



Dielectric elastomers based on silicones filled with transitional metal complexes



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ARTICLE INFO

Article history:

Received 13 October 2015

Received in revised form

24 February 2016

Accepted 11 March 2016

Available online 22 March 2016

Keywords:

Dielectric elastomers

B. Strength

D. Electron microscopy

D. Mechanical testing

ABSTRACT

New composite dielectric elastomers with improved dielectric properties were prepared on the basis of polydimethylsiloxane rubber filled with new types of metal (Mn, Fe, Cr) complexes of the bis-azomethine derived from the condensation of a siloxane diamine, 1,3-bis(aminopropyl)tetramethyldisiloxane, with 3,5-di-bromo-2-hydroxybenzaldehyde. The tetramethyldisiloxane fragment from the structure of the complexes creates the premise for a good compatibility with the silicone matrix without the need for other surface treatments while the complexed metal unit through its polar character changes the dielectric properties of the material. The resulted composites crosslinked at room temperature as dielectric elastomer films were investigated in order to establish if such materials are suitable for use in the structure of electromechanical devices. The introduction of metal complexes in the polymer matrix has led to a slight decrease of the elastic domain but increased the relative dielectric permittivity with up to 100% and the electromechanical sensitivity of the materials, with negligible changes of the thermal behavior and overall moisture sorption capacity, thus preserving the chemical stability and hydrophobic character of siloxanes.

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1. Introduction

Among the classes of polymers that respond to external stimuli such as pH changes, light, temperature, magnetic or electric field, the electroactive polymers are very interesting for use as active elements in actuation and energy harvesting devices. This class of polymers is characterized by the capacity to be actuated almost instantaneously when an electric field is applied and therefore can convert electrical energy into mechanical work or vice versa.

The actuation strain is determined by the mechanical and electric properties of the dielectric elastomers, as shown by the equation of Pelrine [3]:

$$s_z = -p/Y = \epsilon' \epsilon_0 E^2 / Y \quad (1)$$

where Y – the compression modulus in the thickness direction, ϵ' – the dielectric constant, ϵ_0 – the permittivity of free space, E – the electric field.

From this equation results that it is desirable for a dielectric elastomer to have high ϵ' and very low conductivity and low modulus of elasticity: materials with high ϵ' values will generate more output stress and materials with low Y will produce more strain for the same value of the applied electric field.

In the field of the electroactive polymers, dielectric elastomer actuators are of special interest due to the intrinsic simplicity and the large achievable strains [1,2]. There are various categories of elastomers that were tested for use as dielectric elastomers in devices, among them being polydimethylsiloxane [4], polyurethane [5], and acrylate adhesive films [6].

Silicone rubber is a well-known dielectric elastomer tested for use in actuators [7]. Some of the properties that make it desirable for use in actuation devices are: large displacement with high precision and speed, durability and reliability, low stiffness (low Young's modulus), high breakdown strength [8]. Silicones have highly desired elastic behavior [9] but suffer from low values of dielectric constant, thus requiring high driving voltages to induce mechanical work [10].

Various materials were incorporated in silicone polymers for achieving large dielectric constant values: phthalocyanines [11],

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ferroelectric ceramics [12,13], conductive particles [14], and ceramic. The composites of polymers with phthalocyanines are influenced by the humidity in the air [15], the composites with ceramics require a large volume fraction of ceramic, which increases too much the value of the Young modulus [16] and in the composites with conductive fillers as the filler concentration approaches the percolation threshold the conductivity and loss factor values increase very much, affecting the behavior of the membrane [17]. Conductive metal particle fillers have some other unwanted characteristics: high values of Young modulus, thus stiffening the membrane in which they are used, and the high density of metal nanoparticles reduces the weight saving advantage of dielectric elastomers in comparison with mechanical actuation and energy harvesting [18].

In this work, we chose instead of the solutions presented above to use 3d transition metal complexes with bis-azomethine ligands containing siloxane spacers as fillers for a polydimethylsiloxane matrix with medium molecular weight ($M_n = 60,000 \text{ g mol}^{-1}$). The composite elastomer materials were processed as films and cross-linked by condensation at room temperature by using methyltriacetoxysilane as a well-known crosslinking agent leading to silicone films with good flexibility and excellent strain. We made a comparative study of PDMS-metallic clusters composite versus pure PDMS elastomer and highlighted the benefits of such fillers for the mechanical and dielectric properties of the prepared materials.

2. Experimental

2.1. Materials

Three metal complexes containing siloxane bond and manganese (M_1L), iron (M_2L), and chromium (M_3L) in their structure, were used as fillers and have been prepared according to procedure reported in Ref. [19] and described in [Supplementary information \(ESI\)](#).

Octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$, (D_4), supplied by Fluka AG, with the characteristics: b.p. = 175°C ; $n_D^{20} = 1.396$; $d_4^{20} = 0.955$, purity >99% (GC), was dried over sodium wire and freshly distilled before use.

Purolite CT-175, a styrene-divinylbenzene ion exchanger with $-SO_3H$ groups (4.1 mequiv./g) was dehydrated by azeotrope distillation with toluene and vacuumation at $110^\circ\text{C}/10 \text{ mm Hg}$ before use.

The used polydimethylsiloxane- α,ω -diol (PDMS) matrix, with molecular $M_n = 60,000$ as estimated on the basis of GPC analysis, was synthesized according to the already described procedure [20,21]: cationic ring-opening polymerization of octamethylcyclotetrasiloxane in the presence of a cation exchanger as catalyst.

Dibutyltin dilaurate (DBTDL) from Sigma–Aldrich, f.p. = 113°C , $d_4^{20} = 1.066$, was used as received.

Methyltriacetoxysilane (MTS) (yield ~75%, b.p.₁₀ = $95\text{--}97^\circ\text{C}$, $d_4^{20} = 1.17$, freezing point ~ 40°C) was prepared and purified in house by a procedure adapted from the literature [22] and described in Ref. [23].

2.2. Equipments

GPC measurements for the determination of the molar mass of polydimethylsiloxane were made in $CHCl_3$ on a PL-EMD 950 Chromatograph-Evaporative Mass Detector. The calibration was performed with polystyrene standards.

SEM images on film surfaces fractured in liquid nitrogen were taken with Electron Microscope (ESEM) type Quanta 200 operating until 30 kV with secondary and backscattering electrons in low or high vacuum mode.

The presence and ratio of metals were evidenced using an Energy-Dispersive X-ray Fluorescence (EDXRF) system EX-2600 X-Calibur SDD, as fast and non-destructive method, able to use very small amounts of the sample. The measurements were done in the same conditions for all the samples, i.e. current 30 μA , voltage 15 kV, time 200 s, range 10 keV in vacuum. The $K\alpha_1$ peak for elements and its intensity (in Counts) was identified. The samples were measured at least twice on each side.

DSC measurements were conducted with a DSC 200 F3 Maia (Netzsch, Germany). About 10 mg of each sample was heated in pressed and punched aluminum crucibles at a heating/cooling rate of $10\text{--}10^\circ\text{C min}^{-1}$. Nitrogen was used as inert atmosphere at a flow rate of 100 mL/min. The temperature range for the measurements performed with this instrument was $(-150) - (+150)^\circ\text{C}$, using a heating rate of $10^\circ\text{C min}^{-1}$. The temperature against heat flow was recorded. The baseline was obtained by scanning the temperature domain of the experiments with an empty pan. The enthalpy was calibrated with indium according to standard procedures.

The measurements for *Dynamic Vapor Sorption* were performed with an IGA-sorp Dynamic Vapor Sorption apparatus with resolution of 0.1 μg for 100 mg and the sample containers are made out of stainless steel micron size mesh. Before measurements, the samples are dried in a flow of dry nitrogen (250 mL/min) at room temperature until the weight of the sample was in equilibrium, with a relative humidity RH <1%. The measurements involve step increases of 10% for the relative humidity of the controlled flow of nitrogen and recording the mass change of the tested sample for each step, after the sample is first dried with a current of dry nitrogen.

Stress–strain measurements were performed on a TIRA test 2161 apparatus, Maschinenbau GmbH Ravenstein, Germany on dumbbell-shaped cut samples with dimensions of $50 \times 8.5 \times 4 \text{ mm}$. Measurements were run at an extension rate of 20 mm/min, at room temperature. All samples were measured three times and the averages of the obtained values were taken into consideration.

Dielectric spectroscopy was performed using the Novocontrol “Concept 40” broadband dielectric spectrometer (Hundsangen, Germany). The samples were mounted between gold platens and positioned in the Novocontrol Quatro Cryosystem. The dielectric experiment was carried out keeping the temperature fixed but sweeping the frequency. The temperature during testing of samples was 25°C and six decades (log scale) of frequency, i.e. $1\text{--}100,000 \text{ Hz}$, were scanned, with the dielectric constant (ϵ') and loss (ϵ'') were recorded in the frequency domain ($1 \text{ Hz--}1 \text{ MHz}$). The metal complexes were each grounded to a fine powder and then pressed with a 10-ton force press into a pill with 13 mm diameter and 1 mm thickness for dielectric properties tests, in the range of $10^0\text{--}10^6 \text{ Hz}$. The samples of dielectric elastomers (each with thickness <1 mm) were placed between gold plated round electrodes, the upper electrode having a 20 mm diameter.

The measurements for *electric breakdown strength* (EBD) were performed on a Trek installation consisting of: high-speed high-voltage power amplifier, function generator, and oscilloscope. All the samples were allowed to reach equilibrium with the environmental humidity by keeping for 24 h in the equipment room before measurements. The electrodes made of aluminum discs with 2.5 cm diameter were applied on the film samples and the measurements were performed with a voltage increase rate of 500 V s^{-1} at room temperature (20°C) and relative humidity RH ~70% and three tests were made for each sample, with the smallest value taken into account.

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