MULTIFUNCTIONAL COMPOSITES BASED ON VARIOUS NANOLAYERS

Jie Zhang[1] *, Chao Sun,[1] Shanglin Gao[2] and Zuoguang Ye[1,3]

[1]Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education &
International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, China,
jzhang12@mail.xjtu.edu.cn
[2]Leibniz–Institut für Polymerforschung Dresden e.V. Hohe Strasse 6, 01069 Dresden, Germany,
gao@ipfdd.de
[3]Department of Chemistry and 4D LABS, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada, zye@sfu.cn

Keywords: Nanolayer; Interphase; Multifunctional sensor; ALD

Summary

we presented the enhanced the interfacial shear strength of composites with glass fibers deposited by nano-layer (CNTs, ZnO). At the same time, the single modified fiber could be designed as multifunctional sensor based on various nano-layers.

ABSTRACT

Carbon nanotubes (CNTs) and zinc oxide (ZnO) are popular candidates as modifiers to optimize composites' properties, because of their high strength, distinctive electrical, optical properties and high sensitivities towards gas, humidity and so on. In this report, we deposited CNTs and ZnO onto electrically insulating glass fiber surfaces by electrophoretic deposition (EPD) and atomic layer deposition (ALD) methods, respectively. Firstly, we found that the interfacial shear strength of single fiber composites has been singnificantly improved by various nanolayers. Importantly, due to a precisely controlled thickness by ALD, the effect of thickness of nanolayer on the interfacial strength was investigated for the first time, and a critical thickness of nanolayer, corresponding to the maximum interfacial strength has been firstly experimentally obtained.

Subsequently, we utilized single modified fibers to produce the multifunctional sensors. The modified single fiber by CNTs demonstrated a high sensitivity to the stress/strain through the simultaneous measurement of the electrical resistance under tensile loading. The strain sensitivity factor, GF, of CNTs-glass fiber is much higher than those of conventional metallic strain gages with geometrical piezoresistive effect, which displays a potential as *in-situ* micro sensor in materials. At the same time, the CNTs-glass fiber was used as an *in-situ* chemical/physical sensor to characterize the processes of curing or crystallization of polymers through monitoring the low mobility of charge carriers in insulative materials. The glass transition was also interpreted by the resistance measurement.

1 INTRODUCTION

The interphase between reinforcing filler and matrix plays a critical role in performance of composites. Thus, in order to optimize the properties of composite, various experiments have been carried out to improve the interfacial properties, for example, conducting chemical [1,2]or physical[3,4] (heat, plasma) treatments on the reinforced fiber surfaces. Recently, depositing nano-materials onto the fibers surfaces has been regarded as a promising approach to obtain higher quality fiber reinforced composites (FRC). Because the high temperature and chemical atmosphere during the growth process of nano-materials leaded to reduce the tensile strength of the fiber substrate, some low-temperature methods, such as electrophoretic deposition[5,6] and hydrothermal process,[7-10] have been adopted to deposit nano-layers onto the fibers and realized improvement in the IFSS of the composites.

On the other hand, the *in-situ* modification on fibers by different nano-layers has been expected to introduce many new functions into the composites.[5,11-13] In this report, we presented the single fiber deposited by CNTs as a micro-sensor to monitor the deformation or chemical/physical transitions of polymer composites. To investigate the influence of the thickness of nanolayer on the properties of composites, we deposited ZnO on to the glass fibers' surfaces by ALD. While, the single glass fiber modified by ZnO showed us a potential application as UV detector.

2 EXPERIMENTAL

2.1 Deposition of nanolayer

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.

ZnO nano-layers were deposited onto glass fiber at 200 °C by ALD (Picosun R200, Finland) process where diethylzinc (DEZ 99.9999%, Suzhou For nano Electronic Technology Co., Ltd, China) and deionized water were used as precursors for zinc and oxygen. ZnO nano-layers with various thicknesses, from 20 nm to 74 nm, were precisely controlled by the number of ALD cycles.

2.2 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

2.3.1 *Single fibre fragmentation test*

The specimens were tested using a FM-12 tensile test (Beijing Fuyouma Technology Co., Ltd, China) equipment at room temperature, ata 0.0005mm/sstretch rate. Meanwhile, a polarizing microscope system was used to in-situ monitor the processand the birefringent patterns of fiber fragmentation within the epoxy matrix.

Resistance measurement under UV-light:

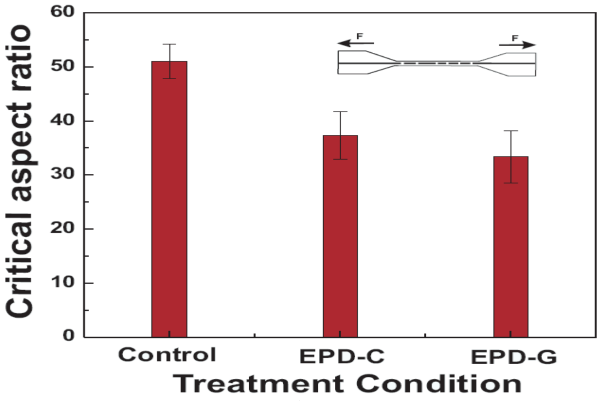
The fiber was connected to two Au electrodes via silver paste on glass substrates. For the sensitivity test of the composites under UV-light, a single fiber was embedded into transparent epoxy. A spectrofluorometer (QuantaMasterTM40, U.S.A.) provided static UV-light and the wavelength of the specific UV-light was 379 nm. Simultaneously, a DC digital multi-meter (Keithley 2002, U.S.A.) was used to record the resistance change through a 2-wire model.

3 RESULTS AND DISCUSSIONS

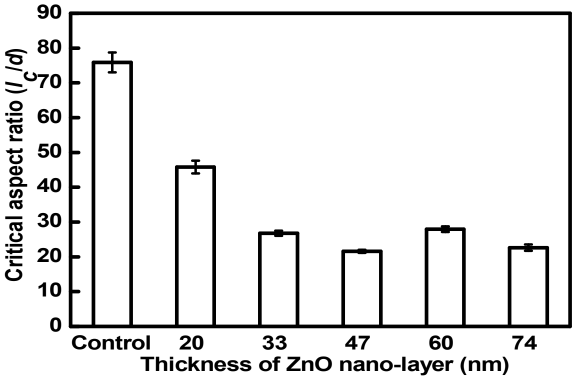
3.1 Interfacial shear strength of single glass fibre composite

Fig. 1a shows the results of the fibre fragmentation tests for differently treated CNT-glass fibre specimens. Based on a force balance in a micromechanical model of Kelly and Tyson [14], the ratio (l_c/d) is an inverse measure of the interfacial shear strength. Thus, the result demonstrates the interfacial shear strength was enhanced by the CNTs coating using EPD, particularly the sample with epoxysilane coupling agent (EPD-G) achieved the maximum interfacial shear strength.

Obviously, the interfacial shear strength of all of the ZnO-modified fiber composites is enhanced compared with the control fiber group, as shown in Fig. 1b. In particular, the sample with 47 nm thick ZnO achieves the maximal improvement, i.e. about 200% over that of the control group. Notably, it is nearly about twice as high as the result (113%) [7] reported in ZnO nanowire-modified carbon fiber composite and much higher than the other result reported nano-materials-modified fiber composites, such as CNT-modified FRC (~ 90%).[15]



(a)



(b)

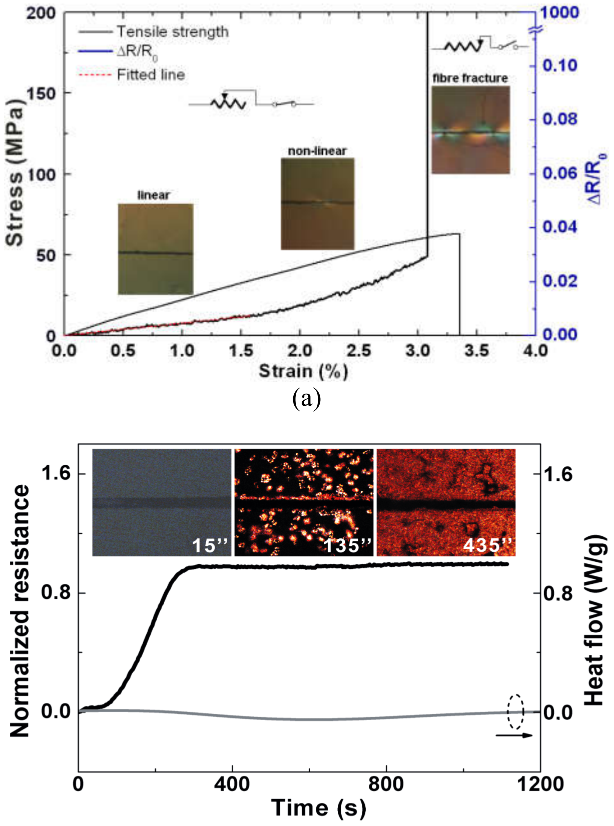
Figure 1: Critical aspect ratios in single (a) CNTs-glass fibre and (b) ZnO-glass fiber composites after fragmentation test

3.2 MULTIFUNCTIONAL COMPOSITE

3.2.1 *In-situ* sensor based on CNT-glass fiber

We investigated the piezoresistive response of the composite with a single CNTs-glass fibre towards external loading (Fig. 2a). The electrical resistance monotonously increases with the applied strain, but the slope of relative resistance ($\Delta R/R_0$) curve is varied, because the CNT networks are disconnected with the initiation and growth of a microcrack within the interphase. This result demonstrates the single MWNTs-glass fibre/epoxy composite can be used as *in-situ* sensor to monitor and to warn early for the damage of materials.

We next investigated more broadly whether the CNT-glass fiber is sensitive towards the crystallization behavior of thermoplastic materials. The formation of crystalline phase of polymer composites, particularly in the interphase region, is a very important issue, which is rarely observed in real time. The structural transition of thermoplastics was gained firstly from the isothermal crystallization (230 °C). In Fig. 2(b), the dramatic ascending resistance after 20 s indicates the appearance of a crystalline phase. It is the result of that the displacement of charge carriers is confined by the rising barrier and the decrease of free volume fraction with the occurrence of a crystalline phase. Through the simultaneous optical images accompanying the resistance test, the gradual growth of crystals can be captured and confirmed. As the completion of crystallization, the resistance reaches the higher plateau as most of charge carriers are restricted.



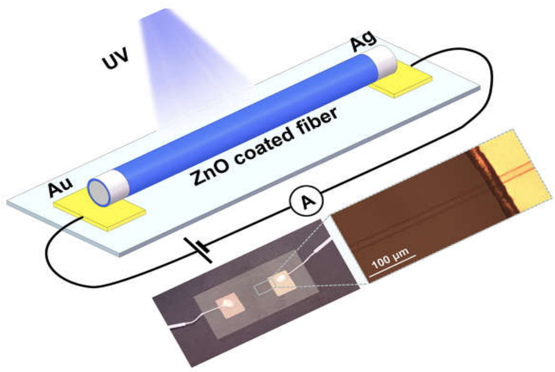
(a)

(b)

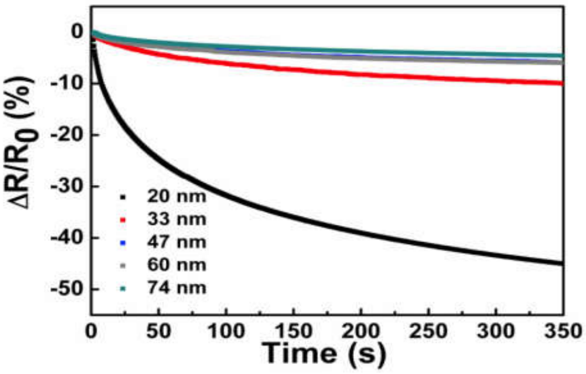
Figure 2: (a) Simultaneous change of electrical resistance depends on the stress and strain for a single CNT-glass fibre/epoxy composite. Inserted figures are the photoelastic profiles during steps of tensile process. (b) The changes of resistance (black lines) based on CNT-glass fiber sensor and heat flow (gray lines) for the isothermal crystallization of PET, at 230 °C. The inserted images are the simultaneous crossed-polarized microscope pictures of the crystallization with the resistance test, at 15 second, 135 second and 435 second, respectively.

3.2.2 UV detector based on ZnO –glass fiber

Fig. 3a schematically shows the test process of single fiber UV detector. We define ΔR/R0 as the UV sensitivity, where R0 refers to the original resistance, and ΔR is a response time dependent value (R-R0) under 379 nm UV-light. The recorded electric responses of modified fibers in air are shown in Figure 3b.When the UV-light is switched on, an instant decrease in the resistance is observed, and clearly, a sharp difference of sensitivity is related to the different thicknesses' ZnO.



(a)



(b)

Figure 3: (a) Schematic drawing of the resistivity testing system on the top and the objective sample for resistivity testing (left down) and the local enlarged optical image of fiber (right down). (b) The sensitivity of the single modified glass fiber with different ZnO nano-layer thickness towards UV-light.

9 CONCLUSIONS

In this report, we presented the enhanced the interfacial shear strength of composites with glass fibers deposited by nano-layer (CNTs, ZnO). At the same time, the single modified fiber could be designed as multifunctional sensor based on various nano-layers.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge support from the National Natural Science Foundation of China (No. 51303148), the Fundamental Research Funds for the Central Universities (No. xjj2013018), the National 111 Project of China (B14040).

REFERENCES

[1] M. A. Sawpan, K. L. Pickering and A. Fernyhough, Effect of various chemical treatments on the fibre structure and tensile properties of industrial hemp fibres, *Composites Part A, **42**, 2011*, pp.888-895.

[2] J. G. Iglesias, J. Gonz´alez-Benito, A. J. Aznar, J. Bravo, and J. Baselga, Effect of glass fiber surface treatments on mechanical strength of epoxy based composite materials, *Journal of Colloid Interface Science,* **250**,*2002*, pp. 251-260.

[3] Z. Dai, B. Zhang, F. Shi, M. Li, Z. Zhang and Y. Gu, Effect of heat treatment on carbon fiber surface properties and fibers/epoxy interfacial adhesion, *Applied Surface Science,* **257**, ***2011***, pp. 8457-8461.

[4] G. M. Wu, Oxygen plasma treatment of high performance fibers for composites, *Materials Chemistry & Phyics,* **85**,*2004*, pp. 81-87.

[5] J. Zhang, R. Zhuang, J. Liu, E Mäder, G. Heinrich and S. Gao, Functional interphases with multi-walled carbon nanotubes in glass fibre/epoxy composites, *Carbon,* **48**, *2010*, pp. 2273-2281.

[6] H. Luo, G. Xiong, X. Chen, Q. Li, C. Ma, D. Li, X Wu and Y. Wan, ZnO nanostructures grown on carbon fibers: Morphology control and microwave absorption properties, *Journal of Alloys & Compounds,* **593**, *2014*, pp. 7-15.

[7] Y. Lin, G. Ehlert and H. A. Sodano, Increased Interface Strength in Carbon Fiber Composites through a ZnO Nanowire Interphase, *Advanced Functional Materials,* **19**, *2009*, pp. 2654-2660.

[8] G. J. Ehlert and H. A. Sodano, Zinc Oxide Nanowire Interphase for Enhanced Interfacial Strength in Lightweight Polymer Fiber Composites, ACS *Applied Material Interfaces,* **1**,*2009*, pp. 1827-1833.

[9] G. J. Ehlert, Y. Lin, U. Galan and H. A. Sodano, Interaction of ZnO Nanowires with Carbon Fibers for Hierarchical Composites with High Interfacial Strength, *Journal of Solid Mechanics & Materials Engineering*, **4**, *2010*, pp.1687-1698.

[10] U. Galan, Y. Lin, G. J. Ehlert and H. A. Sodano, Effect of ZnO nanowire morphology on the interfacial strength of nanowire coated carbon fibers, *Composites Science & Technology,* **71***, 2011*, pp. 946-954.

[11] S. Gao, R. C. Zhuang, J. Zhang, J. W. Liu and E. Mäder, Glass Fibers with Carbon Nanotube Networks as Multifunctional Sensors, *Advanced Functional Materials,* **20***, 2010*, pp. 1885-1893.

[12] J. Rausch and E. Mäder, Health monitoring in continuous glass fibre reinforced thermoplastics: Manufacturing and application of interphase sensors based on carbon nanotubes, *Composites Science & Technology,***70***, 2010*, pp.1589-1596.

[13] Q. Liao, M. Mohr, X. Zhang, Z. Zhang, Y. Zhang and H. J. Fecht, Carbon fiber-ZnO nanowire hybrid structures for flexible and adaptable strain sensors, *Nanoscale,* **5**, *2013*, pp. 12350-12355.

[14] A. Kelly and W.R. Tyson. Tensile properties of fibre-reinforced metals: Copper/tungsten and copper/molybdenum. *Journal of the Mechanics & Physics of Solids,* **13**, *1965*, pp. 329-350.

[15] A. Godara, L. Gorbatikh, G. Kalinka, A. Warrier, O. Rochez, L. Mezzo, F. Luizi, A.W. van Vuure, S.V. Lomov and I. Verpoest, Interfacial shear strength of a glass fiber/epoxy bonding in composites modified with carbon nanotubes, *Composites Science & Technology,* ***70***, ***2010***, pp. 1346-1352.