# Master curves for the mechanical reinforcement of diene elastomers with sp² carbon allotropes

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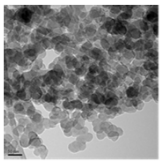
## OBJECTIVES

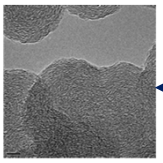
The aim of this work was to develop elastomeric materials for automotive application based on sp² carbon allotropes, to identify a common correlation between features of sp² carbon allotropes and properties of elastomer composites and finally to design composites suitable for automotive application based on this correlation.

### Carbon fillers from a layer of sp²-bonded carbon atoms

**HR-TEM analysis**

CB N326
from Cabot



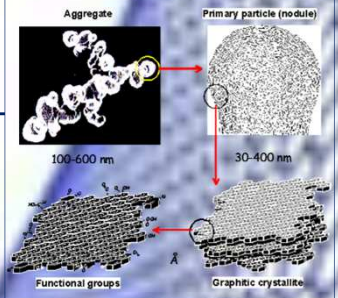


Carbon purity ≈ 98% (TGA)

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

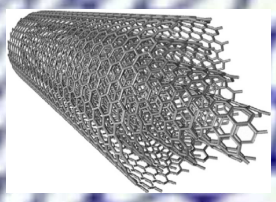
[a] by Boehm titration: carboxy, epoxy, hydroxy groups

**Carbon black**




few stacked layers randomly arranged in spheres

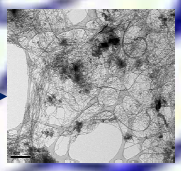
**Multi walled CNT**

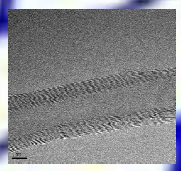


several tubes in concentric cylinders

**HR-TEM analysis**

NANOCYL® NC7000™
from Nanocyl





Carbon purity ≈ 90% (TGA)

| Carbon filler | BET surface area ($m^2/g$) | Acidic groups (mmol/g)[a] | pH |
|---|---|---|---|
| CNT | 275 | 2 | 8.7 |

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

### CB and CNT for the mechanical reinforcement of rubber

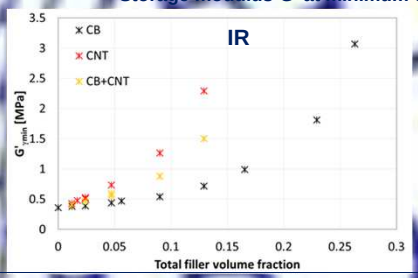
**Recipes of composites**

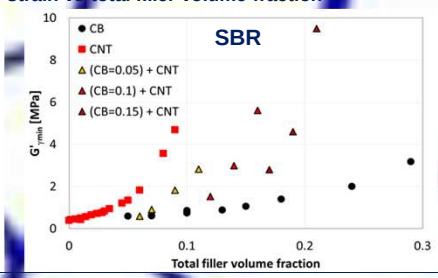
| Volume fractions for **IR** composites* | | | | | |
|---|---|---|---|---|---|
| CNT | 0.012 | 0.024 | 0.047 | 0.090 | 0.129 |
| CB | 0.012 | 0.024 | 0.047 | 0.090 | 0.129 |
| Hybrid composites (CNT/CB) | | | | | |
| CNT + CB | 0.012 | 0.024 | 0.047 | 0.090 | 0.129 |
| CNT | 0.006 | 0.12 | 0.24 | 0.45 | 0.65 |
| CB | 0.006 | 0.12 | 0.24 | 0.45 | 0.65 |

| Volume fractions for **SBR** composites* | | | | |
|---|---|---|---|---|
| CB \ CNT | 0 | 0.02 | 0.04 | 0.06 |
| 0 | 0/0 | 0/0.02 | 0/0.04 | 0/0.06 |
| 0.05 | 0.05/0 | 0.05/0.02 | 0.05/0.04 | 0.05/0.06 |
| 0.1 | 0.1/0 | 0.1/0.02 | 0.1/0.04 | 0.1/0.06 |
| 0.15 | 0.15/0 | 0.15/0.02 | 0.15/0.04 | 0.15/0.06 |

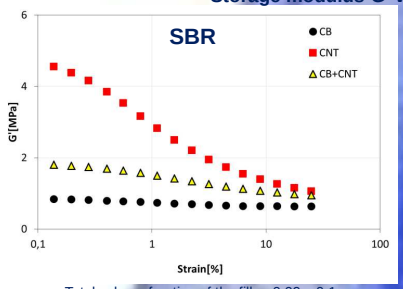
*Composites crosslinked with dicumyl peroxide: 1.40 phr

**Storage modulus G' at minimum strain vs total filler volume fraction**




**Storage modulus G' vs strain amplitude**




Total volume fraction of the filler: 0.09 – 0.1

Larger G' values were clearly obtained with CNT as the reinforcing filler: $G'_{ymin}$ is more than five times higher than $G'_{ymin}$ of the composite based on CB. Storage moduli of the hybrid composites with almost the same amount of CB and CNT are in between, closer to those of CB based composite. It is acknowledged that a nanofiller such as CNT brings about large mechanical reinforcement of polymer melts and elastomers, definitely larger than the one obtained with CB.

**Specific interfacial area**

**i.a. = A · ρ · Φ**

Filler features:

A = BET surface area

ρ = density

Φ = volume fraction

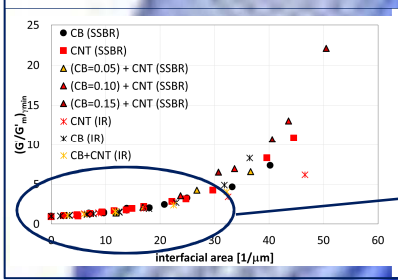
*measure unit:* $m^2 / m^3$

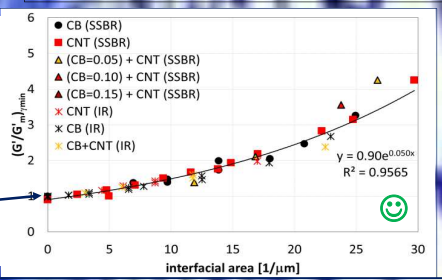
Surface / volume in the composite

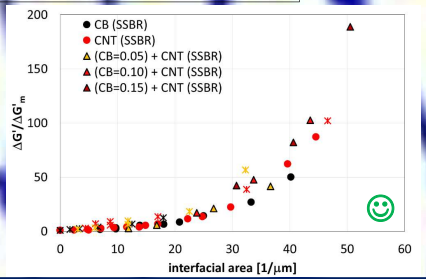
**For binary systems:**

$$i.a. = Ai_{CB} * \rho_{CB} * \phi_{CB} + Ai_{CNT} * \rho_{CNT} * \phi_{CNT}$$

### Master curves for the mechanical reinforcement of rubber




Experimental points can be fitted with a common line up to 27 $\mu m^{-1}$ as the interfacial area values, corresponding to CB and CNT content of about 20 and 12 phr, respectively. The equation of such master curve, $G'_{gmin}/G'_{matrix} = 0.91e^{0.050a}$, was the tool to correlate Storage modulus and Payne effect of the composites.

## CONCLUSIONS

A common master curve for mechanical reinforcement both for IR and SBR elastomeric matrices containing carbon allotropes sp² has been obtained.

Based on this correlation it is possible to predict composite modulus and also the amount of filler volume fraction needed to achieve a desired elastic modulus.