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Highly sensitive and stretchable graphene-silicone rubber composites for strain sensing

Heng Yang, XueFeng Yao*, Zhong Zheng, LingHui Gong, Li Yuan, YaNan Yuan, YingHua Liu

Applied Mechanics Laboratory, Department of Engineering Mechanics, Tsinghua University, Beijing, 100084, China

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ABSTRACT

Flexible strain sensors made by conductive elastomer composites have attracted increasing attention. In this paper, the electromechanical properties of graphene-silicone rubber nanocomposites are studied systematically. First, the conductive nanocomposites composed of graphene and silicone rubber are prepared by means of co-coagulation, which shows a lower percolation threshold with 1.87 wt% (0.94 vol%). Second, the rubber nanocomposites with different graphene contents exhibit a very high strain sensitivity (gauge factor > 143) and a larger strain sensing range (> 170%), also, the good recoverability and reproducibility have been found during the loading-unloading cycle. Finally, the analytical model based on the connectivity of the graphene nanosheets and the viscoelasticity of the rubber matrix is developed to describe the electromechanical properties and explain the 'shoulder peak' phenomenon, also a typical application example about monitoring the operate state of the rubber seal is given.

1. Introduction

Flexible strain sensors made by conductive elastomer composites have attracted increasing attention due to their excellent strain sensing performance, flexible and soft features as well as good reproducibility [1–3], which are widely used in many engineering fields, including bio-signals detection [4], structure health monitoring [5] and smart skins [6]. Conductive polymer composites (CPC) based strain sensors are usually fabricated by dispersing one or more electrically conductive fillers in the polymer matrix. In fact, the selections of conductive fillers and polymer matrix are significant for superior strain sensing performance. Graphene is an important filler for polymers to enhance electrical, mechanical, or barrier properties because of its good mechanical properties, low density, high thermal conductivity and high electron mobility [7–9]. Methyl vinyl silicone rubber has been widely used as sealing materials owing to its excellent thermal stability, anti-aging properties and excellent compression resilience behaviors. However, the mechanical and sensing properties of graphene-silicone rubber nanocomposites have not been explored systematically.

The graphene rubber nanocomposites are mainly prepared by means of the latex blending method, solution blending method and direct blending method. For example, Potts et al. [10] prepared the graphite oxide/natural rubber nanocomposites by means of the latex and direct two-roll mill processing, respectively, which achieved a more uniform dispersion of graphite oxide and the larger property improvements in the nanocomposites by the latex mill processing. Ponnamma et al. [11] reported the synergistic effect of multi-walled carbon nanotubes and the reduced graphene oxides in natural rubber composites fabricated by means of the solution blending method, and found that these composites could be used as a novel organic liquid sensor. Hernandez et al. [12] prepared the nanocomposites with natural rubber and graphene sheets by means of conventional two-roll mill mixing, and the mechanical strength reached maximum at about 0.5 phr graphene. Though some organic solvents will be consumed during the preparation, both the latex blending method and the solution blending method [13,14] are still selected to realize more uniformly dispersion of the nanostructured filler particles in rubber matrix.

Also, the sandwich method is usually used to prepare the graphene rubber nanocomposites. Shi et al. [4] presented high performance strain sensors made by the embedding the graphene platelets film into the polydimethylsiloxane substrate. Actually, the graphene rubber composites made by the sandwich method can only be stretched to a very limited extent, generally less than 30% [15,16]. Although Yan et al. [17] fabricated the high-strain sensors based on stretchable graphene nanopaper exhibiting a gauge factor of 7.1 at 100% strain, the development of high-strain graphene sensors whose maximum strain exceeds 100% by the sandwich method remains technically challenging.

On the other hand, high sensitivity, superior reproducibility, wide

* Corresponding author.
E-mail address: yxf@mail.tsinghua.edu.cn (X. Yao).

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strain scope and long-term stability under cyclic loading are vital for CPC as strain sensors. For instance, Boland et al. [18] produced graphene-natural rubber composites with gauge factors of up to 35 for bodily motion sensors. Lin et al. [19] prepared graphene-based elastomer composites with a segregated nanostructured graphene network with high stretchability (90%) and good reproducibility (~ 400 cycles). However, according to the reported results in the literature (Table S1), strain sensors based on rubber nanocomposites cannot possess high sensitivity (gauge factor > 50) and high stretchability (strain > 100%) simultaneously. Thus, it is still a challenge to prepare the rubber nanocomposites to meet the requirements of both large deformation and high sensitivity. In addition, though the mechanisms of the conductivity and piezoresistivity about the CPC sensor are investigated by numerical simulation [20–22] and theoretical model [4,23], the resistance-strain relationship has not been characterized for the cycle loading, especially for the unloading process. Because of the destruction and reconstruction of conductive paths, the resistance responses are different during the loading and unloading process under the initial cyclic loading stage [2,24]. Thus, it is necessary to establish the quantitative model that completely describes the electromechanical properties for the whole loading and unloading process, in order to understand the mechanisms of piezoresistivity and the re-formation of conductive paths.

In this paper, the graphene-silicone rubber nanocomposites are prepared by the combination of solution method and co-coagulation. The strain sensing behaviors of graphene-silicone rubber nanocomposites are explored under uniaxial tension and cyclic loading. A quantitative model describing the electromechanical properties during the whole loading and unloading process is developed by considering both re-formation of conductive paths and the rubber viscoelastic feature.

2. Experimental details

2.1. Materials

Graphene with less than three layers and its oxygen content 1.84 wt % was purchased from Chengdu Organic Chemicals Co. Ltd, China. Silicone rubber (Methyl-Vinyl-Silicone, MVQ 110-2) was provided by Dong Jue Silicone (Nanjing) Co., Ltd., China. The molecular weight of the used silicone rubber is about 6.2×10^5 g/mol. Curing agent 2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane was obtained from Dongguan TengKai rubber and plastic technology Co., Ltd, China. Tetrahydrofuran (THF, AR) and ethyl alcohol absolute (AR) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd and Fu Yu Fine Chemical Product (Tianjin) Co., Ltd, respectively. All of these chemicals have been used as the received.

2.2. Preparation of graphene-silicone rubber nanocomposites

The graphene-silicone rubber composites were fabricated by the combination of solution method and co-coagulation, as shown in Fig. 1. The preparation process was conducted as follows: (1) Silicone rubber was dissolved in THF at 35°C by vigorous stirring for 120 min. (2) Graphene was dispersed in THF under ultrasonication for 120min to obtain the stable suspension. (3) The silicone rubber/THF and graphene/THF was mixed together, and then sonicated and stirred for 60 min for homogeneous suspension. (4) The mixture was added into anhydrous ethanol drop by drop under vigorous stirring to obtain the flocculate graphene-silicone rubber. (5) The obtained flocculation was filtered, and dried at 50 °C in vacuum oven for 24 h. (6) Curing agent was added into the graphene-silicone rubber mixture, and then the resulting compound was placed in the mold for curing in the vulcanizing machine followed by vulcanizing at 165 °C for 10 min to obtain the composites. The thickness of graphene-silicone rubber composite sample is 1 mm. Fig. 1 (c) shows the prepared neat silicone rubber and graphene-silicone rubber nanocomposites.

2.3. Characterization

Scanning electron microscope (SEM, JSM-7041) was used to characterize nanocomposites morphology. Samples were cryo-fractured in liquid nitrogen. The fracture surfaces were coated with a thin layer of platinum to obtain better images. The Fourier transform infrared spectroscopy (FT-IR) was conducted on a VERTEX 70 V instrument with a resolution of 0.4 cm^{-1} in attenuated total reflection mode. The mechanical properties were obtained by the tension test on an electrical universal testing machine. The dumb bell standard tensile specimen was used in uniaxial tension experiment according to ISO 37:2005(E). Each experiment has been repeated three times with a crosshead speed of 500 mm/min at ambient temperature to ensure the repeatability of the test results. The large deformation extensometer with a gauge length of 40 mm has been used to measure the strain in the tension test.

For the electrically conductive properties test, a high resistance meter (ZC36, Beijing HuaCe Testing Instruments Co., Ltd. China) was applied to measure the volume electrical resistivity above 10^6 Ω cm. The resistance measurement system in (Fig. 1(d)) was employed to measure the volume electrical resistivity below 10^6 Ω cm, including Keithley 6485 picoammeter (20fA-20mA), digitally adjustable voltage source (Shenzhen Zhaoxin Electronic Instrument Equipment Co., Ltd., 0-100VDC) and electrostatic voltmeter (Beijing HuaCe Testing Instruments Co., Ltd., 100 mV–200 V). The dimension of the test sample was 40 mm * 10 mm * 1.0 mm. For each sample, at least five strips were tested. Conductive silver paint has been used to connect the samples and the electrodes to ensure the good contact. The volume conductivity σ is calculated using Eq. (1):

$$\sigma = 1/\rho = L/RS \tag{1}$$

Where ρ, R, S and L are the resistivity, the resistance, the cross-sectional area of the sample, and the distance between the electrodes, respectively.

As for the electromechanical properties, the resistance measurement system and the universal testing machine (Fig. 1(d)) were coupled with a computer to record the real-time current signals, the deformation and the stress. The rectangular strip with dimensions of 40 mm * 10 mm *1.0 mm was clamped with a pair of copper electrodes and a gauge length of 10 mm was created for the resistance response experiments.

3. Results and discussions

3.1. Morphology of composites

Graphene is easily agglomerated in polymer composites because of its large specific surface area, strong van der Waals force between graphene layers and the higher viscosity of the polymer matrix. Thus, the uniform dispersion of graphene in the polymer matrix is significant to obtain high-performance nanocomposites.

The morphology of the freeze-fractured surface for graphene-silicone rubber nanocomposites (3.0 wt%) is shown in Fig. 2(a and b). It can be seen that graphene dispersed homogeneously in the composites and combined firmly with the rubber matrix through the careful observation of the interface.

3.2. Interfacial bonding between graphene and silicone rubber

Graphene surface will possess the remaining oxygenated groups produced during the preparation process. Thus, H-bonding interactions probably exist between silicone rubber chains and graphene sheets owing to oxygenated functional groups, such as −COOH and −OH, on the surfaces of graphene sheets and the oxygen groups on silicone rubber chains.

All the spectra were obtained in the range from 600 to 4000 cm^{-1} as shown in Fig. 2(c). The characteristic absorption peaks at 2962 cm^{-1} and 690 cm^{-1} correspond to the stretching vibrations of CH_3 and Si−C,