FUNCTIONAL PROPERTIES OF NANOCOMPOSITE EPOXY MATRIX SYSTEMS FOR STRAIN SENSING APPLICATIONS

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ABSTRACT

In this paper, electrically conductive nanocomposites based on an epoxy matrix and carbon nanoparticles, namely multi wall carbon nanotubes and carbon black, were investigated concerning their potential for strain sensing applications with electrical conductivity methods. While the detectability of damage in fibre reinforced laminates has already been proven experimentally [1,2], this paper aims to investigate the electromechanical response of the nanocomposite matrices, subjected to mechanical load. It was found that the nanocomposites exhibit a defined exponential resistance vs. strain behaviour in the regime of elastic deformation, which is in good agreement with prevalent theories about charge carrier transport mechanisms in isolator/conductor composites. At higher strain values viscoelastic and plastic deformation dominates, leading to significant deviations from the behaviour observed in the elastic regime. Furthermore, a distinct influence of the nanofiller characteristics on the sensing properties was observed, revealing carbon nanotubes to provide superior sensing characteristics when compared to carbon black nanoparticles.

1. INTRODUCTION

As most structural parts made from FRPs are designed for high load levels and long lifetimes, the fatigue and degradation behaviour of this type of materials is of great interest. Structural monitoring of FRP structures has therefore become increasingly important in recent years and different technical approaches for monitoring strain and damage have been developed, mostly based on different external sensing techniques (e.g. ultrasound, fibre-optical sensors). The direct implication of sensing properties into the matrix of FRP structures is of high interest regarding health monitoring and NDI approaches. Especially the detection of internal failure, such as delamination, is a challenging task with conventional investigation techniques. Recent investigations have shown that the conducting networks of carbon nanoparticles in epoxy matrices are sensitive to applied mechanical load and can be used for damage detection, as well as stress-/strain sensing in composite structures [1-4]. Short carbon fibre/epoxy composites were also found to exhibit piezoresistive behaviour [5].

Electrically conductive polymer-based nanocomposites can be produced by dispersing carbon nanoparticles such as carbon nanotubes (CNTs) and carbon black (CB) in a polymer matrix. In the case of epoxy matrix systems the percolation threshold can be very low because of dynamic percolation processes which occur during the curing process prior to gelation [6]. The implication of sensing properties can therefore be realised at very low filler contents, i.e. 0.3 wt.% of nanoparticles and lower with respect to the matrix [1-3].

The electrical response of isolator conductor composites subjected to mechanical loads has also been extensively investigated in the area of carbon black filled rubber matrices [7,8]. Sensing of stresses/strains and damage evolution via electrical conductivity methods was found to be viable with these type of materials. Of course carbon black filled rubbers differ significantly from the nanocomposites investigated in the present study (e.g. in terms of filler volume fraction, filler type, mechanisms of non-elastic deformation, strain to failure etc.) and therefore the observed sensing characteristics differed significantly.

In case of CFRP structures the intrinsic conductivity of the carbon fibre can be used for electrically monitoring damage evolution [9-11] and also stresses/strains, as carbon fibres exhibit a “piezoresistive” effect [12]. These methods provide limited insight into matrix

related failure mechanisms (e.g. matrix cracking), but the use of an electrically conductive matrix can provide a much more detailed insight into these mechanisms. Furthermore, the application of an electrically conductive matrix allows sensing via electrical methods in composites reinforced with non conductive fibres, e.g. glass or polymer fibres.
In this work, the electromechanical behaviour of a nanocomposite matrix system was investigated in detail. The "piezoresistive" response of different carbon nanoparticle/epoxy based nanocomposites was measured and evaluated for different loading cases in order to gain a fundamental understanding of the observed sensing characteristics.

2. EXPERIMENTS

Epoxy nanocomposites with different volume contents of multi wall carbon nanotubes (MWCNTs) and carbon black (CB) were produced via a high shear mixing process [13]. The matrix system used was the LY556 epoxy system, combined with the CH917 anhydride hardener and D070 accelerator, all provided by Huntsman, Switzerland. As nanoscopic fillers, CVD-grown MWCNTs, provided by Arkema, France, as well as carbon black XE2, provided by Degussa, Germany, were applied. As filler contents, 0.1 and 0.3 wt.% were chosen for the MWCNT nanocomposites and 0.5 wt.% were chosen for the carbon black nanocomposite. This was done to tune the electrical conductivity over a range of two orders of magnitudes and to investigate a possible influence of filler content on the sensitivity of the nanocomposite sensors. The carbon black nanocomposite was investigated for comparative reasons, as the primary particles are of a spherical nature and exhibit an aspect ratio of around one (compared to several hundred for MWCNTs). A filler content of 0.5 wt.% carbon black yields a conductivity in between the two MWCNT composites' conductivities (see Fig. 1).
The tensile tests were performed using a Zwick Z010 universal testing machine, according to DIN EN ISO 527.1. A crosshead speed of 1mm/min was applied. Dog-bone specimens were prepared according to DIN EN ISO 527.2 by countersinking. The elongation of the specimens was measured using a MTS extensometer clip with a gauge length of 25 mm. For the electrical resistance measurements, the samples were contacted at the ends of the parallel part with a surface-ring contact of conductive silver paint. At least seven specimens were tested for each material produced.
A Keithley Sourcemeter 2602 was used for resistance measurements, performed simultaneously to the mechanical tests. A potentiostatic measurement (U = 10V) was applied to the specimens to determine the apparent current and resistance.

3. RESULTS

The conductivities of the nanocomposites produced are shown in Fig. 1. The 0.1 wt.% MWCNT nanocomposite exhibited a conductivity of about $3 \cdot 10^{-4}$ S/m; the 0.3 wt.% MWCNT nanocomposite showed a value of about $1 \cdot 10^{-2}$ S/m. For the carbon black nanocomposite, a conductivity of about $2.5 \cdot 10^{-3}$ S/m was measured.
Exemplary results of the tensile tests are depicted in Fig. 2. The mechanical stress-strain curves are shown in grey. It can be seen that the tensile strength ranges around 85 MPa, which is in very good agreement with the manufacturer's materials data sheet for the LY556/CH917 matrix system. The strain to failure values show the typical scattering, usually varying between 6-7%.

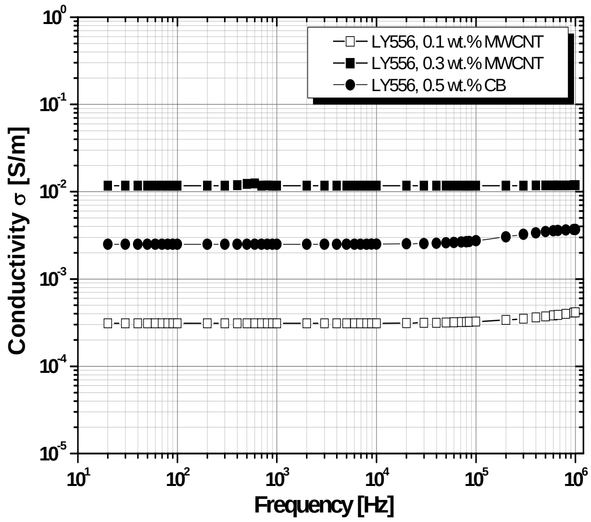

Fig. 1: Conductivity values of the nanocomposites.

The black curves in Fig. 2 are the corresponding resistance measurements. As both MWCNT nanocomposites seemed to behave very similar, only the results from the 0.1 wt.% MWCNT composites are shown in the following discussion. Plotted is the relative resistance change vs. strain. The experiments revealed a pronounced dependency of the electrical resistivity on the mechanical load. The uniaxial tensile tests revealed an exponential variation of resistivity vs. strain in the elastic regime for both, the MWCT and CB nanocomposites (Fig. 2).

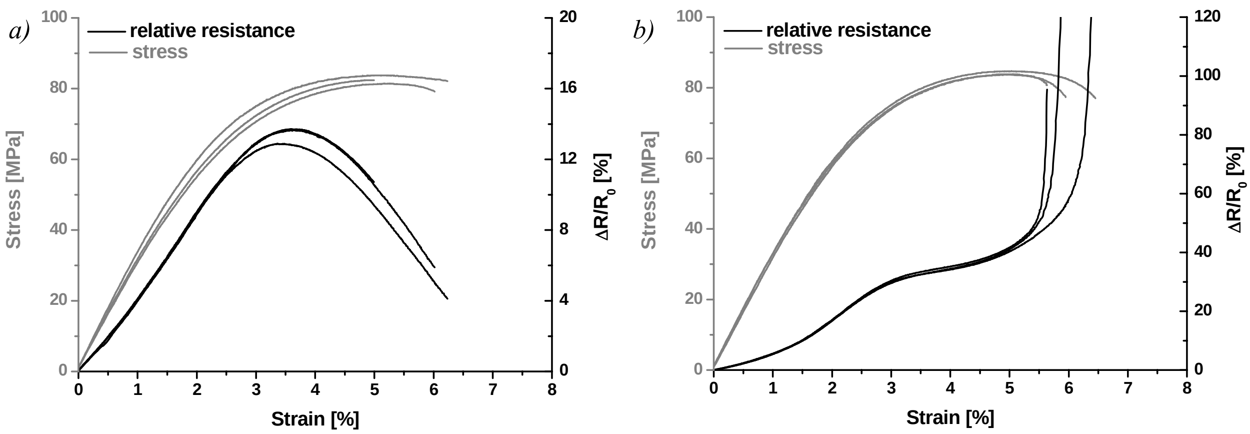

Fig. 2: Stress-strain and resistance-strain curves of different epoxy based nanocomposites: a) 0.1 wt.% MWCNTs, b) 0.5 wt.% carbon black.

Up to a value of ca. 2% of strain the relative resistance change vs. strain can be fitted very well with an exponential function such

$$\frac{\Delta R}{R_0} = r_n + \alpha \cdot e^{\beta \cdot \varepsilon} ,$$

where ΔR is the absolute resistance change, R_0 the initial resistivity of the specimen, r_n is a correction term to account for the resistance change curve starting at the point of origin, and ε is the applied strain. The same resistance vs. strain behaviour was already observed in GFRP laminates with a conductive nanocomposite matrix [2]. In Fig. 3, two exemplary fittings of the resistance change vs. strain curves are shown.

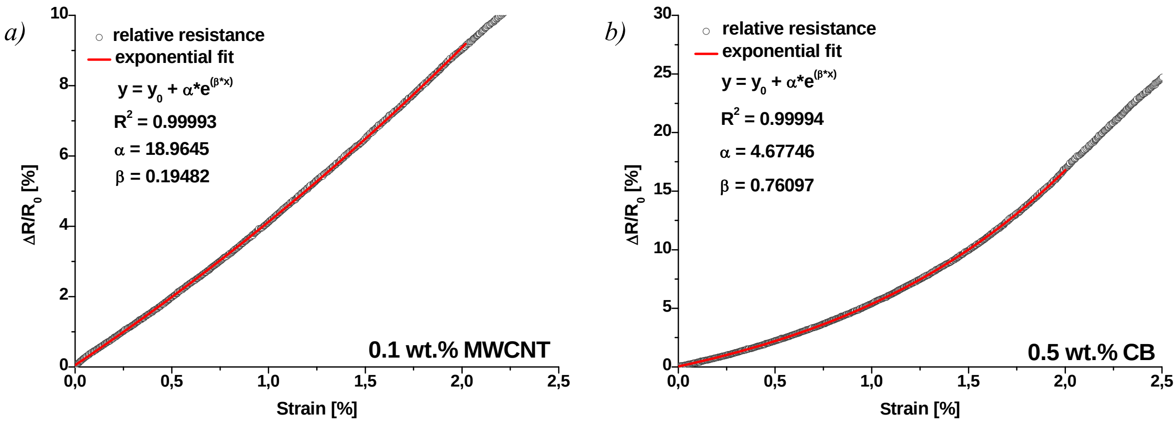

Fig. 3: Resistance-strain curves and exponential fitting functions of different epoxy based nanocomposites: a) 0.1 wt.% MWCNTs, b) 0.5 wt.% carbon black.

The agreement between the measured values and the fitting function is remarkable. A correlation coefficient of $R^2 > 0.999$ was found for all measurements conducted in this work. These findings are in agreement with the fluctuation induced tunnelling theory, describing the charge carrier transport in isolator conductor composites [14-16]. The conductivity is dominated by the tunnelling resistance ρ_t between the conducting particles, which depends exponentially on the interparticle distance: $\rho_t \sim \exp(w/\lambda)$, with w being the junction width. Therefore an exponential resistivity vs. strain behaviour for macroscopic specimens subjected to tensile load can be expected. However, in this case the deformation has to be homogeneous in the whole volume tested.

Comparing the sensitivities of the nanocomposites resistivity vs. strain, one can see from Fig. 3 that the carbon black containing material exhibits a more pronounced exponential behaviour and the resistance increase per strain unit is significantly higher for this material. At 2% of strain, the nanocomposite containing 0.1 wt.% of MWCNTs exhibited a resistance increase of about 9%. The 0.3 wt.% MWCNT-nanocomposite showed an increase of about 6.5% in resistance at this strain value. The carbon black nanocomposite had a 17% resistance increase at 2% of strain. This can be explained by regarding the aspect ratio of the particles and the resulting percolated network structure. As the carbon black nanoparticles are spherical in shape, whereas the MWCNTs may have aspect ratios of up to ~1000, the number of interparticle tunnelling contacts along a conductive pathway is significantly higher in the case of CB nanocomposites. Furthermore, MWCNTs may be in electrical contact to numerous other MWCNTs along their longitudinal axis, thus resulting in a more redundant network structure. As the MWCNTs are randomly oriented in the bulk matrix, intertube contacts may be oriented in a manner, that even though the centres of mass of two contacting CNTs are moving apart by the applied strain, the tunnelling contact distance actually decreases. These orientation effects can not occur with spherical particles. The result of these effects is a significantly reduced sensitivity of the electrical resistance towards strain for MWCNT composites, compared to CB composites.

It is also noteworthy, that in the case of the MWCNT nanocomposites, the resistance change vs. strain in the elastic regime can be approximated reasonably well with a linear function. Up to 1.5% of strain, a linear fit can be applied to all measurements taken, resulting in a correlation coefficient of $R^2 > 0.99$. In view of potential technical applications, this is a significant advantage, as integration into electrical measurement bridges would be facilitated for instance.

Above 2% of strain, the fitting curves start to deviate from the measured data. From Fig. 2 it can be seen that the linear elastic regime of the nanocomposites ends between 1.5 and 2% of strain. At higher strain values, the resistance change vs. strain curves show a strong deviation from the exponential behaviour observed in the elastic regime. In the case of the MWCNT nanocomposites, the slope of resistance change decreases above the elastic regime and passes a maximum at around 4% of strain. This value was found for all measurements, independent of the MWCNT content. The CB nanocomposite exhibits a completely different behaviour. Although the slope of resistance change is also decreasing at strain values higher than 2%, the curves do not pass a maximum, but pass through a point of inflexion, followed by a drastic increase in resistance shortly before final failure. Beyond the elastic regime, viscoelastic and inelastic deformation processes occur in the epoxy matrix, leading to irreversible changes in the percolated network of conductive particles. However, the formation of a maximum in the case of the MWCNT nanocomposites is surprising. Obviously, the pronounced differences in the resistance development at higher strain values can be attributed to the different structure of the network of conductive particles, which itself depends on several factors, such as aspect ratio, interparticle interactions etc.

In order to further investigate the effects occurring in the inelastic regime, modified tensile tests were performed. The specimens were subjected to a tensile strain of 6% (close to strain to failure, see Fig. 2) and subsequently unloaded to zero external stress, while the resistance was again measured simultaneously. Fig. 4 shows an example of such a tensile test.

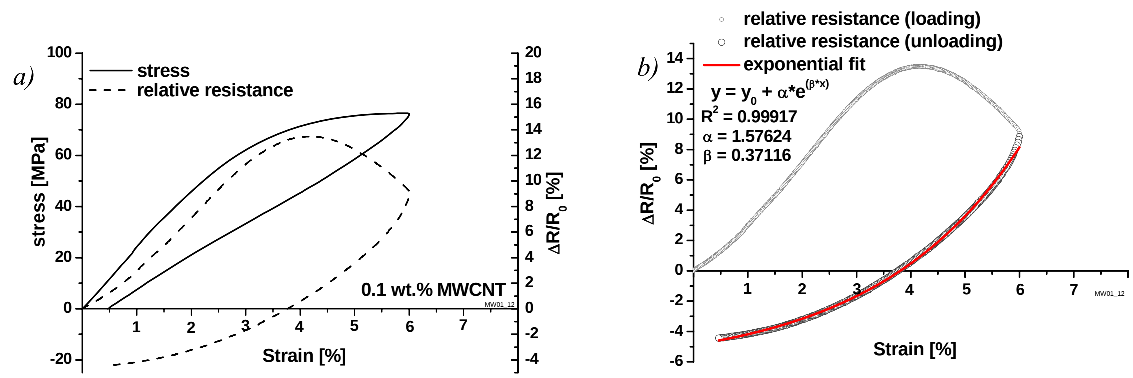

Fig. 4: a) Stress-strain curve and corresponding resistance change for loading and unloading of a 0.1 wt.% MWCNT specimen, b) exponential approximation of the resistance change during unloading .

Looking at the stress-strain curve on Fig. 4a, it can be seen that the residual strain at the end of the test is about 0.5%, i.e. the value of inelastic deformation. As the specimen was subjected to a strain value of 6%, the remaining 5.5% of strain are composed of elastic and viscoelastic deformation. Regarding the resistance change during this test, one can see from Fig. 4a that upon unloading the resistance decreases monotonically with strain. In fact it decreases exponentially with strain, as depicted in Fig. 4b, suggesting a process of elastic resilience. Interestingly the specimen exhibits a lower resistance after testing, even though its length increased by 0.5%. From these results it can be concluded that the conducting network structure of nanoparticles is being irreversibly affected by viscoelastic and plastic deformation processes on the molecular level. In the case of MWCNTs, these effects lead to a reduction in the composite resistance. In the case of spherical carbon black particles only the rate of resistance increase is reduced when the elastic regime is left, but increasing drastically shortly before final failure. At this point it should be noted that local zones of viscoelastic and inelastic deformation processes occur already at low strain values, i.e. the elastic regime. This could explain why the maximum occurs already at 4% of strain, although the overall inelastic deformation of the specimen is only about 0.5% close to final failure.

A further hint for the strong influence of localised inelastic deformation can be found in the resistance development of the carbon black nanocomposites at high strain values. From Fig. 2b, it can be seen that the onset of the final drastic increase of the specimen resistance seems to be correlated to the onset of final failure. At very high strain values (around 5.5% of mechanical strain) the epoxy matrix shows the typical necking behaviour in the area of the final failure. After this point is reached, the specimen deforms mostly locally and high local values of inelastic strain occur. This leads to a significant impairment of the network of spherical particles resulting in the drastic final increase in resistance, as displayed in Fig. 2b.

In Fig. 5, the mechanical stress and the resistance change of three CB nanocomposite specimens is plotted vs. a normalised strain $\varepsilon/\varepsilon_f$, where ε_f is the strain to failure.

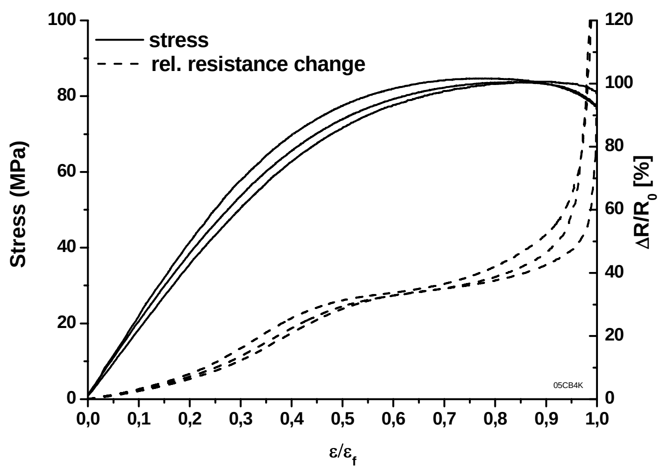

Fig. 5: Stress and relative resistance change vs. normalised strain $\varepsilon/\varepsilon_f$ for the 0.5 wt% CB nanocomposites.

The strong final increase of resistance always occurs at values of $\varepsilon/\varepsilon_f \approx 1$. It should be noted that the maximum resistance values measured directly before the final failure show a high scattering. The resistance behaviour at this point clearly depends on the final strain to failure that is reached and the specific deformation processes occurring in the plastic zone in each specimen. Values between $\Delta R/R_0$ = +120% and +300% have been measured, while the strain to failure values typically ranged in the area from 5.5% to 8%.

The resistance development of the MWCNT nanocomposites seems to be independent of an upcoming final failure, as can be seen in the measured curves. Beyond its maximum at around 4% of strain, the resistance decreases monotonically in a nearly linear manner, with its final value depending on the strain to failure of the specific specimen. A possible explanation may again be the different aspect ratio and more redundant network structure in the MWCNT composites. Instead of a rupture of the conducting pathways, the MWCNTs may be reoriented and aligned in zones of high local deformation, leading to an actual decrease in the network resistivity.

4. CONCLUSIONS

For uniaxial strain, in the elastic regime, the resistance strain characteristics are of an exponential nature. These results are in agreement with the hypothesis that the charge carrier transport between the conducting particles in carbon nanoparticle composites can be explained with the tunnelling effect. The volume content as well as the geometry of the carbon nanoparticles was found to have a distinct influence on the "piezoresistive" response of the nanocomposites. At low strains (below 2.5 %), the CNT based composites exhibit a very weak exponential dependence of resistance vs. strain, allowing a very good linear approximation. Combined with the low volume contents needed to achieve sufficient conductivity values, makes them superior candidates for potential strain sensing applications. At higher strain values, viscoelastic and inelastic deformation processes lead to an irreversible change in the conductive network structure, resulting in irreversible resistance changes. The different behaviour of the nanocomposites containing carbon black, especially at higher strain values in the regime of plastic deformation, can be attributed to the different aspect ratio (being close to one for the carbon black particles and up to several thousands for the CNTs) and network structure of the conducting particles.

5. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of the European Commission Framework 6 Programme, Priority 4, Aeronautics and Space (Aerospace Nanotube Hybrid Composite Structures with Sensing and Actuating Capabilities, NOESIS), Contract No. AST4-CT-2005-516150.

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