

## Strain Sensing with Nanoscale Carbon Fiber – Epoxy Composites

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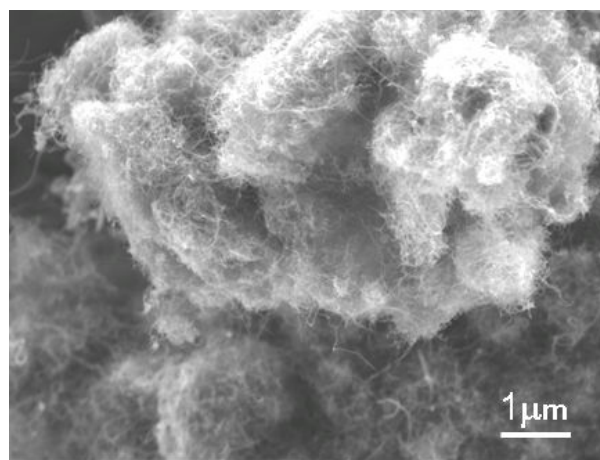
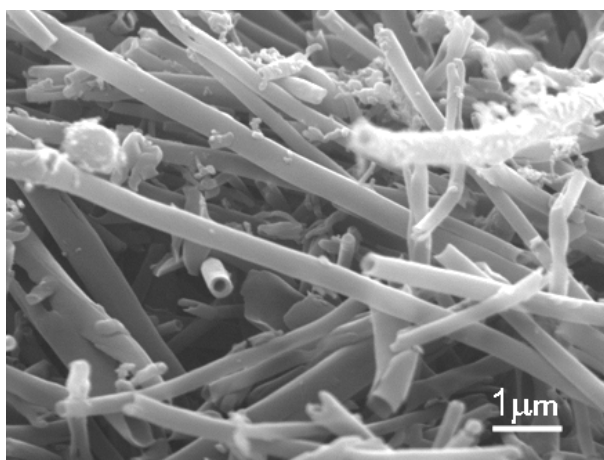
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**Abstract.** To study the electrical behavior of nanoscale carbon fibers (NCF)/epoxy nanocomposites under mechanical load, NCF/epoxy materials were produced using different mechanical dispersion methods like pearl mill and three roll mill. Various preliminary mechanical tests with simultaneous resistance measurements have been conducted. The influence of the filler content, the dispersion quality and the filler geometry on the electrical properties of NCF/epoxy composites was investigated as a function of the mechanical loading. The strain sensitivity strongly depended on the filler content and the filler geometry. In cyclic loading tests at low strains the resistance showed a reversible and linear behaviour. At higher strains irreversible resistance changes were observed. In addition, the specific surface resistance corresponded even during unloading with the highest strain level applied so far. This indicates the potential of NCFs/epoxy nanocomposites to monitor the loading history of a sample.

### Introduction

Nanoscale carbon fibers (NCF), like multi wall carbon nanotubes (MWCNT) and carbon nanofibers (CNF) as seen in figure 1, are well known for their outstanding mechanical as well as unique thermal and electrical properties. At present, considerable research activities are being devoted to “transfer” these properties into composite materials, in particular, into polymer-matrix systems. NCF/epoxy nanocomposites offer multifunctional properties and in addition to the mechanical reinforcement the electrical conductivity increases substantially even at very low filler contents. Both single NCFs [1] and the conductive NCF-substructure materials show piezoresistive effects [2]. The latter are further investigated in this work.



**Fig. 1:** SEM micrographs of carbon nanofibers (left) and multi wall carbon nanotubes (right) bulk material.

The electrical properties of insulating epoxy matrices can be improved by the formation of a conductive NCF network, where the conductive pathway is provided by connected NCFs. To achieve this certain “agglomeration” is needed. The percolation threshold, which is the filler content

needed to transport electric charge, depends mainly on geometry and dispersion of the filler. For NCFs, with an aspect ratio (length to diameter) of up to 1000, percolation thresholds as low as 0.0025 wt% can be achieved [3]. Variation in the NCF contacts for example owing to mechanical deformation results in a change of the electrical properties of the composite material. This may be used for sensing strain and/or the structural integrity of the related composite materials and parts [4-8].

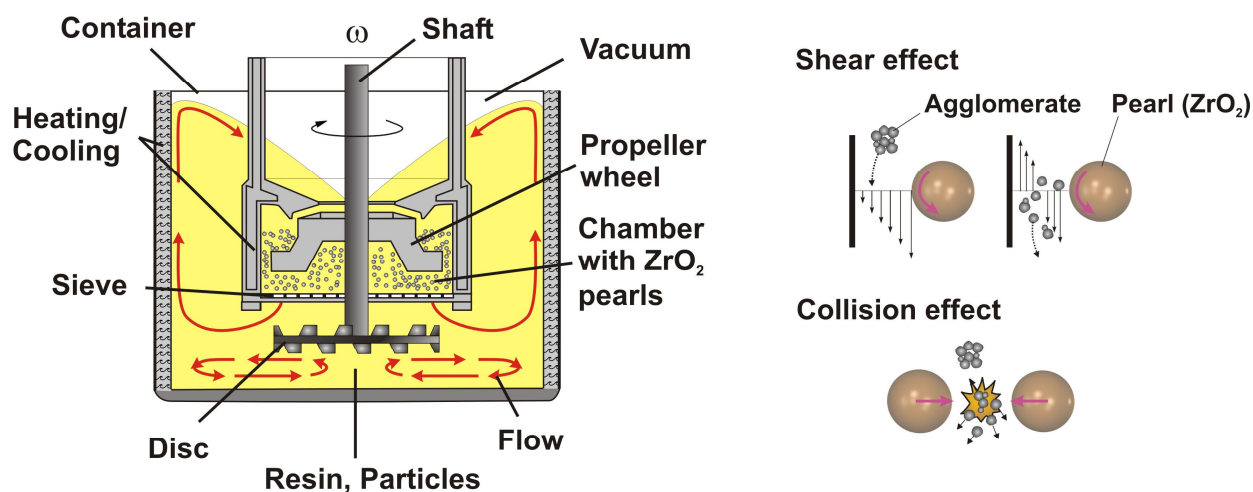
## Experimental

**Materials.** The epoxy matrix material was a two component resin system supplied by Huntsman, composed of the bis-phenol-A resin Araldite LY564 and the amino-curing agent Aradur 2954. The mix ratio in parts by weight is 100:35. The system combines low viscosity with long pot life at elevated temperatures and is additionally suitable for various production processes of fiber reinforced plastics (FRPs) like resin transfer molding (RTM), filament winding and wet lay-up techniques.

Two different kinds of nanoscale carbon fillers, namely multi wall carbon nanotubes (MWCNTs) by Arkema and carbon nanofibers (CNFs) by Grupo Antolin have been used to examine the influence of the filler geometry. The multi wall carbon nanotubes (MWCNT) used are shown in figure 1 (right). The black bulk material has an entangled cotton-like fiber structure and an apparent density of 0.1 g/cm<sup>3</sup>. The average dimension of the nanotubes is 15 nm in outer diameter and more than 500 nm in length. The true density is approximately 2 g/cm<sup>3</sup> and the purity higher than 93 %. In this work, the nanotubes were produced by a catalytic chemical vapor deposition (CVD) technique are used and no further functionalization of structure or surface has been realized.

The carbon nanofibers used were of a stacked-cup type manufactured via CVD. The average dimensions are 100-300 nm in diameter and more than 30 µm in length. Comparing the two systems, the CNFs have an aspect ratio of approximately 100, multi wall carbon nanotubes a value of almost 1000.

**Dispersion Methods.** The properties of NCF reinforced polymers strongly depend on the dispersion quality and the CNT-polymer interface [5]. One basic challenge of CNT-polymer nanocomposites lies in finding a suitable technology for dispersing the CNTs without damaging either them or the polymer. In this work two advanced techniques have been used the pearl mill and the three roller mill. The pearl mill combines a rotating disc used in standard dissolvers with an additional chamber filled with zirconium dioxide pearls. The process runs under vacuum. The pearls had a diameter of 1.2 to 1.7 mm and the working principle is shown in figure 2. Shear and collision effects force the filler agglomerates to break up.



**Fig. 2:** Working principle of the pearl mill.

The second dispersion technique used was a 3 roller mill. With different speeds counterrotating cylinders force the mixture to pass through the gap between them. Figure 3 shows the schematic of the working principle. The speed ratio between the rolls is 1 to 1:3:9 and the minimum gap size 5 microns. With this method very high shear forces are introduced to the whole volume. An advantage of this technique is that more viscous mixtures can be processed. This is important when dispersing nanofillers with a very large surface area as in the case of NCFs, as the viscosity increases significantly even with low filler contents.

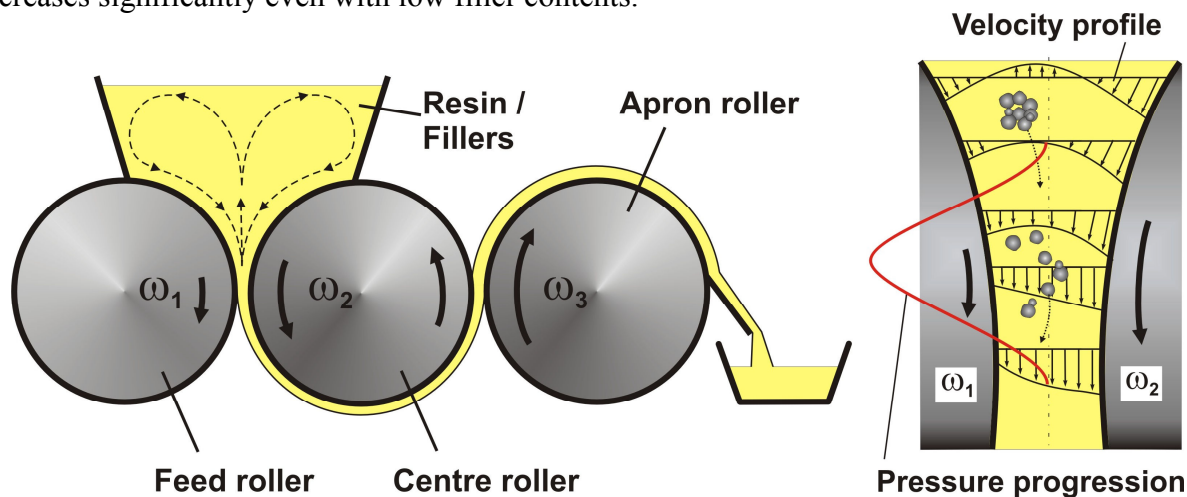


Fig. 3: Working principle of the 3 roller mill.

**Sample preparation.** The NCFs were pre-mixed with the resin systems using an overhead stirrer. For personal safety this was done under an extractor hood. The mixture was then put into a vacuum chamber for degassing, and after that the dispersion process started using one of the following settings:

- Pearl mill: mixing time = 2 h, rotational speed = 2700 rpm, temperature = ~60 °C.
- Three roll mill: speed = 200 rpm, gap size: first run 25 μm; second run 5 μm

After dispersion the mixture was degassed again and cooled down to around 40 °C. Then the respective amount of hardener was added and the whole mixture was stirred in an overhead stirrer at 40 °C for 15 min. For sample preparation specific molds were filled with the nanocomposite and then cured as follows: System NCF + LY 564 + HY 2954: 1 h 80 °C + 8 h 140 °C

**Dispersion Quality.** Figure 4 shows SEM micrographs of a fractured surface of a NCF-epoxy nanocomposite containing 1 wt% MWCNTs dispersed with the pearl mill. Except for a few agglomerates (diameter less than 2 microns) the MWCNTs are quite well dispersed. Nevertheless, the mechanical properties could not be significantly improved by the addition of 1 wt% MWCNTs (not shown here).

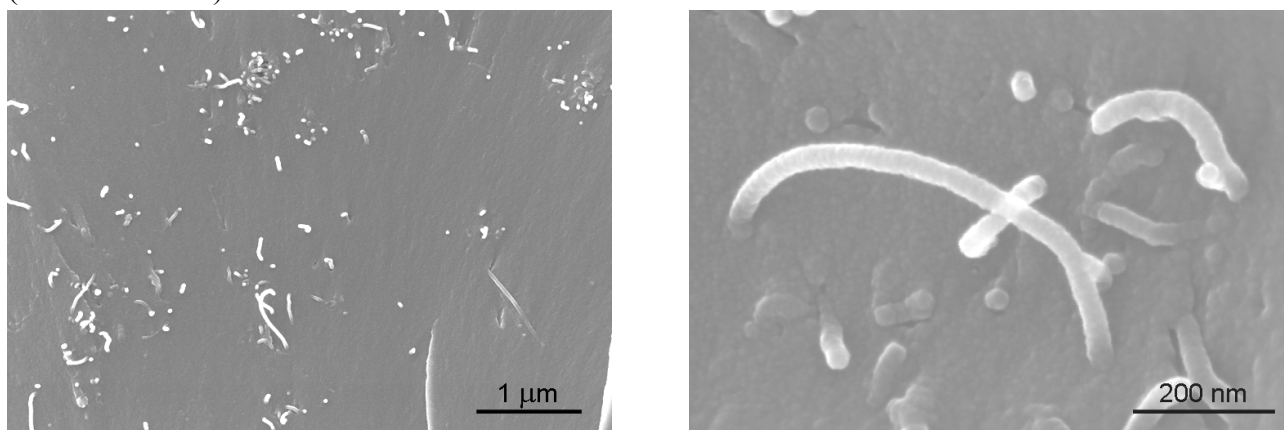


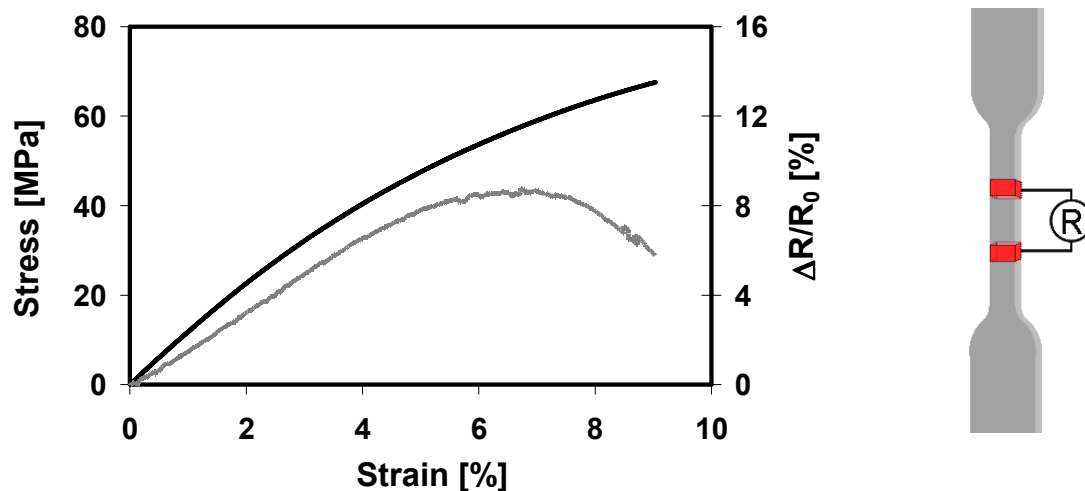
Fig. 4: SEM micrographs of the fracture surface of a sample containing 1 wt% MWCNTs dispersed with the pearl mill.

**Testing.** The electromechanical testing was conducted on a Zwick 1474 universal testing machine. The samples were tested in tension, at a testing speed of 1 mm/min. Simultaneously the resistance between two contacts at a distance of 12 mm was measured with a Keithley 617 electrometer. The contacts were made by using a silver paint and then a silver glue to connect cables to the surface of the sample (see scheme in figure 5).

## Results and Discussion

The formation of a conductive network of nanoscale carbon fibers inside the matrix material is achieved at a certain filler content, the so called percolation threshold. For the system examined in this work a percolation threshold of about 0.1 weight percent for MWCNT and less than 0.5 weight percent for CNF respectively was received. The differences originate from the different filler geometries. The comparison of different dispersion processes showed that the dispersion quality does have an impact on the electrical properties like absolute resistance/conductivity and percolation threshold. But, compared to the impact of the dispersion state on the mechanical properties, the electrical properties are not stronger affected. Furthermore, to form a conductive pathway close contact and a certain degree of agglomeration is needed.

**Static Tests.** Deformation due to mechanical loading can change the conductive pathway. To determine the electrical properties under mechanical load, tensile tests with simultaneous resistance measurements were conducted, as described above. Figure 5 shows a typical stress-strain curve of a tensile test according to DIN ISO 527 (sample type 5a) and the according normalised resistance change in percent. The tested sample contained 0.5 wt% MWCNT dispersed with the pearl mill. The absolute initial resistance was in the order of several kOhm.



**Fig. 5:** Left: tensile test data (black line) with simultaneous resistance measurements (grey line) of a sample containing 0.5 wt% MWCNTs dispersed with the pearl mill. Right: Schema of the tested sample with the electric contacts.

At the beginning the graph shows an almost linear behavior related to the applied strain. At a strain of approximately 60-80% of the failure strain and with increasing strain the resistance decreases. This partly unexpected behavior needs to be further investigated. The most reasonable explanation is the following: The electrical load is transported via conductive pathways represented by the NCF network. Therefore, an increase in resistance (decreasing conductivity) occurs when the conductive pathway breaks and contacts in the network are opened. A decreasing resistance (increasing conductivity) can be explained by closing contacts so that more electrical load can be transported. Under mechanical load the NCF network is deformed and both mechanisms take place. As seen from the graph, at lower strain contact opening seems to dominate whereas at larger strain closing contacts overbalance the opening effect.



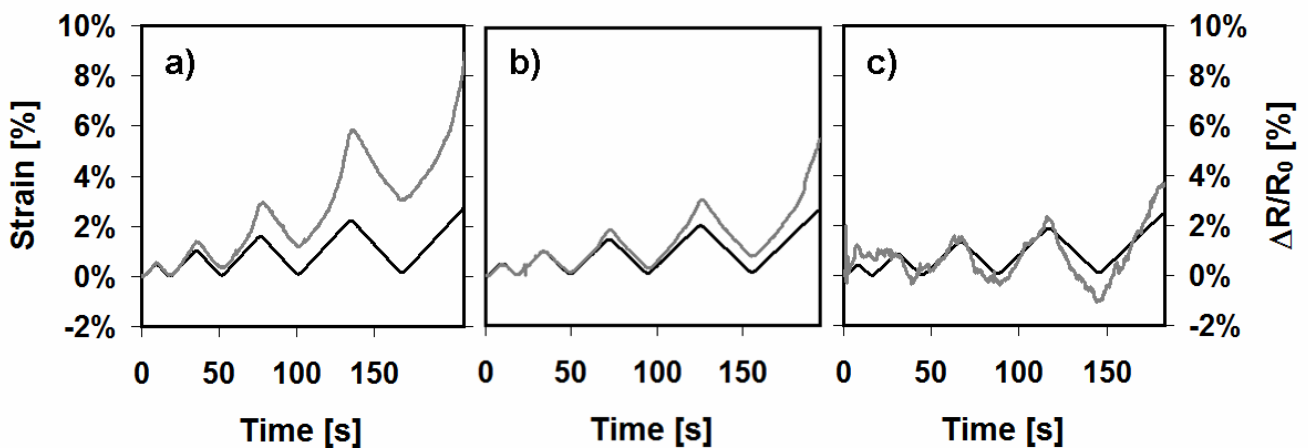
As characteristic values of the resistance curve the slope  $dR/d\varepsilon$ , the strain at maximum resistance  $\varepsilon_{R_{\max}}$ , the relative change of resistance at the maximum  $\Delta R_{\max}/R_0$ , and the final drop in resistance  $\Delta(R_{\max}-R_{\text{end}})/R_0$  were determined. A comparison of samples with 0.5 wt% and 1 wt% MWCNTs showed that with increasing filler content the slope decreases, the maximum in resistance occurs at higher strain, the relative increase at  $R_{\max}$  is lower and the final relative drop in resistance is higher.

**Cyclic Loading.** In order to characterize the conductive NCF network under mechanical load at lower strain values, cyclic loading tests have been conducted. The tests were force controlled using a triangle waveform and increasing maximum loads. The following steps have been used: 10N – 100N – 10N – 200N – 10N – 300N – 10N – 400N – 10N – 500N, while dispersion quality and filler geometry were varied to examine their impact on the electrical behavior.

Figure 6 a) shows the data for a sample containing 0.5 wt% MWCNT dispersed with the three roll mill. During sample manufacture the material passed through the machine two times (first run gap = 25  $\mu\text{m}$ ; second run gap = 5  $\mu\text{m}$ ) to achieve a good dispersion. Graph b) shows data from a sample with the same MWCNT content but with a different dispersion quality because it had passed through the dispersion process just once (first run gap = 25  $\mu\text{m}$ ). This leads to a higher initial resistance value between the contacts of 575 kOhm compared to 43 kOhm for sample a). Furthermore the conductive network seems to be less sensitive to the applied strain even though a clear signal was achieved even at very low strain.

The graph in figure 6 c) corresponds to a sample with 0.5 wt% CNFs processed in the three roll mill (first and second run), too. The initial resistance between the contacts was significantly higher at 80 MOhm. At low strain the electrical response to mechanical load was noisy and therefore less sensitive compared to the MWCNT samples. Therefore exact strain monitoring is more challenging using filler with lower aspect ratio.

Strain values above 2 % were not investigated further, but a tendency of CNF-epoxy samples and MWCNT-epoxy samples with poorer dispersion quality to suddenly increase the sensitivity at higher strain was recognized. However, the filler content of 0.5 wt% CNF is close to the percolation threshold of the applied system. But even small deviations in dispersion quality, filler size distribution, and orientation would change the results substantially.



**Fig. 6:** Results of cyclic loading with samples containing a) 0.5 wt% MWCNT dispersed with the three roll mill (first and second run), b) 0.5 wt% MWCNT (just first run) and c) 0.5 wt% CNF (first and second run).

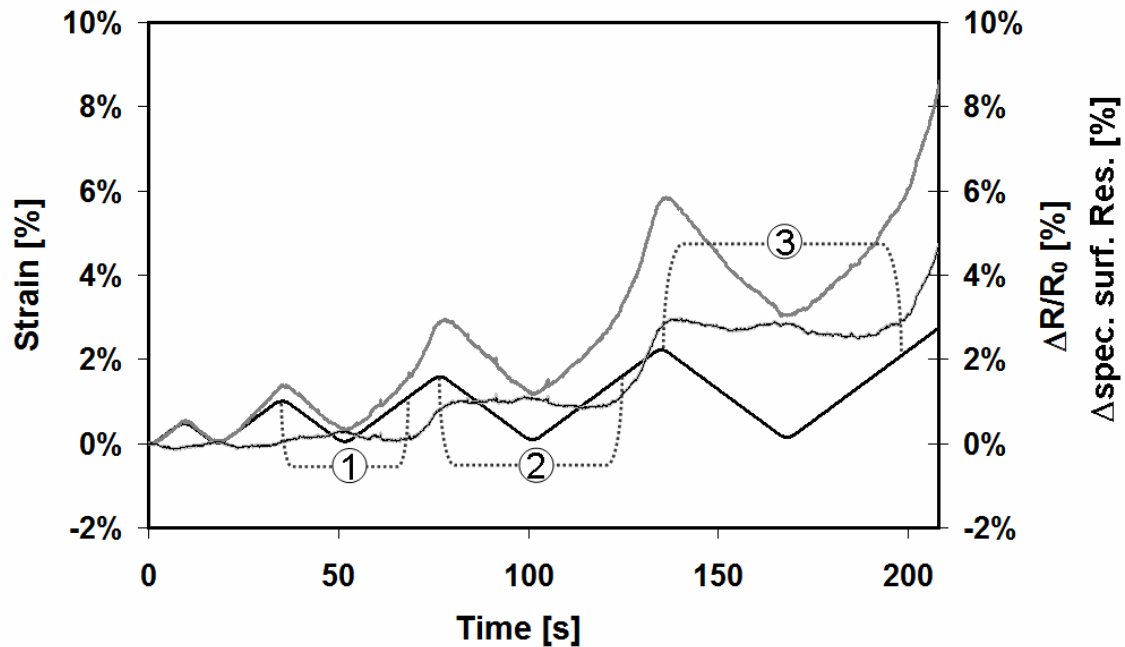
As seen above, at low strain the electrical resistance follows the elongation of the composite. The sensitivity, that means the slope of the resistance change, depends on the filler geometry, filler content and the dispersion quality. Looking at the specific surface resistivity  $\rho_{\text{surf}}$  related to the

surface area between the contacts another interesting effect occurs. The surface resistivity is calculated as follows:

$$\rho_{surf} = R * \frac{D}{L} = R * \frac{4b(1 - \mu * \varepsilon)}{l(1 + \varepsilon)} \quad (1)$$

where R is the resistance, D is the total distance between the electrodes, L the length of the electrodes, b the width of the sample,  $\mu$  the Poisson's ratio (assumed value: 0.3),  $\varepsilon$  the elongation or strain, and l the distance between the contacts on the sample.

As seen in figure 7, loading cycles at low elongations show a totally reversible behaviour of the electrical properties. The specific surface resistivity does not change. But after a certain strain is reached, the specific surface resistance of the material is irreversibly changed. During unloading this specific resistance level is maintained and only when a higher elongation is applied during the next loading cycle, does the specific resistance changes its level again (levels indicated by the dotted lines 1 to 3).



**Fig. 7:** Strain (black), resistance (grey) and calculated specific surface resistivity (fine black) versus time of a sample with 0.5 wt% MWCNTs under cyclic loading.

## Conclusions

The results show that nanoscale carbon fibers (NCFs) dispersed in a polymer matrix form a conductive network that can be used to display mechanical loads by monitoring the residual strain. The electric response of these nanocomposites depends mainly on the filler geometry, the filler content and the dispersion quality. Higher aspect ratios as well as better dispersion quality of the filler improve the sensitivity of the system. Increasing the filler content decreases the slope of the resistance curve (comparable to the Gauge or strain factor).

In addition to monitoring strain the conductive network is able to memorize the load history of the material. At low strain levels the change in resistance is reversible and the resistivity remains constant. At higher strain levels the resistivity is changed and retains information of the highest load applied so far. The mechanisms behind these observations are still under investigation.

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**References**

- [1] C. Stampfer, A. Jungen, R. Lindemann, D. Obergfell, S. Roth, C. Hierold: Nano Letters Vol. 6 (2006), p. 1449.
- [2] W. Peng, X. Feng, D. Tianhuai, Q. Yuanzhen: Journal of material science Vol. 39 (2004), p. 4937
- [3] J.K.W. Sandler, J.E. Kirk, I.A. Kinloch, M.S.P. Shaffer, A. H. Windle: Polymer Vol. 44 (2003), p. 5893.
- [4] I. Kang, M.J. Schulz, J.H. Kim, V. Shanov, D. Shi: Smart Materials and Structures Vol. 15 (2006), p. 737.
- [5] I. Kang, Y.Y. Heung, J.H. Kim, J.W. Lee, R. Gollapudi, S. Subramaniam, S. Narasimhadevara, D. Hurd, G.R. Kirikera, V. Shanov, M.J. Schulz, D. Shi, J. Boeri, S. Mall, M. Ruggles-Wren: Composites Part B Vol. 37 (2006). p. 382.
- [6] J.M. Park, D.S. Kim, P.G. Kim, D.J. Yoon, K.L. de Vries: Composites Part B Vol. 38 (2007), p. 847.
- [7] G.T. Pham, Y.B. Park, Z. Liang, C. Zhang, B. Wang: Composites Part B Vol 39 (2008), p. 209.
- [8] R. Zhang, M. Baxendale, T. Peijs: Physical Review B Vol. 76 (2007), p. 195433.