Materials Letters 140 (2015) 71–74

Contents lists available at ScienceDirect

Materials Letters

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

Temperature sensing of conductive shape memory polymer composites

Hongsheng Luo*, Zhiwei Li, Guobin Yi*, Yunjia Wang, Xihong Zu, Huan Wang, Hailiang Huang, Zhenfei Liang

Faculty of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, PR China

ARTICLE INFO

Article history:
Received 21 July 2014
Accepted 3 November 2014
Available online 11 November 2014

Keywords:
Shape memory
Nanocomposites
Temperature sensing
Conductive
Silver nanowires

ABSTRACT

A novel strategy of stimulus sensing is unprecedentedly presented for conductive shape memory polymer composites. Temperature stimulation makes the composites recover not only the shapes but also the conductivity as the composites experience "memorizing" process from the temporary shapes to the original shapes. Silver nanowires (AgNWs) are incorporated into the surface layer of shape memory polyurethane (SMPU). The AgNW–SMPU composites are stretchable and electrically conductive, particularly exhibiting reversible strain-dependent conductivity. The resistance increases and is subsequently stabilized at relatively higher value as the composites are extended and fixed in a typical shape memory programming. Temperature stimulation enables the composites to recover the shapes, along with large decrease in resistance. The findings disclose that the conductive shape memory composites are able to respond to external stimulus by variation of the electrical signals in a desired manner, which may greatly benefit the development of smart polymer materials in flexible electronics and sensors fields.

1. Introduction

Electrically conductive polymeric nanocomposites have been catching increasingly interest in recent years [1]. Many factors have been found to influence the electrical properties of the composites, including micro-structural factors (nano-fillers content, dispersions, aspect ratio and interface-interaction between the fillers and the matrix) and externally environmental factors (temperature, humidity, and mechanical status of the composites). By virtue of the sensitivity to the environmental stimuli, the conductive nanocomposites are able to serve as a type of sensory materials. For instance, epoxy composites allowed a multifunctional sensor whose electrical properties showed stress/strain, temperature, and relative humidity dependency [2]. Besides, AgNWs are a very important alternative for constructing conductive composites due to the conduction and optical advantages. They were embedded in polydimethylsiloxane (PDMS) for pressure measurements [3]. Although the AgNWs were previously applied to fabricate flexible electrodes for polymer Light-Emitting Diodes (LED) [4], there has been little literature reporting on the AgNW-based conductive sensory shape memory composites. Herein, we present a novel strategy of stimulus sensing for the AgNW-containing conductive shape memory composites. The findings disclosed the capability of the nanocomposites to respond to external stimulus via variations in mechanical and electrical properties, which may extend the application of intelligent polymers in the fields of flexible electronics and sensors.

2. Experimental

The AgNWs were synthesized via polyol process, which was briefly described as following: silver nitrate ($AgNO_3$, Aldrich) and poly(vinyl pyrrolidone) (PVP, Aldrich) were stirred in ethylene glycol (EG) in the presence of $FeCl_3$ at 160 °C for 3 h. The molar ratio of the EG, units of PVP and $AgNO_3$ was 1.0:0.017:0.008. The resultant AgNWs obtained from centrifuge were combined with a glassy shape memory polyurethane (SMPU) by a transfer process [5]. Three composite samples were labeled as PAg01, PAg02 and PAg03 representing the Ag content weight percentages of 6%, 12% and 18%, respectively. The surface morphologies, thermal, structural and electrical properties were investigated by SEM (Hitachi, S-4800), Differential Scanning Calorimetry (DSC, Perkin-Elmer Diamond), UV Laser Raman Spectroscopy (LabRAM HR 800, HORIBA Jobin Yvon) and an electrochemical workstation (CHI660D, Chen-Hua, PR China). The relative resistance (R_r) of the composites was defined as the resistance in the extended state (R_e) divided by the resistance in the original state (R_o). The samples were fixed

* Corresponding authors. Tel.: +86 20 39337174; fax: +86 20 39322231.
E-mail addresses: luohsheng@gmail.com (H. Luo), ygb116@163.com (G. Yi).

http://dx.doi.org/10.1016/j.matlet.2014.11.010
0167-577X/

directly contacted with two conductive clamps during the resistance measurements.

3. Results and discussion

Structural and thermal properties of the composites: The SMPU featured netpoints and thermally switchable chains in the microstructure. The former provided the entropy elasticity for shape recovery while the latter was responsible for shape fixing. The AgNW–SMPU composites maintained the structural characteristics, which is schematically illustrated in Fig. 1a. The glass transition temperatures (T_g) of the composites were determined by DSC measurements (shown in Fig. 1b). It was found that the $T_g$slightly shifted upwards in the range of 73–79 °C as the AgNWs content increased, indicative of the interactions between the AgNWs and the PU molecules. Furthermore, nano-fillers with high aspect ratio tended to constrain the local movement of the polymer molecules incorporated into the polymer matrix [6]. The AgNWs may play restriction effect on the local movements of the PU molecules, leading to the shift upwards of the T_g. The AgNW–SMPU composites in bi-layer structure were fabricated by the transfer process. The surface and bulk morphologies were investigated by SEM, which are shown in Fig. 1c and d, respectively. Drop-casting of the AgNWs suspension in methanol made a conductive percolating film achievable on the substrate surface. The thickness as well as the conduction of the film were controlled by the drop-casting process, such as solid concentration, volume and cover are of the suspensions. Afterwards, the SMPU solution was added and solidified in vacuum before peeling off the final composites. The composites exhibited superior conductivity and flexibility attributed to the nano-silvers and the polymer matrix. The conductive AgNWs network could be clearly observed from the SEM image, one part of which was embedded into the polymer layer while the other part was left on the surface. The partially embedded AgNWs provided sufficient pathway for electrons to go through as electrical voltages were applied. Given that the SMPU was the dominant component of the composites, the AgNW–SMPU composites had mechanics like that of the pristine SMPU, i.e. stretchability and thermally-triggered shape memory effects.

Evolutions of the composites in extension: The composites were extended at 90 °C by different percentages prior to shape fixing. The extension led to deformation of the conductive network constructed by the AgNWs. As a result, the resistance dramatically increased, which was then stabilized along with the shape fixing. The strain-induced changes in the conductivity were observed also in other conductive polymeric nanocomposite systems [7]. Fig. 2a and b shows the SEM images of the AgNW-embedded surface before and after the extension, confirming the deformation of the conductive network under the extension. The composites in different percentages of the extension were investigated with Raman spectroscopy, which is shown in Fig. 2c. Two dominant peaks centrally located at 1367 cm^{-1} and 1587 cm^{-1} were observed which could be assigned, respectively, to the $-CH_2$ deformation and the aromatic stretch from the hard segment [8]. Moreover, the former peak shifted, respectively, from 1367 cm^{-1} to 1343 cm^{-1} and 1335 cm^{-1} as the composite was extended by 10% and 16%, suggesting that the PU matrix enlarged the deformation. The broad peak at 2170 cm^{-1} is expected to be associated with the –CO–NH groups in the PU. The peak disappeared as the extension was up to 16%, perhaps reflecting local structural damage of the composites. The Raman band shift disclosed the deformation of

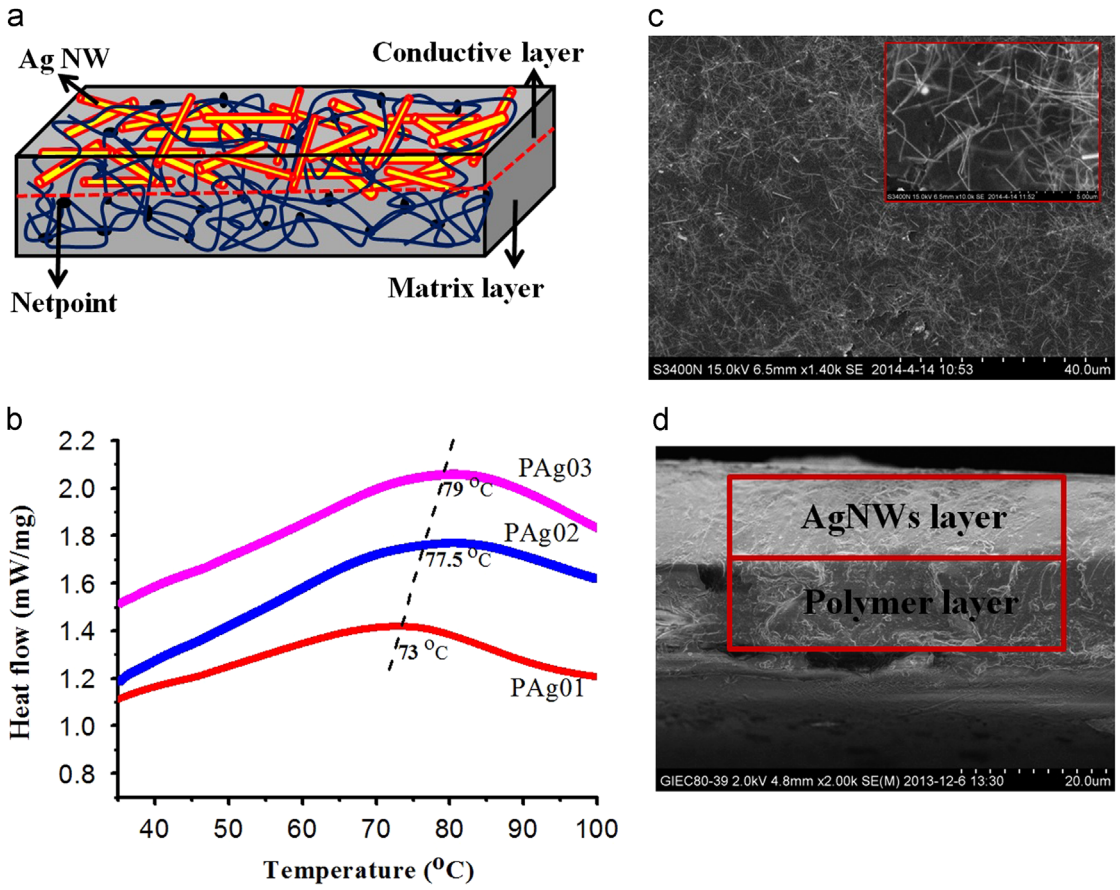

Fig. 1. (a) Schematic illustration of the composite structure; (b) DSC curves of the composites; SEM images of the surface (c) and bulk morphologies (d).