Anisotropic effects and master curves for rubbers with sp² carbon allotropes: towards light weight materials

Maurizio Galimberti¹

Silvia Guerra¹, Giuseppe Infortuna¹, Vincenzina Barbera¹, Andrea Bernardi¹, Giuseppe Mastinu¹, Silvia Agnelli², Stefano Pandini²

¹Politecnico di Milano  ²Università di Brescia

International Elastomer Conference  192nd Technical Meeting ACS Rubber Division  Cleveland (OH) October 9 - 12, 2017
sp² Carbon allotropes

![Image of Carbon black particles with 400 nm scale](image)
### sp\(^2\) Carbon allotropes

**Carbon black**

<table>
<thead>
<tr>
<th>0-D</th>
<th>1-D</th>
<th>2-D</th>
<th>3-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Giant fullerences</td>
<td>(c) Carbon nanotube</td>
<td>(f) Graphene surface</td>
<td>(g) 3D graphite crystal</td>
</tr>
<tr>
<td>(b) C\text{60}</td>
<td>(i) Carbon nanoribbons</td>
<td>(h) Haeckelitte surface</td>
<td>(m) 3D Schwartzite crystals</td>
</tr>
<tr>
<td>(d) Nanocones</td>
<td>(k) Graphene nanoribbons</td>
<td>(p) Nanoribbons 2D networks</td>
<td>(n) 3D Schwartzite crystals</td>
</tr>
<tr>
<td>(e) Nanotoroids</td>
<td>(l) Graphene clusters</td>
<td></td>
<td>(o) Carbon nanofoams</td>
</tr>
<tr>
<td>(j) Short carbon chains</td>
<td>(l) Helicoidal carbon nanotube</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
sp² Carbon allotropes

sp² Carbon allotropes

Various new allotropes to be synthesized

Jin Zhang et al, Carbon 98 (2016) 708e732
Objectives of the contribution to the Rubber Division Meeting

- Rationalization of sp² 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 sp² carbon allotropes. How they look like?

CNT

NANOCYL NC7000
from Nanocyl

CB

CBN326
from Cabot

HSAG

Asbury Synthetic Graphite 8427
## Carbon nanofillers: main features

<table>
<thead>
<tr>
<th>Carbon filler</th>
<th>Carbon Purity (%) (TGA)</th>
<th>Surface area (m²/g) (BET)</th>
<th>DBP absorption number (ml/100g)</th>
<th>Number of stacked layers (XRD)</th>
<th>Acidic groups (mmol/g)(^a) (Boehm titration)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB N326</td>
<td>98</td>
<td>77</td>
<td>85</td>
<td>5</td>
<td>1.3</td>
<td>5.7 – 9.7</td>
</tr>
<tr>
<td>CB N 110</td>
<td>98</td>
<td>137</td>
<td>113</td>
<td>n.d.</td>
<td>n.d.</td>
<td>6.9 – 9.5</td>
</tr>
<tr>
<td>CNT - 1</td>
<td>n.d.</td>
<td>200</td>
<td>316</td>
<td>10</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>CNT - 2</td>
<td>90</td>
<td>275</td>
<td>n.d.</td>
<td>8</td>
<td>2.0</td>
<td>n.d.</td>
</tr>
<tr>
<td>HSAG</td>
<td>99.5</td>
<td>330</td>
<td>162</td>
<td>35</td>
<td>1.1</td>
<td>4.6</td>
</tr>
</tbody>
</table>

\(^a\)carboxy, epoxy, hydroxy groups

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

<table>
<thead>
<tr>
<th>CNT</th>
<th>0</th>
<th>1.25</th>
<th>2.50</th>
<th>5.00</th>
<th>10.00</th>
<th>15.00</th>
<th>30.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>0</td>
<td>1.39</td>
<td>2.78</td>
<td>5.56</td>
<td>11.11</td>
<td>16.67</td>
<td>33.30</td>
</tr>
<tr>
<td>CB N326</td>
<td>0</td>
<td>1.25</td>
<td>2.50</td>
<td>5.00</td>
<td>10.00</td>
<td>15.00</td>
<td>30.00</td>
</tr>
</tbody>
</table>

Fillers with the same volume fraction

Composites crosslinked with dicumyl peroxide: 1.40 phr


## Composites with carbon allotropes, based on IR

### Composites with hybrid filler systems (phr)

<table>
<thead>
<tr>
<th></th>
<th>CNT</th>
<th>CNT/CB</th>
<th>G</th>
<th>G/CB</th>
<th>CB N326</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR = 100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT</td>
<td>0</td>
<td>1.25</td>
<td>2.50</td>
<td>5.00</td>
<td>10.00</td>
</tr>
<tr>
<td>CNT/CB</td>
<td></td>
<td>1.25/1.25</td>
<td>2.50/2.50</td>
<td>5.00/5.00</td>
<td>7.50/7.50</td>
</tr>
<tr>
<td>G</td>
<td>0</td>
<td>1.39</td>
<td>2.78</td>
<td>5.56</td>
<td>11.11</td>
</tr>
<tr>
<td>G/CB</td>
<td></td>
<td>1.39/1.25</td>
<td>2.78/2.50</td>
<td>5.55/5.00</td>
<td>8.34/7.70</td>
</tr>
<tr>
<td>CB N326</td>
<td>0</td>
<td>1.25</td>
<td>2.50</td>
<td>5.00</td>
<td>10.00</td>
</tr>
</tbody>
</table>

Fillers with the same volume fraction

Composites crosslinked with dicumyl peroxide: 1.40 phr

---


Composites with carbon allotropes, based on S-SBR

<table>
<thead>
<tr>
<th>Composites with hybrid filler systems (phr)</th>
<th>SBR = 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>0; 1; 2; 3; 4; 5; 6; 6.5; 7.5; 10; 11; 14; 18; 20</td>
</tr>
<tr>
<td>CB N326</td>
<td>0; 10; 15; 20; 22; 30; 35; 45; 50; 60</td>
</tr>
<tr>
<td>CB N326</td>
<td>10</td>
</tr>
<tr>
<td>CB N326</td>
<td>22</td>
</tr>
<tr>
<td>CB N326</td>
<td>35</td>
</tr>
</tbody>
</table>

Fillers with the same volume fraction

Composites crosslinked with dicumyl peroxide: 1.40 phr
IR based compounds. $G'_{\gamma_{\text{min}}}$ and $\Delta G'$ vs total filler vol%  

Carbon allotropes: CB and CNT

CNT leads to higher values of both $G'_{\gamma_{\text{min}}}$ and $\Delta G'$

Data from shear stress tests, 50°C
SBR based compounds. $G'_\gamma\min$ and $\Delta G'$ vs total filler vol% 

Carbon allotropes: CB and CNT

$G'$

$\Delta G'$

CNT leads to higher values of both $G'_\gamma\min$ and $\Delta G'$

Data from shear stress tests, 50°C
IR based compounds. $G'_\gamma$ vs total filler vol%
SBR based compounds. $G'_\gamma$min and $\Delta G'$ vs total filler vol% 

Carbon allotropes: CB and CNT

Data from shear stress tests, 50°C

M. Galimberti et al  Anisotropic effects and master curves  International Elastomer Conference  Cleveland (OH), October 9-12, 2017 17
SBR based compounds. $G'_{\gamma_{\min}}$ and $\Delta G'$ vs total filler vol% 

Carbon allotropes: CB and CNT

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»

Specific interfacial area

Specific interfacial area \( = A \cdot \rho \cdot \Phi \)

- **filler properties**
  - \( A = \text{BET surface area} \)
  - \( \rho = \text{density} \)
  - \( \Phi = \text{volume fraction} \)

*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»

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 sp² carbon allotropes

Data from shear stress tests, 50°C

Rubber: IR, SBR

\[ y = e^{0.043x} \]

\[ R^2 = 0.9429 \]
Master curve for the initial modulus of elastomers composites with sp² carbon allotropes

Data from shear stress tests, 50°C

Rubber: IR, SBR

Up to

40 phr CB, 12 phr CNT

$y = e^{0.043x}$

$R^2 = 0.9429$
Master curve for the Payne effect of elastomers composites

with sp\(^2\) carbon allotropes

Data from shear stress tests, 50°C
Master curves for the mechanical reinforcement of elastomer composites with sp² carbon allotropes

\[ G' \]

\[ \Delta G' \]

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

M. Galimberti, G. Infortuna, S. Guerra, V. Barbera, S. Agnelli, S. Pandini eXPRESS Polymer Letters, 2017, accepted for publication
Master curves for the mechanical reinforcement of elastomer composites with sp² carbon allotropes

$G'$ and $\Delta G'$

M. Galimberti, G. Infortuna, S. Guerra, V. Barbera, S. Agnelli, S. Pandini eXPRESS Polymer Letters, 2017, accepted for publication
Master curves for the mechanical reinforcement of elastomer composites

with sp² carbon allotropes

What about nanosized graphite?

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

Master curves for the mechanical reinforcement of elastomer composites

with sp² carbon allotropes

What about nanosized graphite?

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

Master curves for the mechanical reinforcement of elastomer composites with sp² carbon allotropes

With DBP absorption - IR as the rubber

![Graph showing mechanical reinforcement of elastomer composites with different allotropes and DBP absorption.]

<table>
<thead>
<tr>
<th>Allotrope</th>
<th>DBP [mL/100g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>85</td>
</tr>
<tr>
<td>CNT</td>
<td>316</td>
</tr>
<tr>
<td>HSAG</td>
<td>162</td>
</tr>
</tbody>
</table>

\[
\phi_c = \phi \left( \frac{1}{\phi + 0.02139 \cdot DBP} \right) \\
\]

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

Anisotropic properties
Carbon allotropes lead to anisotropic properties of rubber compounds?

CNT

CB
"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
## NR based composites with carbon nanofillers

### Recipes and preparation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount [phr (volume fraction)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>100</td>
</tr>
<tr>
<td>Filler</td>
<td>0 (0.02), 4 (0.07), 15 (0.15)</td>
</tr>
<tr>
<td>DCUP</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Fillers
HSAG, CNT, CB: N326

Internal mixer: 50 mL mixing 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

- 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
  - Melt flow direction
Samples preparation and device for shear stress tests

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

melt flow direction

Device for shear stress tests
Shear stress tests: through thickness and in plane

Through-thickness

Stress on faces perpendicular to axis 3

In-plane

Stress on faces perpendicular to axis 1 or 2
Shear modulus vs shear strain amplitude

NR

Shear modulus vs shear strain amplitude for NR:

- **In-plane**
  - Shear modulus: \( G_{21}, G_{12} \)

- **Through-thickness**
  - Shear modulus: \( G_{31}, G_{32} \)

**Isotropic behaviour**

**No Payne effect**

Peroxide crosslinked
Shear modulus vs shear strain amplitude

NR + 35 phr CB N326

Through-thickness

In-plane

(slight) anisotropic behaviour

Peroxide crosslinked
Shear modulus vs shear strain amplitude

NR + 35 phr CNT

Anisotropic Payne Effect

Transversal isotropic behavior

Peroxide crosslinked
Shear modulus vs shear strain amplitude

NR + 35 phr HSAG

Transversal isotropic behavior

Peroxide crosslinked
Transmission electron microscopy

NR + 35 phr CNT

200 nm
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

G' [MPa]

In-plane

Through-thickness

shear strain amplitude [%]

200 nm
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

M. Galimberti et al
Anisotropic effects and master curves
International Elastomer Conference Cleveland (OH), October 9-12, 2017
Anisotropy index as a function of carbon filler content

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

![Graph showing the anisotropy index as a function of carbon filler content.](image)

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

\[
\frac{G'}{G''} = \text{master curve}
\]

Through-thickness

\[
\Delta \text{ through thickness}
\]

interfacial area \( [1/\mu m] \)

CNT (NR)

N326 (NR)

CB

CNT

Through-thickness
Mastercurve and anisotropy

![Graph showing anisotropic effects and master curves.](image)

- CB: Carbon Black
- CNT: Carbon Nanotubes

- In-plane and through-thickness orientation.
Mastercurve and anisotropy

The diagram shows the comparison of in-plane and through-thickness behaviors of CNT (NR) and CB (NR) materials. The graph plots the interfacial area against the master curve for different materials, indicating anisotropic effects. The in-plane behavior is represented by squares, and the through-thickness behavior is represented by triangles. The graph highlights the difference in performance between the two types of materials in different directions.
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
    - filler aspect ratio
Design of materials

Anisotropic electrical properties

Lightweight materials
Design of materials

Anisotropic electrical properties
Electrical resistivity measurements

Measurement setup
Specimens: 3x3x3 mm³. KEITHLEY 2636A System Sourcemeter. Contacts: Copper+silver paste
Electrical resistivity measurements

\[ \rho = R \text{ (S/h)} \]

*Measurement setup*
Specimens: 3x3x3 mm³. KEITHLEY 2636A System Sourcemeter. Contacts: Copper+silver paste
Electrical resistivity measurements - Anisotropy Index

CNT in NR

A.I. = Anisotropy Index = $\rho_{TT}/\rho_{IP}$
Electrical resistivity measurements - Anisotropy Index

HSAG, in NR

\[ A.I. = \text{Anisotropy Index} = \frac{\rho_{TT}}{\rho_{IP}} \]
Electrical resistivity measurements - Anisotropy Index

HSAG, CB in NR

A.I. = Anisotropy Index = \( \rho_{TT}/\rho_{IP} \)
Electrical resistivity measurements - Anisotropy Index

\[ \text{A.I.} = \text{Anisotropy Index} = \frac{\rho_{TT}}{\rho_{IP}} \]

HSAG, CB in NR
Mechanical and electrical anisotropy indexes

![Graph showing mechanical anisotropy index as a function of CNT content. The x-axis represents CNT content in parts per hundred (phr), and the y-axis represents the ratio $(G_{IP}/G_{TT})_{0.025%}$. The graph shows an increase in the ratio with increasing CNT content, reaching a peak at around 20 phr and then declining slightly at higher CNT contents.]
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 sp² carbon allotropes: lightweight materials
To solve the equation of the master curve

\[ G'_{\gamma_{\text{min}}}/G'_m = e^{0.043 \text{i.a.}} \]

Target density

\[ \rho_C = \rho_{CB} \cdot \phi_{CB} + \rho_{CNT} \cdot \phi_{CNT} + \rho_m \cdot (1 - \phi_{CB} - \phi_{CNT}) \]
Target modulus and density as a function of relative CNT content

Relative CNT content = $\phi_{\text{CNT}}/(\phi_{\text{CB}}+\phi_{\text{CNT}})$
Target modulus and density as a function of relative CNT content

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

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

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

LiDuP
Lightweight Construction and Durability Performance

www.lidup.polimi.it

Fabrizio Torricelli, Paolo Romele  University of Brescia

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

Thanks for the attention!