GLASS FIBRE WITH CARBON NANOTUBE NETWORKS AS MULTI-FUNCTIONAL SENSOR

SL Gao, RC Zhuang, J Zhang, JW Liu, E Mäder
Leibniz Institute of Polymer Research Dresden
Hohe Strasse 6, 01069 Dresden, Germany
gao@ipfdd.de

SUMMARY

A single glass fibre sensor has been manufactured by depositing multiwalled carbon nanotubes on fibre surface. The single fibre and their epoxy matrix composites show linear and nonlinear piezoresistivity, temperature and relative humidity dependencies of electricity. Unidirectional composites exhibit an ultra-high anisotropic semiconducting property and an ultra-low electrical percolation threshold.

Keywords: glass fibre, sensor, nanotube, epoxy, composites, interphase

INTRODUCTION

A glass fibre is an electrically insulating material and is the most widely used reinforcement (over 80%) in composites globally. Functionalisation of traditional glass fibre surfaces by nano-reinforcements is leading to the tremendous potential for multi-functional composites [1]. The development of novel glass fibre reinforced plastics (GFRPs) with the electrical conductivity is very attractive for a broad range of applications including electrostatic dissipation, electric field shielding, damage detecting, packaging, etc.

Traditionally, the electrical conductivity of GFRPs was achieved by either adding conductive particles, such as carbon blacks and carbon nanotubes in polymer matrix, or composite surface treated with metallic fabrics, foils, or antistatic or conductive coatings. These methods may cause ageing, maintenance and manufacture problems as well as an increase in weight and cost. As outstanding candidates for sensing materials, carbon nanotubes (CNTs) with high aspect ratio and an excellent conductivity (10^5–10^8 S m^{-1}) have stimulated the development of multi-functional nanotube/fibre composites [2-5]. Recently, the GFRPs with multiwalled carbon nanotube networks (MWNTs) as well as carbon black in polymer matrix were developed and the electrical resistance method was performed to monitor the damage initiation and evolution [6,7]. The approaches, however, are less sensitive to the fracture of the load-carrying fibers and provide less information on the development of cracks in the fibre/polymer matrix interphase, where the microscale damage is usually initiated.

To achieve light-weight and low-cost conductive GFRPs, lowering loading of CNTs is a critical issue. The electrical percolation threshold (PT) is the minimal loading of CNTs required to form a network that spans the whole system. The CNTs/epoxy composites in general show a much lower PT than other polymer systems, but the reported values are very different from less than 0.01 wt% to over 4 wt% [8,9]. In order to experimentally

obtain the low theoretical PT, the CNTs should be unbundled/disentangled and CNT surface should be functionalised, since the introduced functional groups prevent rebundling/reentanglement through electrosteric and/or electrostatic repulsion [10]. Recent experiments on the percolation of CNTs in aqueous dispersions have shown that a remarkable lowering of the percolation threshold can be achieved by making use of weak attractive interactions between the CNTs [11]. To achieve low PT and anisotropic electrical properties, aligning homogeneously the nanotubes in composite matrix is very interesting and challenging. Many methods are used so far, such as electrospinning, magnetic field, liquid crystal, shear flow, melt spun, mechanical stretching methods and so on. In the nanotube aligning direction, the conductivity is normally much higher than the value perpendicular to the nanotube orientation, e.g. three orders of magnitude higher for CNT/epoxy composite along the mechanical stretching direction [12]. Overall, the dispersion and orientation of CNTs remain a hindrance in exploiting the exceptional CNT properties in polymer matrix composites.

Aimed at multi-functional applications, here, we present a sample fabrication method that introduces electrical conductivity to glass fibre surface by depositing a layer of MWNTs networks, and in turn, specifically forming an interconnected MWNTs-rich interphase within an epoxy matrix. The surface morphology of the fibre and the glass transition temperature of composites were studied by AFM and DSC. We further utilize the direct current (DC) electrical resistance method for the detection of the influence of various environmental factors, i.e. stress/strain, temperature, relative humidity (*RH*), on electrical properties of the single glass fibre and unidirectional MWNTs-glass fibre reinforced composites where no additional nanotubes were added to the epoxy matrix.

EXPERIMENTAL

The alkali-resistant glass (ARG) fibres with an average diameter of 17 μm utilized in this work were made at our institute by a continuous spinning process. We used commercial carboxyl functionalized MWNTs (Nanocyl-3101, Nanocyl S.A., Belgium) produced via the catalytic carbon vapor deposition (CCVD) process, with purity in excess of 95%, average diameter of 9.5 nm and length of 1.5 μm. The nanotubes were dispersed in the aqueous dispersions at 0.5 wt% with the pH value of 5~6, in presence of non-ionic, cationic or anionic surfactants, namely Igepal CO970, Aquard S-50, and sodium dodecyl sulfate (SDS), respectively. Then, the glass fibre rovings were dipped into MWNTs dispersion for 15 mins, withdrawn with their axes perpendicular to the solution surface and dried in a vacuum oven at 40 ^{o}C for 8h. Finally, the concentration of nanotubes on glass fibre surface was 2.3 wt% measured with an electronic balance. A commercial DGEBA-based epoxy (Rütapox L20) with hardener (Rütadur SL) in a weight ratio of 100:34 manufactured by Bakelite AG was used as matrix and the composites were cured at identical conditions (80 ^{o}C, 6 h).

We first measured the DC electrical resistance of single MWNTs coated glass fibre between two copper electrodes at distances of 0.29, 0.30, 0.50, 1.04, and 2.20 mm, respectively. We further performed in-situ electrical resistance measurements of the single glass fibre at different strains, temperatures, relative humidities (*RH*). The experiments of the resistance changing with the temperature or the humidity were carried out in a hot-stage (Linkam LTS350 Heating/Freezing, UK) from -150 ^{o}C to +180 ^{o}C with a heating rate of 1 ^{o}C/min in a nitrogen atmosphere and a conditioning

cabinet (Weiss Umwelttechnik, Germany) from 20% to 80% *RH* at temperature of 30±0.2 ^{o}C condition, respectively. To investigate the piezoresistive effect, the electrical resistance was recorded as the single glass fibre underwent uniaxial tensile. The specimen was clamped between two plates with conductive silver paste (Acheson Silver DAG 1415M), which served also as electrodes.

Using the Favigraph ME testing machine (Textechno, Germany) equipped with a 1 N load cell, the single fibre tensile test was conducted according to DIN EN ISO 5079 standard at gauge length of 20 mm and the cross head velocity of 0.2 mm/min. Four-point conductivity measurements were carried out to monitor the DC electrical resistance change of the loaded specimen with a Keithley 2000 multimeter and two-point conductivity was also carried out with LCR-digital multimeter (VC-4095) for the resistance value higher than 100 MΩ. In order to further detect composite piezoresistive effect, mechanical tensile/compression strain were performed using a self-made screw-driven tensile stage and simultaneous resistance was reordered at each strain step. We prepared unidirectional fibre/epoxy composites over a very wide range of volume fraction from 4×10^{-3} % to 50 %, including a dog-bone shaped sample ($20\times1\times1.8$ mm^3) and rectangular-shaped sample ($20\times7\times1.8$ mm^3) for electrical and mechanical testing along either longitudinal or transverse fibre directions to assess whether significantly different electrical properties arise due to glass fibre alignment with carbon nanotube.

The fibre surface topography was characterised using atomic force microscopy (AFM, a Digital Instruments D3100, USA) in tapping mode. Image mean roughness and maximum height roughness within the cursor box derived from ASME B46.1 are calculated for six fibre surfaces. In addition, the glass transition temperature (T_g) was measured for the composite sample with fibre volume fraction of 40% by the modulated differential scanning calorimetry (Q2000 MDSC, TA Instruments, UK) at the rate of temperature change of 3 K/min.

RESULTS AND DISCUSSION

First, we present the results of electrical resistance measurement of the single glass fibre coated with anionic dispersant individualized MWNTs (Fig.1). The measured DC resistance *R* of the fibre was in the range of 10^4 up to 10^7 Ω. It in general increases with increasing electrode-electrode distance, *L*. Accordingly, for our MWNTs-glass fibre with diameter of *D*, the calculated specific conductivity $\sigma_{glass}= 4L/\pi D^2R$, is typically in the range of 0.1 up to 30 S m^{-1} and the fibre surface resistance values is in the range of 10^3 to 10^7 Ω/sq. It is evident from the AFM images that the nanotube networks with generally curved rather than straight nanotubes are aligned randomly. The orientations of nanotubes shorter than 5 μm are reported strongly influenced by Brownian motion [13]. Thus, our nanotubes with average length of 1.5 μm tend to randomize the distribution of orientations on the curved fibre surface. Such nanotube networks with locally isotropic and heterogeneous distribution create conductive pathway. The data presented here could be explained most readily if it is assumed that there is a nanotube layer having conductivity, $\sigma_{cnt,}$ on fibre surface with thickness, *t*, as schematically shown in Fig.1. The specific conductivity of glass fibre, σ_{glass}, parallel to the fiber axis is therefore given by

$$\sigma_{glass} = 4\left(\frac{t}{D} + \frac{t^2}{D^2}\right)\sigma_{cnt} \approx \frac{4t}{D}\sigma_{cnt} \quad (1)$$

Taking a rough estimate $D \sim 17$ μm for the glass fibre and t is in range of a few tenths to a few hundred nanometres based on fibre surface roughness data (average roughness of 6±3 nm, maximum height roughness 107±64 nm by the AFM characterisation), we see the ultra-thin nanotube networks with $\sigma_{cnt} \approx 10^2$ to 10^3 $\sigma_{glass} \approx 10$ to 10^4 S m^{-1}. It possess conductivity approach to the highest conductivities, typically 10^4 to 10^5 S m^{-1}, of the nanotube only buckypapers with an aggregate of high dense carbon nanotube networks [14-16]. It suggests that the high conductivity of the networks is achieved on our glass fibre surface. One may note, however, that a large variation in the resistance data is obtained. It is attributed to inhomogeneous distribution of nanotubes on the fibre surface using ionic SDS surfactant, such inhomogeneous distribution being more pronounced in the cases of using nonionic and cationic dispersing agents (results not show). As previously reported, at high SDS concentration, a depletion attraction is induced due to the unbalanced osmotic pressure between the SDS-stabilized nanotubes colloids and/or SDS micelles [17]. Consequently, nanotube bundles in a surfactant solution could form clusters. A percolated network depending on the aggregates features can form in both aqueous sizing and in turn fibre surface, which are influenced by different surfactants. A further optimization of uniformity and density of the nanotubes on glass fibre surface by applying electrophoretic deposition and controlling the degree of dispersion will be reported elsewhere [18].

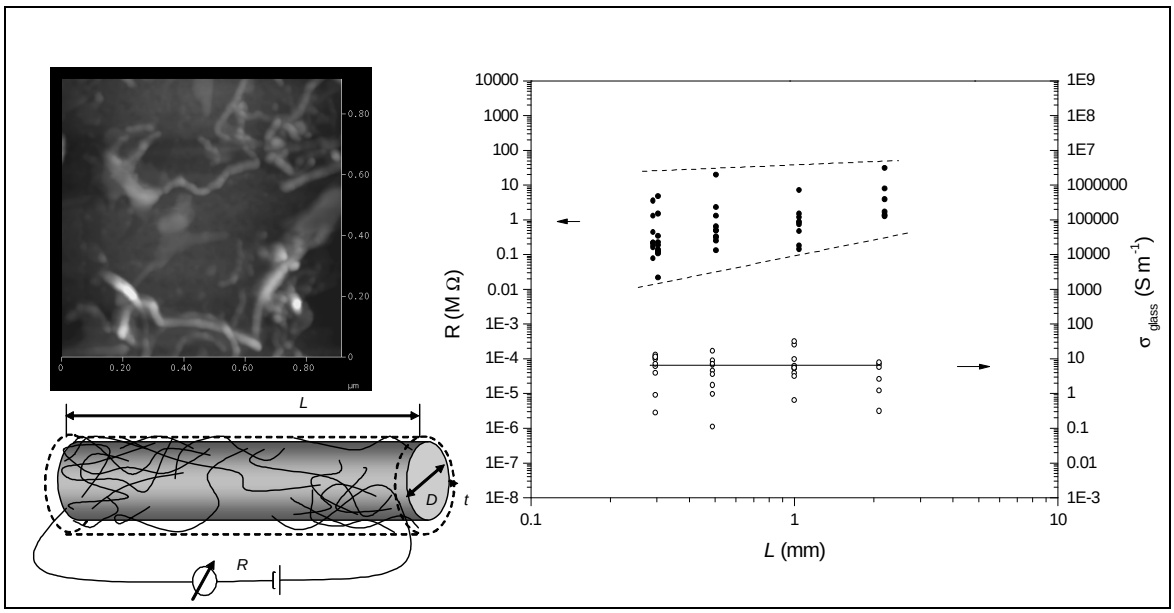

Figure 1. The DC electrical resistance measurements performed on single glass fibres in length of L with MWNT networks on glass fibre surface (shown in AFM image). Also schematically illustrates the fibre diameter and MWNT network thickness given by D and t, respectively, where t is much less than D.

As compared with traditional nanotubes containing polymer nanocomposites, our MWNTs coated unidirectional glass fibres reinforced epoxy matrix composites have an ultra-high anisotropic electrical property. The conductivities along the direction of glass fibres are typically four orders of magnitude higher than those of perpendicular to them (Table 1). Such anisotropic ratio of conductivity is approximately ten times higher than

the value of the aligning-CNTs/epoxy nanocomposites [19]. Thus, it permits low loading levels of nanotubes, along fibre direction, to achieve comparable or higher conductivities to conventional CNTs filled nanocomposites, and simultaneously, to keep insulation along other specific directions. Most interestingly, the specific conductivity of our composites parallel to the fibre axis is about 3.6×10^{-6} S m^{-1} at 5.7×10^{-4} wt% MWNTs, which is to our knowledge, the highest conductivity value yet reported for CNTs nanocomposites at this loading level [20]. Such nanotube loadings are significantly lower than the previously reported percolation threshold values. These results suggest that our MWNTs-glass fibres combined with a high aspect ratio at millimetre and higher scale are attractive fillers for making electrically conductive composites with anisotropic, antistatic and electrostatic shielding features.

Table 1. Anisotropic electrical properties of unidirectional glass fibre/epoxy composites.

Glass fibre fraction (vol %)	MWNTs concentration (wt %)	Specific conductivity in longitudinal fibre direction ($\times10^{-2}$ S/m)	Specific conductivity in transverse fibre direction ($\times10^{-6}$ S/m)
1.1×10^{-2}	5.7×10^{-4}	3.6×10^{-4}	NA
20	0.87	4.77	1.66
40	1.34	6.86	4.84
50	NA	33.03	22.27

We next investigated whether our semiconductive glass fibre is sufficient to show similar piezoresistivity for strain sensing as carbon fibre for a basic ability of smart structures. We started with the simultaneous measurement of the single MWNTs-glass fibre resistance change, stress, σ_{glass}, and strain, ε, during tension up to fracture (Fig.2a). We found that the fractional resistance increase ($\Delta R/R_o$) of the fibre increases approximately linearly with tensile strain up to fracture, which can be defined by:

$$\varepsilon = \frac{1}{GF}\frac{\Delta R}{R_o} + \varepsilon_o \qquad (2)$$

where R_o is the initial resistivity of the specimen without applying stress, $\Delta R=R-R_o$ is the resistance change, and the parameter ε_o refers to the initial strain for piezoresistivity effect of CNT network. GF is the strain sensitivity factor (or known as gage factor) which is 10.3 determined by the regression analysis. This value is comparable to the piezoresistive effect of semiconductor sensors but much higher than the geometrical piezoresistive effect in metallic sensors with the sensitivity factors usually a little over 2. The piezoresistivity of carbon nanotubes has been known for several years, i.e., nanotube electrical resistance changing by benting or stretching [21]. The significant resistance change of nanotube network on our glass fibre surface can be attributed to not only the stress dependent resistivity of the nanotube structure, but also the stress dependent change of nanotube network geometry, nanotube-nanotube interspace, contact area and density (junction point per unit volume). It should be noted that below the small strain level, $\varepsilon_o \approx 0.27\%$, the main part of individual nanotubes on fibre surface might not undergo mechanical stress and nanotube-nanotube interspace as well as network shape might not being changed recognizably. We subsequently addressed the strain sensing ability of an epoxy matrix composite with the continuous unidirectional

MWNTs-glass fibres. Fig. 2b shows the longitudinal strain and $\Delta R/R_o$ obtained simultaneously during both tension and compression region. The $\Delta R/R_o$ increased upon tensile loading and decreased upon compression loading almost linearly in the studied strain range, which can also be described by Eq. (2). The obtained strain sensitivity factor, however, is only about 1.3 which is essentially an order magnitude below that of single fibre shown in Fig. 2a. This phenomenon is very similar as the aforementioned conductivity variation before and after imbedded in epoxy. A possible main mechanism for reduction of sensitivity factor is attributed to the epoxy constriction effect, that is to say, the polymer chains limit lose or increase of nanotube-nanotube junction points/area during tension and compression, respectively. Secondly, part of fibre might not subject to load due to inhomogeneous stress distribution. Despite our still limited knowledge of the identity of the exact mechanisms, our findings clearly indicate that the piezoresistive effects of semiconductive MWNTs-glass fibre and composites provide a unique opportunity and a high potential for an in-situ load and damage detection of the most widely used glass-fibre-reinforced-polymer structures, which, unlike other attempts, does not require additional sensors and dispersion of CNTs in polymer matrix.

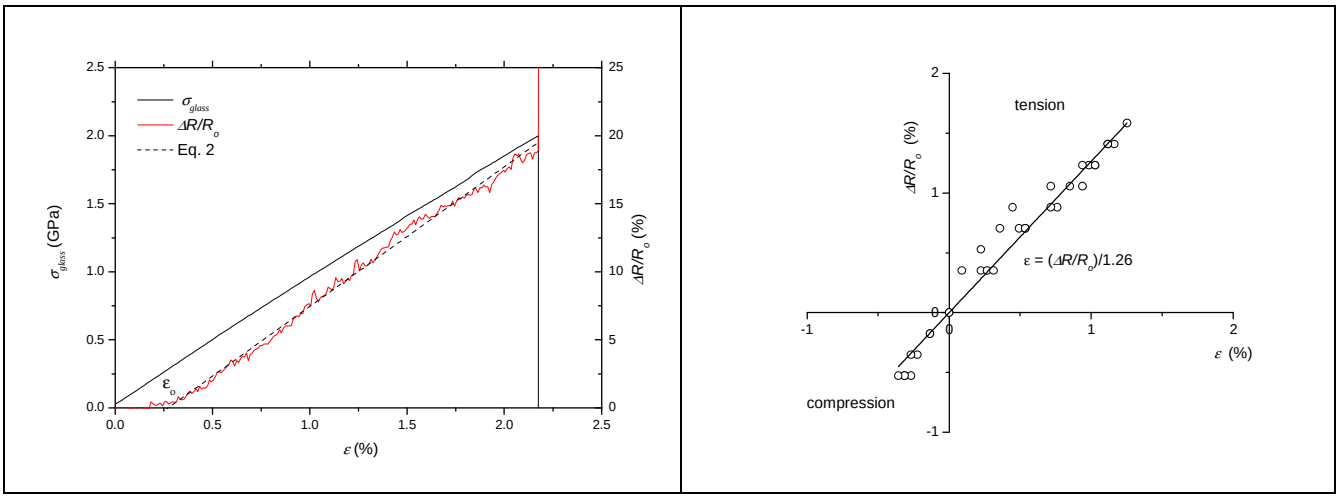

Figure 2. The piezoresistive effects of (a) single MWNTs-glass fibre during static tensile testing up to fracture, and (b) MWNTs-glass fibre (20 vol %) reinforced epoxy composites in both tension and compression.

To explore more broadly how our semiconductive glass fibre in composites is sufficient for temperature sensing, we assessed that the temperature dependence of the electrical resistivity for single and unidirectional fibre composites at different directions (Fig. 3a). It can be observed, in general, that the resistance of all samples decreased monotonically with the increase of temperature, indicating a negative temperature coefficient (NTC) effect and reflecting a typically semiconductive characteristic of MWNTs. The highest and lowest temperature sensitivities were found for composites at transverse direction and longitudinal direction, respectively. The single fibre composite showed similar behaviour with a composite in longitudinal direction. Interestingly, we found a transition range of all curves starting from around 70~74 °C, which was almost

coincident with the glass transition temperature, $T_g \approx 68\sim71$ °C measured by DSC [20]. We can thus infer that the transition temperature detected through the semiconductive interphase is related to the brittle-ductile transition of epoxy in or near interphase when the temperature increases up to T_g. The transition of epoxy network possibly induces break of some nanotube junction points and elongation of the interspaces between the CNTs, resulting in the variation of the resistance trends. Of particular interest is whether the entangled nanotube network influences the local cross-linking density of epoxy in interphase resulting in different T_g to bulk matrix. Experiments attempting to measure this by our in-situ MWNTs-glass fibre sensor and nano-TA technology are under way.

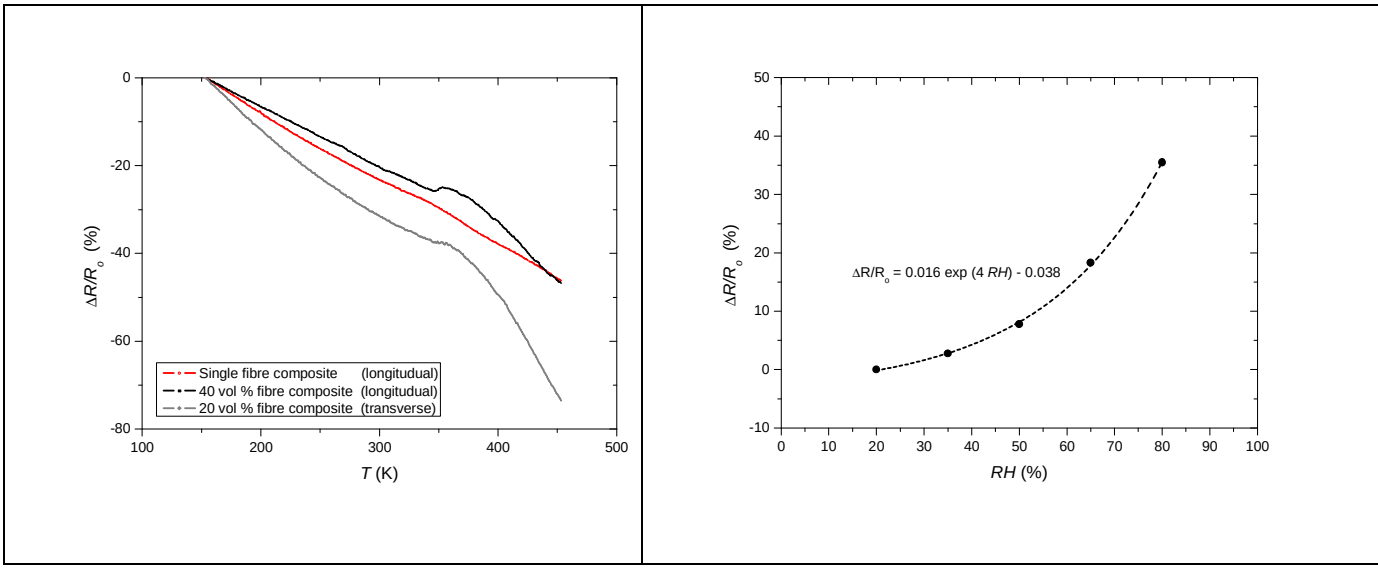

Figure 3. (a) The temperature dependence of the resistance changes of single fibre composite and unidirectional fibre composites with different volume fraction of MWNTs-glass fibres; (b) relative humidity dependence of the resistance changes of single MWNTs-glass fibre.

Moreover, the resistance of the single MWNTs-glass fibre was found to be sensitive to the humidity of the environment, which is shown in Figure 3b. It can be observed that the fractional resistance increased quickly up to about 40% with the increase of the humidity. The adsorption of electron-donating water molecules compensates for the hole carriers in p-type MWCNTs, causing the electrical resistance of nanotube to increase with humidity [22]. We found that the changes of the resistance had an exponential relationship with the humidity $\Delta R/R_o \propto \exp(bRH)$, where b is a positive constant. This is inconsistent with previously reported linear relationship for the pure CNT array and polymer/CNT-array composite film [23]. The mechanisms behind this are still unclear. Generally, the sensitivity to *RH* was reported very low for CNTs/hydrophobic polymer composite materials as humidity sensors [24]. The high humidity sensitivity of our single MWNTs-glass fibre hints that the fibre may also has potential as humidity sensor.

In conclusion, we have presented, for the first time, the glass fibre surface depositing with multiwalled carbon nanotube networks (MWNTs) leading to the formation of an electrically semiconductive glass fibre and in turn fibre/polymer interphase. As an in-situ multifunction sensor, the single MWNTs-glass fibre and corresponding epoxy

matrix composites show stress/strain, temperature and relative humidity dependences of electrical conductivity, which are capable of detecting composite piezoresistive effect and the local glass transition temperature in or near interphase. Moreover, the unidirectional composite fabricated via the MWNTs-glass fibres exhibit an ultra-high anisotropic semiconducting electrical property and an ultra-low electrical percolation threshold.

ACKNOWLEDGEMENTS

This work was supported by the German Research Foundation (DFG) Priority Programme SPP 1369 "Polymer-Solid Contacts: Interfaces and Interphases". The authors wish to thank Dr. Rüdiger Häßler, Werner Ehrentraut, Birgit Schulze for experimental assistance and helpful discussions

References

1. S.L. Gao, E. Mäder, R. Plonka, *Acta Materialia* 55 (2007) 1043.
2. R. H. Baughman, A. A. Zakhidov, W. A. de Heer, *Science* 297 (2002) 787.
3. E. Bekyarova, E. T. Thostenson, A. Yu, H. Kim, J. Gao, J. Tang, H. T. Hahn, T.-W. Chou, M. E. Itkis, R. C. Haddon, *Langmuir* 23 (2007) 3970.
4. V.P. Veedu, A.Y. Cao, X.S. Li, K.G. Ma, C. Soldano, S. Kar, P.M. Ajayan, M.N. Ghasemi-Nejhad, *Nat. Mater*. 5 (2006) 457.
5. Y. Dzenis, *Science* 319 (2008) 419.
6. L. Böger, M.H.G.Wichmann, L.O. Meyer, K. Schulte, *Compos. Sci. Technol.* 68 (2008) 1886.
7. L.M. Gao, Erik T. Thostenson, Z.G. Zhang, T.W. Chou, *Adv. Funct. Mater.* 19 (2009) 123.
8. J. Sandler, M.S.P. Shaffer, T. Prasse, W. Bauhofer, K. Schulte, A.H. Windle, *Polymer*, 40 (1999) 5967.
9. A. Allaoui, S. Bai, H.M. Cheng, J.B. Bai, *Compos. Sci. Technol.* 62 (2002) 1993.
10. J.H. Sung, H.S. Kim, H. Jin, H.J. Choi, I. Chin, *Macromolecules* 37 (2004) 9899.
11. B. Vigolo, C. Coulon, M. Maugey, C. Zakri, P. Poulin, *Science* 309 (2005) 920.
12. Q. Wang, J.F. Dai, W.X. Li, Z.Q. Wei, J.L. Jiang, *Compos. Sci. Technol.* 68 (2008) 1644.
13. M.D. Lynch, D.L. Patrick, *Nano Lett.*, 2 (2002) 1197.
14. Z. Wu, Z. Chen, X. Du, J.M. Logan, J.Sippel, M. Nikolou, K. Kamaras, J.R. Reynolds, D.B. Tanner, A.F. Hebard, A.G. Rinzler, *Science* 305 (2004) 1273.

15. U. Dettlaff-Weglikowska, V. Skakslova, R. Graupner, S.H. Jhang, B.H. Kim, H.J. Lee, Y.W. Park, S. Berber, D. Tomanek, S. Roth, *J. Am. Chem. Soc*. 127 (2005) 5125.

16. D. Zhang, K. Ryu, X. Liu, E. Polikarpov, J. Ly, M.E. Tompson, C. Zhou, *Nano Lett*. 6 (2006) 1880.

17. B. Vigolo, A. Penicaud, C. Coulon, C. Sauder, R. Pailler, C. Journet, P. Bernier, P. Poulin, *Science* 290 (2000) 1331.

18. J. Zhang, S.L. Gao, R.C. Zhuang, J.W. Liu, E. Mäder, Submitted.

19. Q. Wang, J.F. Dai, W.X. Li, Z.Q. Wei, J.L. Jiang, *Compos. Sci. Technol.* 68 (2008) 1644.

20. S.L. Gao, R.C. Zhuang, J. Zhang, J.W. Liu, E. Mäder, R. Häßler, submitted.

21. T.W. Tombler, C.W. Zhou, L. Alexseyev, J. Kong, H.J. Dai, L. Liu, C.S. Jayanthi, M. Tang, S.Y. Wu, *Nature* 405 (2000) 769.

22. O.K. Varghese, P.D. Kichambre, D. Gong, K.G. Ong, E.C. Dickey, C.A. Grimes, *Sens. Actuators B* 81 (2001) 32.

23. Z.H. Yang, Z. Cao, H. Sun, Y. Li. *Adv. Mater*. 20 (2008) 2201.

24. P.G. Su, C.S. Wang, *Sens. Actuators B* 124 (2007) 303.