diene elastomers with sp^2 carbon allotropes

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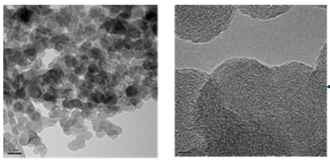
OBJECTIVES

The aim of this work was to develop elastomeric materials for automotive application based on sp^2 carbon allotropes, to identify a common correlation between features of sp^2 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 sp^2-bonded carbon atoms

HR-TEM analysis

CB N326
from Cabot

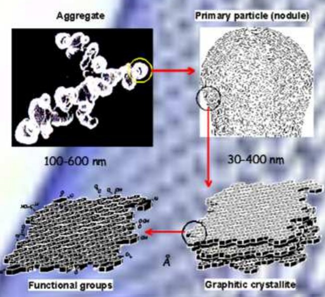


Carbon purity ≈ 98% (TGA)

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

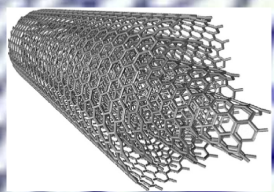
[a] by Boehm titration: carboxy, epoxy, hydroxy groups

Carbon black



few stacked layers randomly arranged in spheres

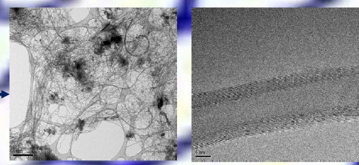
Multi walled CNT



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

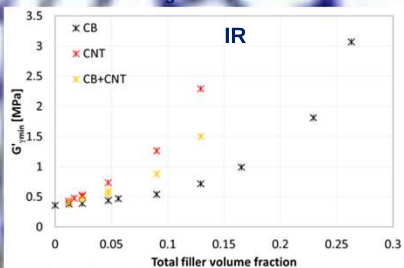
Recipes of composites

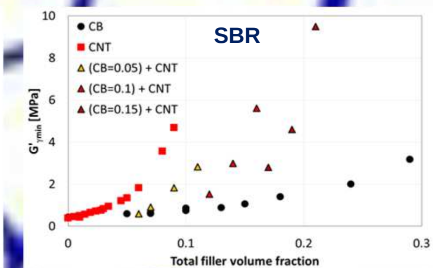
Volume fractions for **IR** composites*					
CNT	0.012	0.024	0.047	0.090	0.129
CB	0.012	0.024	0.047	0.090	0.129
Hybrid composites (CNT/CB)					
CNT + CB	0.012	0.024	0.047	0.090	0.129
CNT	0.006	0.12	0.24	0.45	0.65
CB	0.006	0.12	0.24	0.45	0.65

Volume fractions for **SBR** composites*				
	CNT			
CB	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

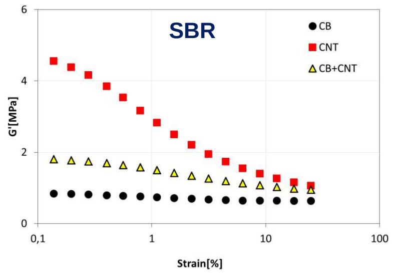
*Composites crosslinked with dicumyl peroxide: 1.40 phr

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

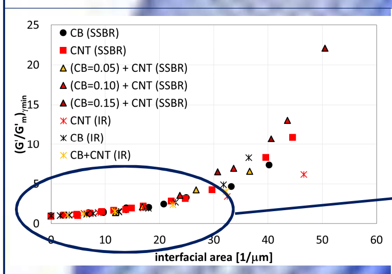
measure unit: m^2 / m^3

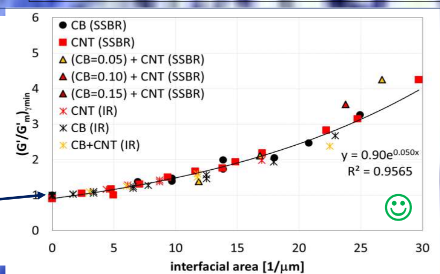
Surface / volume in the composite

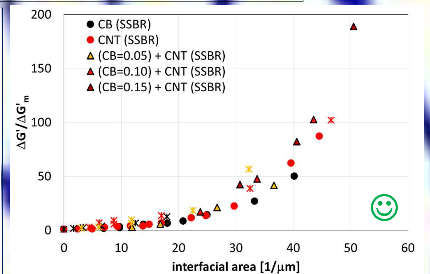
For binary systems:

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

Master curves for the mechanical reinforcement of rubber







Experimental points can be fitted with a common line up to 27 µm^{-1} as the interfacial area values, corresponding to CB and CNT content of about 40 and 12 phr, respectively. The equation of such master curve, G'$_{ymin}$/G'$_{matrix}$ = 0.91e$^{0.05 i.a.}$, was the tool to compute 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 sp^2 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.