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Preparation of electromechanically active silicone composites and some evaluations of their suitability for biomedical applications

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ABSTRACT

Some films based on electromechanically active polymer composites have been prepared. Polydimethylsiloxane-α,ω-diols (PDMSs) having different molecular masses (Mv = 60 700 and Mv = 44 200) were used as matrix in which two different active fillers were incorporated: titanium dioxide *in situ* generated from its titanium isopropoxide precursor and silica particles functionalized with polar aminopropyl groups on surface. A reference sample based on simple crosslinked PDMS was also prepared. The composites processed as films were investigated to evaluate their ability to act as efficient electromechanical actuators for potential biomedical application. Thus, the surface morphology of interest for electrodes compliance was analysed by atomic force microscopy. Mechanical and dielectric characteristics were evaluated by tensile tests and dielectric spectroscopy, respectively. Electromechanical actuation responses were measured by interferometry. The biocompatibility of the obtained materials has been verified through tests *in vitro* and, for valuable films, *in vivo*. The experimental, clinical and anatomopathological evaluation of the *in vivo* tested samples did not reveal significant pathological modifications.

1. Introduction

Electromechanically Active Polymers (EAPs) with muscle-like properties such as high flexibility, strain, and energy density are a relatively new technology, which, depending on their fabrication and configuration, has numerous potential applications [1–8]. Compared to other smart materials, they have the advantage of being light weight, are relatively easy to be obtained and processed through scalable procedure, and in general are low cost [4–8]. The most attractive characteristic of EAPs is their ability to emulate the operation of biological muscle with large actuation strain and inherent vibration damping [9,10]. They are highly compliant thus easily interfacing with human or other environmental sources of motion. Combined with their high energy output, these features make them attractive for a variety of energy harvesting applications. Among the candidates for artificial muscles, the dielectric elastomers, as a class of electroactive polymers, have typical characteristics of these, such as, low density, are chap, easy to obtain, *etc.* of these *etc.* [2]. In addition, they have a versatile chemistry, and thus the performance of elastomer actuators can be tailored by choosing the appropriate elastomers, changing the cross-linking chemistry of polymer chains, adding functional entities, or modifying preparation techniques [11]. They have already found applications as artificial muscles and also mobile robots, micro-pumps, micro-valves, disc drives, flat panel speakers, intelligent endoscope, *etc.* [2]. A type of dielectric elastomer actuator consists of a soft elastomer sandwiched between two compliant electrodes generally made of carbon powder. When a voltage is applied between the electrodes, an electrostatic force is generated that compresses the elastomer thickness, expanding it in-plane [3]. Current artificial muscles are often limited due to the high power necessary to obtain reasonable displacement values [2]. Therefore, many studies are in progress now to create new materials and compositions suitable to act as performant artificial muscles.

Silicones and acrylic elastomers, both dielectric amorphous elastomers, have shown the best performance as artificial muscle actuator materials. Acrylic elastomer is a powerful material with regard to its strain response, but shows high viscoelastic losses, while silicone has a faster response time. Therefore, silicones can operate at frequencies greater than 1 kHz, while acrylic elastomers currently have an upper limit of 100 Hz. Silicones have also better coupling efficiency, good temperature and humidity tolerance making it an attractive actuator material [9].

In a previous work [12], we have reported a series of silicone composites filled with mixtures of commercial SiO_2 and TiO_2 powders

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in different ratios. While the first was introduced as reinforcement filler, the second was added in order to increase the dielectric constant of the material. A high molecular mass (Mv = 346 000) polydimethylsiloxane-α,ω-diol (PDMS) was used as matrix, which after the filler incorporation was crosslinked by radicalic mechanism with organic peroxides when organic bridges are formed between chains somewhat restricting the sliding of these in relation to each other. Thus, composites with higher dielectric constant values were obtained but showing also high values for Young's modulus. Traverse strain responses in the range 1.24–5.09 nm/V/mm thickness were obtained.

In order to decrease the modulus value, a request for applications in actuation, in the present paper we have prepared composites based on home-made PDMS with moderate molecular masses, lower than those used in our previous work but higher than those reported in the literature [13,14], and cross-linked through the ends of the chains with a trifunctional silane, methyltriacetoxysilane, without any catalyst. Either *in situ* generating titania or silica particles functionalized with polar groups were used as filler to increase the dielectric constant of the composites, without addition of silica as hardener. The composites processed as films were further investigated from points of view of mechanical, dielectric and electromechanical behaviours which are of interest for actuation. As a result of the structural changes (chain length, crosslinking pattern, filler), electromechanical performances different from the previous ones were obtained. In addition, some evaluations (*in vitro* biocompatibility tests and *in vivo* clinical and anatomopathological evaluation) on the suitability of the obtained composites for biomedical applications were performed this time.

2. Experimental

2.1. Materials

Fumed silica, Aerosil 380 (Degussa), 100% purity, specific surface 380 m^2/g, particle diameter 0.003–0.015 μm was treated with 3-aminopropyltriethoxysilane (APTES) in vapour state (NH_2–SiO_2).

Polydimethylsiloxane-α,ω-diols, PDMSs, of different molecular masses, PDMS1 (Mv = 44 200) and PDMS2 (Mv = 60 700) were prepared according to the already described procedure [15]: cationic ring-opening polymerization of octamethylcyclotetrasiloxane in the presence of a cation exchanger as catalyst.

Methyltriacetoxysilane, MTAS, $(CH_3CO_2)_3SiCH_3$, assay—90%, bp—94–95 °C/9 mm Hg, and density—1.20 g/mL at 20 °C (Aldrich).

Titanium(IV) isopropoxide, $Ti[OCH(CH_3)_2]_4$, TIP, assay ≥97.0%, bp = 232 °C, and density = 0.96 g/mL at 20 °C (Aldrich).

Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly (ethylene glycol), Pluronic L 31, average M_n ~1,100, PEG — 10 wt.%, surface tension — 47 dyn/cm, 25 °C, and 0.1 wt.% in H_2O (Aldrich).

2.1.1. Materials and reagents for in vitro tests

DMEM (Dulbecco's Modified Eagle Medium, with 4500 mg/mL glucose, 110 mg/L sodium pyruvate and 0.584 mg/L L-glutamine); BFS (Bovine Fetal Serum, heat inactivated, non-USA origin, sterile-filtered, suitable for cell culture); P/S/N (Penicillin/Streptomycin/Neomycin solution with 5000 units penicillin, 5 mg streptomycin and 10 mg neomycin/mL, sterile-filtered, suitable for cell culture); PBS solution (Phosphate Buffered Saline solution, sterilised, suitable for cell culture); MTT (3-(4,5-Dimethyl-2-thiazolyl)-2,5-diphenyl-2H-tetrazolium bromide); and DMSO (dimethyl sulfoxide). All materials and reagents were purchased from Sigma-Aldrich unless otherwise mentioned.

2.2. Measurements

The surface images were obtained with a Solver PRO-M scanning probe microscope (NT-MDT, Russia), in atomic force microscopy (AFM) configuration. Rectangular silicon cantilevers NSG10 (NT-MDT, Russia) with tips of high aspect ratio were used. All images were acquired in air, at room temperature (23 °C), in tapping mode, at scanning frequency of 1.56 Hz. The scan length ranged between 5 μm and 20 μm.

Stress–strain measurements were performed on dumbbell-shaped cut samples from thin films on a TIRA test 2161 apparatus, Maschinenbau GmbH Ravenstein, Germany. 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. To test the fatigue resistance, cyclic tests were performed. Five cycles were run with: stationary time at maximum strain — 5 s, stationary time at minimum strain — 5 s, maximum strain — 100%, minimum strain — 2%, and applied stress is similar with the one read in the breaking stress–strain curve tested previously.

Novoncontrol setup (Broadband dielectric spectrometer Concept 40, GmbH Germany), integrating an ALPHA frequency response analyzer and a Quatro temperature control system, was used to investigate the dielectric properties of the polymer composites over a broad frequencies window, 10^0–10^6 Hz, at room temperature. The bias voltage applied across the sample was 1.0 V. Samples having uniform thickness in the 0.15–0.38 mm range were placed between gold plated round electrodes, the upper electrode having a 20 mm diameter.

The electromechanical actuation measurements were made using an AGILENT5529A LASER interferometer with 10 nm resolution setup to measure linear displacement. The samples were placed on the reference surface between two copper electrical electrodes (20 mm × 20 mm), the sandwich being pressed by the retro-reflector of the interferometer which followed the deformation of the samples as various electrical voltages were applied to the electrodes.

2.3. Procedure

2.3.1. Preparation of series I (samples **1**–**3**)

3.000 g (0.049 mmol) PDMS having $\overline{Mv}$ = 60 700 was mixed with various amounts of TTIP (0, 0.3, and 0.6 g corresponding to the samples **1**, **2**, and **3**, Table 1) by magnetically stirring for 60 min, after that 0.42 g (1.909 mmol) MTS (8%) was added and the stirring continued for another 5 min. Then, the mixture was poured as thick film on a Teflon substrate and left to crosslink under the influence of the atmospheric moisture.

Table 1
Recipes for preparing composites.

Sample	Mv of PDMS	PDMS amount, g	Surfactant, g	Filler		MTAS, g
				Added precursor, g (type)	Calculated filler, wt.%	
Series I						
1	60700	3.0	–	–		0.42
2	60700	3.0	–	0.3 (TIP)	2.7 (TiO_2)	0.42
3	60700	3.0	–	0.6 (TIP)	5.4 (TiO_2)	0.42
Series II						
4	44200	7.0	0.21	0.21 (NH_2–SiO_2)	2.9 (NH_2–SiO_2)	0.67