Accepted Manuscript

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A temperature sensor based on a MWCNT/SEBS nanocomposite

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Abstract. The fabrication of a temperature sensor based on multi-walled carbon nanotubes (MWCNTs)/styrene-b-(ethylene-co-butylene)-b-styrene (SEBS) triblock copolymer composite is reported. The device was realized by drop casting 10 μl of a MWCNTs dispersion in a toluene solution of SEBS onto gold electrodes fabricated onto a polyimide support. Thermogravimetric and electrical resistance measurements highlighted a good reproducibility of film composition and sensing properties. A negative temperature coefficient with an absolute value comparable to the highest values in metals was measured when a substantial amount of MWCNTs was incorporated into the nanocomposite (40% by weight), and a five-fold increase was observed close to the percolation threshold. Though such sensitivity seems to be partly lost after the first heating, the results allowed us to be optimistic about the feasibility of realizing nanocomposite films with temperature sensitivities comparable to that of common thermistors in the range 20-60 °C.

Keywords. MWCNT, SEBS, polymer nanocomposite, temperature, sensor

1. Introduction

Since their discovery in 1991[1], carbon nanotubes (CNTs) have raised enormous interest for their excellent mechanical, thermal, and electrical properties [2, 3], which make them promising materials for a large number of potential applications [4-12]. Their possible use in the production of nanocomposites is a further reason for interest [12]. Experiments have shown that nanoscale reinforcement of polymers can remarkably change the properties of these materials [13], and the excellent characteristics shown by CNTs suggested that their incorporation into polymeric matrices could allow for the creation of new nanostructured materials characterized by unprecedented properties [12, 14-16]. For example, the tubular molecular structure and the high conductivity of CNTs provide functional materials with a very low percolation threshold [17]. Percolation thresholds as low as 0.002 vol % have been achieved in polymer composites with long flexible ropes of aligned multi-walled carbon nanotubes (MWCNT, [18]). CNTs with either semi-conducting or metallic character have shown a resistivity strictly dependent on temperature and this made us think that such property could be translated into nanocomposites to be used for the fabrication of small-sized temperature sensors.

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However, preparation procedures produce mixtures of nanotubes with different dimensions and chirality, as well as with a variable level of impurities and structural defects. Such variability hampers the comparison of results obtained by different researchers with different samples. Furthermore, the existence of strong secondary interactions between individual nanotubes makes it difficult to separate them from each other and to obtain uniform dispersions at the nanoscale level, which are required for an effective translation of CNT properties to the composite. At present, solution blending is the most used and effective method for preparing CNT nanocomposites [17]. This procedure involves the preparation of a nanotube dispersion in a suitable solvent, the mixing with a polymer or a polymeric solution and the preparation of the film by precipitation, drop casting or spin coating.

Ultrasonication and functionalization or addition of opportune amounts of surfactant to the solvent are widely used to disperse CNTs. Commercially available styrene-b-(ethylene-co-butylene)-b-styrene (SEBS) triblock copolymer, consisting of physically crosslinked polystyrene (PS) hard domains and polybutadiene (PB) soft segments, may be successfully used as a surfactant for CNT exfoliation thanks to the effective interactions between the styrenic moieties of the polymer and the carbon nanotube [19-21].

A possible use of CNTs for the realization of miniaturized temperature sensors has been suggested [22-24], but to the best of our knowledge no paper has been published regarding the preparation of a temperature-sensitive MWCNT nanocomposite.

This work focuses on the development of a thermoresistive MWCNT/SEBS nanocomposite to be used for the realization of miniaturized temperature sensors in the form of thin films to be deposited on different support materials. We believe that this kind of device could find successful application wherever low cost and possibility of tailoring shape and dimensions of the monitored surface are fundamental issues. For example, wireless and disposable temperature sensors working in the 30-40 °C range could be used for the remote monitoring of chronic wounds.

2. Materials and methods.

2.1 Materials

Multiwall carbon nanotubes (MWCNTs, Baytubes C150 P), a generous gift from Bayer Material Science, were used as received. These nanotubes are vapour grown and typically consist of 3–15 graphitic layers wrapped around a hollow 4 nm core. Typical diameters range from 13 to 16 nm, whereas lengths are between 1 and 10 μm. The density is approximately 1.4-1.6 g/cm^3 [25].

Poly(styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS, Europrene Sol TH 212) was supplied by Enichem Elastomeri and used as such. This triblock copolymer (M_w = 65–70 x10^3, M_w/M_n =1.03–1.11) consists of 19% units of styrene, 32.4% units of 1,2 butadiene and 48.6% units of 1,4 butadiene respectively. The –EB–block has a glass transition temperature (T_g) of about -57 °C and a melting temperature (T_m) of about 17 °C, whereas polystyrene blocks have a glass transition temperature of about 80°C [26]. Toluene was supplied by Sigma Aldrich and used without any purification.

2.2 Preparation of the dispersions

A stock solution was prepared by dissolving SEBS (0.4 g) in toluene (100 mL). Aliquots of this solution (3 ml) were poured in vials containing 12 mg of MWCNTs, thus obtaining a 1:1 w/w ratio with SEBS. Uniform dispersions were then obtained by ultrasonicating (UP 400 S, Hielscher) the MWCNTs mixtures for 60 min at full power (50 W) and at a frequency of 30 kHz. The immersion of the vials in a water/ice bath allowed us to minimize the evaporation of toluene during sonication to negligible levels. The resulting dispersions were centrifuged at 4000 rpm for 30 min and then filtered to remove the residual MWCNT agglomerates. The actual MWCNTs/SEBS weight ratio was evaluated by thermogravimetric analysis (TGA). Thermogravimetric scans were carried out by a Mettler Toledo Starc System (TGA/SDTA851^e). The samples were heated from 25 to 600°C at 10°C/min under a nitrogen flow, and from 600 to 900°C under an air flow.

2.3 Fabrication of the sensors

Sensor supports were fabricated by Cad Line (Pisa, Italy) onto a polyimide film (Kapton®, thickness 50 μm). This material was chosen due to chemical inertia and low permeability to water and vapours, which helps in protecting the sensing film. Copper tracks were prepared by photolithography and then electroplated with nickel and gold to fabricate the electrodes (dimensions: length 7 mm, width 1 mm, distance 2 mm; thickness of copper 35 μm, nickel 3.0 μm, gold 1.2 μm). Each support contained two couples of electrodes and so allowed the fabrication of two sensors. A drop (10 μl) of the MWCNT/SEBS dispersion was cast onto each sensor spot and then left to evaporate at room temperature for two hours to fabricate the sensing film. Once dried, the sensing film was protected by gluing a polyimide cover (thickness 25 μm) onto the sensor support under a pressure of 200 GPa for a minute (press model 200M, Collin). A schematic diagram of the sensor is reported in Figure 1. Scanning electron micrographs (SEM) of the sensing film were taken by a Hitachi S3400 microscope.

2.4 Calibration of sensors

The temperature sensors were sandwiched between two aluminium plates heated by two mica plate heaters (RS 615-1700, RS Components). A temperature controller (dTRON 316, Jumo) connected to a J-type thermocouple embedded in one of the plates allowed for a fine regulation (0.1 °C) of the set-point temperature. Sensor resistance was measured by a digital multimeter (U1242A, Agilent).

3. Results and Discussion.

In the fabrication of sensors reproducibility is always a fundamental issue, especially if the production is carried out at prototype level. For this reason, many sensors were produced from different dispersions and characterized. The evaluation of the typical sensor parameters revealed that inter-batch variability was far larger than intra-batch variability, suggesting that preparation of the dispersions more than sensor fabrication was the critical step.

Several authors reported that the preparation of carbon nanotube dispersions was tricky, and stated that reproducibility was an issue but without adding quantitative details [1, 4]. In fact, the efficiency of the ultrasonic processing depends on many parameters, such as sonication conditions (duration, power), solvent and nanotube characteristics [12]. The release of high power over a long time period allows one to untangle more nanotubes but shortens their length, thus reducing the aspect ratio and deteriorating the composite properties. Slight variations in the sonication conditions can significantly affect the conductivity of fibres even when CNTs are from the same batch. For example, fibres prepared with exactly the same tubes and chemicals can exhibit conductivity differences of almost 2 orders of magnitude [27].

The characteristics of the polymer used for the preparation of composites also plays an important role. In our case, the presence of π-electron-rich styrene and butadiene blocks in the macromolecular backbone allows strong interactions between the carbon nanotubes and the polymeric dispersant, which acts as an efficient surfactant for the untangled MWCNTs.

The dispersion preparation procedure was analyzed step by step and improvements were made to reduce variability. An effective refrigeration with a stirred water/ice bath allowed us to limit to about 8°C the increase in temperature over 60 minutes of sonication. At the same time, it also allowed us to decrease the loss of solvent in the absence of a stopper to negligible levels (less than 0.4% in weight). The ultrasonic device was fixed so that its sonotrode could be reproducibly dipped into the dispersion, which was contained every time in vials of the same volume and shape. This solution, together with accurate weighing, allowed us to limit the variability of the fraction of the dispersed nanotubes measured by TGA to 2%. The typical result of a thermogravimetric scan performed on a nanocomposite film obtained from 5 mL of dispersion is reported in Figure 2. It can be seen that the polymer matrix starts degrading at about 405°C, whereas the pyrolysis of the residual carbon nanotubes is activated at 600°C when the purge gas is switched from nitrogen to air. A MWCNT untangling efficiency of about 80-85 % was typically obtained under our conditions when starting with a 1:1 weight ratio between MWCNTs and SEBS.

Figure 3a shows the calibration curves relevant to sensors at their first use produced with three replicate dispersions. Three sensors were prepared with each dispersion and characterized by determining the calibration curve. The response time of the sensors was about 5 seconds. Average values of the electrical resistance were calculated and plotted at each temperature value. Percentage variations of the resistance values were used so that individual differences in the sensor baseline resistance values could be normalized. Standard deviations obtained from three sensors produced with the same dispersion are shown as error bars. The curves show a light deviation from linearity in the 20 – 50°C range (≤ 4% from the best fit line). Even though single sensors have a certain degree of variability, the "average" calibration curves relevant to the three dispersions are quite similar. This was confirmed by the thermogravimetric analyses, which measured a MWCNT weight percentage of 40.7, 41.2 and 42.4 for the dispersions A, B and C respectively, therefore with only a 2% relative standard deviation. Figure 3b shows the calibration curves for three sensors prepared with the dispersion C. Results were quite reproducible, the maximum deviation of sensor resistance from the

average resistance value through the whole range of temperatures was 8%. As expected, inter-batch variability (about 43%) was higher than intra-batch variability (about 8%).

Figure 4 reports a series of five different calibrations performed on the same sensor over a time span of nine months. It is evident that a remarkable change in sensitivity occurred the first time the sensor was used and then its characteristics settled down and remained stable for 9 months. The same behaviour was observed in all the sensors. The typical sensitivity observed at 35°C in newly-made sensors was -20 ± 5 Ω/°C, which became $-3 \pm 0,4$ Ω/°C after use. The first value corresponds to a negative temperature coefficient of about $-0,005$ K^{-1}, whose absolute value is comparable to the highest values found in metals ($0,0037 - 0,006$ K^{-1}, $0,00385$ K^{-1} for a Pt_{100} sensor) and is about an order of magnitude lower than common thermistors ($-0,044$ K^{-1}). After use, the temperature coefficient dropped to values of about $-0,0006$ K^{-1}, whose absolute value is close to the temperature coefficient of amorphous carbon ($0,0005$ K^{-1}). This loss of sensitivity after heating up to 55-60°C could be due to a modification of the MWCNTs phase dispersion within the SEBS phase.

We hypothesize that the sensor resistance results from three contributions:

$$R_f = R_{MWCNT} + R_{IT} + R_c \qquad (1)$$

where R_{MWCNT}, R_{IT} ed R_c are the intrinsic MWCNT resistance, the intertube resistance and the contact resistance among MWCNTs and gold electrodes respectively. We assume that this last contribution can be neglected compared to the others. Electrical conductance is allowed in MWCNTs by delocalized π electrons, which hop between neighbouring MWCNTs thanks to the tunnel effect. A semiconducting behaviour was observed in vertically aligned films of MWCNTs which is compatible with our observations [28]. A temperature increase thermally excites electrons into the conduction band and favours intertube mobility, leading to lower resistances. In the fresh composite, MWCNTs are distributed in the solid thermoplastic matrix to form a network of disentangled conducting regions, which provide temperature coefficients comparable to metals. The heating up to temperatures higher than 40-50°C likely alters the morphology of the SEBS matrix, as this polymer shows a small but significant percentage of crystalline phase which melts with a broad endotherm just above room temperature [29]. This phenomenon may increase the mobility of carbon nanotubes within the polymer matrix and allow their reorganization into a more connected network, thus conferring to the system a higher conductivity but less sensitivity towards temperature variations.

Dispersions with different MWCNT weight percentages were prepared to find the percolation threshold. In all the samples, the effective amount of MWCNT incorporated within the polymer was evaluated by TGA. Some authors affirm that a slight aggregation produces a lower percolation threshold by increasing the local interactions between nanotubes [30, 31]. In any case, the intertube contribution to the overall resistance should be enhanced close to the percolation threshold. The orientation of the nanotubes in the polymer matrix has a profound effect on both electrical conductivity and percolation threshold. In composites with highly aligned nanotubes, a reduced number of contacts between the tubes results in an increased electrical conductivity and in a higher percolation threshold compared to composites with randomly oriented

nanotubes. Since no care was taken to align MWCNT when preparing the dispersion, we expected nanotubes to be randomly oriented in our composites. This was confirmed by scanning electron microscopy (Fig. 5). The electrical conductivities of nanocomposite films prepared with the different dispersions were measured at room temperature (25°C) and compared (Fig. 6). As expected, a monotonic increase of the conductivity values was observed when increasing the MWCNT content. A step increase in resistance was observed in correspondence to the percolation threshold (Fig. 6a). In this condition, the electrical conductivity follows a power law [32-33]:

$$\sigma_c = \alpha\,(v - v_c)^{\beta} \qquad\qquad (2)$$

where σ_c is the composite conductivity, v is the MWCNT volume fraction, v_c is the percolation threshold, α is a constant and β is the critical exponent. Since the densities of the polymer and the MWCNT are similar (1.2 and 1.5 g/cm^3 respectively), the volume fraction v of the MWCNT can be approximated by the mass fraction m. Figure 6b shows that the MWCNT/SEBS conductivity agrees well with the percolation behaviour modelled by Eq. 2. The straight line corresponding to a percolation threshold m_c= 11.8 %, with $\alpha = 3.2$ and $\beta = 2.0$ provides an excellent fit to the data, with a correlation factor of 0.993. The value of the critical exponent is only related to the dimensionality of the system, and a value close to the theoretical value 1.9 indicated the formation of a 3D percolative network. Figure 7 shows the calibration curves of two sensors fabricated with dispersions containing MWCNT weight percentages of 12.5% and 35% respectively. The sensor fabricated with a MWCNT content close to the percolation threshold had a sensitivity about five times higher than the other and a temperature coefficient of -0,028 K^{-1}, which is halfway between a metal and a thermistor. As expected, decreasing the amount of MWCNTs down to the percolation threshold is an effective way to enhance sensitivity. In practical applications, a high sensor resistance leads to a low power consumption and reduced self-heating effect during the measurements. On the other hand, a more complex and expensive circuitry may be needed to acquire sensor data, which is not advisable in cases like wearable body sensors.

4. Conclusions

MWCNT/SEBS nanocomposite films were prepared with a variable content of carbon nanotubes. Thermogravimetric analyses demonstrated that the procedure for the preparation of the dispersions was reproducible (coefficient of variation about 2%). The sensing properties of the films were also reasonably reproducible. In three sensors prepared from the same dispersion, the maximum deviation of electrical resistance from the average resistance value through the whole range of temperatures was 8%. As expected, inter-batch variability was higher (about 43%). A negative temperature coefficient was observed when the nanocomposite film contained a substantial amount of MWCNTs (40% by weight), whose absolute value is comparable to the highest values found in metals. Under these conditions, the temperature-sensing properties of the film were directly related to the MWCNTs properties, confirming the semiconductor-like behaviour observed by several authors. The formation of a three-dimensional percolative network was hypothesized

when the amount of MWCNTs approached the percolation threshold, which was calculated to be 11.8 % by weight. A five-fold increase in sensitivity was obtained in this case.

Though improvable, these results show that the fabrication of MWCNT nanocomposite temperature sensors with a temperature coefficient comparable to that of common thermistors may be possible. Future work will involve the optimization of the dispersion preparation procedure (to lower the percolation threshold and improve sensitivity) and a testing of other polymers with a larger dependence of their properties from temperature in the range of interest.

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Captions

Figure 1. Schematic diagram of the sensor: a) section, b) top view.

Figure 2. Thermogravimetric scan of a MWCNT/SEBS nanocomposite with a nanotube weight percentage of about 40%.

Figure 3. Sensor calibration curves: a) sensors fabricated from three dispersions with a nanotube weight percentage of about 40% at their first use, b) sensors fabricated from the same dispersion. Percentage and absolute variations of resistances versus temperature are plotted respectively.

Figure 4. Repeatability of a sensor containing a nanotube weight percentage of 35%. Percentage variations of the baseline resistance values (25°C) with temperature at different times after fabrication: $t_0 = 0$ days, $t_1 = 3$ days, $t_2 = 2$ weeks, $t_3 = 3$ months, $t_4 = 9$ months.

Figure 5. Scanning electron micrograph of a nanocomposite film containing a percentage of 41.5 w/w of MWCNTs.

Figure 6. Room temperature electrical conductivity of MWCNT/SEBS nanocomposites versus nanotube loading showing a typical percolation behaviour (a) and versus reduced mass fraction (b).

Figure 7. Percentage variation of resistance versus temperature in sensors with MWCNT weight percentages of 12.5% and 35%.

Vitae

Giusy Matzeu was born in 1985. She earned her B. Sc. in Biomedical Engineering from University of Cagliari (2007) and M. Sc. in Biomedical Engineering from University of Pisa (2010). At present, she is a Ph. D. student in Chemistry into the ASG Group, Dublin City University, under the supervision of Professor Dermot Diamond and Dr. Claudio Zuliani. Her research interests spread from electrochemistry to chemical sensors for environmental and biological applications.

Andrea Pucci received his M.S. in Chemistry (1999) and his Ph.D. (2003) in Chemical Science from the University of Pisa. He is currently a research assistant and contract professor of Chemistry of Nanotechnology in the Department of Chemistry and Industrial Chemistry at the University of Pisa. He was visiting scientist at ETH in Zurich, at Centre of Molecular and Macromolecular Studies of the Polish Academy of Science and at University of Manchester. His research interests focus on the preparation of new functional macromolecules including the development of field responsive thermoplastic materials, ion conductive polymers for fuel cells and polymeric dispersants for lubricants.

Stefania Savi received her M.S. in Chemistry (2000) from the University of Pisa. She is currently a degree technician at the Department of Chemistry and Industrial Chemistry at the University of Pisa. She is primarily involved in the preparation and characterization of polymer blends and composites from post-consumer polymers or renewable sources containing vegetable fibres or fillers of natural origin.

Marco Romanelli, MD PhD, is a Board certified, Consultant Dermatologist who received a PhD in Experimental Dermatology from the University of Naples. He is currently Assistant Professor at the Department of Dermatology, University of Pisa and Director of the Wound Healing Research Unit. He leads a research group actively involved in the wound assessment using physical measurements, in the management of inflammatory ulcers, and in the evaluation of biochemical markers related to wound healing.

Fabio Di Francesco graduated in physics (1994) and received his Ph.D. (2000) at the University of Pisa. In 2000-2006 he has been a researcher of the Institute of Clinical Physiology (National Research Council). Since 2006, he is researcher at the Department of Chemistry and Industrial Chemistry of the University of Pisa. At present he is developing non invasive diagnostic and patient monitoring tools along two research lines: identification of chemical markers in body fluids (breath, sweat, saliva) and development of sensors for real time measurements.

Highlights

A multi-walled carbon nanotubes (MWCNTs)/styrene-b-(ethylene-co-butylene)-b-styrene (SEBS) triblock copolymer composite was used to fabricate a temperature sensor.
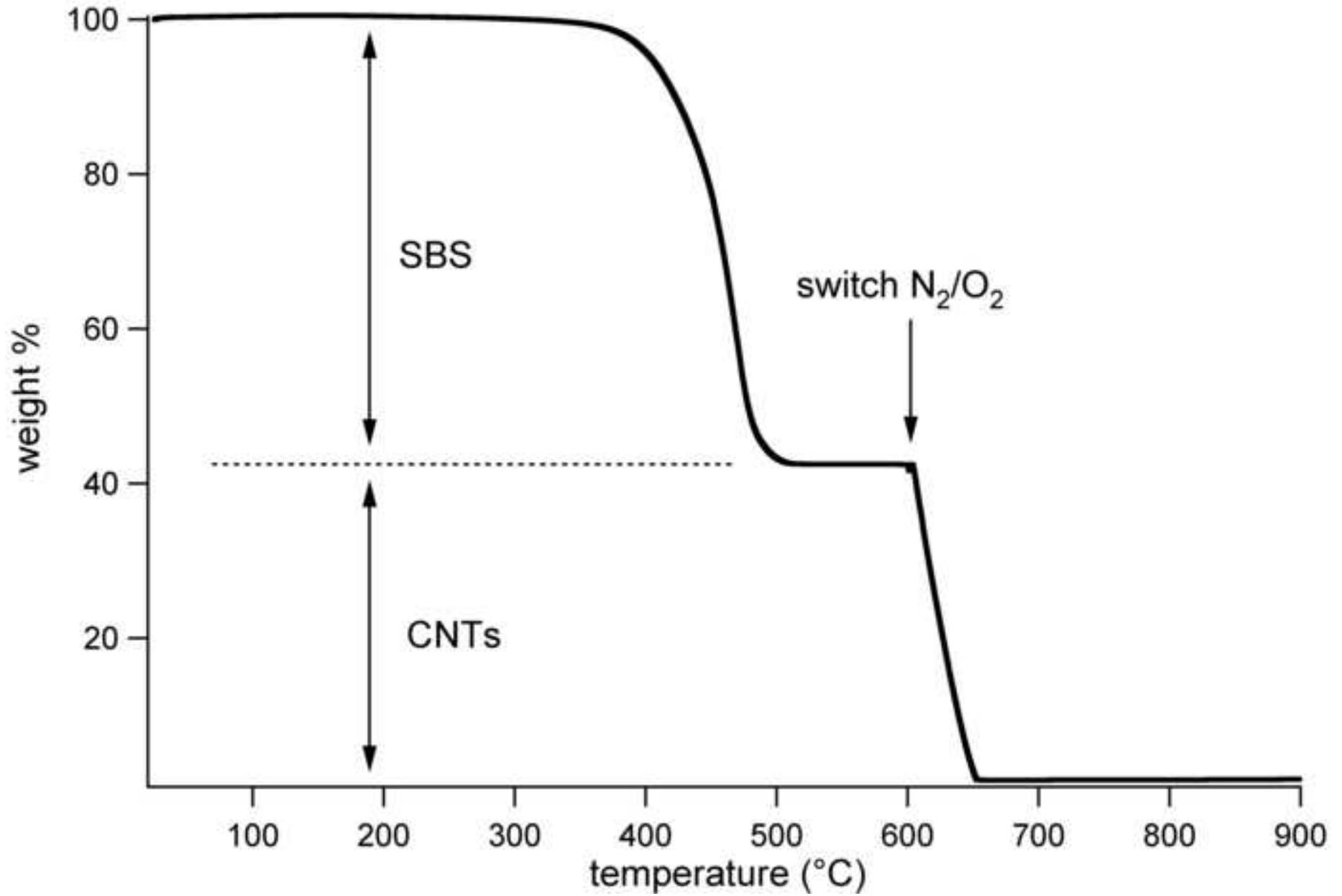
Negative temperature coefficients with absolute values comparable to the highest values in metals were measured with substantial amounts of MWCNTs in the composite (40% by weight)

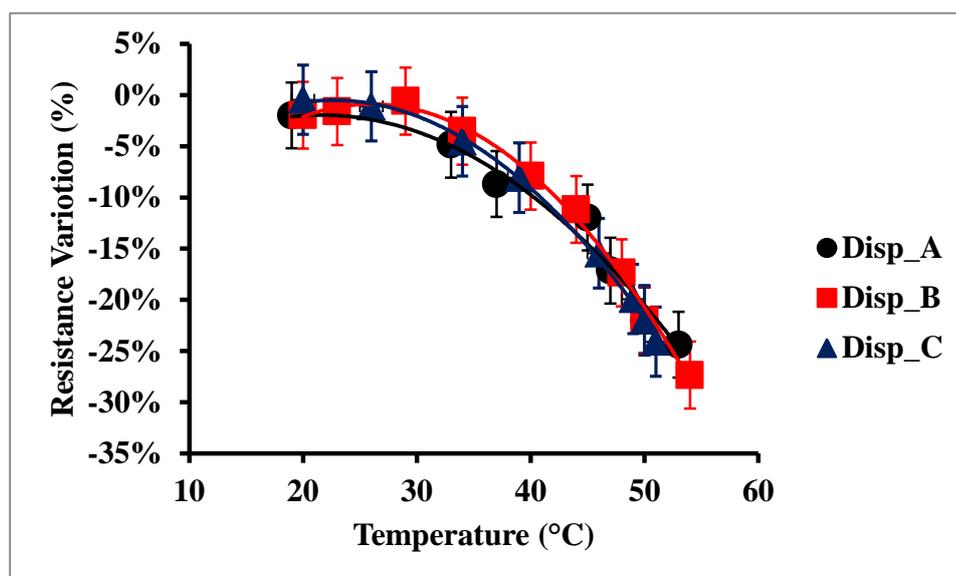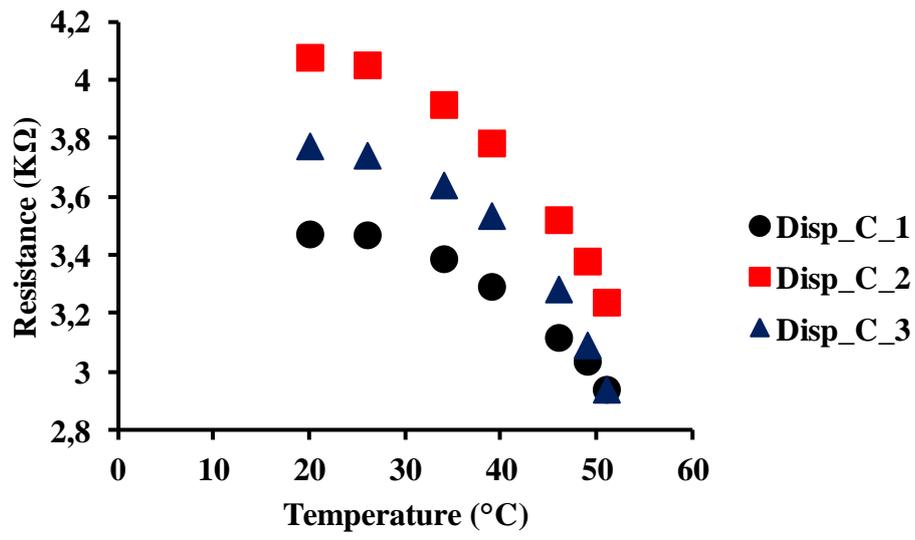A five-fold increase of sensitivity was observed close to the percolation threshold
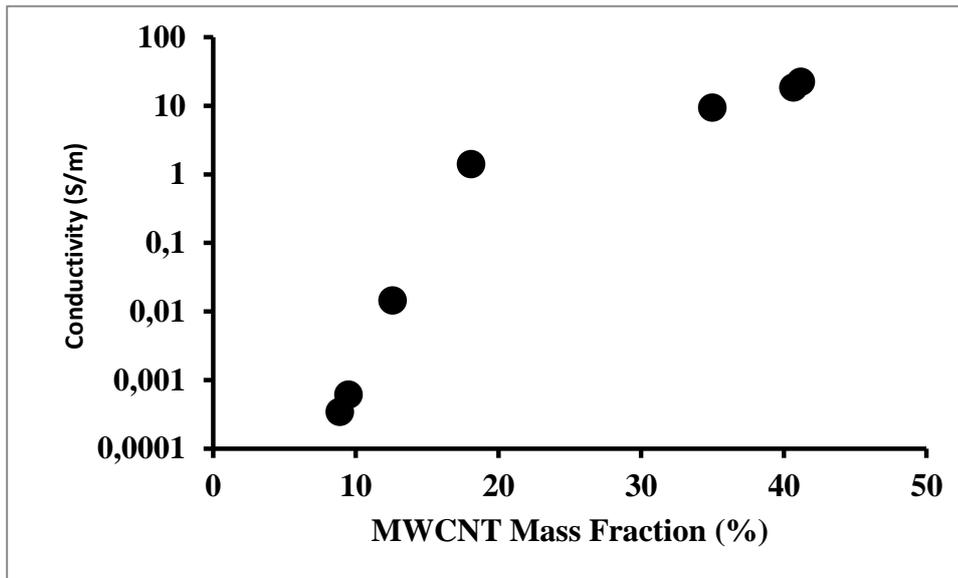
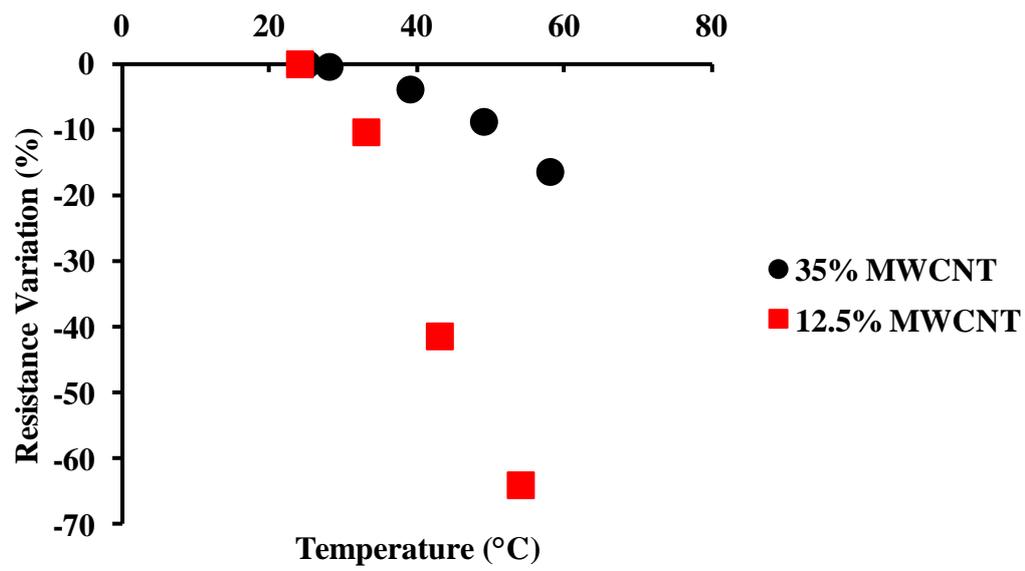**Figure(s)**

5 mm   2 mm

a)

7 mm

20 mm

20 mm

b)
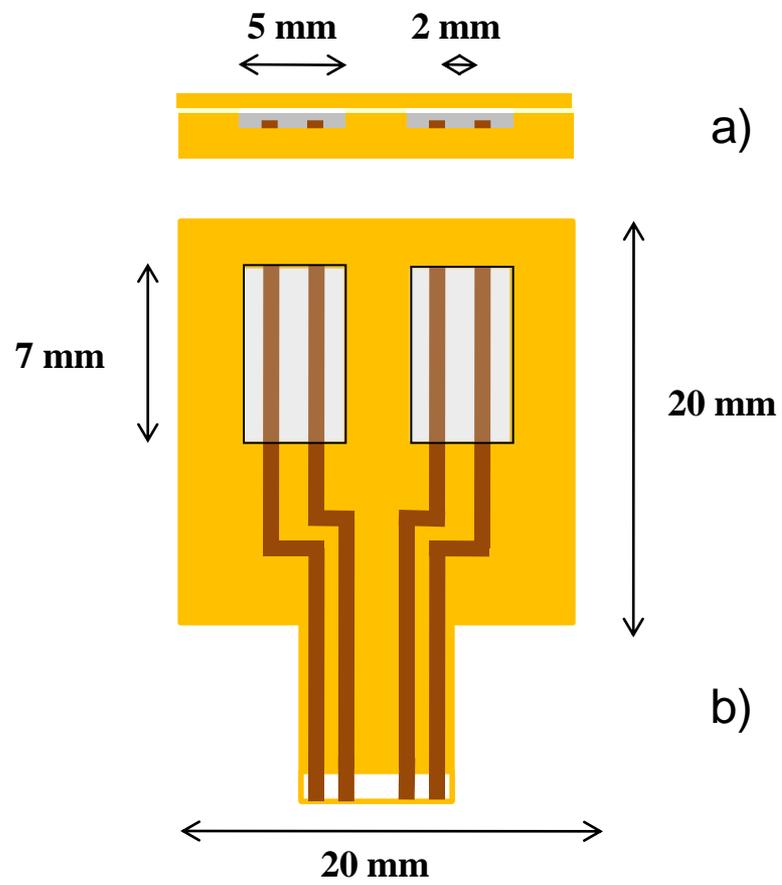
Figure 3a

Figure 3b
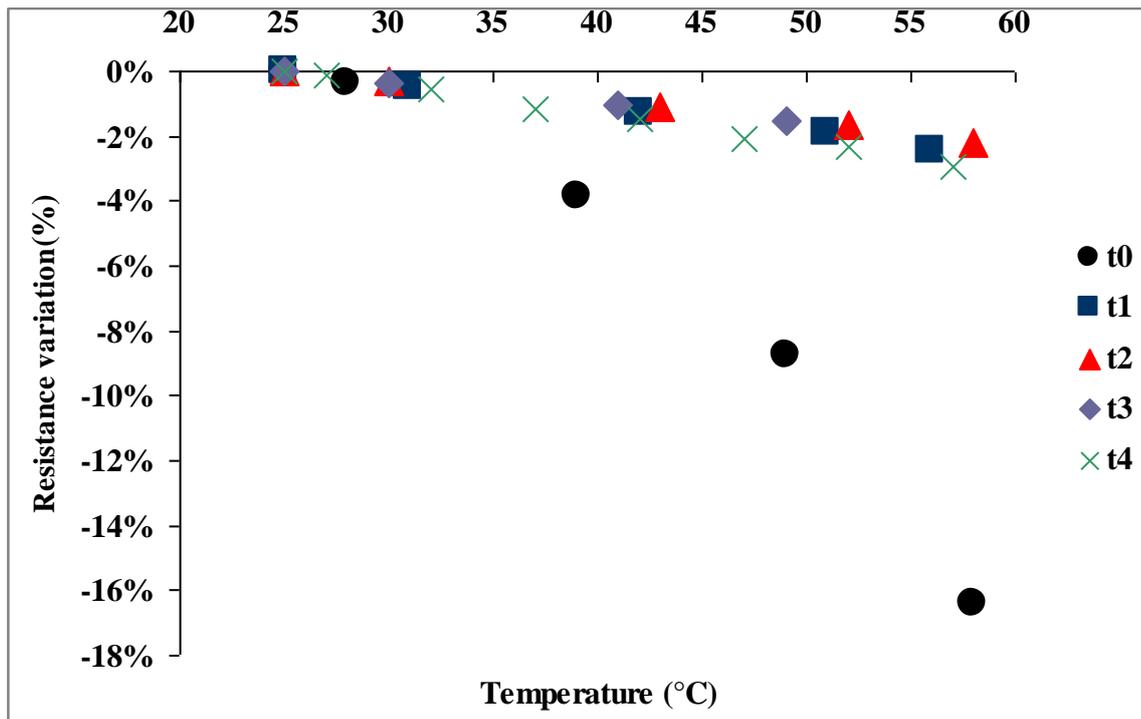
Figure 4
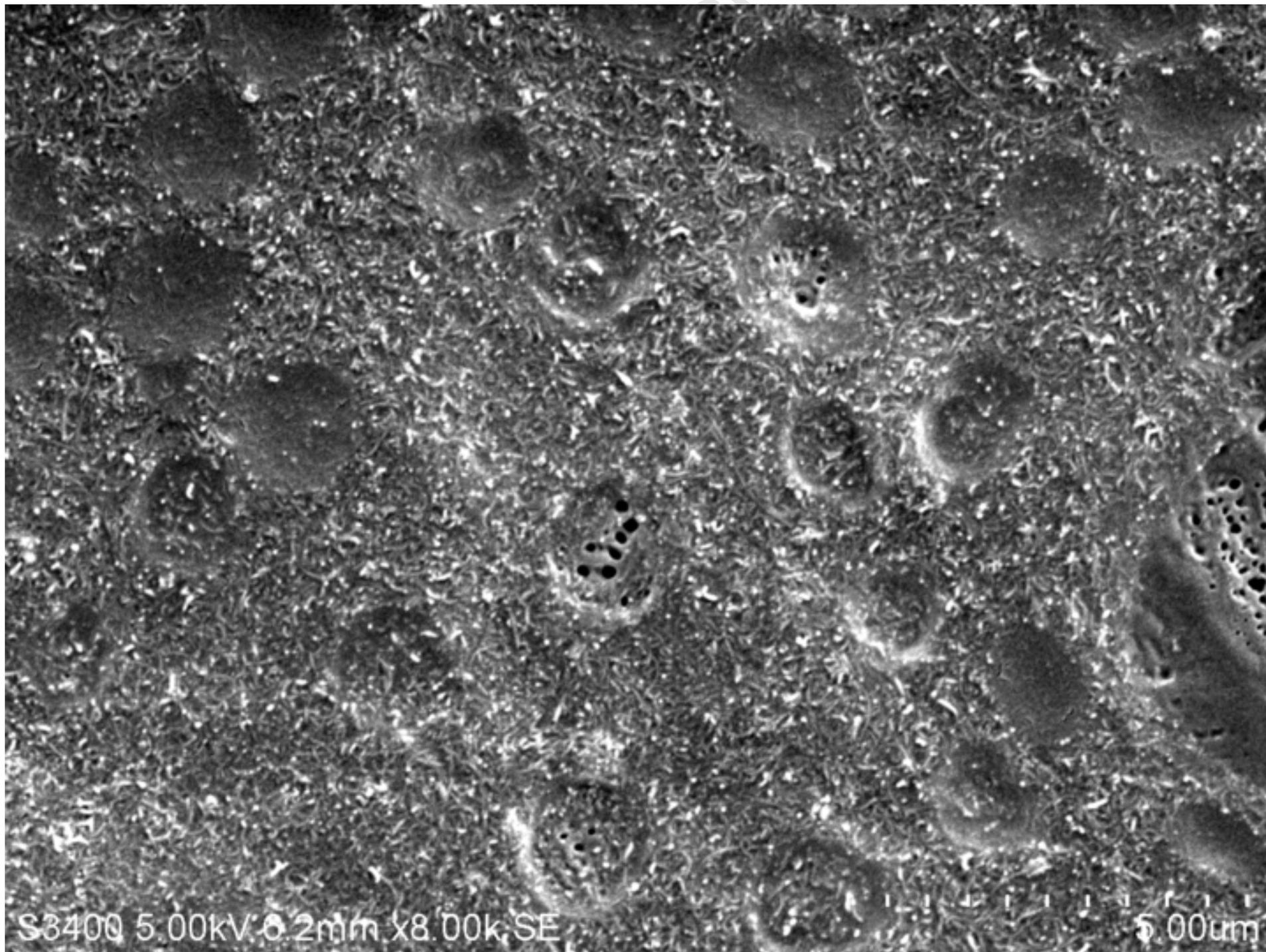
Figure 6a

Figure 6b

Figure 7