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Conductive herringbone structure carbon nanotube/thermoplastic polyurethane porous foam tuned by epoxy for high performance flexible piezoresistive sensor

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In this paper, we used epoxy (EP) as a third component to tune the electromechanical performances of the conductive porous foam. A directional ice-template freezing method was utilized to fabricate a carbon nanotubes (CNTs)/EP/thermoplastic polyurethane (TPU) porous foam with a herringbone-like structure. CNTs were homogeneously distributed in the skeleton of the foam. The microstructure of the herringbone-like foam was studied in detail from both the directions perpendicular and parallel to the freezing front movement direction. An ultralow percolation threshold (0.088 vol%) of the conductive foam was achieved. The strength of the CNTs/TPU/EP foam was significantly enhanced with the increase of the CNTs and EP contents. When the foams were exposed to a compression strain from 0 to 70%, the resistance of the porous material decreased in a good linear manner. The foams showed a good differenciation capability towards different compression strain amplitude. Upon multiple cyclic compressive process, the change of the resistance tended to be stable after several compression loading-unloading cycles' measurement. After a pre-compression treatment, the resistance response also became much stable on the basis of the re-arrangement of the conductive network and the stabilized cells structure of the foam. The porous foam possesses a rapid response speed (about 160 ms). Our flexible porous foam with a good chemical resistance can be used in ethanol to sense the finger pressing, and it showed excellent sensing performances when applied to monitor human body motions.

1. Introduction

Conductive polymer composites (CPCs) are usually fabricated by dispersing single or hybrid conductive ingredients (carbon black, carbon nanotube(CNT), metal particles or conducting polymers, etc.) into insulating polymer matrix [1,2]. On the basis of the excellent properties, such as light weight, good flexibility, ease of manufacturing and good chemical resistance, etc., widespread attention on tuning of the structure and properties of CPC has been received in many application areas, such as electromagnetic interference shielding [3,4], electrostatic discharge protection [5–7] and sensors [8–13], etc. As one of the most interesting applications, CPC based flexible piezoresistive material have been demonstrated to possess a vast practical future in health monitoring [14–18], wearable electronics [19–22] and movement sensor [23–25], etc.

Piezoresistive behavior is generally defined as the resistance variation induced by external mechanical stimulus, which is one of the most essential performances of the CPC based piezoresistive sensors [26–29]. Traditional piezoresistive sensors are generally fabricated by metallic or inorganic semiconductor materials. These materials are typically rigid, heavy and brittle when subjected to external force, largely hindering their utilization in many fields [30,31]. Recently, a considerable amount of investigations has been

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performed on piezoresistive sensors with good flexibility and excellent recoverability. For example, Lou et al. fabricated an ultra-sensitive graphene pressure sensor with long-term stability and rapid response rate based on a natural viscoelastic material poly(vinylidene fluoride) @ reduced graphene oxide film [21].

Porous polymer materials filled with conductive fillers are often utilized as piezoresistive sensors to obtain excellent flexibility and favorable piezoresistive performances. These three dimension nanocomposites always have high porosity, ultra-low density and good energy conversion and storage properties. The porous CPCs have been intensively studied in many pressure electronic fields [32–34]. For example, Li et al. reported a novel strategy for fabricating a flexible and stretchable piezoresistive porous material through a simple dip-coating method [35]. Although the structure and properties of conductive porous CPC piezoresistive foam have been studied extensively, the sensing mechanism is not fully clear and the piezoresistive stability of the materials is still needed to be improved.

On the other hand, in recent years, various approaches about the fabrication of porous CPCs have been proposed, including salt-leaching [36,37], bio-template synthesis [38] and ice-templating [39–41], etc. Among these methods, the ice-templating has been considered as a promising simple technique. Aligned porous materials can be prepared and tuned by controlling the growth of ice crystals by a directional freezing process [39]. Roberts et al. prepared hierarchical porous nitrogen-rich carbon monoliths via ice-templating approach, the monolith could be used as lithium-ion battery anode materials [42]. Kuang et al. produced hierarchically structure graphene foams with superb compression recoverability via the directional freezing method followed by a high-temperature thermal treatment [43].

On the basis of the excellent flexibility, thermoplastic polyurethane (TPU) composites based strain sensors have been studied frequently by many researchers [44–46]. We also reported a CNTs/TPU nanocomposite foam prepared by a thermally induced phase separation (TIPS) technique previously, which presented a good piezoresistive recoverability [47]. Nevertheless, the strength of the TPU based porous piezoresistive materials is very low, the sensing durability is still poor. On the other hand, thermosetting materials, such as epoxy (EP), have provoked widespread attention due to their high strength and stiffness properties. It is known that EP can be used in many fields, such as coatings, adhesives, hardware components and semiconductor encapsulation. EP composites as strain sensor not only possess a higher strength but also exhibit excellent recoverability and stability [48,49]. To the best of our knowledge, few works have been carried out by using EP as a component to tune the piezoresistive performances of a flexible conductive porous material.

In the present work, to achieve a promising material with a favorable porous structure, good piezoresistive properties as well as high strength, we fabricated a novel herringbone structure conductive composite foams based on the combination of EP with TPU via the directional ice-template freezing technique. CNT was chosen as the conductive filler arising from its excellent mechanical properties and superior electrical conductivities. Mechanical properties tuned by different EP content and CNT content were conducted under compression test. Piezoresistive properties towards different deformation amplitude and compression rate were studied during multiple cyclic compressive loading. The capability of the porous nanocomposite on human motions detections was also demonstrated by monitoring the jump, piaffe, tiptoe and walk, etc. The results indicate that our herringbone-like porous nanocomposite has great prospect as high performance flexible piezoresistive sensor.

2. Experimental section

2.1. Materials

Polyester-based TPU (Elastollan 1185A) was purchased from BASF Co. Ltd., China. EP resin (LT-5078A) and hardener (LT-5078B) were supplied by RuiGao New Materials Co. Ltd., China. The amine functionalized multi-wall CNTs were bought from Chengdu Organic Chemicals, Chinese Academy of Science. Dioxane was purchased from Zhiyuan Reagent Co., Ltd. Tianjin, China and was used as received without further purification.

2.2. Fabrication of porous CNTs/TPU/EP nanocomposites

In a typical run, CNTs and EP (LT-5078A: LT-5078B = 3:1) were dispersed in dioxane (40 ml) by ultrasonication to reach a homogenous mixture. The TPU pellets were then dissolved in dioxane (40 mL) under vigorously stirring at 40 °C for 30 min. After that, TPU solution was added into the prepared CNTs/EP solution and stirred at room temperature until a uniform mixture was obtained. The mixture was then stored in a freezer at −25 °C for 12 h to completely freeze the solution and then freeze-dried at −80 °C for 72 h in a freeze drier. Finally, the as-prepared nanocomposites were annealed at 80 °C for 8 h for piezoresistive behavior test.

2.3. Characterizations

The microstructure and morphology of the fabricated CNTs/TPU/EP nanocomposites were observed by a field emission scanning electron microscope (FE-SEM, Model JEOL JSM-7500F). Samples were immersed in liquid nitrogen for an hour and cut off quickly by a blade. Before the SEM observation, the fractured surfaces were sputtered with a thin layer of platinum for better imaging. The interactions between components of the CNTs/TPU/EP composite were investigated by using the fourier transform infrared spectroscopy (FTIR). The spectra of the samples was taken at 400-4000 cm^{-1} wavelength by using a Thermo Fisher Nicolet iS50 spectrometer in the attenuated total reflection (ATR) mode. Compression tests were performed at room temperature using a universal testing machine (UTM2203, Shenzhen Suns Technology Stock Co. Ltd., China). The schematic of the experiment set-up for measuring piezoresistivity and compressive strain-resistance variation of the nanocomposite foams were illustrated in Fig. S1. The fixture used in the present paper was shown in Fig. S2. The dimensions of all the cylindrical porous samples were 11 mm in diameter and 10 mm in height. In cyclic compression test, two aluminum plates were used as the electrodes and connected to a precision digital resistor (Model TH2683, Changzhou Tonghui Electronics Co. Ltd., China). In order to ensure a good contact between electrodes and samples, the top and bottom cross-sections of the samples were coated with a layer of silver paste. The results were averaged over at least five foam samples. The electric resistance upon cyclic compression was recorded simultaneously using the precision digital resistor.

3. Results and discussion

3.1. Morphology

Ice-templating method is an effective way to produce a structured macroporous material. Fig. 1 schematically shows the freezing mechanism for the conductive porous CNTs/TPU/EP foam. As in nature, during the freezing process of 1, 4-dioxane, polymer molecules and CNTs concentrate in the slurry, impurities have a very low solubility in ice crystals, thus they are ejected from the