



Largely improved electromechanical properties of thermoplastic polyurethane dielectric elastomers by the synergistic effect of polyethylene glycol and partially reduced graphene oxide

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ABSTRACT

In this study, moderate content of polyethylene glycol (PEG) with ionic conductivity and low content of graphene oxide (GO) were simultaneously introduced into thermoplastic polyurethane (TPU) followed by in-situ chemical reduction of GO (rGO) to prepare TPU/PEG/rGO dielectric elastomer (DE) composites with largely improved electromechanical performance. The results showed that PEG remarkably disrupted the hydrogen bonds between TPU chains in TPU/PEG/rGO composites and formed new hydrogen bonds with TPU. In addition, PEG molecules can also form hydrogen bonds with rGO, leading to the coating of PEG on GO and thus the separation of rGO from TPU. Interestingly, PEG and rGO showed significant synergistic effect on the dielectric constant (ϵ') of the composites, resulting in the large increase in ϵ' at 10^3 Hz from 7 for pristine TPU to 71 for TPU/PEG/rGO composite. This was attributed to the increase in dipole polarizability of TPU chains caused by the disruption of hydrogen bonds and the increase in interfacial polarizability caused by the favorable electron transfer from partially reduced GO coated by PEG to TPU. The elastic modulus (Y) of the TPU/PEG/rGO composites largely decreased because of the plasticizing effect of PEG and the separation of GO from TPU. Owing to the simultaneous increase in ϵ' and decrease in Y , the composite showed 49 times increase in electromechanical sensitivity (β) and 6.5 times increase in actuated strain at a certain electric field over that of pristine TPU.

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1. Introduction

Over the last decade, dielectric elastomer (DE), as a promising candidate for advanced electro active polymers, have drawn much attention [1–3]. A DE film sandwiched between two compliant electrodes can form a dielectric elastomer actuator (DEA) which acts as electromechanical transducers that transform electrical energy to mechanical energy [2,4]. Owing to their large active strain and stress, fast response, flexibility, and high energy density, DEA

find applications in many fields such as eyeball actuators, tactile displays, sensors, and biologically inspired robots. However, the potential application of DEA is significantly restricted by the high electric field and/or high operating voltage required to drive them, since high electric field could be harmful to human body and could damage equipment. Thus, the preparation of DEs with large actuated strain at low electric field is one of the biggest challenges for DEA.

Based on linear-elasticity and free boundary approximations, the actuation strain S_z in thickness direction is given by

$$S_z = -\frac{P}{Y} = -\frac{\epsilon_0 \epsilon' E^2}{Y} = -\beta E^2$$

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where ϵ_0 and ϵ' are the permittivity of free space and the dielectric constant of the material, respectively. Y is the elastic modulus, and E is the applied electric field. Thus, a reasonable route to reduce the operating voltage is to improve the electromechanical sensitivity (β), which is defined as the ratio of ϵ' to Y ($\beta = \epsilon'/Y$). Thus, an increase in ϵ' and a decrease in Y is a reasonable solution. To improve ϵ' , the most widely used approach is introducing high- ϵ' ceramics into the elastomer matrix. A high content (up to 50 vol.%) of ceramics is usually required to improve the ϵ' , resulting in high Y , low flexibility, and poor processability. Another effective method to increase ϵ' is to prepare percolative composites by adding conductive fillers such as silver particle, graphene [5], CNTs [6], and conductive carbon black into the matrix. For example, Wang reported that the ϵ' of CNTs DE composites is significantly improved as the volume percent of CNTs is higher than 6 vol% [6]. Owing to the good conductivity and layered structure with a large aspect ratio of graphene [7,8], a small amount of graphene can greatly improve the ϵ' of DEs. A disadvantage of the graphene/elastomer composites is the increase in Y and a loss in flexibility because of the reinforcing effect of graphene [9] that lowers the deformability of DEs. As a result, the increase in β and the actuated strain were far less than expected.

On the other hand, some studies were focused on improving the actuated strain by decreasing the Y of DEs through introducing plasticizers such as polyethylene glycol (PEG) [10,11], dioctyl phthalate (DOP) [12], and epoxidized soybean oil (ESO) [13] into the elastomer matrix. According to previous study, the actuated strain of TPU DEs can be improved by more than ten times by adding a large number of plasticizers, but accompanied with a decrease in Y to less than 0.25 MPa that results in poor mechanical strength. In addition, adding a large number of plasticizers leads to severe phase separation of plasticizer from the elastomer matrix. On the other hand, the large number of plasticizer molecules can be lost by evaporation, migration, or extraction.

The most promising DE for DEA application are acrylic, silicone and polyurethane [2,4,14]. In this study, we used TPU as DE because of its good mechanical strength, easy processability (vulcanization is not required), and recyclability. We added moderate content of PEG into TPU matrix to disrupt the hydrogen bonds between TPU chains, and thus improve the dipole polarizability of TPU chains for the enhancement of dielectric constant. On the other hand, the introduction of PEG can significantly decrease the elastic modulus of TPU. Meanwhile, we simultaneously added a low content of graphene oxide into TPU matrix and partially reduce GO to increase the interfacial polarizability of the composites for the further increase in the dielectric constant. Since PEG could have strong hydrogen bonding interaction with both TPU and GO, whereas the interaction between GO and TPU is weaker, PEG could be coated on GO and thus separated TPU with GO. Because of the ionic conductivity of PEG, the PEG coated GO could show strong interfacial polarizability on TPU, and thus could largely increase the dielectric constant of TPU, and maintain the low elastic modulus due to the separation of PEG from GO. Because of the moderate content of PEG and low content of GO, the as prepared composites could also hinder the large increase in dielectric loss and thus hinder the large decrease in breakdown strength. Thus, the simultaneous increase in ϵ' and decrease in Y are expected to be obtained by the introduction of moderate content of PEG and low content of rGO. Therefore, a large increase in β and actuated strain at a low electric field is expected to be obtained. We aim to explore the method to improve the actuated strain at a low electric field of DEs for widening its application in biological and medical fields. In addition, we also aim to study the synergistic effect of the plasticizer and high- ϵ' filler on the electromechanical properties of DEs.

2. Experimental

2.1. Materials

Thermoplastic polyester-polyurethane (TPU, Elastollan Soft 45A, 1.18 g/cm³) was purchased from BASF Polyurethane Specialties (China) Co., Ltd. and dried at 60 °C for 5 h before use. Polyethylene glycol (PEG, purity > 99.9%) with an average molecular weight of 600 was obtained from Longxi Chemical Co., Ltd. (China). Natural graphite (1000 mesh, purity > 99%) was provided by Huadong Graphite Factory (China). *N,N*-dimethylformamide (DMF, 99.5%), tetrahydrofuran (THF, 99.0%) and the chemicals used for the preparation of graphene oxide nanosheets (GONS) were supplied by Beijing Chemical Reagents Co., Ltd. (China). L-ascorbic acid (L-AA, purity > 99%) was purchased from Alfa Aesar Co., Ltd (USA). All chemicals were used as received.

2.2. Preparation of TPU/PEG/rGO composites

GONS was prepared from natural graphite by the modified Hummers method as described in our previous study [5]. TPU/PEG/rGO composites were prepared by the in situ chemical reduction method and solution casting method. First, TPU and PEG were dissolved in THF by magnetic stirring at 60 °C for 30 min to form a transparent and homogenous solution. Subsequently, GONS suspension was mixed with the TPU/PEG solution under stirring for 2 h to obtain a uniform TPU/PEG/GONS suspension. The L-AA (ten times as high as that of GONS by weight) serving as a reducing agent was added into the suspension under vigorous stirring. The in situ chemical reduction was allowed to continue for 24 h under stirring at 23 °C. TPU/PEG/rGO suspension was concentrated with a spin flash drying apparatus (Re 3000, Shanghai Yarong, China) under reduced pressure at 60 °C. The concentrated suspension was cast in a petri dish and completely dried in a vacuum for 24 h at 60 °C. The composition of TPU/PEG/rGO composites was denoted as TPU-x-y, where x represents the content of PEG and y represents the content of GONS. For example, TPU-10-1.5 represents the composite contains 10 parts per hundred rubber (phr) of PEG and 1.5 phr of rGO.

2.3. Characterization

An atomic force microscope (AFM, Multimode 8, Nano Scope Analysis, Bruker, Germany) was used to observe the morphology of GONS and rGO in tapping mode. The samples were prepared by dropping the dilute solution on freshly cleaved mica and drying under room temperature. A Fourier transform infrared spectrophotometer (FT-IR, Tensor 27, Bruker Optik GmbH., Germany) at a resolution of 4 cm⁻¹. A minimum of 24 scans were signal averaged. The frequency scale is internally calibrated with a reference helium–neon laser to an accuracy of 0.01 cm⁻¹. An X-ray photoelectron spectroscope (XPS, ESCALAB 250, Thermo Fisher Scientific Company, USA) was conducted with X-ray source of Al K α . The C1s peak at 284.8 eV was applied to calibrate the binding energy scale. A Raman spectrometer (JY-HR 800, HORIBA Ltd., France) with laser excitation at 514 nm.

The Fourier transform infrared spectrophotometer equipped with an attenuated total reflectance (ATR) probe was used to study the change in hydrogen bonds of TPU composites. All the spectra were obtained at a resolution of 4 cm⁻¹ in a wave number range of 400–4000 cm⁻¹. The microstructure of the TPU composites was characterized by a transmission electron microscope (TEM, H-800, Hitachi Co., Japan). The samples for TEM observations were cryogenically cut by a glass knife in a Reichert–Jung Ultracut microtome (Leica Camera AG, Germany) and then collected on 400-mesh

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