Simultaneously improved actuated performance and mechanical strength of silicone elastomer by reduced graphene oxide encapsulated silicon dioxide

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(Received 29 September 2015; final version received 8 December 2015)

Herein, graphene oxide (GO)-encapsulated silica (SiO$_2$) hybrids (GO@SiO$_2$) were prepared via electrostatic self-assembly of the 3-aminopropyltriethoxysilane (APS)-modified SiO$_2$ and GO. The as-prepared GO@SiO$_2$ was introduced into polydimethylsiloxane (PDMS) elastomer to simultaneously increase the dielectric constant ($k$) and mechanical properties of PDMS. Then, the in situ thermal reduction of GO@SiO$_2$/PDMS composites was conducted at 180°C for 2 h to increase the interfacial polarizability of GO@SiO$_2$. As a result, the values of $k$ at 1000 Hz are largely improved from 3.2 for PDMS to 13.3 for the reduced GO@SiO$_2$ (RGO@SiO$_2$/PDMS elastomer). Meanwhile, the dielectric loss of the composites remains low (<0.2 at 1000 Hz). More importantly, the actuated strain at low electric field (5 kV/mm) obviously increases from 0.3% for pure PDMS to 2.59% for the composites with 60 phr of RGO@SiO$_2$, an eightfold increase in the actuated strain. In addition, both the tensile strength and elastic modulus are obviously improved by adding 60 phr of RGO@SiO$_2$, indicating a good reinforcing effect of RGO@SiO$_2$ on PDMS. Our goal is to develop a simple and effective way to improve the actuated performance and mechanical strength of the PDMS dielectric elastomer for its wider application.

Keywords: graphene oxide (GO)-encapsulated silica (SiO$_2$) hybrids; electrostatic self-assembly; polydimethylsiloxane (PDMS) elastomer; dielectric constant ($k$) and mechanical properties; actuated strain at low electric field

1. Introduction

Dielectric elastomers (DEs), as an attractive branch of electro-active polymers (EAPs), can give rise to surprisingly large deformation when stimulated by an electric field, and work efficiently over a broad frequency range. Thus, they have received much attention in the past two decades [1,2]. A dielectric elastomer actuator (DEA) can shrink in the thickness direction and expand in the plane direction by applying an electric field across the film thickness [3]. By virtue of the excellent properties such as large strain, fast response, lightweight, reliability, high energy density, and high electromechanical coupling efficiency, DEAs find applications in artificial muscles, sensors, micro air vehicles, flat-panel speakers, micro-robotics, and responsive prosthetics [4–8]. A key limitation for the practical application of DEAs is the requirement of high electric field (>100 kV/mm) to drive them [9–11], which could be harmful to humans and can damage equipment.
particularly in biological and medical fields [12]. Therefore, getting a large actuated strain at a low electric field is the biggest challenge for DEAs.

Based on the assumption of constant modulus and free boundary conditions for a DE film, the thickness strain $S_z$ can be approximated by [13].

$$S_z = -P/Y = -\varepsilon_0 \varepsilon_r E^2 / Y$$

where $P$ is Maxwell’s stress on the material, $\varepsilon_r$ is the relative permittivity, $\varepsilon_0$ is the permittivity of free space, $E$ is the applied electric field, and $Y$ is the elastic modulus of a DE film. According to the law of volume constancy [14], the planar strain $S_p$ can be approximated by:

$$S_p = 1/(1 + S_z) - 1$$

According to Equations (1) and (2), to obtain a DE with high actuated strain at a low electric field, a high electromechanical sensitivity ($\beta$) is required, which is defined as the ratio of the dielectric constant ($k$) to the elastic modulus ($Y$) ($\beta = k/Y$) [1]. However, most DEs such as silicone elastomer and acrylic rubber have quite low values of $k$, which are 2.8 and 4.8, respectively [15]. Therefore, a key issue is to increase the $k$ of DEs, while retaining other excellent properties such as low dielectric loss, low modulus ($Y$), and good flexibility. One common method to obtain a DE with high $k$ is to introduce high-$k$ ceramics such as TiO$_2$ into the elastomer matrix [10,15–17]. Usually, a high content (up to 50 vol%) of ceramics is required to obtain high $k$, leading to low flexibility and poor processability, and thus largely limiting the wide application of DEs [18]. Another method is to add conductive fillers such as carbon nanotubes (CNTs) into the matrix, or blending with chemical modification of silicone with organic dipoles is a promising approach to increase $\varepsilon'$ (dielectric constant) [19]. Because of the curl and entanglement of CNTs with fibrous nanostructure, even quite a low content of CNTs can result in the formation of CNT network, thus leading to the large increase in $k$ [19,20]. However, in this case, a high dielectric loss was also obtained owing to the high direct current (DC) conductance caused by the direct connection of CNTs [21].

Compared with CNTs, graphene sheets are usually synthesized from natural graphite, which is abundant, cheap, and easily available. In addition, graphene sheets have a larger aspect ratio, and thus have been considered as good fillers to improve the dielectric constant of elastomers, as has been reported in previous studies [19,20,22,23]. For instance, Romasanta et al. [24] reported that the value of $k$ of polydimethylsiloxane (PDMS) increased from 2.7 to 23 at low frequency (10 Hz) by addition of 2.0 wt.% of thermally expanded graphene sheets. Obviously, the increase in the value of $k$ of these polymers by addition of graphene oxide (GO) is far less than expected. The main reasons are the poor dispersion of graphene in matrix, the restacking of graphene sheets during preparation caused by $\pi-\pi$ stacking and hydrophobic interactions, and/or weak interfacial adhesion between graphene sheets and the polymer matrix [25–27]. A good dispersion of GO in the polymer matrix and a strong interfacial adhesion between GO and the matrix can be obtained via the organic functionalization of GO [28,29]. A disadvantage of this approach is that it is complicated and time-consuming. In addition, the coating of GO on silica (SiO$_2$), metal oxide particles, or carbon nanosphere is an efficient method to prevent GO from self-agglomerating, as reported in previous studies [25,30–32].

In addition, a disadvantage of GO is that the graphite structure is disrupted by oxidation, resulting in a decrease in the dielectric constant [33,34]. Thus, reduction of
GO is required to obtain a DE with both high $k$ and low dielectric loss. In most cases, GO was reduced via chemical reduction using hydrazine hydrate [35], Vitamin C [36], etc., leading to a high reduction degree, and thus a good electric conductivity of the composites. Thus, chemical reduction of GO can result in a high dielectric loss of the composites because of the large DC conductance [10]. In recent years, some studies reported that in situ thermal reduction of graphene oxide nanosheets (GONSs) at a moderate temperature (180–200°C) within a polymer is a simple and effective technique for the moderate reduction of graphitic structure [26,30].

PDMS, as one of the most important DEs, has a rather low modulus, a good thermal stability over a wide temperature range, a fast speed of response, high efficiency, and excellent biocompatibility for artificial muscle. However, its dielectric constant and mechanical strength are too low for practical application. Racles et al. [37] developed where cyanopropyl-groups were distributed along the backbone of PDMS chains. Good overall results were obtained for blends of the cyanopropyl-functional PDMS and PDMS.

Herein, GO-encapsulated silica (SiO$_2$) (GO@SiO$_2$) hybrids were prepared via electrostatic self-assembly in which the 3-aminopropyltriethoxysilane (APS) acts as a ‘glue’ molecule to connect GO and SiO$_2$. Therefore, in this study, GO@SiO$_2$ is introduced in the PDMS matrix to simultaneously increase the dielectric constant and mechanical properties of PDMS. Then, the reduced GO@SiO$_2$ (RGO@SiO$_2$)/PDMS composites were obtained by in situ thermal reduction of GO@SiO$_2$/PDMS composites to increase the interfacial polarizability, and thus increase the $k$ of the composites. Our goal is to develop a simple and effective way to improve the actuated performance and mechanical strength of PDMS DE for its wider application.

2. Experimental

2.1. Materials

Natural graphite flakes with a mean size of 18 μm were supplied by Huadong Graphite Factory (China). Submicron-sized silica (average diameter: 3 00 nm) was supplied by Guangdong Shengyi Technology Co., LTD (China). APS was supplied by Momentive Performance Materials (Shanghai). A commercial grade of siloxane (PDMS) (DC3481 184) and the curing agent (81-F) were purchased from Dow Corning Co., Ltd. (America). The viscosity and density of PDMS material used are 22.1 Pa s and 1.213 g/cm$^3$, respectively. Potassium permanganate (KMnO$_4$, 99.5%), sulfuric acid (H$_2$SO$_4$, 98%), sodium nitrate (NaNO$_3$, 99.0%), hydrogen peroxide (H$_2$O$_2$, 30%), hydrochloric acid (HCl, 37%), and methanol (CH$_3$OH, 99.5%), which were all used for the preparation of graphite oxide, were supplied by Beijing Chemical Reagents Co., Ltd. (China). Tetrahydrofuran (THF) was used as a solvent to dissolve PDMS and was purchased from Beijing Chemical Reagents Co., Ltd. (Beijing, China).

2.2. Preparation of graphene oxide-encapsulated silica (GO@SiO$_2$) hybrids

The graphene oxide-encapsulated silica (SiO$_2$–NH$_2$–GO) hybrids were prepared in two steps: the modification of silica particles with APS coupling agent and the surface assembly of GONSs with the modified silica microspheres.

Graphite oxide was prepared from natural graphite by Hummers method. The as-prepared graphite oxide was then dispersed in an aqueous solution (1 mg/mL) and exfoliated via sonication for 1 h using a GA 98-III ultrasonic cell disruptor (Shangjia
Biological Technology, Shanghai, China) with a power of 1000 W to form a uniform colloidal suspension of GO. The nonexfoliated GO sheets were removed by centrifugation at 8000 rpm for 10 min. The surface modification of SiO$_2$ with APS coupling agent was carried out in a mixture of ethyl alcohol and water. In a typical process, SiO$_2$ powder (1 g) was first dispersed well in 400 mL of ethyl alcohol by sonication for 1 h, followed by the addition of 40 mL water. Subsequently, 1 mL of APS coupling agent dissolved in a small amount of ethyl alcohol was added to the above solution, and the mixture was stirred at 60°C for 8 h until the grafting reaction was realized. The obtained particles (SiO$_2$−NH$_2$) were centrifuged from the mixture, washed with ethyl alcohol and deionized water thrice.

The GO@SiO$_2$ hybrids were simply fabricated by mixing the neutral aqueous suspension of SiO$_2$−NH$_2$ and GO solution. A total volume of 400 mL of SiO$_2$−NH$_2$ suspension (2.5 mg/mL) was added to 200 mL of aqueous GO solution (0.1 mg/mL) under mild stirring for 4 h. When stirring stopped, the GO precipitated with SiO$_2$−NH$_2$ at the bottom of the beaker, leaving a transparent aqueous solution. The sediment solid (GO@SiO$_2$) was collected and washed with deionized water several times to remove the unbound GO and then freeze-dried under vacuum.

### 2.3. Preparation of PDMS-based composites with solution compounding

The preparation of GO@SiO$_2$/PDMS composites is schematically illustrated in Figure 1. First, a certain weight of GO@SiO$_2$ hybrids was dispersed in THF by ultrasonic treatment and mild magnetic stirring. Meanwhile, 3 g of PDMS was dispersed in 20 ml THF by mild magnetic stirring for 1 h to form a stable solution. Then, the uniform GO@SiO$_2$/THF suspension was mixed with PDMS/THF solution under stirring for 2 h, followed by the addition of a curing agent. After mechanical stirring for 10 min, the GO@SiO$_2$/PDMS/THF solution was poured into a mold to remove the solvent and cure at room temperature in a fume cupboard with a thickness of 0.5 mm. The GO@SiO$_2$/PDMS film was obtained after the removal of solvent, and the RGO@SiO$_2$/PDMS composites were obtained by in situ thermal reduction of GO@SiO$_2$/PDMS composites at 180°C for 2 h at a pressure of

![Figure 1](image_url). The schematic illustration of the fabrication of SiO$_2$−APS−GO hybrids.
4 MPa. The composites with different contents of GO@SiO2 (30 wt%, 60 wt%) were achieved by changing the content of GO@SiO2. For the purpose of comparison, a pure PDMS film was also prepared by the same method. Here, it should be noted that the GO content is only 0.6 and 1.2 wt% for the composites with 30 and 60 wt% of GO@SiO2, respectively.

2.4. Characterization

The morphology and microstructure of SiO2 and GO@SiO2 were investigated by scanning electron microscopy (SEM, S-4800, Hitachi Co. Japan), transmission electron microscopy (TEM, Tecnai G² 20, FEI Co. Hong Kong), and high-resolution transmission electron microscopy (HRTEM, JEM-3010, Hitachi, Japan). Samples for TEM and HRTEM observation were prepared by suspending GO@SiO2 in water at a concentration of 0.005 mg/mL under ultrasonication for 30 min, dropping the suspension on micro grids, and then drying in a vacuum oven.

Zeta potential measurements were performed using a Zetasizer 90 (Malvern Instruments, Malvern, England). The aqueous suspensions of silica, SiO2–NH2, and GO were diluted to 0.05 mg/mL and sonicated for 30 min to form a homogeneous solution before conducting the measurements.

Raman spectra of GO and GO@SiO2 dried powder samples were obtained by using a multichannel confocal micro spectrometer (Renishaw in Via, England) with a laser wavelength of 633 nm.

The chemical compositions of GO, SiO2–NH2, and GO@SiO2 were obtained using an ESCALAB 250 X-ray photoelectron spectrometer (XPS) purchased from Thermo Fisher Scientific Company (American).

The volume resistivity (\(\rho_v\)) of GO@SiO2/PDMS composites was measured using a high-resistance meter (EST121, Beijing Huajinghui Technology Co., Ltd, China). \(\rho_v\) is calculated as follows: \(\rho_v = (R_V \cdot S)/L\), where \(R_V\) is the volume resistance of the specimen, \(S\) is the contact area between the composite and the electrode, which is 2122.64 mm² for this instrument, and \(L\) is the average thickness. The conductivity is the reciprocal of volume resistivity.

Dielectric properties were measured using an HP4294A impedance analyzer (Agilent, USA) in the frequency range of 10²–10⁶ Hz at room temperature. The volume resistivity of the composites was tested using a high-resistance meter (EST 121, Beijing HuajingHui Scientific and Technical Co., Ltd., China) at room temperature. Mechanical properties were obtained using a tensile apparatus (CMT4104, Shenzhen SANS Testing Machine Co., Ltd., China); 5–10 samples were tested in the tensile test for each material at a strain rate of 50 mm/min, and the \(Y\) of pure PDMS and GO@SiO2/PDMS composites was obtained by calculating the slopes of the stress–strain curves at the strain of 5%, which was obtained using a tensile apparatus.

The actuated strain was measured using a circular strain test and the diameter of the active area is 1 cm. The samples for actuated strain tests had a thickness of about 0.5 mm and a diameter of 5 cm, and compliant electrodes with a diameter of 11 mm were applied to each side of the DE. Before the test, two main surfaces of the films were sprayed with graphite suspension using an airbrush to fabricate compliant electrodes. The film was first fixed on two circular frames without a pre-strain, and electric field was applied on both sides of the film. The electric field needed was equipped with a high-voltage DC generator (DTZG-60, Wuhan Dotek Electric Co., Ltd.). The strain was calculated as the change of the pixel of the electrode area divided by the original pixel. A video camera was fixed at
the same focal length to capture the actuator plain before and after voltage exertion. Three actuators were studied three times for each composition, and the average values are reported. The thickness of pure PDMS and GO@SiO$_2$/PDMS composites was 0.5 mm. The electric breakdown field was obtained by testing the actuated stains of composites until electric breakdown occurred.

3. Results and discussion

3.1. Self-assembly of GO and APS-modified silica

The overall synthetic procedure of GO coated on silica is demonstrated in Figure 1. GONSs are negatively charged in aqueous solution because of the ionization of the carboxylic acid groups and phenolic hydroxy groups on their surface. When GO is mixed with other positively charged particles, the assembly can be realized by the electrostatic force. However, a silica (SiO$_2$) particle in an aqueous solution is also negatively charged because of the ionization of H$_2$SiO$_3$ on its surface. So the surface modification of SiO$_2$ is necessary to realize the assembly of GO on silica. APS molecules with amino groups can ionize to form a positively charged surface and APS can also undergo condensation reaction with materials that have hydroxyl groups.

Here, SiO$_2$ was first modified by APS to form a positively charged surface. Therefore, it is easy to assume that electrostatic driving force can take place between SiO$_2$−NH$_2$ and GO. To clarify this process, zeta potential was tested to examine the surface charges of GO, SiO$_2$, and SiO$_2$−NH$_2$ aqueous suspensions, as shown in Table 1. With a pH value of 7.0, GO had a highly negative surface charge with a zeta value of −42.5 mV. Meanwhile, the surface charges of the SiO$_2$ switched from negative (zeta = −26.8 mV) to positive (zeta = 39.1 mV) after the modification, suggesting the successful graft of APS on SiO$_2$. When the oppositely charged GONSs and SiO$_2$−NH$_2$ particles collided through simple solution mixing, the electrostatic assembly might have been triggered, forming the core−shell structure of GO@SiO$_2$ hybrid afterward.

The morphology and microstructure of the GO@SiO$_2$ hybrids and the pristine SiO$_2$ were observed by SEM, TEM, and HRTEM, as shown in Figure 2. Compared with the SiO$_2$ particles (specific area ~ 120 m$^2$/g) that have a microsphere morphology and a smooth surface (Figure 2a), GO@SiO$_2$ hybrids show crinkled and rough textures that are associated with the presence of flexible GO sheets. In most cases, the edges of individual as well as overlapping GO layers can be observed, particularly at the interface between aggregated particles, where the graphene layers appeared to link the neighboring spheres together (Figure 2b). The typical TEM and HRTEM images of GO@SiO$_2$ hybrid (Figure 2c, d) also confirm that the flexible GO sheets are successfully wrapped around the SiO$_2$−NH$_2$ microspheres, with the GO shell thicknesses of about 3 nm. The core−shell structure of the GO@SiO$_2$ hybrids can prevent the restacking of GO and the self-aggregation of SiO$_2$. Considering the large specific surface area gap between GO and silica (the specific surface area of an individual GO sheet is 2600 m$^2$/g), it is easy to

| Sample          | SiO$_2$ | SiO$_2$−NH$_2$ | GO    |
|-----------------|---------|---------------|-------|
| Zeta value (mV) | −26.8   | 39.1          | −42.5 |
understand why only 2 wt% GO is needed to assemble on the SiO$_2$ when the equilibrium coverage is reached.

The encapsulation of GO on SiO$_2$ can be confirmed by XPS, as shown in Table 2. The nitrogen content of 3.39\% in SiO$_2$–NH$_2$ suggests a successful introduction of amino groups on SiO$_2$. The increase in carbon content from 25.12\% of SiO$_2$–NH$_2$ to 33.79\% of GO@SiO$_2$ also indicates the immobilization of GO on SiO$_2$. Fourier transform infrared spectroscopy (FT-IR) was also used to confirm the covalently attached APS coupling agent and the GO wrapping on the SiO$_2$, as shown in Figure 3. The main peaks of SiO$_2$ spectra curve at 1621 and 3430 cm$^{-1}$ are designed as stretching vibration of Si–O–Si, blending vibration of O–H, and stretching vibration of –OH, respectively. Several minor bands at around 2800–3000 cm$^{-1}$ were detected in the spectra of SiO$_2$–NH$_2$, which were attributed to the C–H stretching vibration of the hydrocarbon chains of the grafting APS. A weak band at 1725 cm$^{-1}$ appeared in the SiO$_2$@GO spectra curve, which is the

### Table 2. The element analysis of SiO$_2$, SiO$_2$–NH$_2$, GO@SiO$_2$, and GO.

| Samples       | C    | Si   | O    | N    |
|---------------|------|------|------|------|
| GO            | 69.73| –    | 30.27| –    |
| SiO$_2$       | 19.7 | 29.86| 50.44| –    |
| SiO$_2$–NH$_2$| 25.12| 25.98| 45.51| 3.39 |
| GO@SiO$_2$    | 33.79| 22.23| 42.56| 1.42 |

Figure 2. The SEM images of (a) pristine SiO$_2$ (b) GO@SiO$_2$ hybrid; (c)TEM; and (d) HRTEM of GO@SiO$_2$ hybrid.
characteristic of the C=O stretching vibration band of GO. As GO has a large amount of –OH groups, the peak at 3429 cm$^{-1}$ of SiO$_2$–GO is higher than that of SiO$_2$–NH$_2$.

Raman spectroscopy has been used as a powerful tool for the characterization of graphene and its derivatives. Therefore, it was also employed to further confirm the GO shells on SiO$_2$ hybrids. As shown in the Figure 4, there are two peaks at about 1337 and 1595 cm$^{-1}$ in the Raman spectroscopy of graphite oxide, corresponding to the D and G bands. The existence of the two bands was also observed in the spectroscopy of GO@SiO$_2$, which demonstrates the successful assembly of GO on SiO$_2$. Meanwhile, it was reported that both G and 2D bands can be used to monitor the number of layers [38–40]. The G peak of the single-layer graphene shifts to lower wavenumbers, and the 2D band decreases in intensity and lower frequency peaks after stacking more GO layers. In this study, the peak positions of the G bands of the GO and GO@SiO$_2$ were centered at about 1595 and 1602 cm$^{-1}$, respectively. This indicates that GO@SiO$_2$
contains less layers compared to original GO. However, the 2D peaks of the two materials are not obvious in this study and cannot demonstrate the change in number of GO layers.

3.2. **In situ thermal reduction of GO@SiO$_2$/PDMS**

Many researchers have demonstrated that the increase in $k$ is far less than that expected using GO as the dielectric filler because of the severe disruption of the graphite structure of GO [41]. Therefore, the reduction of GO@SiO$_2$/PDMS composites is required to increase the interfacial polarization ability of GO@SiO$_2$. So, the in situ thermal reduction of GO@SiO$_2$/PDMS composites was conducted at 180°C for 2 h because of the following advantages. First, the directional distribution of GO@SiO$_2$ around PDMS latex particles and network structure can be retained during in situ thermal reduction at 180°C. Second, the method is simple and efficient for the partial reduction of GO shells of GO@SiO$_2$.

Thermal reduction of pure GO was conducted under the same conditions to evaluate the degree of reduction of GO shells. The degree of reduction was characterized using XPS and TGA, and the results are shown in Table 3 and Figure 5. The oxygen content obviously decreases from 28.88% for GO to 21.38% for RGO, as shown in Table 3, and the carbon oxygen ratio increases from 2.46% for GO to 3.73% for RGO, suggesting partial reduction of GO. Figure 5 shows the XPS C1s core-level spectra of pure GO. We can observe four characteristic peaks corresponding to carbon atoms in different functional groups: C–C (unoxidized graphite carbon skeleton) at 284.79 eV, C–O (hydroxyl

Table 3. The element analysis of GO and in situ thermal reduction of graphene.

| Samples          | C     | O     | C/O   |
|------------------|-------|-------|-------|
| GO               | 71.12 | 28.88 | 2.46  |
| 180c 2h RGO      | 78.87 | 21.14 | 3.73  |

![Figure 5](image_url)  
Figure 5. The C1s X-ray photoelectron spectroscopy of GO and RGO.
and epoxy groups) at 286.59 eV, C=O (carbonyl group) at 287.69 eV and COOH (carboxyl and ester groups) at 288.69 eV. The presence of the same peak in Figure 5(b) suggests that there are still some oxygen-containing groups in RGO. But the peaks corresponding to the oxygen-containing groups in the spectrum of RGO are weakened, especially that of C=O (carbonyl), indicating that GOs have been partially reduced during thermal reduction at 180°C.

The mass loss of pure GO, RGO was measured at a heating rate of 10°C min\(^{-1}\) in nitrogen atmosphere, as shown in Figure 6. The mass loss below 100°C of GO is due to the removal of absorbed water. The maximum rate of mass loss, corresponding to the loss of most of the oxygen-containing groups, occurs at 150–200°C for both GO and RGO. The mass loss of RGO continues with further increase in temperature because of the remaining oxygen-containing groups caused by the partial reduction of GO during thermal reduction at 180°C.

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3.3. Microstructure of RGO@SiO\(_2\)/PDMS composites

The fracture surfaces of RGO@SiO\(_2\)/PDMS composites with different filler content were observed by SEM, and the results are shown in the Figure 7. A uniform distribution of RGO@SiO\(_2\) in PDMS matrix is observed in both composites filled with 30 phr and 60 phr of RGO@SiO\(_2\), as shown in Figure 7(a) and 7(b), respectively. To clearly observe the interspace between the fillers, the SEM images of the composites with larger magnification were obtained, as shown in Figure 7(c) and Figure 7(d), respectively. Obviously, although some agglomeration of RGO@SiO\(_2\) in the matrix is observed with the increase in the content of RGO@SiO\(_2\) to 60 phr, the interspace between the filler particles largely decreases. As a result, a strong filler network is observed in the composite with 60 phr of RGO@SiO\(_2\), facilitating the increase in conductivity and dielectric constant.
3.4. Electromechanical properties of GO@SiO$_2$/PDMS composites

The stress–strain curves of pure PDMS and the RGO@SiO$_2$/PDMS composites with 30 phr and 60 phr of RGO@SiO$_2$ are shown in Figure 8 and the corresponding mechanical properties are summarized in Table 5. We can observe that both the tensile strength and elastic modulus of PDMS obviously increase with the increase in the content of RGO@SiO$_2$, indicating the good reinforcing effect of RGO@SiO$_2$ on the PDMS matrix. For example, the tensile strength increases from 1.0 MPa for pure PDMS to 1.5 MPa for...
the composite with 60 phr of RGO@SiO$_2$, and the corresponding elastic modulus increases from 0.27 to 0.9 MPa. Although the elongation at break decreases with increasing the content of RGO@SiO$_2$, the elongation at break of the composites is larger than 200%, facilitating the practical application of DE. (The standard deviation is ±0.3.)

The dielectric properties of pure PDMS and RGO@SiO$_2$/PDMS composites as a function of frequency at room temperature are shown in Figure 9. As expected, the $k$ of all the RGO@SiO$_2$/PDMS composites is largely decreased with an increase in frequency, suggesting a strong frequency dependence of $k$ of all the composites. The strong dependence of $k$ is ascribed to interfacial polarization effect (also named as the Maxwell–Wagner–Sillars (MWS) effect) of RGO@SiO$_2$ on PDMS molecules caused by the accumulation of many free charges at the internal interfaces between RGO@SiO$_2$ and PDMS [42]. Is has enough time to accumulate charge at the interfaces between RGO@SiO$_2$ and the rubber matrix at low frequency, resulting in the high $k$ of the composites. However, the interfacial polarization cannot catch up with the change in electrical field frequency at high frequency, leading to the large decrease in $k$ at high frequency [43].

Interestingly, a significant increase in $k$ is observed with the increase in the content of RGO@SiO$_2$ at the same frequency (see Figure 9(a)) in the whole frequency range. The dielectric loss slightly increases with the increase of filler content, especially in the high frequency range of $10^3$–$10^6$ Hz. For example, the $k$ of the RGO@SiO$_2$/silicone rubber (SR) composite with 60 wt% of RGO@SiO$_2$ at 100 and 1000 Hz is 16.8 and 13, respectively, which is much higher than that of pure SR (3.6). The increase in $k$ is ascribed to the high increase in the interfacial polarizability of RGO@SiO$_2$ caused by the in situ thermal reduction of GO. The dielectric loss of RGO@SiO$_2$/SR composite (see Figure 8(b)) at $10^3$ Hz with 30 wt% and 60 wt% GO@SiO$_2$ remains low (<0.2), much lower than that of many other conductive filler/polymer dielectric composites. The relatively low loss is mainly attributed to the low DC conductance of RGO@SiO$_2$ caused by the partial reduction of GO shells by in situ thermal reduction at 180$^\circ$C, as demonstrated by the relatively low electrical conductivity of all the composites, as shown in Table 4.

The elastic moduli of pure PDMS and RGO@SiO$_2$/PDMS composites are summarized in Table 5. We can observe that the elastic modulus increases from 0.27 MPa for pure PDMS to 0.6 and 0.9 MPa for the composites with 30 and 60 phr of RGO@SiO$_2$,
respectively. There is a large increase in $k$ and a mild increase in the elastic modulus of PDMS composites by addition of RGO@SiO$_2$.

Figure 10 shows the actuated strains of pure PDMS and RGO@SiO$_2$/PDMS composites as a function of the electric field. The actuated strain of all the samples obviously increases with the increase in electric field, because it has a quadratic relationship with the applied electric field. Although the maximum actuated strain of the composites is lower than that of pure PDMS and the breakdown strength of PDMS obviously decreases with the increase in RGO@SiO$_2$ content, the actuated strain of the composites at low electric field is much higher than that of pure PDMS, as summarized in Table 6. For example, the actuated strain at 10 kV/mm obviously increases from 0.58% for pure PDMS to 3.48% for the composites with 60 phr of RGO@SiO$_2$. The $k$ of the RGO@SiO$_2$/SR composite with

Table 4. The conductivity of RGO@SiO$_2$/PDMS composites.

| RGO@SiO$_2$ content (phr) | Conductivity (S/m) |
|---------------------------|--------------------|
| 0                         | $8.5 \times 10^{-12}$ |
| 30                        | $2.4 \times 10^{-11}$ |
| 60                        | $1.2 \times 10^{-10}$ |

Table 5. The electromechanical properties of RGO@SiO$_2$/PDMS composites.

| RGO@SiO$_2$ content (phr) | Dielectric constant $k$ at $10^3$ Hz | Dielectric loss tangent at $10^3$ Hz | Elastic modulus $Y$ (MPa) | $\beta = k/Y$ | Tensile strength (MPa) | Elongation at break (%) |
|---------------------------|-------------------------------------|-------------------------------------|---------------------------|---------------|-----------------------|------------------------|
| 0                         | 3.2                                 | 0.006                               | 0.27                      | 5.3           | 1.03                  | 329.4                  |
| 30                        | 5.2                                 | 0.021                               | 0.60                      | 8.6           | 1.52                  | 234.1                  |
| 60                        | 13.3                                | 0.156                               | 0.90                      | 14.8          | 1.53                  | 210.3                  |

Figure 10. Lateral actuation strain of PDMS and RGO@SiO$_2$/PDMS composites as a function of electric field.
60 wt% of RGO@SiO$_2$ at 100 and 1000 Hz is 16.8 and 13, respectively, which is much higher than that of pure SR (3.6). According to the equation $S_z = -\varepsilon_r\varepsilon_0E^2/Y$, the $Y$ of composites with 60 wt% of RGO@SiO$_2$ is close to the $Y$ of composites with 30 wt% of RGO@SiO$_2$. The $\beta$ of 60 wt% RGO@SiO$_2$ has been increased due to the significantly improved dielectric constant of composites. So the actuator strain of 60 wt% RGO@SiO$_2$ composites has been enhanced, as the electric field strength increased, the composites with 60 wt% of RGO@SiO$_2$ possess high dielectric loss. So the electrical energy conversion to heat energy leads to the actuator strain non-linear increase. More interestingly, the actuated strain at 5 kV/mm obviously increases from 0.3% for pure PDMS to 2.59% for the composites with 60 phr of RGO@SiO$_2$, an eightfold increase in the actuated strain, much higher than that of other previously reported DEs [13,43–47], as summarized in Table 6. The improvement in the actuated strain at low electric fields is in favor of the application of DE in the biological and medical fields (such as synthesis of artificial skin), tactile displays, and braille displays, etc. [47].

3.5. Conclusions

We developed a simple and efficient method to simultaneously improve the actuated performance and mechanical strength of a silicone elastomer. GO@SiO$_2$ were first prepared via electrostatic self-assembly of APS-modified SiO$_2$ and GO, and then introduced into PDMS matrix to prepare GO@SiO$_2$/PDMS dielectric composites. RGO@SiO$_2$/PDMS composites are then prepared by in situ thermal reduction of GO@SiO$_2$/PDMS composites at 180°C for 2 h to increase the interfacial polarizability. The results show that the $k$ of PDMS largely increases by adding 60 phr of RGO@SiO$_2$, whereas the dielectric loss of the composites remains low (<0.2 at 1000 Hz). The actuated strain at low electric field (5 kV/mm) obviously increases from 0.3% for pure PDMS to 2.59% for the composites with 60 phr of RGO@SiO$_2$, an eightfold increase in the actuated strain. On the other hand, both the tensile strength and elastic modulus are obviously improved by adding 60 phr of RGO@SiO$_2$ due to the good reinforcing effect of RGO@SiO$_2$ on PDMS.

Disclosure statement

No potential conflict of interest was reported by the authors.
Funding
We would like to express our sincere thanks to the National Natural Science Foundation of China [grant number 51173007], [grant number 51103090], [grant number 51221002] for financial support.

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