Enhanced performance of porous silicone-based dielectric elastomeric composites by low filler content of Ag@SiO₂ Core-Shell nanoparticles

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ABSTRACT

In the present work, micropores and a low filler content of Ag@SiO₂ nanoparticles (NPs) are synchronously introduced into polydimethylsiloxane (PDMS) film to obtain porous dielectric elastomeric composites. The morphology and dielectric and mechanical properties of the composites are investigated. The resulting composites possess high dielectric permittivity, low dielectric loss and low Young’s modulus, which is beneficial to the requirements of a dielectric elastomer actuator. This study provides an effective method to prepare high-performance PDMS-based dielectric porous dielectric elastomeric composites filled with low filler contents of Ag@SiO₂ NPs.

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1. Introduction

Dielectric elastomers are promising materials for advanced electromechanical applications such as actuators, generators and sensors, thanks to their simple and flexible working principle [1–4]. The high dielectric permittivity and low Young’s modulus are two key parameters to improve the electromechanical sensitivity of dielectric elastomers [5]. A remarkably increase of dielectric permittivity can be achieved by adding conductive particles, such as carbon nanotubes [6], metal particles [7], and graphene sheets [8, 9] into the polymer matrix until reaching the percolation threshold [10, 11]. However, at percolation dielectric loss factor increases and Young’s modulus significantly increases, limiting the application of dielectric elastomers [12].

Introducing an insulating shell between conductive fillers, using core–shell nanoarchitecture strategies, would be a reasonable route to decrease the dielectric loss meanwhile improving the dielectric permittivity of the composites [13]. Nan has fabricated Ag@C core-shell structure fillers and incorporated into epoxy. The dielectric permittivity of an epoxy nanocomposite increased by more than two orders of magnitude when the Ag nanoparticle concentration was larger than 20% [14, 15]. DM Opris reported PANI@PDVB/PDMS composites, which presented higher dielectric permittivity 3.4@10³Hz [16]. Such insulating shells on conductive fillers can prevent these conductive fillers from contacting each other directly, which favors a reduction in dielectric loss [17]. Moreover, the Young’s modulus of composite based on dielectric elastomers should be considered prudently. James Wang et al. [18] presented an exponential equation to predict porosity-related modulus relations for porous materials. As expected, polymer porous membranes exhibited the same exponential relationship between modulus and porosity [19]. It can therefore be an interesting
strategy to improve the dielectric permittivity and decrease the Young's modulus through introducing micropores and conductive nanoparticles into the matrix simultaneously.

In this study, silver coated silicon dioxide nanoparticle (Ag@SiO₂ NP) suspension was squeezed into polydimethylsiloxane (PDMS) through intense agitation. After the volatilization of water and cross-linking of PDMS, micropores were introduced into the matrix along with Ag@SiO₂ NPs. The dielectric and mechanical properties of the PDMS/Ag@SiO₂ NPs composites were investigated in terms of porosities and content of the Ag@SiO₂ NPs.

2. Experimental

170 mg Silver nitrate (AgNO₃, Tianjin Yingda Rare Chemical Reagent Factory) and 200 mg poly (vinyl pyrrolidinone) (PVP, Mₕ:58000, Aladdin) were mixed in deionized water followed by adding 400 µL of 5.0 M NaCl solution. Then the solution was added into the mixed solution of 2800 mg L-ascorbic acid and 40 mL 0.5 M NaOH and stirred for 2h [20]. The obtained Ag NPs were dispersed in 200 mL deionized water (DI water) after centrifugation. Silica coating was performed based on the modified Stober method [21]. 3.0 g PVP (Mₕ: 24000, Aladdin) was dissolved in the 200 mL Ag NPs solutions. Then the solutions were centrifuged and the supernatant was removed, and the sediments were redispersed in a solution of ammonia in 50 mL ethanol (4.2 vol%). 5 mL tetraethyl orthosilicate (TEOS, Tianjin Bodi Chemical Co. LTD.) solution (10 vol % in ethanol) was added immediately. After stirring for 12 h, the solution was centrifuged to obtain Ag@SiO₂ NP suspension. The Ag@SiO₂ NP suspension was squeezed into PDMS mixture (base monomers and the curing agent was in a mass ratio of 10: 1) (Sylgard 184, Dow Corning) through stirring for 30 min. The mixture was cast to come a 1 mm film after the air being removed by a vacuum process and cured at atmospheric pressure at 80 °C. Samples are named as PDMS/Ag@SiO₂-x-y, where x represents the mass fraction (wt.%) of Ag@SiO₂ and y represents the volume fraction (vol.%) of DI water.

The Ag@SiO₂ NPs were characterized with transmission electron microscopy (TEM, FEI Tecnai G2F20S-TWIN, USA) and X-ray diffraction analysis (XRD, Rigaku Ultima IV, Japan). Fractured cross sections of the PDMS/Ag@SiO₂ composites were investigated by scanning electron microscopy (SEM, Inspect F, FEI, USA) with an acceleration voltage of 20 kV. The dielectric properties of the composites were measured by a Novocontrol Concept 50 Frequency Analyzer in the frequency range 10⁵ Hz to 10⁷ Hz. The tensile tests were performed using a universal tensile testing machine (AGS-J Shimadzu) at a crosshead speed of 12 mm/min.

3. Results and discussion

Figure 1 shows the XRD patterns of Ag NPs and Ag@SiO₂ NPs. The peaks at 38.0°, 44.1°, 64.4°, 77.3° and 81.6° are assigned to the 111, 200, 220, 311 and 222 lattice planes respectively, which are indexed to be cubic-phase Ag [20]. A broaden peak at 21.0° observed from XRD patterns of Ag@SiO₂ NPs confirms the existence of amorphous SiO₂. From the TEM images (Fig.1 insets), the Ag nanoparticles are basically spherical and their average particle size is about 25 nm. The aggregates of several Ag particles are covered by a smooth and homogeneous silica shell to obtain Ag@SiO₂ NPs with an average particle size of 200 nm. The SEM images in Fig.2 show the porous structures and Ag@SiO₂ NPs distribution of the PDMS/Ag@SiO₂-2-y composite film. When the Ag@SiO₂/DI water suspension was squeezed into the hydrophobic PDMS, phase separation happened and the water phase in the PDMS solution attempted to form

![Figure 1. XRD patterns and TEM images (inset) of silver nanoparticles and Ag@SiO₂ nanoparticles.](image-url)
spherical droplets. During the curing of PDMS, DI water was volatilized and the micropores stayed with relatively uniform pore size distribution (Fig. 2 A1-C1). The porosity is approximately equal to the volume fraction of DI water, which ranges from 0% to 40%. With increasing volume fraction of DI water, the pore size increases and the average diameter of the pores in these composite films is 2.02\(\mu\)m, 3.10\(\mu\)m and 3.47\(\mu\)m, respectively (see insets in Fig. 2 A1-C1). Composite with various porosities and Ag@SiO\(_2\) NPs inside the pores wall (Fig. 2 A2-C2, the Ag@SiO\(_2\) NPs are featured as small bright spots) were fabricated successfully.

The stress-strain curves and Young’s modulus of the composites are presented in Fig. 3. All as-fabricated composites show elastic behaviors even though the nanoparticle and micropore are introduced into it. The Young’s modulus of the composites decreases with increasing porosity. As expected, an evident increase in the Young’s modulus is observed by increasing the Ag@SiO\(_2\) from 0 to 3 wt% (Fig. 3(b)), but they are all below the Young’s modulus of pure PDMS’s (1.80MPa). Because micropores and NPs are introduced into the matrix simultaneously, a relatively low Young’s modulus of the composites is ensured.

Figure 4(a) presents the frequency dependence of dielectric permittivity of PDMS/Ag@SiO\(_2\)-2-\(y\) and PDMS/Ag@SiO\(_2\)-x-30 composites. The dielectric permittivity of all composites shows a low frequency dependence in the measured frequency range, which can be attributed to the fact that SiO\(_2\) shells interact

\[\text{Figure 2. SEM images of the fractured cross sections of PDMS/Ag@SiO}_2-2-\(y\) composites with porosities of 20\% (A), 30\% (B), 40\% (C) respectively: 2000X, 10000X (from top to bottom). The insets show the core size distributions of the composites.}\]

\[\text{Figure 3. Stress–strain curves of PDMS/Ag@SiO}_2\) composites with various porosity (a) and content of Ag@SiO\(_2\) NPs (b).}\]
with PDMS matrix, confining the rotation of amorphous dipoles in PDMS. The dielectric permittivities are enhanced with increasing porosity (6.9@10^3Hz for PDMS/Ag@SiO2-2-40). Also, the dielectric permittivity of the composites increases with the increasing of the NP (Fig. 4(c)). When the content of Ag@SiO2 NPs is 3 wt%, the dielectric permittivity of the composites reaches 6.8@10^3Hz which is nearly 2.5 times that of composites containing 1 wt% Ag@SiO2 NPs. The increased dielectric permittivity is mainly attributed to Maxwell–Wagner–Sillars (MWS) polarization, which occurs at the interface between two materials with an accumulation of charge carriers. Porosity and filler contents show little effect on dielectric losses of the PDMS/Ag@SiO2 composites, which are all less than 0.02@10^3Hz (Fig. 4(b) and (d)). Table 1 summarizes the dielectric properties and mechanical properties of the composites containing different kinds of fillers. We can see that PDMS-based porous dielectric elastomeric composites filled with 2 wt% of Ag@SiO2 NPs in this study show a relatively higher dielectric permittivity, lower dielectric loss and Young’s modulus, compared with others’ researches.

4. Conclusions

High-performance porous PDMS-based dielectric elastomeric composites filled with low filler contents of Ag@SiO2 NPs were successfully prepared.

![Image](https://example.com/image.png)

**Figure 4.** (a) Dielectric permittivity, (b) loss of PDMS/Ag@SiO2 composites with different porosities; (c) Dielectric permittivity, (d) loss of PDMS/Ag@SiO2 composites with different content of Ag@SiO2 NPs.

**Table 1.** PDMS-based elastomers containing different fillers.

| Base elastomer | Filler          | Content | ε’@10^3Hz | tanδ@10^3Hz | Y[MPa] | Ref. |
|---------------|----------------|---------|-----------|-------------|--------|------|
| PDMS          | TiO2           | 11 vol% | 5.5       | 0.060       | 2.20   | 22   |
| PDMS          | Ag@SiO2 Particles | 20 vol% | 5.9       | 0.078       | 1.44   | 23   |
| PDMS          | BaTiO3         | 30 wt%  | 5.7       | 0.005       | –      | 24   |
| PDMS          | PMN            | 20 vol% | 5.2       | –           | 1.00   | 25   |
| PDMS          | Expanded graphite | 2 wt%  | 4.5       | 0.090       | 0.80   | 26   |
| PDMS          | PANi@PDVB      | 20 wt%  | 3.4       | 0.050       | 2.32   | 16   |
| PDMS (Porous) | Ag@SiO2 particles | 2 wt%  | 6.9       | 0.001       | 0.82   | This study |
The Young's modulus decreased significantly when micropores were incorporated into the composites. The dielectric permittivity was improved significantly with increasing porosity even at low nanoparticle content. The dielectric losses of the all composites were less than 0.02 at 10^3 Hz. Overall, this work provides a feasible way of preparing high-performance dielectric porous composites, which have great prospects for advanced electromechanical applications.

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