Influence of temperature and humidity on resistance of carbon nanotube based coatings

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1 Abstract

In this work multi walled and single walled carbon nanotube (CNT) based coatings are tested on their temperature dependent resistance. Both CNT-types were applied as CNT-dispersant coating and as CNT-silicone-compound. To clarify a possible error source the influence of humidity on resistance at 20 °C is determined. For the multi walled CNT-silicone-compound the influence of filler content on temperature dependent resistance is tested.

2 Introduction

The motivation for this work comes from the idea of using a temperature sensitive coating on circuit boards to be able to monitor all electrical circuits on the board for excess temperature. Especially in explosion protected mobile devices this could be advantageous. At the moment much effort is been taken to prevent excess temperature by covering the circuit board with resin for spreading heat and applying passive cooling units to guarantee temperatures below ignition point of critical atmospheres. Ignition sparks are prevented by energy control of capacity and current monitoring of the device.

A temperature sensitive coating with response in electrical measurable properties could be of great use for monitoring individual integrated circuits. Through proper positioning of electrodes a whole area could be read out by voltage-current measurements and the temperature affected signals could be interpreted by use of information technologies. This would make explosion protected mobile devices much smaller and would reduce the addition of weight from passive cooling units or resin.

State of the art temperature measurement systems have different technological disadvantages for such measurement scenarios. Temperature sensitive resistances or thermo elements cover only small sections of an area. Whereas measurement systems like pyrometers use complex equipment and need image processing technologies.

Carbon nanotubes are used for the development of a temperature sensitive coating because investigations at IPA have shown that the resistance of CNT-compounds exhibits reasonable decrease in value with rising temperature. In addition, CNT show many useful properties for conductive compounds. Their high aspect ratio results in low filler content for reaching the percolation threshold. They exhibit a high conductivity which results in a good conductivity of compound structures. Additionally the resulting composite structures behave mechanically similar to the matrix polymer, which means they partially retain their flexibility and easy processing.

3 Experimental

In this work, two different compositions of carbon nanotube based coatings are tested. One coating consists of CNT and dispersing agent based on water as solvent, whereas the other consists of CNT in silicone-matrix.

Following the raw materials, the production, processing and characterisation methods for both kinds of coatings are shown.

3.1 Raw Materials

Different brands and types of nanotubes were used to produce water based nanotube dispersion. An overview can be found in table 1.

Brand	Ctube 100	Nanocyl™ NC 7000	Baytubes® C150P	Shenzhen SWNT
Abbreviation	CT	NC	BT	SZ
Manufacturer	CNT Co., Ltd.	Nanocyl S.A.	Bayer AG	Shenzhen Nanotech Port Co. Ltd.
Country	Korea	Belgium	Germany	China
Length	1 - 25 µm	1,5 µm	1 - 10 µm	< 20 µm
Diameter	10 - 40 nm	9,5 nm	13 - 16 nm	< 2 nm
Type	MWNT	MWNT	MWNT	SWNT
Specific surface	150 - 250 m^2/g	250 - 300 m^2/g	not specified	450 m^2/g
Purity	93%	90%	95%	90%
Availability	Not specified	40 t/a	60 t/a	5 t/a

Table 1: Overview of nanotubes used. All values are taken from the respective supplier (official MDS or website).

For multi walled carbon nanotubes (MWNT) Gum Arabic (GA) was taken as dispersing agent, whereas for single walled carbon nanotubes (SWNT) Sodium Dodecyl Sulphonate (SDS) was used.
For the silicone-compound a two component room temperature curing system Elastosil RT601 from Wacker Silicones was used. Silicone was chosen because of its high thermal stability and its low humidity capacity.

3.2 Fabrication process

The aqueous CNT-dispersions were produced via use of ultra sonication. The procedure was as follows: The dispersant was dissolved in water by aid of magnetic stirring. Then nanotubes were added while the mixture was continuously stirred to incorporate them into the liquid. This mixture was sonicated with a Sonotrode KE76 Bandelin with 30W RMS for about 30 minutes. Centrifugation was done at 5000 rpm with an Eppendorf centrifuge 5804 (rotor A-4-44) for 10 minutes to separate the stabilized nanotubes from their agglomerates. Then the mixture was decanted and used for spray coating of samples.

The CNT dispersion in the silicone matrix was made with a three-roll-mill Exakt 80E. The last step of the grinding process was done in a force control mode which enabled fineness below 5 µm but with an uncontrolled gap. Before this step the nanotubes were pre dispersed in the silicone for 1 hour by a Heidolph rotor-stator-mixer “Silent Crusher” with 30 µm gap at 5000 rpm. The nanotubes were only dispersed in the A-component. After addition of the B-component the paste was intensely kneaded to receive a homogenous compound for application.

3.3 Preparation of the coatings

The aqueous nanotube dispersion was applied on ceran glass substrates via spray coating. Resistance was in the range of 500 – 1000 Ohm/sq. Five millimeter wide electrodes were applied on the surface with conductive silver paint. After preparation the samples were temperature treated at 120 °C for 1 hour.
For the MWNT-silicone-compound, as substrate conductor-boards with pre-patterned 4-wire electrodes were used. The coatings were applied with a coating knife. The SWNT-silicone-compound was applied on glass substrates with the same technique. Electrodes for 4-wire measurement, made of conductive epoxy, were placed on the surface of the SWNT-samples. All the silicone based coatings were tempered for 24 h at 120 °C before electrical characterization.

3.4 Characterization

For determination of humidity influence a climate chamber Vötzsch VCV 4060-5 were set to 20 °C. Starting at 20 rH% the relative humidity was increased by 10 % every 15 minutes. During this procedure, the relative humidity in the chamber and the resistance of the samples were monitored.
Resistance-temperature values of the CNT-dispersant coatings were measured on a heating plate in lab conditions. Temperature was determined with an infrared temperature measurement pistol. For comparison of the different coatings the surface resistance was calculated and normalized to the value of 25 °C.
For measurement of the CNT-silicone compounds, heating and cooling ramps with an absolute slope of 1 °C/min in the climate chamber were used to measure the temperature dependent resistance.
For resistance measurements a system from National Instruments (NI 9205, NI 9265 and NI 9213) was used. To compensate temperature differences, all samples were temperature monitored individually with NiCr-Ni thermo elements.

4 Results of measurements

In this chapter the temperature- and humidity-dependent electrical properties of the different coatings are presented. A main result is that the resistance of CNT-dispersant coatings is strongly influenced by humidity and exhibits a rather low temperature dependency. Resistance of CNT-silicone compounds are nearly immune to humidity and exhibit a well measureable change of resistance in the explored temperature range.

4.1 CNT-dispersant coatings

4.1.1 Influence of humidity on resistance

Figure 1 shows how the relative resistance of BT-GA-coating behaves while a change of relative humidity at 20 °C. It appeared that a change of relative humidity from 10 % to 90 % resulted in a rise of resistance of nearly 30 %. This behavior can be explained as follows: since nanotubes themselves show hydrophobic nature, most dispersants however have a high affinity to polar media. Therefore high humidity will cause an adsorption of water-molecules to the dispersant, which will lead to a volume increase. By this volume increase some conducting pathways become isolated and thus increase the resistance of the nanotube network.

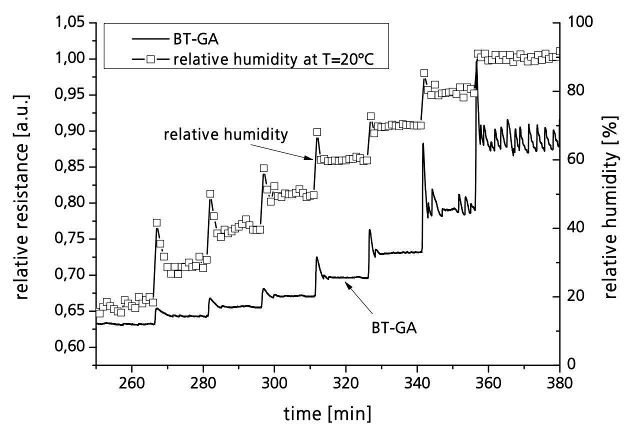

Figure 1: Variation of relative humidity at 20 °C and resulting variation of relative resistance of two different BT-GA coatings plotted over time.

4.1.2 Correlation between resistance and temperature

In figure 2 and 3 a comparison of thermal behavior of resistance at initial and subsequent heating is shown. The initial heating (see figure 2) to 220 °C shows for MWNT-GA-based coatings a discontinuity at high temperature around 180 °C. Follow-up heating (see figure 3) shows a more continuous behavior up to 220 °C. It is assumed that the behavior at initial heating is caused by a decomposition of the dispersant gum Arabic. This is further supported by the later observed continuous characteristic of resistance.
In subsequent heating it can be seen, that all the MWNT-GA-coatings show negative temperature coefficient of resistance (TCR) while the SWNT-SDS-coating behave like metals

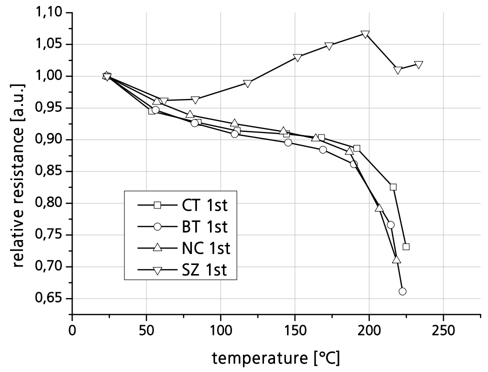

Figure 2: Resistance behavior at initial heating of CNT-dispersant coatings

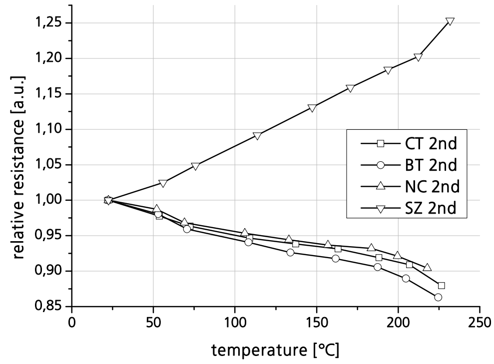

Figure 3: Subsequent temperature-resistance behavior of CNT-dispersant coatings after initial heating

with positive TCR.
From the MWNT-coatings the BT-based coating shows the maximum decrease in resistance, followed by the CT-nanotubes. All together, the MWNTs show decrease in resistance of absolute value in the range of -5 % till -7 % per 100 °C. This effect appears a factor of 3 to 6 smaller than the impact of humidity at 20 °C.
The positive temperature coefficient of the single walled nanotube coating could have different reasons. Oxygen doping of the semiconducting nanotubes like reported from Philip G. Collins et al. (Science, Vol. 87, 1801-1804) could be a factor for this metal like TCR, a higher volume expansion of SDS compared to GA could also explain such behavior.

4.2 CNT-silicone coatings

Based on the results of CNT-dispersant coatings, BT-MWNT and SZ-SWNT were chosen for test of CNT-silicone compounds. BT was taken because they show the strongest temperature response of the MWNTs. SZ as only SWNT-type in this work, were taken as comparison to the MWNT-type.
Both CNT-type compounds were produced with 1.5, 3 and 5 phr of nanotube content. For the SZ only with 5 phr resistance in measureable region was obtained. For the BT-based compounds the resistivity for different filler amount is shown in figure 4. Resistivity of the silicone-compounds with 5 phr SZ was around 300 Ohm*cm.

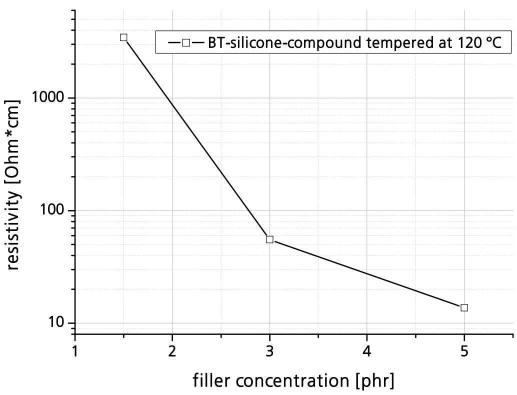

Figure 4: Resistivity of BT-silicone compound at different filler contents

4.2.1 Influence of humidity on CNT-silicone compounds

Before further testing, the influence of humidity was determined. As figure 5 shows, the influence in the explored region of humidity is below 1 % of resistance. This very small influence of humidity is neglected in the further measurements for characterization of silicone compounds.

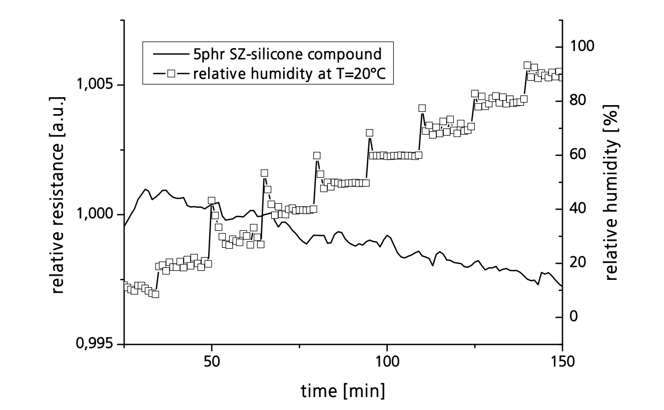

Figure 5: Relative humidity at 20 °C and resistance of SZ-silicone-compound measured over time.

The small change for silicone-compounds further strengthens the assumption that the dispersing agent is responsible for the high impact of humidity on CNT-dispersant coatings. Because silicone itself is permeable to water vapor, the nanotubes inside would also react on adhesion of water molecules if there would be a significant interaction.

4.2.2 Correlation between resistance and temperature of CNT-silicone compounds

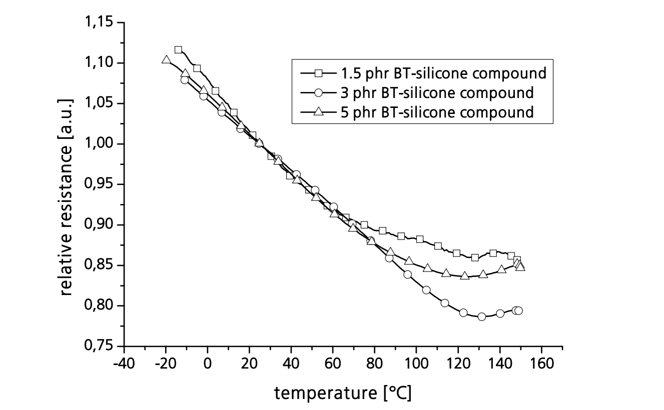

Figure 6: Influence of filler content on temperature dependent resistance of BT-silicone compound

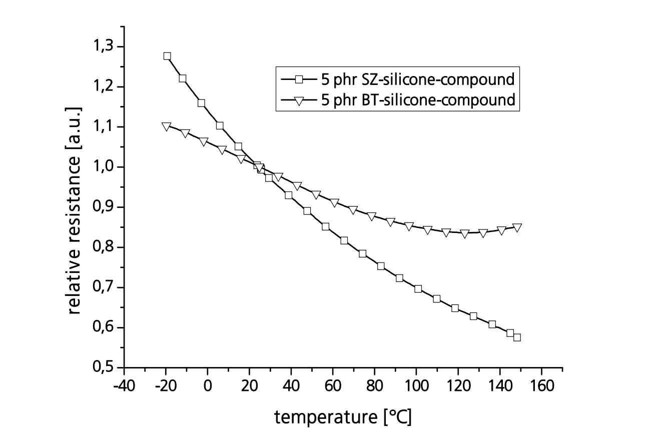

Figure 7: Temperature dependent relative resistance of silicone-compound based on BT or SZ (partial data of figure 6)

At first, investigation on the influence of filler content to the BT-compound was done (see figure 6). One can suspect that with lower amounts of conducting filler and resulting wider barriers between particles, an influence of temperature could become much more intensive. But as figure 6 shows, for all tested contents of BT the sensitivity stayed almost the same. Furthermore, with low filler content of 1.5 phr BT the resistance becomes irregular at temperatures above 70 °C; although a slightly higher sensitivity at temperatures below 20 °C is achieved. The 3 phr BT-compound shows up to 70 °C sensitivity near to the compound with 5 phr BT but has at temperatures above 80 °C a better performance.

Finally the SZ-compound and the BT-compound with same filler content are compared. A comparison of the relative resistance over temperature (see figure 7) shows that the SZ-compound exhibits a much higher sensitivity to temperature than the BT-compound. Furthermore the SZ-compound shows a decreasing slope to higher temperatures but does not result in an inflection point like the MWNT-compound shows. Over the whole measured temperature range of 170 °C the SZ-compound varies about 70 % whereas the BT-based coating shows a difference of 26.7 % from the highest value to the inflection point at 125 °C. Roughly this is a 3-times lower sensitivity to temperature for the BT-compound. A possible explanation for this higher sensitivity of the SZ-compounds could be the band gap of SWNTs which causes higher carrier density with rising temperature. Increased carrier density would lead to lower resistance of single CNT which could account for lower resistance of the complete nanotube structure in the compounds.

5 Conclusions

In this work CNT-dispersant-coatings and CNT-silicone-coatings, made of MWNTs and SWNTs were tested on their response in resistivity to the environmental conditions humidity and temperature.
It could be shown that the resistance of BT-GA coatings is highly influenced by humidity while SZ-silicone-compound is hardly affected. Varying humidity increases the resistance of BT-GA coating up to 30 %. Contrarily, resistance of SZ-silicone compounds only change about 0.5 % under the same conditions.
A temperature dependent resistance is found for all investigated compositions. While the NC-dispersant coating shows the smallest decrease with rising temperature the SZ-compound exhibits the widest resistance variation caused by temperature.
Furthermore it is shown that by variation of BT-content only small changes of temperature behavior are achieved.
To some extent the SZ-silicone coating can find application as temperature sensing materials. An advantage of this composition is that by the use of silicone a good temperature stability is achieved and only minor influence of humidity distorts the measurement.

6. Acknowledgment

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