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Effect of carbon nanotube type and functionalization on the electrical, thermal, mechanical and electromechanical properties of carbon nanotube/styrene–butadiene–styrene composites for large strain sensor applications

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ABSTRACT

Thermoplastic elastomer tri-block copolymer, namely styrene–butadiene–styrene (SBS) composites filled with carbon nanotubes (CNT) are characterized with the main goal of obtaining electro-mechanical composites suitable for large deformation sensor applications. CNT/SBS composites with different filler contents and filler functionalizations are studied by morphological, thermal, mechanical and electrical analyses. It is shown that the different dispersion levels of CNT in the SBS matrix are achieved for pristine or functionalized CNT with strong influence in the electrical properties of the composites. In particular covalently functionalized CNTs show percolation thresholds higher than 8 weight percentage (wt%) whereas pristine CNT show percolation threshold smaller than 1 wt%. On the other hand, CNT functionalization does not alter the conduction mechanism which is related to hopping between the CNT for concentrations higher than the percolation threshold.

Pristine single and multiwall CNT within the SBS matrix allow the preparation of composites with electro-mechanical properties appropriate for strain sensors for deformations up to 5% of strain, the gauge factor varying between 2 and 8. Composites close to the percolation threshold show larger values of the gauge factor.

1. Introduction

Composite materials research in order to tailoring material properties for novel applications has resulted in important advancements in materials science and engineering. In particular, the use of carbon nanoallotropes as fillers in polymer matrices resulted in applications in the areas of sensors, relying on the electrical properties of the carbon nanoallotropes [1,2], low weight aerospace structural materials [1], optoelectronics [3], antistatic protection [4,5], capacitors [4] and electromagnetic interference shielding materials [4,5], among others.

Thermoplastic elastomers (TPE) are an important class of polymers that combine the mechanical properties of rubbers (e.g., high deformation materials) with the processability and recyclability of thermoplastics [6]. Tri-block copolymer poly(styrene-b-butadiene-b-styrene) (SBS) is a TPE known for its microphase separation into soft and hard domains, including spherical, cylindrical, gyroid and lamellar morphologies [7]. Tailoring the molecular architecture and the morphology of SBS block copolymers offers the possibility to tune the mechanical properties of the materials from thermoplastic elastomers to tough thermoplastics [7]. This requires a detailed understanding of the interrelations between the molecular architecture, the microphase separated morphology, the thermal and mechanical history and the resulting mechanical behavior [7]. SBS was first industrialized as a thermoplastic elastomer of styrene via anionic polymerization [7]. It did not find wide use in biomedical applications due to the biostability problem of the double bonds in the elastomeric block. However, after the entire saturation of the butadiene segments in SBS, the obtained poly(styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS) shows a better oxidative stability [7], allowing biomedical applications such as medical

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gloves, transfusion bags, catheters, ureteral stents, microfluidic devices and DNA chips [7].

SBS can be manufactured by solvent casting using solvents such as toluene [8], ethanol and acetone [9], or by melt flow processes such as extrusion [10,11]. It can be also used without vulcanization [12] which is an advantage as there is no degradation of the mechanical and electrical properties of the composites obtained from this copolymer [12]. The excellent mechanical properties of SBS such as its high deformation (can be larger than 1000% [8]) and the value of initial modulus depend on the styrene/butadiene ratio and copolymer architecture. SBS has two glass transition temperatures (T_g) due to the distinct T_g of poly-butadiene (PB), around −80 °C, and poly-styrene (PS), around +80 °C [13–15]. This copolymer has a good thermal stability and its degradation temperature is around 230 °C for PB and 430 °C for PS [16], the incorporation of carbon nanoallotropes not inducing major variations on the thermal properties of the SBS matrix [16].

SBS is an interesting material for the development of force sensors for robotic and industrial automation [17] in order to replace silicones-based sensors that are not capable of sustaining large deformations and sudden impacts [17]. For these and related applications, the TPE insulator matrix needs conductive nanofillers for modifying its electrical properties. Carbon nanoallotropes have been studied as suitable fillers for the development of polymeric matrix composites. Carbon black, carbon nanofibers and carbon nanotubes have been investigated for the development of composites with TPE matrices in order to tune mechanical, electrical or thermal properties for specific applications as antistatic devices [4,18,19], electrostatic discharge [14,18,20], pressure [14,18] or large deformation sensors [21–23] and also for better understanding of the matrix/filler interactions in order to achieve tuned composite properties [9,24,25]. From the different carbon nanoallotropes, CNT allow the lowest electrical percolation [22] thresholds in composites due to the high aspect ratio and lower defects [4,9,26]. Differences in the CNT characteristics strongly affect the overall performance of the composites [4] and, in particular, the functionalization of the CNT surface is commonly used to tailor composite response and polymer/CNT compatibility and dispersion [9,25]. Chemical functionalization is based on the covalent linkage of functional entities onto CNT surfaces [27]. It can be performed at the termini or the sidewalls of CNT. Direct covalent sidewall functionalization is associated to a change of hybridization from sp^2 to sp^3 and simultaneous loss of the π-conjugation system on the graphene layer [27]. Non-covalent functionalization is other method for tuning the interfacial properties of CNT where a suspension of CNT in the presence of polymers leads to the wrapping of the polymer around the CNT to form supermolecular complexes of CNT [27]. The polymer wrapping process is achieved through van der Waals interactions and π–π stacking between CNTs and polymer chains [27]. Together with polymers, surfactants have also been employed to functionalize CNT [27].

The preparation method is also important to determine the properties of composites, in particular due to its effect on filler dispersion and orientation (in the case of high aspect ratio nanofillers) within the polymer matrix [9,28]. Composite materials prepared by solvent casting generally show lower electrical percolation thresholds and homogeneous dispersion of CNT than extruded composites [14,29].

All together it is recognized that the addition of CNT into an insulator matrix allows to tune the electrical and mechanical properties of the composites to suit specific applications as pressure or deformation sensors [30,31]. Using a TPE matrices, this sensors can be large deformation sensors, with deformations up to 20% [8]. This is an important fact due to the large interest of those sensors and the few material possibilities to develop them. The piezoresistivity, the variation of the electrical resistivity when a deformation is applied to a material, can be taken as advantage for the development of such sensors [30,31] and, in the case of carbon nanofiller/polymer composites, this effect is mainly attributed to variations of the conductive network with strain due to loss of contact between the fillers, tunnelling or hopping effects in neighboring fillers and/or conductivity variations due to the deformation of CNT [32–34]. These electro-mechanically active composites are characterized by a high piezoresistive sensitivity [32] and can be used in applications such as strain sensors for structural health monitoring [24,35], damage and fracture detection [36] and in biomechanical applications [37].

The electro-mechanical properties are determined by the mechanical and, mainly, by the electrical conductivity value and the electrical conductivity mechanism [30] within the composite. Further, the addition of CNT to the SBS matrix can also influence the overall conduction mechanism, i. e., with addtion of CNT to the composite the main contribution to the conduction mechanism can be ascribed to hopping or tunneling between CNT [34,38].

This work aims at understanding how the different PB/PS ratio in the polymer matrix as well as the CNT characteristics, single- and multi-walled and functionalized, influences the mechanical, electrical and electro-mechanical properties of CNT/SBS composites.

2. Experimental

2.1. Materials and processing

Four different commercial thermoplastic elastomers SBS matrix Calprene C401, C411, C500 and C540, supplied by Dynasol Elastomers, S.A (Spain), were used. The main characteristics of these thermoplastic elastomer tri-block copolymers are summarized in Table 1. Butadiene corresponds to the soft component of the copolymer and styrene to the hard one. The investigated SBS matrices are composed by different ratios of styrene and butadiene and two different structures (Table 1), radial and linear.

The carbon nanofillers used are three different types of carbon nanotubes (CNT):

- Multi-walled CNT (MWCNT) from Baytubes with reference C150P; purity >95%, outer mean diameter of 13–16 nm and length of 1–10 μm) supplied from Bayer Materials Science;
- MWCNT from Nanocyl with reference NC7000; purity 90%, outer mean diameter of 9.5 nm and length of 1.5 μm); and
- Single Walled CNT (SWCNT) purity 60–70% with 30% of metal content, mean diameter of 1.4 nm and 0.5–3 μm length for individual CNT. For CNT bundles, the length and diameter is, respectivelty, 1–5 μm and 2–10 nm, from Carbon Solutions with reference AP-SWNT.

Preparation of the composites using pristine CNT, both single and multi-wall, was performed in two steps. To promote good dispersion and disintegration of the CNT in the suspension, these were placed inside an Erlenmeyer with toluene and tip sonicated (Hielscher DRH-P400S; 400 W maximum power; 24 kHz maximum frequency) for 30 min (60% amplitude and 0.5 cycle time). After this stage, SBS was added to the solution and stirred until complete dis-

Table 1
Main relevant characteristics of the used styrene–butadiene–styrene (SBS) matrices.

Company Reference	C401	C411	C500	C540
Block copolymer Structure	Radial	Radial	Linear	Linear
Styrene/butadiene (%)	20/80	30/70	30/70	40/60