

Short communication

One-pot preparation of porous piezoresistive sensor with high strain sensitivity via emulsion-templated polymerization



Lei Yang^{a,b,*}, Ruiying Wang^a, Qingting Song^b, Yu Liu^a, Qiangqiang Zhao^{a,b}, Yifeng Shen^{a,b}

^a Engineering Research Center for Eco-Dyeing and Finishing of Textiles, Zhejiang Sci-Tech University, Hangzhou 310018, Zhejiang, China

^b Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, College of Materials and Textiles, Zhejiang Sci-Tech University, Hangzhou 310018, Zhejiang, China

ARTICLE INFO

Article history:

Received 17 February 2017

Received in revised form 24 May 2017

Accepted 4 June 2017

Available online 17 June 2017

Keywords:

B. Electrical properties

B. Mechanical properties

A. Foams

A. Polymer-matrix composites (PMCs)

ABSTRACT

Flexible conductive polymer composite foams (CPCFs) are considered as promising materials for piezoresistive sensors. However, most of them have low strain sensitivity with gauge factor (GF) of around 1.0. Herein, for the first time, W/O emulsion-templated polymerization is developed to fabricate graphene-based flexible CPCFs with high strain sensitivity. Compared to the literature-reported CPCFs, our materials have conductive network with higher specific surface area, improving conductive pathways formation between fillers under compression. In the vicinity of conductive percolation threshold, the CPCF has highest GF of 6.0 within 0–5% strain range and piezoresistive stability, demonstrating its high strain sensitivity and promising applicability in strain sensors.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Wearable sensors for monitoring biological activities of human beings is of great importance, which have potentials in health monitoring and disease diagnosis [1–3]. Piezoresistive pressure sensors represent a type of wearable sensors with low energy consumption in operation, easy read-out signals, and easy fabrication process. CPCFs, which is an excellent candidate for porous piezoresistive pressure sensors, possess better sensitivity and is able to work in low loading regions when compared to those sensors with planar structure [4].

Up to now, flexible CPCFs are mainly fabricated by solid-templated method, including polymer-templated method [5–8] and ice-templated method [9]. Yao et al. prepared reduced graphene oxide@polyurethane (rGO@PU) CPCFs by dipping PU sponge into GO aqueous dispersion [5]. This method demanded the polymer template have high porosity and very big cells for the intake of GO sheets, 200 μm in diameter for example [5]. Because the produced CPCFs were low modulus materials, a low compressive stress would cause a high strain response, and marked reconstruction of internal conductive pathways of conductive fillers. Therefore, these CPCFs exhibited highly sensitive towards stress [5–9]. On the other hand, the high porosity and very big pore size led

to a very low specific surface area in the conductive network inside these CPCFs. It restricted the growth of conductive pathways at small compressive strains, leading to poor strain sensitivity of the CPCFs as indicated by the low GF of around 1.0 [5,8,9]. Substitution of conductive nanoparticles, like carbon black (CB) [6] and Ag [7], for big GO sheets could produce CPCFs with higher GFs under compression. However, they usually required a sophisticated procedure, for example 15 lay-by-lay deposition cycles in the case of CB [6]. Thus, it is still challenging to prepare CPCFs with high strain sensitivity.

Herein, we report the one-pot development of flexible CPCFs through emulsion-templated polymerization (ETP). Before polymerization, GO aqueous dispersion was pre-emulsified with a lipophilic monomer phase, in which the dispersed aqueous phase droplets acted as template [10,11]. During polymerization, GO was reduced by Vitamin C (VC) [12] in the dispersed droplets. Finally, after removing water, flexible CPCFs were obtained, in which rGO particles covered the frameworks, as shown in Fig. 1. The microstructures and electromechanical properties were also investigated.

2. Experimental section

2.1. Materials

The inhibitor in styrene (St), butyl acrylate (BA), divinylbenzene (DVB) and 2-ethylhexyl methacrylate (EHMA) were removed via

* Corresponding author at: College of Materials and Textiles, Zhejiang Sci-Tech University, Hangzhou 310018, Zhejiang, China.

E-mail address: yanglei@zstu.edu.cn (L. Yang).

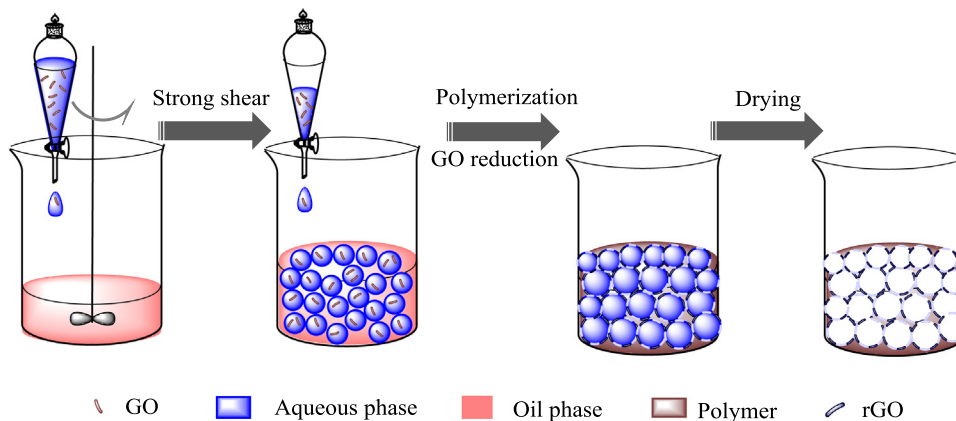


Fig. 1. Scheme for the preparation of CPCFs via emulsion-templated polymerization (ETP). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

washing with sodium hydroxide aqueous solution (10 wt.%). 2,2'-azobis (isobutyronitrile) (AIBN) was recrystallized twice from methanol. *S*-1-Dodecyl-*S'*-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate (TTCA) was synthesized and purified according to the literature [13]. Span 80, GO aqueous dispersion (2–10 μm , 5 mg/mL), and VC were used as received.

2.2. Emulsion-templated polymerization

The fabrication of CPCFs is schematized in Fig. 1. The aqueous phase was added drop-wise into the oil phase under strong shearing. The obtained emulsion was then transferred into a glass-stopped test tube and further heated in an oven at 65 $^{\circ}\text{C}$ for 24 h. The obtained CPCFs were removed from the tubes and dried to a constant weight. Monomer conversions exceeded 95% for each runs. The detailed recipes were collected in Table S1.

2.3. Characterization

The microstructure of the CPCF was examined on scanning electron microscopy (SEM, Phenom) and transmission electron microscope (TEM, JSM-100X). The reduction efficiency of GO within CPCF was examined on X-ray photoemission spectroscopy (XPS, K-Alpha, Thermo Scientific, America). Before XPS analysis, the sample was purified by Soxhlet extraction with methanol. The mechanical properties were measured on a mechanical testing machine (Instron 5543). The porosities of CPCF were calculated by dividing the volume of aqueous phase by gross volume of reaction mixture based on the recipes. The piezoresistive properties were measured in real-time by a two-point measurement with a Keysight E4980AL. GF is calculated from the equation: $GF = (\Delta R/R_0)/\varepsilon$, where $\Delta R/R_0$ is the resistance change rate, ε is the compressive strain.

3. Results and discussion

The recipes in Table S1 indicated that the internal phase (aqueous phase) volume ratios of all runs were as high as 82%. Therefore, the produced CPCFs had low density of around 0.2 g mL^{-1} , and could rest on the green bristlegrass (Graphic abstract). The representative SEM images for CPCF1–7 are shown in Fig. 2a–g, respectively. The insets in Fig. 2a–g showed the wrinkled morphologies of cell walls, which were more obvious for samples with higher GO loadings. In Figs. 2h and S1, the ultrathin-section TEM micrograph of CPCF4 demonstrated that rGOs covered the inner wall of pores. XPS analysis was employed to examine the reduction degree of rGO within CPCF4. Although residual oxygen was still obvious,

the relative contribution of those oxygen-containing components of the C1s envelop decreased significantly in the spectrum of rGO within CPCF4. Consequently, O/C atomic ratios decreased from 0.5 for raw GO to 0.2 for rGO within CPCF4, indicating that the GO particles had been effectively reduced by VC during polymerization (Fig. S2). The growing hydrophobicity drove the rGO particles towards the oil phase. However, being blocked by the newly formed cell walls, rGOs finally attached to the walls of polymer skeleton. As indicated by SEM, all the rGO-covered pores had closed-cell structure and broad pore size distribution. The average pore diameter was less than 70 μm (Table S1), which were 1/10–1/3 of the reported values for the solid-templated CPCFs [5–9]. Moreover, unlike the pores in the literature-reported CPCFs [5–8], the pores in our CPCFs from ETPs had walls instead of thin struts, which ensured increased specific surface area of conductive network along the polymer skeleton. Then, the mechanical and piezoresistive properties of such a novel type of CPCFs were investigated.

The obtained CPCFs showed superior mechanical flexibility. Taking CPCF4 as an example, its stress-strain curves for the cyclic compression with different strains are presented in Fig. 3a. During compression, the deformation process was divided into three stages: a linear elastic region for $\varepsilon < 10\%$, a plateau region for $15\% < \varepsilon < 35\%$, and a densification region for $\varepsilon > 35\%$. Such deformation behavior is typically observed for cellular solids [9,14]. The releasing curves almost returned to the original point, suggesting complete shape recovery. The inset in Fig. 3a show that the cyclic hysteresis curves with 40% strain perfectly overlapped even after 800 cycles, demonstrating very small plastic deformation and excellent mechanical robustness of CPCF4.

The incorporation of rGOs endowed the foams with improved electrical conductivity [15–17]. Fig. 3b showed the dependence of volume electrical conductivity of CPCF on rGO concentration. The prediction by the percolation equation [18] inserted in Fig. 3b gave the conductive percolation threshold $\Phi_c = 0.055$ vol.% with respect to the total foam volume. This value was one order of magnitude lower than that for reported dense conductive polymer composites [19]. The low percolation threshold was ascribed to two reasons. The first one was the selective location of rGO at the CPCF cell wall surfaces [20]. It resulted in an efficient arrangement of rGO particles, forming an rGO conductive network around the pores. The second one was termed as “volume expansion effect”, referring to the volume expansion of the composites due to the presence of pores [21]. Below the Φ_c , the conductivities were considerably low and relatively constant. CPCF4 had $\Phi = 0.056$ vol.% being very close to Φ_c . Fig. S3 was the proposed piezoresistive mechanism

Download English Version:

<https://daneshyari.com/en/article/5439400>

Download Persian Version:

<https://daneshyari.com/article/5439400>

[Daneshyari.com](https://daneshyari.com)