Materials Letters 159 (2015) 276–279

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Tunable resistivity–temperature characteristics of an electrically conductive multi-walled carbon nanotubes/epoxy composite

Xiaohan Cao, Yan Lan, Yue Wei, Guoqiang Zheng, Kun Dai*, Chuntai Liu*, Changyu Shen

College of Materials Science and Engineering, The Key Laboratory of Advanced Materials Processing & Mold of Ministry of Education, Zhengzhou University, Zhengzhou 450002, PR China

ARTICLE INFO

Article history:
Received 11 May 2015
Received in revised form
27 June 2015
Accepted 6 July 2015
Available online 7 July 2015

Keywords:
Carbon nanotubes
Epoxy resin
Temperature sensors
Composite materials

ABSTRACT

Resistivity–temperature characteristics of conductive multi-walled carbon nanotubes (MWCNT)/epoxy (EP) composite were studied during a heating-cooling run (HCR) with different top test temperatures. The values of R_e (room-temperature resistance at the end of a HCR) decrease with increasing the top test temperature. The fluctuation-induced tunneling conduction (FITC) and the hysteresis effect developing in MWCNT/EP composite are responsible for this fascinating phenomenon. In order to understand this result further, resistivity–temperature characteristic at different cooling rates was studied. The values of R_e also decrease with rising the cooling rate. This paper provides an effective approach to acquire a tunable temperature sensor.

1. Introduction

Electrically conductive polymer composites (CPCs) which possess resistivity–temperature characteristics have been studied persistently for several decades, for the fact that they are the basis of many popular industrial applications including thermal detectors, over-temperature protection devices and self-regulating heaters, etc [1]. Polymer-based resistivity–temperature materials have advantages over the conventional inorganic materials, such as excellent formability, low cost, flexibility and lightweight, etc. The positive temperature coefficient (PTC) effect and negative temperature coefficient (NTC) effect are the typical resistivity–temperature behaviors of CPCs. Conceptually, PTC and NTC of thermistors display a conspicuous increase and a succeeding gradual decrease in electrical resistance with increasing temperature, respectively.

Up to now, although a large variety of studies have been carried out to analyze the mechanisms of resistivity–temperature characteristics in CPCs, the mechanisms are still incomplete [2,3]. For semi-crystalline thermoplastic matrices, it has long been recognized that the expansion of the matrix resulted from the melting or glass transition leads to the PTC effect [4]. On the other hand, it is often admitted that the formation of a flocculated structure at elevated temperatures when the viscosity of the matrix is adequately low results in NTC effect [2]. However, for CPCs with cross-linked matrices, the origin of PTC and NTC effect is hard to perfectly discuss due to their complex nature [3]. Besides, the majority of the aforementioned works about the resistivity–temperature behaviors of thermoset CPCs were implemented during heating process, while the resistivity–temperature behaviors during cooling process have almost been failed to be considered. Therefore, further studies are still necessary.

It is known that cured epoxy (EP) resins have excellent chemical resistance, high strength, fine size stability and nice processability. Additionally, chemical functionalization of nanofiller is found to improve the interfacial interaction between filler and polymer matrix as well as the dispersion of the filler. In this research, the resistivity–temperature characteristics of amino multi-walled carbon nanotubes (MWCNT)/EP CPCs with different top test temperatures during a heating-cooling run (HCR) were investigated. Additionally, the resistivity–temperature characteristics during cooling were concerned specifically.

2. Experimental

The main materials used in the present paper include MWCNT and EP. MWCNT with an average length of 50 μm was supplied by Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. EP resin (LT-5078A) and hardener (LT-5078B) were obtained from RuiGao New Materials Co. Ltd., China.

To prepare the composites, the MWCNT was first dispersed in

* Corresponding authors.
E-mail addresses: kundai@zzu.edu.cn (K. Dai), ctliu@zzu.edu.cn (C. Liu).

http://dx.doi.org/10.1016/j.matlet.2015.07.028
0167-577X/

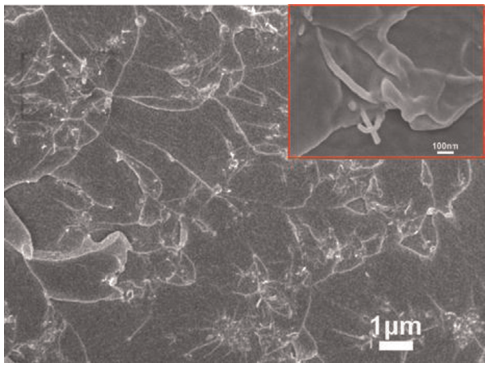

Fig. 1. SEM micrograph of MWCNT/EP composite (MWCNT content 0.3 wt%).

acetone by sonicating for 30 min to form a suspension. Then it was mixed with quantitative EP by stirring for 30 min and sonicating for another 30 min. The mixture was kept in a vacuum oven to remove the acetone. The hardener was added to the mixture in a stoichiometric ratio. After degassing, the mixture was poured into a mold and cured at a schedule (25 °C for 24 h and then 80 °C for 8 h). To ensure contact resistance stability, copper electrode was immersed into the liquid EP before curing. The composite with 0.3 wt% MWCNT was chosen to evaluate the resistivity–temperature characteristics. This content is just beyond the percolation region (percolation threshold 0.025 wt%), thus the sample would be sensitive to the thermal stimuli. The morphology of the MWCNT/EP composite was observed using a field emission scanning electron microscope (SEM, JSM-7500F).

In resistivity–temperature test [5], specimens were immersed in a silicone oil bath of a temperature-controlled device to avoid oxidation (see Fig. S1). Before resistivity–temperature test, the specimens ($60 \times 10 \times 4$ mm^3) were all heated to 180 °C and isothermal treated for 5 min; then cooled to 25 °C to eliminate the effect of thermal history developed during the preparation process. Thereafter, the specimens were heated from 25 °C to different top test temperatures (100 °C, 120 °C, 140 °C, 160 °C, 180 °C) at 3 °C/min and held at this temperature for 5 min, then cooled to

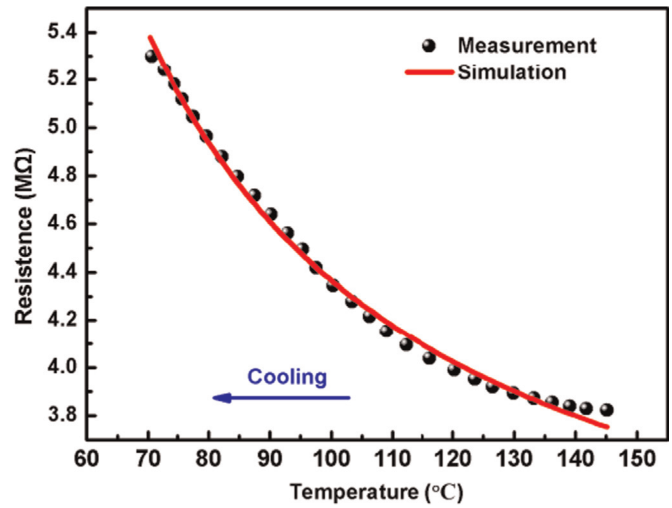

Fig. 3. Comparison of electrical resistance-temperature relationship of MWCNT/EP composite at the top test temperature 160 °C, measured during the last cooling cycle, with simulations using the Eq. (1).

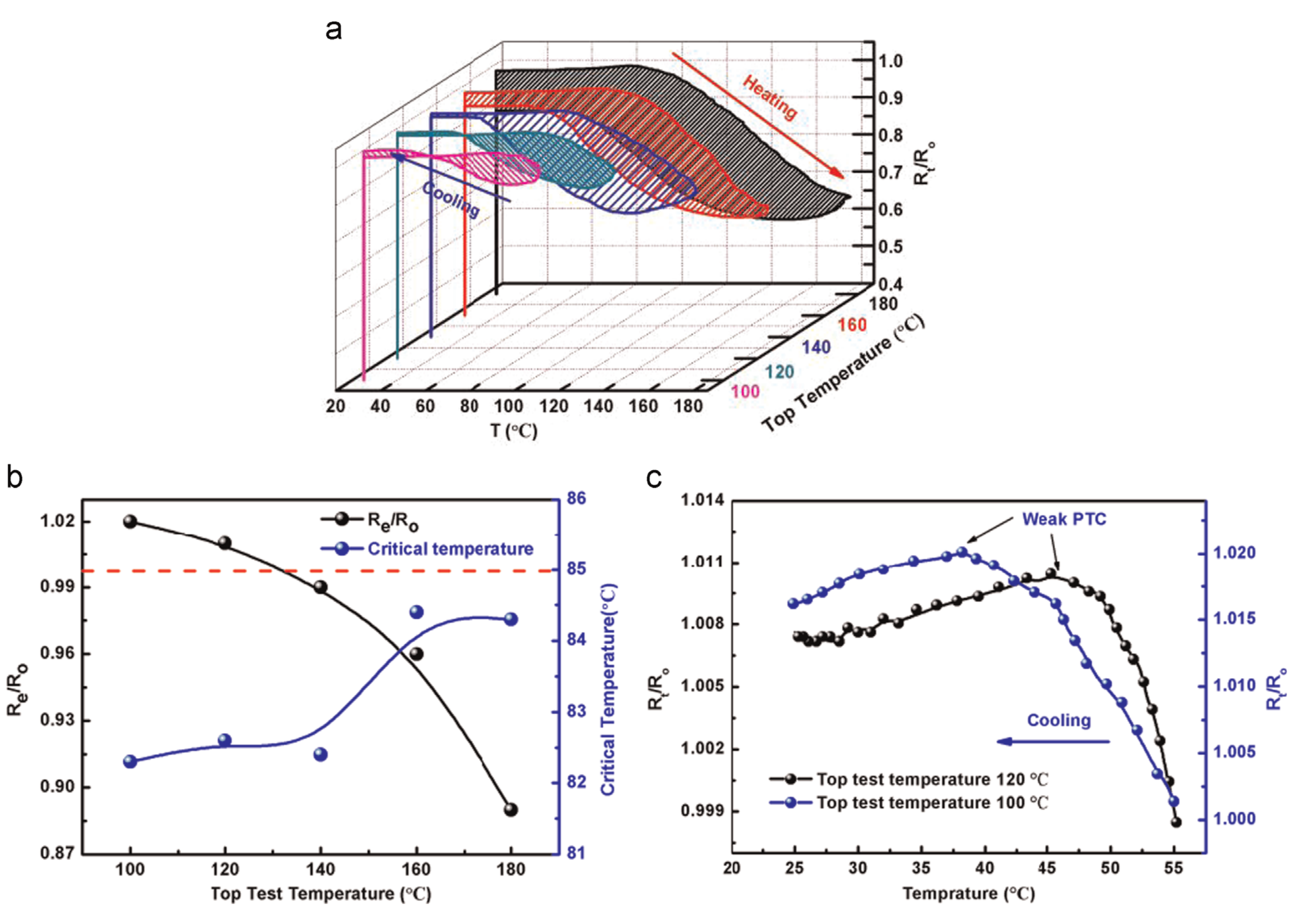

Fig. 2. (a) Resistivity–temperature behaviors of MWCNT/EP composite with different top test temperatures; (b) relationships of R_e/R_o and critical temperature vs. the top test temperature; (c) resistivity–temperature behaviors of MWCNT/EP composite with the top test temperatures of 120 °C and 100 °C during the end of the cooling cycle.