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Thermomechanical behavior of SBR reinforced with nanotubes functionalized with polyvinylpyridine

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ABSTRACT

The mechanical and thermal behavior of composites consisting on a styrene–butadiene rubber (SBR) matrix with a sulphur/accelerator system and multiwalled carbon nanotubes functionalized with poly-4-vinylpyridine (MWCNT-PVP) as reinforcement, were studied. The materials were tested with stress-strain tensile tests, DMTA and DSC for thermal properties. A strong increase in the plastic behavior with slight decrease of its elastic Modulus and *Tg* led to unexpected results.

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1. Introduction

SBR are usually reinforced with mineral fillers such as carbon black and/or silica in order to get substantial improvements in both their mechanical properties and their antistatic behavior. Recently, carbon nanotubes (CNTs) have shown the effectiveness in reinforcing the polymeric materials instead of carbon black, although one of the biggest problems is obtaining an homogeneous dispersion of carbon nanotubes in the polymer matrix [1]. Surface modification of CNTs enhances their compatibility and dissolution properties into the polymer matrix and this is one of the most efficient methods to achieve a proper adhesion [2]. Up to date, the use of CNTs functionalized with a polymer has not been tested on SBR. So far, Perez et al. [3] informed that multiwalled carbon nanotubes (MWCNT) show the influence of the introduction of hydroxyl and carbonyl functional groups on the CNTs surfaces. They observed that filler–matrix interaction improve properties, such as resistance to solvent swelling and enhanced glass transition temperature. The functionalization of MWCNT with a polymer compatible with one block of the matrix reduces their agglomeration, increasing their dispersion within the polymeric matrix and leading to an increment in the mechanical properties by way of a good stress transfer through the MWCNT-SBR interface [4].

In a previous work, in which we showed that the presence of non-functionalized MWCNT, although changing the mechanical properties, the improvements were less than those predicted by theoretical models. A possible explanation of this fact is that N-t-butylbenzothiazyl-2-sulfonamide (TBBS) could adhere to the MWCNT walls, thus becoming ineffective to accelerate the vulcanization process [1a]. Therefore, the use of nanotubes wrapped in a polymer creates a steric hindrance preventing that adhesion. In this work, we chose 4-vinylpyridine (VP) to functionalize the MWCNT because VP is a monomer structurally similar to styrene, which has an aromatic ring able to interact by means of π–π interactions with the MWCNT. Indeed, VP has been chosen over styrene because it could be doped with metal, which could not only increase the electrical conductivity but also improve the mechanical properties of the composite material [5].

2. Material and methods

SBR of the 1502 type, which contains 23.5 wt% styrene and 55 wt% trans-1,4, 9.5 wt% of cis-1,4 and 12 wt% of cis-1,2 butadiene was used. The matrix was composed by dissolving this rubber with toluene (25 ml/g). Once it reached a liquid state, 24 h later, vulcanization reagents were added according to Table 1.

For the reinforcement (composite material), we used MWCNT (Nanocyl 3100). The MWCNT-PVP was made according to the report by Kong et al. [6] using VP as monomer. The polymer bonded chemically to the MWCNT's wall effectively. From Thermogravimetric Analysis (TGA) (TGA-51 Shimadzu thermogravimetric analyzer) we could conclude that the mass relation of polyvinylpyridine (PVP) to MWCNT is only 10%, as shown in Fig. 1.

Reinforcement content of 0.33 wt%, 0.66 wt% and 1 wt% was chosen. The mixtures, with or without MWCNT-PVP, were then spilled onto a glass at room temperature for 4 days. The thin films were later mixed mechanically to prepare them for vulcanization.

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Table 1
Matrix composition.

Material	PHR (per hundred rubber)
Sulphur	2
Stearic acid	2
Zinc oxide	5
TBBS	1
Antioxidant	1.2
SBR1502	100

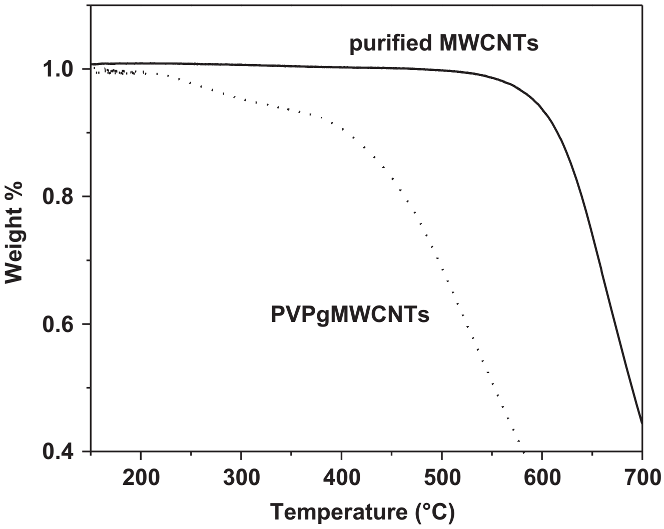

Fig. 1. TGA curves of the crude MWCNT and the functionalized MWCNTs.

All samples were directly vulcanized into a mold with the dumb-bell form according to DIN 53504, type S3. The vulcanization temperature was set to 150 °C for 1 h, and then the samples were rapidly cooled in water [1a].

The cuasi-static behavior of all the composites was studied at room temperature with an Instrom TM Testing machine with a 50 N load cell, and a deformation rate of 2.12 10^{-4} m/s. To determine the Young Modulus with high precision, the tensile test was also analyzed using a Dynamic Mechanical Thermal Analyzer (DMTA IV) Rheometric Scientific equipment in the Rectangular Tension mode at 1 Hz. For thermal properties, a Differential Scanning Calorimetry (DSC) was made to determine the influence in the Glassy-Transition Temperature (Tg) of the MWCNT with PVP after the vulcanization. DSC was performed on a TA Q series^{TM} Q20-1041. Sample weights of 15–20 mg were used under a N_2 nitrogen atmosphere and introduced in aluminum pans. The equipment was calibrated with indium standard. The heating rate was 5 °C/min from −70 to 25 °C.

3. Results and discussion

3.1. Mechanical properties

Before analyzing any result, it is important to note that although the PVP interacts with zinc [7], in this particular case, the mass amount of zinc is 50 times greater than the PVP, so this reaction should not be considered.

The stress-strain curves for the matrix and different composites, according to their MWCNT-PVP content, are shown in Fig. 2. It can be observed that the matrix behaves as a pure elastomer. Tensile Strength increases constantly as the elongation increases, with a gradual change in the slope. This behavior is similar to the previously reported with the same SBR [1a]. On the other hand, the addition of MWCNT-PVP, causes a sudden change of slope while losing tensile strength. So, the composite loses its elastomeric properties, leading to the typical behavior of plastic materials. Note that the strain to failure seems unaffected by the addition of MWCNT-PVP, except for the composite with 1 %wt filler content. This fact could be explained taking into account that the filler content was so high, that as a consequence the MWCNT-PVP could have agglomerated, facilitating the fissure propagation.

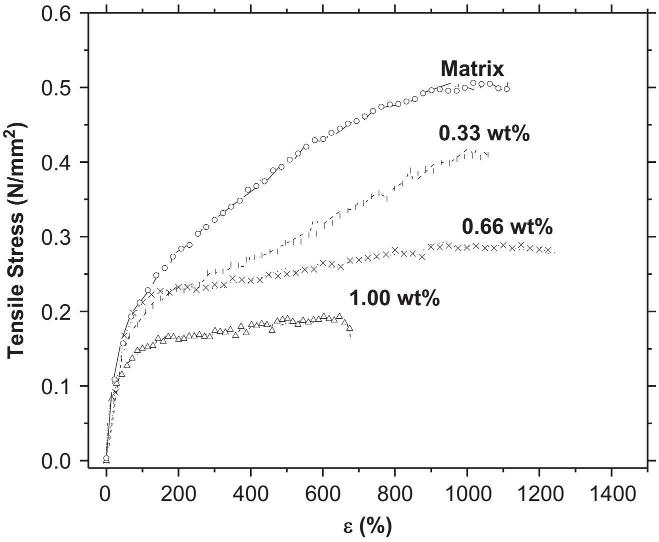

Fig. 2. Stress-Strain tensile tests.

In Fig. 2 we show the change observed to deformations greater than 100%, indicating that part of the material is flowing, suggesting that the addition of MWCNT-PVP either changes the crosslink type or the entanglement density type, allowing the non-entangled polymer chains to be even freer, generating this plasticity which allows this typical yield behavior. Also, from Fig. 2, apparently the Young Modulus is not much affected with the addition of filler content.

The Young Modulus (E′) was determined from the stress-strain curves from the DMTA. In all samples the modulus (E′) happened to be in the order of 1 MPa, showing only a slight decrease with the addition of functionalized MWCNT, being only 10% less for the sample with 1% filler content.

The results of the stress-strain curves are very interesting because they mean that the addition of MWCNT-PVP changes the behavior from elastic to elasto-plastic, which was not expected given the results obtained with the addition of non-functionalized MWCNT [1a].

The vulcanized elastomers may have different types of crosslinks: monosulphidic, in which two polymer chain are bonded by a bridge with only one sulphur atom and polysulphydic where two polymer chains are bonded by a bridge consisting in two or more sulphurs. There is also the entanglement, caused by the long polymer chains.

So, these important changes could be related either to a change to the crosslink type or that there is an important number of polymer chains that are not enough crosslinked. Therefore, they could disentangle themselves by deformation, leading to this plastic behavior, meaning a reduction in the crosslink density. Both effects would lead to lower values in the Tg.

3.2. Thermal properties

The thermal behavior of the composites was performed by DSC experiments. The results of these measurements are summarized in Table 2.

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Table 2
DSC results.

Sample	ΔT	ΔHeat flow (W/g)	Tg (°C)
Cured matrix	18.28	0.0397	−54.52
0.33 wt% MWCNT-PVP and cured	16.22	0.0421	−53.66
0.66 wt% MWCNT-PVP and cured	14.89	0.0539	−57.10
1 wt%MWCNT-PVP and cured	13.34	0.0408	−57.52

It could be observed that increasing the amount of MWCNT-PVP effectively reduces the temperature range (ΔT) involved in the glassy transition. Indeed, the Tg are also reduced, except in the sample with 0.33% of MWCNT-PVP, in which the possible differences were not significant. As the transition breadth is linked to the distribution of mobility of polymer segments, and thus may be taken as a measure of the structural inhomogeneity of the polymer network, these results are consistent with the presence of monosulfide crosslinks.

Note that a decrease in the Tg (shift to lower temperatures) means either that there are less crosslinks, or that the material wrapped onto itself more compactly, reducing the mean free volume. It is known that the temperature at which the glassy transition happens is related to the temperature at which a certain amount of free volume can be found.

The latter could also be attributed to a greater amount of monosulphidic links. So, the packing is more compact and avoids the entanglement of the polymer chains, so the molecules not fixed by the entanglement can flow.

This is an interesting and novel result from the standpoint of technology, as it shows that not always the addition of dispersed MWCNT improves the properties. The addition of MWCNT-PVP to achieve good dispersion and good interactions with the polymer chains, can lead to other interaction phenomena that radically change the properties of the material. Comparing these results with those previously reported [1a], which showed that added MWCNT in SBR matrix did not change the behavior of Stress-Strain curves, we can conclude that the large effective area of the functionalized MWCNT can interact with both styrene and butadiene moieties or vulcanization reagents through π interactions, affecting the vulcanization process. As a result of this, significant changes can be observed in both mechanical and thermal properties.

4. Conclusions

We showed that the mechanical behavior of materials obtained from the addition of MWCNT-PVP, regarding the addition of MWCNTs, in a SBR matrix changed from hyperelastic to elasto-plastic. Furthermore, the addition of MWCNT-PVP produced significant changes in Tg and its temperature range.

In summary, covalent functionalization of MWCNT, even with a low percent of polymer, changes significantly the mechanical and thermal properties of the composites.

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