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Multiphysics characterization of multi-walled carbon nanotube thermoplastic polyurethane polymer nanocomposites during compression

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ABSTRACT

Multiphysics properties of polymer nanocomposites (PNCs) are of interest for polymer-based microelectromechanical systems, tactile sensors, and flexible electronics. Coupling of mechanical (e.g., strain, stiffness, mechanical shock, etc.), electrical (e.g., resistance), and thermal (e.g., thermal expansion) effects has received little previous attention and is critical for performance and reliability. Compression experiments needed for sensitive touch sensors at low force and strain are rare with insufficient understanding of multiphysics mechanisms. This study investigates mechanical, electrical, and thermal properties of multi-walled carbon nanotube (MWCNT)/thermoplastic polyurethane PNCs during localized compression experiments. A novel correlation was established between increased electrical conduction through a spanning path(s) and higher stiffness giving insight into the mechanism of load transfer to MWCNTs. The correlation is attributed to MWCNT shell buckling-induced growth in the real area of contact between the metal contact electrodes and the PNC that occurs when a spanning path is compressed and begins to conduct electric current. Modulating electric current and power dissipation in a contact shows PNC thickness modulation, where higher power results in localized PNC elongation. The observed PNC thickness modulation is attributed to thermal expansion of the polymer.

1. Introduction

Nanocomposite elastomers are being developed for polymer-based microelectromechanical systems tactile sensors and for printed traces and die attach/solder replacements for flexible electronics boards [1–6]. Mechanical, electrical, and thermal properties of polymer nanocomposites (PNCs) have been extensively investigated, but the relationship between their macro-behavior and nanostructural properties is still poorly understood [7]. Less research has focused on the coupling between mechanical, electrical, and thermal properties, especially during localized compression experiments at low strain, which are needed to develop sensitive touch sensors.

Mechanical properties and structural reinforcement have been the focus in the development of PNCs [8]. Physical mechanisms of mechanical reinforcement in PNCs are still not well established [9,10], but some progress has been made linking chemistry, structure, and mechanical properties. The ability of nanocomposites to transfer load from the host matrix to the nanotubes is critical [11]. Load transfer mechanisms from the polymer to carbon nanotubes (CNTs) are not completely understood and a multiphysics approach is needed to extend the state-of-the-art.

Mechanical properties of CNTs have been investigated, and there are reviews discussing the mechanics of CNTs and their bundles [12,13]. Tensile mechanical properties of multiwalled CNTs (MWCNTs) and carbon nanofibers (CNFs) are excellent with tensile strengths of 11–63 GPa and 2.8–3.3 GPa, respectively [14–17]. However, for compression and bending loads, elastic buckling of CNTs above a critical force was established as a deformation mechanism that limits strength [18–22]. For example, the compressive buckling strength of MWCNTs was found to be only 50 MPa [23]. For MWCNTs under compression, the structures

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exhibited either Euler buckling for high aspect ratio or brief Euler buckling followed by asymmetrical shell buckling (i.e., kinking) for small aspect ratio above a critical force/strain [18,21,23,24]. CNFs exhibited symmetric shell buckling during compression [23]. Localized kinking occurred for high aspect ratio MWCNTs with an abrupt decrease in stiffness to near zero, and subsequent displacement was bending about the kink [25].

Multiscale modeling of the compressive behavior of PNCs under axial loading was conducted earlier, and both normal and shear stresses are present near the CNTs, but fall off rapidly in the polymer over a distance of about two CNT diameters [26]. In PNCs, the polymer matrix provides support to CNTs to resist buckling under compression, and provides a path for load sharing between CNTs [27]. Sideways buckling was observed in compressed MWCNT PNCs [19,28,29]. Bending, looping, and kinking of MWCNTs embedded in an epoxy resin were observed with compressive buckling strengths between 100 and 150 GPa [28]. The mechanical properties of the matrix are expected to affect MWCNT buckling strength in a PNC, but no data was found in the literature other than for an epoxy polymer [28]. A concern for PNCs is that buckling-induced reduction in nanotube stiffness will impair the ability of CNTs to sustain external loads [30]. However, there have been no studies of buckling of CNTs within a spanning load-bearing path in a PNC, and whether it happens and how it affects mechanical and electrical properties is not known making this study timely.

Similar to mechanical properties, additional understanding of electrical conductivity in CNT PNCs is needed [31]. Electrical transport occurs within spanning CNT networks in nanocomposites [32]. Tunneling between neighboring CNTs was considered and PNCs followed a fluctuation induced tunneling model [31,33]. Conductive path theory and quantum tunnel effect theory were combined to explain nanocomposite electrical conduction [34]. The electrical resistance of an individual conductive path is primarily determined by inter-tube tunneling and the individual tube resistance can be neglected [35]. Junction resistance increases exponentially with increased separation, and insertion of a polymer chain in the gap between CNTs reduces current by 4 orders of magnitude [36]. This study was undertaken to develop a better understanding of the conductive network including interactions and formation/destruction of conductive paths [9,37].

Thermal properties of PNCs are important for heat dissipation applications where metals can be replaced with PNCs for weight reduction, corrosion resistance, easy processing, and low manufacturing cost [38]. However, most published literature state that enhancement in thermal conductivity of PNCs over the neat polymers is less than theoretical predictions [38]. Point interactions and small area in well-dispersed random nanotube networks limit phonon transfer [38,39]. Low interface thermal resistance leads to better heat flow between nanotubes, but allows more heat transfer to the matrix along the tube [39]. Thus, thermal transport in CNT composites always involves the low thermal transport efficiency matrix [38,39].

PNCs offer promise as large area, high sensitivity, and low manufacturing cost flexible smart sensors [11,40–42]. PNC sensors concentrate current through resistive insulating barrier nanoconstrictions leading to high local current densities and temperatures [43]. Thermal expansion properties of CNT-reinforced nanocomposites were investigated previously [44]. Electrothermal PNC actuators were developed as adaptive structures with strains on the order of a few percent [45]. Electrothermal effects in piezoresistive sensors have not been previously investigated and warrant exploration here. Additional rationale for studying electrothermal effects and multiphysics is that new opportunities for PNC devices and applications will exploit the dynamic behavior of PNCs in response to physical stimuli [46].

The aim of this study was to investigate the multiphysics properties of PNCs at low compressive force and strain leading to new and improved understanding of relevant mechanisms. A novel correlation was established between increased electrical conduction through a spanning path(s) and higher stiffness giving insight into the mechanism of load transfer to MWCNTs. The correlation is attributed to MWCNT shell buckling-induced growth in the real area of contact (RAC) between the metal contact electrodes and the PNC that occurs when a spanning path is compressed and begins to conduct electric current. Modulating electric current and power dissipation in a contact shows PNC thickness modulation, where higher power results in localized PNC elongation. The observed PNC thickness modulation is attributed to thermal expansion of the polymer. Significant multiphysics coupling was observed and should be considered for ultrahigh performance and reliability devices utilizing PNCs.

2. Experimental section

A micro/nanocontact apparatus was used for this study and is shown schematically in Fig. 1a. The apparatus was described in detail in an earlier study that investigated the electromechanical behavior of carbon fibers and CNT-coated carbon fibers (fuzzy fibers) [22]. This type of test was selected due to its ability to measure small compressive force and displacement along with the ability for electric current flow and electrical resistance measurement. This makes the test suitable for multiphysics studies. Briefly, a ball-on-flat electrode configuration is used with Au-coated GaAs wafers and Au-coated 1.6 mm diameter Grade 100 440C stainless steel balls. The PNC was sandwiched between the electrodes in compression experiments as shown in Fig. 1b. Peak forces used were generally less than 30 mN and peak displacements less than 25 μm. A thermohygrometer was used to monitor the temperature and relative humidity (RH) inside the chamber. The temperature and RH inside the chamber during experiments was 22 ± 1 °C and 45 ± 5%, respectively.

Fig. 1b shows a close up view of the ball-PNC-wafer contact along with the electrical circuit used for electrical resistance measurements. Compression experiments on the neat polymer or PNC sandwiched between Au electrodes were conducted using a movable platform and a piezoelectric actuator for ball displacement. Controlled displacement of the ball electrode initiated PNC compression against the flat electrode, and the resulting compression force and displacement of the lower electrode were measured with the high sensitivity load/displacement cell shown in Fig. 1a. A constant open circuit voltage of 10 V was used along with a fixed resistor of 1 kΩ assembled in series with gold plated electrodes to limit the current to less than 10 mA (Fig. 1b). Voltage drop across the series resistor was monitored with an oscilloscope and stored in a computer. Simple circuit analysis was used to calculate the electrical resistance of the sandwiched PNC. The maximum measurable electrical resistance with the circuit and instrumentation is 10^9 Ω. The above procedure was found to be a reliable way to conduct the experiments.

The fabrication of the MWCNT/thermoplastic polyurethane (TPU) PNC used in this study is discussed in detail in earlier studies [47–49]. This material was selected due to its being of interest for polymer MEMS sensors/actuators [3] and strain resilient electronic interconnect materials [50]. Polyurethanes are of interest for polymer MEMS because of their superior tear resistance and adherence to substrates compared to more commonly used polydimethylsiloxane (PDMS) [51]. MWCNTs (PRT-HT-19, Applied Science Inc.) with an average diameter of 100 nm, length greater than 10 μm, and a purity of 99.9% were combined with polymer (Morthane PS455-203, Huntsman Polyurethanes, aromatic polyester