Sensors and Actuators A 271 (2018) 76–82

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

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

Poisson effect enhances compression force sensing with oxidized carbon nanotube network/polyurethane sensor

Petr Slobodian[a,*], Pavel Riha[b], Robert Olejnik[a], Jiri Matyas[a], Michal Kovar[a]

[a] Centre of Polymer Systems, University Institute, Tomas Bata University, Tr. T. Bati 5678, 760 01 Zlin, Czech Republic
[b] Institute of Hydrodynamics, Academy of Sciences, Pod Patankou 30/5, 166 12 Prague 6, Czech Republic

ARTICLE INFO

Article history:
Received 8 November 2016
Received in revised form
27 November 2017
Accepted 15 December 2017

Keywords:
Compression force sensor
Carbon nanotubes
Polyurethane
Polymer composite
Nano-cracks

ABSTRACT

Poisson effect when a sensor made of multi-walled carbon nanotube network embedded in the elastic polyurethane was compressed in one direction and expanded in the other two directions perpendicular to the direction of compression several fold enhanced the sensing owing to nano-sized cracks of the network. The composite sensitivity was further multiplicatively enhanced by $KMnO_4$ oxidation of carbon nanotubes. As an example of the composite use as a compression sensor, a pressure on the shoe sole was monitored as well as a ball bullet impact on the sensor.

1. Introduction

Stretchable and flexible polymeric composites with integrated carbon nanotubes pose great potential in area of new material design with high performance properties. Such strain or stress sensing composite materials have attracted considerable attention specially because of their unique characteristics lying in superior mechanical properties as deformability and easy adjustment to limited space and/or shape, electromechanical sensitivity, the ease of composite processing and low cost, which surpass conventionally used materials. Their potential applications are in the area of wearable sensors for healthcare related use [1], soft robotics [2], smart textiles [3], structural health monitoring [4], or bio-interactive electronic devices [5]. From the array of different solutions and various types of transducers available for the mentioned applications, piezo-resistive strain or stress sensors belong to the most investigated ones [6–16]. In most cases they are usually polymer based composites with conductive filler such as carbon nanotubes, carbon fibers, etc. The filler can be *in situ* polymerized with the matrix [17] or it can be also deposited on the surface of a stretchable polymer by various methods as direct printing [6] or transferring of a conductive layer from another polymeric substrate [7,8]. The carbon nanotube films are usually deposited on a thicker flexible polymer, which acts as a mechanical support and transfer strains or stresses to the sensitive layer [6–16]. This kind of new materials can overcome limitation of traditional metallic and semiconducting deformation sensors, which are not suitable for high deformation measurements since they can sustain only ~5% of elongation before fracture [6]. On the other hand, the polymer based sensors can be elongated as much as several hundred percent.

Thermoplastic polyurethane elastomers (TPUs) are usually used as elastomeric matrices. TPU can be prepared by thermally induced phase separation technique [18] or by high shear twin screw extrusion mixing and phase separation of a single TPU-CO_2 solution [19]. TPU matrix sensors can be prepared by infiltration of multi-walled carbon nanotube forests into polyurethane binder, which measure reproducible changes in resistivity at elongation up to 40% [16].

Deformation sensors made of layered carbon nanotube/polymer composites usually consists of conducting filler network together with fracturing filler/composite strain sensitive film. The detection sensitivity increases when the nanotube structure breaks into gaps and islands [15,20,21]. The electrical resistance of conductive carbon nanotube networks is mainly affected by the nanotube/nanotube contacts since the nanotubes cannot create a continuous conductive path within the entire length of the sensing film [13]. Synergic effects of the contact resistance and bulk resistance mechanisms were also studied [22]. The maximum tunneling distance between crossing nanotubes is about 1.8 nm [23]. Previous work shows that a higher tunneling resistance or higher ratio of the tunneling resistance to the total sensor resistance increases the sensor sensitivity [24]. Our work reveals that chemical or plasma oxidation of MWCNTs increases the network contact resistance and

* Corresponding author.
E-mail address: slobodian@cps.utb.cz (P. Slobodian).

https://doi.org/10.1016/j.sna.2017.12.035
0924-4247/

thus enhanced the sensor sensitivity [11,12]. Several methods are proposed to enhance the strain sensitivity of polymer composite sensors further. For instance, mixed multiwalled carbon nanotubes (MWCNTs) and carbon black reduce entanglement in the conductive network, which increases its strain sensitivity [8]. Similarly, the incorporation of additional functionalized MWCNTs into composite sensor, which can facilitate the interfacial interaction between the filler and polymer matrix enhances also its sensitivity [8].

The aim of this study was to develop a sensitive sensor for compressive force sensing. The sensor was made from $KMnO_4$ oxidized multi-walled carbon nanotube network embedded in elastic polyurethane and then stimulated by pre-strain deformation, which caused the cracking of the nanotube network. Further we described differences in sensing efficiency of the stimulated sensor due to cracking of MWCNT network and MWCNT/TPU sensor without stimulation. The observed differences in electromechanical properties of sensors are discussed on basis their structure, which was examined by means of the scanning electron microscopy.

2. Experimental

2.1. Materials

Desmopan 385S polyester based TPU was supplied by Bayer MaterialScience. The limited information on TPU properties provided by the manufacturer revealed its mass density of 1200 kg/m^3, injection molding temperature 210–230 °C, shore hardness 85 (method A), ultimate tensile strength 40 MPa and strain at break 450%. The >90% pure multi-walled carbon nanotubes with electrical resistivity of 0.12 Ωcm produced by acetylene chemical vapor deposition method by Sun Nanotech Co. (China). We determined by the transmission electron microscopy (TEM) [25] that the diameter of individual nanotubes was between 10 and 60 nm and their length from tens of micrometers up to 3 μm, Fig. 1a. The maximum aspect ratio of the nanotubes was about 300. Oxidized MWCNTs were prepared in a glass reactor with a reflux condenser filled with 250 mL of 0.5 M H_2SO_4, into which 5 g of potassium permanganate ($KMnO_4$) as oxidizing agent and 2 g of MWCNTs were added. Dispersion was sonicated at 85 °C for 15 h using a thermostatic ultrasonic bath (Bandelin Electronic DT 103H) and filtered. Then MWCNTs were washed with concentrated HCl to remove MnO_2 and after that washed with water until pH reached 7. The oxidized nanotubes were denoted MWCNT($KMnO_4$).

2.2. Compression force sensor

Aqueous dispersion of MWCNTs was prepared by sonication using UZ Sonopuls HD 2070 for 15 min at room temperature. The nanotube concentration in the dispersion was 0.3 wt.%, concentration of added surfactant sodium dodecyl sulfate and 1-pentanol were 0.1 M and 0.14 M, respectively. Ultimately, the pH was adjusted to 10 by addition of aqueous solution of NaOH [26].

The polyurethane non-woven porous membrane for MWCNT dispersion filtration was prepared by electrospinning from Desmopan 385S solution in polyurethane dimethyl formamide/methyl isobutyl ketone (volume ratio 1:3). The polymer weight concentration was 16%. In order to optimize the electrospinning process, NaCl was added to adjust electrical conductivity to 30 μS/cm. The distance of the steel multi-jet spinning electrode and the steel plate acting as the collecting electrode of the electrospinning equipment was 180 mm. The total number of nozzles was 18, the length of nozzles 30 mm, the distance between nozzles 20 mm, the nozzle internal diameter 1.2 mm and the outer diameter 2.2 mm. The electric voltage was set to 75 kV (Matsusada DC power supply), the flow rate of polyurethane solution in one nozzle 1.6 μl/min. The final thickness of TPU non-woven filters was about 200 μm. Scanning electron microscope (SEM) micrograph of TPU membrane is in Fig. 1b.

To prepare MWCNT network, homogenized MWCNT dispersion was filtered through TPU non-woven filters fixed on a funnel of diameter 90 mm. The network of typical thickness of about 35 μm was washed several times with deionized water at 65 °C, followed by methanol *in situ* and dried between two filtration papers for 24 h. SEM analyses of upper surface of both CNT layers prepared from pure MWCNTs and from $KMnO_4$ oxidized MWCNTs are presented in Fig. 1c and d, respectively.

The polyurethane filter with MWCNT network was melt welded at 175 °C to the surface of pure TPU plate to create stress sensor covered by another crosswise TPU plate and stacked together at edges (see Fig. 1e). The adequate compression molding temperature was chosen 175 °C according to the differential scanning calorimetry measurement (Perkin-Elmer Pyris 1) performed at a heating rate of 10 °C/min. Electrodes (Cu wires) for two-point lengthwise resis-

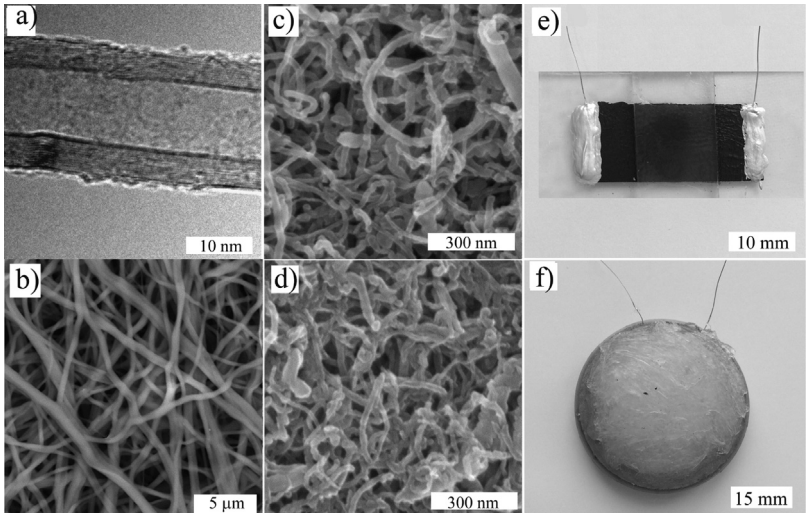

Fig. 1. a) TEM micrograph of a pristine nanotube, b) SEM micrograph of polyurethane non-woven filtering membrane, c) SEM micrograph of the surface of entangled pristine MWCNTs, d) SEM micrograph of the surface of entangled oxidized MWCNTs, e) the sensor with protecting TPU strip and two silver painted electrodes for two-point resistance measurement, f) the sensor covered by a two-component silicone rubber.