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Bridging the segregated structure in conductive polypropylene composites: An effective strategy to balance the sensitivity and stability of strain sensing performances

Shuaiguo Zhao[a], Dandan Lou[a], Guojie Li[a], Yanjun Zheng[a], Guoqiang Zheng[a], Kun Dai[a,*], Chuntai Liu[a], Yuanli Jiang[b], Changyu Shen[a]

[a] School of Materials Science and Engineering, The Key Laboratory of Advanced Materials Processing & Mold of Ministry of Education, Zhengzhou University, Zhengzhou, Henan 450001, People's Republic of China

[b] Henan Energy and Chemical Industry Group Research Institute Co., Ltd., Zhengzhou, Henan 450001, People's Republic of China

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ABSTRACT

Conductive polymer composites (CPCs) based strain sensors have been studied intensively recently. For a desirable strain sensor, a high sensitivity, a nice recoverability together with a good stability are required synchronously. In this study, the design of a segregated carbon black (CB) conductive network was demonstrated to be crucial for preparing polypropylene (PP)-based strain sensors with fine recoverability and stability, but a low sensitivity. The incorporation of carbon fibers (CFs) with large aspect ratio into the segregated CB/PP was utilized to build a bridged-segregated structure, leading to a synergistic conductive network. As a result, an improved sensitivity as well as a good stability was both achieved for the CF/CB/PP composite. The origin of these results was further explained on the basis of the tunneling model proposed by Simmons and the synergetic effect. This work provides a strategy for improving the performance of strain sensor with balanced sensitivity and stability by introducing a bridged-segregated structure.

1. Introduction

Conductive polymer composites (CPCs) have attracted enormous interest from both industry and academia over the last couple of decades [1–6]. By monitoring electrical signals transduced from the tensile stimuli, CPCs have been exploited as strain sensors, which shows great promise in automobile and infrastructural health, etc [7,8].

A desirable strain sensor requires a high sensitivity, a nice recoverability together with a good stability. To achieve these performances, carbonous filler based CPCs have been extensively investigated. However, a nice reproducibility (*i.e.,* the stability) of strain sensors is difficult to achieve, and the performance of strain sensor depends strongly on the category of conductive filler. For example, Wichmann et al. [9] found that the resistance of high-aspect-ratio carbon nanotubes (CNTs) filled epoxy CPCs first increases and then decreases with rising strain, while the resistance of low-aspect-ratio carbon black (CB) filled epoxy increases monotonically. Zhao et al. [10] reported that the resistance peak of CB/polypropylene (PP) increases gradually with cycle number, while it decreases for CNTs/PP. In addition, as the loading-unloading cycle progresses, the resistivity peak in CNTs/thermoplastic polyurethane (TPU) [11], carbon fiber (CF)/polyether sulfone (PES) [12] and carbon nanofibers (CNFs)/PP [13] decreases; however, that in graphene/polylactic acid (PLA) increases gradually [14]. These developments are related to the nonequivalent breakage and reconstruction of the conductive network. In addition, there is a “trade-off” relationship between the sensitivity and stability of a CPC sensor [11], which is closely related to the evolution of the conductive network structure. In others words, it is still a great challenge to achieve good sensitivity and stability synchronously in a CPC based strain sensor.

The distribution state of conductive fillers also has a strong influence on the strain sensing behaviors. Wu et al. [15] improved the strain sensing reproducibility of segregated CB/cellulose nano-whiskers (CNs)/natural rubber (NR) CPCs by selectively dispersing CB coated CNs nano-hybrid at the interfaces between NR microspheres. Amjadi et al. [16] successfully reduced the resistance hysteresis of silver nanowire (AgNW)/Polydimethylsiloxane (PDMS) by designing sandwiched PDMS/AgNW/PDMS composites, where the selectively dispersion of AgNW between PDMS enhanced the robustness of conductive network and decreased the buckling of AgNWs. In addition, Nanni et al.

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[*] Corresponding author.
E-mail address: kundai@zzu.edu.cn (K. Dai).

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[17] reported that the resistance of CB/epoxy composite containing CB aggregates first increases and then decreases with the increasing loading, while the sample with uniform CB dispersion increases monotonically. Based on this discussion, a segregated conductive network would be more stable to strain stimuli, and CB particles in CPC would have two capability, that is, the usual breakage effect of CB conductive network and the reconstruction effect of some CB conductive paths by applied strain, which provides promise in balancing the conductive network evolution.

To this end, a unique segregated conductive network constructed by CB particles is selected as a candidate in this paper [18,19]. In this case, the damage of conductive paths would only occur at the interface region, and the reconstruction of conductive paths would be achieved by the effectively involvement of CB particles in polymer matrix under applied strain. These two effects might balance each other and lead to a stable conductive network. On the other hand, although the synergistic effect of hybrid fillers has been used to improve the sensitivity, the mechanism is still not fully clear [20]. Namely, the previous reports mainly focus on the uniform dispersion of two types of conductive fillers. To our knowledge, few studies have been reported on combing the segregated structure with hybrid fillers in rational design of ternary CPCs.

In the present paper, the two strategies-a segregated structure and hybrid filler were combined. We proposed a bridged-segregated structure in CF/CB/PP composite to tune the sensitivity and the stability of strain sensing behaviors. In the composite, CB particles excluded by PP particles formed the segregated conductive network; CF was utilized to string the segregated conductive paths. CB/PP and CF/PP composites with a segregated structure were also fabricated for comparison. The percolation thresholds of CF/CB/PP, CB/PP and CF/PP were *ca.* 0.94 vol %, 2.34 vol % and 0.27 vol %, respectively based on the percolation curves of our previous work [21]. The strain sensing behaviors of these composites were studied and compared in detail. The mechanism of the unique segregated structure and the incorporation of CF on the strain sensing performances are discussed.

2. Experimental

PP (T30s, Dushanzi Petroleum Chemical Co., China) was used as the polymer matrix with a Mw of 3.99×10^5 g/mol, a molecular weight distribution of ca. 4.6 and a melt flow index (MFI) of 3.0 g/10 min (230 °C, 2.16 kg). CB (VXC-605, Cabot Co. Ltd. USA) with a with a dibutyl phthalate (DBP) absorption value of 148 ± 15 cm^3/100 g and a primary particle size of 30–50 nm, and CF with mean length L = 5 mm and aspect ratio AR = 657 (T300-3K, Toray Inc., Japan) were used as conductive fillers. To prepare the CPCs, PP particles with the size of 10–50 μm were first prepared by a dissolving-smashing method developed in our lab [21]. For the fabrication of CF/CB/PP, the desired amount of CB and PP particles were initially mixed together in a mortar, and then CFs was added, followed by mechanical stirring in ethanol for 1 h and ultrasonication for 1 h. After complete evaporation of ethanol, the mixed powders were compression-molded into $100 \times 100 \times 0.6$ mm^3 sheets at 190 °C with a pressure of 15 MPa. CF/PP and segregated CB/PP were also prepared with the same conditions for comparison. For simplicity, CB/PP with a segregated structure is denoted as s-CB/PP. According to the reported literatures [12], conductive network constructed with low filler concentration is more sensitive to the strain stimuli, and the largest strain sensitivity usually emerges around the percolation threshold [13]. Based on this guidance and the optimization ratio between CB and CF (Fig. S1), the conductive filler concentrations were fixed at 2.36 vol % for s-CB/PP, 0.35 vol % for CF/PP and 0.16/0.92 vol % for CF/CB/PP, respectively, which were all close to the percolation threshold as shown in the three percolation curves in our previous work [21].

The tensile test was conducted using a displacement controlled Suns UTM2203 universal testing machine. Synchronism of electrical and mechanical response is recorded during both monotonic and cyclic tension. The program of cyclic tension includes 10 loading-unloading cycles at different strain (2%, 3% and 4%) and different tensile speed (0.5, 5 and 10 mm/min). Electrically resistance (*R*) was in-situ measured using a resistivity meter (model TH2683, Changzhou Tonghui Electronics Co., Ltd.). A tensile rate of 0.5 mm/min was applied for all the resistance-strain tests except the measurements at different tensile speeds. The sample has a dimension of $100 \times 10 \times 0.6$ mm^3 and a gauge length of 50 mm, while two pieces of copper net separated 40 mm were bonded with silver paint to ensure the good contact.

Scanning electron microscopy (SEM) was conducted to study the fractured surfaces of specimens using a field emission SEM (7500F JEOL, Japan). For optical microscope (OM) observation, the samples were cut into slices (15 μm) utilizing a microtome. The mechanical properties and thermal properties were also investigated (Fig. S2 and Fig. 3).

3. Results and discussion

3.1. Morphology

Fig. 1 shows the optical and SEM images of s-CB/PP, CF/PP and CF/CB/PP CPCs, respectively. In Fig. 1a&a', CB particles were selectively localized at PP matrix boundaries, forming a segregated CB conductive network. The thickness of this conductive paths (~0.5–20 μm) is much larger than that in common segregated CPCs, such as CNTs/UHMWPE (~0.5–2 μm) [18]. These thick conductive paths are attributed to the migration of CB particles from interface region into PP region, resulting from the low melt viscosity of PP. In Fig. 1b&b', CFs have relatively large dimension and can span across PP domains over long distance. Only a minute amount of CFs are needed to reach the percolation threshold, leading to a sparse CF conductive network. For CF/CB/PP composite (Fig. 1c&c'), the segregated CB conductive paths are successfully constructed and further bridged by CFs, forming a synergetic CF and CB conductive network. In this case, the CF provides charge transport over long ranges and the segregated CB particles transport electron over short ranges. We therefore refer to this conductive network as bridged-segregated structure to reflect (i) a segregated structure and (ii) a synergetic conductive network.

3.2. Mechanical properties and strain sensing behaviors under monotonic tension

Fig. 2 displays the typical stress (σ), normalized resistance change (R/R_0%)-strain curves of the three CPCs. Here, R and R_0 refer to the instantaneous resistance and initial resistance of the sample, respectively. In Fig. 2 a, b&c, it is observed that the stress increases gradually with the strain for the three CPCs. However, the R/R_0% of CF/PP and CF/CB/PP increases much faster than that of s-CB/PP, showing a rapider response rate and a higher sensitivity. This difference in sensitivity can be experimentally evaluated by the gauge factor (GF) [14]:

$$GF = \frac{\Delta R/R_0}{\varepsilon} = \frac{R/R_0 - 1}{\varepsilon} \tag{1}$$

Here, ΔR represents the instantaneous change in resistance. In Fig. S4a, the GF is 311.5 for CF/PP, 53.4 for s-CB/PP and 253.8 for CF/CB/PP, respectively. This GF is much higher than many reported thermoplastic and thermoset based CPCs [12,22], but lower than that of elastomeric CPCs [11,20]. It is related to the microstructure of the conductive network and the flexibility of the polymer matrix. The difference in GF for the three composites can be ascribed to the discrepancy in conductive network. For s-CB/PP, a dense and robust conductive network is constructed by massive CB nanoparticles and connected by a substantial of conductive channels. Destruction of few conductive channels or their contact points would not induce a considerable change in resistance. In contrast, in CF/PP, a sparse