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Siloxane-based thin films for biomimetic low-voltage dielectric actuators

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ABSTRACT

Molecular beam deposition of siloxane-based polymer thin films was employed to realize single-layer dielectric elastomer actuators. With molecular weights of 6000 and 28,000 g/mol, vinyl-terminated polydimethylsiloxane (PDMS) was evaporated under high-vacuum conditions at crucible temperatures between 100 and 180 °C. Both deposition rate and realizable film thickness showed linear dependency with respect to the crucible temperature and were significantly higher for PDMS with lower molecular weight. Optimized growth conditions for 6000 g/mol were obtained at 180 °C with a deposition rate of (130 ± 5) nm per hour and a maximal film thickness of (530 ± 1) nm. Thermally induced polymerization was observed to limit the maximum accessible evaporation temperature for hydride-terminated PDMS above 180 °C and for vinyl-terminated PDMS above 230 °C. Ultraviolet (UV) light induced polymerization of vinyl-terminated PDMS was successfully established via radicalization at the functional vinyl end groups of the chains. Atomic force microscopy nanoindentation of the UV-polymerized network reveals that the oligomer chain length determines the elastic modulus of the polymer layer. Manufactured as asymmetric cantilever structures, the bending characteristic gave evidence that a 200 nm-thin film, activated in the voltage range between 1 and 12 V, maintains the actuation compared to a 4 μm-thick, spin-coated film, operated between 100 and 800 V. The force of the presented 200 nm-thin film cantilever actuator was about 10^{-4} N. This means that a multilayer actuator with more than 10^4 layers would reach forces comparable to natural muscles. Therefore, such nanostructures can qualify for medical applications for example to treat severe incontinence.

1. Introduction

Research on dielectric, electrically activated polymer (EAP) actuators for biomimetic implants focuses toward a significant reduction of the actuation voltages [1,2]. Micrometer-thick, silicone-based polymer films, prepared for example by spin-coating, require voltages in the range of several 100 V to a few kV to reach thickness strains of 25 to 48% [3,4]. Although the generation of high voltages through electromagnetic transformers is established, the limitations are large component size and often relatively low efficiency. Associated costs and potential health risks for medical device applications within the human body are further drawbacks. Therefore, one should either increase the dielectric constant of the polymer, for example by adding fillers in the elastomer network [5,6], or decrease the film thickness to reduce the operation voltage. Taking advantage of molecular beam deposition (MBD), we follow the pathway to reduce the film thickness to the sub-micrometer range. Compared with the well-established spin coating [7], solvents are not required. In order to reach the necessary actuation forces/pressures, however, stack actuators [8] have to be realized. This approach implies the reliable preparation of both polymer and stretchable electrode multilayers. Although MBD is known for excellent film homogeneity and relatively low defect densities, reliable MBD for polymer layers is challenging as heating in the crucible often causes dissociation to lower molecular weight components, pyrolysis, and even polymerization [9]. Such processes significantly modify evaporation rates and beam composition. These complex phenomena limits the evaporation temperature ranges typically to values between 150 and 450 °C and the deposition rates of the material to values below the desired range of about 1 μm/h or 1 monolayer/s. Nevertheless, once vacuum deposition of appropriate organic and electrode materials is available, one can prepare and characterize in situ film growth of multi-stack actuators under well-defined high-vacuum (HV) conditions.

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It is hypothesized that MBD of vinyl-terminated polydimethylsiloxane (PDMS) with molecular weights M_w of 6000 and 28,000 g/mol allows for the preparation of low-voltage DEAs under HV conditions. We know that siloxane-based polymers are dielectric elastomers in actuator configurations because of their elasticity and dielectric behavior. Strain levels of 30 to 40% were reached [10]. Especially the millisecond response and the acceptance as a biocompatible material for applications within the human body make silicone suitable for biomimetic applications in artificial muscles [10,11].

Cross-linking of PDMS is achievable through the presence of functional groups either at the chain end or in the form of a copolymer. Covalent bonding can be realized either by heat-induced curing using a catalyst [12] or applying ultra-violet radiation to force the photo-initiated reaction of radicals [13,14]. Mid-infrared (MIR)-spectroscopy, for example, can support the analysis of polymerization in vinyl-terminated PDMS under continuous illumination by means of a deuterium broadband lamp, avoiding any use of cross-linkers or catalysts.

To characterize the performance of planar EAP actuators one can place them on a rectangular cantilever and measure the bending as a function of the applied voltage. Recently, experimental results of such a cantilever bending system [15] were published. Here a 200 nm-thin silicone film was embedded between two Au electrodes each 10 nm-thin. This EAP actuator was placed on a 25 μm-thick polyetheretherketone (PEEK) cantilever to obtain an asymmetric structure, which notably bends through the application of a voltage as small as a few volts. The cantilever bending approach is known from atomic force microscopy and similar methods to be extremely sensitive, see e.g. [16]. Therefore, this approach has also been applied for the current study.

It can reasonably be expected that low-voltage DEAs prepared by means of biocompatible materials with intrinsic properties, which include millisecond response and remarkable energy efficiency [10], will not only become parts of medical implants but find applications in a wide variety of other fields.

2. Materials and methods

2.1. Silicones used

The study on thermal evaporation is based on vinyl-terminated dimethylsiloxane DMS-V21 (Gelest Inc., Morrisville, PA, USA), vinyl-dimethylsiloxane copolymer AB116647 (abcr GmbH, Karlsruhe, Germany) and hydride-terminated hydride-dimethylsiloxane copolymer HMS-H271 (Gelest Inc., Morrisville, PA, USA). Elastosil 745 A/B (Wacker Chemie AG, München, Germany) is solely used for spin coating of micrometer-thick films.

2.2. Thermal characterization of PDMS

The characterization of thermal degradation was carried out with thermal gravimetric analysis (TGA) using a TGA/SDTA851e system (Mettler Toledo, Greifensee, Switzerland). The data were acquired with a heating rate of 10 K per minute under nitrogen atmosphere for PDMS terminated with hydride and vinyl groups. The temperature at which thermally induced crosslinking occurs was determined by heating micrometer-thin films with a rate of 5 K per hour, starting from 150 °C under atmospheric conditions.

2.3. Thermal evaporation of PDMS

The deposition experiments were carried out under high-vacuum conditions. After bake-out at a temperature of 120 °C for two hours, a base pressure of 10^{-8} mbar was achieved using a Agilent SH-110 dry scroll pump (Swissvacuum Technologies SA, Marin-Epagnier, Switzerland) with a pumping speed of 110 l/min in combination with Agilent V-81-M turbo pump (Swissvacuum Technologies SA, Marin-Epagnier, Switzerland) with a pumping speed of 77 l/s for N_2 at a rotation frequency of 1350 Hz. We utilized a low temperature effusion cell (Dr. Eberl MBE Komponenten GmbH, Weil der Stadt, Germany) with precise regulation and high temperature stability in order to realize a homogeneous temperature distribution inside the crucible (NTEZ crucible with a volume of 2 cm^3). The temperature ramp of the evaporator was adjusted to a heating rate of 10 K per minute. When the shutter of the evaporator was opened a rise of the vapor pressure was detected to 1×10^{-6} mbar and up to 5×10^{-6} mbar at 120 °C and 180 °C source temperature, respectively. The pressure was detected with a FRG-700 Varian inverted Magneton Pirani Gauge (Swissvacuum Technologies SA, Marin-Epagnier, Switzerland) in front of the turbo pump, at a distance of 600 mm to the evaporator. The substrate was placed 300 mm in front of the evaporation source. A quartz crystal microbalance (LewVac, Ote Hall Farm, Burgess Hill, UK) served for the film thickness measurement.

2.4. Crosslinking of poly-dimethylsiloxane (PDMS)

Photodecomposition of Si-vinyl bonds occurs as a result of direct UV radiation with a wavelength below 300 nm [17]. To obtain the radicalization wavelength of the Si-vinyl bonds, a UV–vis measurement was performed with an Agilent 8453 Spectrometer (Agilent Technologies, Basel, Switzerland). The solvent hexane (HPLC grade, Fischer Scientific, Wohlen, Switzerland) was utilized.

The UV radicalization was realized with a deuterium D2 broadband UV lamp (Yuyu Lightning, China) covering a spectral range between 180 and 450 nm with maximum intensity at a wavelength of 210 nm.

Mid-infrared (MIR) spectroscopy with a Varian 670-IR spectrometer (Varian Inc., Santa Clara, USA) was used to investigate the resulting polymer network by analyzing the absorption bands of bond-vibrations from 600 to 4000 cm^{-1} with steps of 4 cm^{-1}.

2.5. Nanoindentation of PDMS cross-linked networks

The nanomechanical properties of the deposited polymers were quantified using the FlexAFM ARTIDIS system (Nanosurf AG, Liestal, Switzerland). The nominal spring constant of the cantilevers (CONTSCR, Nanosensors, Neuchatel, Switzerland) was determined to be 0.2 N/m using the Sader method [18]. The ARTIDIS system allows systematic sampling at selected points of interest. The size of each spot was either 15×15 μm^2 or 20×20 μm^2. Each spot was overlaid with a 64×64 points array. The array defines the locations of the 4096 nanoindentation tests. The FlexAFM ARTIDIS automatically acquired the data and generated a stiffness map and histogram for each spot. The power law method by Oliver & Pharr [19] was used to calculate the Young's modulus. The CONTSCR-cantilever tip radius was 7 nm. The approach was done with a speed of 6 μm/s while the measurements were taken at a force setpoint of 4 nN.

2.6. Preparation and mechanical characterization of asymmetric EAP structures

The polymer films, either grown by MBD (see Section 2.3) with a thickness of 200 nm or spin-coated (Spincoater WS-400B-6NPP, Laurell Technologies, North Wales, USA) with a thickness of 4 μm (Elastosil A/B at 3000 rpm for 150 s, heat cured for 2 h at 120 °C), were embedded between two 10 nm sputtered Au-electrodes (Magnetron sputter system, Balzers Union SCD040,