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Dimensional effect of SrTiO₃ particles on functional performance optimization of polydimethylsiloxane-based composites for dielectric elastomer actuators

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Abstract

Dielectric elastomer materials have a great application potential in electromechanical sensing and energy-harvesting fields. However, the realization of high electro-actuation properties under a relatively low electric field is still a critical challenge. Herein two series of polydimethylsiloxane (PDMS)-based dielectric elastomer composites incorporated SrTiO₃ (STO) with distinguishing diameters were prepared through solution-blending and compression moulding methods. The resultant STO/PDMS composites showed significantly enhanced dielectric permittivity and Young’s modulus. Moreover, the PDMS-based composite filled with 4 vol.% nano-scaled STO exhibited an improved electro-actuation strain of 3.3% at a very low electric field of 24 V μm⁻¹, which was 30% larger than that of the neat PDMS. The experimental results revealed that the electro-active performance of dielectric elastomer composite under low electric fields can be influenced by the size of incorporating functional units, and be also successfully optimized by regulating the fillers-matrix interfacial interaction. This study provides a promising strategy to design and fabricate novel dielectric elastomers with advanced low-field driving electro-active properties.

Introduction

Dielectric elastomer (DE) as one typical electroactive polymer is capable of providing a relatively large electrical field actuated response, which has shown a great application potential in Braille devices, haptic displays, soft robots and electromechanical sensors etc in recent years [1–6]. In comparison with other traditional electro-actuated materials, there are several distinguished merits such as large strain, fast response, ease-processing, and low cost can be found in DE system [7].

However, both large field-driving stress and strain of DE are always obtained at a relatively high driving electrical field, which greatly limits its practical application range [8]. For instance, artificial alternative biomaterial is one of the most promising applications of DE in future. However, the main potential biological and medical applications of DE such as artificial prosthesis, heart pump and retina etc cannot allow such a high voltage to be operated in vivo [9–11]. Thus, how to effectively improve the electro-active performance of DE at a low driving field is a critical issue to be solved urgently.

It is widely considered that the electro-active performance of a DE material is mainly determined by its dielectric permittivity (εr), Young’s modulus (Y) and electrical breakdown strength (E₀) [12]. From the perspective of material design, the functional performance of a DE material can be optimized through a rational regulation of both inner structure and above key characteristics [13]. Although the method of reducing Y was reported to be benefit to elevate both the flexibility and electro-actuated strain of DE, the obtained material is too soft to provide sufficient output force, which also limits a majority of application conditions for DE materials.
Taking DE-based artificial muscle as an example, a large actuated-stress is more important than strain to drive muscle fibers to realize the lifting motion of prosthesis or mechanical arm in a robot sensor. Therefore, to optimize the $\varepsilon_r$ values is a feasible and reasonable strategy for the fabrication of DE materials and devices in the next generation with advanced electro-active properties.

In recent decades, conductive fillers were widely adopted in polymer-based composites for promoting their overall $\varepsilon_r$ values, according to the percolation theory [17–19]. Be different from polymer-based film capacitors, DE materials can become thinner and thinner along the applied voltage direction with an increasing voltage. The true electrical field that applied onto a DE film augments exponentially, resulting in that the electrical breakdown is easily happened in DE system [20]. Thus, it is necessary to avoid utilizing conductive fillers directly in DE composites, in order to impede the growth of inner conductive paths. Compared with conductive fillers, ceramics particles with high $\varepsilon_r$ are also able to improve the overall $\varepsilon_r$ of composites and show a less influence on the reduction of $E_b$. Carpi et al reported a series of TiO$_2$ filled silicone-based DE films with significantly improved dielectric and electro-actuation performances [21]. Yang et al prepared a surface-functionalized BaTiO$_3$ (BT) loaded DE composites, where an optimal electro-actuated strain of 26% was obtained at a low electric field of 12 kV mm$^{-1}$ [22]. In addition, several types of ceramic with a much higher $\varepsilon_r$ value such as lead magnesium niobate, etc were also employed to improve the dielectric and electro-active performance of DE composites [23].

Besides its intrinsic $\varepsilon_r$ value, the size of functional filler also plays a critical role in influencing the dielectric property and mechanical flexibility of DE composites. Generally, fillers with a small size show larger specific surface area and more severe aggregation in polymer matrix than those large-sized fillers. Both the dielectric polarization and mechanical reinforcement are positively related to the interfacial area and interfacial interaction between fillers and matrix [19]. However, these two effects make opposite contributions to electro-active performance of DEs. Thus, how ceramic particle size influences the electro-active performance of a DE composite is an important issue needed to be carefully studied.

SrTiO$_3$ (STO) is a semi-conductive anatase material, and is also one of the most important precursors of BaSrTiO$_3$ (BSTO) and various element-doped BSTO. By virtue of its high $\varepsilon_r$ (~300), low loss and excellent thermo-stability, STO have been widely used in insulating material and capacitors [24–27]. Polydimethylsiloxane (PDMS) has been widely utilized as DE matrix due to its fast response, low hysteresis, outstanding bio-compatibility, ease-processing and low cost [28–30]. In fact, the electro-active performance of STO/PDMS composite has been rarely reported, especially the influence of STO size on dielectric, mechanical and electro-actuated performances of PDMS-based DE composites.

Herein, a series of flexible and insulating PDMS-based composites with different-sized STO particles were successfully prepared by solution blending and compress-moulding approaches, which exhibits both improved dielectric performance and mechanical modulus. At a same volume fraction, STO with different sizes make a distinguishing contribution on functional property optimization. Furthermore, the STO/PDMS composites can be applied as DE film actuator, which exhibited an enhanced electro-actuated strain. These results demonstrate that the size of functional units is a key parameter to regulate electro-active performance of STO/PDMS composites. The STO/PDMS composites have great application potential in dielectric elastomer actuator and energy storage.

**Experimental section**

**Material**

A hydroxyl-terminated PDMS was obtained from Shandong Wancheng chemical company (China). Anatase STO particles with two different average sizes donated respectively as m-STO (micron-STO) and n-STO (nano-scaled STO), which were purchased from Shanghai Macklin Biochemical Co., Ltd (China). Dibutyltin dilaurate, ethyl silicate (TEOS), and absolute ethanol were all provided by Tianjin Kernel Chemical Company (China) in analytical grade (analytical reagent, AR). Tetrahydrofuran (THF, AR) was supplied by Sinopharm Chemical Reagent Company. All chemicals were used as received without further purification.

**Preparation of STO/PDMS composites**

The as-received STO particles were ultrasonically dispersed in ethanol for 30 min to obtain a well-dispersed suspension. Meanwhile, PDMS was dissolved into THF with magnetic stirring until the solution becomes homogenous. Then, the two suspensions were blended and vigorously stirred at 45 °C for 5 h, followed by 50 °C for another 2 h to vaporize THF in a vacuum oven. Consequently, TEOS and dibutyl tin dilaurate were added and well-dispersed into the solvent-removed blend with the mass ratio of 20:3. The obtained mixture was casted into a lab-fabricated metallic mould at room temperature for 12 h under a pressure of 15 MPa, in order to make PDMS-based composites cross-linked completely.
Characterization of the microstructure of two types of STO particles and fractured surfaces of STO/PDMS composite was performed by SEM (EM-30 PLUS, OPTONLIMITED, China). Both powder and composite samples were sputtered a thin layer of gold onto the surface. X-ray diffraction (XRD) patterns of different-sized STO particles were determined by diffractometer (D8 Advance A25, Germany) with Cu radiation source. Dielectric permittivity and loss tangent were acquired using a Keysight E4990A impedance analyzer. The mechanical properties were evaluated using a Shimadzu EZ Test (EZ-LX) machine at a crosshead speed of 10 mm min$^{-1}$. The samples of mechanical test were prepared in dumbbell shape according to GB/T-528 IV. The corresponding Young’s modulus values were determined by calculating the slope of the tensile stress-strain curve in the linear region. Electro-actuated strain and dielectric breakdown strength measurements were performed on an ultra-high voltage source (CS9920, China) accompanying a lab-established real-time recording system.

Results and discussions

The morphology of as-received STO particles are shown in figures 1(a) and (b). The average diameters of spherical m-STO and n-STO are 2 μm and 500 nm, respectively. It is assumed that both m-STO and n-STO have same surface structure and are homogeneously distributed and separately dispersed in PDMS matrix without any aggregation. At a same loading volume fraction, the total interfacial area is similar to the surface area of STO particles [31]. The interfacial area of n-STO/PDMS composites is 400% larger than that of m-STO/PDMS composites. Such a large difference in structure feature is helpful to investigate its regulating effect on functional properties of composites effectively. Figure 1(c) demonstrates the typical XRD pattern of m-STO and n-STO, where the observed 2θ characteristic peaks at 32.42°, 39.98°, 46.48°, 57.79°, 67.80° and 77.17° represent the typical anatase-crystallized STO. Moreover, there is no significant difference in both position and relative
intensity of characteristic peaks between m-STO and n-STO. It indicates that the selected STO particles have not obvious difference in crystallization structure but just distinguishable size.

SEM images of the fractured surface of the STO/PDMS composite are shown in figures 2(a) and (c). Both m-STO and n-STO particles were found to be homogeneously distributed in the PDMS matrix without significant agglomeration, indicating that as-received STO particles aggregation can be effectively separated by ultrasonication and magnetic stirring procedures. According to the theory of solid physics, the atoms on surface are unstable, and have more energy than internal atoms. For a same material, the surface energy enhances with its reducing size. The particles with high surface energy tend to form aggregations, in order to reduce the overall surface energy. Therefore, compared with n-STO, m-STO particles have a smaller surface energy and could be more easily separated from aggregation and dispersed into PDMS matrix through the completely same composite-preparation procedures. Good compatibility of the inorganic and organic phases was confirmed in large-scale SEM images of m-STO or n-STO loaded PDMS composites (see figures 2(b) and (d)). It is observed that the interface between STO and PDMS is not sharp, which implies an intact interfacial adhesion. The interfacial adhesion between fillers and matrix plays a critical role in influencing the maximum electro-actuated stress and strain of a DE film. The weak interfacial adhesion allows air gaps to exist in the interface between fillers and matrix, these air gaps are able to be filled through the frequently-adopted approach of surface modification, where hydrocarbon chains are grafted onto the surface of fillers. However, no matter the air gaps or additional hydrocarbon chains could result in the local electrical-sensitive defects, which would further deteriorate the dielectric strength of composites [32].

Figure 3 exhibits the dielectric performances of n-STO/PDMS and m-STO/PDMS composites with different STO contents. The dielectric permittivity values of both two series of composites show a negligible dependence on the frequency from 3 kHz to 10 MHz, as shown in figure 3(a). Be different from fluoropolymers, the observed frequency-independent behavior of STO/PDMS composite is mainly determined by the inherent feature of crosslinked PDMS matrix. It can be seen that the dielectric permittivity enhances with increasing both m-STO and n-STO volume fractions. Typically, the ε_r values of 16 vol% n-STO and m-STO loaded PDMS-based composites are 7.3 and 6.8 at 3 kHz, which are 120% and 106% higher than that of PDMS, respectively. It is observed that the loss tangent values of two series of composites firstly decrease and are then kept below 0.01, independently from the increasing testing frequency, as depicted in figure 3(b). The relatively high loss tangent at

Figure 2. SEM images of the fractured surfaces of PDMS-based composites loaded with (a) m-STO and (c) n-STO; (b) and (d) are high-magnification images of m-STO and n-STO particles embedded in the matrix, respectively.
low frequency range may be ascribed to the typical interfacial polarization between STO particles and PDMS matrix. STO particles with an inherent low loss tangent are able to endow DE composites with a high electromechanical energy conversion efficiency. It is worth noting that at same volume fractions, n-STO/PDMS composites show a higher $\varepsilon_r$ values than m-STO/PDMS composites. Moreover, the $\varepsilon_r$-difference is gradually significant with increasing STO loading content. It is due to their larger specific surface area, n-STO particles exhibit a stronger interfacial interaction to PDMS matrix in comparison with m-STO, which is responsible for the greater $\varepsilon_r$ values of the composites.

A uniaxial tensile measurement was performed to evaluate the mechanical properties of neat PDMS and STO/PDMS composites. Dumbbell-shaped specimens were prepared according to the testing standard of GB/T 528. Figures 4(a) and (b) show the stress-strain curves of the PDMS composites loaded with different fraction of n-STO and m-STO, respectively. The elongation at break of PDMS-based composites generally reduces with increasing STO volume fraction. It can be explained as that the movement of PDMS macromolecular chains can be greatly impeded by their tight interfacial bonding with STO particles. However, for the n-STO/PDMS composites, the elongation at break of the sample-4 vol.% is larger than that of the sample-2 vol.%. It may be ascribed to the physical crosslinking effect of n-STO particles to PDMS matrix. Moreover, the tensile strength of composites basically increases with increasing filler volume fractions, which is closely related to its inner interfacial interaction and filler dispersion. However, the tensile strength of 2 vol.% m-STO/PDMS composite is lower than that of neat PDMS. It could be ascribed to as that in comparison with n-STO, m-STO has a lower inherent surface energy and a weaker interfacial adhesion with PDMS matrix. With an increasing m-STO loading, the interfacial strengthen effect dominates its competition against the cavity weaken effect. More and more applied stress can be transferred from PDMS matrix to m-STO particles, leading to that an enhanced tensile strength of composites with increasing m-STO loading. It is noteworthy that both the tensile strength and elongation at break of n-STO/PDMS composites are larger than those of m-STO/PDMS composites. Compared with m-STO filled composites, nano-sized n-STO particles are able to provide a stronger interfacial interaction with matrix. Moreover, the macromolecular chains movement is limited by a larger bulk volume and steric hindrance of m-STO, resulting in the lower elongation at break values than n-STO/PDMS composites at the same volume fractions [33]. In addition, Young’s modulus is one of the most important features in determining the electro-active strain of DE materials. As exhibited in figure 4(c), Y values of both m-STO/PDMS and n-STO/PDMS composites increase with rising the filler content. The n-STO filled composites show higher Y values than m-STO loaded counterpart at all filler fractions, which mainly ascribed to its stronger filler-matrix interfacial interaction.

Figure 5 illustrates the actuation strains of PDMS-based composites loaded with various contents of m-STO and n-STO particles against an applied low electric field (from 0 to 24 V $\mu$m$^{-1}$). It is observed that all DE composite samples show augmenting actuated strains with increasing driving electric field. Particularly, when applying an electric field, all composites show the gradually enlarged actuated strains. However, the actuated strains of both m-STO/PDMS and n-STO/PDMS composites at low filler volume fraction are larger than those of high volume fraction filled counterparts. It is mainly ascribed to the developing competition between dielectric polarization improvement and mechanical reinforcement, which plays an opposite role in influencing the electro-active strain of DEs. Compared with m-STO filled counterpart, n-STO/PDMS composites exhibit a more obvious exponential relationship between actuation strain and applied electric field, which is consistent
with the Maxwell electro-actuation theory. It implies that the nanoparticle-filled composite is more sensitive to applied electric field than micron-filler loading system. As shown in figure 5(b), the PDMS-based composite loaded with 4 vol.% n-STO displays the highest actuated strain at a given electric field. Specifically, its actuated strain of 3.3% is obtained at 24 V μm⁻¹ without any pre-strain, which is 13% and 30% larger than that of 4 vol.% m-STO filling counterpart and neat PDMS, respectively. Notably, the largest actuated strains of two series of composites are all achieved when filler loading is about 4 vol.%. It is indicated that at this volume fraction, the inner interfacial interaction between fillers and matrix achieves an optimal compromise between dielectric...
property and flexibility. Furthermore, a little inherent steric effect of nano-scaled STO might be also responsible for the larger actuated strain of n-STO/PDMS composites.

Conclusions

In summary, the n-STO/PDMS and m-STO/PDMS composites were successfully prepared by using methods of solution-blending and pressure-moulding. A large electro-actuated strain of 3.3% at a low applied field of 24 V μm\(^{-1}\) is obtained in DE composite loaded with 4 vol% n-STO, which is 30% larger than that of neat PDMS. The higher \(\varepsilon\) and \(\Upsilon\) values achieved in n-STO/PDMS composites have been mainly attributed to the enhanced interfacial interaction between nano-scaled STO and elastomer matrix in comparison with m-STO filled composites. It is indicated that the electro-actuated strain of a 0–3 heterogeneous DE composite at a low applied field can be influenced by not only the balance between volume fraction-dependent dielectric and mechanical performances, but also the size-related steric effect of functional fillers. This study provides a useful experimental evidence for the material design of dielectric elastomers in next generation with improved electro-active performance at low electrical fields.

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References

[1] Brochu P and Pei Q B 2010 Advances in dielectric elastomers for actuators and artificial muscles Macromol. Rapid Commun. 31 10–36
[2] Biggs J et al 2013 Electroactive polymers: developments of and perspectives for dielectric elastomers Angewandte Chemie-International Edition 52 9409–21
[3] Mirvakili S M and Hunter I W 2018 Artificial muscles: mechanisms, applications, and challenges Adv. Mater. 30 1704407
[4] Chen Y F, Zhao H C, Mao J, Chirarattananon P, Hellingf B E, Hyun N S P, Clarke D R and Wood R J 2019 Controlled flight of a microrobot powered by soft artificial muscles Nature 575 324
[5] Shintake J, Cacucciolo V, Florzano D and Sheh H 2018 Soft robotic grippers Adv. Mater. 30 1707035
[6] Yin T H, Wu T H, Zhong D M, Liu J J, Liu X J, Han Z L, Yu H H and Qu S X 2018 Soft display using photonic crystals on dielectric elastomers ACS Appl. Mater. & Interf. 10 24758–66
[7] Anderson I A, Gibly T A, McKay T G, O’Brien B M and Calais E P 2012 Multi-functional dielectric elastomer artificial muscles for soft and smart machines J. Appl. Phys. 112 041101
[8] Carpi F, Bauer S and De Rossi D 2010 Stretching dielectric elastomer performance Science 330 1759–61
[9] Carpi F, Frediani G, Turco S and De Rossi D 2011 Bioinspired tunable lens with muscle-like electroactive elastomers Adv. Funct. Mater. 21 4152–8
[10] Qiu Y, Zhang E, Plamhottam R and Pei Q B 2019 Dielectric elastomer artificial muscle: materials innovations and device explorations Acc. Chem. Res. 52 316–25
[11] Acome E, Mitchell S K, Morrissey T G, Emmett M B, Benjamin C, King M, Radakovic M and Keplinger C 2018 Hydraulically amplified self-healing electrostatic actuators with muscle-like performance Science 359 61–5
[12] Dang Z M, Yuan J K, Zha J W, Zhou T, Li S T and Hu G H 2012 Fundamentals, processes and applications of high-permittivity polymer–matrix composites Prog. Mater. Sci. 57 660–723
[13] Kong L B, Li S, Zhang T S, Zhang J W, Boey F Y and Ma J 2010 Electrically tunable dielectric materials and strategies to improve their performances Prog. Mater. Sci. 55 840–93
[14] Yang D, Huang S, Ruan M N, Li S X, Wu Y B, Guo W L and Zhang L Q 2018 Improved electromechanical properties of silicone dielectric elastomer composites by tuning molecular flexibility Compos. Sci. Technol. 155 160–8
[15] Zhang F X, Li T F and Luo Y W 2018 A new low modulus dielectric elastomer nano-structured composite with high permittivity exhibiting large actuation strain induced by low electric field Compos. Sci. Technol. 156 151–7
[16] Zhao H, Wang D R, Zha J W, Zhao J and Dang Z M 2013 Increased electroactuation through a molecular flexibility tuning process in TiO\(_2\)-polydimethylsilicone nanocomposites J. Mater. Chem. A 1 3140–5
[17] Panahi-Sarmad M, Zahiri B and Noroozi M 2019 Graphene-based composite for dielectric elastomer actuator: a comprehensive review Sensors and Actuators a-Physical 293 222–41
[18] Panahi-Sarmad M and Razaghi-Kashani M 2018 Actuation behavior of PDMS dielectric elastomer composites containing optimized graphene oxide Smart Mater. Struct. 27 085021
[19] Dang Z M, Yuan J K, Yao S H and Liao R J 2013 Flexible nanodielectric materials with high permittivity for power energy storage Adv. Mater. 25 6334–65
[20] Dorfmann L and Ogden R W 2019 Instabilities of soft dielectrics Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences 377 20180077
[21] Carpi F and De Rossi D 2005 Improvement of electromechanical actuating performances of a silicone dielectric elastomer by dispersion of titania dioxide powder IEEE Trans. Dielectr. Electr. Insul. 12 835–43
[22] Yang D, Ge F X, Tian M, Ning N Y, Zhang L Q, Zhao C M, Ito K, Nishi T, Wang H M and Luan Y G 2015 Dielectric elastomer actuator with excellent electromechanical performance using slide-ring materials/barium titanate composites J. Mater. Chem. A 3 9468–79
[23] Yang D, Zhang L Q, Liu H L, Dong Y C, Yu Y C and Tian M 2012 Lead magnesium niobate-filled silicone dielectric elastomer with large actuated strain J. Appl. Polym. Sci. 125 2196–201
[24] Yao L M, Pan Z B, Zhai J W, Zhang G Z, Liu Z Y and Liu Y H 2018 High-energy-density with polymer nanocomposites containing of SrTiO3 nanoﬁbers for capacitor application Composites Part a- Applied Science and Manufacturing 109 48–54
[25] Wu L W, Wang X H, Gong H L, Hao Y N, Shen Z B and Li L T 2015 Core-satellite BaTiO3@SrTiO3 assemblies for a local compositionally graded relaxor ferroelectric capacitor with enhanced energy storage density and high energy efﬁciency J. Mater. Chem. C 3 750–8
[26] Lu Y-C, Yu S, Zeng X, Sun R and Wong C-P 2018 High energy density polymer nanocomposites with Y-doped barium strontium titanate nanoparticles as ﬁllers IET Nanodielectrics 1 137–42
[27] Feng Z, Hao Y, Bi M, Dai Q and Bi K 2018 Highly dispersive Ba0.6Sr0.4TiO3 nanoparticles modiﬁed P(VDF-HFP)/PMMA composite ﬁlms with improved energy storage density and efﬁciency IET Nanodielectrics 1 60–6
[28] Cheng W, Yu L W, Kong D S, Yu Z W, Wang H T, Ma Z, Wang Y M, Wang I Z, Pan I J and Shi Y 2018 Fast-response and low-hysteresis ﬂexible pressure sensor based on silicon nanowires IEEE Electron Device Lett. 39 1069–72
[29] Opris D M, Molberg M, Walder C, Ko Y S, Fischer B and Nuesch F A 2011 New silicone composites for dielectric elastomer actuator applications in competition with acrylic foil Adv. Funct. Mater. 21 3531–9
[30] Zhao H, Yang M H, He D L, Liu Y, Bai J T and Bai J B 2019 Effects of the shape features of graphite nanoplatelets on electrically-conductive behaviors of polydimethylsiloxane-based stretchable electrodes Mater. Res. Exp. 6 085001
[31] Sahbi A and Manfred K 2014 Magneto-rheological response of elastomer composites with hybrid-magnetic ﬁllers Smart Mater. Struct. 24 025016
[32] Yifei W, Linxi W, Qibin Y, Jie C, Qing W and Hong W 2017 Ultrahigh electric displacement and energy density in gradient layer-structured BaTiO3/PVDF nanocomposites with an interfacial barrier effect J. Mater. Chem. A 5 10849–55
[33] Yang D, Ruan M, Huang S, Wu Y, Li S, Wang H, Ao X, Liang Y, Guo W and Zhang J 2016 Dopamine and silane functionalized barium titanate with improved electromechanical properties for silicone dielectric elastomers RSC Adv. 6 90172–83