

Mechanical reinforcement of rubber by sp² carbon allotropes such as carbon black and carbon nanotubes: The role of interfacial area and filler orientation

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The large variety of reinforcing fillers nowadays available proves their importance for enhancing the properties of rubber compounds (refs. 1-4).

Besides the so-called traditional fillers, such as the nanostructured carbon black and silica (refs. 5 and 6), new generations of fillers are being developed, as for example nanofillers, i.e., particles with at least one dimension below 100 nm (ref. 7). Such a low size results in a very high surface to volume ratio, and therefore in a higher reinforcing efficiency in a rubber-based composite (refs. 8-11). Major interest is for carbon nanofillers: carbon nanotubes (CNT), both single-walled and multi-walled (refs. 7, 8 and 12), and graphene and graphene related materials (GRM), such as graphene nanoplatelets made by a few stacked layers of graphene (nanoG) (refs. 13-16). It is indeed worth underlining that new types of carbon nanofillers are continuously appearing (refs. 17 and 18).

It is clear nowadays that, particularly for large scale applications, nanofillers cannot replace CB. Indeed, increasing interest is for hybrid systems based on CB-CNT and CB-graphene related materials (refs. 19-22), developed by partially substituting CB with nanometric carbon allotropes.

In spite of such large interest for carbon nanofillers and for hybrid filler systems, the theoretical study of their effects on the properties of a rubber compound does not have the same space, and this limits their rational use and exploitation.

Some of the authors studied the effects of sp² carbon allotropes on the mechanical properties of a rubber matrix: a single filler or hybrid filler systems were used (refs. 9 and 23-26). A common rationalization of the mechanical reinforcement by different families of sp² carbon allotropes has been proposed recently by the authors (refs. 9 and 24). A common correlation was found between the composites' modulus and the surface made available by the filler per unit volume of composite, meaning with the specific interfacial area.

In such a common frame for the behavior of sp² carbon allotropes, it is definitely interesting to identify the distinctive features of the nanometric ones, mainly CNT and GRM. They are characterized by a high aspect ratio (or shape anisotropy); i.e., the ratio of the maximum over the minimum dimension of the particle. Hence, CNT and GRM can present a preferential orientation in the elastomeric matrix and, as a consequence, they can impart anisotropic properties, which means directionally dependent properties. Preferential orientation and alignment of

nanoparticles is an effective way to selectively improve the composite properties along specific directions. However, in soft matrices such as rubbers, anisotropic effects promoted by nanoparticles have never been thoroughly analyzed. A remarkable anisotropic behavior of the dynamic moduli has been documented by some of the authors for composites based on natural rubber (NR), filled with either CNT or a nanosized graphite (nanoG) (refs. 23 and 26). Properties along transversal directions were experimentally measured, and it was found that the structuring of nanofillers induced an orthotropic and transversally isotropic response. As a result, the dynamic moduli were very similar to each other when measured in the sheet plane, and nearly twice as much when measured in the orthogonal direction (i.e., perpendicular to the sheet plane).

The aim of this work was to go more in depth into such investigation: The separate and combined effects of filler surface area and filler orientation were studied. Comparison was made between a nanostructured and a nanometric filler, CB and CNT, respectively. Common features and differences in their influence on the mechanical behavior are highlighted and explained on the basis of their main parameters.

Experimental

Materials

Composites were prepared with three different matrices: isoprene rubber (IR), styrene butadiene rubber (SBR) and natural rubber (NR).

Synthetic poly(1,4-cis-isoprene) (IR) was SKI3 (Nizhnekamskneftechim Export, Nizhnekamsk, Russia), with 70 Mooney units (MU) as Mooney viscosity (ML [1+4] 100°C).

Synthetic poly(styrene-co-butadiene) (SBR) was from solution anionic polymerization: Nipol NS 522 (Zeon Corporation, Düsseldorf, Germany), with 39 mass% of bound styrene, 37.5 mass% of extension oil and 62 Mooney units (MU) as Mooney viscosity (ML [1+4] 100°C).

Poly(1,4-cis-isoprene) from *Hevea brasiliensis* (natural rubber, NR) was SMR GP, with 65 Mooney units as Mooney viscosity (ML [1+4] 100°C), from Lee Rubber.

Organic peroxide was 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane supported on silica/CaCO₃ (45 mass %), from Arkema Inc.

Two types of multiwall carbon nanotubes were used.

CNT(B) are Baytubes C150 P from Bayer Material Science. They are characterized by chemical purity ≥95 wt. %, length of 1-10 μm, number of walls of 3-15, outer and inner diameters of 10-16 and 4 nm, respectively, according to the technical data sheet. Their surface area, measured by the BET method, is 200 m²/g.

Table 1 - filler amount in phr of composites based on IR, with CNT(B) and CB as the carbon allotropes; other ingredients: IR 100 phr, dicumyl peroxide 1.40 phr

CNT(B)	0	1.25	2.50	5.00	10.00	15.00	30.00
CNT(B)/CB	-	-	1.25/	2.50/	5.00/	7.50/	15.00/
CB N326	0	1.25	2.50	5.00	10.00	15.00	30.00

Table 2 - filler amount in phr of composites based on SBR, with CNT(N) and CB as the carbon allotropes; other ingredients: SBR 100 phr, dicumyl peroxide 1.40 phr

CNT(N)	0; 1; 2; 3; 4; 5; 6; 6.5; 7.5; 10; 11; 14; 18; 20
CB N326	0; 10; 15; 20; 22; 30; 35; 45; 50; 60
CB N326	~10 + CNT(N): from 0 to 14 (vol. fraction: 0.05)
CB N326	~22 + CNT(N): from 0 to 14 (vol. fraction: 0.10)
CB N326	~35 + CNT(N): from 0 to 14 (vol. fraction: 0.15)

CNT(N) are Nanocyl NC7000 series from Nanocyl (Sambreville, Belgium), with carbon purity of 90%, average length of about 1.5 μm and BET surface area of 275 m^2/g .

Carbon black N326 (CB) from Cabot is characterized by 30 nm as the mean diameter of spherical primary particles, a nitrogen adsorption number of 77 m^2/g and a DBP adsorption number of 85 $\text{mL}/100 \text{ g}$.

In IR based systems, composites with only CB, only CNT(B) or hybrid fillers (CB+CNT) were prepared. The composition in phr (weight parts per hundred parts of rubber) is reported in table 1. In hybrid filler composites, the filler content was divided into two equal parts of the two fillers.

Composites based on SBR are filled with CNT(N), CB or hybrid fillers (table 2). In this case, hybrid fillers were prepared by adding to the fixed contents of CB increasing amounts of CNT(N). The contents were chosen to uniformly cover a wide range of total filler surface area.

Finally, NR based composites were prepared by adding only CNT(N) or CB, as shown in table 3.

Preparation

Composites, based on either IR, SBR or NR, were prepared using a Brabender type internal mixer (Brabender PL-2000 Plasti-Corder torque rheometer, Brabender GmbH & Co. KG, Duisburg, Germany), with a 50 mL mixing chamber. The following procedure was adopted for the preparation of all the samples: 50 g of the polymer were introduced into the Brabender type internal mixer and masticated at 80°C for one minute with rotors rotating at 60 rpm. The filler was then added, mixing was performed for four minutes, and the composite was then discharged at a temperature of about 90°C. The composite, so prepared, was left to reach room temperature and was fed again to the Brabender mixer kept at a temperature of

Table 3 - filler amount in phr (and volume fraction in brackets) of composites based on NR, with CNT(B) and CB as the carbon allotropes; other ingredients: NR 100 phr, dicumyl peroxide 1.40 phr

CNT(B)	0	4	15	35
		(0.02)	(0.07)	(0.15)
CB N326	0	4	15	35
		(0.02)	(0.07)	(0.15)

about 50°C. Peroxide was added, mixing was performed for three minutes with rotors rotating at 60 rpm, and the composite was finally discharged. Composites were finally further homogenized by passing them five times through a two-roll mill operating at 50°C, with the front roll rotating at 30 rpm and the back roll rotating at 38 rpm, and 1 cm as the nip between the rolls.

Crosslinking reaction was performed at 170°C for 10 minutes for IR compounds, and at 170°C for 20 minutes for SBR compounds using a Monsanto oscillating disc rheometer (MDR 2000) (Alpha Technologies, Heilbron, Germany).

NR sheets were compression molded for 10 minutes at 170°C with 3.5 MPa pressure into square plates with 3 mm thickness and 100 mm edge.

Characterization

Dynamic mechanical characterization

For SBR and IR based composites, dynamic shear moduli were measured by a Monsanto RPA 2000 rheometer (Alpha Technologies, Heilbron, Germany) in the torsion mode. For each sample, a first strain sweep (0.1-25% shear strain amplitude) was performed at 50°C and 1 Hz, then the sample was kept in the instrument at the minimum strain amplitude ($\gamma_{\text{min}} = 0.1\%$) for 10 minutes, to achieve fully equilibrated conditions. Finally, dynamic tests were performed at 50°C at increasing strain amplitude (0.1-25% shear strain amplitude) with a frequency of 1 Hz. Dynamic moduli of NR based composites were measured by a dynamic mechanical analyzer Q800 (TA Instruments) in a shear sandwich configuration, in strain sweep mode. Parallelepiped specimens were cut from cured sheets of rubber with dimensions of about 3 x 3 x 8 mm^3 . Figure 1a shows a schematic representation of the test configuration. Two specimens are compressed between the fixed plates and the moving plate of the machine. Strain sweeps were carried out in the range 0.02% to 25% of strain amplitude, at room temperature and 1 Hz. Thanks to the small dimensions of the specimens, different directions of strain could be applied in order to study the variation of material properties with the loading direction.

The various strain directions applied are shown in figures 1b and 1c, where the rubber plate is sketched with a broken line, and Cartesian coordinates are displayed: Plane 1-2 corresponds to the main plane of the rubber sheet, and direction 3 is the direction perpendicular to such plane and also the direction of the pressure applied during the compression molding phase. Two main configurations are shown, including through-thickness (TT) and in plane (IP). In TT configuration, the shear strain is applied as in

Figure 1 - schematic representation of test configurations, a) parallelepiped samples were taken from a crosslinked nanocomposite sheet and tested in the shear sandwich configuration by a dynamic mechanical analyzer, b) representation of direction of shear strains applied to specimens in b) “through-thickness” and c) “in-plane” configurations; the coordinates of the reference system (long arrows) and the applied strain directions (short arrows) are also displayed

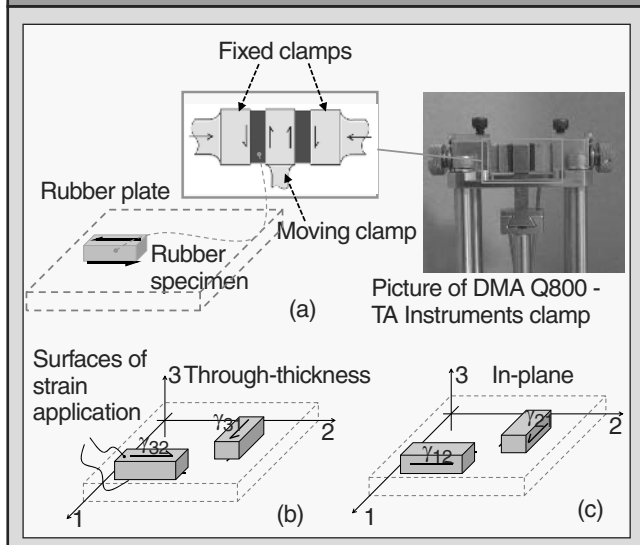
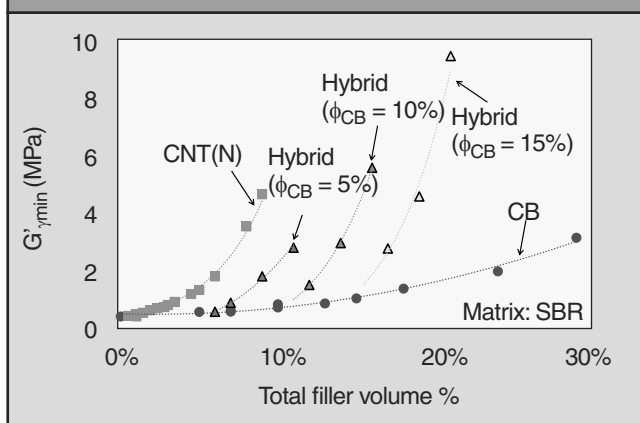


figure 1b, i.e., through the sheet thickness; while in IP configuration, the shear strain is applied as in figure 1c and lies in the 1-2 plane.

It is worth pointing out that TT configuration is similar to the test configuration carried out by the RPA, in the sense that the strain is applied on a surface perpendicular to the pressure applied during the curing phase.

Figure 2 - $G'_{\gamma_{min}}$ versus total filler volume % of composites based on SBR filled with only CB, only CNT(N) or hybrid filler systems (CB+CNT[N])



Results

Structural chemical characterization of fillers

Both CB and CNT were characterized to get their morphological, chemical and structural characteristics.

In brief, CNT(B) was characterized in (ref. 9), and has: BET surface area equal to 200 m²/g, DBP absorption number of 316 mL/100 g and number of layers stacked in crystalline domain of about 10, measured by WAXD analysis.

CB and CNT(N) were characterized and compared in (ref. 24). Carbon purity was investigated by means of thermogravimetric analysis and was found to be larger for CB (about 98%) than for CNT(N) (about 90%). Indeed, infrared spectra of CNT(N) showed features compatible with hydrocarbon, as well as oxygenated functional groups, and Boehm titration revealed a larger amount of acidic oxygenated groups. Disordered structure was shown for both CB and CNT(N) by Raman spectroscopy and WAXD analysis.

Role of filler interfacial area for the mechanical reinforcement

Storage modulus at small strains, $G'_{\gamma_{min}}$, was selected as the parameter to study the mechanical reinforcement of rubber composites. It can be reasonably expected that different fillers provide different initial modulus values, hence different levels of mechanical reinforcement. As an example, figure 2 shows the results obtained for SBR based composites, listed in table 2.

At the same filler volume fraction, CNT(N) leads to a modulus much higher than that obtained only with CB. It is indeed worth observing the dramatic increase of modulus of a CB based composite by adding even a low CNT(N) amount. The graph in figure 2 clearly shows the higher reinforcing efficiency of CNT and the fact that CNT is able to impart its higher efficiency also to hybrid filler composites.

One of the main reasons for the higher efficiency of CNT is its higher surface area. To support this claim, the data obtained for systems with different filler type and matrix type are plotted as a function of the specific interfacial area in figure 3. The specific interfacial area is the total surface area of filler normalized

Figure 3 - $(G'/G'_m)_{\gamma_{min}}$ versus specific interfacial area for composites based on SBR or IR; black line indicates the master curve

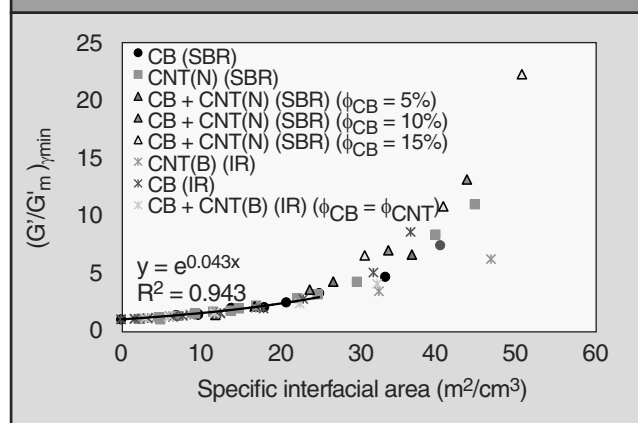
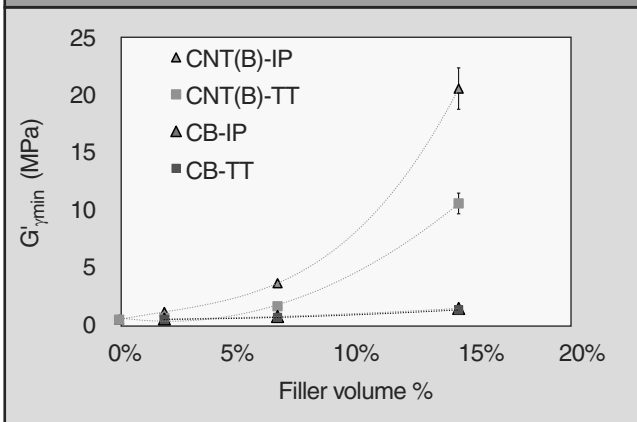


Figure 4 - $G'_{\gamma_{min}}$ versus filler volume % of composites based on NR filled with CB or CNT(B), tested in two different configurations: in-plane (triangles) or through-thickness (squares) (figure 1)



over the volume of the composite, calculated according to equation 1:

$$\text{Specific interfacial area} = \rho * A_{CB} * \phi_{CB} + \rho * A_{CNT} * \phi_{CNT} \quad (1)$$

Where ρ is the filler density, equal to 1.8 g/cm^3 for both CB and CNT, A is the surface area measured by BET method, and ϕ is the filler volume fraction in the composite. As, for example, for an SBR based composite filled with 0.1 CB and 0.06 CNT(N) as the volume fractions, the specific interfacial area is $1.8 * 77 * 0.1 + 1.8 * 275 * 0.06 = 43.6 \text{ m}^2/\text{cm}^3$. Equation 1 provides an estimation of the filler-polymer interfacial area under the hypothesis that all the filler surface is available to contact the polymer.

In figure 3 are reported both the data shown in figure 2, with SBR as the elastomer, and the data of IR based composites (listed in table 1). In order to compare data with different matrices, the stiffness values reported in figure 3 were normalized over the modulus of the neat matrix (G'_m).

Figure 3 shows that up to about $25 \text{ m}^2/\text{cm}^3$, the storage modulus values seem to follow a common trend, irrespective of the different fillers used, nanostructured or nanometric, single or hybrid, and even irrespective of the polymer matrix. By fitting the data with an exponential curve, a sort of master curve was calculated, displayed by a black curve in figure 3. The master curve is calculated up to $25 \text{ m}^2/\text{cm}^3$, a remarkable content, which corresponds to 45 phr of CB and 11.5 phr of CNT(N), which are contents typical of many elastomer composites reported in the scientific literature and also available at the commercial scale.

The calculated master curve establishes a quantitative correlation between moduli at low strain amplitude, and could be used as a tool for the rationalization of reinforcement, with many potential advantages. For example, in (ref. 24), it was used as a quantitative tool to design lightweight elastomeric materials.

At contents higher than $25 \text{ m}^2/\text{cm}^3$, the data are more scattered. This could be due to an increased difficulty of dispersion at such high contents, particularly with CNT.

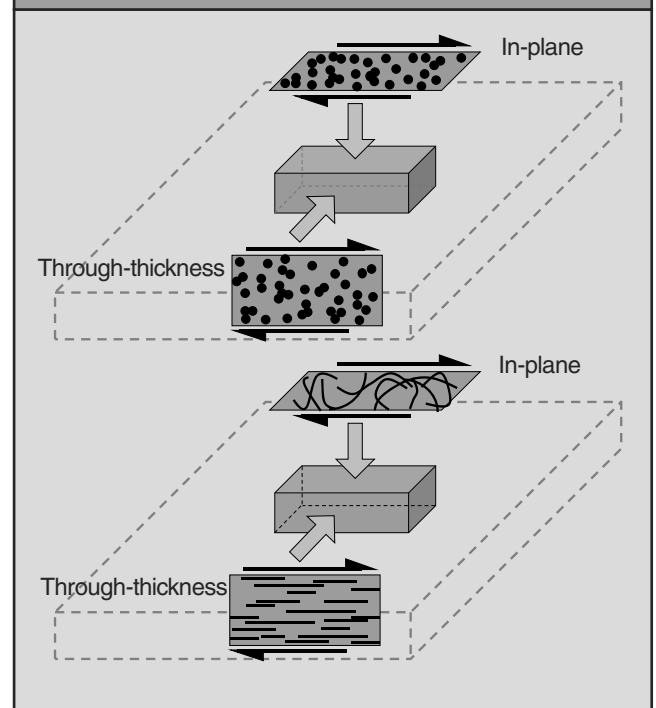
The role of filler orientation on the mechanical properties

Correlation discussed in the previous paragraph is based on the assumption that the specific interfacial area can be representative of the interaction between the polymer and the filler. This assumption could be disputed. However, the correlation was based on experimental data and the fit was remarkable. Other parameters to represent the polymer filler interaction, such as CTAB or DBP absorption, are under investigation. A question could arise: Whatever the parameter is to represent the polymer-filler interaction, can the reinforcing effects of the fillers be modeled only on the basis of this parameter? As mentioned in the Introduction, nanometric fillers such as CNT are characterized by high aspect ratio. It was commented that fillers with high aspect ratio could have preferential orientation in the rubber composite, and could thus promote anisotropic effects. In this work, anisotropic effects were investigated by dynamic mechanical tests carried out on parallelepiped specimens. As shown in figure 1, different loading directions were applied: They can be classified with two test configurations, i.e., TT and IP configurations.

Systems based on NR filled with CB or CNT(B) were investigated, and $G'_{\gamma_{min}}$ values are reported in figure 4 as a function of filler volume %.

Figure 4 shows anisotropic properties of CNT(B) filled composites. In fact, for systems filled with CNT(B), the modulus is higher in IP configuration than in TT configuration. On the other hand, the same values of moduli were measured for composites with CB in TT and IP configurations, and curves are overlapped: This reveals an isotropic behavior. The anisotropy index of

Figure 5 - schematic representation of the hypothesized organization of CB (left side) and CNT (right side) with a lateral view in "through-thickness" tests and with a top view in "in-plane" tests



CNT(B) filled composites, i.e., the ratio of IP modulus over TT modulus, is: 1.88 ± 0.04 (4 phr), 2.25 ± 0.04 (25 phr) and 2.07 ± 0.04 (35 phr).

Therefore, for a tubular filler characterized by a high aspect ratio (CNT[B]), the stiffness measured by the application of the strain in the plane of the rubber plate is about twice as much as the stiffness measured by the application of strain through the thickness. This effect is due to filler structuring in the rubber matrix. Figure 5 shows a schematic representation of hypothesized filler structuring.

CB particles are nearly isometric and are randomly distributed in the whole volume of rubber. CNT(B)s are flexible tubes and present a planar random orientation inside parallel layers, partially interconnected and structured through the sheet thickness. Only for CNT(B), therefore, different moduli values are obtained as a function of applied stress direction.

The hypothesis of filler structuring depicted in figure 5 was confirmed by the analysis with a transmission electron microscope (TEM) applied on sections, allowing one to observe the filler structure through the sheet thickness. The application of an electron diffraction technique to TEM images allows one to

identify CNT(B) preferential orientation, and to highlight their layered structuring, with alternate layers having high or low filler concentration (ref. 23). Such filler structuring is in agreement with the transversally isotropic mechanical behavior revealed by dynamic mechanical tests.

Master curves and anisotropic properties

In the previous paragraph, the anisotropy of the mechanical reinforcement of rubber compounds based on an anisometric filler such as CNT(B) has been documented. The question which arises is how to combine this finding with the results which led to the master curve shown in figure 3. Why CB and CNT give the same initial modulus at the same specific interfacial area (figure 3) and the same filler, CNT gives different values of initial modulus as a function of the direction of the applied stress? As a matter of fact, the question could be the following: Is it possible to take into account both the role of filler surface area and of filler orientation?

To answer these questions, the data of figure 4 were plotted in figure 6a as a function of the specific interfacial area.

In the graph in figure 6a, the points due to CB, both in TT and IP configuration, and to CNT(B) in TT configuration, lie on the same master curve. Only the points due to CNT(B) in IP configuration are above this curve, as the composite revealed higher modulus for a same specific interfacial area, when stress was applied in IP configuration. At least for TT configuration, the concept of a master curve common to both CB and CNT, based on specific interfacial area, still seems to also be valid for an anisometric filler such as CNT.

It is interesting, therefore, to compare the new master curve found for NR based systems in TT configuration with the master curve obtained with IR and SBR based systems (shown in figure 3). At this aim, the data of NR of figure 6a were normalized over the matrix modulus and plotted in figure 6b, where the original data of IR and SBR based systems are also displayed as black circles, without distinction of filler or matrix type. They are very close to the data of NR composites in TT configuration, at least up to $25 \text{ m}^2/\text{cm}^3$, as already observed for the SBR/IR mastercurve.

The data of the SBR/IR mastercurve were obtained by a torsional rheometer (Monsanto RPA 2000 rheometer). This test configuration has similarities with the TT test realized in shear sandwich configuration: In both cases, the strain is applied on a surface perpendicular to the pressure applied during the curing phase.

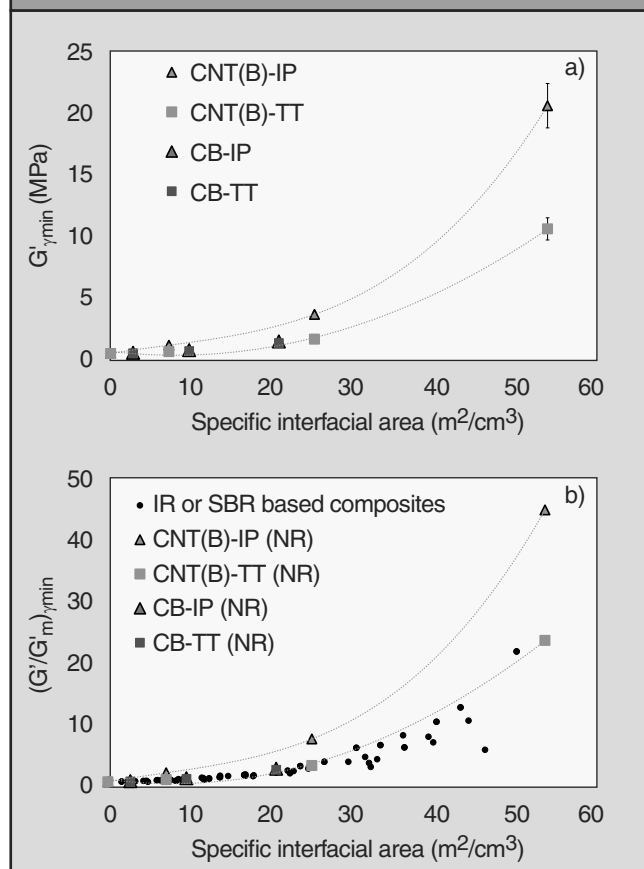
Conclusions

This work is a contribution for the rationalization of the mechanical reinforcing effects of a rubber matrix promoted by sp^2 carbon allotropes, both nanostructured, such as CB, and nanometric, such as CNT. CB and CNT, which were used as the only filler or as a hybrid filler system.

Differently from a nearly isometric filler such as CB, fillers with high aspect ratio, such as CNT, promote anisotropic properties. This is due to filler structuring: CNT presents a planar random orientation inside parallel layers, partially interconnected, and structured through the sheet thickness.

In spite of the anisotropic properties of CNT filled composites, a common equation (master curve), able to correlate the

Figure 6 - a) $G'_{\gamma_{\min}}$ and b) $(G'/G'_m)_{\gamma_{\min}}$ versus specific interfacial area of composites based on NR filled with CB or CNT(B), tested in two different configurations: in-plane (triangles) or through-thickness (squares) (revisit figure 1); in b) black circles are data of composites based on SBR or IR



mechanical reinforcement (initial modulus) with the interfacial area made available by fillers, was obtained for composites based on CB, CNT or hybrid filler systems, and isoprene or styrene/butadiene rubber. This occurs when the load acts parallel to the orientation of filler particles. In this case, there is no dependence of moduli on filler aspect ratio. On the other hand, if the load acts perpendicular to the fibers' direction, the modulus depends not only on filler volume fraction and interfacial area, but also on filler aspect ratio.

A master curve for the mechanical reinforcement could be used as a predictive tool for designing composites with target modulus and density values. Moreover, the possibility to selectively increase composites' reinforcement along specific directions could be exploited in advanced design of rubber composites.

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