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Piezoresistive characterization of multi-walled carbon nanotube-epoxy based flexible strain sensitive films by impedance spectroscopy

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ABSTRACT

In this study, we investigate the piezoresistive properties of flexible, strain sensitive multi-walled carbon nanotubes (MWCNTs)/epoxy composites. The deformation over the sensor area was tested by digital image correlation (DIC) under quasi-static uniaxial tension. The piezoresistive characteristics of the films were investigated quantitatively by electrochemical impedance spectroscopy (EIS) over a wide range of frequencies from 40 Hz to 110 MHz. Scanning electron microscopy (SEM) images confirmed that MWCNTs/epoxy composites with different CNT concentrations have a good homogeneity and dispersion. Additionally, in order to tailor the piezoresistivity of the strain sensor, an RC equivalent circuit was derived based on the impedance responses and the corresponding parameters were extracted under tensile strain. Compared with traditional strain gauges, higher sensitivity is obtained in particular at the concentrations close to the percolation threshold (13.6 for 0.3 wt.%). Due to the tunneling effect, a non-linear piezoresistivity is observed at low concentrations. It was found that sensors with 1 wt.% shows the highest linearity with a correlation coefficient of 0.999. The standard deviation of the cyclic readings was found to be 0.05%, indicating a high repeatability.

1. Introduction

Carbon nanotubes (CNTs) have been studied intensively for decades and they have attracted a great deal of attention owing to their superior electrical [1,2], mechanical [3,4] and thermal properties [5,6]. Compared with the other nanofillers, i.e. metallic particles or carbon black, CNTs are considered as an effective filler due to their high aspect ratios ($\approx$100–1000) which results in the formation of conductive paths at very low CNTs concentrations [7,8]. Due to CNTs outstanding electrochemical, thermal and physical properties, integration of CNTs into a polymer matrix would make the composites as a potential candidate for smart sensing applications including chemical, pressure, gas, flow and mechanical sensors [9–13]. For the realization of CNTs based strain sensors, numerous approaches were demonstrated in the form of CNTs films as buckypapers [14–17] and CNTs/polymer composites [18–38]. However, CNTs buckypapers strain sensors have many drawbacks in terms of repeatability, linearity, fragility and weakness in stress transfer since the CNTs are bonded only by van der Waals forces [23,24]. To overcome these limitations, CNTs/polymer based nanocomposites should be used to minimize the slip between the adjacent CNTs and to increase the stress transfer of the material. Thus, CNTs/polymer based nanocomposites are considered as the best choice for strain sensor applications.

Today, there are numerous studies based on CNTs/polymer nanocomposites, including CNTs/polyisoprene (PI) [22], CNTs/polyurethane (PU) [23], CNTs/polydimethylsiloxane (PDMS) [26], CNTs/polymethylmethacrylate (PMMA) [18,27], CNTs/polycarbonate (PC) [28], CNTs/polysulfone (PSF) [29,30], CNTs/polyelectrolyte (PE) [19,20,46], CNTs/poly(vinylidene fluoride (PVDF) [31] and CNTs/epoxy [32–37] aiming to ensure highly sensitive and stable strain sensors. Among the aforementioned polymers, epoxy resin is chosen due to its superior thermal and mechanical properties as well as its good adhesion to many substrates, dimensional stability and good heat and chemical resistance [39].

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However, the dispersion of CNTs in epoxy polymer is challenging due to the low solubility and weak dispersibility of CNTs. Therefore, an effective dispersion process and fabrication process should be performed and the processing parameters should be well characterized in order to realize the potential of CNTs/epoxy based flexible strain sensors. One of the first attempt of using CNTs in epoxy matrix was performed by Park et al. [32] to assess the damage in continuous fibers by nondestructive acoustic emission. Later, Zhang et al. [23] has shown the strong potential of CNTs/epoxy composites for *in situ* health monitoring, i.e. crack or fatigue damage detection and healing of laminated composite structures. Furthermore, Wichmann et al. [34] studied the directional sensitivity of MWCNTs/epoxy composite to bending deformations. Moreover, Hu et al. [33,36] have performed extensive numerical simulations and experimental measurements to reveal the effects of processing parameters on the piezoresistivity of CNTs/epoxy based composites. Yin et al. [35] investigated the linear and anti-symmetric piezoresistivity of CNTs/epoxy based nanocomposites with two different CNTs aspect ratios. It was found that the working mechanism for the CNTs with a lower aspect ratio is the tunneling resistance change, which results in nonlinear static piezoresistivity, while for higher aspect ratios the main working mechanism is found to be the piezoresistivity of the MWCNTs themselves.

To characterize the structure, texture and morphology of the nanocomposites, so far, various methods such as Raman spectroscopy [37,40,41], impedance tomography [42], electron [43] and atomic force microscopy [44] have been used. Among these characterization methods, electrochemical impedance spectroscopy (EIS) is a well-developed real-time non-destructive frequency domain process that quickly provides a wide range of information about the complex conduction mechanisms and dielectric properties of nanomaterials [45]. By using EIS, not only the change the piezoresistivity but also the complex conduction network of the nanocomposites can be clarified [20,46–49]. For instance, Loh et al. [20] fabricated thin-film strain sensors by dispersing SWNTs into poly(sodium 4-styrene-sulfonate) and poly(vinyl-alcohol) by layer-by-layer processing. The non-linearity, decay and hysteresis of the strain sensors were predicted using an R–C equivalent circuit. Lynch et al. [46] optimized the wireless read-out mechanism of the SWCNTs/polyelectrolyte (PE) strain sensitive thin films by EIS. Loyola et al. [47] used EIS to characterize the strain sensing and environmental sensitivity of the fiber-reinforces composites for structural health monitoring (SHM) applications. Parmar et al. [48] has indirectly quantified the effect of CNTs alignment on the strain sensing capability of CNTs-PC composites by EIS. Stassi et al. [49] has utilized the EIS to analyze the electrical conduction mechanism based on the tunneling effect of copper-PDMS composite for pressure sensor applications. An exponential decrease in the tunneling resistance and linear capacitance under pressure was indicated, thus confirming that tunneling effect is dominant conduction mechanism. However, to the best of our knowledge, there is no study addressing piezoresistive investigation MWCNTs/epoxy based nanocomposite by EIS on a flexible thin substrate.

In this study, unlike the other fabrication methods such as surface modification or in-situ polymerization where quite complex chemical treatments take place, a cost-effective, simple direct mixing method is used. MWCNTs/epoxy nanocomposites for different MWCNTs concentrations ranging from 0.3 wt.% to 1 wt.% were prepared, and their piezoresistive properties were investigated by EIS. A corresponding R–C equivalent model under tensile strain was proposed, with the aim of revealing the complex conduction mechanism of MWCNTs/epoxy nanocomposites under quasi-static tensile loading.

2. Materials and methods

2.1. Materials and nanocomposite preparation

The MWCNTs were purchased from SouthWest NanoTechnologies and they were used without any further chemical treatment. The as-received MWCNTs have 95% purity, 6–9 nm outer diameter and <1 μm length. The epoxy resin L20 (Bisphenol A-epichlorohydrin) and hardener (EPH-161) was obtained from Faserverbundwerkstoffe GmbH, Waldenbuch, Germany. MWCNTs with contents of 0.3, 0.4, 0.5, 0.75 and 1 wt.% were mixed directly with epoxy and the mixture was then subjected to the sonication (30 min, 30 W, 25 °C) using a horn sonicator (Bandelin GM 3200). After the sonication process, the dispersion was mixed by magnetic stirring at 400 rpm for 2 h. Then, hardener was added to the dispersion at a volume ratio of 100:5 and mixed by magnetic stirring at 400 rpm for 10 min. It is important to note that the low amount of epoxy resin-hardener was found to be the most suitable quantity to allow for a flexible, thin substrate. After that, samples were put into a vacuum chamber to allow degassing.

2.2. Substrate form and digital image correlation analysis

In this work, owing to its dimensional stability at elevated temperatures and its flexibility, a Kapton HN polyimide substrate with the thickness of 132 μm was used. For the tensile tests, substrates were cut in two different shapes (rectangular and dog-bone shape, respectively). Dog-bone shape is a standard configuration for tensile tests and the dimension is defined according to the "Deutsches Institut für Normung" (DIN) EN-ISO-3167 [50] standard. In order to determine the most appropriate specimen shape, and to measure the surface strain fields over the sensor area during deformation, two specimens with the different geometries were tested using the in-situ optical technique known as digital image correlation (DIC) under quasi-static uniaxial tension.

DIC is an accurate 2-D (or 3-D) full-field image analysis technique that uses a mathematical correlation algorithm to determine surface displacements and strains by tracking the non-uniform random speckle patterns on the specimen surfaces [51]. In our experiments, such random gray intensity distributions were artificially produced by spraying black and white paints on the MWCNTs/epoxy composite deposited substrate surfaces using airbrush equipment. Since the MWCNTs/epoxy layers exhibit excellent adhesion to the Kapton film, the strains determined by DIC are also characteristic for the strain values in the thin film functional layer. A single CCD camera with a resolution of 2358 × 1728 pixels was used to record images during the deformation. By means of the DIC software, the (2D) displacement of each surface point (pixel) is evaluated by comparing the digital images captured at different times during the deformation. By using the ARAMIS software package [52], DIC-data were analyzed in terms of local deformations and surface strain fields.

From Fig. 1 a, it can be seen that strains are relatively evenly distributed on the entire rectangular substrate for small macroscopic strains, but some strain fluctuations are also observed, e.g. at a macroscopic strain of 1%. In the dog-bone shape (Fig. 1b) the deformation is homogeneous in the parallel gauge length (which corresponds to the sensor area in this study), while strain concentrations occur near the grips. Therefore, in this study, dog-bone shape samples were used for the impedance spectroscopy measurements under tensile loading. In order to determine the elastic loading region of the dog-bone specimen, a tensile strain up to 3% was applied to the substrate. The deformation (axial strain) was measured by DIC and the forces were measured using a 100 N load cell. The elastic region was then defined by fitting a straight line to