Composites Science and Technology 97 (2014) 34–40

Contents lists available at ScienceDirect

Composites Science and Technology

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

Investigation on the piezoresistive behavior of high-density polyethylene/carbon black films in the elastic and plastic regimes

Shaodi Zheng, Jie Deng, Luqiong Yang, Danqi Ren, Shinlin Huang, Wei Yang, Zhengying Liu *, Mingbo Yang

College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, Sichuan, People's Republic of China

ARTICLE INFO

Article history:
Received 23 January 2014
Accepted 5 April 2014
Available online 16 April 2014

Keywords:
A. Polymer-matrix composites (PMCs)
A. Smart materials
B. Electrical properties
C. Deformation
B. Piezoresistivity

ABSTRACT

The piezoresistive behavior of two kinds of films, cast film and pressed film, based on high-density polyethylene/carbon-black composites is investigated for specimens loaded in axial tension. The tests are performed under a low number of cycles and different levels of applied strain. The normalized electrical resistance of the cast film is almost constant with strain in the elastic region and then it starts to increase with strain in the plastic region. However, for the pressed film, the normalized electrical resistance increases monotonically with strain. This unique behavior of resistance change of cast films can be applied to identify the elastic and plastic deformation in the composite. Moreover, two completely different strain sensing behaviors are presented in the cast film which undergo the cyclic tensile within the elastic regime and plastic regime. Finally, the normalized electrical resistance is simulated by using a mathematical model, taking into account the number of conductive paths and tunneling effect.

1. Introduction

The research on the electrical properties of carbon black (CB) filled polymer has attracted a lot of interests [1–7]. With an appropriate amount of carbon black in polymer matrix, the composites possess flexibility and piezoresistivity at the same time. These attributes have been utilized for developing smart materials which are able to measure their own strains through the variations in their electrical resistance [8–13]. The piezoresistive signal of these CB/polymer composites can also be used as structural health monitoring of advanced composite materials [2,6,7,11]. Besides the morphologies and electrical properties of the conductive network, the piezoresistive capability of these CB filled composite materials is strongly dependent on the matrix mechanical behavior, loading type (tension, compression, impact) and loading time or loading history [4,5,9,12,14]. Especially under cycling loading, reversible phenomena such as elasticity and irreversible phenomena such as plasticity of polymer may affect the electrical response of the CB-polymer composites.

The study on the relation between applied strain and the resistance of composite is the key to investigate the strain sensor [1,5,8,11,15–19]. The piezoresistivity observed in the strain sensors made from polymer/CB composites can be mainly attributed to the tunneling effect in adjacent fillers and the loss of contact between the fillers with the variation of strain. Zhang et al. [20] found that the resistance of conductor-filled polymer composites decreases with increasing uniaxial pressure and uses a concept of conducting path to describe this phenomenon. They considered that the total resistance in conducting composites is decided by the resistance between adjacent conductive particles. Based on the theory of tunneling current, the total resistance of the composite can be calculated by:

$$R_{tunnel} = \frac{M}{N}\frac{h^2 s}{Ae^2\sqrt{2m\varphi}}\exp\left(\frac{4\pi s\sqrt{2m\varphi}}{h}\right) \quad (1)$$

where M is number of particles forming a single conducting path, N is number of conducting paths, h is Plank's constant, s is thickness of insulating film between the adjacent particles, A is effective cross-sectional area, e is electron charge, and φ is height of potential barrier between adjacent particles, m is electron mass.

Maris Knite et al. [21] studied the relation between strain and electrical resistance of carbon-black-filled polyisoprene composite. Chiacchiarelli et al. [19] studied the piezoresistive behavior of graphene epoxy nanocomposites. They all found that the composite resistance increases with strain. To explain this phenomenon, the tunneling effect and destruction of conducting paths were taken into account. They hypothesized that the conducting path might actually be reduced when deformation increases, due to

* Corresponding author. Tel./fax: +86 28 85405324.
E-mail address: liuzhying@scu.edu.cn (Z. Liu).

http://dx.doi.org/10.1016/j.compscitech.2014.04.001
0266-3538/

the growth of micro-cracks within the material. The number of conducting paths can be calculated by:

$$N_{(\varepsilon)} = \frac{N_0}{\exp(A\varepsilon + B\varepsilon^2 + C\varepsilon^3 + D\varepsilon^4)} \quad (2)$$

where ε is the deformation, $N_{(\varepsilon)}$ represents the amount of conduction paths at a specific deformation. N_0 is the initial amount of conducting paths and A, B, C and D are fitting parameters. Based on the analysis on the relation among the deformation of matrix, the particle separation, and the number of conducting paths, the changes in the electrical resistance of the composite can be fitted by Eq. (3):

$$\ln R = \ln R_0 + \ln(1+\varepsilon) + A\varepsilon + B\varepsilon^2 + C\varepsilon^3 + D\varepsilon^4 \quad (3)$$

where R_0 is the initial electrical resistance, R is the instantaneous electrical resistance at a specific deformation. This model quite well described the experimental data at large deformations in Ref. [21].

However, the mass ratio of CB to the polymer in composite was required to be close to the percolation threshold in this model. In addition, the size of the carbon black was neglected in the process of derivation of the Eq. (3). Thus, the existing models cannot be used to explain the complicated piezoresistive phenomena for the composites which fabricated with the mass ratio of carbon black far more than the percolation threshold. Furthermore, it is found that the size of carbon black is non-negligible in the process of derivation of mathematical model for the piezoresistive of composites.

In this work, the piezoresistivities of carbon-black-filled conductive films prepared by different methods are investigated quantitatively. A particular interesting scenario occurs in the strain sensing behavior of HDPE/CB film which was fabricated by cast film extrusion. When the cast film subjected to the uniaxial tensile, an almost constant normalized electrical resistance is displayed in the elastic region, and the normalized electrical resistance starts to increase when strain entered into plastic region. The piezoresistive behavior of the cast film can be applied to identify the elastic and plastic deformation in the composite as a smart material. Moreover, two completely different strain sensing behaviors are presented when cast film undergo the cyclic tensile within the elastic regime and plastic regime. To explain the complex piezoresistive phenomena, we conducted detailed investigation into the underlying mechanisms responsible for the piezoresistivity of the cast film, with a focus on the decrease of the number of conductive paths and tunneling effect. The normalized electrical resistance is simulated by using a mathematical model, taking into account the number of conductive paths and the tunneling effect.

2. Experiment

2.1. Materials

Carbon Black (PrintexXE2-B, mean particle size of 30 nm, specific surface area of 1000 m^2/g, and dibutyl phthalate absorption of 420 ml/100 g) was supplied by Evonik degussa Corporation, Germany. A commercial high-density polyethylene (HDPE 3300F), with a melt flow rate of 0.3 g/10 min, supplied by Yanshan petroleum Chemical Co., Ltd., Beijing, was used as the matrix material.

2.2. Preparation of HDPE/CB conductive films

HDPE/CB (5 vol%) composite was melt blended through a twin-screw extruder (SHJ-20, L/D ratio of 20, Nanjing Giant Machinery Co., Ltd.) set as temperature profile of 170, 185,190 and 185 °C from hopper to die. The extruded strands were pelletized and then the carbon black was added (to ensure good conductivity) under the same extrusion processing conditions to get HDPE/CB (7.2 vol%) composite. The HDPE/CB conductive film with draw ratio 16 (the linear velocity of rotation of take-up roll divided by the velocity of melt outflow from die exit) was prepared by cast film extrusion method using a single-screw extruder (SJ-20BX25) equipped with a film die. In addition, the HDPE/CB pellets were compression molded at 200 °C for 5 min and then cooled to 25 °C under pressure for 2 min. All the films were annealed at 110 °C for 2 h.

2.3. Sample characterizations

The dispersion of carbon black and crystalline morphology of the conductive films were observed with a Scanning Electron Microscopy (Inspect F, FEI Company, USA). An acceleration voltage is 20 kV. For studying the dispersion of filler, the specimens were placed laterally on the stage without any metal coating. For morphological observation, the surfaces of specimens were etched by permanganic etching technique [22,23], washed, dried and then covered with a thin layer of gold. The piezoresistivity measurements were performed on a homemade apparatus (Fig. 1a). The uniaxial tension and release was carried out by the Shimadzu universal testing machine (AGS-J) with a constant rate of 1 mm/min. Two-probe electrical resistivity measurements were performed using an electrometer Keithley 6517B (Keithley Instruments, Inc, Ohio, USA) connected to a computer. The strain (ε) and resistance data were recorded through a LabVIEW program in a real-time manner. Both ends of the dumbbell samples were coated by silver paint prior to test in order to reduce the contact resistance. Five specimens for each sample were tested and the averaged data were reported in this work.

3. Results and discussion

3.1. Morphology

The results of the scanning electron microscope (SEM) analysis of HDPE/CB films, prepared by compression-molded process and cast film extrusion process, are shown in Fig. 2. As seen from Fig. 2a and b, the SEM micrograph of the surface of films showed that carbon black particles homogeneously dispersed in HDPE matrix, with no visible agglomerates, which ensures the formation

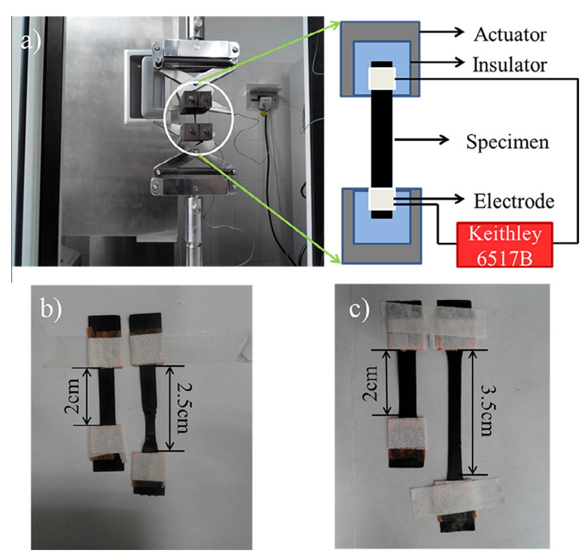

Fig. 1. (a) Experimental setup for the piezoresistivity measurements. Photographs of the pressed film (b) and cast film (c): the left one is the original sample and the right one is the stretching sample with strain in which the electrical resistivity could not be obtained by our equipment.