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Influence of electrical stress on printed polymer resistors filled with carbon nanomaterials*

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Superior electrical properties of carbon nanotubes were utilized by the authors in the fabrication of printed resistors. In common applications such as electrodes or sensors, only basic electrical and mechanical properties are investigated, leaving aside other key parameters related to the stability and reliability of particular elements. In this paper we present experimental results on the properties of printed resistive layers. One of the most important issues is their stability under high currents creating excessive thermal stresses. In order to investigate such behavior, a high direct current stress test was performed along with the observation of temperature distribution that allowed us to gain a fundamental insight into the electrical behavior at such operating conditions. These experiments allowed us to observe parametric failure or catastrophic damage that occurred under excessive supply parameters. Electrical parameters of all investigated samples remained stable after applying currents inducing an increase in temperature up to 130 °C and 200 °C. For selected samples, catastrophic failure was observed at the current values inducing temperature above 220 °C and 300 °C but in all cases the failure was related to the damage of PET or alumina substrate. Additional experiments were carried out with short high voltage pulse stresses. Printed resistors filled with nanomaterials sustained similar voltage levels (up to 750 V) without changing their parameters, while commonly used graphite filled polymer resistors changed their resistance value.

Keywords: *carbon nanotubes; printed electronics; polymer resistors; high current stress*

1. Introduction

Stability of resistance under different electrical and non electrical stresses is one of the most important resistor properties. Besides mechanical and thermal stress, along with humidity influence, electrical stress is the main factor that has major contribution to the stability of resistance. In the field of printed electronics where usually elastic polymer substrates are used, the devices are subjected to high voltage electrical stress, namely to electrostatic discharge [1, 2]. On the other hand, supply parameters in every day use may vary in value, both for expected or unknown origins. In certain cases there might be a need to supply electronic devices with higher current for short periods of time, and still to maintain primary electrical parameters of the elements. This is very important in case of elements with small dimensions such as printed electronic elements, where the thickness of printed layers can range from few to dozens of micrometers.

In order to investigate the behavior of printed thick film resistors under excessive current values, especially at high current densities, a high direct current stress was applied to the printed polymer-nanotube composite resistors on elastic PET and rigid alumina substrates. Along with high current stress, the observation of temperature distribution was also conducted to detect overheating of the structures, which is considered to be the main failure mechanism of resistors under excessive supply conditions [3]. Resistors were also subjected to high voltage pulse stresses from 250 V to 1000 V. Carbon nanotubes are known to sustain high current densities [4, 5], and therefore the idea of eval-

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uating composite layers filled with CNTs under the influence of high current stresses was proposed.

2. Experimental methods and results

Investigated resistors were made by screen printing technique from the developed polymer-nanotube compositions on elastic PET foil and rigid ceramic alumina substrates. After printing the samples were thermally cured to obtain final layers.

2.1. Materials preparation

The used compositions consisted of poly(methyl methacrylate) (PMMA), organic solvent and carbon nanotubes (CNTs) as a functional conductive phase. The materials used for printed electronics should be low cost and easy to obtain because of their use in disposable and large-area structures. Therefore, as the main material, as prepared multiwalled carbon nanotubes (MWCNTs) synthesized by catalytic chemical vapor deposition method (CCVD) were used. CCVD method is commonly used for large scale mass production of MWCNTs. Material prepared in this way usually contains other carbon structures and residues of metal catalyst, what causes the low purity of CNT load (less than 95 %), but it is more than ten times less expensive than segregated and purified CNTs. The morphology of used MWCNTs was evaluated by HRSEM (Fig. 1), which allowed us to characterize the diameter and the length to be 10 – 40 nm and 0.5 – 5 μm, respectively, though longer structures were also observed.

Additionally, segregated doublewalled carbon nanotubes (DWCNTs) with the diameter of 2 – 4 nm, length up to 50 μm and purity up to 60 % were used. The observations proved that this material was heavily agglomerated, with nanotubes packed in long stripes. Another evaluated material was graphite platelet nanofibers (GPNs) with similar properties as those of MWCNTs, with the diameter of 50 – 250 nm, length of 0.5 – 5 μm and purity above 99 %. All materials were subjected to HRSEM observations to evaluate their morphology. Results of these observations are presented in Fig. 1. For synthesis of polymer resin, poly (methyl methacrylate) polymer powder with Mw ∼ 350 000 from Sigma-Aldrich was used and dissolved in diethylene glycol n-butyl ether acetate organic solvent. Dissolving process was conducted with magnetic blade mixer for 48 h at 40 °C. Vehicle concentrations (8 – 12 wt.%) were selected with respect to rheology of the compositions, and electrical properties of the final composite layers.

To obtain final compositions, CNTs and GPNs were dispersed in polymer resin. Electrical and optical properties were controlled by the amount of CNTs in the compositions. Nanomaterials were added to selected resins and mixed in an agate mortar at the first phase of initial homogenization. Diluted samples were also ultrasonically homogenized in IS-1K ultrasonic bath for 30 minutes. The last stage was three-roll-milling to break the remaining agglomerates, carried out in an Exakt tree-roll-mill with silicon carbide rolls, and 5 μm gap between the rolls.

The final layers were fabricated from the compositions deposited on elastic polyester substrate by screen printing technique. The layers were cured at 130 °C for 15 min to evaporate the organic solvent. Additional silver contacts were also screen printed to allow repeatable resistance measurements. Fig. 2 presents a macroscopic photograph of the samples made from compositions containing 1 wt.% of DWCNTs and 3 wt.% MWCNTs.

To compare the obtained results with commonly used materials for such elements, resistors printed from Acheson PF407a graphite paste as well as ITO transparent electrodes were also evaluated.

2.2. Experimental procedures

Electrical properties of final layers were evaluated after printing and curing the compositions. All samples were electrically conductive, with resistance values ranging from 10^1 Ω/□ to 10^5 Ω/□. Moreover, the layers with low amount of DWCNTs were optically transparent, with transmittance up to 65 %.

For the primary test evaluating the change in resistance under high currents, a specially designed laboratory stand was used, allowing the supply with

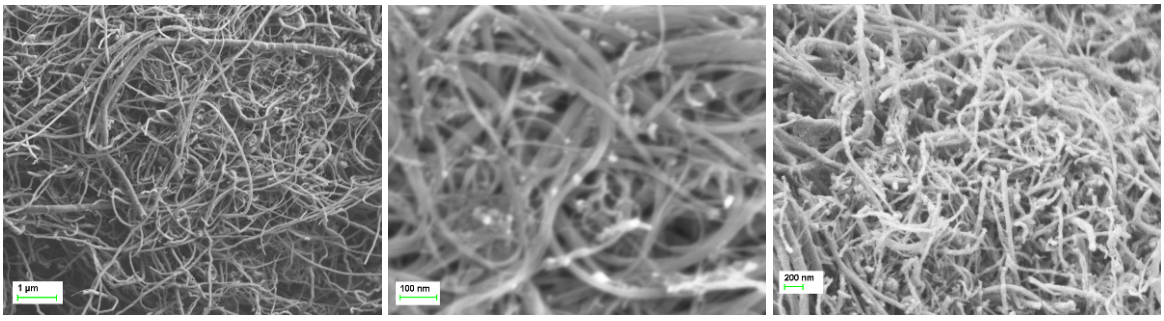

Fig. 1. HRSEM micrographs of used carbon nanomaterials: MWCNTs (left), DWCNTs (center), GPNs (right).

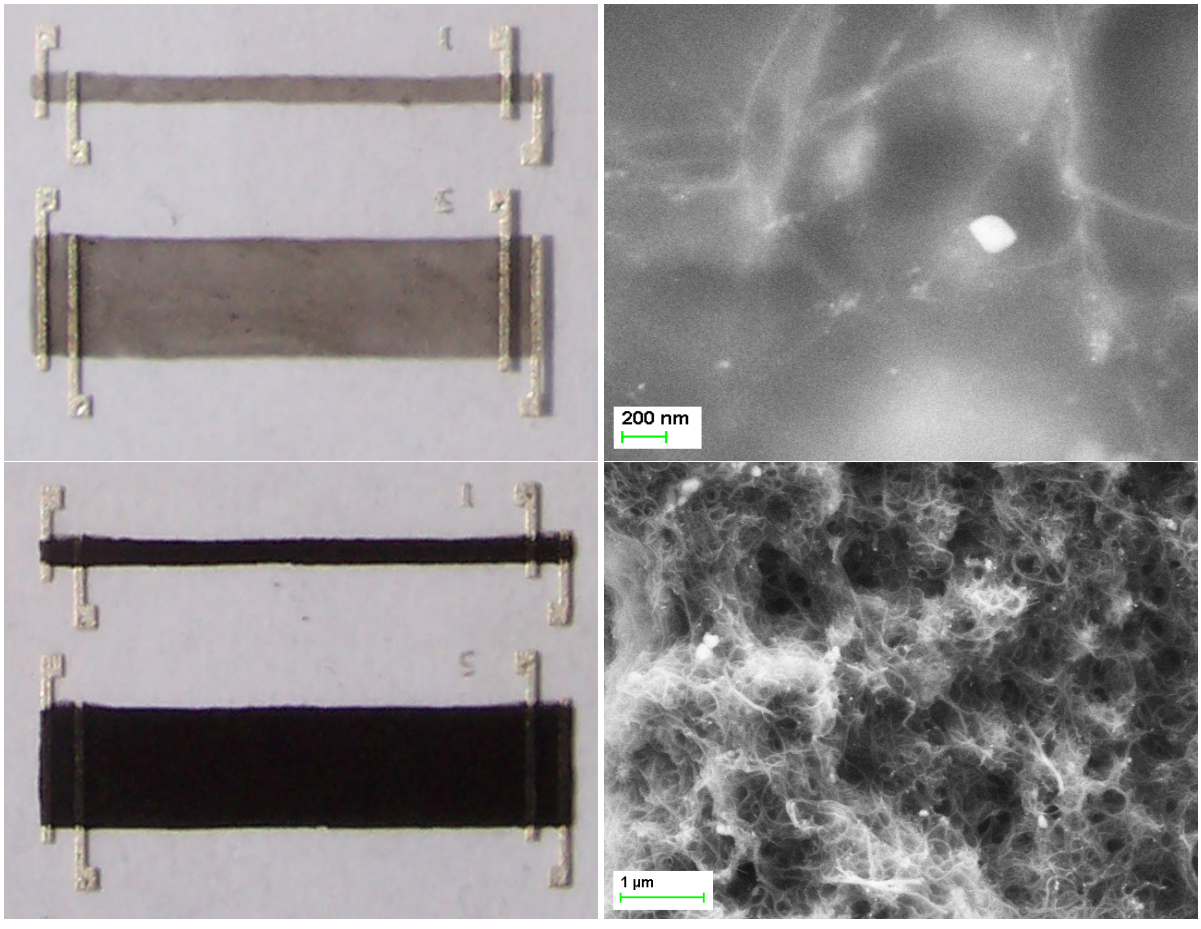

Fig. 2. Screen printed and cured compositions with 1 wt.% DWCNT (top) and 3 wt.% MWCNT (bottom).

adjustable DC voltage up to 200 V. Voltage and current measurements were carried out with Escort 3145A laboratory multimeters. The observations of temperature distribution were made with VIGOcam v50, allowing to measure the changes in temperatures up to 350 °C.

Resistance stability under high current load was determined basing on the relative changes in resistance of the layers according to the formula:

$$\frac{\Delta R}{R_0} = \frac{(R_{load} - R_0)}{R_0} \tag{1}$$

where R_{load} is the sample resistance after current load, measured at 20 °C, R_0 is the primary sample resistance.

Usually, in such experiments pulsed measurement techniques are used with single pulses [6] and multiple pulses [7]. In our experiment, a constant value of high current load was provided on the tested samples. Such current load first induced slow increase of temperature up to 130 °C (primary curing temperature) and after cooling down to room temperature, fast increase up to 200 °C with short time of current rise. Such procedure makes possible to partially eliminate long time exposure to high temperatures, but allows one to observe the failures related to electrical breakdown and fast overheating.

Second type of the tests consisted in subjecting the evaluated samples to high voltage pulses generated from discharging capacitor stack. Depending on resistors value (from 500 Ω to 1 kΩ) the time constant of discharging pulse was around 30 ms.

2.3. Results and discussion

First set of the samples made of PMMA vehicle and 21 wt.% of GPNs, 3 wt.% of MWCNTs and PF407 a graphite paste was printed on an alumina substrate, and tested for resistance stability under changing supply current. Resistance of samples was measured for the samples treated with three current values: the one that was not inducing any increase of temperature, and with the currents causing an increase of temperature up to 130 °C and around 200 °C. Resistance changes in function of induced temperature are presented in Fig. 3, and relative changes in resistance are presented in Table 1. Resistive layers filled both with carbon nanotubes and graphite nanofibers remained stable up to 130 °C. Major change in resistance was noted above this temperature. This was due to additional hardening processes that were caused by higher values of temperature than in the primary curing process. This is a known case for carbon-polyesterimide resistors where a further polycondensation process occurs [8] which was also observed for PF407a layers. In the case of CNT and

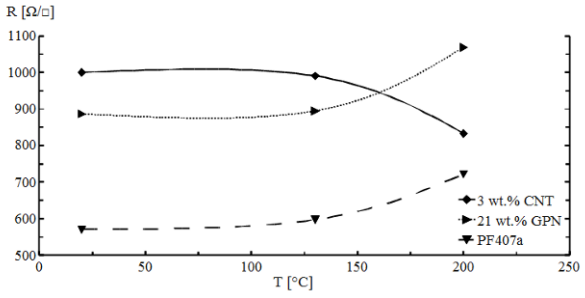

Fig. 3. Values of resistance measured at 20 °C for the samples treated with the currents inducing an increase of temperature.

GPN filled resistors it was related to further evaporation of solvent remained in the cured layers. Above 200 °C, the composite layers filled with carbon nanotubes decreased their resistance what was also previously observed during other thermal experiments with these materials [9]. The increase of resistance in graphite nanofibers filled composites might be related to higher amount of filler in the composite (21 wt.%). With an increase of temperature more local microcracks in polymer base were formed decreasing the number of active conducting paths which contributed to the increase of resistance. Additionally the same type of samples was subjected to the current, whose value was gradually increased and during that process, the measurements of resistance were made (without cooling). The goal was to observe the changes in resistance under the current load and to register the failure points at which the resistors would be burned due to the influence of high temperature. Changes in resistance in function of temperature for 21 wt.% GPNs layers, 3 wt.% MWCNTs layers and PF407a graphite paste are presented in Fig. 4.

Unfortunately, in both cases (CNT and GPN) during the measurements substrate, failures occurred around 300 °C, what is presented in Fig. 5. Rapid increase of the layer temperature caused the high gradient of temperature near the region of the tested resistors. The substrate was unable to dissipate the induced thermal energy, which resulted in the rapid increase of mechanical stresses within the substrate, causing it to brake. Failure of the substrate occurred along the line of resistors, as

Table 1. Resistance stability after high current load.

Stress temperature	$\Delta R/R_0$ for 21 wt.% GPNs	$\Delta R/R_0$ for 3 wt.% MWCNTs	$\Delta R/R_0$ for PF407a
130 °C	0.01	−0.01	0.05
200 °C	0.21	−0.17	0.27

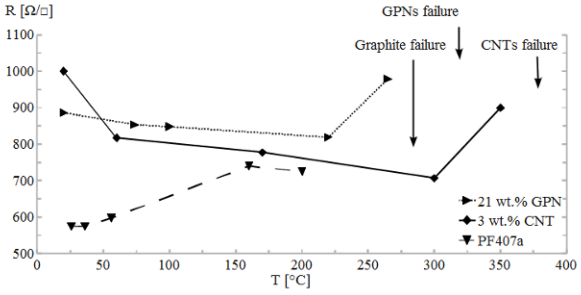

Fig. 4. Changes in resistance in function of temperature for GPNs, MWCNTs and graphite resistive layers.

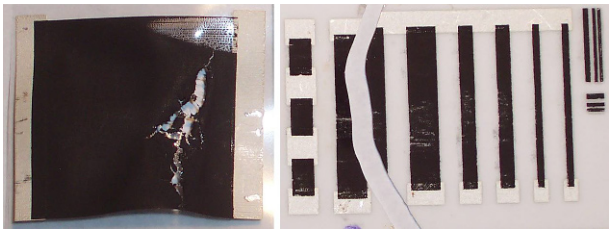

Fig. 5. Micrograph presenting substrate failure for 3 wt.% MWCNTs samples on PET (left) and alumina (right).

in that direction most of the thermal stresses were generated. In all cases this had an influence on the printed resistors, as the thick polymer resistors could not withstand the strong strains caused by substrate failure. In both cases (CNT and GPN) large parts of resistors remained, leaving most of the primary resistor, so we only noted discrete changes in resistance.

For the samples filled with GNPs the major increase of resistance was noted above 250 °C and for the samples filled with CNTs such increase was noted above 320 °C, but it was related to the substrate failure and change in sample geometry. Nevertheless, after substrate failure, the current value was still increasing linearly and the samples were monitored for the increase of temperature. Burnout of GPNs layer was observed around 320 °C. For CNTs sample, the measurement was more difficult as the layer had been destroyed after few seconds when the camera noted 350 °C which was the limit value for that device. We can only estimate that the samples sustained the temperature around 370 °C induced by 250 mA current. Also the samples filled with 3 wt.% CNTs were printed on the polyester substrate and treated in the same way with linearly increasing current. Around 220 °C failure of polyester substrate was observed (Fig. 5), but the resistive layer remained electrically conductive, changing its resistance value by few percent. Second type of tested samples was a composition of the same PMMA vehicle filled with DWCNTs, screen printed on elastic transparent polyester substrate, and cured in the same conditions. The obtained sample was optically transparent with the transmittance around 65 % and sheet resistance of 27 kΩ/□. Similar type of electrode was used previously by the authors for the fabrication of electroluminescent structures and fotovoltaic devices [10, 11]. In this case high resistance of the layers was limiting the supplying current, therefore only temperatures around 130 °C were possible to obtain during the current induced heating of the layers.

The resistance of DWCNTs samples was measured at a gradually increasing current (without cooling). The goal was to observe the changes in resistance under current load and to register possible failure (what wasn't the case for those samples). The changes in resistance in function of temperature for 1 wt.% DWCNTs layers are presented in Fig. 6. In the same figure thermographs for

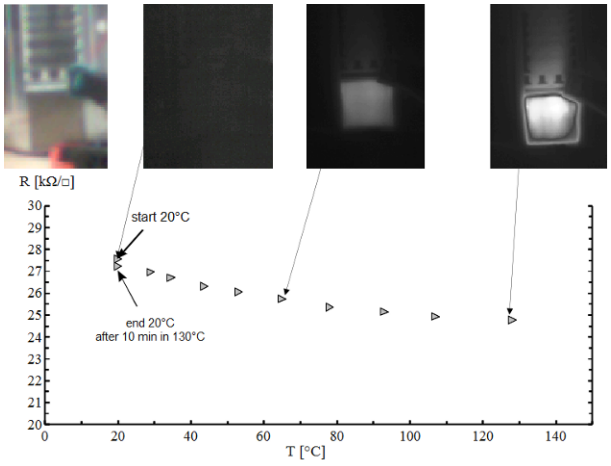

Fig. 6. Changes in resistance in function of temperature for DWCNTs filled resistive layers.

Table 2. Resistance change for printed resistors after one and five HV pulses.

[V]	250	500	750	1000
MWCNTs 3 wt.% [Ω] – initial 738.8 Ω				
1st	738.5	739.2	742.2	747.8
5th	738.5	738.9	738.6	802
GPNs 21 wt.% [Ω] – initial 695.6 Ω				
1st	696.2	696.2	697.8	701.7
5th	696.3	696	696.5	698.9
PF407a [Ω] – initial 594.6 Ω				
1st	594.4	595	594.4	594.6
5th	594.7	594.7	594.4	594.6

selected temperatures are also presented. Optical transmittance in visual range observed with naked eye did not change during the whole experiment. After 10 min exposure to the current induced temperature of 130 °C the samples were cooled down to 20 °C and the resistance was measured. Only 1.2 % change in resistance, calculated with $\Delta R/R_0$ formula, was noted.

In similar way ITO transparent electrodes sputtered on PET foil were tested. Unfortunately, it turned out that thin ITO electrodes could not sustain even remarkably lower currents that the nanotube electrodes did. The highest current value observed for ITO electrodes was below 1 mA which induced a temporary increase of temperature to 28 °C. For the second time the composite layers with CNTs were outperforming ITO as transparent electrodes. Other experiments done by the authors proved that the composite layers with carbon nanotubes were more durable under cyclical bending tests than ITO electrodes on elastic substrates [12].

Finally high voltage pulse tests were carried out. The measurements were conducted at different values of voltage, and the resistance of the layers was measured before shocks, after one shock and after five shocks. Detailed values of resistance change are presented in Table 2.

It can be observed that no major increase in resistance was noted for all samples. Only resistors with MWCNT's showed 7 % growth of resistance after five pulses with the amplitude of 1000 V. Though MWCNT's resistors showed a change in resistance, they also sustained the highest voltage among all the samples. While the graphite resistors were destroyed with 1500 V pulse, the nanotube resistors were still conductive but increased their resistance by above 50 %, and only 2000 V pulse created there destructive short circuit.

3. Conclusions

The high current behavior of printed polymer resistors filled with carbon nanotubes and nanofibers on alumina and elastic polyester substrates has been investigated. A high current load along with pulse stress test were applied to the tested samples. The supplied current load induced an increase of temperature up to 130 °C, 200 °C and above 350 °C. Such procedure allowed us to observe the failures caused by electrical breakdown and fast overheating. Investigated samples filled with CNTs sustained the currents inducing 130 °C for a period of few minutes with negligible change in resistance (less than 2 %). Composite layers with high amount of multiwalled nanotubes and nanofibers can be used as elastic thick film heaters. This type of resistors was able to sustain induced temperatures above 350 °C which resulted in substrate failure caused by thermal stresses in the substrate. These materials might be used in fabrication

of high power printed and elastic resistors but also for ohmic contacts in printed and elastic electronics. Investigated transparent electrodes filled with doublewalled nanotubes might be used as transparent heaters or infrared emitters optically transparent in visible wavelength range.

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