

NEW INSIGHTS IN THE CNT-RUBBER STRUCTURE FOR A RATIONAL DEVELOPMENT OF ADVANCED MATERIALS

Juan L. Valentín^{1*}, Pilar Bernal-Ortega¹, M. Mar Bernal², Antonio González-Jiménez¹, Rodrigo Navarro¹

1. Institute of Polymer Science and Technology (ICTP-CSIC). C/Juan de la Cierva 3, 28006 – Madrid, Spain

2. Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Torino, 10129, Italy

Abstract: In this work, a systematic characterization of CNT-rubber structure has been performed by using a combination of experimental techniques (including advanced ¹H time-domain NMR methods) and the last developed analysis procedures (including stress and strain amplification factors) in order to improve the understanding about the mechanical and viscoelastic properties of these nano-composites. According to the obtained results, these promising materials could have some limitations to be applied in high-performance tire tread compounds (mainly related to the rolling resistance and fuel consumption) because of the difficulty of dispersion of CNT in rubber matrices (high filler networking), the strong influence of CNT in the vulcanization process (low cross-link density and high network defects) and the nature of filler-rubber interactions (high energy dissipation associated to the rupture of filler-rubber interactions at high strain amplitudes). To overcome these issues, the CNT have been surface-modified with oxygen-bearing groups and sulfur.

Keywords: rubber reinforcement; viscoelastic properties; composite structure; ¹H DQ-NMR

1 Introduction

Among others, one of the most important paradigms on high-performance tire tread rubber compounds is to obtain a reinforcing system that preserve the unbeatable viscoelastic properties of the rubber matrices (in terms of wet grip and rolling resistance) but enhancing their wear and mechanical properties, in order to reach the durability requirements^[1-2]. One possible way to address this issue is based on the use of nano-fillers, since their small size and higher effective surface area allow reaching similar mechanical properties than the conventional rubber micro-composites (based on silica/silane and carbon black fillers) but at much lower volume fraction^[3].

In this sense, carbon nanotubes (CNT) have attracted great attention in both academia and industry, due to their exceptional mechanical, electrical and thermal properties and also for their large aspect ratio, low density and high flexibility^[4]. However, the proved difficulty for dispersing CNT into the rubber matrix^[4-5] seem to be the main reported reason which reduces the expected improvement on the compound properties and the main technological limitation for using CNT-rubber compounds in advanced applications, e.g. high-performance tire tread rubber compounds.

The main aim of this work is to perform a fun-

damental and systematic characterization of CNT-rubber structure (based on combination of experimental techniques and the last developed analysis procedures) in order to understand and quantify the different structural factors (at molecular level) that determine the reinforcement mechanism and viscoelastic properties of CNT-based nanocomposites. These novel structural insights will provide i) more detailed arguments to understand why CNT-rubber composites do not reach the expected properties and ii) novel and more efficient strategies to overcome the defined limitations for developing rubber materials with advanced properties.

2 Experimental section

CNT-NR nanocomposites were prepared by using a conventional sulfur vulcanization system and different filler loading (from 1 to 20 phr). Multi-walled carbon nanotubes purchased from NanocylTM S.A. (NC7000TM with average diameter 9.5 nm, average length 1.5 μm, surface area 250-300 m²·g⁻¹ and carbon purity 90 %) were used as provided.

Composites with traditional fillers, carbon black (N121) and silica (Z1165MP modified with TESPT

silane coupling agent) were also prepared for to be used as reference in order to compare the physical and viscoelastic properties of CNT-NR nanocomposites.

In order to measure some key-properties in rubber compounds for tire tread compounds i) the Payne effect was evaluated on vulcanized samples in a TA Q8000 dynamic mechanical analyzer, in tension mode at 10 Hz frequency with a pre-strain of the samples of 5 mm. Measurements were performed at 40 °C at different shear strain amplitudes (from 0.04 to 60 %); ii) Dynamic mechanical measurements were also made on tension mode with an amplitude of 20 μm and 1 Hz frequency for performing a temperature sweep from -80 to 100 °C, with a heating rate of 2 °C min^{-1} .

The advanced structural characterization of NR composites were performed by combining different experimental methods, e.g. ^1H double quantum (DQ)-NMR^[6-8], equilibrium swelling^[9] and uniaxial stress-strain experiments, under a common and unified physical framework that provide an enhanced analysis procedure^[10-12].

3 Results and discussion

In tire industry, especially for tire tread compounds, the development of rubber compounds with high mechanical properties and low energy dissipation us a great challenge. Addition of high amount of fillers, especially carbon black and silica, is needed in order to achieve the requirements for stiffness, wear resistance, tear resistance and durability. However, the addition of these particles leads to a worse viscoelastic behavior (especially in terms of rolling resistance) when it is compared to the unfilled counterpart.

In the case of CNT-NR nanocomposites, the addition of 4.5% v/v of nanoparticles provides the same reinforcing effect (in terms of modulus at 100% deformation) than ~24% v/v of carbon black (grade N121). The observed reinforcement is much higher than it was expected according to the pure hydrodynamic effect, being this behavior more pronounced in the samples with higher filler volume fraction. This behavior should be explained by the presence of other mechanisms such as the filler-matrix and filler-filler interactions.

The effect of different structural parameters on the reinforcing effect of CNT in NR compounds is shown in Figure 1. It demonstrates that although the

filler-rubber interactions in CNT-NR composites could be around 6 times higher than in the carbon black interface (see Figure 2), the formation of a filler network is the main factor related with the enhancement of the storage modulus in the linear regimen.

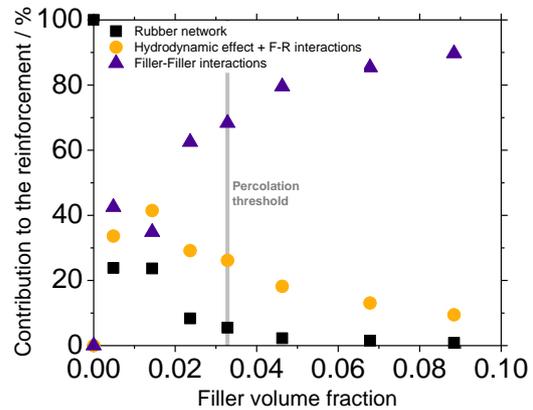


Figure 1. Contribution to the reinforcement of the different structural factors with the filler volume fraction for CNT-NR nanocomposites.

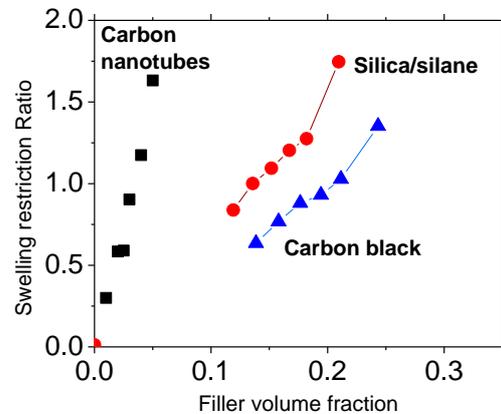


Figure 2. Equilibrium swelling ratio obtained by combining ^1H DQ-NMR and equilibrium swelling experiments for NR compounds filled with carbon nanotubes, carbon black and silica modified with silane (TESPT). This ratio is related with the number of filler-rubber interactions^[8].

Nevertheless, this hierarchical structure based on CNT aggregated in bundles is the main reason for the critical reduction of the effective shape factor from ~160 (i.e. the theoretical value according the measured length and diameter ratio of a single CNT) to 20

for the samples with higher CNT volume fraction. As consequence, the contribution of the hydrodynamic effect to the rubber reinforcement is continuously decreasing with the filler volume fraction (see Figure 1). In addition, the breakdown of the filler network (mainly based on van der Waals interactions) is the main reason for the non-linear drop of the modulus with the strain amplitude (Payne effect) and the maximum in the loss modulus, G'' , observed at intermediate strain amplitudes.

However, the high G''_{∞} values in the high strain regime (see Figure 3) should be related to structural factors associated to the rubber matrix but not to filler effects, i.e. reduction in the cross-link density and increasing in the non-elastic network defects (dangling chains, chain ends, loops...) with the concentration of CNT (see Figure 4).

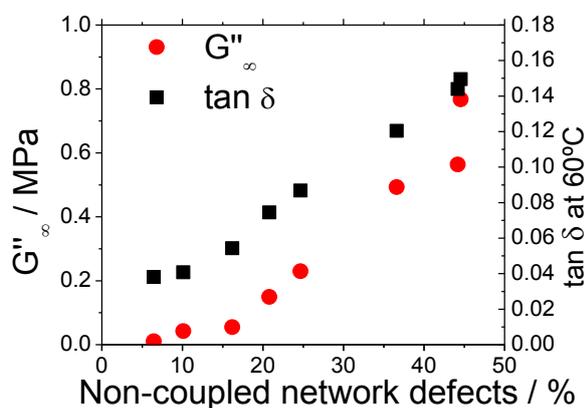


Figure 3. Variation of loss modulus at high strain regime, G''_{∞} , and $\tan \delta$ at 60°C (related to rolling resistance in tire tread compounds) with the non-elastic network defects for NR-CNT compounds.

It is important to remark that addition of CNT provokes an evident broadening of the dipolar coupling distribution of NR matrix (see Figure 4a). In one hand, the appearance of a well-defined tail at higher dipolar couplings (it does not appear in NR samples filled with carbon black) should be related with an intense filler rubber interactions that promotes a measurable contrast in the constrain density at the filler interface, i.e. the molecular weight between constraints at the CNT interface seems to be shorter than in the bulk. However, the maximum of the distribution is gradually shifted to lower residual dipolar couplings, it should be related with a strong decrease in the cross-link density in the rubber matrix with the addition of CNT. As consequence, the

non-coupled network defects (dangling chains, chain ends, loops, etc) increase almost linearly with the CNT volume fraction reaching values around 50% for the samples filled with 9% v/v of nanoparticles (see Figure 4b).

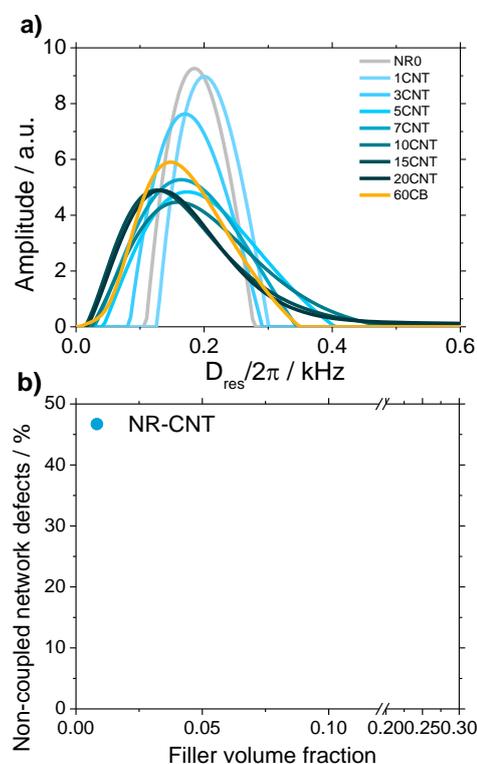


Figure 4. Variation of structural parameters of CNT-NR nanocomposites with the filler volume fraction: a) the dipolar coupling distribution and b) elastically inactive coupled defects.

According the new insights in the CNT-rubber structure, these promising materials (according to the high number of interactions between the rubber chains and the CNT surface) could have some limitations to be applied in high-performance tire tread compounds (mainly related to the rolling resistance and fuel consumption) because of i) the difficulty of dispersion of CNT in rubber matrices (well developed filler networking), the strong influence of CNT in the vulcanization process (low cross-link density and high network defects) and the adsorptive nature of the filler-rubber interactions (high energy dissipation associated to the rupture of filler-rubber interactions with the deformation).

In order to minimize these issues, CNT nanoparticles have been surface-modified with oxygen-bearing groups and sulfur. The sul-

fur-modification of the CNT (FCNT) was developed in two different steps: 1) Oxidation of CNT to introduce hydroxyl and carboxyl groups into the surface and 2) functionalization of the oxidized carbon nanotubes with elemental sulfur by sonication in carbon disulfide followed by melting at 155 °C. In order to maintain the amount of sulfur of the recipe constant for all samples, the sulfur grafted in the FCNT were taken into account in order to prepare the FCNT-NR compounds.

The addition of FCNT provides a better dispersion of these nanoparticles and a lower aggregation and agglomeration in a complex hierarchical structure. As consequence, a smaller Payne effect was observed as shown in Figure 5.

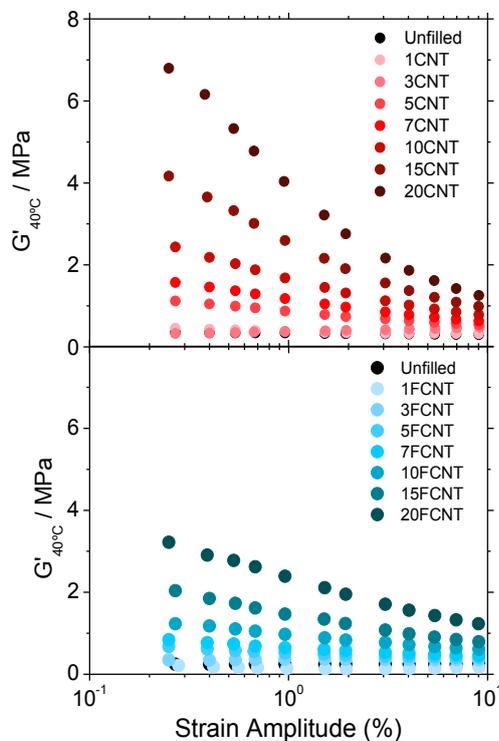


Figure 5. Dependence of the storage modulus with the strain amplitude (Payne effect) for NR samples filled with pristine (CNT) and modified (FCNT) carbon nanotubes.

In addition, the adverse effect of CNT on the vulcanization is minimized by the grafting sulfur moieties in their surface. The network structure of FCNT-NR samples shows a narrower dipolar coupling distribution (related to the molecular weight between constraints), with a more effective use of the available Sulphur that promotes higher cross-link density and lower network defects (see Figure 6).

Additionally, FCNT promotes the formation of covalent bonds between rubber chains and the nano-particle surface.

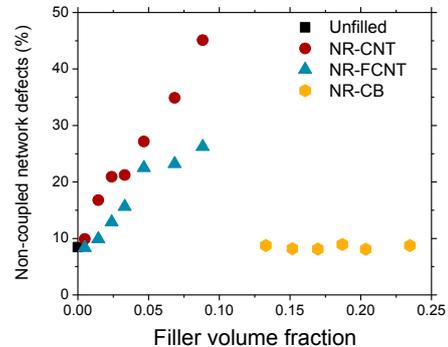


Figure 6. Variation of the elastically inactive coupled defects for NR composites filled with different volume fraction of CNT, FCNT and carbon black.

All described changes in the FCNT-NR structure do possible the reduction in the energy dissipation phenomena at 60°C (as it is shown in Figure 7), enhancing the overall features of these materials for being used in high-performance tire tread compounds.

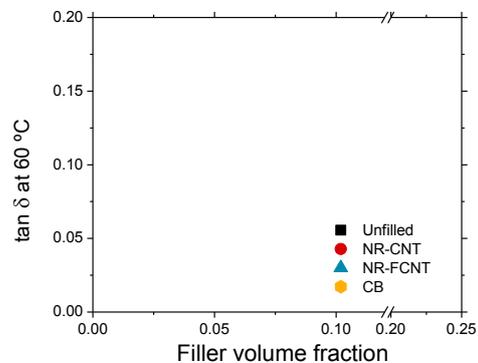


Figure 7. Variation of $\tan \delta$ at 60 °C (related to rolling resistance in tire tread compounds) with the filler volume fraction for NR compounds reinforced with CNT, FCNT and carbon black.

4 Conclusions

According the new insights in the CNT-rubber structure, these promising materials could have some limitations to be applied in high-performance tire tread compounds (mainly related to the rolling resistance and fuel consumption) because of the difficulty of dispersion of CNT in rubber matrices (high filler networking), the strong influence of CNT in the vul-

canization process (low cross-link density and high network defects which contribute to the energy dissipation at the high-strain regimen) and the adsorptive nature of filler-rubber interactions (high energy dissipation associated to the rupture of filler-rubber interactions). To overcome these issues, the CNT have been surface-modified with oxygen-bearing groups and sulfur (FCNT), in order to achieve i) better dispersion of CNT in the elastomeric matrices, ii) formation of covalent bonds between rubber chains and the CNT surface and iii) reduction of network de. As consequence, FCNT-NR compounds show improved performance as compared with their pristine counterpart for using in tire tread compounds.

5 Acknowledgements

The authors thank the financial support provided by the Ministerio de Ciencia e Innovación (MCINN) through the Project MAT2014-52644-R, MAT2017-87204 and an FPI grant.

References:

- [1] Wang, M.-J. Effect of polymer-filler and filler-filler interactions on dynamic properties of filled vulcanizates. *Rubber Chemistry and Technology*, 1998, 71: 520-589.
- [2] Donnet, J.-B. Black and white fillers and tire compounds. *Rubber Chemistry and Technology*, 1998, 71: 323-341.
- [3] Vilgis, T. A.; Heinrich, G.; Klüppel, M. Reinforcement of polymer nano-composites: theory, experiments and applications. Cambridge: Cambridge University Press, 2009.
- [4] Bokobza, L. Enhanced Electrical and Mechanical Properties of Multiwall Carbon Nanotube Rubber Composites. *Polymers for Advanced Technologies*. 2012, 23: 1543-1549.
- [5] Das, A.; Stöckelhuber, K. W.; Jurk, R.; Saphiannikova, M.; Fritzsche, J.; Lorenz, H.; Klüppel, M.; Heinrich, G. Modified and Unmodified Multiwalled Carbon Nanotubes in High Performance Solution-Styrene-butadiene and Butadiene Rubber Blends. *Polymer*. 2008, 49: 5276-5283.
- [6] Saalwächter, K. Proton multiple-quantum NMR for the study of chain dynamics and structural constraints in polymeric soft materials. *Progress in Nuclear Magnetic Resonance Spectroscopy*. 2007, 51: 1-35.
- [7] Valentín, J.L.; Posadas, P.; Fernández-Torres, A.; Malmierca, M.A.; González, L.; Chassé, W.; Saalwächter, K. *Macromolecules*. 2010, 43: 4210-4222.
- [8] Valentín, J.L.; Mora-Barrantes, I.; Carretero-González, J.; López-Manchado, M.A.; Sotta, P.; Long, D.R.; Saalwächter, K. *Macromolecules*. 2010, 43: 334-346.
- [9] Valentín, J.L.; Carretero-González, J.; Mora-Barrantes, I.; Chassé, W.; Saalwächter, K. *Macromolecules*. 2008, 41: 4717-4729.
- [10] Basterra-Beroiz, B.; Rommel, R.; Kayser, F.; Westermann, S.; Valentín, J.L.; Heinrich, G. New insights into rubber network structure by a combination of experimental techniques. *Rubber Chemistry and Technology*. 2017, 90: 347-366.
- [11] Basterra-Beroiz, B.; Rommel, R.; Kayser, F.; Westermann, S.; Valentín, J.L.; Heinrich, G. Swelling of polymer networks with topological constraints: Application of the Helms-Heinrich-Straube model. *Express Polymer Letters*. 2018, 12: 731-739.
- [12] Basterra-Beroiz, B.; Rommel, R.; Kayser, F.; Valentín, J.L.; Westermann, S.; Heinrich, G. Revisiting Segmental Order: A Simplified Approach for Sulfur-Cured Rubbers Considering Junction Fluctuations and Entanglements. *Macromolecules*. 2018, 51: 2076-2088.