Increased electromechanical sensitivity of polysiloxane elastomers by chemical modification with thioacetic groups

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HIGHLIGHTS

• Novel silicone-based elastomers modified with thioacetic groups were prepared.
• Surface treated silica particles improve the mechanical properties of the formed elastomers.
• The increased permittivity and the optimized elasticity allowed construction of DEA responsive to a low electric field.
• The elastomers can be processed in thin films from which actuators operated at low voltages were constructed.

ABSTRACT

Chemically cross-linked polydimethylsiloxane (PDMS) elastomers have gained importance as a dielectric in elastic capacitor actuators, which elongate when electrically charged. Common PDMS elastomers have a dielectric permittivity of only about 3 and thus elongations interesting for real applications occur only at high voltages. In this work, a new class of silicone-based elastomers with increased permittivity are synthesized starting from polymethylvinylsiloxane and thioacetic acid via a photo-induced thiol–ene reaction, whereby polar thioacetate groups are introduced at every siloxy unit. The silanol end-groups of the formed polymer are subsequently used for cross-linking into thin films using a condensation reaction with poly(methylhydrosiloxane-co-dimethylsiloxane). These films show good mechanical properties and have a low glass transition temperature (-58 °C), which allows for a wide range of use temperatures. Further they have an increased permittivity ($\varepsilon^\prime = 4.7$) and an increased sensitivity to electric field as compared to regular polydimethylsiloxane elastomers. Our new elastomers are easily accessible and can be processed into very thin films, which allows access to actuators operable way below 1000 V. An actuation strain of 12.8% at an electric field of 21.5 V/µm was measured.

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1. Introduction

Dielectric elastomer actuators (DEAs) are electromechanical transducers which have properties that remind of those of natural muscles [1]. They are lightweight elastic capacitors that have a
2. Experimental

Prior use. The functionalization of SiO2 nanoparticles was realized according to the literature [25].

2.1. Materials and chemicals

Tetramethylammonium hydroxide pentahydrate (TMAH), 1,3,5,7-tetravinyl-1,3,5,7-tetramethylocyclosiloxane (V4) and (25–35\% methylhydrosiloxane)-dimethyilsiloxane copolymer (CL) were purchased from ABCR. Thioacetic acid (TAA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), 2,2′-(ethylenedioxy)dithioanethiol, dibutyltin dilaurate (Sn cat.), benzene and toluene were purchased from Aldrich. Amorphous SiO2 particles (60–70 nm) were purchased from US Research Nanomaterials Inc., Houston, and 1,1,1,3,3,3-hexamethydisilazane from Alfa Aesar. Methanol and tetrahydrofuran were purchased from VWR. All chemicals were reagent grade and used without purification; only THF was dried over sodium and distilled prior use. The functionalization of SiO2 nanoparticles was realized according to the literature [25].

2.2. Methods

1H and 13C NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer using a 5 mm BBO Prodigy™ CryoProbe at 400.18 and 100.63 MHz, respectively. Chemical shifts (δ) in ppm are calibrated to residual solvent peaks (CDCl3: 7.26 and 77.16). Size-exclusion chromatograms were recorded with an Agilent 1100 Series HPLC (Columns: serial coupled PSS SDV 5 μm, 100 Å and PSS SDV 5 μm, 1000 Å, Detector: DAD, 235 nm and 360 nm; refractive index). THF was used as mobile phase, polydimethylsiloxane (PDMS) standards were used for the calibration, and toluene as internal standard. Differential scanning calorimetry (DSC) investigations were undertaken on a Pyris Diamond DSC (PerkinElmer USA) instrument under nitrogen flow (50 ml × min−1), in aluminum crucibles shut with pierced lids and using about 10 mg sample mass. Tensile tests were performed on a Zwick 2010 tensile test machine with a crosshead speed of 50 mm/min. Tensile test specimens with a gauge width of 2 mm and a gauge length of 18 mm were prepared by die-cutting. The strain was determined over the traverse movement sensor. The curves were averaged from 3 replicates per material (see ESI), and the values reported are averaged. The Young modulus Y100% was determined from the slope of the stress-strain curves using a linear fit to the data points from 0 to 10%. The Young modulus Y50% and Y10% was determined from the slope of the stress-strain curves using a linear fit to the data points within ±10% strain. For the cyclic hysteresis tests, one sample for each material was subjected to cyclic loading (up to 50% strain) at a ramp rate of 20 mm/min and unloading for 5 cycles. Dynamic mechanical analysis was carried out on a RSA 3 DMA from TA Instruments. Stripes of 10 mm width and 2 cm long were measured under a dynamic load of 2.5 g, at 2% strain in the frequency range of 0.05–10 Hz at 25 °C and 65% humidity. Dielectric permittivity measurements at room temperature were done in the frequency range of 1 Hz to 1 MHz, using a Novocontrol Dielectric Spectrometer equipped with an Alpha-A Frequency Analyzer. The samples were prepared by sputtering gold electrodes with a thickness of 20 mm. The Vrms (root mean square voltage) of the probing AC electric signal applied to the samples was 1 V. Electromechanical tests were performed using circular membrane actuators at ambient temperature and humidity. The films were biaxial prestretched by 30% and fixed between two circular rigid frames that have an inner diameter of 25 mm. Circular electrodes (8 mm diameter) of carbon black powder were applied to each side of the film. A FUG HCL-35–12/500 high voltage source served as a power supply for actuator tests. The voltage was increased by 100 V or 50 V steps every 2 s up to maximum 5.6 kV. The actuation strain was measured optically as the extension of the diameter of the electrode area via a digital camera, using an edge detection tool of a LabView program to detect the boundary between the black electrode area and the transparent silicon film. Photoreactions were conducted with a UVAHAND 250 GS H1 mercury vapor UV lamp from Dr. Hoenle AG.

2.3. Procedure for polymer synthesis and material preparation

Synthesis of P1: The polymer was prepared according to the literature [14].

1H NMR (400 MHz, CDCl3, 6 ppm): 0.14–0.20 (m, 3H, –Si–CH3); 5.75–5.82 (m, 1H, –Si–CH=CH2); 5.89–6.03 (m, 2H, –Si–CH=CH2); 13C NMR (100 MHz, CDCl3, 6 ppm): 0.43 (–Si–CH3); 133.24 (–Si–CH=CH2); 136.88 (–Si–CH=CH2); GPC: Mn = 78 kg mol−1, Mw = 769 kg mol−1, PDI = 2.2.

Synthesis of P2: To P1 (10 g, 0.116 mol, 1 eq) dissolved in dry THF (200 ml), TAA (17.66 g, 0.232 mol, 2 eq) and DMPA (0.2973 g, 1.16 mmol, 0.01 eq) were added. The solution was irradiated with a UV light twice for 15 min. The reaction mixture was concentrated under vacuum and precipitated with methanol (50 ml) and washed few times with methanol. The viscous liquid was kept as a solution in THF. Prior thin film formation, the solution was concentrated. 1H NMR
and sandwiched between a second glass plate. The thickness of the film was adjusted by two spacers with a thickness of 1 mm. The film was irradiated with a UV light for 5 min. Thereafter, the top glass plate was removed and the films were detached from the Teflon coated glass substrate. They were left at room temperature for 24 h and then dried at 70 °C for 2 days prior further characterizations.

3. Results and discussion

To prepare silicone elastomers modified with polythioacate groups, two synthetic paths were followed (Fig. 1). The first started with a poly(methylhydrosiloxane) (P1) which was modified first with thioacate groups and then cross-linked into thin films [44]. The second approach used a one-step process in which the modification of P1 with thioacetic acid (TAA) and the cross-linking occurred simultaneously within the thin films. The starting polymer, P1, was prepared from 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (V4) monomer by anionic ring-opening polymerization in presence of tetravinylsiummonium hydroxide. P1 carries a vinyl group at every silox unit which we used to introduce thioacetate groups by thio-ene addition of TAA in presence of 2,2-dimethoxy-2-phenylethylacetoephene (DMPA) triggered by UV light. The structure and molecular weight of the synthesized polymers were analyzed by 1H NMR and GPC. The complete disappearance of the vinyl and thiol groups proton signals of the starting reagents and the appearance of new signals in the aliphatic region of the 1HN M RaCy t r e c t ra o n complete disappearance of the vinyl and thiol groups proton signals of the starting reagents and the appearance of new signals in the aliphatic region of the 1HN M R s p e c t r a confirmed the reaction to be complete and thus the formation of thioacetate functionalized polymer (P2) (Fig. 2). The thio-ene addition reaction gave predominantly the Cn% (Fig. 2). The thio-ene addition reaction gave predominantly the

a A solution of dibutyltin dilaurate (50 vol%) in toluene was used. 
b a dispersion of hexamethyldisilazane treated silica particles (0.5 g) in toluene (10 ml) was used.

2.4. Preparation of thin films

Material \( A_n \): A solution of P2 (1 g), CL and Sn catalyst in toluene (4 ml) was processed in thin films on a Teflon substrate by doctor blade technique. For the amounts of reagents used please see Table 1. The films were left at room temperature for 24 h to cross-link, followed by 2 days at 70 °C to remove any residual solvent. Different elastomers named \( A_n \) were prepared for which the amount of reagents used is listed in Table 1.

Material \( B_n \): A solution of P2 (1 g), CL, Sn catalyst and different amount of hexamethyldisilazane treated silica particles in toluene (4 ml) was processed into thin films on a Teflon substrate by doctor blade technique. The reagents and amounts used for the synthesis of materials \( B_n \) are listed in Table 1. The films were left to cross-link at room temperature for 24 h and at 70 °C for 2 days.

Material C: A solution of P1 (1 g), surface functionalized silica particles (0 wt%, 5 wt%, and 10 wt% for CMS, C05, and C105 respectively), TAA (0.85 ml), 2,2′-(ethylenedioxy)diethanethiol (17 µl), and DMPS (5 mg) in toluene (2 ml) was placed on a glass plate coated with a Teflon film and sandwiched between a second glass plate. The thickness of the

![Fig. 1. Synthesis of poly(methylhydrosiloxane) (P1) from monomer V4, functionalization of P1 by thio-ene addition with thioacetic acid to polymer P2, which is cross-linked with poly (methylhydrosiloxane-co-dimethylsiloxane) CL to form materials \( A_n \) (a) and a one-step process to materials \( C_n \) in which the functionalization and cross-linking of P1 occur simultaneously in thin films (b).](image-url)
fit to the data points from 0 to 10% strain, while for the Young moduli at 50% and 100% a linear fit to the data points within ±10% strain was used.

For the synthesis of materials \( A_n \) the amount of catalyst was kept constant, while the amount of cross-linker used was gradually increased from 20, 40, 60, to 160 \( \mu \)mol per 0.5 g \( P_2 \). With increasing the amount of cross-linker used, the materials \( A_n \) became stiffer, except for \( A_4 \) which was softer as compared to \( A_3 \). This indicates that for \( A_4 \) an excess of CL was used which acts as a plasticizer. Material \( A_1 \) showed a strain at break of 198% and a \( Y_{10\%} \) = 68 kPa, material \( A_3 \) had a strain at break of 124% and a \( Y_{10\%} \) = 110 kPa, and material \( A_4 \) showed a strain at break of 141% and a \( Y_{10\%} \) = 80 kPa. All films prepared from materials \( A_n \) were rather sticky and difficult to work with. In an attempt to optimize the properties of \( A_n \), surface treated silica particles were used and the corresponding materials \( B_{0\%}, B_{2\%}, B_{5\%}, B_{10\%} \) with 0 wt%, 2 wt%, 5 wt%, and 10 wt% were prepared, respectively. As expected, with increasing silica amount in the elastomers, the materials become stiffer (Fig. 4). Thus, the elastic modulus at 10% strain increased from 79 kPa for \( B_{0\%} \), to 119 kPa for \( B_{2\%} \), and reached a maximum value of 210 kPa for \( B_{10\%} \). The strain at break increased with silica content from 175% to 265%, for materials \( B_{0\%} \) and \( B_{10\%} \), respectively. These materials were not sticky and therefore handling thin films of \( B_n \) was easier as compared to \( A_n \).

Materials \( C_{0\%}, C_{5\%}, C_{10\%} \) showed a strain at break of 125%, 64%, and 110%, and a tensile strength of 135 kPa, 385 kPa, and 362 kPa, respectively. Because the properties of materials \( C_{0\%} \) were inferior to those of \( B_{0\%} \), these materials were discarded and no further investigations were conducted with them.

Because of the good processability into thin films and promising mechanical properties of materials \( B_{n\%} \), further investigations were conducted. Cyclic relaxation tests showed no hysteresis for \( B_{2\%} \) and \( B_{5\%} \), and a very small hysteresis for \( B_{10\%} \), but all materials recovered immediately the initial shape after the stress was removed (Fig. 4). The very good elastic properties of materials \( B_{n\%} \) modified with silica are further supported by the dynamic mechanical analysis (DMA) tests conducted at room temperature and at frequencies between 0.01 to 10 Hz and at a stress value of 30 Pa. With increasing the amount of silica in materials \( B_{n\%} \), an increase in the storage modulus can be observed from 64 kPa, 136 kPa–242 kPa for \( B_{2\%}, B_{5\%}, B_{10\%} \), respectively (Fig. 5). The storage modulus remained almost constant from 0.01 Hz to 1 Hz and then increased slowly at higher frequencies. The loss factor at low frequency was below 0.1, but it increased at higher frequencies.

### Table 2

| Sample | Young’s modulus [kPa] | Strain break* [%] |
|--------|-----------------------|------------------|
|        | \( Y_{10\%} \) | \( Y_{50\%} \) | \( Y_{100\%} \) |
| \( A_1 \) | 68 ± 1 | 58 ± 1 | 50 ± 1 | 198 ± 28 |
| \( A_2 \) = \( B_{0\%} \) | 79 ± 1 | 75 ± 1 | 47 ± 1 | 175 ± 8 |
| \( A_3 \) | 110 ± 1 | 107 ± 1 | 87 ± 1 | 124 ± 3 |
| \( A_4 \) | 80 ± 1 | 77 ± 1 | 72 ± 1 | 141 ± 28 |
| \( B_{2\%} \) | 119 ± 1 | 73 ± 1 | 60 ± 1 | 248 ± 33 |
| \( B_{5\%} \) | 122 ± 1 | 67 ± 1 | 78 ± 1 | 252 ± 18 |
| \( B_{10\%} \) | 210 ± 1 | 161 ± 1 | 213 ± 1 | 265 ± 47 |
| \( C_{0\%} \) | 135 ± 16 | 87 ± 13 | 73 ± 11 | 125 ± 10 |
| \( C_{5\%} \) | 385 ± 75 | 245 ± 56 | – | 64 ± 9 |
| \( C_{10\%} \) | 362 ± 15 | 223 ± 7 | – | 110 ± 10 |

* The average strain at break of three different samples. The stress-strain curves of materials \( A_n \) and \( B_{n\%} \) were superimposable.
frequencies, which may indicate that these materials are not suitable for actuators operated at high frequencies.

The dielectric properties of \(B_{n\%}\) were investigated by dielectric spectroscopy at room temperature between 1 Hz to 10^6 Hz. Fig. 6 shows the variation in permittivity \(\varepsilon'\), dielectric loss \(\varepsilon''\), loss factor \(\tan(\delta)\) and conductivity \(\sigma\) for \(B_{n\%}\). Table 3 summarizes the dielectric properties measured at 10^3 Hz. Compared to conventional polydimethylsiloxanes elastomers, for which \(\varepsilon'\) is around 3, the newly developed materials show an increased permittivity of up to 4.7. The permittivity of the materials slightly decreased with the addition of silica. The conductivity values at low frequencies varied between \(1.3 \times 10^{-12} \text{ S cm}^{-1}\) for \(B_{2\%}\) and to \(1.7 \times 10^{-11} \text{ S cm}^{-1}\) for \(B_{10\%}\). An increase in permittivity at low frequencies was observed for all materials due to electrode polarization, which is increasing with the silica addition.

Materials \(B_{n\%}\) (except \(B_0\%\) which was too sticky to allow handling) as well as one commercial reference material, silicone Elastosil, were evaluated regarding their actuation strain at different electric fields using circular actuators having 8 mm carbon black electrodes. A biaxial prestrain of 30% was applied to all films to avoid wrinkling of the electrode during actuation. The prestrained films were placed between two rigid plastic frames that have an inner diameter of 25 mm. The voltage applied was increased gradually.

Fig. 4. The stress-strain curves for materials \(A_n, B_{n\%}\) and \(C_{n\%}\). Cyclical uniaxial extension tensile over 5 cycles at 50% strain for \(B_{2\%}, B_{5\%}\) and \(B_{10\%}\) of varying silica content.

Fig. 5. Dynamic mechanical analysis conducted on \(B_{2\%}, B_{5\%}\) and \(B_{10\%}\) elastomers at different frequencies and room temperature.

Fig. 6. Dielectric permittivity \(\varepsilon'\), dielectric loss \(\varepsilon''\), loss factor \(\tan(\delta)\) and conductivity \(\sigma\) of the \(B_{n\%}\) materials at room temperature and different frequencies.
using a step of 100 V. Fig. 7 shows the lateral actuation strain as a function of nominal electric field for \( B_{2\%} \) and Elastosil, where the nominal electric field is the applied voltage divided by the initial actuator thickness. From all materials investigated, \( B_{2\%} \) showed the poorest actuation, and the breakdown field was only 16.5 V/\( \mu \)m. Material \( B_{2\%} \) showed the best performance, a lateral actuation strain of 11.4% at an electric field of 20 V/\( \mu \)m. This material showed a maximum actuation strain of 12.8% when the breakdown was reached at 21.5 V/\( \mu \)m. As expected, the actuation of \( B_{2\%} \) occurred at higher electric fields as compared to \( B_{5\%} \), which is due to the fact that this material was stiffer as compared to \( B_{2\%} \). A maximum actuation of 14.5% at the maximum voltage of 29 V/\( \mu \)m was measured for \( B_{2\%} \). For the actuation strain of a different actuators made from \( B_{2\%} \), see Fig. 5.13. Because of the reduced elastic modulus and increased dielectric permittivity, the actuation of \( B_{2\%} \) occurred at significantly lower electric fields as compared to the regular silicone film, which has an elastic modulus in the range of 1.3 MPa (Fig. 7). The dielectric breakdown of our materials is not very high, likely because the actuators entered the electromechanical instability, an effect often observed in soft elastomers. Electromechanical instability can be avoided with elastomers that stiffen above a certain strain [46]. Unfortunately, our elastomers do not show strain-stiffening. One possible approach to alter the stress-strain curve and thus to increase the dielectric breakdown is by synthesizing prestrain-locked silicone interpenetrated networks [47,48]. Such networks showed better performance as compared to standard silicone films. Although interpenetrated networks can be in principle synthesized using the materials developed here, more synthetic effort has to be invested to achieve such them.

Cyclic actuation tests were also conducted for materials \( B_{5\%} \) and \( B_{10\%} \) at different frequencies of 0.33 Hz (for 50 cycles), 3.33 Hz (for 100 cycles) (Fig. 8) and show some hysteresis in actuation which increases with the frequency. DMA tests show for all materials \( B_{n\%} \) an increase in the mechanical losses with increasing the frequency. These mechanical losses are likely the reason behind the hysteresis observed in the cyclic actuation tests. Material \( B_{5\%} \) seems to have slightly lower hysteresis as compared to \( B_{10\%} \) which is in agreement with the DMA which shows slightly more mechanical losses for \( B_{10\%} \).

An actuator constructed from thin films of \( B_{2\%} \) (-24 \( \mu \)m) responded to rather low voltages (Fig. 8). For example at 600 V, which represents an electric field of 25 V/\( \mu \)m in an actuator, a lateral actuation strain of 4.5% was measured. We gradually increase the voltage of the actuator to 800 V (Fig. 5.14). The dielectric breakdown of this actuator was reached at 31 V/\( \mu \)m, at 750 V, where a lateral actuation strain of 7.2% was measured. Actuators operable at low voltages were reported before by Shea et al. [9] and Sheima et al. [42]. The first used a 3 \( \mu \)m thick polydimethylsiloxane based elastomer as dielectric, while the latter was 35 \( \mu \)m thick. A lateral actuation strain of 7.3% was observed at a voltage as low as 245 V (82 V/\( \mu \)m). Sheima used a polystyrene-lacel elastomer modified with nitrile groups which has a \( \varepsilon_{r} \) of 18 and an elastic modulus in the range of 350 kPa. A 35 \( \mu \)m thick actuator gave 7% lateral actuation strain at 300 V (8.6 V/\( \mu \)m). While this material was processible into thin films, the detachment of films from the substrate was tedious because the strain at break was only 80%. The most promising materials in the current work develop the interesting work is attractive. Because of the promising actuation at low voltages, further research will be carried out to reduce the mechanical losses, to increase the dielectric breakdown field, and to construct stacked actuators with these materials.

4. Conclusions

We have developed a synthetic strategy to polysiloxane elastomers modified with thioacetic groups which showed promising properties for actuation. They were prepared in two steps starting from polyvinylpolysiloxane which was chemically modified with thioacetic acid and subsequently cross-linked via a condensation reaction in presence of Sn catalyst. The mechanical properties of the obtained elastomers were tuned by blending with different amounts of surface treated silica. The glass transition temperature of the formed elastomers of -58 °C suggests an attractively broad temperature range in which these elastomers can be used. Because of the increased dielectric permittivity and the rather low elastic moduli, the actuators constructed with these elastomers responded to low electric fields. By reducing the thickness of the dielectric films, it was possible to construct devices that gave about 5.6% lateral actuation strain at 650 V, which is significantly lower as compared to most dielectric elastomers reported to date. Thus, the materials developed here are promising candidates as dielectric in actuators. Future efforts will be directed towards mastering the remaining challenges such as hysteresis between actuation cycles and lifetime evaluation.

Conflicts of interest

There are no conflicts to declare.

CRediT authorship contribution statement

Elena Perju: Data curation, Formal Analysis, Investigation, Methodology, Writing - original draft. Yee Song Ko: Investigation, Writing - Review & editing. Simon J. Dünkli: Investigation. Dorina M. Opris: Conceptualization, Funding acquisition, Project Administration, Supervision, Writing - review & editing.

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| Sample | \( \varepsilon_{r} \) | \( \sigma \) [S cm\(^{-1}\)] | Lateral actuation strain \( a \) [%] | \( s_{\text{max}} \) [%] | \( E_{\text{B act}} \) \( a \) | \( d \) [\( \mu \)m] \( b \) |
|--------|------------------|------------------|------------------|------------------|------------------|------------------|
| \( B_{2\%} \) | 4.7 | 1.3 \( \times 10^{12} \) | 1.8 | 5.8 | 7.1 | 16.5 | 90 |
| \( B_{5\%} \) | 4.58 | 5.0 \( \times 10^{12} \) | 1.8 | 5.1 | 11.4 | 13.8 | 21.5 | 87, 93 |
| \( B_{10\%} \) | 4.53 | 1.7 \( \times 10^{11} \) | 1.3 | 3.2 | 6.2 | 14.5 | 29.0 | 62, 69 |

\( a \) 30% bilateral prestrain was applied.

\( b \) thickness of the dielectric films used.
Fig. 8. Cyclic actuation at 0.33 Hz 50 cycles, at 3.33 Hz 100 cycles and at 6.66 Hz and 1000 V of B_{max} (left) and 1500 V of B_{max} (middle). The thicknesses of the actuators were 62 μm and 87 μm for B_{max} and B_{max}, respectively. Lateral actuation strain of a 24 μm thick film of B_{max} tested using a voltage ramp of 50 V per 2 s up to 650 V (right).

**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matdes.2019.108319.

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