U.P.B. Sci. Bull., Series B, Vol. 78, Iss. 4, 2016 ISSN 1454-2331

AN EXPERIMENTAL INVESTIGATION OF THE EFFECTS OF WEIGHT FRACTIONS OF REINFORCEMENT AND TIMING OF HARDENER ADDITION ON THE STRAIN SENSITIVITY OF CARBON NANOTUBE/POLYMER NANOCOMPOSITES

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The excellent mechanical, electrical and thermal properties of carbon nanotubes, besides the significant reduction of their cost in the past decade, has aroused intense interest of researchers to utilize them as an alternative to conventional smart materials. One of the recent interests in application of CNTs is in fabricating CNT-based strain sensors. In this regard, CNT/polymer nanocomposites have attracted the most attention. Hence, in the present investigation CNT/epoxy nanocomposite have been fabricated by in situ polymerization technique and piezoresistive responses of the samples have been recorded and evaluated. Among the various effective parameters (such as intrinsic structure of CNTs, fabrication process, etc.), here, effects of the weight fraction of CNTs and timing of hardener addition on the strain sensitivity of nanocomposite are investigated. In order to evaluate the functionality of the samples under static loading as a strain sensing element, the fabricated composite films are attached to a macroscopic aluminum beam. The changes of the electrical resistivity are also recorded with a LCR meter. Our findings indicate that initial mixing of epoxy resin and hardener lead to higher sensitivity of the nanocomposites. Furthermore, weight fraction of CNTs plays a key role on piezoresistive behavior of the sensors. Thus, a lower loading of reinforcements culminates sensor sensitivity. The dispersion state of the CNTs in the epoxy matrix is also characterized by scanning electron microscopy (SEM).

1. Introduction

Capability of sensing and responding to different environmental situations of smart materials, has made them suitable for a wide range of applications.

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Among the various types of smart materials, carbon nanotubes (CNT)/epoxy nanocomposite has triggered world-wide attention in building highly sensitive strain sensors [1-3]. Carbon nanotubes possess phenomenal physical and mechanical properties such as large aspect ratio, low mass density and high Young modulus and ultimate strength [4], which made them perfect candidates to produce polymer composites for commercial applications [5, 6]. Their superior electrical and piezoresistive (change in resistance with strain) properties of CNTs have made them an attractive reinforcement for strain sensors [7-10]. The sensitivity of these novel strain sensors was higher than that of conventional ones. From the accumulated knowledge until now, the observed sensitivity can be mainly related to the following three parameters [1, 8, 11], namely: (1) significant variation of conductive networks formed by CNTs, such as loss of contact among CNTs [12, 13]; (2) tunneling effect in neighboring CNTs due to distance changes [8, 14, 15] and (3) conductivity change or piezoresistivity of CNTs due to mechanical deformation [16].

In the case of CNT/polymer sensors, influences of various factors in fabrication process and material properties have been reported in literature. Hu et al. [17] experimental results demonstrated that the curing temperature and the mixing conditions are key factors in the fabrication process, which remarkably influence the formation of conducting network. Ayatollahi et al. [18] showed that the aspect ratio of CNTs is another important factor which affects both mechanical and electrical properties of nanocomposite. Their results revealed that longer multi-walled carbon nanotubes (MWCNTs) with small diameters (i.e. higher aspect ratios, l/d) lead to better dispersion quality and further improve conductivity and mechanical properties. The same trend was also reported by Zhang et al [19]. They reported that fatigue crack growth rate can be significantly reduced due to reducing the nanotube diameter, increasing the nanotube length and improving the nanotube dispersion. Damian et al. [20] reported an improvement on mechanical and thermal properties of the epoxy composites due to functionalization of MWCNTs. Jiang et al. [21] investigated effect of aspect ratio on resistance-pressure sensitivity of CNT/rubber nanocomposite. Their results confirmed that composite with low concentration of nanotubes, at low aspect ratio shows great piezoresistive sensitivity. In an attempt to obtain an ultra-high sensitive piezoresistive strain sensor, Hu et al. [1] fabricated metal-coated carbon nanofiller/epoxy nanocomposite. The experimental results represented that the sensor made of carbon filler with silver coating has the gauge factor around 80 times higher than that in a metal-foil strain gauge. In another research, Moniruzzaman et al. [22] introduced a new fabrication method for the preparation of the single-walled carbon nanotube (SWCNT)/epoxy nanocomposites. Significant improvement in flexural modulus and flexural strength at 0.05 wt. % nanotubes was observed.

In the current study, the authors endeavour to investigate strain sensing capabilities of MWCNTs at the nanoscale and develop strain sensors at the macroscale. In order to explore the effect of weight fractions of MWCNTs on strain sensitivity, 0.05-1.5 wt. % of MWCNTs was added to an epoxy matrix. Owing to the lack of detailed information on the influence of fabrication process on the strain sensitivity of MWCNT/epoxy composites, the effect of adding sequences of constituent materials is also investigated and discussed.

2. Experimental Procedure

MWCNTs grade of ~20 µm length and 30-50 nm diameter, produced by in situ polymerization technique, with purity of ~ 95% was supplied from Shenzen Co. Ltd. The epoxy matrix used in this study consists of Diglycidyl ether of bisphenol-A based epoxy resin (CY-219) with an amine hardener (HY-5161), supplied by Hunstman Co. Ltd. CNT/epoxy nanocomposite with different weight fractions of MWCNTs (from 0.05 to 1.5 wt. %) were fabricated by two kinds of mixing procedure. Mechanical mixer was used as the mixing machine for both methods. In the first approach, epoxy resin was mixed with the chosen MWCNT contents and stirred at 2000 rpm for 30 min at room temperature. Afterwards, the hardener was added while the mixture was being stirred at 500 rpm for 1 min to allow for the dispersion of the hardener. Finally, a stirring rate of 240 rpm was applied for 3 min and rectangular samples were cast in the Teflon mold.

For a second set of samples, the epoxy and hardener were first mixed at 2000 rpm for 1 min at ambient temperature. Then, MWCNTs were added in to the blend, which was mixed again for 2 min at 2000 rpm. Finally, the mixing process was ended by a stirring rate of 500 rpm for 1 min. For all samples, the weight ratio of epoxy to hardener was 2:1, according to the instruction of manufacturer. All the samples were subsequently cures for 2 h at 80 ºC. In order to examine the capabilities of MWCNT/epoxy films as a strain gauge, rectangular sections of 10 mm × 5 mm with the thickness of ~200 µm were cut from the cured samples and bonded to the aluminum cantilever beam. Silver paste was also placed on the two sides of the sensors to act as terminals for electrical resistance measurements by producing good contact between the surfaces and copper cables. Electrical resistivity changes were recorded with a LCR meter. The overall test setup for calculating piezoresistive responses of samples is shown in Fig. 1.
Fracture surfaces of the nanocomposite were also characterized on a scanning electron microscopy (SEM, Hitachi S4160).

Fig. 1: Experimental setup for piezoresistivity measurement

3. Results and Discussion

The piezoresistivities of the two MWCNT/epoxy sensors, with different fabrication processes, under static loading are demonstrated in Fig. 2:

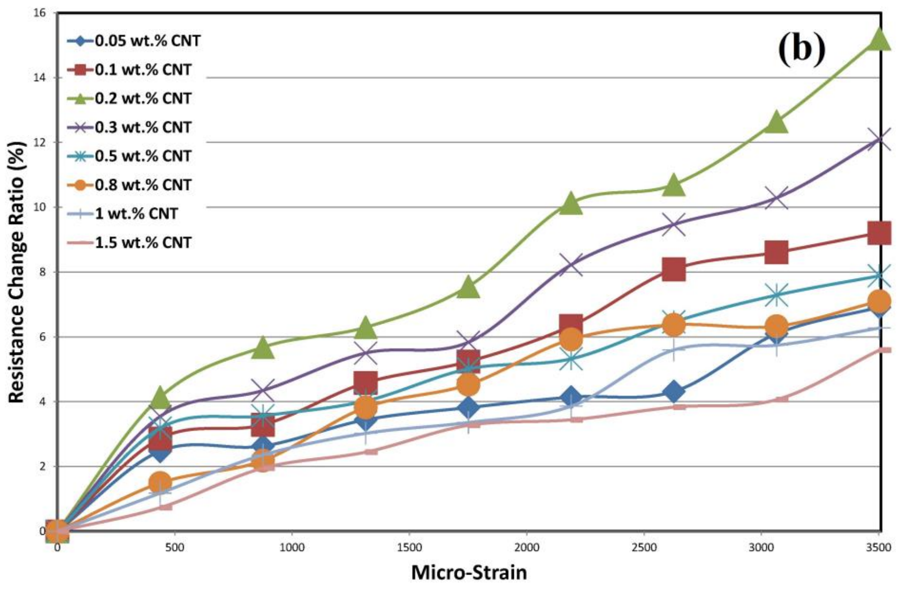


Fig. 2 **a)**: Piezoresistive responses of sensors with: a) preliminary mixture of resin and MWCNT

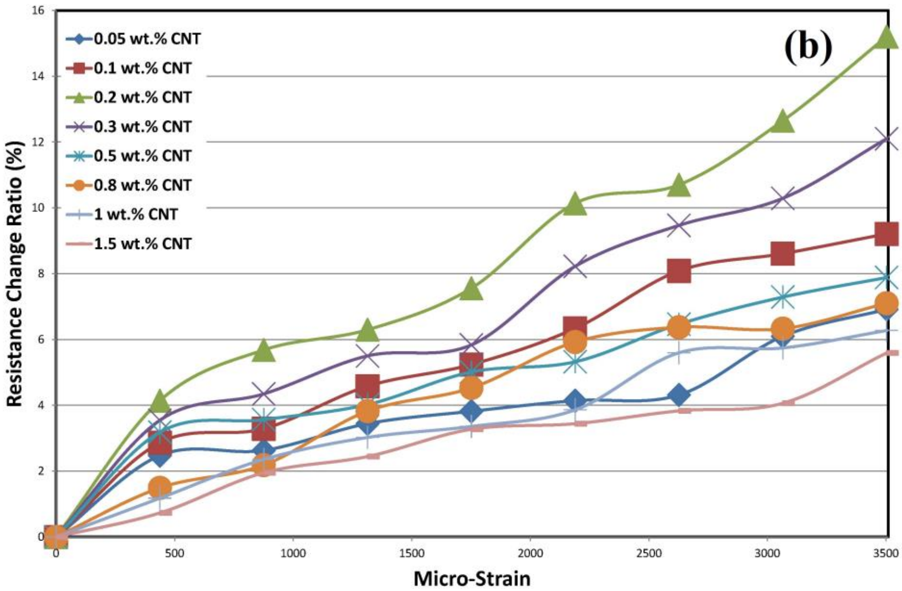


Fig. 3 **b)** Piezoresistive responses of sensors with: b) preliminary mixture of resin and hardener

As it is obvious, it can be found that the piezoresistivities of the MWCNT/epoxy are highly nonlinear. According to Simmons' theory, when the distance between the CNTs increases gradually, due to applied strain, the tunneling resistance will increase significantly in nonlinear form. Therefore, the total resistance of the sensors has increased nonlinearly [11]. It is important to notice that loss of contact among the CNTs or breakup of conductive paths of CNTs also affects the resistance changes, but it may mainly work under the small strain. Moreover, due to weak interface strength of CNTs and epoxy matrix, very limited deformation is expected to sense by CNTs. Thus, the contribution of piezoresistivity of CNTs themselves to the total piezoresistivity of nanocomposite sensors can be neglected [11].

MWCNT weight fraction has a significant effect on the sensor sensitivity, whereas in general, with the decrease of CNT loading, the sensor gauge factor (= $(\Delta R/R0)/\varepsilon$), with the initial resistance R0, the resistance change ΔR, and the applied strain ε) becomes higher. This phenomenon can be explained as follow: for an intensive conductive network, if one conductive path is broken down, the total nanocomposite resistance showed minor variation. On the contrary, for a sparse conductive network, the variation of resistivity is much higher. In other words, the samples of higher resistances possess the higher sensor sensitivity [11].

Influence of timing for adding hardener on sensitivity of the samples is explored in Fig. 3. By comparing the results of two samples, we can interestingly find that initial adding of epoxy and hardener lead to higher sensitivity. No clear explanation can be mentioned for this phenomenon, but what is evident is that preliminary mixing of epoxy and hardener can partially avoid the encapsulation or coating of CNTs which itself affects the piezoresistive response of nanocomposite [17].

Furthermore, for all weight fractions, it was found a fourth-degree polynomial which adequately fits the complete R/R0 vs. ε. (see equations in Fig. 3). Thus, for application usage, four fitting coefficients can be employed to calibrate the sensor [23].

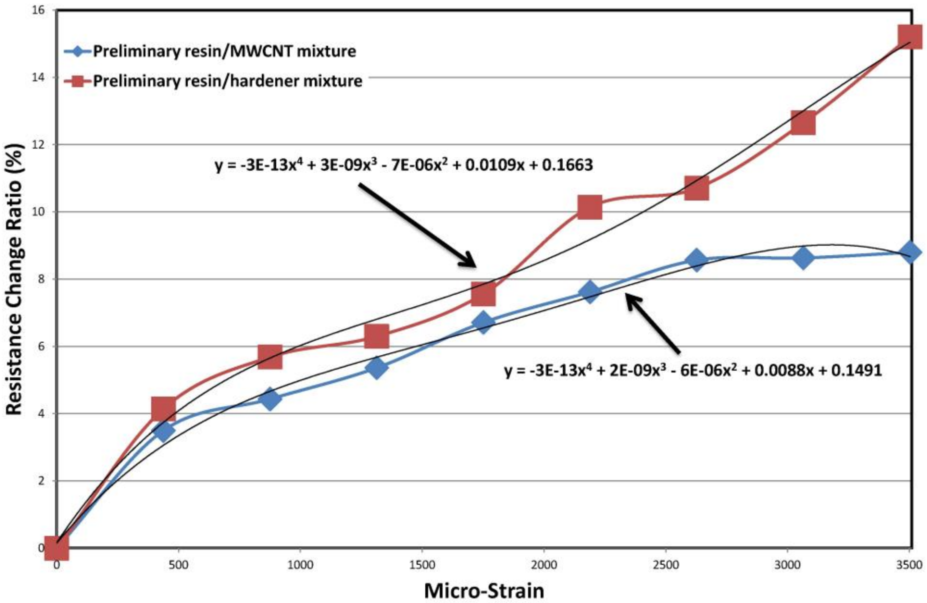
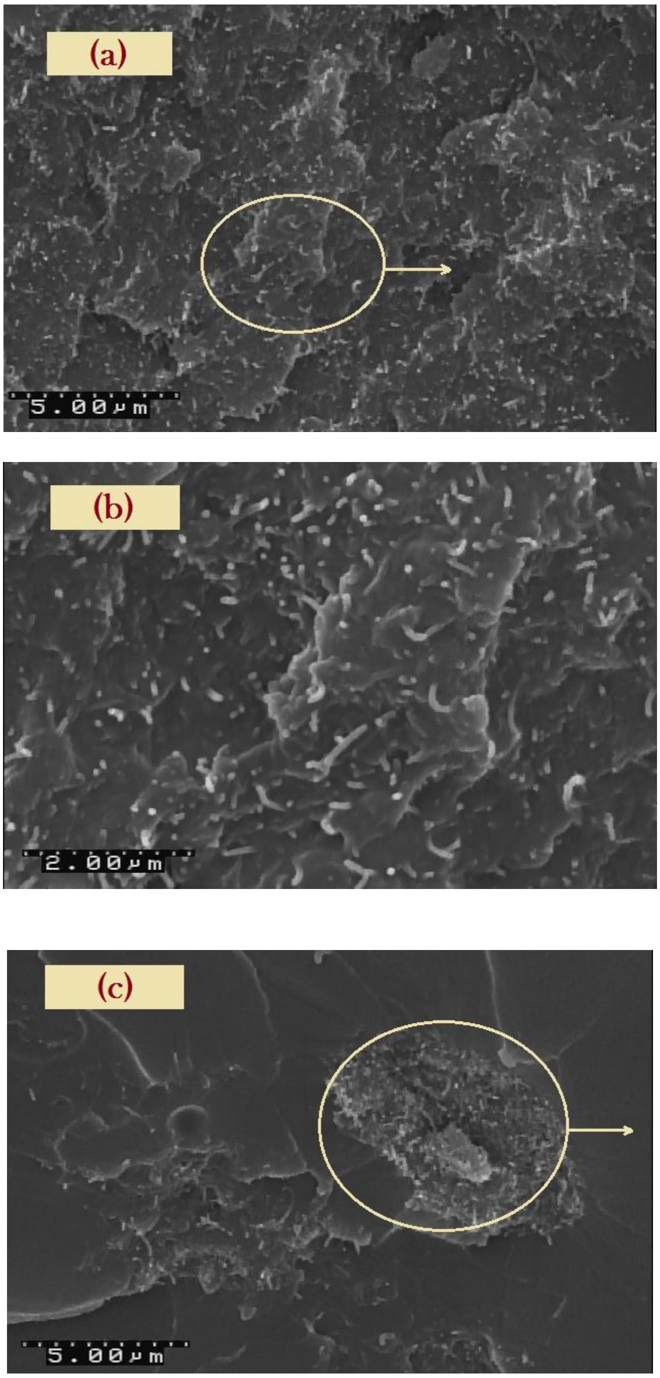


Fig. 4: Comparison of piezoresistive responses of 0.2 wt.% MWCNT/epoxy nanocomposite with different fabrication methods

Fig. 4 shows the fractured surfaces of 1 wt. % MWCNT/epoxy nanocomposite made from two different fabricating procedure. As illustrated in Fig. 4a and b, the better dispersion of MWCNTs can be observed in preliminary mixture of resin and MWCNTs. While, in the case of initial mixing of resin and hardener, severe aggregates were produced (Fig. 4c and d). Precise observations of the pulled out MWCNTs also clarify a weak interface between the MWCNTs and the matrix.


(a)
5.00μm
(b)
2.00μm
(c)
5.00μm

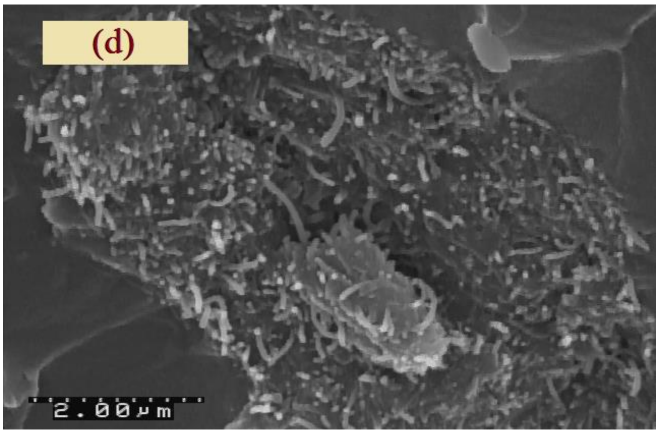


Fig. 5: SEM images of fractured surfaces of 1 wt.% MWCNT/epoxy nanocomposite with: a) preliminary mixture of resin and MWCNT; b) higher magnification of Fig. 4a shows good dispersion of MWCNTs ,and c) preliminary mixture of resin and hardener; d) higher magnification of Fig. 6c shows the produced aggregates in the matrix

4. Conclusions

In the current study, the effects of weight fractions of CNTs and timing of hardener addition on the strain sensitivity of MWCNT/epoxy nanocomposites were investigated. Our results showed that lower loadings of MWCNT lead to better strain sensitivity. In other words, a sparse conductive network with high resistance may be favorable for obtaining higher sensor sensitivity. On the other hand, fabrication process (timing of hardener addition for instance) is one the most important parameter that should be considered thoroughly. In future, the authors will explore more comprehensive study on the fabrication process parameters to accurately extract more convenient concepts.

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