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

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Department of Mechanical Engineering

Department of Civil and Environmental Engineering
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
Objectives of the work

- To develop lightweight elastomeric materials for automotive application
- To prepare elastomer composites based on sp² carbon allotropes
- To identify a common correlation between features of sp² 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

<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)</td>
<td>(c)</td>
<td>(f)</td>
<td>(g)</td>
</tr>
<tr>
<td>C60</td>
<td>C60</td>
<td>Graphene surface</td>
<td>3D graphite crystal</td>
</tr>
<tr>
<td>Giant fullerene</td>
<td>Carbon nanotube</td>
<td>(h)</td>
<td>(m)</td>
</tr>
<tr>
<td>(b)</td>
<td>(i)</td>
<td>Haeckel surface</td>
<td>3D graphite crystal</td>
</tr>
<tr>
<td>Nanocones</td>
<td>Graphene nanoribbons</td>
<td>(p)</td>
<td>(n)</td>
</tr>
<tr>
<td>(d)</td>
<td>(j)</td>
<td>Nanoribbons 2D networks</td>
<td>3D Schwarzite crystals</td>
</tr>
<tr>
<td>Nanotoroids</td>
<td>Graphene nanoribbons</td>
<td>(k)</td>
<td>(o)</td>
</tr>
<tr>
<td>(e)</td>
<td>(l)</td>
<td>Helicoidal 2D networks</td>
<td>Carbon nanofoams</td>
</tr>
<tr>
<td>Short carbon chains</td>
<td></td>
<td>(l)</td>
<td>3D nanotube networks</td>
</tr>
</tbody>
</table>

## Carbon allotropes

<table>
<thead>
<tr>
<th>0-D</th>
<th>1-D</th>
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<td>(a)</td>
<td>(c)</td>
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<td>(g)</td>
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<tr>
<td>C60</td>
<td>Carbon nanotube</td>
<td>Graphene surface</td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td>Giant fullerenes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d)</td>
<td>Nanocones</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e)</td>
<td>Nanotoroids</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i)</td>
<td>Graphene clusters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(j)</td>
<td>Short carbon chains</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(l)</td>
<td>Helicoidal carbon nanotube</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Various new allotropes to be synthesized

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

- Graphene
  - Stacked
  - Wrapped
- Carbon black
  - Few stacked layers randomly arranged in spheres
- CNT
  - Single walled
  - Multi walled

- Few layers graphene
- Grades with different shape anisotropy
- Many stacked layers
- Graphite
  - Few stacked layers
  - Many stacked layers
Carbon fillers from a layer of sp$^2$-bonded carbon atoms

- **graphene**
  - stacked
  - wrapped

- **carbon black**
  - few stacked layers randomly arranged in spheres

- **CNT**
  - single walled
  - multi walled
Analysis of mechanical reinforcement
CNT and CB as the sp² carbon allotropes

**CNT**
- Carbon purity ≈ 90% (TGA)

**CB**
- Carbon purity ≈ 98% (TGA)

NANOCYL® NC7000™ from Nanocyl
- CBN326 from Cabot
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

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

<table>
<thead>
<tr>
<th>Carbon filler</th>
<th>BET surface area (m²/g)</th>
<th>Acidic groups (mmol/g)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB N326</td>
<td>77</td>
<td>1.3</td>
<td>7.6</td>
</tr>
<tr>
<td>CNT</td>
<td>275</td>
<td>2</td>
<td>8.7</td>
</tr>
</tbody>
</table>

<sup>a</sup> by Boehm titration: carboxy, epoxy, hydroxy groups
Analysis of mechanical reinforcement
Composites with carbon allotropes, based on IR

<table>
<thead>
<tr>
<th>Composites with only one filler (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR = 100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<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>CNT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></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>
<td>16.67</td>
<td>33.30</td>
<td></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>
<td></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>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>1.25</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>1.39</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>

IR = 100

Fillers with the same volume fraction

Composites crosslinked with dicumyl peroxide: 1.40 phr


# Composites with carbon allotropes, based on S-SBR

## Composites with hybrid filler systems (phr)

<table>
<thead>
<tr>
<th></th>
<th>CNT</th>
<th>SBR = 100</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0; 1; 2; 3; 4; 5; 6; 6.5; 7.5; 10; 11; 14; 18; 20</td>
<td></td>
</tr>
<tr>
<td>CB N326</td>
<td>0; 10; 15; 20; 22; 30; 35; 45; 50; 60</td>
<td></td>
</tr>
<tr>
<td>CB N326</td>
<td>10</td>
<td>+ CNT: 0 ÷ 14</td>
</tr>
<tr>
<td>CB N326</td>
<td>22</td>
<td>+ CNT: 0 ÷ 14</td>
</tr>
<tr>
<td>CB N326</td>
<td>35</td>
<td>+ CNT: 0 ÷ 14</td>
</tr>
</tbody>
</table>

**Fillers with the same volume fraction**

**Composites crosslinked with dicumyl peroxide: 1.40 phr**
Initial Modulus as a function of the total filler content

Data from shear stress tests, 50°C

IR

CB

CNT

CB+CNT

$G_{\text{min}}$ [MPa]

0 0.05 0.1 0.15 0.2 0.25 0.3

Total filler volume fraction

$G_{\text{min}}$ [MPa]
Initial Modulus as a function of the total filler content

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

\[ 0.09 - 0.1 \text{ as total filler volume fraction} \]

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
To identify a common correlation between features of sp² 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*

\[ A = \text{BET surface area} \]
\[ \rho = \text{density} \]
\[ \Phi = \text{volume fraction} \]

*measure unit:* \(\text{m}^2 / \text{m}^3\)

Surface / volume in the composite
Master curve for the initial modulus of elastomers composites

with \( sp^2 \) carbon allotropes

![Graph showing data from shear stress tests, 50°C]

Elastomers: 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

Elastomers: IR, SBR
Master curve for the initial modulus of elastomers composites with sp² carbon allotropes

Data from shear stress tests, 50°C

Elastomers: IR, SBR

Up to 40 phr CB, 12 phr CNT
Master curve for the Payne effect of elastomers composites

with sp² carbon allotropes

Data from shear stress tests, 50°C

Elastomers: IR, SBR

M. Galimberti et al  From master curve to lightweigth materials  Rubber Con 2017  Prague (CZ), May 23-25, 2017
Master curves for the mechanical reinforcement of elastomer composites with \( sp^2 \) carbon allotropes

\[ G' \quad \Delta G' \]

IR, SBR as the elastomers

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

with sp² carbon allotropes

Data from shear stress tests, 50°C

IR, SBR as the elastomers

M. Galimberti et al

From master curve to lightweight materials

Rubber Con 2017 Prague (CZ), May 23-25, 2017
CNT and CB as the sp² carbon allotropes
CNT and CB lead to anisotropic properties of composites?

"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

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

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
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

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

- **CNT**
  - Graph showing the relationship between G'IP/GETT and nanofiller content [phr].
  - CNT is represented by a red line with data points.

- **CB**
  - Graph showing the relationship between G'IP/GETT and nanofiller content [phr].
  - CB is represented by a blue line with data points.

Diagram showing the orientation of CNT and CB in composite materials.
Transversal isotropic behaviour …

NR composites with CNT, nano graphite

... for carbon fillers with high aspect ratio

Grand Canyon
Master curve for the initial modulus of elastomers composites with sp² carbon allotropes

Data from shear stress tests, 50°C

Elastomers: IR, SBR
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 sp² carbon allotropes

Objective:
lightweight materials
What to do?

1. Master curve based on interfacial area
2. To solve the equation of the master curve:
   equation to correlate modulus and interfacial area
3. To define target modulus and density
4. Best combination of sp² carbon allotropes
To solve the equation of the master curve

\[
\frac{G'_{\gamma_{\text{min}}}}{G'_m} = 0.90e^{0.050 \text{i.a.}}
\]

Target density

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

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

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

- 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
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)

#### Table

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

Mastinu, G, Plochl, 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)

- $A$ is the 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 $p_3 = m$

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

\[
\frac{\partial E}{\partial p_1} = \frac{\partial E}{\partial C_x} = A \cdot 1.9 \cdot 10^4
\]

\[
\frac{\partial E}{\partial p_2} = \frac{\partial E}{\partial f_R} = m \cdot 8.4 \cdot 10^2
\]

\[
\frac{\partial E}{\partial p_3} = \frac{\partial E}{\partial m} = a \cdot C_x \cdot 1.9 \cdot 10^4 + f_R \cdot 8.4 \cdot 10^2 + 10
\]
### E percent variations for 10% variation of $p_i$

<table>
<thead>
<tr>
<th>Vehicle type</th>
<th>Data</th>
<th>% variation of E due to 10% variation of $p_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rated Power kW</td>
<td>A m$^2$</td>
</tr>
<tr>
<td>Mid-range</td>
<td>140</td>
<td>2.2</td>
</tr>
<tr>
<td>Compact</td>
<td>55</td>
<td>2.0</td>
</tr>
<tr>
<td>Sports</td>
<td>310</td>
<td>1.95</td>
</tr>
<tr>
<td>SUV</td>
<td>200</td>
<td>2.3</td>
</tr>
</tbody>
</table>

- 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

<table>
<thead>
<tr>
<th>Tyre size</th>
<th>Tyre mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>155/70 R13</td>
<td>6.5 kg</td>
</tr>
<tr>
<td>185/70 R13</td>
<td>7.0 - 7.2 kg</td>
</tr>
<tr>
<td>175/65 R14</td>
<td>6.5 - 7.2 kg</td>
</tr>
<tr>
<td>195/65 R15</td>
<td>8.2 - 9 kg</td>
</tr>
<tr>
<td>&gt;R20</td>
<td>&gt;15 kg</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Vehicle type</th>
<th>Tyre</th>
<th>Vehicle mass reduction</th>
<th>% Energy saved due to mass reduction only</th>
<th>% Energy saved due to RR reduction</th>
<th>Total % Energy saved due to mass reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mid-range</td>
<td>195/70 R15</td>
<td>4 kg</td>
<td>0.1</td>
<td>4</td>
<td>4.1</td>
</tr>
<tr>
<td>Compact</td>
<td>155/70 R13</td>
<td>3 kg</td>
<td>0.2</td>
<td>3</td>
<td>3.1</td>
</tr>
<tr>
<td>Sports</td>
<td>245/45 R19</td>
<td>&gt;5</td>
<td>&lt;0.5</td>
<td>4</td>
<td>4.5</td>
</tr>
<tr>
<td>SUV</td>
<td>&gt;R20</td>
<td>&gt;6</td>
<td>&lt;0.2</td>
<td>4</td>
<td>4.2</td>
</tr>
</tbody>
</table>
Conclusions

![Graphs and images related to conclusions]
Acknowledgments

Prof. Gianpiero Mastinu  Politecnico Milano
Pirelli Tyre
Thanks for the attention!

www.lidup.polimi.it