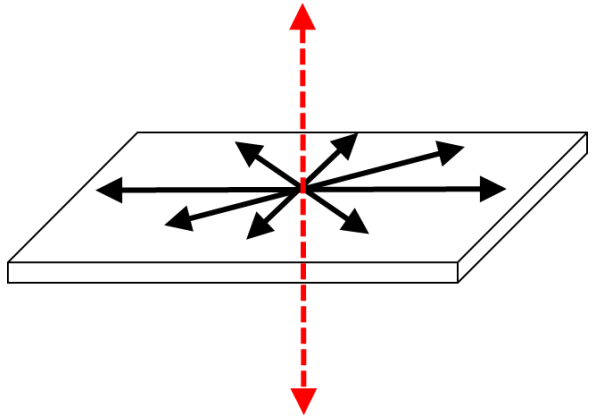
Agnelli et al., Macromolecules 2016, 49, 8686−8696

Results

NR + 35 phr CNT



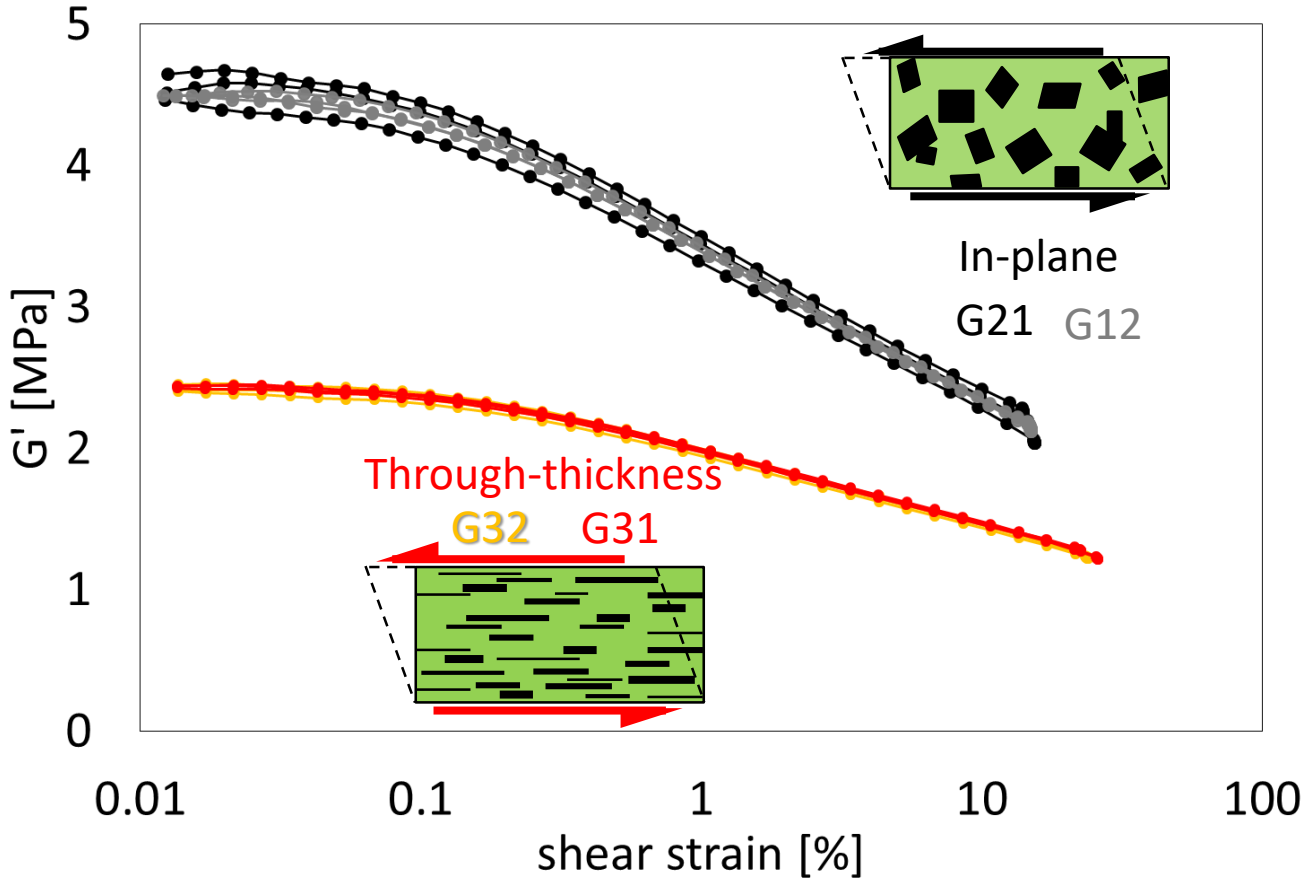
Transversal isotropic behavior

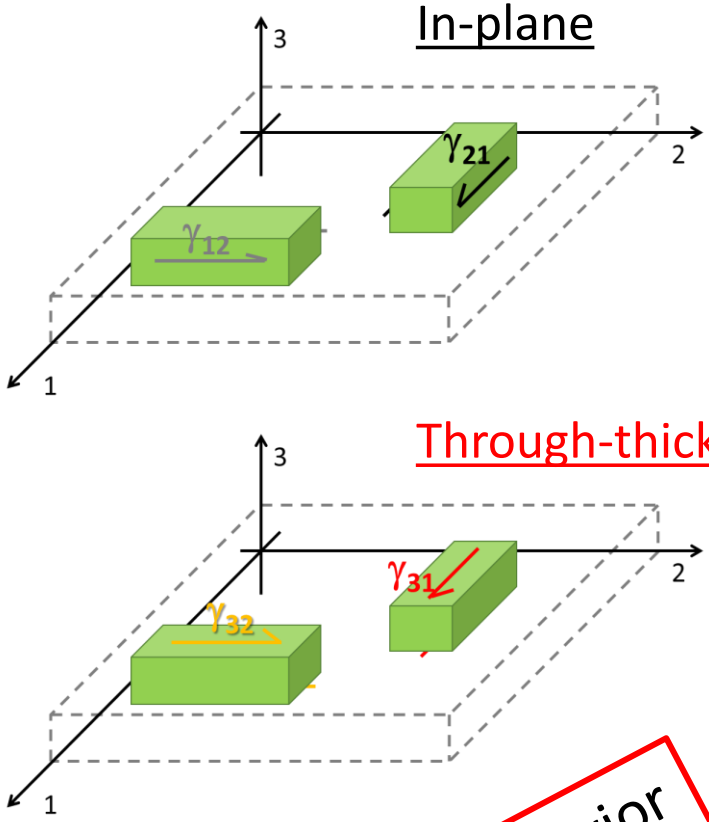


Agnelli et al., Macromolecules 2016, 49, 8686−8696

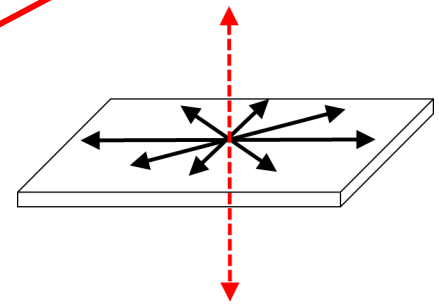
Results

NR + 35 phr nanoG



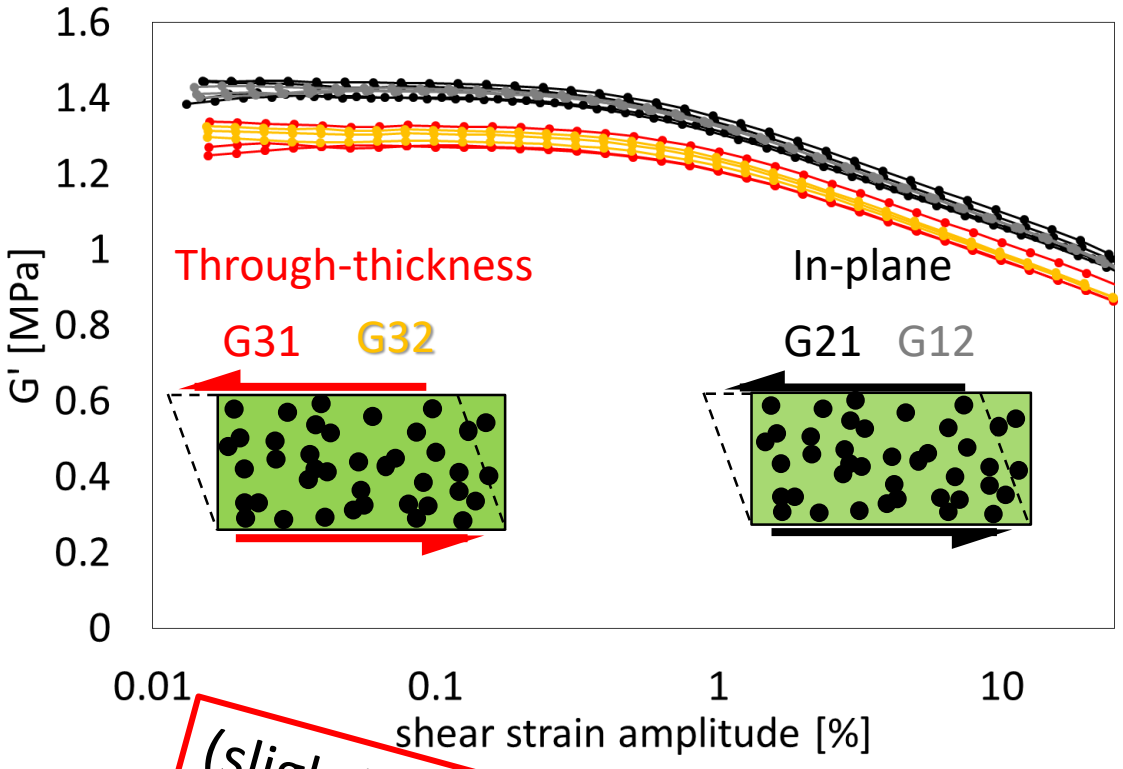


Transversal isotropic behavior



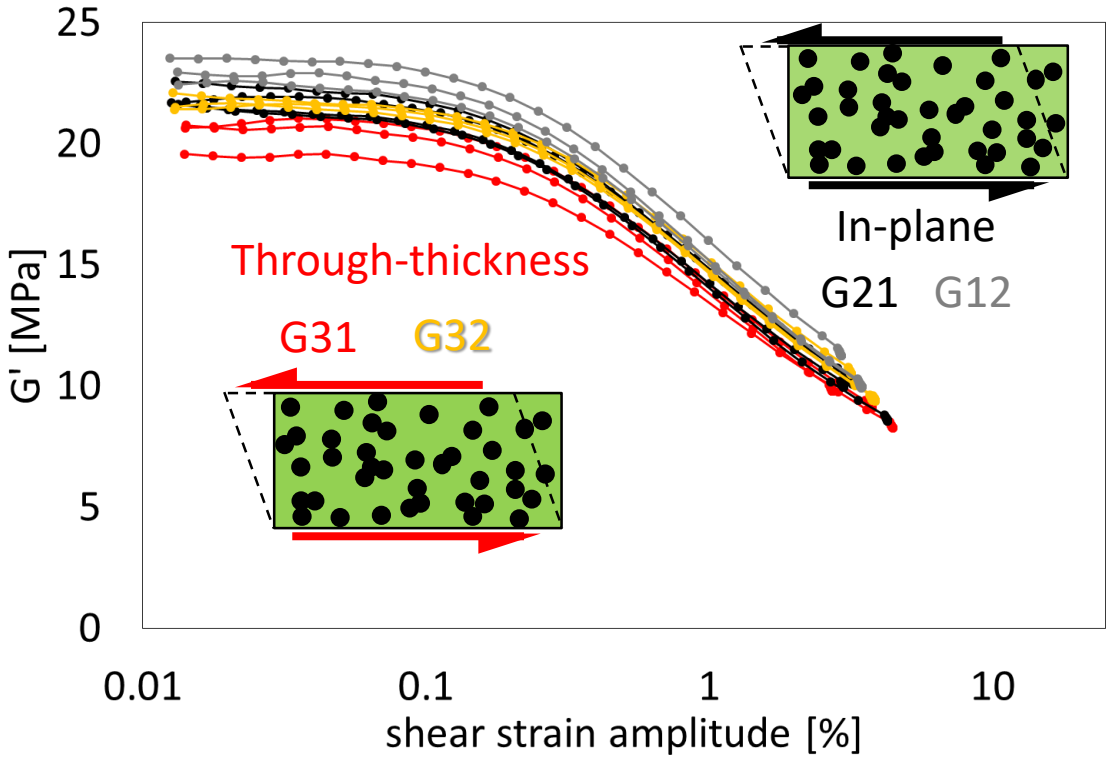
Results

NR + 35 phr N326



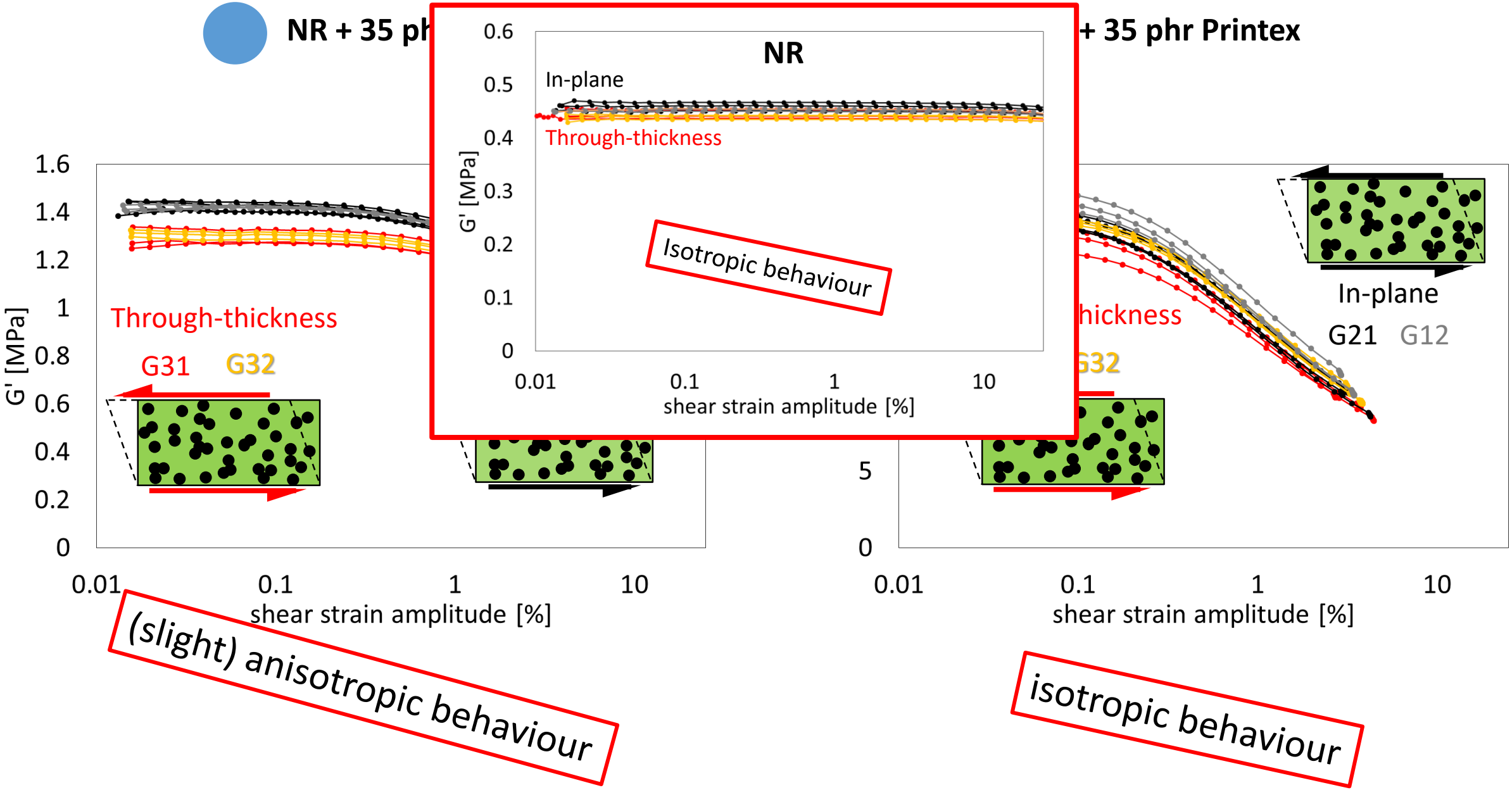
(slight) anisotropic behaviour

NR + 35 phr Printex



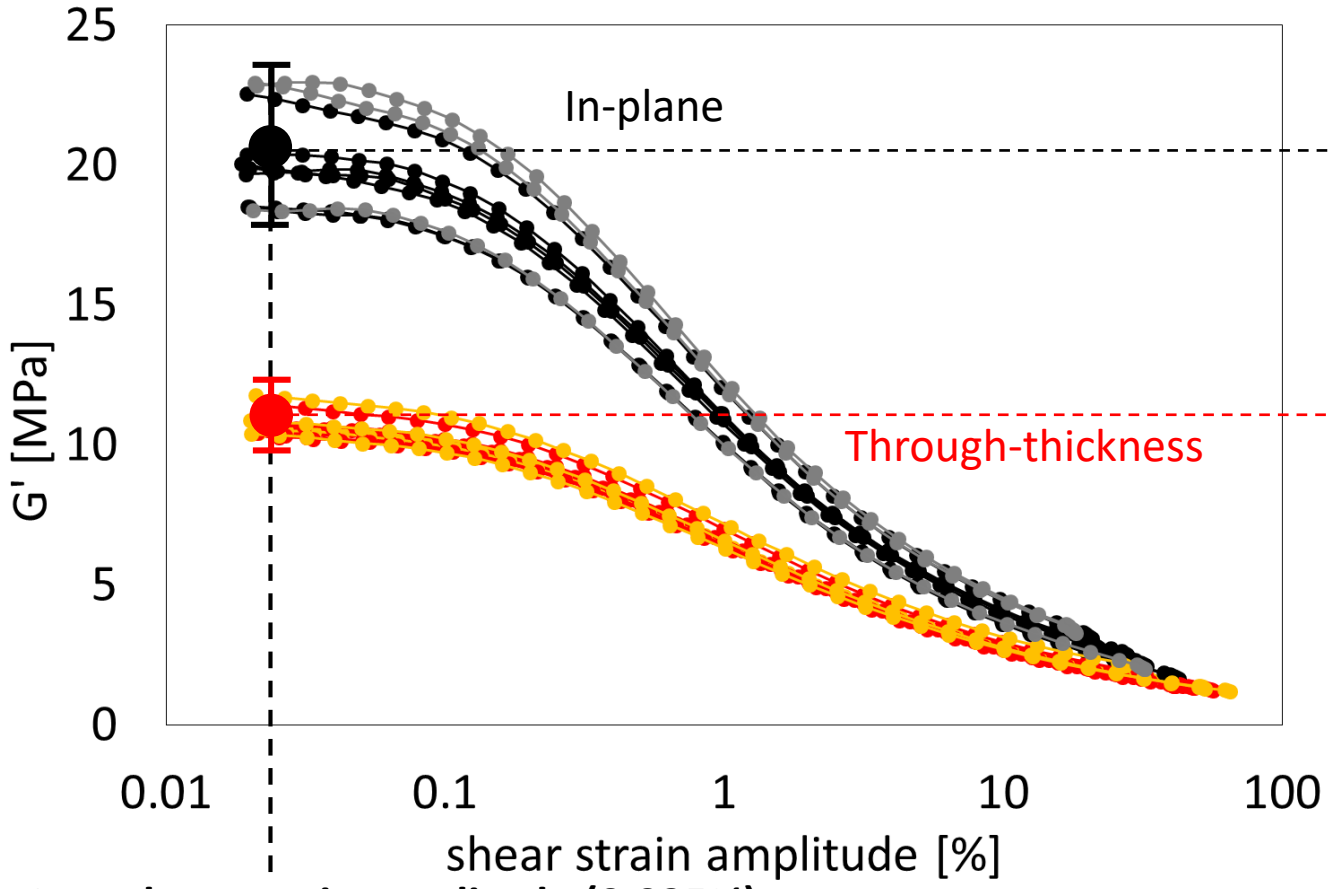
isotropic behaviour

Results


NR + 35 ph
+ 35 phr Printex
NR
In-plane
Through-thickness
Isotropic behaviour
G' [MPa]
shear strain amplitude [%]
Through-thickness
G31
G32
hickness
G32
In-plane
G21
G12
(slight) anisotropic behaviour
isotropic behaviour

Results

Anisotropy index



Low shear strain amplitude (0.025%)

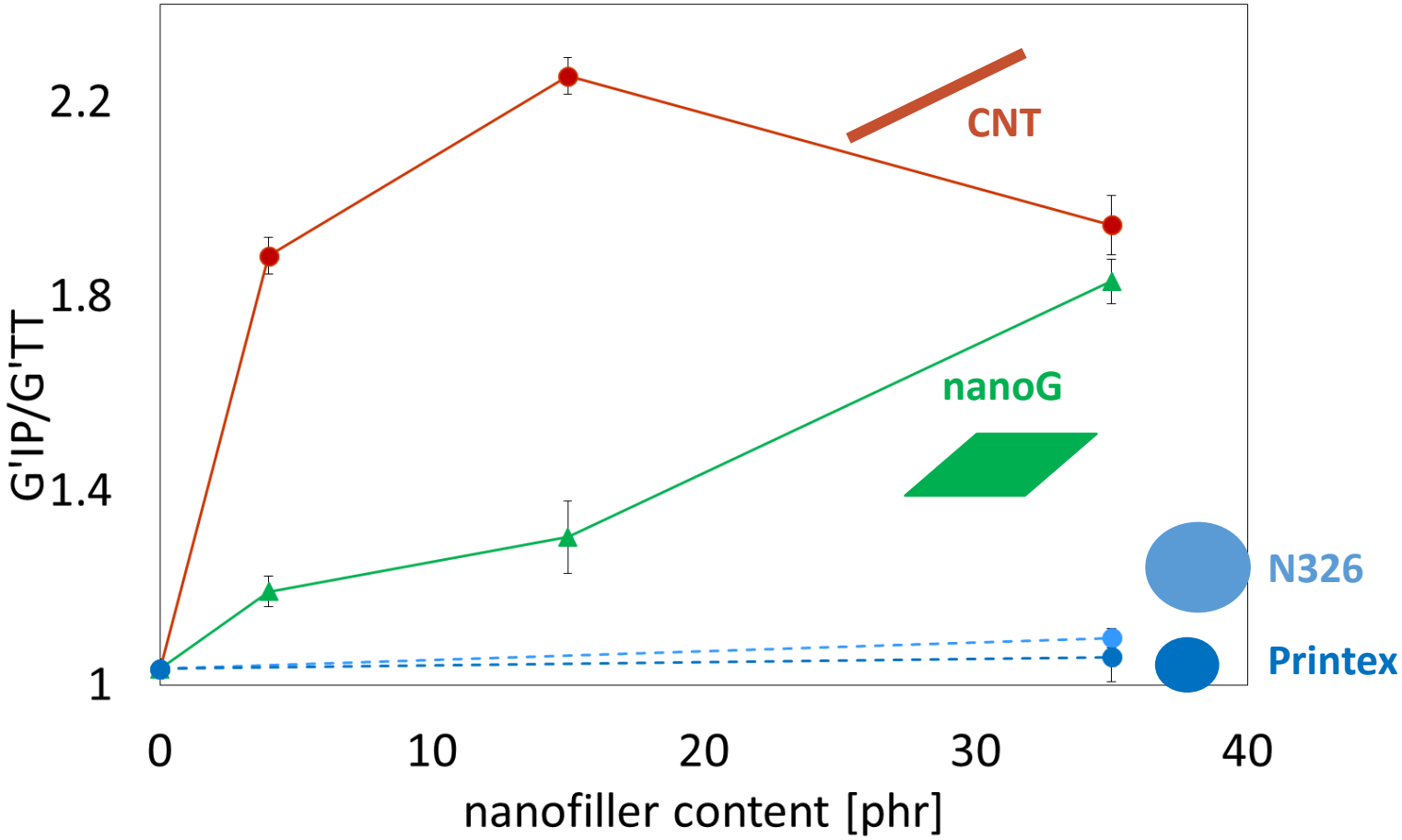
Anisotropy index:

$$\frac{G'IP}{G'TT}$$

Results

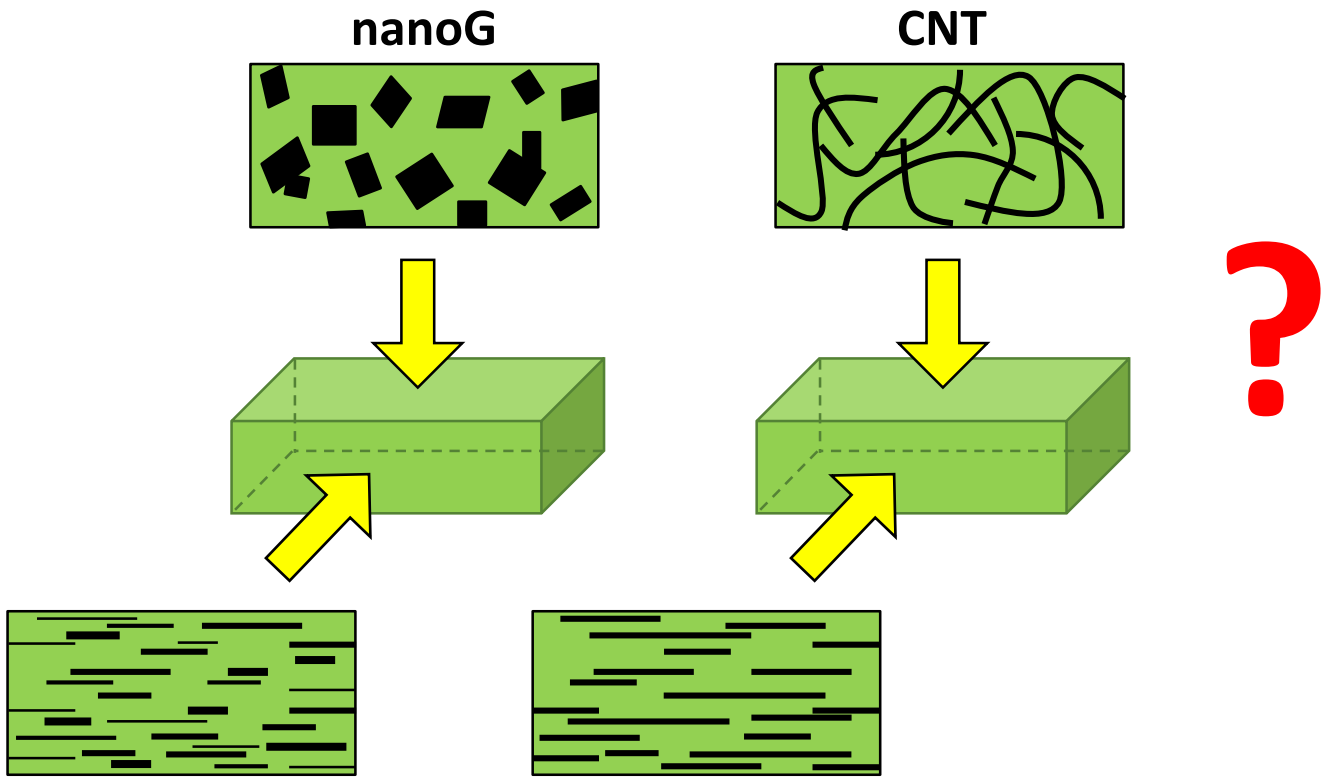
Anisotropy level of storage modulus

Low shear strain amplitude (0.025%)



Results

Investigations of filler structuring



Analyses

- Transmission electron microscopy (TEM) analysis
- Electrical resistivity measurements

Preliminary data on:

- **NR + 15 phr CNT**
- **NR + 35 phr CNT**

Results

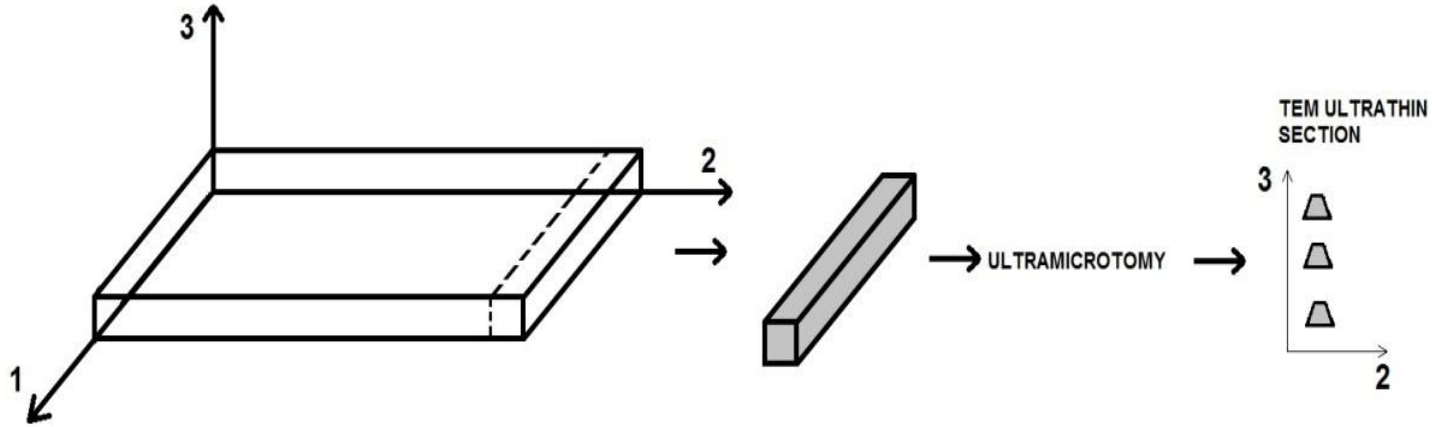
Transmission electron microscopy (TEM) analysis

TEM:
Philips CM200 electron microscope
200 kV
Field Emission Gun filament

Materials:

- **NR + 15 phr CNT**
- **NR + 35 phr CNT**

Ultrathin sections obtained perpendicular to the reference axis 1



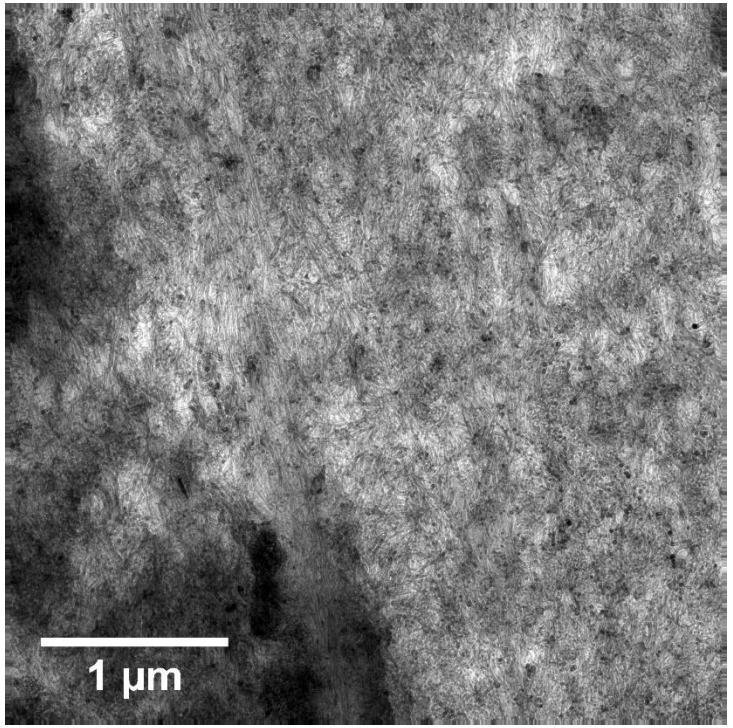
Sketch of expected CNT structuring:

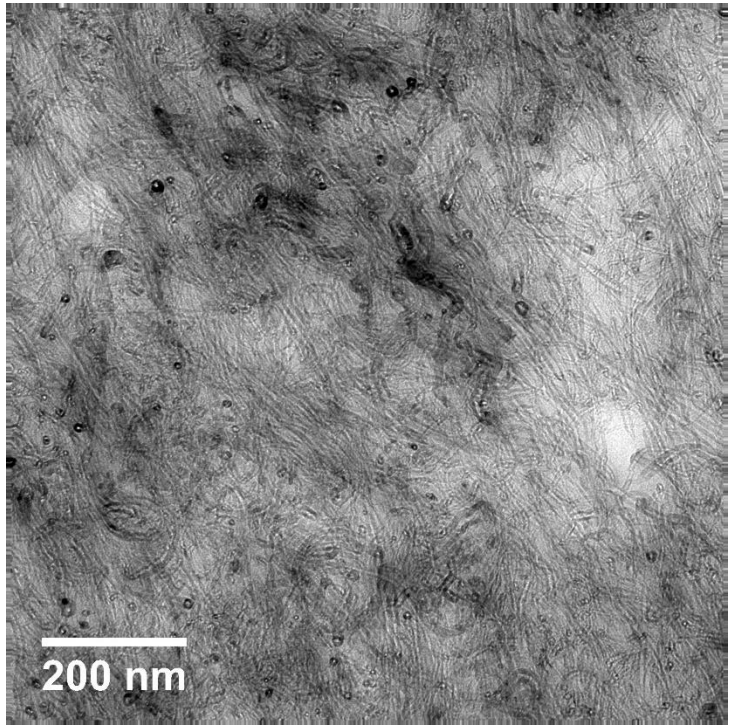
Ultrathin slice (approximately 70–100 nm thick) preparation by ultramicrotomy technique.
(sample temperature: -130° C; diamond knife)

Results

Bright field Transmission electron microscopy (TEM-BF) analysis

NR + 35 phr CNT





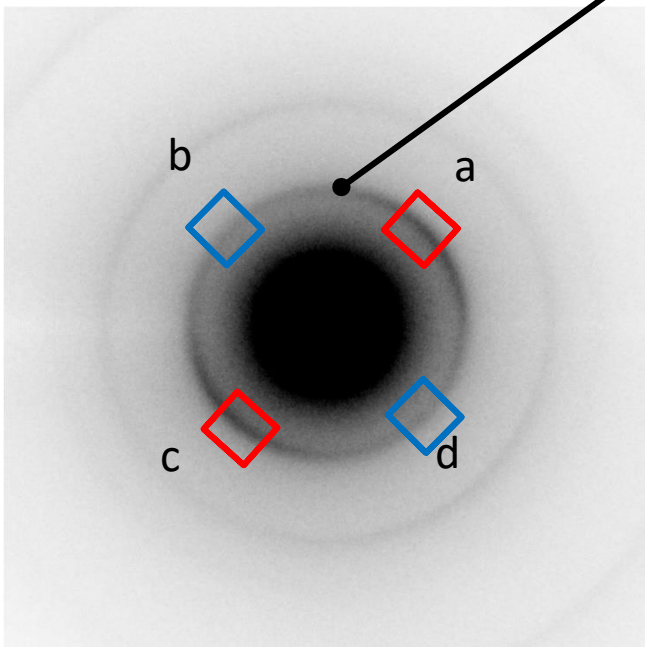
Results

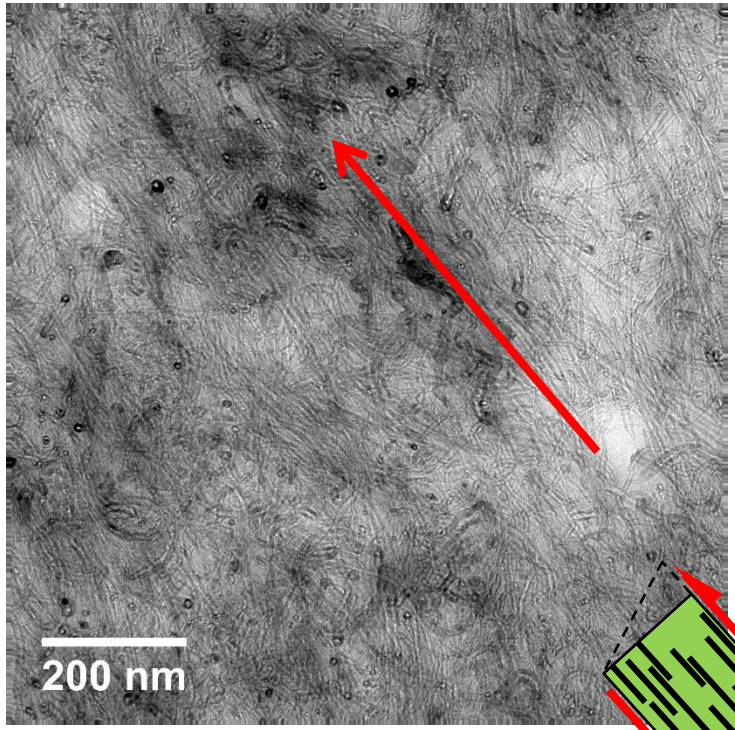
Electron diffraction measurements
by Selected Area Electron Diffraction (SAED) Patterns

NR + 35 phr CNT

SAED ring pattern

(002) Debye-Scherrer ring → d-spacing of 0.34 nm → concentric arrangements of the nanotubes walls



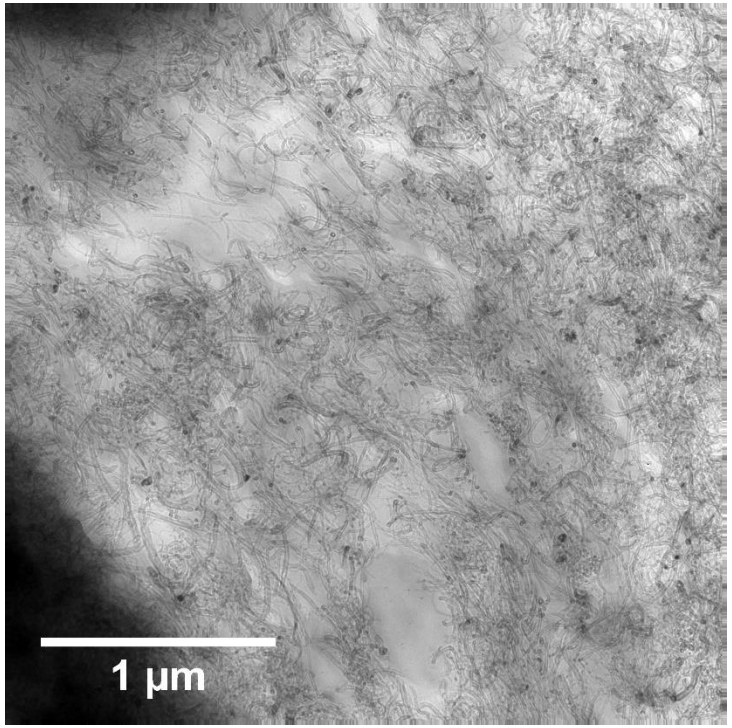


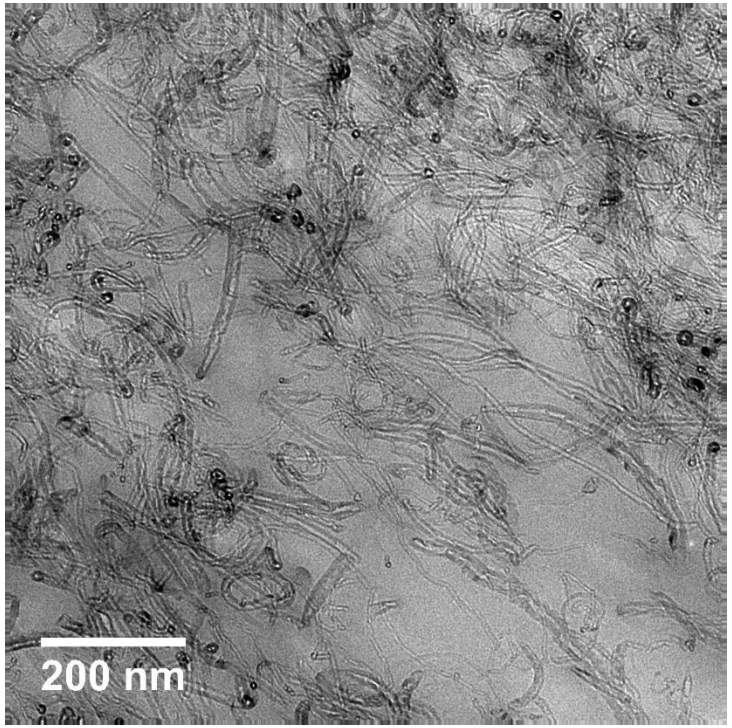
CNT preferential orientation by SAED analysis

Results

Bright field Transmission electron microscopy (TEM-BF) analysis

NR + 15 phr CNT





Results

Electron diffraction measurements by Selected Area Electron Diffraction (SAED) Patterns

NR + 15 phr CNT

SAED ring pattern

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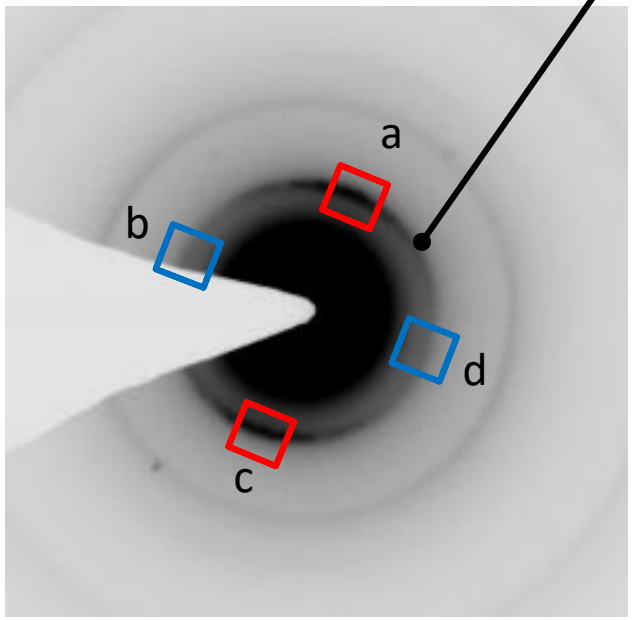
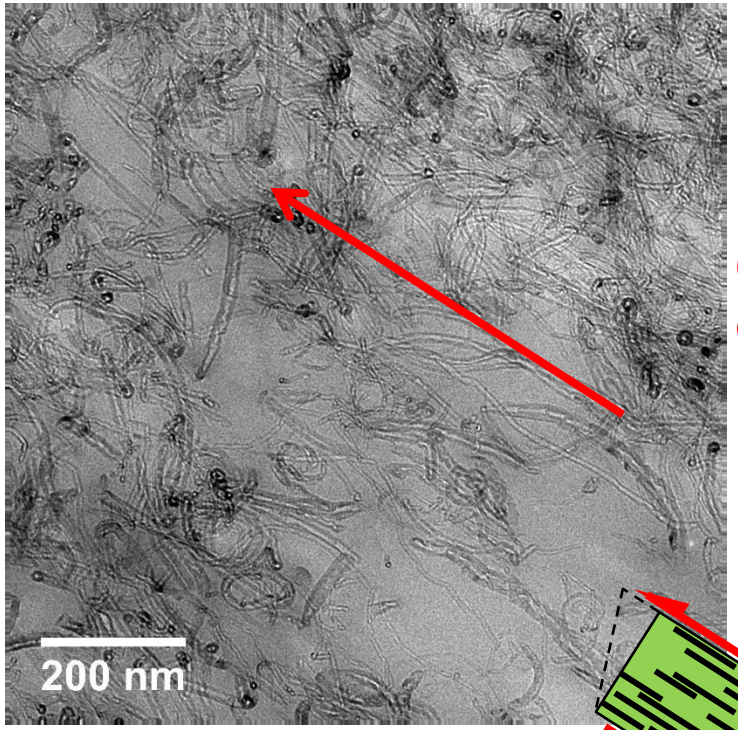




CNT preferential orientation by SAED analysis

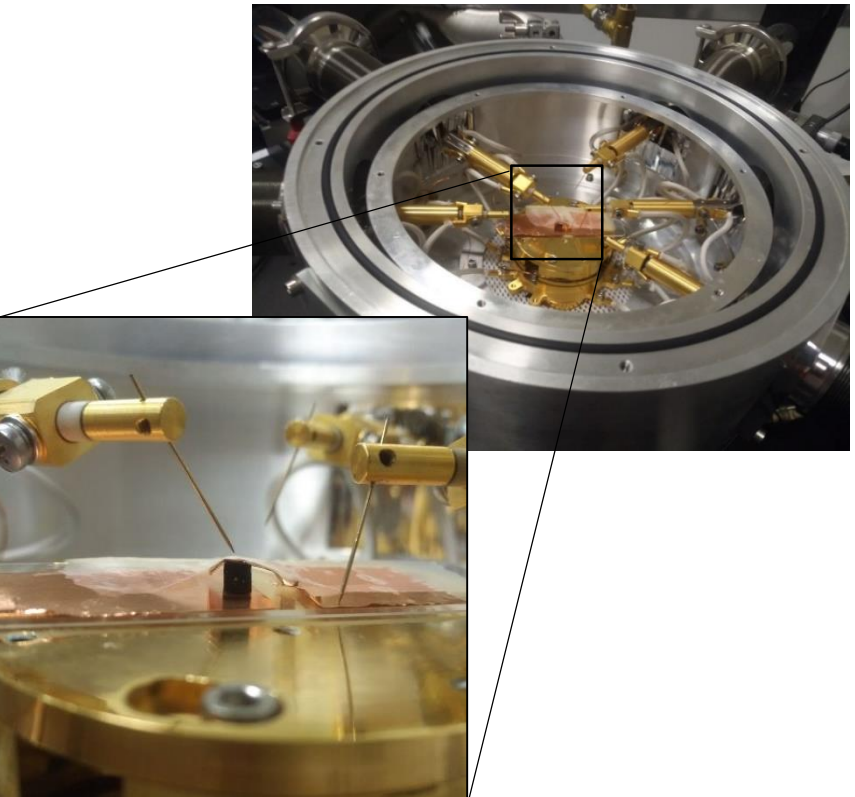
Results

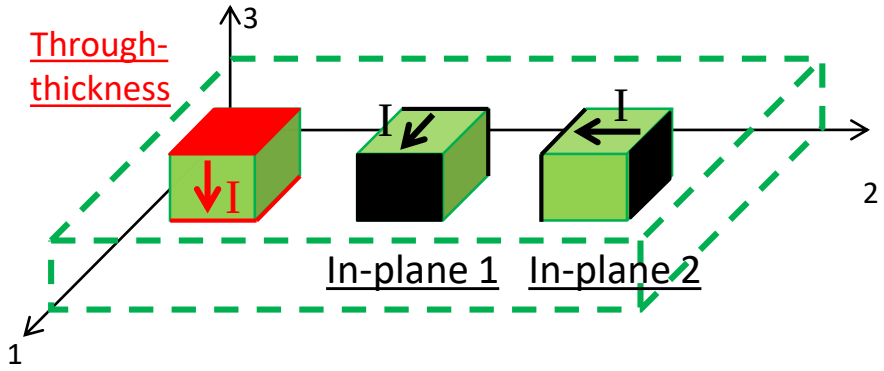
Electrical resistivity measurements

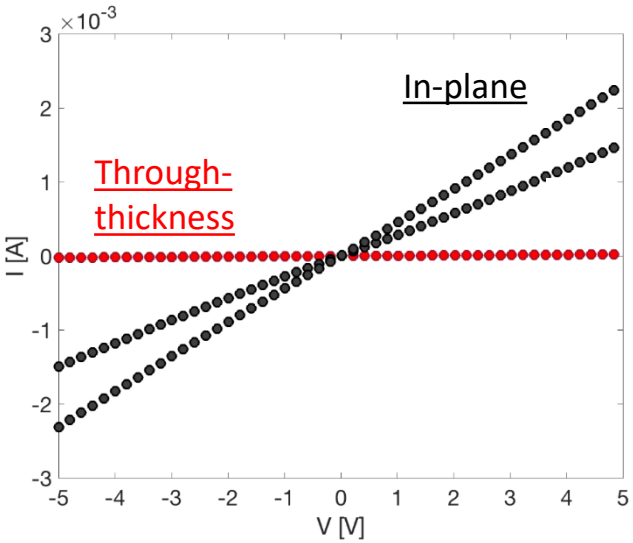
Measurement setup:
Specimens: 3x3x3 mm^3
KEITHLEY 2636A System Sourcemeter
Contacts: Copper+silver paste

Materials:

- **NR + 15 phr CNT**
- **NR + 35 phr CNT**



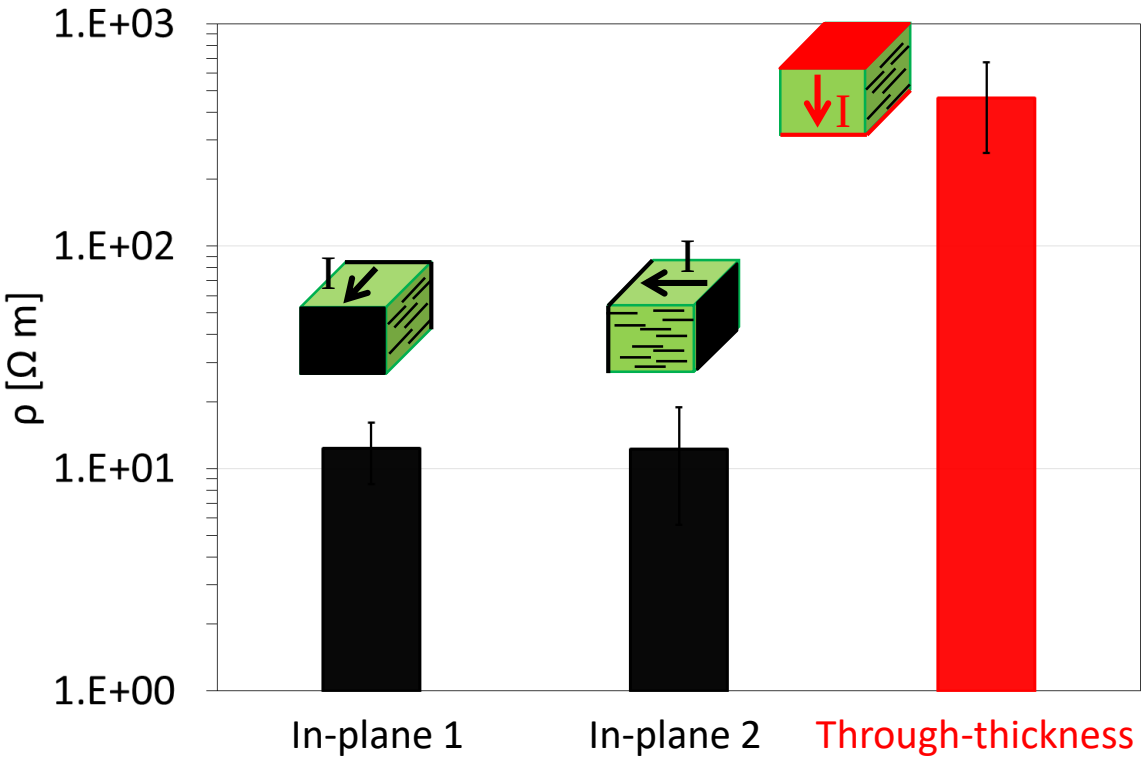




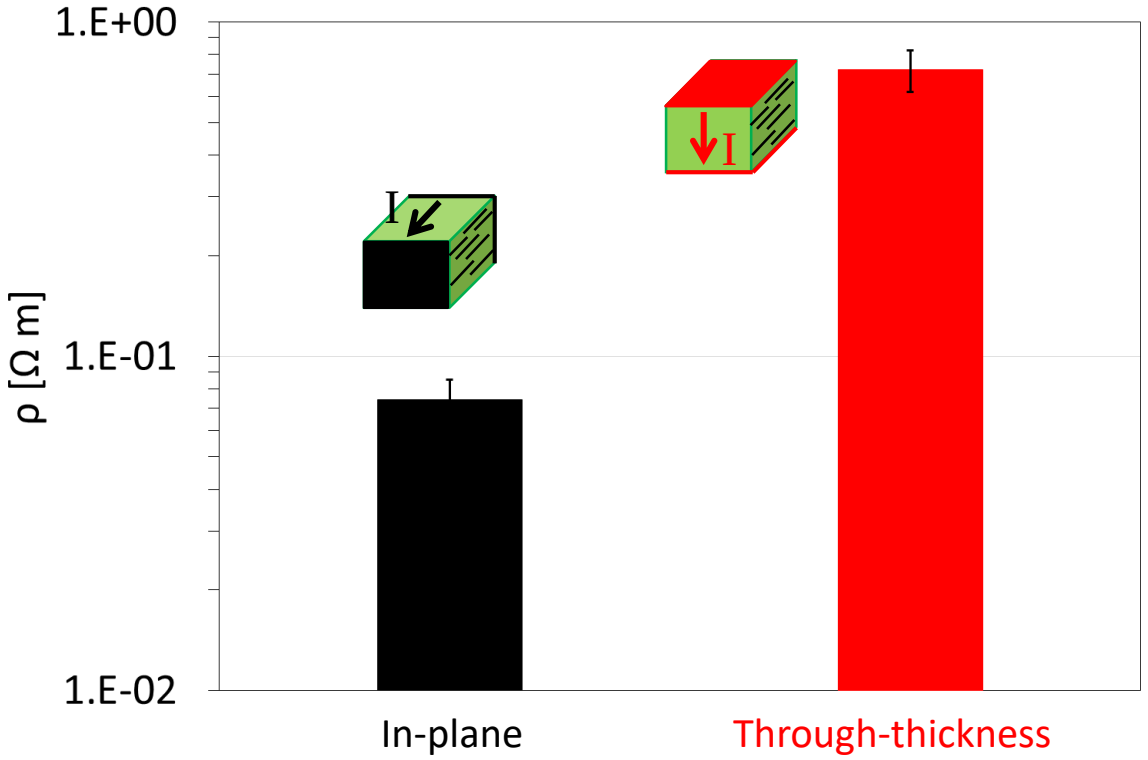
Results

Electrical resistivity measurements

NR + 15 phr CNT



NR + 35 phr CNT



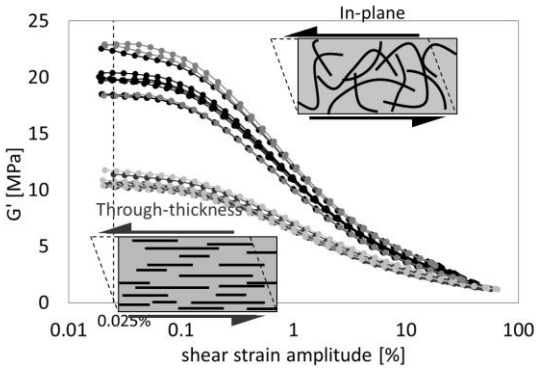
Anisotropy index:

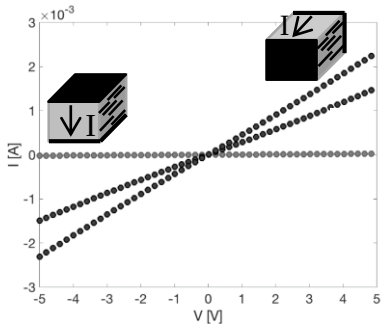
$\rho_{TT}/\rho_{IP} = 38$

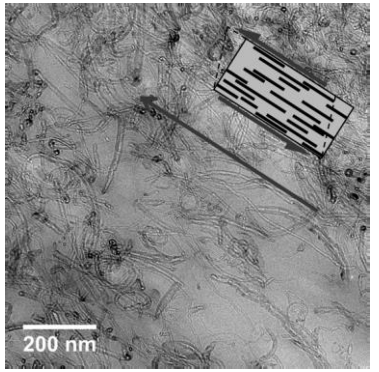
$\rho_{TT}/\rho_{IP} = 10$

Conclusions

- Dynamic shear characterization allowed to **estimate the mechanical anisotropy level** in a thin rubber plate.
- In a homogeneous compression molded rubber plate, **CNT** and **nanoG** confer a **transversal isotropic behavior,** whose intensity depends on filler content .







- This behavior could be interpreted as a consequence of a random orientation of the filler particles in the sheet plane, and of their planar piling up through the sheet thickness.
- A combined microscopy approach (**TEM+SAED**) and **electrical measurements** provided confirmation of CNT structuring.

Thank you for you attention!

Transverse isotropy is observed in sedimentary rocks at long wavelengths.