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Conduction mechanisms in conductive multi-walled carbon nanotube filled polydimethylsiloxane nanocomposites

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ABSTRACT

This work presents an investigation of the electrical behavior of below percolation threshold CNTs-filled PDMS nanocomposites. Fabricated films were assessed with the aid of current-voltage characteristic and charging/discharging current transient method. The obtained results revealed the presence of a non-negligible hysteresis and the electrical conduction is found to be dominated by internal field emission processes. Finally, the role of change of direction of the applied voltage on the conduction processes has been investigated for the first time.

1. Introduction

Carbon Nanotubes (CNTs) exhibit unique physical properties including mechanical, thermal and electrical, which find industrial application in the fields of switching elements [1], piezoresistive sensors [2], flow sensors [3], electromagnetic shielding [4] and applications where controlled mechanical, thermal and electrical properties are required. A polymer of particular interest is polydimethylsiloxane (PDMS). PDMS is a non-conductive silicone based elastomer which has been under special focus due to its flexibility and ease of micro-molding for prototyping [5], thus representing the most widely used silicon-based organic polymer. The addition of CNTs into PDMS matrix improves the mechanical, thermal and electrical properties of the composites. The electrical conductivity of the polymer can be enhanced abruptly by several orders of magnitude with only a few percent of CNT loading [6,7] following the percolation mechanism [8]. At the onset of the percolating network, the electrical conductivity obeys the power law relation $\sigma_c \propto (v - v_c)^{\beta}$ [9], where σ_c is the composite conductivity, v the CNT volume fraction, v_c the percolation threshold and β is the critical exponent.

The electrical conductivity of bulk CNT network composites has been intensively investigated in nanocomposites. In the case of flexible silicone elastomer polydimethylsiloxane rubber (PDMS) with CNT filler it has been reported that the conductivity varies with the applied voltage and the current-voltage characteristics showed nonlinear relationships, which can be fitted to quadratic functions [7]. The assessment of high density polyethylene (HDPE) and carbon nanofiber (CNF) has revealed the presence of two competing processes in the composite: internal field emission and electrical conduction relaxation of which the former dominates at lower filler concentrations or under low electric field, while the latter is pronounced under the application of strong electric field [10,11]. Moreover, it has been shown that combining Zener tunneling effect with percolation theory, a novel current density–electric field relationship can be developed that can be applicable to carbon/polymer composites below and above the percolation threshold [12,13]. Finally, a statistical-thermodynamic model was introduced for prediction of electrical conductivity of polymer-based carbon composites containing micro and nanofiller [14].

The aim of the present work is to investigate the electrical behavior of below percolation threshold CNTs-filled PDMS composites. The fabricated films were assessed with the aid of current-voltage (I–V) in a close loop. The obtained results revealed the presence of a non-negligible hysteresis and the electrical conduction is found to be dominated by internal field emission processes. The role of change of direction of the applied voltage on the conduction process has been investigated for the first time and the results indicate that the electrical behavior during the ascending of the applied voltage differs from the one obtained during the descending. The latter has been attributed to polarization phenomena of CNTs.

2. Experimental details

2.1. CNT material

The CNTs used were commercial pristine MWCNTs (ONEX MW 1000C1) supplied by Glonatech S.A. (Athens, Greece). Their purity is

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>94%, the diameter is in the range of 25–30 nm and the length is estimated around 5 μm. These MWCNTs are produced by Fluidized Bed Chemical Vapor Deposition (FBCVD). The PDMS silicone resin (Polydimethylsiloxane Type I) is a two constituent resin (PPG Coatings SPRL/BVBA, Belgium). Organic solvents xylene (Carlo Erba Reagents S.r.l.) and toluene (fisher scientific) were used in order to facilitate the dispersion of carbon nanotubes inside the PDMS matrix.

2.2. Preparation of PDMS/MWCNTs nanocomposites

The nanocomposites preparation involved different combinations of the above materials. Two groups of PDMS/MWCNTs nanocomposites were prepared by using two different processing methods. In method A, MWCNTs were initially mixed with xylene, using ultrasonication, under water bath for half hour. Subsequently, the CNTs/solvent suspension was mixed with the PDMS resin, again using ultrasonication. For samples fabricated with Method B, the only parameter that changed compared to method A, was the solvent used (toluene instead of xylene). In both processing methods, the mixing of the suspension of CNTs/solvent was realized in part A of the PDMS resin until the solvent was fully evaporated. The temperature under which the mixing took place did not exceed 60 °C degrees, because the PDMS resin has a temperature limit above which it should not be processed. For each processing route, the hardener (Part B) was added to the PDMS/MWCNTs mixture after the dispersion process and magnetic stirring took place for half an hour, until there was no phase separation between the two parts of the resin. Finally, the suspensions were poured into molds and they were left to cure at room temperature for 24 h. After fully curing of the samples, conductive contacts were formed onto the surfaces of the samples, by applying silverpoint epoxy with the aid of a rectangular shaped mask. Final samples with concentrations in CNTs 0.1, 0.5 and 0.7% w/w were synthesized by both processing methods (Table 1).

2.3. Characterization techniques

2.3.1. Structural characterization

The fine surface morphology of MWCNTs was observed using Zeiss Supra 35VP Scanning Electron Microscope. The diameter of MWCNTs has been found to be in the range of 25–30 nm. Information about their length was provided by conducting Transmission Electron Microscopy (TEM) measurements. The CNTs length is estimated at 5 μm. The purity of MWCNTs was assessed with thermogravimetric analysis (TGA) using TA Instruments TGA Q500, which revealed that the amorphous carbon is low and the purity >94%. Finally, Raman spectra were obtained to certify the high quality of the graphitic layer.

2.3.2. Electrical characterization

Electrical measurements were carried out to obtain current-voltage (I–V) and capacitance-voltage (C–V) curves of the neat matrix and the nanocomposites. Moreover, Discharge Current Transient (DCT) method has been applied after charging the utilized samples with 20 V for 6 h. The devices capacitance was measured with a Boonton 72B capacitance meter with a resolution of about 0.05fF. The DC applied bias was provided by a Keithley 6487 source-meter/electrometer and the voltage ramp-up (ascending) and down (descending) was performed with a rate of 100 mV/s in the range 0 to +20 V denoted (1), +20 V to 0 denoted (2), 0 to −20 V denoted (3) and −20 V to 0 denoted (4) in the figures with I–V characteristics. The thickness of the samples was 1–2 mm and the contact area was of the order of 0.25 cm^2. Symmetric contacts were formed with silver loaded epoxy [15,16] (inset of Fig. 1). Finally, all measurements were performed under vacuum and at room temperature ($T = 300$ K).

Table 1
Samples according to their processing method and materials used.

Sample	Processing method	Solvent	CNTs content
REF	–	Not used	0%
A0.1	A	Xylene	0.1%
A0.5	A	Xylene	0.5%
A0.7	A	Xylene	0.7%
B0.1	B	Toluene	0.1%
B0.5	B	Toluene	0.5%
B0.7	B	Toluene	0.7%

3. Results and discussion

The reference material (REF) (Fig. 1), which is representative for samples A0.1 and B0.1, exhibits high resistivity leading to noisy current-voltage characteristic, due to the limitations of the experimental setup. Specifically, the I–V characteristic is rather linear with a slope of about 10^{-15} S that corresponds to a specific resistivity of about 2.1×10^{15} ohm cm, which is in good agreement with the reported upper limit of PDMS materials resistivity of 1.4×10^{15} ohm cm [17]. Moreover, the I–V characteristic shows a clockwise hysteresis, which can be attributed to both the trapping of injected charges near the injecting electrodes and the large dielectric relaxation time (the sample capacitance is $C \cong 1.35 \times 10^{-12}$ pF, including low frequency electrodes parasitic capacitances).

As already mentioned the aim of the present work is to investigate the effect of CNTs concentration on the electrical properties of PDMS below percolation threshold. Thus, in order to determine if the CNTs concentration is below percolation threshold we plotted the dependence of conductance G (at 0 V and 20 V) and capacitance C (at 0 V) vs CNT concentration in Fig. 2. Both the conductance and the capacitance were found to increase monotonously with CNTs concentration indicating that the percolation threshold has not been exceeded for the CNTs concentrations used in the present work.

The current-voltage characteristics of sample A0.5 (Fig. 3A) that is also representative for sample B0.5, and sample A0.7 that is also representative for sample B0.7, were found to be non-linear exhibiting an asymmetric counterclockwise loop, which means that the loop area is larger in the first quadrant, in both cases. In order to obtain a better insight for the physical mechanism responsible for the non-linear behavior of the current-voltage characteristic, the experimental data of each region (1), (2), (3) and (4) were compared with the hopping law: $J = [\sigma_{hop} \cdot E \cdot \exp(\alpha \cdot E)]$, the Frenkel-Poole law: $J = [\sigma_{FP} \cdot E \cdot \exp(\frac{-\Phi_b + \sqrt{\beta \cdot E}}{kT})]$ and a power law [18]: $J = (\gamma \cdot E^n)$ that depending on the value of n may

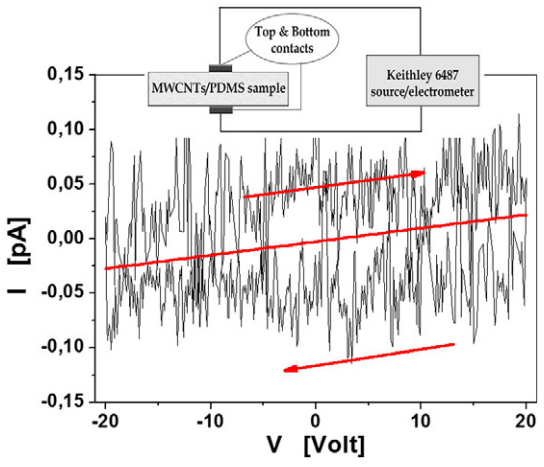

Fig. 1. Current–Voltage (I–V) characteristic curve for the reference material. This I–V characteristic is also representative for samples A0.1 and B0.1 that exhibit high resistivity. The slope of I–V is presented with a red line and it is about 10^{-15} S. The inset picture on top presents the experimental set-up.