Materials Letters 118 (2014) 161–164

Contents lists available at ScienceDirect

Materials Letters

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

Influence of the second filler on the positive piezoresistance behavior of carbon nanotubes/silicone rubber composites

Jun-Wei Zha [a], Wei-Kang Li [b], Jing Zhang [b], Chang-Yong Shi [c], Zhi-Min Dang [a,b,*]

[a] Department of Polymer Science and Engineering, School of Chemistry and Biological Engineering, University of Science & Technology Beijing, Beijing 100083, People's Republic of China
[b] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China
[c] Department of Elements, Beijing Institute of Fashion Technology, Beijing 100029, People's Republic of China

ARTICLE INFO

Article history:
Received 8 November 2013
Accepted 15 December 2013
Available online 22 December 2013

Keywords:
Hybrid fillers
Silicone rubber composites
Aspect ratio
Piezoresistivity
Electrical properties

ABSTRACT

To investigate the influence of the second filler on piezoresistive properties of the composites, silica (SiO_2) and carbon black (CB) as the insulating and conductive particles were incorporated into the carbon nanotube (CNT)/silicone rubber (SR) composites. Both SiO_2 and CB can serve as "seesaw" to support the CNT, but their effect on the piezoresistivity of CNT/SR composites was remarkably different. Besides, the introduction of SiO_2 and CB has a distinct CNT aspect ratio (AR) effect on the piezoresistivity. Lower AR endows higher piezoresistivity in the (SiO_2–CNT)/SR composites, but higher AR is more favorable for the (CB–CNT)/SR composites.

1. Introduction

Carbon nanotubes (CNTs) have been considered as a realistic alternative to conventional smart materials owing to their extraordinary mechanical and electrical properties [1,2]. More attention has been paid to the CNT/polymer composites which can serve as pressure sensors [3–7]. Silicon rubber (SR) with superior electrical insulation, low modulus, high elasticity and flexibility as well as outstanding environmental stability has widely served as a typical engineering polymer material and opened opportunities for its applications in the high deformable and reversible piezoresistive composites [8–10]. As is well known, the improving CNT dispersion within the polymer matrix is the key objective for achieving favorable properties in the composites. In order to solve this problem, as is more recently reported, the opinion of utilizing hybrid fillers composed of CNT and other fillers has already been proposed and their synergistic effect has been mainly focused on [11,12]. It has revealed that desired performance of the composite could be achieved by combining the advantages of each filler [13]. However, there is a lack of research on the electrical performance of the second filler on the piezoresistive behaviors of the CNT/polymer composites, and it is still a challenge to understand the mechanisms behind the piezoresistive effect of the three-component composites. Moreover, understanding the effect of CNT AR on the piezoresistivity of the second filler/CNT hybrids filled polymer composites is extremely required in order to fully take advantage of the combinations to adjust the piezoresistivity.

In this letter, a strategy was designed to disclose the piezoresistivity mechanism of the composites by respectively introducing different concentrations of insulating (SiO_2) and conductive (CB) particles as the second filler into the MWNT filled room temperature vulcanization silicone rubber (RTVSR) composites. RTVSR is well known for its excellent properties such as low modulus (<1 MPa), convenient in processing and high elongation stress–strain properties. It is preferred to be used as polymer matrix in preparing pressure-sensitive rubber composites. Different piezoresistive behaviors of the (SiO_2–MWNT)/RTVSR and (CB–MWNT)/RTVSR hybrid composites were investigated. The influence of the second filler on the piezoresistivity of the composites was discussed based on the mechanisms, and the distinct CNT aspect ratio (AR) effect on the piezoresistivity resulted from the addition of the second filler was also investigated.

2. Experimental

Acetylene CB with ~50 nm in diameter and 60–70 $mm^2\,g^{-1}$ in surface area, SiO_2 with diameter of ~50 nm and CNTs with ARs of ~117 and ~437 were used as fillers. In order to achieve uniform dispersion, prior to use, the filler surface was first chemically

* Corresponding author at: Department of Polymer Science and Engineering, School of Chemistry and Biological Engineering, University of Science & Technology Beijing, Beijing 100083, People's Republic of China. Tel./Fax: +86 10 6233 2599.
E-mail address: dangzm@ustb.edu.cn (Z.-M. Dang).

0167-577X/$ - see front matter Crown Copyright © 2013 Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matlet.2013.12.065

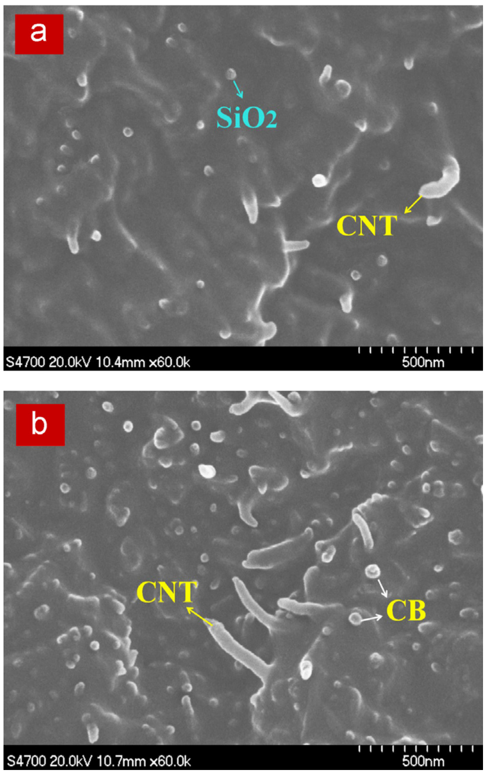

Fig. 1. SEM images of fracture surfaces of the SR composites with (a) 1.3 vol% CNT and 3 vol% SiO_2 and (b) 1.3 vol% CNT and 3 vol% CB.

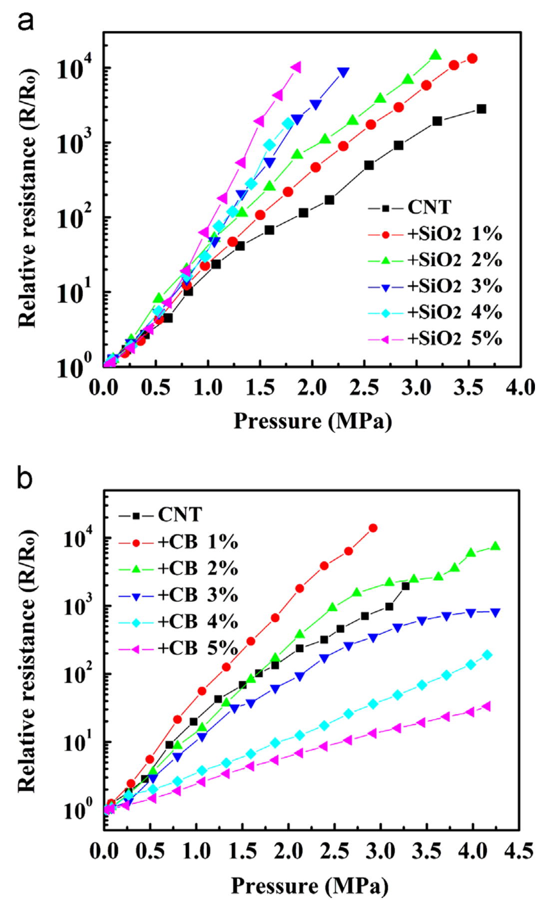

Fig. 2. Piezoresistive behaviors of the (a) (SiO_2–CNT)/SR and (b) (CB–CNT)/SR composites.

modified by γ-aminopropyltriethoxy silane (KH550). The fillers were well dispersed in the matrix by solution blending and then high shear mixing (three roll-mill) techniques. Then the vulcanizing agent and activator at proper ratios were added, and the mixture was compressively molded at 15 MPa for 12 h at room temperature. The (SiO_2–CNT)/SR and (CB–CNT)/SR samples with a diameter of ~12 mm and a thickness of ~1 mm were achieved. Their fracture surfaces were characterized by scanning electron microscopy (SEM, Hitanchi S-4700). For the electrical testing, both surfaces of the samples were sprayed with gold using ion beam sputtering (ETD-200) in order to reduce the contact resistance. The applied pressure was measured using a vertical electric test stand (Japan, JSV-500D) and the corresponding electrical resistance was measured by a digital multimeter (F-45). Five samples for the composites with the same filler content are measured.

3. Results and discussion

SEM images of the fractured surfaces of the (SiO_2–CNT)/SR and (CB–CNT)/SR composites with 1.3 vol% of CNT and 3 vol% of SiO_2 and CB are presented in Fig. 1. We can see that the modified CNT, SiO_2 and CB are uniformly dispersed in the SR matrix. There is no extraction trace, suggesting a strong interfacial adhesion between the fillers and silicone rubber matrix.

The piezoresistive behaviors of the composites described by the relative resistance (R/R_0) vs. pressure curves are demonstrated in Fig. 2. Here, R is the resistance of the composites at some pressure and R_0 is the initial resistance of the composites at no pressure. From Fig. 2a and b, it is clearly seen that both (SiO_2–CNT)/SR and (CB–CNT)/SR composites display positive piezoresistive effect. Namely, the relative resistance consistently increases with the pressure. Compared to the CNT/SR composites, the addition of SiO_2 results in larger piezoresistivity, and it increases with the SiO_2 concentration, as shown in Fig. 2a. It is well known that the applied pressure can lead to the movement of rubber chains, which gives rise to the orientation of CNTs along the direction perpendicular to the pressure, as illustrated in Fig. 3a. And this orientation behavior will break the CNT conductive networks. With the introduction of SiO_2, it could act as "seesaw", supporting the CNTs in the matrix, as shown in Fig. 3b. Due to the "seesaw", the CNT orientation appears more easily under a given pressure. With the increase of pressure, more and more conductive pathways in the composites are destroyed by the insulating SiO_2 (the blue circles in Fig. 3b). Thus, the relative resistance consistently increases and the composites display positive piezoresistance effect. With increasing the SiO_2 concentration, more CNT conductive networks are easily damaged and thus stronger piezoresistivity is observed.

With regard to the (CB–CNT)/SR composites (Fig. 2b), when $f_{CB} \leq 2$ vol%, it can be seen that the addition of CB results in higher piezoresistivity compared to the CNT/SR composites. However, when $f_{CB} > 2$ vol%, the piezoresistivity becomes lower, and it deceases with the increase of CB concentration. Like SiO_2, the CB particles also act as "seesaw", which could support the CNTs and break the CNT networks. However, these conductive CB fillers also play important roles on the reformation of conductive channels. This is different from the insulating SiO_2 which mainly destroys the networks. One can see from the red circles in Fig. 3c that the CB can connect with each other or the adjacent CNTs to form conductive networks. In this case, the broken conductive pathways of CNTS can be reconnected by the CB particles. By comparing the curves in Fig. 2a and b with 1 vol% SiO_2 and CB, in case of the low CB concentration, it is possible that more CNT networks are broken