FUNCTIONAL EPOXY COMPOSITES WITH MWNTS-GLASS FIBRES

J. Zhang[1*], S. L. Gao[1], E. Mäder[1]J. W. Liu[1], R.C. Zhuang[1]

Department Composite Materials, Leibniz-Institut für Polymerforschung Dresden e. V. (Leibniz Institute of Polymer Research), Dresden, Germany
[*]Corresponding author (zhang@ipfdd.de)

Keywords: *Carbon nanotube; Glass fibre; Interphase; Sensor; Switch*

1 Introduction

The interphase between reinforcement and matrix plays a critical role in performance of both bio-composites and man-made composites. For glass-fibre-reinforced plastics (GFRPs), the strength of composites and the environmental stability can be improved significantly through introducing the appropriate nanoscale interphase by nanoparticles. Recently, various nanoscale materials have been used for enhancing the interfacial strength of composites [1,2]. Since their excellent mechnical strength [3-5], carbon nanotubes (CNTs) are regarded as a ideal candidate of interphase modifiers to reinforce the interfacial strength. Besides, CNTs with small diameter open the door to future miniaturized and multifunctional materials, such as micro/nanoscale transistors, which could act as metals or semiconductors [6,7]. We deposited multi-walled carbon nanotubes (MWNTs) onto electrically insulative glass fibre surfaces for the first time [8-10], leading to the formation of semiconductive MWNTs-glass fibres and the improvement of the interfacial shear strength. Furthermore, we manufacture the single MWNTs-glass fibre not only as an *in-situ* sensor tracking the microcrack in composite, but also as an electromechanical switch utilizing the microcrack.

2 Experimental

2.1 Materials

The alkali-resistant glass (ARG) fibres with an average diameter of 12 µm utilized in this work as control fibre were manufactured by a continuous spinning process without sizing at our institute. Commercially available carboxy functionalized MWNTs (NC3101, Nanocyl S.A., Belgium) with an average diameter of 9.5 nm and an average length of 1.5 µm were used. Nonionic surfactant Igepal CO 970 was used to disperse CNTs. Silane coupling agent 3-Glycidyloxypropyltrimethoxysilane (Dynasylan® Glymo, Evonik Degussa Corporation, Germany) was added into CNT dispersion to introduce functional groups onto fibre surface and to improve the interfacial shear strength. A commercial DGEBA-based epoxy resin (resin EPR L20 and hardener EPH 960 in a weight ratio of 100:34, manufactured by Hexion Specialty Chemicals Stuttgart GmbH) was used as polymer matrix in the present study.

2.2 Deposition of MWNTs

Firstly, the 0.05 wt% MWNTs dispersion was prepared. Then MWNTs were deposited onto the insulating glass fibre surface through electrophoretic deposition (EPD) method, at constant voltages, deposition time of 10 min, and an electrode distance of 8 mm. The coated samples were dried at 40 ºC in a vacuum oven for 8 h. For optimization of coating morphology and thickness, the second time deposition was conducted under the same conditions as the first cycle. The morphology of MWNTs-glass fibre is shown in Fig.1.

2.3 Fabrication of single fibre model composite

Single filaments were mounted in a dogbone shaped silicone rubber mould. The epoxy resin and curing agent were thoroughly mixed and degassed prior to pouring into the mould. The samples were isothermally cured at 80 ºC for 12 h.

2.3 Characterization

2.1.1 *Topographic morphology*

The morphologies of MWNT coatings on the glass fibre surface were investigated using a SEM (Ultra 55, Carl Zeiss SMT AG, Germany), after sputtering a 5 nm thick platinum layer onto samples.

2.1.2 *Single fibre fragmentation test*

The interfacial shear strength was assessed by using the fragmentation test of single fibre model composites. The dimensions of single fibre composite specimen for fragmentation test were: 20

mm gauge length, 1.8 mm width and 1.5 mm thickness. Optical microscopes (Nikon Optiphot-2 and Keyence VHX-600) with transmitted polarized light were used to *in-situ* detect the lengths and fringe patterns of fibre fragments within the epoxy matrix.

2.1.3 *Electromechanical tests of single fibre composites*

The electrical resistances of the single fibres and single fibre model composites under tensile load were monitored simultaneously with mechanical stress-strain measurement under tensile loading. The specimen dimensions of single fibre model composite were 0.4 mm thickness, 1.5 mm width, and 5 mm gauge length.The stress-strain curve was detected by FAVIGRAPH Semiautomatic Equipment(Textechno Company, Germany) with test velocity 0.2 mm/min. Keithley 2000 multimeter and Keithley 6517A high resistance meter were used for the electrical resistance measurement and the ends of samples and test grips were painted by silver paste in order to form Ohmic contact.

The experiments of the resistance changing with temperature were carried out in a hot-stage (Linkam LTS350 Heating/Freezing, UK) from 25 °C to 80 °C with a heating rate of 5 K/min. At room temperature, the resistance of switch was immeasurable (above 210 GΩ), which was acquiesced to equal with the resistance value of epoxy (10^{15} Ω) in order to normalize the resistance value.

3 Results

3.1 Interfacial shear strength of single glass fibre composite

Fig. 2 shows the results of the fibre fragmentation tests for differently treated fibre specimens. Based on a force balance in a micromechanical model of Kelly and Tyson [11], the critical aspect ratio (l_c/d) is an inverse measure of the interfacial shear strength. Thus, the result demonstrates the interfacial shear strength was significantly enhanced by the MWNT coating using EPD, particularly the sample with epoxy silane coupling agent (EPD-G) achieved the maximum interfacial shear strength. The reason of enhancement might be the micro-interlocking between carbon nanotubes and epoxy as well as chemical bonding from silane coupling agent.

3.2 Multifunctional composite

3.2.1 *In-situ sensor*

First, we measured the DC resistance R of the single MWNTs-glass fibre which was in the range of 10^4 up to 10^8 Ω, and the resistance increased with increasing the space between electrodes. Accordingly, the calculated specific volume resistivity $\rho_{glass} = \pi d^2 R / (4L)$, for our glass fibre with diameter of 12 µm, was typically in the range of 2 up to 2.5×10^4 Ω·cm, which was in the semiconductive range and significantly lower than the volume resistivity over 10^{15} Ω·cm of the common electrical insulative glass fibre. We found the resistance of single fibre is sensitive to the small strain (Fig. 3a), and the strain sensitivity factor (or known as gage factor) is larger than commercially available metallic strain gages [9,12]. Consequently, an opportunity of *in-situ* sensor could be offered.

We investigated the piezoresistive response of the composite with a single MWNTs-glass fibre towards external loading (Fig. 3b). The electrical resistance monotonously increases with the applied strain, but the slope of relative resistance ($\Delta R/R_0$) curve experiences three stages: i) linear, ii) non-linear, and iii) abrupt changes, which correspond to the initiation and growth of a microcrack within the interphase. The electrical conductive path is completely damaged by microcracks and the resistance jumps to “infinity” (out of measurable range) before the composite failure. This result demonstrates the single MWNTs-glass fibre/epoxy composite can be used as *in-situ* sensor to monitor the propagation of microcrack and predict the damage of materials in advance.

To get more timely predictive signal, we embedded three individual fibres into the matrix and monitored the variation of resistance (Fig. 3c). The resistance sharply step-wise increases with the three fibres broken one by one, which acted as three variable resistors connected in parallel. Obviously, the multi-individual fibres composite improves the early warning capability and sensitivity for material health.

3.2.2 *Electromechanical switch*

We then examined whether the disconnected MWNT networks bridging across microcracks could be connected repeatedly under cyclic loading conditions. An alternative function, the electromechanical "switch" was found, where the electrical signals turn ON and OFF states with a variation of strain (see Fig. 4a). During the first cycle loading, the local microcrack is enlarged (see Fig. 4b) to completely break any junctions of carbon nanotube networks, where a natural trench structure is formed and the switch presents the "OFF" state. During the unloading, subsequently, the microcracks are closing and the disconnected nanotubes are approaching each other. Whenever the microcrack is less than the critical gap (microcrack width), some of disconnected carbon nanotubes re-connect and rebuild Ohmic contacts or approach very near to each other to form tunnelling current, the switch turns into "ON" state. The conversion of ON-OFF states occurred at almost same strains of all cycles, except the first cycle associated with the structure formation of switch. According to the axial fibre stress distribution in the single fibre composite, the critical gap, $\Delta\delta_c$, could be evaluated [10,13,14]. It is worthwhile to note that the effective service life of the switch should be influenced by multiple factors, such as, magnitude of loading force, speed, temperature and so on. Under the peak stress of 50 MPa, the observed service life of our switch could reach up to 50 times indicating a reasonable good repeatability [10]. In contrast to the generally designed gap in the electromechanical devices through complicated micro-fabrication processes [15], the MWNTs bridging microcracks result in a micro switch with the "junction-break" (connection-disconnection of CNTs network) mechanism, which integrates the electrode and contact gap structure in one single fibre model composite.

We subsequently further confirmed the "junction-break" mechanism by temperature actuated switch, (Fig. 5a). With the increase of temperature, the composite starts to expand and the microcrack on interphase shrinks where the disconnected carbon nanotubes would approach each other. Once the disconnected carbon nanotubes re-bridged, the electric circuit is immediately conducted and the resistance drops down sharply, at which the temperature is defined as the switch temperature. Notably, the variation of resistance during cooling is opposite with that during heating. Thus, the switch could be reproducibly actuated through heating and cooling.

Further work along these lines will be needed to explore whether the switch is possibly actuated by other kind of sources, such as laser, ultraviolet (UV), visible, infrared (IR) light or others. It is confirmed by the preliminary results of the small thermomechanical deformation caused by visible light illumination driving the switch (Fig. 5b).

4 Conclusion

Owing to MWNTs deposited onto the surface of the insulative glass fibre, the semiconductive MWNTs-glass fibres have been formatted and the interfacial shear strength in single fibre model composite has been improved. Subsequently, we have demonstrated that the MWNTs-glass fibres were able to detect and make utility of microcracks as real-time *in-situ* sensors for in advance warning catastrophic failure of materials and switches for sensitive control of micro systems.

Figures

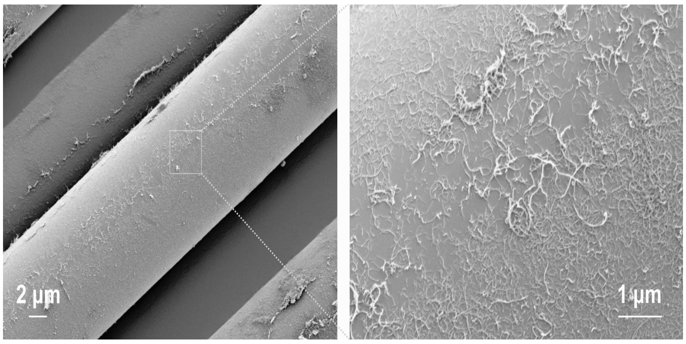


Fig. 1 FE-SEM images for the morphologies of the glass fibres coated by MWNTs.

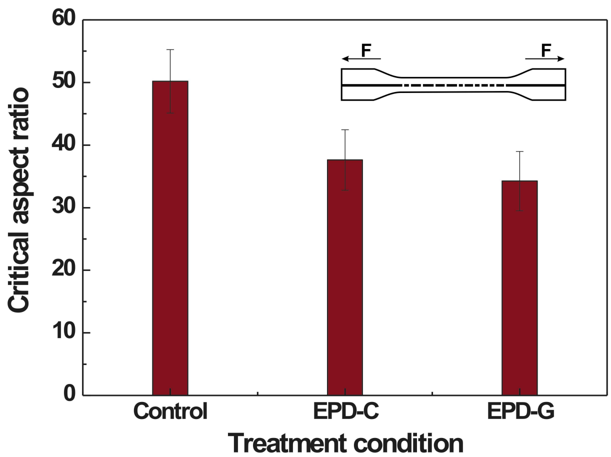
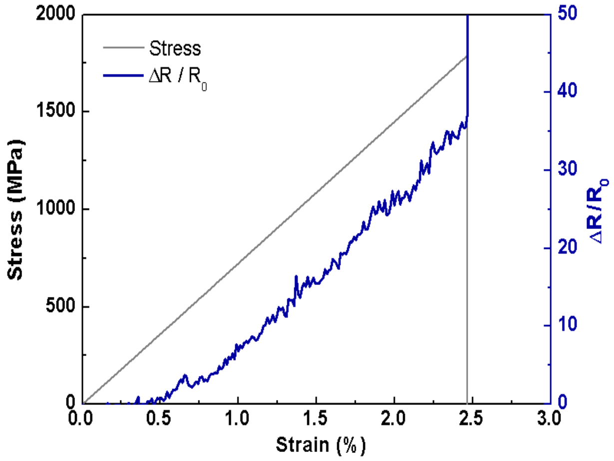
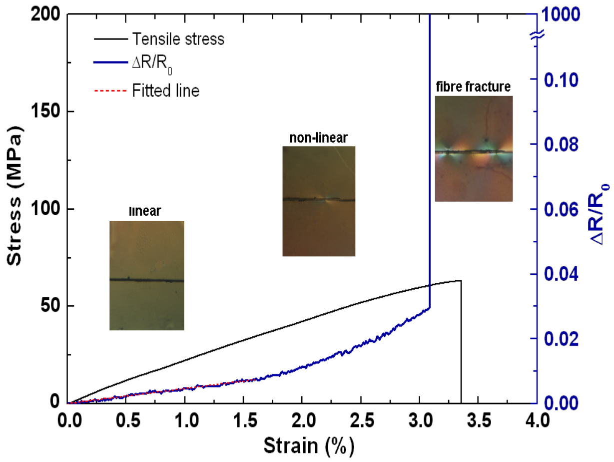


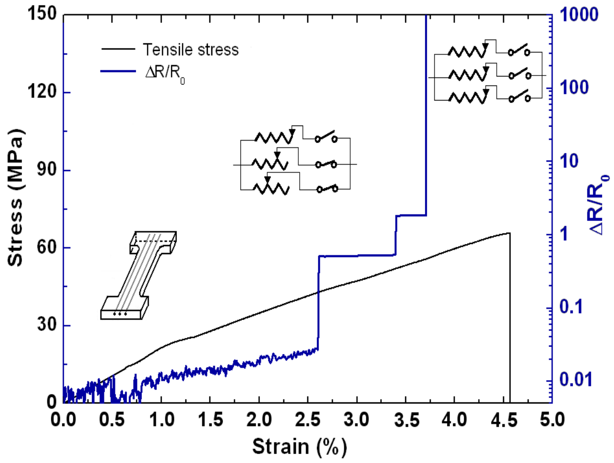
Fig. 2 Critical aspect ratios in single fibre composites after fragmentation with differently treated fibre surfaces.



a

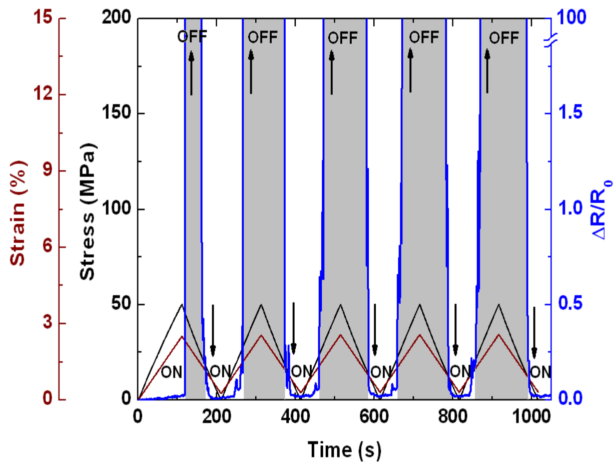


b

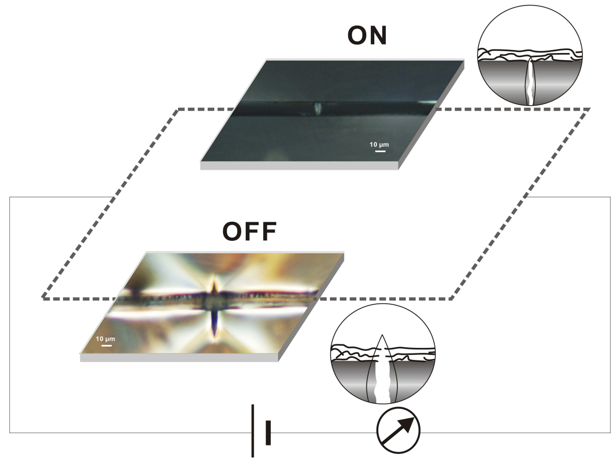


c

Fig. 3 a) The resistance various of single MWNTs-glass fibre with external stress/strain. b) Simultaneous change of electrical resistance depends on the stress and strain for a single coated fibre/epoxy composite. Inserted figures are the photoelastic profiles during steps of tensile process. c) The function of early warning is optimized through three individual fibres in the composite.

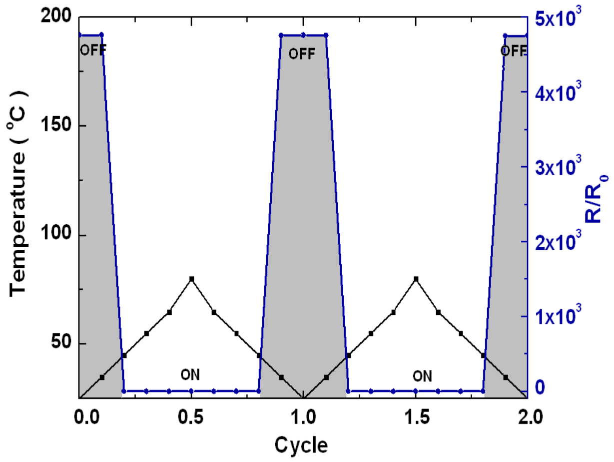


a

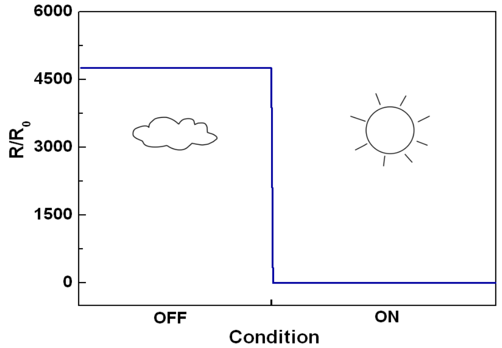


b

Fig. 4 a) Electromechanical switch acts during cyclic tensile tests. b) The switch turns ON or OFF state with the closing or opening of microcrack.



a



b

Fig. 5 a) The relative variation of the resistance and temperature dependence on cycle time (R_0 is 210 GΩ). b) The switch actuated by visible light. The switch presents ON or OFF state with turning on or off the visible light illumination (a lamp of 60 W). The distance between lamp and sample was about 200 mm.

Reference

[1] L. M. Gao, E. T. Thosteson, Z. G. Zhang and T.W. Chou "Sensing of damage mechanisms in fiber-reinforced composites under cyclic loading using carbon nanotubes", *Advanced Functional Materials*, Vol. 19, No. 1, pp 123-130, 2009.

[2] N. Shahid, R. G. Villate and A. R. Barron "Chemically functionalized alumina nanoparticle effect on carbon fiber/epoxy composites", *Composites Science and Technology*, Vol. 65, No. 14, pp 2250-2258, 2005.

[3] J-P Salvetat-Delmotte and A. Rubio "Mechanical properties of carbon nanotubes: A fiber digest for beginners", *Carbon*, Vol. 40, No. 10, pp 1729-1734, 2002.

[4] M. M. J. Treacy, T. W. Ebbesen and J. M. Gibson "Exceptionally high Young's modulus observed for individual carbon nanotubes", *Nature*, Vol. 381, p. 678, 1996.

[5] E. W. Wong, P. E. Sheehan and C. M. Lieber "Nanobeam mechanics: Elasticity, strength, and toughness of nanorods and nanotubes", *Science*, Vol. 277, pp 1971-1975, 1997.

[6] S. V. Ahir and E. M. Terentjev "Photomechanical actuation in polymer-nanotube composites", *Nature Materials*, Vol. 4, No. 6, pp 491-495, 2005.

[7] A. B. Kaul, E. W. Wong, L. Epp and B. D. Hunt "Electromechanical Carbon Nanotube Switches for High-Frequency Applications", *Nano Letters*, Vol. 6, No. 5, pp 942-947, 2006.

[8] J. Zhang, R. C. Zhuang, J. W. Liu, E. Maeder, G. Heinrich and S. L. Gao "Functional interphases with multi-walled carbon nanotubes in glass fibre/epoxy composites", C*arbon*, Vol. 48, No. 8, pp 2073-2281, 2010.

[9] S. L. Gao, R. C. Zhuang, J. Zhang, J. W. Liu and E. Maeder "Glass fibre with carbon nanotube networks as multifunctional sensor", *Advanced Functional Materials*, Vol. 20, No. 12, pp 1885-1893, 2010.

[10] J. Zhang, J. W. Liu, R. C. Zhuang, E.Maeder G. Heinrich and S. L. Gao "Single MWNTs-Glass Fibre as Strain Sensor and Switch", Adva*nced Materials*, Accepted, 2011.

[11] A. Kelly and W. R. Tyson "Tensile properties of fibre-reinforced metals: Copper/tungsten and copper/molybdenum", *Journal of Mechanics and Physics of Solids*, Vol. 13, No. 6, pp 329-350, 1965.

[12] G. T. Pham, Y. B. Park, Z. Liang, C. Zhang and B. Wang "Processing and modeling of conductive thermoplastic/carbon nanotube films for strain sensing", Comp*osites Part B: Engineering*, Vol. 39, No. 1, pp 209-216, 2008.

[13] J. M. Whitney and L. T. Drzal "Toug*hened Composites ASTM STP 937"*, Norman J.Johnston, American Society for Testing and Materials. 1987.

[14] F. A. Ramirez, L. A. Carlsson and B. A. Acha "A method to measure fracture toughness of the fiber/matrix interface using the single-fiber fragmentation test", Comp*osites Part A: Applied Science and Manufacturing*, Vol. 40, No. 6-7, pp 679-686, 2009.

[15] S. W. Ryu, C. J. Kim, S. Kim, M. Seo, C. Yun, S. Yoo and Y. K. Choi "Fullerene-Derivative-Embedded Nanogap Field-Effect-Transistor and Its Nonvolatile Memory Application", *Small*, Vol. 6, No. 15, pp 1617-1621, 2010.