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Extruded thermoplastic elastomers styrene–butadiene–styrene/carbon nanotubes composites for strain sensor applications

P. Costa [a], C. Silvia [b], J.C. Viana [b], S. Lanceros Mendez [a,*]

[a] Center/Dept. of Physics, University of Minho, 4710-058 Braga, Portugal
[b] Institute for Polymers and Composites IPC/I3N, University of Minho, 4800-058 Guimarães, Portugal

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ABSTRACT

Tri-block copolymer styrene–butadiene–styrene (SBS) composites with different butadiene/styrene ratios and multi-walled carbon nanotubes (MWCNTs) can be used for the development of electro-mechanical sensors for large strains applications. Extruded CNT/SBS composites show percolation thresholds around 5 wt%, electro-mechanical properties with high sensibility at larger strain and the gauge factor reach values up to 30 at strains of 20%. The butadiene/styrene ratio has influence in the mechanical and electro-mechanical properties. In one hand, the increase of the styrene content in copolymer increasing initial mechanical modulus, on the other hand, the increase of the butadiene content leads to larger maximum deformations and higher electro-mechanical sensibility for strains up to 20%. Further, applied initial pre-stress increases the electro-mechanical sensibility of the composites.

1. Introduction

Conducting polymer composites based on an insulator polymeric matrix with an electrical conducting nanofiller dispersed within the matrix have been extensively studied for their applications as antistatic materials, electromagnetic interference, capacitors [1–4], temperature, pressure, gas and piezoresistive sensors [1,2].

The most widespread uses of industrial polymer composites with carbon nanoallotropes are as packing and structural materials. The majority of polymers are thermally and electrically insulators but for packing purposes it is required that polymers do not accumulate static charge during manufacturing, assembling, storage and service [3]. The amount of carbon nanoallotropes necessary for obtaining a given level of electrical conductivity depends on the type of nanofiller. In the case of carbon black (CB), widely used due to its low cost, a loading between 15% and 20% by weight (wt%) is necessary for reaching the percolation threshold [3,4]. These large filler contents, on the other hand, brings negative effects on the processability of the composites and their mechanical properties [3]. The use of carbon nanotubes (CNT) lead to composites with superior electrical and mechanical properties when compared to other carbon allotropes such as carbon black or vapor grown carbon nanofibers (CNF) and these properties are achieved with lower nanoallotropes loadings [5,6]. CNF have higher density and diameter than CNT [7]. Electrical percolation threshold in composites with CNF as filler materials is around 4–6 wt% [7]. The unique mechanical, electrical and thermal properties of CNT have largely accelerated their applications in the development of structural and electrical components [8]. CNT/polymer composite materials have further enhanced multifunctionality in terms of stress and strain sensing capabilities, even at the nanofiller-matrix interface level [9].

As polymer matrix, the thermoplastic elastomer tri-block copolymer styrene–butadiene–styrene (SBS) is widely studied and used in industry due to its high elongation at break, abrasion resistance and durability [10–13]. SBS can be used without vulcanization, which is an advantage as it does not degrade the mechanical and electrical properties obtained in composites [8]. SBS copolymers can be composed by different ratios of styrene and butadiene, which strongly influences its mechanical, electrical and thermal properties. Usually, butadiene is the component in larger quantity with the styrene content being up to 50%.

The SBS has high thermal stability with the butadiene glass transition (Tg) around −80 °C [10] and the styrene around 100 °C [10]. The incorporation of carbon nanotubes within the copolymer matrix does not change them significantly, being observed just a slight shift of the glass transitions to higher temperatures [14,15]. The most outstanding property of CNT/SBS composites is therefore their mechanical properties, showing strains higher than 1000% for CNT contents up to 8 wt% independently of the styrene/butadiene ratio within the SBS (20/80, 30/70 or 40/60) [2]. Further, the initial modulus increases with decreasing butadiene (softer phase) in SBS and the electrical percolation threshold is independent of the SBS matrix [2].

* Corresponding author. Tel.: +351 253604073.
E-mail address: lanceros@fisica.uminho.pt (S. Lanceros Mendez).

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Properties of polymer composites strongly depend on the processing, characteristics and functionalization of the nanoallotropes, as well as on the dispersion and distribution level of the nanofillers in the polymer matrix [7,16].

Processing methods typically used in this type of composites are solvent casting, in situ polymerization, melt blending and chemical modifications [16,17]. The ability to disperse individual CNT homogeneously within matrix has a strong influence in composite characteristics and therefore in their application potential [17].

Percolation threshold below 0.01 wt% [18] have been reported under specific processing conditions such as solvent casting [19], but values around 1–3 wt% are most typically found for composites based on thermoplastic polymers with CNT processed with industrially-viable methods such as melt compounding and extrusion [19]. Thus, up scaled industrial processes for composites preparation typically lead to an increase of carbon nanofiller loading for achieving similar electrical properties when compared with solvent casting methods processed in laboratory environment.

The percolation threshold can be further tailored in polymer extrusion by adding a second filler working in synergy with the CNT [19], but this second filler can have both positive implications such as decreasing the percolation threshold and adding novel functionalities to the polymer matrix, but also negative, such as increasing fragility, price and difficult recyclability of composites [19]. Nanoclays are of the best example of second fillers added in polymer/carbon nanofiller composite [20,21].

It has been shown that CNT/SBS composites prepared by solvent casting show excellent piezoresistive properties appropriate for the development of large deformation sensors with good and linear sensibility [22], when compared to traditional strain gages [23]. Composites with percolation thresholds near 0.5 wt% and good piezoresistive properties characterized by gauge factors (GF) up to 100 for 4 wt% CNT of composites have been achieved [22].

This work investigates the electrical, mechanical and electro-mechanical performance of CNT/SBS composites prepared by extrusion in the form of wire in order to evaluate the possibly of up-scaled production and performance of these materials for sensor and actuator applications.

2. Experimental

2.1. Materials and sample processing

Thermoplastic elastomers tri-block copolymer styrene–butadiene–styrene (SBS) Calprene, from Dynasol, with different butadiene/styrene ratios, 80/20 and 60/40 for C401 and C540, respectively were used. C401 shows a radial structure and C540 a linear one [24].

Multi-walled carbon nanotubes (MWCNTs) from Baytubes were used as carbon nanoallotropes. The CNT with reference C150P are characterized by purity over 95%, inner and outer diameter of 4 and 13 nm, respectively, length larger than 1 μm and bulk density between 130 and 150 kg/m^3.

The CNT/SBS composites were processed on a co-rotating Microlab Twinscrew extruder from Rondol Technology Ltd., designed to process small amounts of material while retaining the characteristics of larger equipment. The screw has a diameter of 10 mm and a length of 200 mm, and the die, with a circular channel with a diameter of 2 mm. Prior to extrusion, the raw polymer was milled to reduce its original size until 1 mm in average in order to guarantee a continuous feeding of the twin-screw extruder. Both polymer and nanoallotropes were previously dried in a dry air dehumidifier according to the supplier instructions, pre-mixed in powder form and fed into the extruder by gravimetric feeding. Along the barrel and at the die, the temperature profile was set, after an optimization procedure for CNT/SBS composites, from 150 °C (at the feed zone) to 190 °C (at the die) (Table 1) and the rotational velocity was set at 35 rpm.

After extrusion, the obtained composite wire was cooled down to room temperature. Composites from SBS with 4%, 6%, 8% and 10% CNT in weight were prepared for both C401 and C540 SBS types.

2.2. Sample characterization

Scanning electron microscopy (SEM) experiments were performed in a Quanta 650 FEG (FEI) with high-vacuum mode (<6^{-4} Pa) at a voltage of 10 kV and a distance of 5 mm.

The FTIR–ATR analyses were carried out using a Bruker OPUS/IR PS 15 in the spectral range from 4000 to 400 cm^{-1}. The spectra were the results of 64 interferograms at a spectral resolution of 4 cm^{-1}.

Thermogravimetric experiments (TGA) were conducted under Argon atmosphere between 50 °C and 700 °C at a heating rate of 10 °C/min in a TGA-7 thermo balance (Perkin–Elmer) apparatus. The degradation temperature was calculated as the onset in the weight loss versus temperature curve.

Differential scanning calorimetry (DSC) was performed from −20 to 200 °C at a rate of 10 °C min^{-1} using a DSC-2010 (TA instruments) under dry nitrogen atmosphere.

Stress–strain mechanical tests were performed using a universal testing machine from Shimadzu, model AG-IS with load cell of 1 KN in tensile mode at test velocities from 1 to 50 mm/min at room temperature (~23 °C) on wire composites with 4–5 mm of diameter and with a distance between clamps of 10–20 mm. The uniaxial displacement was applied at the upper clamp whereas the bottom clamp remained fixed (Fig. 1).

Electrical resistance of the composites was calculated from the slope of current–voltage, *I–V* curves, measured with an automated Keithley 487 picoammeter/voltage source. *I–V* data points were collected between silver painted contacts in the extruded yarn composite with 5 mm of distance between them. Resistivity was measured applying a voltage ranging between ±10 V and measuring the current, *I*.

Electro-mechanical tests were performed by measuring the electrical resistance of the composite sample through silver painted electrodes with an Agilent 34401A multimeter during the uniaxial mechanical deformation (Fig. 1) of the sample, applied with a universal testing machine from Shimadzu on samples with 4–5 mm of diameter and a distance between clamps of ~10 mm. The silver painted electrodes were placed inside the clamps during the mechanical tests, not suffering therefore any deformation during the stress–strain measures.

The evaluation of the piezoresistive response during the uniaxial stress tests was performed at different test velocities (from 1 to 50 mm/min) and strain levels (1–20%). Further, experiments were conducted at different levels of pre-stress up to 20%. In order to obtain an average electro-mechanical response, 10 loading–unloading cycles were measured for each sample.

Variations of the electrical resistance due to mechanical deformation are quantitatively evaluated by the Gauge Factor, defined as:

Table 1
Temperature profile along the extruder.

	Die	Zone 3	Zone 2	Zone 1	Feed zone
Temperature (°C)	190	180	170	160	150