Contents lists available at ScienceDirect



Sensors and Actuators A: Physical



journal homepage: www.elsevier.com/locate/sna

Electro-mechanical properties of triblock copolymer styrene-butadiene-styrene/carbon nanotube composites for large deformation sensor applications



P. Costa^a, A. Ferreira^a, V. Sencadas^{a,b}, J.C. Viana^c, S. Lanceros-Méndez^{a,*}

^a Centro/Dept. de Física da Universidade do Minho, 4710-058 Braga, Portugal

^b Escola Superior de Tecnologia, Instituto Politécnico do Cávado e do Ave, Campus do IPCA, 4750-810 Barcelos, Portugal

^c Institute for Polymers and Composites IPC/I3N, University of Minho, 4800-058 Guimarães, Portugal

ARTICLE INFO

Article history: Received 24 March 2013 Received in revised form 2 August 2013 Accepted 4 August 2013 Available online 12 August 2013

PACS: 62.20.D 62.20.F 62.23.Pq

Keywords: Piezoresistive Gauge factor Carbon nanotube composites Polymers

1. Introduction

Elastomeric polymers are promising materials for the development of composite samples for sensors and actuator applications, among other factors, due to their large deformation, flexibility and impact resistance [1].

In order to expand their range of applicability, in particular to the sensor field, the electrical properties of elastomers can be tailored through the incorporation of carbon nanotubes (CNT). Applying this approach, composites using carbon allotropes and thermoplastic elastomeric materials (TPE) have found applications in electrostatic charge dissipation, electromagnetic interference shielding, field emission devices, pressure or deformation sensors [2]. Due to the large strains and the high impact resistance, such materials are also promising for the substitution of silicon based force and deformation sensors, as well as strain gages [3]. Conductive TPE composites exhibit excellent mechanical and electrical properties and can be used as artificial muscles, electromechanical actuators, touch control, switches and shape-memory polymers [2]. Small

ABSTRACT

Thermoplastic elastomer/carbon nanotube composites are studied for sensor applications due to their excellent mechanical and electrical properties. Piezoresisitive properties of tri-block copolymer styrene–butadiene–styrene (SBS)/carbon nanotubes (CNT) prepared by solution casting have been investigated. The initial elastic modulus of the SBS/CNT composites increases with increasing the CNT filler content present in the samples, without losing the high deformation capability of the polymer matrix (~1500%). Furthermore, above the percolation threshold these materials are unique for the development of large deformation sensors due to the strong piezoresistive response. Piezoresistive properties evaluated by uniaxial stretching in tensile mode and 4-point bending showed gauge factors up to 120. The linearity obtained between strain and electrical resistance makes these composites interesting for large strain piezoresistive sensors applications.

© 2013 Elsevier B.V. All rights reserved.

amounts of CNT incorporated in the TPE matrix can enhance the mechanical properties, electrical and thermal conductivity. The filler can be randomly distributed or oriented within the TPE matrix, by applying a magnetic or electric field, in order to optimize the piezoresistive properties in the desire direction [4].

The dispersion of CNT in a polymer matrix is one of the most studied issues in polymer composites, and physical and chemical strategies for CNT cluster segregation are commonly used. Several chemical agents are used for this purpose, including xylene [2], dehydrated ethyl alcohol [5], toluene and ethanol [6], among others, in order to achieve higher composite homogeneity [2,7] and reduced the clusters size [2]. By applying such dispersion agents, the aims are to obtain a better dispersion of the fillers within the polymer matrix and, as a result, to decrease the percolation threshold and enhance electrical properties while maintaining proper elastomeric behavior [5,8].

Thermoplastic elastomers based on a tri-block copolymer styrene–butadiene–styrene (SBS) have similar properties than rubber without the need of the vulcanization step. They show good chemical stability, low temperature flexibility and damping properties [9]. SBS is an interesting elastomer material for scientific and technological applications due to its large elongation at break and durability and when obtained

^{*} Corresponding author. Tel.: +351 253 604073; fax: +351 253 604061. *E-mail address:* lanceros@fisica.uminho.pt (S. Lanceros-Méndez).

^{0924-4247/\$ -} see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.sna.2013.08.007

without the vulcanization chemical treatment, no degradation of the mechanical and electrical properties occurs [10]. The different butadiene/styrene ratio and architecture in the copolymer influences the material morphology, mechanical, electrical and thermal properties. Usually, butadiene is the larger component and the quantity of styrene can go up to 50%.

Studies on polymer/CNT composites can be found regarding the evaluation of dispersion, mechanical, electrical and thermal properties, as well as the development of applications [5,8]. Within this field, thermoplastic elastomeric polymers with CNT are gaining increasing attention [2,5,8,11]. The electrical properties of these composites are strongly dependent on CNT type and concentration present in the composite [2,5,8] and on chemical modification of the surface of the CNT's [5,8,12].

SBS shows a good thermal stability with the glass transition at -80 °C, due to the butadiene phase, and at 100 °C, assigned to the styrene compound present in the copolymer [2], and the incorporation of the CNT filler does not change them significantly [2]. Furthermore, the SBS/CNT composites have excellent mechanical properties like strain higher than 1000%, similar stress–strain curves with amount of CNT and several ratios of styrene and butadiene in matrix of these composites. The elastic modulus increases with decreasing butadiene in SBS and electrical percolation threshold is similar for the different SBS matrices [13].

One key issue of these composites for piezoresistive sensor development is the linearity between electrical resistivity and the strain. The gauge factor (GF) can be tailored by changing CNT concentration or pre-strain to the material, in order to obtain sensors with tailored sensibility [13]. The gauge factor of polymer/CNT composites with different CNT type and polymer matrix can lie within a quite wide range, 0.74–50 [14]. The piezoresistivity depends on parameters related to CNT conductivity, surface characteristics and dispersion and polymer matrix, the GF being typically larger for filler concentrations in the composite around the percolation threshold [14]. Piezoresistivity composites with thermoplastics or thermosetting polymer matrixes have been most often studied than elastomeric composites [15]. Epoxy composites with carbonaceous fillers show typically gauge factors between 3.4 and 4.3 [13]. Poly(methyl methacrylate) and polycarbonate as matrix and CNT as fillers show higher gauge factors for $\sim 0.6\%$ of strain which are 3.5 times more sensitive than metallic strain gages [15].

Elastomeric silicon composite have been studied for pressure sensors [16] and piezoresistive sensors based on polyurethane are being developed [15].

In the present work, SBS/CNT composites with different SBS morphologies, radial and linear, and with different filler contents were prepared by solvent casting in order to study the influence of the carbon nanotubes in the piezoresistive properties of the composite samples and to evaluate the performance of the composites for sensor applications. Four-point bending and uniaxial tensile mechanical tests were performed, while monitoring the variation of electrical resistance in composites samples.

2. Experimental

2.1. Materials and processing

High purity multi-walled carbon nanotubes (MWCNT) were provided by Bayer Materials Science, Germany (Baytubes C 150P; purity > 95%, outer mean diameter = 13-16 nm; length = $1-10 \mu$ m) and commercial Calprene C401, C411, C500 and 540 tri-block SBS copolymer was supplied by Dynasol Gestión, S.A (Spain). All composites samples were processed using the Baytubes C 150P pristine

Table 1

Main characteristics of the SBS copolymers.

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

carbon nanotubes as received. The elastomeric matrix is composed by different relative contents of styrene and butadiene and morphologies, radial and linear (Table 1).

To promote a good dispersion and disentanglement of the MWCNT bundles, the fillers were placed inside an Erlenmeyer with toluene and kept in an ultrasound bath (*Bandelin*, Model Sonorex Super RK106) during 6 h. After this stage, the SBS copolymer was added to the solution and stirred at room temperature until complete dissolution. The relation of the SBS to toluene is 1 g for 5.5 ml, respectively. The amount of pristine MWCNT in the solution was selected to result in concentrations between 0 and 8%wt of MWCNT in the SBS matrix. After complete dissolution, the solution was spread on a clean glass substrate and the solvent evaporation was performed at room temperature, resulting in highly flexible composite films with thickness between 150–300 μ m, using a coater measurement gauge Fisher DualScope MPOR. Further details on the preparation, morphological, mechanical and thermal characteristics of the composites can be found elsewhere [13].

2.2. Morphological analysis

Scanning electron microscopy (Leica Cambridge apparatus at room temperature) was performed in order to evaluate the composites microstructure and the dispersion of the fillers within the polymer matrix. All the specimens were coated with a conductive layer of sputtered gold with a Polaron, model SC502 sputter coater.

2.3. Electrical conductivity measurements

Electrical resistance of the composites was calculated from the slope of *I*–*V* curves measured with an automated Keithley 487 picoammeter/voltage source. *I*–*V* data points were collected between Au contacts, deposited on both sides of the samples with a Polaron SC502 sputter coater. Volume resistivity was measured with circular contacts of 5 mm diameter with an applied voltage ranging between ± 10 V, and measuring the current. The resistivity of the samples (ρ) was calculated by [13]:

$$\rho = \frac{R \cdot A}{d} \tag{1}$$

where R is the resistance of the sample, d its thickness and A the area of the electrodes. The electrical measurements were performed at room temperature.

2.3.1. Electro-mechanical characterization

Electro-mechanical tests were performed by measuring the electrical resistance of the sample, through gold electrodes deposited by sputtering with a Polaron Coater SC502, with an Agilent 34401A multimeter during the mechanical deformation of the sample, applied with an universal testing machine from Shimadzu (model AG-IS, with a load cell of 1 kN) on samples with approximately $60 \text{ mm} \times 20 \text{ mm}$ and a thickness ranging from 150 to $300 \,\mu\text{m}$.

Two different mechanical solicitations were applied to the samples. During the so-called method 1, mechanical experiments were performed in the tensile mode under a pre-strain (Fig. 1); in the method 2, 4-point-bending deformation was applied to the sample (Fig. 2).



Fig. 1. Schematic representation of the experimental configuration of the clamps for the stress–strain experiments with simultaneous electrical measurements for electro-mechanical response evaluation of the samples by applying uniaxial stress.



Fig. 2. Representation of the 4-point bending tests (method 2) apparatus where *z* is the vertical displacement, *d* is the thickness of the sample (between 150 and 300 μ m) and *a* is the distance between first and second bending points (15 mm). The electrodes are in the center of the sample.

The evaluation of the piezoresistive response during the uniaxial stress tests was performed at different speed rates (from 1 to 50 mm/min) and strain levels (1–50%). In the same uniaxial stress tests using a pre-strain until 30% was applied, were the composite sample is stretched before stress–strain tests. In order to obtain an average electro-mechanical response, 10 loading-unloading cycles were measured for each sample, being the gold electrodes in contact with the clamps, in order to prevent any deformation during experiments. All this experiments are performed at room temperature.

For the 4-point-bending measurements (Fig. 2), the sample was glued to the bottom of a poly(propylene) board. Gold electrodes with an area of $6 \text{ mm} \times 1 \text{ mm}$ were placed at the bottom of the sample. For all experiments, 4 loading-unloading cycles were performed and the average electro-mechanical response evaluated at room temperature.

The experimental conditions for the electro-mechanical measurements are summarized in Table 2.

Variations of the electrical resistance due to mechanical deformation are quantitatively evaluated by the gauge factor (GF), defined as:

$$GF = \frac{dR/R_0}{dl/l_0}$$
(2)

Table 2

Experimental conditions of electro-mechanical tests for two mechanical deformation methods.

	Description	Stress-strain cycles	Strain	Speed (mm/min)
Method 1	Uniaxial stress	10	1–50%	1–50
Method 2	4-point bending	4	0.1–1 mm	1–50

where R is the sample electrical resistance without mechanical deformation and dR is the resistance change caused by the variation in length (dl) [13]. The GF can be also written as:

$$GF = \frac{dR/R_0}{\varepsilon_l} = \frac{d\rho/\rho_0}{\varepsilon_l} + 1 + 2\nu$$
(3)

where $\varepsilon_l = dl/l_0$ (strain) and ν is the Poisson ratio. From Eq. (3) it is possible to observe that the GF has a contribution from the intrinsic piezoresistive effect ($(d\rho/\rho_0)\varepsilon_l$) and another from a geometrical effect (1+2 ν) [17].

In uniaxial stretching mode experiments (method 1) Eq. (2) was used for the calculation of the GF, using the evolution of the resistance during the stress–strain measurements. In 4-point-bending mode experiments (method 2), the strain was calculated from the theory of a pure bending of plates, valid between the inner loading points, and given by [14]:

$$\varepsilon = \frac{3dz}{5a^2} \tag{4}$$

where *d*, *z* and *a* are represented in Fig. 2. Experiments were performed in samples of the different polymer matrices shown in Table 1 for CNT filler contents between 0 and 8 wt%. The GF value was calculated for each cycle, from the *z*-displacement and the electrical resistance data, by taking the fit curve by a linear regression. Finally, an average GF value was calculated for each sample.

3. Results and discussion

Elastomeric materials are known for their outstanding deformation, that can reach ~1500%, and it was observed that the incorporation of CNTs up to 8 wt% into the polymer matrix does not influence the maximum strain. On the other hand it is observed an increase of the initial modulus from ~1.5 MPa obtained for the SBS matrix up to 150 MPa for a CNT concentration of 8 wt% [13].

3.1. Morphological characterization

Dispersion and interaction between CNT and the SBS matrix are shown in the SEM images of different SBS matrix (C401, C411, C500 and C540) with 4 wt% of CNT in Fig. 3. Composite samples with higher loadings of CNT present similar dispersion patterns for all the SBS matrix.

SBS/CNT composites processed by solvent casting present a good cluster distribution of CNT for the different SBS matrix. CNT are agglomerated in clusters with $\sim 1-2 \,\mu$ m in size for all composites. As it will be shown later, the SBS matrix does not has an important role in electrical conductivity network in composite samples, which correlated to the similar filler dispersion, results in overall similar electrical macroscopic response. It is also observed a good wetting between individual CNT and the SBS matrix (inset in Fig. 3 for the C540 SBS/CNT composite).

Electrical conductivity of composites depends on CNT distribution within the polymer matrix. It has been demonstrated that a distribution of well distributed small agglomerates or clusters is more important for achieving higher electrical conductivity [5,18] than a good dispersion of individual fillers. The same is not the case for the mechanical properties [18]. Different parameters such as dispersion method and dispersion agent [19] and structural quality of carbon nanofillers [19] have influence in electrical properties of polymer/carbon composites. In the present case, nevertheless, it is observed that the used polymer matrix does not influence the overall dispersion of the fillers.

Good wetting is observed SBS matrix and CNT in the composites as shown in Fig. 3, inset, and by the fact that during the piezoresistive tests for large deformations up to 20% no degradation of the electromechanical cycles is observed (see later), indicating



Fig. 3. SEM images for SBS/CNT composites with different SBS matrix (C401, C411, C500 and C540) filler loading of 4 wt% of pristine CNT.

reversible electromechanical processes and therefore no detachment or irreversible reconfigurations of the filler network [12,13].

3.2. Mechanical hysteresis

The mechanical properties of SBS polymers, like initial modulus, maximum strain or hysteresis are key issues for their applications as piezoresistive sensors, where mechanical properties play an important role in sensor response and reliability. The mechanical hysteresis is important to analyze reproducibility of stress–strain tests in sensor applications. Good linearity of electrical resistance depends on the mechanical properties of composites. The mechanical hysteresis of these nanocomposites was characterized in stress–strain tests for ten cycles for several deformations levels of 5%, 10% and 20% (Fig. 4). It was observed that loading and unloading curves do not coincide during two successive cycles, given evidence of a mechanical hysteresis in these composites. The mechanical hysteresis decreases with increasing number of cycles in the composite, in particular for the first few cycles (Fig. 4a), and increases for increasing strain (Fig. 4b). For elastomeric matrices filled with carbon nanofillers, the mechanical hysteresis increases with the increment of nanofiller content in the composite, both in uniaxial tension and compression [20]. Initial stiffness (and initial modulus) and subsequent stretch-induced stiffening at larges



Fig. 4. Example of hysteresis for experimental stress-strain curves for composites SBS-C540 with 4% of CNT. (a) With individual color for 10 curves for 5% of deformation and (b) 10 cycles for 5%, 10% and 20% of deformation.



Fig. 5. Hysteresis for the different SBS copolymers as a function of strain during 10 cycles for 4 different matrixes and 5%, 10% and 20% of deformation.

strains were both found to increase with increasing filler content [13,20].

The hysteresis energy loss values are calculated by the area under the cycles in J/m^3 (Fig. 5) for the SBS copolymers. As mentioned, this value increases for increasing strain and decrease with increasing number of cycles for each composite.

Comparing the different ratios of butadiene/styrene in the polymer matrices, the larger hysteresis value is found for the harder copolymer (C540 with 40% of styrene), followed by C411 matrix for 20% of strain, as presented in Fig. 5. The copolymer with lower mechanical hysteresis is C401, the one with lower styrene content (20%). For copolymers with same styrene content (C411 and C500, with 30% of styrene), the larger hysteresis is for C411, as the radial structure shows slower recovery dynamics than the linear one [13]. This behavior is related to the one observed for the elastic modulus, with higher values for matrices with more styrene, and for same values of styrene, the radial structure showing superior Young modulus values [13].

3.3. Electrical and electro-mechanical response

Electrical measurements on SBS/CNT composite samples prepared with different SBS ratios and morphologies (Table 1) and with several amounts of conductive filler show that the composite electrical conductivity is not strongly dependent on the



Fig. 6. Log of electrical conductivity as a function of MWCNT content for the four different matrices, C401, C411, C500 and C540, as specified in Table 1.

matrix morphology or styrene/butadiene relative content (Fig. 6), the conductivity being nevertheless higher for the sample with less butadiene present in the sample and with linear morphology (C540). The percolation threshold is found to occur at around 1 wt% CNT concentration present in the material. The sample with less styrene and with radial structure (C401) showed a smaller value of electrical conductivity until percolation threshold, when compared to the other samples.

Composites near electrical percolation threshold generally show the largest variation of the electrical resistance with the applied mechanical deformation [21,22]. In the present case of these elastomeric materials, the GF is also large around the percolation threshold, but due to the small filler content at the threshold, just small deformations (below 5%) can be applied before a strong decrease of the electrical conductivity occurred due to the strong decrease of the local concentration of the filler, which destroys the conductive path between fillers [23,24]. Therefore, for large deformation sensors, composites with larger concentration of CNT, above the percolation threshold, have to be considered in order to undergo strains up to ε ~ 50% with linear variation of the electrical resistance and with resistance values compatible with the development of strain sensors [13]. Thus, we use in further electromechanical measurements, composites samples with 4 wt% CNT to analyze GF for larges deformation.



Fig. 7. (a) Electro-mechanical measurements during uniaxial deformation (method 1) for the C411 elastomeric SBS matrix with 4 wt% MWCNT, obtained for a maximum strain of 5% and nominal strain-rate of 1 mm/min. (b) $\Delta R/R_0$ vs $\Delta L/L_0$ and corresponding linear fit for the determination of gauge factor of composite samples with 4 wt% CNT within a C401 SBS matrix for A: 5%, B: 10% and C: 20% of strain.



Fig. 8. Values of GF of method 1 for different matrix of composites with 4 wt% MWCNT/SBS at v = 2 mm/min without pre-stress and (b) values of the GF for C540 composite at deformation of $\varepsilon = 20\%$ and test velocity of v = 2 mm/min for different pre-stresses strains.

3.3.1. Electro-mechanical response under uniaxial stress

Electro-mechanical response was measured under uniaxial stress and in 4-point bending tests. In uniaxial tensile tests, the mechanical measurements were performed with the composite with filler content of 4 wt% CNT (Fig. 7a) and the GF was determined by the variation of resistance during the loading and unloading cycles (Fig. 7a), according to Eq. (2). In Fig. 7b are shown different data points to demonstrate how the GF (relation between the variations of the electrical resistance with the mechanical deformation) was obtained for the different composite samples through the respective linear fits. The higher is the slope in linear fit, the larger is the GF value for composites, i.e., increasing their sensibility.

It was observed that the electrical response of the SBS/MWCNT composites follows linearly the mechanical deformation, both during the loading and the unloading cycles (Fig. 7a). Moreover, it is possible to observe that $\Delta R/R_0$ has a linear trend and fits well with $\Delta L/L_0$ in the data points for all cycles (Fig. 7a). In Fig. 7b, there are shown three different responses of the electrical resistance variation with mechanical strain of the SBS filled with 4 wt% of CNT and respective linear fits for different GF values. This demonstrates the different sensibility of the composites samples, related to the different test velocity or pre-strain applied during the measurements, as it will be discussed later. It is important to notice that the thermoplastic SBS elastomer composites fully recover the original properties after loading-unloading cycles at different pre-strains and experiments performed at different strain rates.

The piezoresistive response for uniaxial stress method was analyzed for C401, C411, C500 and C540 SBS matrices with 4 wt% CNT as a function of the deformation, between 5% and 20%. C540 SBS matrix was also pre-stressed (until 30%) and deformed until a maximum deformation of 20%, and for several speed at four different deformation (5%, 10%, 20% and 50%). The GF was determined applying Eq. (2).

The four different elastomeric matrices have distinct behavior for GF at different deformations (at a velocity of v = 2 mm/min) as shown in Fig. 8a. SBS matrix with a linear structure (C540) showed a higher GF than the SBS samples with a radial morphology. This is influenced by the mechanical hysteresis, with radial structure showing slower recovery dynamics than the linear ones [13]. For the same butadiene/styrene ratios, the GF is higher for the SBS linear matrix structures, as observed by comparison of the C500 and C411 composite samples. C500 SBS/CNT samples with 4% filler content show a GF \approx 9, whereas the GF for composites with C411 SBS matrix have a GF less than GF < 4 for all strains (Fig. 8a). Moreover, the amount of butadiene present in the composites influences the GF, which is lower for the samples with more butadiene in their composition (Table 1), for strains up to 10% with C401 (low styrene content matrix) SBS/CNT shows a higher GF than for the SBS samples with 30% of butadiene at 20% of strain. C401, C411 and C500 SBS matrix have a lower GF value (GF < 10) and distinct behavior with deformation. Composite with higher amount of styrene with linear structure (C540 with 40% styrene) has the highest value of GF and an increase of the GF was observed with increasing deformation (up until a maximum of 20%). This GF behavior is related to the mechanical response of the these composites, as the initial elastic modulus is around 5 times higher for the C540 than for other elastomeric matrixes filled with 4 wt% CNT [13]. The results show that polymer morphology and styrene/butadiene ratio influence the mechanical behavior of the matrix.

Due to the nanoscale dimensions of the carbon nanotubes, the interfacial regions that surround the filler are also in nanometer dimensions and the applied load can be easily transferred from the matrix to CNT's network. There are three synergizing aspects of interactions in carbon nanotube based nanocomposites, i.e., polymer-nanotube interaction, nanotube-nanotube and intra polymer interactions. Despite an increase interest in carbon nanotube filled polymer composites, the mechanism and magnitude of load transfer between the polymer matrices and the filler are still unclear [25]. In the present work, it seems that the CNT's present in the SBS matrix with radial structure are poorly wrapped by elastomeric amorphous chains, and when a mechanical load is applied to such a nanocomposite, and due to the nature of such anisotropic structure, polymer chains will not aligned easily in the direction of the mechanical loading and consequently, the conductive filler will suffer minor spatial rearrangements due to the poor wrapping between the filler and the matrix, and the change in the electrical resistance will be smaller, giving origin to reduced GF values. On the other hand, it seems that for the linear structure, the SBS amorphous chains wrapped with more contact points the CNT's, and when the mechanical load was applied, the chains are more easily aligned in the stretch direction, giving origin to a local decrease of the concentration of CNT by increasing the distance between the each neighbor filler. Consequently there is an increment on the electrical response of the material, contributing for the highest GF values found in the samples with linear structure when compared to the radial ones.

Small values of uniaxial stretching do not change the CNT and consequently, the effect on the electrical response is not influenced in a strong manner by this type of loading [24]. The average number of electrical paths seems similar for stretching until 3% [24] and CNT displacements would not be sufficiently large to break the percolations network [24]. On the other hand, larger strains induce reorientation of the filler in the direction of the applied mechanical load, and therefore, stronger variations in the electrical properties of the composites [26].

In order to maximize the GF response of the elastomeric nanocomposites, a pre-stress from until 30% of strain, was performed to the C540 matrix sample. In these measurements, the composites were pre-stressed at 30% of initial distance between jaws and then the electromechanical tests were performed at 20% of deformation at 2 mm/min. The obtained results shows an increase of the GF value with a small increase of the pre-stress of 5% of strain from GF of \sim 20 up to GF of \sim 100, and remaining almost constant for higher pre-stress values (Fig. 8b). Pre-stretching will cause both an increase of the apparent Elastic modulus and a reorientation of the fillers to an unstable configuration. In this situation, a further increase of the stretching will lead both to larger internal stresses [27] and to larger variations on the CNT conductive network, leading to larger values of the GF. Theoretical predictions showed that aligned CNT make composites more sensitive (increase GF value) that non-aligned CNT [24] and this can be important to increase GF for higher deformations, if the CNTs align with the applied deformation during the electromechanical tests.

Proceeding on the search f maximizing the piezoresistive properties of SBS matrix composites, an effort was devoted to the understanding of the influence of the test velocity during mechanical solicitation on the GF values. This study was performed for several deformations of 5%, 10%, 20% and 50% at different velocities of 1–50 mm/min for the C540 SBS matrix filled with 4% of MWCNT. The results are presented in Fig. 9. The gauge factor increase with velocity until 20 mm/min, decreasing for higher speeds (50 mm/min) for low strains analyzed. For the minimum and maximum velocities (5 and 50 mm/min) the behavior of GF is constant and the values are similar, being around 15–30 as function of the strain until 50%. For intermediate velocities, GF shows higher values at low strains (up until 10%) decreasing thereafter down to the values of others velocities. The obtained results suggest that an applied pre-strain improves the piezoresistive response of the nanocomposites. It seems that an increase of the GF values occurs, but this increase is especially stronger for the smaller pre-strain values and for intermediated deformation velocities. For smaller pre-stress, the alignment of the CNT's will be poor and their orientation will be similar to the obtained after processing and when a load is applied, especially at smaller velocities, the mechanical load transferred from the polymer matrix to the filler is not enough to promote alignment of the conductive filler in the loading direction due to the poor wrapping of the polymer amorphous chains on the CNT. Consequently the electrical response of the nanocomposites will be smaller. On the other hand, for higher deformation rates, the mechanical load is too fast and, due to the week bonding between the polymer chains and the conductive filler that only occurs at nanoscale points in the MWCNT, such higher mechanical solicitation will quickly destroy the bonds between the filler and the matrix. Consequently the polymer chains will align in the direction of the applied stress, but the MWCNT's only not suffer the same mechanical load and the electrical response will be smaller, being the effect similar to the one observed for the strain rate of 5 mm/min (Fig. 9). Further, when the strain was applied at 10 and 20 mm/min, the rate was not enough to destroy the bonds between the matrix and the conductive filler. Consequently the MWCNT's can follow the direction of the mechanical solicitation, contributing for higher alignment and local decrease of filler concentration, which promotes an increase of the GF values obtained (Fig. 9). The results for this SBS composite show that the variations on the electrical resistance follows the stress-strain tests at a velocity of around 10 mm/min, and denoting a major difficulty on this match for higher velocities.

3.3.2. Electro-mechanical response under 4-point-bending

Typical results from the 4-point-bending experiments are show in Fig. 10, where four loading-unloading cycles are shown for the C411 sample with 4 wt% of CNT content. The variation of electrical



Fig. 9. GF values for C540 SBS with 4 wt% CNT at different strains (5%, 10%, 20% and 50%) for speeds of 5, 10, 20 and 50 mm/min.



Fig. 10. Electro-mechanical measurements with 4 point-bending mechanical solicitation (method 2) for the C411 elastomeric SBS matrix with 4 wt% MWCNT. Maximum deformation: 1 mm; deformation velocity: 0.1 mm/min.

resistance follows linearly the mechanical deformation over time. The deformation in this method 2 is quite different from those applied in method 1: the applied force is parallel to the cross-section of the composite sample unlike the method 1 that is normal to the cross section. This implies a different stress and strain distribution through the cross section of the loaded samples. In method 1, the stress is uniform through the cross section, whilst in method 2 there is a non-uniform stress distribution along the cross section, which is maximum at the outer surfaces of the specimen (being the surface where load is applied in a compressive state, and in a tensile in the opposed surface).

The GF obtained for the different SBS sample composites with 4 wt% CNT for different maximum deformations and deformation velocities are shown in Fig. 11a and b, respectively. It was observed that the composite samples with SBS radial structure show higher GF values (C401 and C411), and the ones with large content of butadiene (C401 with 80%) present the highest GF values (Fig. 11a). The GF for SBS C540 varies between 40 and 100 for several strain levels. The remaining composites have GF values lower than 30. In general, the samples with linear structure (C500 and C540) present similar piezoresistive response, and the composite samples with large butadiene amount present in their composition have the highest GF values. An increase of the deformation velocity reveals that the amount of butadiene phase in the elastomeric composition is responsible for the highest GF values found (Fig. 11b). The values of GF as function of velocity are practically constant up to until 50 mm/min for the SBS matrices C411, C500 and C540 and are similar to the values of the GF obtained for varying strains. For the C401 SBS matrix, the GF values are around 100 and they increase for lower velocity up to a maximum value, similar to the results obtained for method 1, and decrease thereafter with the increase of the velocity until 50 mm/min. This electro-mechanical behavior is related to the viscoelastic nature of the polymer matrix and therefore to the mechanical time response [13].

The two different electro-mechanical methods (tensile and bending) show how important is the SBS matrix in the piezoresistive of the nanocomposites. In uniaxial uniform stress (tensile loading), the SBS matrix with the lowest butadiene content shows a higher GF value, as well as the highest mechanical properties (namely, the initial modulus). In 4-point bending the SBS matrix with higher GF values is that with the largest butadiene content.

There are two different effects contributing to the GF values: the intrinsic piezoresistive effect and the geometric variation effect (Eq. (3)). For this type of materials, the Poisson ratio goes from 0.35 to 0.5 [28-30], which means that the geometric variation effect contribution to GF varies among 1.7-2. Metallic strain gauges show similar gauge factors of ~ 2 for strains smaller than 4%, which are ascribed to geometrical variations [31,32]. In elastomeric composites, the piezoresistivity values up to ~ 2 are also mostly due to geometrical contributions, being the larger contributions to the GF due to electrical resistance variation of network fillers in composites and therefore to intrinsic contributions. Fig. 11 shows that for concentrations of the 4 wt% CNT, the geometric variation factor can be dominant for small deformations and C500 or C540 SBS matrix, but for larger deformations the intrinsic effect due to straininduced modification of the conductive network is dominant. For C401 SBS/MWCNT composite samples, the intrinsic piezoresistive effect is dominant for several deformations and speed stress-strain tests.

4. Conclusions

The SBS tri-block copolymers have excellent properties for piezoresistivity sensors at large deformations when mixed with carbon nanotubes at percolation threshold or above, offering electrical properties to the isolator matrixes. The electrical percolation threshold is less than 1 wt% for all different matrices of SBS composites and it has a similar behavior for electrical conductivity.

Electrical and mechanical properties generally depend on CNT distribution on the polymer matrix. In the present case, SEM images show a similar small cluster distribution of CNT in all SBS matrixes, which results in similar high electrical conductivity for all studied polymer/carbon nanotubes matrixes.



Fig. 11. (a) GF for 4-point-bending as a function of strain up to 1 mm and (b) GF as a function of speed up to 50 mm/min for C401, C411, C500 and C540 SBS matrix composites with 4 wt% CNT.

The nanocomposites with 4 wt% of CNT can be used as sensors for larges deformations, up to 50% of deformation, with high gauge factor values.

For uniaxial stress method, the SBS matrix that has the highest GF is C540 (linear copolymer architecture and lowest content of butadiene), which increase with deformation. For enhanced sensibility and GF values, to these composites is applied an initial pre-strain until 30%. Applying a pre-strain of 5% or higher, the GF increase for values around 100 for the C540 SBS/CNT composite with 4 wt% CNT. The gain in sensibility of the composite is huge with the application of pre-stress and can be as high as GF = 120. The GF as function of test velocity increases up to 10 mm/min, and have a distinct behavior for the superior velocities for the different matrices. Thus, the maximum GF is obtained using a pre-strain (5% or 10%), velocity of around 10 mm/min. These SBS/MWCNT nanocomposites can be used in sensor for larger deformation, up to 50% of strain, with a high GF.

For method 2 (bending) the behavior of the GF for several velocities and deformations for all SBS matrices was measured. As function of deformation, the matrix that shows the highest values of GF is C401 (copolymer with a radial architecture, and high content of butadiene) and the values ranging between 40 < GF < 100. For the other matrices GF values are lower than 30. As function of the test velocity, the behavior is similar to the behavior of strain and it is varying from 80 < GF < 120 for C401 SBS, and for others matrices the GF shows similar values as function of the applied strain.

These composites present also a mechanical hysteresis that increase with strain and it is higher for the initial loading cycles, decreasing in the course of the cyclic loading. Mechanical hysteresis is higher for the matrices with high content of styrene.

Overall, this investigation demonstrates the suitability of these materials for the development of large deformation piezoresistive sensors.

Acknowledgements

This work was co-funded by FEDER funds through the "Programa Operacional Factores de Competitividade - COMPETE" and by national funds by FCT - Fundação para a Ciência e a Tecnologia, through project references: PTDC/CTM-NAN/112574/2009 and NANO/NMed-SD/0156/2007. PC, AF and VS would also to acknowledge FCT for the SFRH/BD/64267/2009, SFRH/BD/69796/2010 and SFRH/BPD/63148/2009 grants, respectively. The authors also thank support from the COST Action MP1003, 2010 'European Scientific Network for Artificial Muscles' and MP0902 "Composites of Inorganic Nanotubes and Polymers, COINAPO" and funding from "Matepro - Optimizing Materials and Processes", ref. NORTE-07-0124-FEDER-000037", co-funded by the "Programa Operacional Regional do Norte" (ON.2 - O Novo Norte), under the "Quadro de Referência Estratégico Nacional" (QREN), through the "Fundo Europeu de Desenvolvimento Regional" (FEDER). The authors also thank to Dynasol Elastomers (Madrid) (http://www.dynasolelastomers.com) for kindly supplying the SBS used in this work. Thanks to Instituto de Carboquimica (CSIC) in Zaragoza, Spain, for providing the SEM images.

References

- [1] W. Zhi Feng, W. Pei, Y. Xiong Ying, J. Bo, Processing and modeling of multi-walled carbon nanotube/styrene-butadiene-styrene (SBS) composites for force sensing, in: IEEE-NANO 2009. 9th IEEE Conference on Nanotechnology 2009, 2009, pp. 756–757.
- [2] L.G. Pedroni, M.A. Soto-Oviedo, J.M. Rosolen, M.I. Felisberti, A.F. Nogueira, Conductivity and mechanical properties of composites based on MWCNTs and styrene-butadiene-styrene block[™] copolymers, Journal of Applied Polymer Science 112 (2009) 3241–3248.

- [3] P. Wang, S. Geng, T. Ding, Effects of carboxyl radical on electrical resistance of multi-walled carbon nanotube filled silicone rubber composite under pressure, Composites Science and Technology 70 (2010) 1571–1573.
- [4] A.I. Oliva-Avilés, F. Avilés, V. Sosa, Electrical and piezoresistive properties of multi-walled carbon nanotube/polymer composite films aligned by an electric field, Carbon 49 (2011) 2989–2997.
- [5] H. Lorenz, J. Fritzsche, A. Das, K.W. Stöckelhuber, R. Jurk, G. Heinrich, M. Klüppel, Advanced elastomer nano-composites based on CNT-hybrid filler systems, Composites Science and Technology 69 (2009) 2135–2143.
- [6] A. De Falco, S. Goyanes, G.H. Rubiolo, I. Mondragon, A. Marzocca, Carbon nanotubes as reinforcement of styrene–butadiene rubber, Applied Surface Science 254 (2007) 262–265.
- [7] Y.-T. Liu, X.-M. Xie, X.-Y. Ye, High-concentration organic solutions of poly(styrene-co-butadiene-co-styrene)-modified graphene sheets exfoliated from graphite, Carbon 49 (2011) 3529–3537.
- [8] A. Das, K.W. Stöckelhuber, R. Jurk, M. Saphiannikova, J. Fritzsche, H. Lorenz, M. Klüppel, G. Heinrich, Modified and unmodified multiwalled carbon nanotubes in high performance solution-styrene–butadiene and butadiene rubber blends, Polymer 49 (2008) 5276–5283.
- [9] J.-H. Wu, C.-H. Li, Y.-T. Wu, M.-T. Leu, Y. Tsai, Thermal resistance and dynamic damping properties of poly (styrene-butadiene-styrene)/thermoplastic polyurethane composites elastomer material, Composites Science and Technology 70 (2010) 1258–1264.
- [10] S.B. Munteanu, M. Brebu, C. Vasile, Thermal and thermo-oxidative behaviour of butadiene–styrene copolymers with different architectures, Polymer Degradation and Stability 89 (2005) 501–512.
- [11] C. Ocando, A. Tercjak, İ. Mondragon, Nanostructured systems based on SBS epoxidized triblock copolymers and well-dispersed alumina/epoxy matrix composites, Composites Science and Technology 70 (2010) 1106–1112.
- [12] C. Li, E.T. Thostenson, T.-W. Chou, Sensors and actuators based on carbon nanotubes and their composites: a review, Composites Science and Technology 68 (2008) 1227–1249.
- [13] P. Costa, J. Silva, V. Sencadas, R. Simoes, J.C. Viana, S. Lanceros-Méndez, Mechanical, electrical and electro-mechanical properties of thermoplastic elastomer styrene–butadiene–styrene/multiwall carbon nanotubes composites, Journal of Materials Science 48 (2013) 1172–1179.
- [14] W. Zhifeng, Y. Xiongying, A numerical investigation on piezoresistive behaviour of carbon nanotube/polymer composites: mechanism and optimizing principle, Nanotechnology 24 (2013) 265704.
- [15] J.R. Bautista-Quijano, F. Avilés, J.V. Cauich-Rodriguez, Sensing of large strain using multiwall carbon nanotube/segmented polyurethane composites, Journal of Applied Polymer Science 130 (2013) 375–382.
- [16] L. Wang, X. Wang, Y. Li, Relation between repeated uniaxial compressive pressure and electrical resistance of carbon nanotube filled silicone rubber composite, Composites Part A: Applied Science and Manufacturing 43 (2012) 268–274.
- [17] J.H. Kang, C. Park, J.A. Scholl, A.H. Brazin, N.M. Holloway, J.W. High, S.E. Lowther, J.S. Harrison, Piezoresistive characteristics of single wall carbon nanotube/polyimide nanocomposites, Journal of Polymer Science Part B: Polymer Physics 47 (2009) 994–1003.
- [18] P. Cardoso, J. Silva, D. Klosterman, J.A. Covas, F.W.J. van Hattum, R. Simoes, S. Lanceros-Mendez, The role of disorder on the AC and DC electrical conductivity of vapour grown carbon nanofibre/epoxy composites, Composites Science and Technology 72 (2012) 243–247.
- [19] K. Tsuchiya, A. Sakai, T. Nagaoka, K. Uchida, T. Furukawa, H. Yajima, High electrical performance of carbon nanotubes/rubber composites with low percolation threshold prepared with a rotation-revolution mixing technique, Composites Science and Technology 71 (2011) 1098–1104.
- [20] S. Cantournet, M.C. Boyce, A.H. Tsou, Micromechanics and macromechanics of carbon nanotube-enhanced elastomers, Journal of the Mechanics and Physics of Solids 55 (2007) 1321–1339.
- [21] A. Ferreira, P. Cardoso, D. Klosterman, J.A. Covas, F.W.J. Van Hattum, F. Vaz, S. Lanceros-Mendez, Effect of filler dispersion on the electromechanical response of epoxy/vapor-grown carbon nanofiber composites, Smart Materials and Structures (2012) 21.
- [22] J.C. Dawson, C.J. Adkins, Conduction mechanisms in carbon-loaded composites, Journal of Physics: Condensed Matter 8 (1996) 8321.
- [23] J. Silva, S. Ribeiro, S. Lanceros-Mendez, R. Simões, The influence of matrix mediated hopping conductivity, filler concentration, aspect ratio and orientation on the electrical response of carbon nanotube/polymer nanocomposites, Composites Science and Technology 71 (2011) 643–646.
- [24] T.C. Theodosiou, D.A. Saravanos, Numerical investigation of mechanisms affecting the piezoresistive properties of CNT-doped polymers using multi-scale models, Composites Science and Technology 70 (2010) 1312–1320.
- [25] D. Bikiaris, Microstructure and properties of polypropylene, Carbon Nanotube Nanocomposites Materials 3 (2010) 2884–2946.
- [26] Y. Jiang, H. Fan, A micromechanics model for predicting the stress-strain relations of filled elastomers, Computational Materials Science 67 (2013) 104–108.
- [27] C. Grimaldi, P. Ryser, S. Strassler, Gauge factor of thick-film resistors: outcomes of the variable-range-hopping model, Journal of Applied Physics 88 (2000) 4164–4169.
- [28] C.P. Buckley, C. Prisacariu, C. Martin, Elasticity and inelasticity of thermoplastic polyurethane elastomers: sensitivity to chemical and physical structure, Polymer 51 (2010) 3213–3224.

- [29] M. Motamedi, M. Eskandari, M. Yeganeh, Effect of straight and wavy carbon nanotube on the reinforcement modulus in nonlinear elastic matrix nanocomposites, Materials & Design 34 (2012) 603–608.
- [30] T. Aoyama, A.J. Carlos, H. Saito, T. Inoue, Y. Niitsu, Strain recovery mechanism of PBT/rubber thermoplastic elastomer, Polymer 40 (1999) 3657–3663.
- [31] M.H.G. Wichmann, S.T. Buschhorn, J. Gehrmann, K. Schulte, Piezoresistive response of epoxy composites with carbon nanoparticles under tensile load, Physical Review B 80 (2009) 245437.
- [32] C.L. Cao, C.G. Hu, Y.F. Xiong, X.Y. Han, Y. Xi, J. Miao, Temperature dependent piezoresistive effect of multi-walled carbon nanotube films, Diamond and Related Materials 16 (2007) 388–392.

Biographies

Pedro Costa graduated in Physics in 2007 and obtained a Master degree in Advanced Materials Physics in 2009, both degrees obtained at Minho University in Portugal, specializing in the area of functional materials or nano and microtecnologies. In 2010 he started the PhD in Materials Engineering at the University of Minho focusing on the development of composite materials for large strain sensor applications.

A. Ferreira received the B.Sc. and the M.Sc. degree in Physics from the University of Minho, Braga, Portugal, in 2007 and 2010, respectively. He is currently working toward the Ph.D. at the Physics Department, University of Minho. His thesis work consists in the development of a pressure sensor network system for static and dynamic measurement for lower limb prosthesis pressure mapping.

Vitor Sencadas received Ph.D. in Physics in 2009 from University of Minho, Portugal and in 2010 joined the Center of Physics of Minho University as a Research

Fellow. His research interests are related to electroactive materials, especially piezoelectric and piezoresistive materials for applications as scaffolds and membranes for tissue and biomedical engineering. In 2011 he joined at IPCA as an invited member.

Júlio C. Viana is an Associated Professor at the Department of Polymer Engineering at the University of Minho, Portugal, since 2009. He joined the Polymer Engineering Department at the University of Minho in 1992. He graduated in Production Engineering – Polymers (University of Minho) in 1991, completed the M.Sc. in Computer Aided Mechanical Engineering Design at Queens University in Belfast in 1993 and the PhD in Polymer Science and Engineering at University of Minho (in collaboration with CEMEF/Ecole des Mines de Paris, Fr) in 2000. The main areas of scientific and technological interests dealt with mechanical behavior of polymers (characterization, deformation mechanisms, impact); relationships between processing, morphology and properties of polymers; advanced polymeric material systems (active/smart polymers, mechanically active polymers); non-conventional molding techniques (for property enhancement and multifunctional behavior).

S. Lanceros-Mendez graduated in physics at the University of the Basque Country, Leioa, Spain, in 1991. He obtained his Ph.D. degree in 1996 at the Institute of Physics of the Julius-Maximilians-Universität Würzburg, Germany. He was Research Scholar at Montana State University, Bozeman, MT, from 1996 to 1998 and visiting scientist at the A.F. Ioffe Physico-Technical Institute, St. Petersburg, Russia (1995), Pennsylvania State University, USA (2007) and University of Potsdam (2008). Since September 1998 he has been at the Physics Department of the University of Minho, Portugal, where he is associate professor and since 2012 he is also associate researcher at the INL – International Iberian Nanotechnology Laboratory. His work is focused in the area of polymer based smart materials for sensors and actuators, energy and biomedical applications.