A built-in sensor with carbon nanotubes coated by Ag clusters for deformation monitoring of glass fibre/epoxy composites

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Abstract. A multiwalled carbon nanotube network embedded in a polyurethane membrane was integrated into a glass fibre reinforced epoxy composite by means of vacuum infusion to become a part of the composite and has been serving for a strain self-sensing functionality. Besides the pristine nanotubes also nanotubes with Ag nanoparticles attached to their surfaces were used to increase strain sensing. Moreover, the design of the carbon nanotube/polyurethane sensor allowed formation of network micro-sized cracks which increased its reversible electrical resistance resulted in an enhancement of strain sensing. The resistance sensitivity, quantified by a gauge factor, increased more than hundredfold in case of a pre-strained sensor with Ag decorated nanotubes in comparison with the sensor with pristine nanotubes.

1. Introduction

Strain sensing composite materials have attracted considerable attention for their unique characteristics exceeding conventionally applied sensors. Between different solutions and various types of transducers available for these applications, piezo-resistive strain sensors are among the most investigated ones [1-6]. They are usually based on conductive polymer composites (CPCs) prepared by embedding of electrically conductive fillers as carbon nanotubes (CNTs) into a polymeric matrix. Here the carbon nanotube films are usually deposited on thicker flexible polymeric substrate which acts as a mechanical support and transfer mechanical stimulus to carbon strain sensitive layer [1-6]. The electric resistance response of a CNT film/polymer composite to extension is determined by the local resistance in nanotube contacts and the straightening and buckling of nanotubes, which affects the number of contacts between nanotubes [1]. It was found that the resistance change at deformation above approx. 1% is due to the crack formation in carbon nanotube layer [11-13]. To modify the nanotube contacts itself in the course of strain sensitivity increase, different chemical functionalization
or plasma oxidation of carbon nanotubes are used [5,7]. Moreover, decorating CNTs with Ag nanoparticles enhance also the strain sensing [8-10]. Finally, there were published results that show that increase in the sensitivity of CNT film/polymer composite to applied strain can be significantly increased by composite pre-straining method [11-13].

In the present paper the combination of MWCNTs functionalization by Ag nanoparticles (AgNPs) together with a controlled pre-straining are used to prepare a strain sensor with enhanced sensitivity to applied strain. It composes of electrically conductive entangled network of Ag-decorated multiwalled carbon nanotubes supported by polyurethane filtering membrane integrated into a glass fibre/epoxy resin composite by vacuum infusion technique.

2. Experimental methods

Materials
Purified MWCNTs produced by chemical vapour deposition of acetylene were supplied by Sun Nanotech Co. Ltd., China. According to the supplier, the nanotube diameter is 10-30 nm, the length 1-10 μm, the purity ~ 90% and the volume resistivity 0.12 Ωcm. MWCNTs decorated by Ag clusters were prepared by sonication of nanotube dispersion in Bandelin thermostatic ultrasonic bath for 30 min. Then 80 ml of 0.1 M silver nitrate (AgNO₃) and 20 ml of 1 wt.% of sodium salt of citric acid was added to dispersion and boiled in a glass reactor connected with the reflux condenser for 1 hour. Polyurethane (TPU), Desmopan 385S was used for fabrication of filtering membrane by technology of electrospinning supplied by Bayer MaterialScience (ultimate tensile strength 40 MPa and strain at break 450 %). As an epoxy matrix EPIKOTETM as resin and EPIKURETM RIMH 1366 as curing agents mixed in weight ratio 100:30 were used. Woven glass textiles were supplied by Lange+Ritter (03G080LT.VR080). The textile had a plain weave structure and weight 80g/m².

Polyurethane/MWCNT sensor integrated into glass fibre/epoxy composite
Aqueous dispersion of MWCNTs/AgNPs was prepared by sonication in an apparatus UZ Sonopuls HD 2070 for 15 minutes at room temperature. The nanotube concentration in the suspension was 0.3 wt.%. Dispersion contained also surfactants, namely sodium dodecyl sulfate and 1-pentanol with concentration 0.1M and 0.14M, respectively. Moreover, NaOH aqueous solution was added to adjust pH to 10. For making an entangled MWCNTs/AgNPs network, a porous polyurethane membrane and a vacuum filtration method was used. 30 ml of homogenized dispersion was filtered through the funnel of diameter 90 mm. Polyurethane filtering membrane was prepared by technology of electrospinning of TPU solution in dimethyl formamide/methyl isobutyl ketone solution, 3:1. This semi product was integrated by epoxy vacuum infiltration according schematic illustration in Fig. 1., and cured during 24 hours at room temperature. The size of tested MWCNTs layers integrated into epoxy composites was approx. 50x10 mm. Cu wires were fixed to the sensor by a silver-colloid electro-conductive paint Dotite D-550 (SPI Supplies) and dried before vacuum infusion process.

![Fig. 1 The schematic illustration of fabrication process of epoxy/glass fibre composite with integrated MWCNT/TPU strain sensitive layer.](image-url)
Tests and measurements
The morphology of the MWCNTs and MWCNTs decorated with Ag nanoparticles were investigated by means of TEM analysis using the microscope JEOL JEM 2010 at the accelerating voltage of 160 kV. The structure of MWCNT films was analysed by the scanning electron microscope (SEM) NOVA NanoSEM 450. Elongation and relaxation of a glass fibre/epoxy composite with integrated strain sensor was measured during the composite bending over a cylindrical surface. Seven different cylindrical surfaces with diameters from 70 to 315 mm were used. The pre-strained composites were prepared by bending around cylindrical surface of diameter 37 mm. The achieved strain $\varepsilon$ was calculated according to Euler-Bernoulli beam bending theory, $\varepsilon = \frac{y}{\rho}$, where $y$ denotes the sensor distance from neutral axis and $\rho$ denotes radius of neutral axis, according schematics illustration in Fig. 2.

Detection ability of applied strain by integrated MWCNT layer was tested by its resistance change with deformation. The sensor resistance was monitored during bending with help of the two-point technique measured lengthwise using Multiplex datalogger 34980A with storage of data once per second.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig2.png}
\caption{The schematic of bending of glass fibre/epoxy composite over a cylindrical surface.}
\end{figure}

3. Results and Discussion
High-resolution transmission electron microscopy (HRTEM) micrographs in Fig. 3a show the structure of one individual MWCNT which consist of about 15 rolled layers of graphene. Fig. 3b is TEM analysis of MWCNT with deposited Ag clusters. The size of Ag clusters on MWCNT surface was in the range $\sim$3-10 nm.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig3.png}
\caption{a) HRTEM micrograph of the structure of individual nanotube; b) TEM micrographs of individual nanotube with deposited Ag clusters.}
\end{figure}
The scanning electron microscope (SEM) analysis of PU non-woven filtering membrane is presented in Fig. 4 a). Individual nanotubes are entrapped by filtering membrane in the course of MWCNTs aqueous dispersion vacuum filtration. The nanotubes infiltrate into membrane pores which are finally blocked and a filtering cake made of pure network of entangled MWCNTs is created. SEM micrograph in Fig. 2 b) shows the upper surface of MWCNTs network and Fig. 2 b) of network from MWCNTs/AgNPs. Both networks are porous and electrically conductive structures created by entangled nanotubes with electrical conductive junctions between individual tubes.

Final epoxy composite with integrated MWCNTs/PU composite sensor consisted of six layers of glass fibre textile, then a stripe of MWCNTs/PU composite sensor and finally one covering layer of glass textile, Fig. 5a. This configuration assured that the sensor was placed above the neutral axis of the glass fibre/epoxy composite. Hence, when the glass fibre/epoxy composite was bent, the sensor underwent an extension and it measured a corresponding electrical resistance change of a nanotube film.

The resistance change of the sensor made of pristine or Ag decorated MWCNTs integrated into the glass fibre/epoxy composite was tested in the course of the composite elongation by bending over the rigid cylinders of different diameters. The maximum strain of the sensor located above the neutral axis and calculated in the middle of MWCNTs layer was 0.48 %. The results of five cycles of stepwise elongation/relaxation of the composite are shown in Fig. 6 for not pre-strained and pre-strained samples. Part a) the results for the sensor with pristine nanotubes show firstly a residual strain after the sample relaxation which was not observed in tests of the integrated sensor with MWCNTs/AgNPs.
Also in comparison with data in Parts b) the resistance change is relatively small. On the other hand, the sensor with Ag decorated nanotubes did not have any residual strain and the resistance change in comparison with the sensor with pristine nanotubes substantially increased which is favourable for the effective measurement of deformation of the glass fibre/epoxy composite. A fundamental parameter of the strain sensor is its sensitivity to strain expressed usually by means of the gauge factor (GF). GF is the ratio of the fractional change in electrical resistance to the fractional change in length, or strain $\epsilon$, $GF = (\Delta R/R_0)/(\Delta L/L) = \Delta R/R/\epsilon$, where $(\Delta R/R_0) = (R - R_0)/R_0$. $R_0$ represents initial resistance (undeformed sensor) and R in deformed state. The sensor sensitivity to strain measured by the gauge factor was as high as 500 for the sensor with Ag decorated MWCNTs while metallic foil sensors usually have a gauge factor slightly over 2.

Fig. 6 The glass fibre/epoxy composites with the integrated sensors subjected to five elongation/relaxation cycles. The resistance change as well as the gauge factor corresponding to respective resistance data in the course of elongation and relaxation is denoted by circles and squares, respectively. The results for not pre-strained sensor are denoted by open symbols and the results for the pre-strained sample by 0.94 % strain are denoted by filled symbols. a) The sensor with pristine MWCNTs, b) the sensor with MWCNTs/AgNPs.

4. Conclusion
MWCNTs layers embedded in epoxy composites reinforced by glass fibres are proposed as a novel material that can be used for composite itself deformation detection. Further, it has been proven that modification of pure MWCNT with Ag clusters together with application of well-defined prestrain stimulation significantly increase composite sensitivity to applied strain defined by GF. Sensitivity for sensor with pure MWCNTs reaches GF values 6-8. When comparing with GF for composite with MWCNTs/AgNPs layer coming up to 500. This is a substantial increase ranks the polyurethane sensor integrated into the glass fibre/epoxy composite among strain gauges with the highest electromechanical sensitivity.
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