High performance dielectric elastomers by partially reduced graphene oxide and disruption of hydrogen bonding of polyurethanes

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ABSTRACT

Thermally reduced graphene oxide (TRG)/thermoplastic polyurethanes (TPU) dielectric elastomer with high dielectric constant (k), low dielectric loss and greatly improved actuated strain at low electric field was prepared by solution blending followed by in situ thermal reduction. The results showed that a good dispersion and alignment of TRG in the TPU matrix was obtained. The k at 10^3 Hz was sharply increased from 7 for pure TPU to 1875 for the composite with 2 vol. % of TRG because of the partial restoration of graphite structure and the great increase in dipole polarizability of TPU caused by the disruption of hydrogen bonds of TPU chains. The dielectric loss at 10^3 Hz of the composite with 2 vol. % of TRG remained low (0.43). Despite of the increase in elastic modulus with the increase in the content of TRG, the great increase in k lead to the great increase in electromechanical sensitivity (β). As a result, a 106 times increase in β at 10^3 Hz and 17 times increase in actuated strain at low electric field (250 V/mm) were achieved by adding 2.0 vol% of TRG. This study provides a simple and effective method for the improvement of actuated strain at low electric fields through partial reduction of graphene oxide and the disruption of hydrogen bonds in TPU, facilitating the applications of dielectric elastomers in the biological and medical fields, where a low electric field is required.

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1. Introduction

Dielectric elastomers (DEs), as an attractive branch of electroactive polymers (EAPs), deform when stimulated by an electric field, and work efficiently over a broad frequency range. Thus, they have been receiving much attention [1]. Dielectric elastomer actuators (DEAs) consist of a thin elastomeric film sandwiched between two compliant electrodes. A DEA shrinks in the thickness direction and expands in the plane direction by applying an electric field across the film thickness [2,3]. DEAs find many applications in industries such as artificial muscles, sensors, micro air vehicles, flat-panel speakers, micro-robotics, and responsive prosthetics because of their large strain, fast response, lightweight, reliability, high

energy density, and high electromechanical coupling efficiency [2,4,5]. A key limitation for the practical application of DEAs is the requirement of high electric field (>100 kV/mm) [6–8], which could be harmful to humans and damage equipment, particularly in biological and medical fields [7–9]. Getting a large actuated strain at a low electric field is the biggest challenge for DEAs.

To obtain a DE with high actuated strain at a low electric field, a high electromechanical sensitivity (β) is required, which is defined as the ratio of the dielectric constant (k) to the elastic modulus (Y) ($\beta = k/Y$). Thus, a reasonable solution to improve the actuated strain at a low electric field is to increase the k and decrease the Y of DE [10–12]. However, the k of common DEs is very low (less than 8). Thus, a key issue is to increase the k of DEs, but retain other excellent properties such as low dielectric loss and good flexibility. One common method to improve the k of DEs is to introduce high-k ceramics into the elastomer matrix [13,14]. A high content (up to 50 vol.%) of ceramics is usually required to effectively improve the k, resulting in high Y, low flexibility, and poor processability, all of which limit the applications of DE. Another method is to prepare

percolative composites by adding conductive fillers [15] such as carbon nanotubes (CNTs) [16,17] into the matrix. Because of the curl and entanglement of CNTs, even quite a low content of CNTs leads to the formation of a CNT network, and thus a large increase in k [18]. However, the dielectric loss is also quite high owing to the leakage current caused by the direct connection of CNTs [19]. In addition, CNTs are usually prepared by a complicated process, and they are quite expensive.

Graphene sheet has superior electrical conductivity and has been considered to be an ideal candidate for high-k filler. Compared with CNTs, it has a layered structure with a larger aspect ratio, and thus it is easier to form a large number of parallel micro-capacitors at low filler content, facilitating the preparation of DE composites with high k [19–21]. In addition, graphene is usually synthesized from natural graphite, which is cheap and easily available. On the other hand, a large number of oxygen functional groups (C—O—C, C—OH, and C=O) are easily introduced on graphene oxide nanosheet (GONS) during the preparation by using the Hummers' method [22]. These oxygen functional groups enable GONS to form homogenous colloidal suspensions in organic or aqueous solvents. The strong interaction between GONS and some elastomer matrices with polarized groups such as polyurethane (PU) [23,24], could prevent the direct connection of GONS, and thus could lead to a low dielectric loss. However, the oxidation of graphite could also lead to severe disruption of the graphite structure [25], resulting in a decrease in k [26]. Therefore, reduction of GONS is required to obtain a DE composite with both high k and low dielectric loss. In recent years, several studies have found that in situ partial thermal reduction of GONS at moderate temperatures within a polymer is a simple and effective technique to partially restore the graphite structure [27,28].

In recent years, some studies have been carried out to increase the dielectric properties of polymer by introducing graphene nanosheets or graphene oxide into the matrix. For example, Romasanta et al. [19] reported that the k of poly(dimethyl) siloxane was increased from 2.7 to 23 at 10 Hz with the addition of 2.0 wt.% of thermally expanded graphene sheets by using the melt blending method. In addition, Seveyrat et al. [20] reported that the k of polyurethane composites filled with graphene nanosheets was about 60 at 10^3 Hz near the percolation threshold (7.2 vol.%). The increase in k of these polymers by adding graphene sheets is far less than expected. The poor dispersion of graphene sheets in the matrix, the aggregation or restacking of graphene sheets during preparation, and the weak interfacial adhesion between the graphene sheets and polymer matrices are the main reasons. Recently, an interesting work was conducted by Jiang et al. [21]. A hyperbranched aromatic polyamide functionalized graphene sheets (GS—HBA) were first prepared and used to increase the dielectric properties of thermoplastic polyurethane (TPU). A uniform dispersion of GS—HBA in the TPU matrix and a strong adhesion between GS—HBA and TPU were successfully achieved. As a result, the k of the composite with 5 wt.% of GS—HBA at 10^3 Hz was 920, 158 times higher than that of pure TPU. More importantly, the hyperbranched chains also suppressed the leakage current by isolating the GS—HBA in the TPU matrix, resulting in a low dielectric loss (lower than 1.5 at 10^3 Hz).

Silicones, acrylics, and polyurethanes are the three most promising groups of DEs. Of these materials, TPU has received much attention in recent years because of its recyclability, high force output, high mechanical properties, and high dielectric constant [2]. A large number of hydrogen bonds exist in TPU, in which the NH group acts as the donor and either the carbonyl group from the hard segment or the ester oxygen group from the soft segment acts as the acceptor [29]. These hydrogen bonds limit the mobility of the polarized groups of TPU chains, thus limit the dipole orientation polarization ability of TPU, restricting the increase in k of TPU. Previous studies revealed that the

hydrogen bonds among the urethane groups of TPU can be disrupted by adding functionalized graphene [24,30]. The disruption of hydrogen bonds of TPU could increase the dipole orientation polarization ability of TPU chains and thus the k of TPU.

Therefore, in the present study, we first prepared GONS/TPU composites by solution blending followed by a special spin flash drying technique to obtain a strong interaction between GONS and TPU, a uniform dispersion of GONS in the TPU matrix, and a good alignment of GONS in the matrix. Then, we used the in situ thermal reduction technique to partially reduce the GONS in the GONS/TPU composites by hot pressing at a low temperature (180 °C) for 1 h. The increase in the interfacial polarization ability of thermally reduced graphene oxide (TRG) is expected by the partial restoration of the graphite structure of GONS, which could lead to the increase in the number of charge carriers accumulated at the interface between TRG and TPU matrix, and thus the increase in k at low filler contents. The remaining oxygen functional groups could disrupt the hydrogen bonds between the TPU chains, increase the mobility of the polarized groups of TPU chains, and thus increase the dipole orientation polarization ability of TPU, further increase the k of TPU. On the other hand, these oxygen groups could increase the interaction between TRG and TPU, suppress the leakage current by isolating TRG in the TPU matrix, and thus decrease the dielectric loss of the composites. Our goal is to develop a simple and effective way to improve the actuated strain at low electric field of DE by improving the k of TPU for its application in biological and medical fields, where a low electric field is required.

2. Experimental

2.1. Materials

Natural graphite (1000 mesh, purity > 99%) was provided by Huadong Graphite Factory (China). Thermoplastic polyester-polyurethane (TPU, Elastollan Soft 45A, 1.18 g/cm^3) was purchased from BASF Polyurethane Specialties (China) Co., Ltd. and dried at 60 °C for 5 h before use. N, N-dimethylform-amide (DMF, 99.5%), tetrahydrofuran (THF, 99.0%), concentrated sulfuric acid (H$_2$SO$_4$, 98%), sodium nitrate (NaNO$_3$, 99.0%), potassium permanganate (KMnO$_4$, 99.5%), hydrogen peroxide (H$_2$O$_2$, 30%), hydrochloric acid (HCl, 37%), and methanol (CH$_3$OH, 99.5%) were supplied by Beijing Chemical Reagents Co., Ltd. (China). All chemicals were used as received.

2.2. Preparation of graphene oxide nanosheet (GONS)

Graphite oxide was first prepared from natural graphite by the modified Hummers method [31]. The as-prepared graphite oxide was then dispersed in DMF solvent (1 mg·ml^{-1}) and exfoliated via ultrasonication for 1 h by using a GA 98-IIIultrasonic cell disruptor (Shangjia Biological Technology, China) with a power of 1000 W to form a uniform colloidal suspension of graphene oxide nanosheet (GONS). The exfoliated graphene oxide solution was then centrifuged at 8000 rpm for 10 min to remove the non-exfoliated graphite oxide particles and other impurities.

GONS powder was obtained by vacuum filtration onto microporous membranes (pore size: 0.22 μm) and then dried in a vacuum oven at 60 °C for 24 h. For comparison purposes, TRG was also prepared by reducing GONS powder at 180 °C under vacuum for 1 h. The reduction condition was the same as that used for the in situ partial thermal reduction of TRG/TPU composites.

2.3. Preparation of GONS/TPU and TRG/TPU composites

A schematic representation of the preparation of TPU composites is shown in Fig. 1. GONS/TPU composites were prepared by the