



Silicone elastomers with high dielectric permittivity and high dielectric breakdown strength based on dipolar copolymers



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ABSTRACT

Dielectric elastomers (DEs) are a promising new transducer technology, but high driving voltages limit their current commercial potential. One method used to lower driving voltage is to increase dielectric permittivity of the elastomer. A novel silicone elastomer system with high dielectric permittivity was prepared through the synthesis of siloxane copolymers, thereby allowing for the attachment of high dielectric permittivity molecules through copper-catalysed azide-alkyne 1,3-dipolar cycloaddition (CuAAC). The copolymers have a high degree of chemical freedom, as the dimethylsiloxane spacer units between the functional groups, as well as the degree of functionalisation, can be varied. Thus, the best overall properties were obtained for an elastomer prepared with a copolymer with a 1200 g mol^{-1} dimethylsiloxane spacer unit and 5.6 wt% of the high dielectric permittivity molecule 1-ethynyl-4-nitrobenzene. Here, a high increase in dielectric permittivity (~70%) was obtained without compromising other favourable DE properties such as elastic modulus, gel fraction, dielectric loss and electrical breakdown strength.

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1. Introduction

Dielectric elastomers (DEs) are a new and promising transducer technology and are often referred to as ‘artificial muscles’, due to their ability to undergo large deformations when stimulated by electric fields. DEs consist of a soft and thin elastomeric film sandwiched between compliant electrodes, thereby forming a capacitor [1]. There are, however, certain issues that currently limit the commercial potential of the technology, including high driving voltages (several kVs) and short device lifetime. Consequently, there is a need to optimise DE materials, in order to overcome the current shortcomings of the technology. One of the most important components of a DE is the elastomer, as it governs dielectric permittivity and the breakdown strength of the DE. Polydimethylsiloxane (PDMS) elastomers are one of the most used materials for DEs, due to their high efficiency, fast response and low viscous losses, which means that the material can be operated at higher frequencies but with lower losses [2,3]. Furthermore, silicone elastomers can be operated across a broad temperature range [3]. The major disadvantage of silicone elastomers is that they

possess relatively low dielectric permittivity, which means that a high electrical field is necessary to actuate the DE. The necessary electrical field can be lowered by increasing the energy density of the elastomer, which can be done by creating elastomers with higher dielectric permittivity, i.e. with a higher ability to store electrical energy.

Dielectric permittivity of silicone elastomers has been improved by various techniques, most commonly through metal oxide fillers such as TiO_2 [4–9], BaTiO_3 [9–11], and Al_2O_3 [9]. A number of conducting fillers have also been employed, such as expanded graphite [12], carbon nanotubes [13,14], a copper-phthalocyanine oligomer [15,16], and calcium copper titanate ($\text{CaCuTi}_4\text{O}_{12}$) [17]. These composite-type systems, despite higher dielectric permittivity, exhibit major drawbacks such as large dielectric losses and reduced breakdown strengths, as increases in dielectric permittivity are achieved at loadings near the percolation threshold; thus, the systems are prone to filler agglomeration and consequent significant changes in mechanical properties. Furthermore, the Young’s modulus usually also rises significantly, which consequently reduces achievable strain. Various techniques have been developed in order to avoid agglomeration and increasing stiffness when raising dielectric permittivity, including the preparation of encapsulated polyaniline (PANI) particles with insulating polymeric shells that prevent the agglomeration of the PANI particles [18].

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Furthermore, blends of PDMS/poly(hexylthiophene) [19] and PDMS/polyethylene glycol [20] have been developed to increase homogeneity between the matrix (PDMS) and filler (high dielectric permittivity polymer) and to maintain suitable elastic moduli.

Another approach is to graft organic dipoles chemically to the PDMS elastomer network. This approach potentially leads to a more controlled network structure, as it does not rely on the efficient and perfect mixing of particles or blends. Furthermore, such covalently grafted systems should provide a more stable elastomer system upon continued activation of the material [21]. Several interesting systems have been developed. Kussmaul et al. [22] and Risse et al. [23] added the synthesised dipolar molecule *N*-allyl-*N*-methyl-*p*-nitroaniline, together with compensating amounts of a hydride-functional cross-linker, to a PDMS matrix and a commercial silicone elastomer system, respectively, in one-step processes. Madsen et al. [24,25] developed a new silicone-compatible cross-linker that allowed for specific functionalisation with high dielectric molecules at the cross-linking point of polymer networks. This was done using a copper-catalysed azide-alkyne 1,3-dipolar cycloaddition (CuAAC) reaction, which is orthogonal, so that functionality could be added without compromising the network-forming reaction. Racles et al. [26] developed another approach 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. High permittivities have been obtained by these methods, as two-fold increases of permittivity were usually achieved. When increasing dielectric permittivity, however, it is important to keep in mind other essential properties that govern the lifetime of the DE, such as elastic modulus, dielectric loss and electrical breakdown strength. Upon chemical manipulation of the polymer network these properties are also easily compromised.

The aim of this work is to create new and improved silicone elastomer systems with high dielectric permittivity while maintaining reasonable levels of other favourable properties such as viscous and dielectric losses and electrical breakdown strengths. We report herein on a new and controlled silicone elastomer system based on functionalisable siloxane copolymers that allow for the attachment of high dielectric permittivity molecules through CuAAC reactions. The synthesised copolymers allow for a high degree of chemical freedom, as several parameters can be varied during the preparation phase. Thus, the space between the functional groups can be varied, by using different dimethylsiloxane spacer units between the high dielectric permittivity molecules. Furthermore, the degree of functionalisation of the copolymers can be varied accurately by changing the feed of the high dielectric permittivity molecules. As a result, a completely tuneable elastomer system, with respect to functionalisation, is achieved. We have investigated how the different functionalisation variables affect essential DE properties, including dielectric permittivity, dielectric loss, elastic modulus and dielectric breakdown strength, and we have also determined the optimal degree of chemical functionalisation where important properties are not significantly compromised.

2. Experimental

2.1. Materials and methods

Hydride-terminated PDMS, DMS-H11 ($\bar{M}_w \approx 1200 \text{ g mol}^{-1}$ as determined by $^1\text{H NMR}$), 3-(chloropropyl)methyldimethoxysilane, allyldimethylsilane and a hydride-functional cross-linker, HMS-301, were acquired from Gelest Inc. The platinum cyclovinylmethyl siloxane complex catalyst (511) was purchased from Hanse Chemie. Hydride-terminated PDMS ($\bar{M}_w \approx 580 \text{ g mol}^{-1}$ as stated by supplier) and vinyl-terminated PDMS ($\bar{M}_w \approx 25,000 \text{ g mol}^{-1}$ as stated by

supplier) were purchased from Sigma–Aldrich. Silicon dioxide amorphous hexamethyldisilazane-treated particles (SIS6962.0) were purchased from Fluorochem. All other chemicals were acquired from Sigma–Aldrich and used as received, unless otherwise stated.

FTIR was conducted on a PerkinElmer Spectrum One model 2000 Fourier Transform Infrared apparatus equipped with a universal attenuated total reflection accessory on a ZnSe/diamond composite. Spectra were recorded in the range of 4000–650 cm^{-1} with 4 cm^{-1} resolution and 16 scans. ^1H and ^{13}C NMR experiments were performed on a Bruker 300 MHz spectrometer in CDCl_3 . Size-exclusion chromatography (SEC) was performed on a Tosoh EcoSEC HLC-8320GPC instrument equipped with RI and UV detectors and SDV Linear S columns from PSS. Samples were run in toluene at 35 °C at a rate of 1 mL min^{-1} , and molar mass characteristics were calculated using WinGPC Unity 7.4.0 software and linear polydimethylsiloxane (PDMS) standards acquired from PSS. Differential scanning calorimetry (DSC) measurements were performed on a DSCQ1000 from TA Instruments. Mechanical characterisation of the prepared films was performed with a TA Instruments TA 2000 Rheometer set to a 1% controlled strain mode, which was ensured to be within the linear viscoelastic regime. The measurements were performed with a parallel plate geometry of 25 mm in the frequency range of 100–0.01 Hz. Dielectric relaxation spectroscopy (DRS) was performed on a Novocontrol Alpha-A high performance frequency analyser (Novocontrol Technologies GmbH & Co.) operating in the frequency range 10^{-1} – 10^6 Hz at room temperature. The diameter of the tested 1 mm thick samples was 25 mm. Electrical breakdown strengths were measured on an in-house built device based on international standards. The polymer film (~150 μm) was slid between two spherical electrodes, and a stepwise increasing voltage was applied (50–100 V/step).

2.2. Syntheses

All reactions were carried out in a nitrogen atmosphere. Structures for ^{13}C NMR assignment can be found in the [Supporting Information](#).

2.2.1. α,ω -Allyl-poly((azidopropyl)methylsiloxane-co-dimethylsiloxane) with a 1200 g mol^{-1} pre-polymer **1**

1 was synthesised according to a recently published procedure [27] using 3-chloropropylmethyldimethoxysilane (7.23 g, 39.6 mmol), hydride-terminated dimethylsiloxane (1200 g mol^{-1}) (50 g, 41.7 mmol), tris(pentafluorophenyl)borane (2 mL, 0.04 M, 0.2 mol%), dimethoxydimethylsilane (19.4 g, 163 mmol), allyldimethylsilane (9.76 g, 97.4 mmol), NaN_3 (12.4 g, 191 mmol) and tetrabutylammonium azide (1.09 g, 3.82 mmol) to produce a slightly yellowish oil (50.0 g, 96.6%). IR (cm^{-1}): 2960 (C–H stretch); 2095 ($-\text{N}_3$ stretch); 1630 (C=C stretch); 1410 (Si– CH_2 stretch); 1260 (Si– CH_3 stretch); 1010 (Si–O stretch). $^1\text{H NMR}$ (CDCl_3 , δ_{H} , ppm): –0.05–0.09 (m, CH_3 –Si), 0.58 (m, –Si– CH_2 – CH_2 –), 1.50 (d, 4H, $^3J = 8.1 \text{ Hz}$, CH_2 – $\text{CH}=\text{CH}_2$), 1.65 (m, – CH_2 – CH_2 – CH_2 –), 3.23 (t, $^3J = 7.1 \text{ Hz}$, N_3 – CH_2 – CH_2), 4.83 (m, 4H, $\text{CH}=\text{CH}_2$), 5.77 (m, 2H, $\text{CH}=\text{CH}_2$). $^{13}\text{C NMR}$ (CDCl_3 , δ_{C} , ppm): –0.55–1.03 ($d + e + i$), 14.50 (f), 22.77 (g), 23.40 (c), 54.14 (h), 112.51 (a), 135.32 (b). SEC (toluene): $\bar{M}_w = 23,000 \text{ g mol}^{-1}$.

2.2.2. α,ω -Allyl-poly((azidopropyl)methylsiloxane-co-dimethylsiloxane) with a 580 g mol^{-1} pre-polymer **5**

5 was synthesised according to a recently published procedure [27] using 3-chloropropylmethyldimethoxysilane (15 g, 82.1 mmol), hydride-terminated dimethylsiloxane (580 g mol^{-1}) (45.7 g, 78.8 mmol), tris(pentafluorophenyl)borane (4.2 mL, 0.04 M, 0.2 mol%), dimethoxydimethylsilane (39.6 g, 329.4 mmol),

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