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Tensile piezoresistivity and disruption of percolation in singlewall and multiwall carbon nanotube/polyurethane composites

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ABSTRACT

Carbon nanotube elastomeric composite films were fabricated by solution casting using singlewall and multiwall carbon nanotubes (SWCNTs and MWCNTs) and two thermoplastic-elastomers polymer matrices, an in-house synthesized segmented polyurethane and a commercial one. The CNTs are first characterized and the electrical conductivity, mechanical properties and piezoresistive response of the SWCNT and MWCNT composites with 8 wt% are evaluated. For both polymer matrices, the electrical conductivity of composites made from MWCNTs is higher than that achieved for composites made from SWCNTs. Evaluation of the strain–electrical resistance relationship of the composites shows a dependency of the piezoresistive sensitivity on the kind of CNT (SWCNT or MWCNT) and matrix electrical and mechanical properties. Above a specific strain threshold, electrical percolation is disrupted under tensile loading. The strain level at which this happens is larger for composites made with MWCNTs than for composites made with SWCNTs.

1. Introduction

The fast growth of new tendencies in material science has led to the investigation of smart materials based on polymer composites [1]. Among the most promising smart materials, carbon nanotube (CNT)/polymer composites are one of the most aggressively investigated, because of the physical properties of CNTs and the versatility of polymers [2]. CNT/polymer composites have shown sensory properties [3–5] and piezoresistive capabilities [6–9]. The variation of electrical resistance with applied strain (piezoresistivity) has been used to fabricate composite materials with strain sensing capabilities using different polymers, including elastomers [8–10]. It has also been reported that CNT/elastomer composites can have actuating properties [11], and some CNT/elastomer composites are being studied for possible application as artificial muscles [12]. Bokobza [13] report that for a 10 wt% MWCNT/styrene-butadiene-rubber composite, the relationship between the normalized change in electrical resistance ($\Delta R/R_0$) and the applied tensile strain is nearly linear. Contrary to the results of Bokobza, Kang et al. [14] found a nonlinear behavior of the piezoresistive response for a 20 wt% MWCNT/ethylene-propylene-diene rubber composite. Zhang et al. [15] studied the tensile piezoresistive properties of a MWCNT/polyurethane-urea composite, finding that the relationship between resistivity and strain shows an exponential relationship. Some elastomers such as segmented polyurethanes (SPU) can be tailored to exploit the processing properties of thermoplastics. The mechanical properties of SPUs are due to physical interactions of the soft (e.g. polyol) and hard (e.g. diisocyanite) segments. These processing advantages make the application of thermoplastic-elastomer composites with piezoresistive capabilities more feasible.

CNT/SPU composites could also provide a large range of strain sensing. Under tensile loading, the maximum strain measurable by the change in the electrical resistance of the composite depends on the strain at which the electrically percolated network is disrupted, i.e. electrical percolation ceases, see e.g. [16]. Although, the piezoresistive properties of CNT/polymer composites for strain sensing applications have been studied, there are few works that deal with elastomeric matrices, and direct comparison of the piezoresistive response of composites using SWCNTs and MWCNTs are scarce. Therefore, the aim of this work is to investigate the piezoresistive properties of CNT/SPU composites using SWCNTs and MWCNTs, focusing on the role of CNT type. Characterizations of both CNTs as well as electrical and mechanical characterization of the CNT/SPU composites are conducted in order to better understand the observed piezoresistive phenomena.

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2. Materials and methods

2.1. Materials

Commercial MWCNTs grown by chemical vapor deposition ("Baytubes C150P") were supplied by Bayer Material Science.[1] The MWCNTs have inner and outer diameters of approximately 4 and 13 nm, respectively, and length in the range of 1–4 μm [17]. The MWCNTs were subjected to a mild oxidative treatment based on nitric acid and peroxide, as reported elsewhere [18]. SWCNTs were synthesized using a furnace-based pulsed laser ablation method using a Nd:YAG laser and circular pellets as targets; details on the SWCNTs synthesis are described elsewhere [19,20]. The elements employed as catalyst for the synthesis of the SWCNTs were Ni:Co:Mo with a weight ratio of 5:4:1. After synthesis, the SWCNTs were purified, obtaining SWCNTs with 95% purity.

Two thermoplastic-elastomers were used in this work: Tecoflex (TF) SG-80A ("Thermedics Polymer Products"[2]), which is a commercial segmented polyurethane with a number average molecular weight (M_n) of ~40,000 g/mol, and an in-house-synthesized segmented polyurethane ($M_n \sim 38{,}000$ g/mol) which will be hereafter named simply "SPU". SPU was synthesized using a molar ratio of 2.05:1:1 of 4,4′-methylene bis (cyclohexyl isocyanate):1,4-butanediol:poly (tetramethylene ether glycol), as described in [21]. Both polymers (TF and SPU) are segmented polyurethanes of ultimate strains above 600% and similar chemical composition, see [21].

2.2. Characterization of SWCNTs and MWCNTs

The morphology of both CNTs was examined using an FEI Tecnai-F30 transmission electron microscope (TEM) operating at 300 kV. For the TEM studies, a small amount of dry CNTs were deposited on a standard Cu TEM grid for analysis.

The structural quality of the CNTs was analyzed by Raman spectroscopy (Thermo Scientific DXR SmartRaman) using a 532 nm laser, 5 accumulations and 10 s per accumulation. The Raman spectrum of the SWCNTs was used for determination of its mean diameter by using the relation between the diameter and the radial breathing mode (RBM) feature of the spectra of SWCNTs as described in [22].

A Bruker IFS 113V spectrometer was used to obtain the optical absorption spectra (OAS) in a spectral range of 3000–15,000 cm^{-1}. Samples for OAS measurements were prepared by dispersing the CNTs in acetone using an ultrasonic bath and subsequently depositing the solution onto a heated KBr pellet, yielding a thin homogeneous film on top of the KBr pellet. In the OAS spectrum, the absorption at ~5520 cm^{-1} (S_{11}) is a band that corresponds to the first semiconducting transition energy. The known relationship between S_{11} and the mean diameter of SWCNTs was also used to estimate the SWCNT diameter (d) as [19],

$$S_{11} - \Delta = \frac{2\gamma\alpha}{d} \tag{1}$$

where $\gamma = 2.9$ eV is the value of the tight binding overlap integral, α is the C–C distance (0.142 nm) and Δ is an excitonic correction factor which depends on the nanotube diameter and CNT to CNT interactions; Δ was taken as 70 meV for bundled SWCNTs [19].

[1] Bayer Material Science, Leverkusen, Germany; www.baytubes.com.
[2] Thermedics Polymer Products, Ohio, U.S.A.; www.lubrizol.com.

2.3. Fabrication of nanocomposite films

0.30 mm thick rectangular films were fabricated by solution casting of 8 wt% SWCNT and MWCNT composites made of TF or SPU. To fabricate the films, 1 g of neat polymer (TF or SPU) was dissolved into 10 ml of chloroform ($CHCl_3$) to obtain a viscous solution (SOL1); in parallel, the required amount of CNTs (oxidized MWCNTs or purified SWCNTs) were dispersed in 15 ml of $CHCl_3$ (SOL2) using an ultrasonic probe (VC750, Sonics & Materials, 150 W, 20 kHz) for 1 min and then an ultrasonic bath (70 W, 42 kHz) for 2 h. Then SOL1 and SOL2 were mixed together and mechanically stirred for 2 h and the CNT/polymer/$CHCl_3$ solution was cast onto a Teflon mold and allowed to dry at room temperature for 24 h to evaporate the solvent. Finally, the solid composite film in wafer form was released from the Teflon mold and cut to size according to the corresponding characterization. At least five specimens were obtained from each wafer and employed for mechanical, electrical or piezoresistive characterization. The four kinds of composites fabricated using either SWCNTs or MWCNTs (all at 8 wt%) were labeled MWCNT/TF, MWCNT/SPU, SWCNT/TF and SWCNT/SPU, depending on the CNT and polymer matrix used.

2.4. Characterization of nanocomposite films

The electrical resistance of the composite films was measured at room temperature with a Fluke 289 multimeter. Two silver painted areas located at the film edges were used as electrodes for the resistance measurements. The specimen length was 25 mm with 5 mm long electrodes, leaving an effective span (L) of 15 mm between the silver electrodes. The specimen width was 6 mm and its nominal thickness was 0.30 mm. The electrical conductivity (σ_e) was calculated from the measured electrical resistance (R) as,

$$\sigma_e = \frac{L}{AR} \tag{2}$$

where A is the cross-sectional area of the specimen, and L is the distance between electrodes.

For the mechanical and piezoresistive characterization, 0.30 mm thick rectangular films of dimensions 60 mm × 10 mm were tested in uniaxial tension. End tabbing was achieved by wrapping 10 mm of the film ends with masking tape, defining a gauge length of 40 mm. Tensile load was applied to the film using a Shimadzu AGI-100 universal testing machine at a displacement rate of 5 mm/min, while the corresponding force was measured by the machine load cell and converted to axial stress. Mechanical strain (ε) was calculated from the machine cross-head displacement normalized by the gauge length of the specimen. A different set of samples were used for piezoresistive characterization, where two copper wires were centered at the midspan of the specimen separated 30 mm to define the electrodes. In order to cement the wires, the tip of the wires was heated and gently pierced through the film thickness and further bonded by silver paint. Electrical resistance was measured in situ during the tension test employing a portable Fluke 289 electrometer with data logging capabilities. Before stretching the samples, the electrical resistance was recorded for 30 s without any mechanical loading for inspection of the signal stability. After 30 s without significant variation in R, the sample was loaded in tension recording the electrical resistance.

3. Results and discussion

3.1. Characterization of carbon nanotubes

3.1.1. Morphology of SWCNTs and MWCNTs

Fig. 1 shows TEM images of the as-synthesized SWCNTs (Fig. 1a) and as-received MWCNTs (Fig. 1b). Fig. 1a shows that SWCNTs tend