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Improved electromechanical properties of silicone dielectric elastomer composites by tuning molecular flexibility

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ABSTRACT

Silicone rubber (SR) composites exhibited significantly improved electromechanical properties via tuning the molecular flexibility by adding plasticizer. To decrease the enhanced elastic modulus of SR composites filled with high-dielectric-constant $BaTiO_3$ (BT) particles, silicone oil (SO) plasticizer was incorporated into the BT/SR composite to weaken the intermolecular interactions and break the structure of the filler network as result of swelling effect. The obviously decreased elastic modulus resulted in a high electromechanical sensitivity β and a relatively large actuated strain of 10.6% for 20 phr BT/SR composite filled with 50 phr SO at a low electric field of 25 kV/mm, approximately 380% increase compared to that of pure SR at the same electric field. The result indicates that tuning flexibility of composites is a good strategy to obtain high-performance dielectric elastomers.

1. Introduction

Dielectric elastomer actuators (DEAs), consisting of a thin elastomer film sandwiched between two compliant electrodes, act as a new and promising soft transducer technology [1,2]. DEAs have ability to expand large deformation when responded to electric stimuli (shown in Fig. 1) or generate electric energy when subjected to mechanical motion. By virtue of their outstanding actuated strain, fast response, and high energy density, DEAs have been empolyed in a wide range of advanced applications such as braille displays, wave energy harvesters, bio-inspired robots, optical devices, and health monitors [3,4]. As dielectric, several soft materials such as polyacrylate [5], polyurethanes [6,7], natural rubber [8], nitrile-butadiene rubber [9], silicone rubber (SR) [10,11], and (polystyrene-co-ethylene-cobutylene-co-styrene-g-maleic anhydride) [12,13] as well as composites thereof have been investigated. Among them, silicone elastomers characterized by a high flexibility of the Si-O bond are the most promising materials for electroactive dielectric actuator [14]. In addition, they have high stability, high dielectric strength, small mechanical hysteresis, and fast response time. However, silicone elastomer has low dielectric constant, thus requiring a high electric field to drive them, causing security risk and increasing costs of devices [11].

The thickness strain S_z is given by the ratio of electrostatic pressure P to the elastic modulus Y of the elastomer. Equation (1) gives a simple prediction of the resulting deformation based on the assumptions that a dielectric elastomer film is an ideal elastomer (with a Poisson's ratio of 0.5) with small deformation

$$S_z = -P/Y = -\varepsilon_r \varepsilon_0 E^2 \Big/ Y \quad (1)$$

where ε_0 and ε_r are the permittivity of free space and the relative dielectric permittivity (dielectric constant) of the dielectric elastomer material, respectively; E is the applied electric field. For large deformation, this assumption is no longer valid and is replaced by a more complicated nonlinear hyper-elastic equivalent, because Y generally depends on the strain itself [15]. In addition, the change in the thickness and dielectric constant of elastomer material during actuation should be considered [16]. Considering the actuated stains are not very large, simple Equation (1) was used in this

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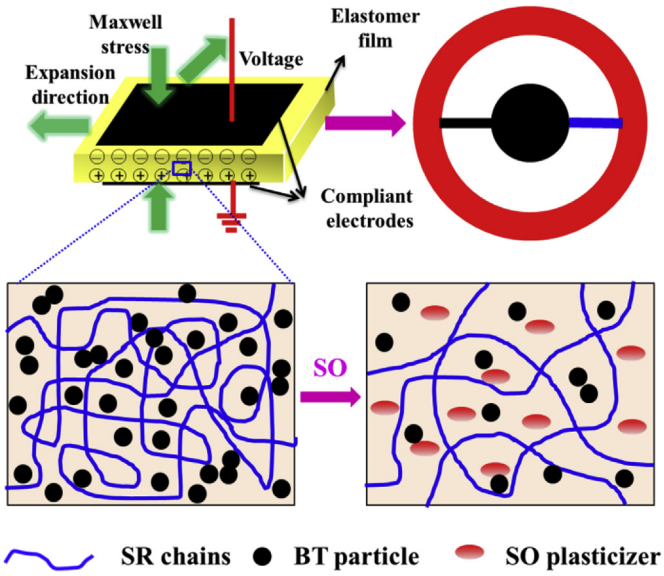

Fig. 1. Operational principle of circular dielectric elastomer actuator and schematic diagram of the BT/SR composite and SO/(BT/SR) composite.

study for easily understanding the mechanism of actuation. In order to obtain a large actuated strain at a low electric field, a high electromechanical sensitivity (β) defined as the ratio of dielectric relative permittivity (dielectric constant) to elastic modulus ($\beta = \varepsilon_r/Y$) is needed. Thus, an increase in β is a reasonable solution to decrease the operating voltage [4,17].

The most popular methods of increasing dielectric constant of silicone elastomer are incorporating high-dielectric-constant ceramics or conductive fillers and attaching polar molecules and groups, such as p-nitroaniline, nitrobenzene, nitrile, and cyanopropyl [18–22]. However, the polar molecules and groups will decrease the dielectric strength of the polymer and increase the sensitivity to moisture. In addition, the limited amount of molecules and groups will lead to an unsatisfactory increase in the dielectric constant [11,23,24]. Conductive fillers such as polyaniline [25], multi-walled carbon nanotubes [26], graphite [27], and conductive carbon black [28] can sharply increase the dielectric constant of silicone elastomer when the concentration of conductive fillers approaches the percolation threshold. However, it is usually accompanied by a dramatic increase in the dielectric loss, resulting in a part of electric energy dissipation during the actuation, thus imposing a number of limitations on the long-term stability and lifetime of materials [29,30].

Recently, much studies have been foucusing on incorporating high-dielectric-constant ceramics (e.g., TiO_2 and $BaTiO_3$) into the polymeric matrix to improve the dielectric constant of silicone elastomer composites, as the dielectric nature of ceramic particles will not induce high dielectric loss. In addition, this method can not only lead to high energy density but also decrease the necessary driving electric field [19,20]. However, the elastic modulus is significantly increased, leading to undesirable increase in the electromechanical sensitivity β. As a result, the elastic modulus of ceramic particles/silicone elastomer composites is usually decreased by adding plasticizer such as silicone oil (SO) [31], polyethylene glycol [15], and cyanopropyl-functionalized polydimethylsiloxane [18]. Because of the synergistic effect of the increased dielectric constant and decreased elastic modulus, a much improved electromechanical strain was obtained at low driving electric field. For example, Nguyen et al. [32] added dioctyl phthalate and titanium dioxide (TiO_2) into acrylonitrile butadiene rubber matrix to prepare dielectric elastomer composite with a high elastic energy and a large deformation at a low driving voltage. In our previous studies, TiO_2 and epoxidized soybean oil were blended into a hydrogenated nitrile-butadiene rubber matrix to form a dielectric elastomer with a high actuated strain at a low electric field [33]. However, in these studies, the compatibility between the plasticizer and polymeric matrix is not very good. Therefore, in this study, SR and SO were used because of the good compatibility between them and the silicone chains are swollen by the SO, enhancing interaction between them.

In this study, $BaTiO_3$ (BT) particles were used as the dielectric filler because of their high dielectric constant (~1700 at room temperature), low cost, and environmentally friendly characteristics [34]. SO was used as the plasticizer to decrease the elastic modulus by tuning the molecular flexibility of the silicone elastomer composite. Through tuning the intermolecular interactions and structure of filler network, a much increased electromechanical sensitivity β was expected to obtain by blending BT and SO into the silicone elastomer matrix. Thus, we aimed to prepare a silicone dielectric elastomer with a large actuated stain at a low driving electric field for widening its application in biological and medical fields.

2. Experimental

2.1. Materials

Commercial methylvinyl silicone rubber (type110-2) was supplied by Chenguang Research Institute of Chemical Industry, China. BT particles with an average size of 100 nm were provided by Nantong New Electronic Technology Co. LTD (China). SO with viscosity of 0.1 Pa s was purchased from Beijing Chemical Reagents Co., Ltd. (China). The crosslinking agent dicumyl peroxide (DCP) was obtained from Beijing Chemicals Company, Beijing, China.

2.2. Preparation of dielectric composites

The uncured SR dielectric composites were mixed with DCP and filler particles using a 6-inch two-roll mill. Recipe 3.1 contained 100 of phr (parts per hundred parts of rubber) SR, 2 phr of DCP, and different contents of BT (0 phr–30 phr); Recipe 3.2 contained 100 phr of SR, 2 phr of DCP, 20 phr of BT, and different contents of SO (0 phr–50 phr). The filled SR composites were cured by hot compression molding (at a pressure of 25 MPa and a temperature of 160 °C) for their optimum curing time as determined using a GT-M2000-FA disk oscillating rheometer (Goteah Testing Machines Inc., Taiwan).

2.3. Characterization

The fractured surfaces of the SR composites filled with BT and/or SO were observed by scanning electron microscopy (SEM, Nano-SEM 430, FEI). The stress-strain curves of the samples were measured using an Instron 3366 tensile apparatus according to ASTM D412 at a crosshead speed of 50 mm min^{-1}. The elastic modulus of the samples was determined by calculating the slope of the stress-strain curve within 0–10% of strain. The largest strain of cyclic stretching stress-strain curves was controlled at 50%. The dielectric properties of the samples were determined using an impedance analyzer (Concept-49/50, Novochtrol, Germany) in the frequency range from 1 to 10^6 Hz under a voltage of 1 V. The frequency of the dielectric constant was used to calculate the electromechanical sensitivity β is 1 kHz. Actuated strain tests were measured using a circular membrane actuator without any pre-strain following the methods described in our previous study