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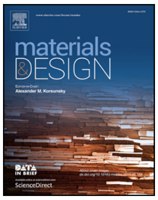

Ceramic nanotubes-based elastomer composites for applications in electromechanical transducers

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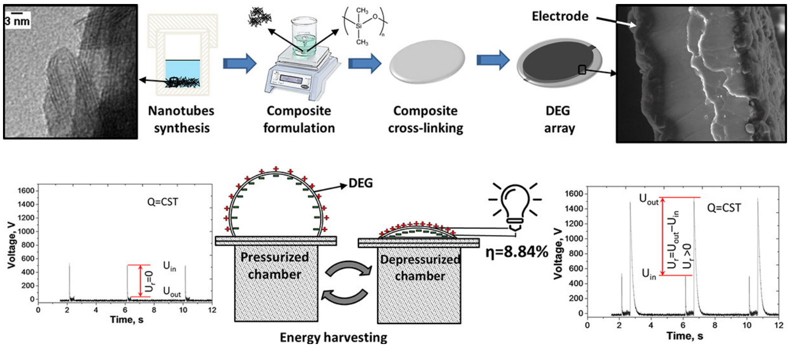
HIGHLIGHTS

- 2 or 5 wt% TiO_2 nanotubes added increases the silicones dielectric permittivity at 0.1 Hz of 2.4 and 3.6 times, respectively
- Surface treatment of TiO_2 with hexamethyldisilazane leads to an 18.9% increase in the dielectric strength of the composite.
- Composites show up to 4.2% lateral strain at 40 $V \cdot \mu m^{-1}$ applied electric field.
- Composite film sandwiched between electrodes behaves like an energy generator.
- An energy conversion efficiency up to 8.84% at 2.5 $V \cdot \mu m^{-1}$ is reached.

GRAPHICAL ABSTRACT



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ABSTRACT

Titanium dioxide-based nanoparticles with nanotube morphology were synthesised and used in low fractions (2 and 5 wt%) as dielectric permittivity enhancers for high molecular weight polydimethylsiloxane matrix (M_n = 350,000 g mol^{-1}). In order to ensure good dispersability in, and compatibility with the silicone matrix, the filler was treated with hexamethyldisilazane. The polymer composites were processed as films and stabilized by condensation of the chain ends with a trifunctional silane, resulting in low density cross-linking elastomers. The films were characterized for morphology, dielectric and mechanical behavior. The evaluated properties were compared with those measured in similar conditions for a pure cross-linked silicone matrix and a commercial dielectric elastomer taken as references. The results indicated an increase in dielectric permittivity (up to 33%), as a result of filler incorporation without significantly damaging dielectric strength (>60 V μm^{-1}) and mechanical properties (elastic modulus as low as 0.4 MPa and high strains at break up to 600%). Electromechanical measurements revealed the best performance in actuation for the composite containing 2 wt% nanotubes (4.2% lateral strain at 40 $V \cdot \mu m^{-1}$). Initial tests for energy harvesting performed with dielectric elastomer generators built with the same material sandwiched between two highly compliant electrodes yielded promising energy conversion efficiency (up to 8.84% at 2.5 $V \cdot \mu m^{-1}$).

1. Introduction

Dielectric elastomers are smart, highly deformable polymer-based materials belonging to Electroactive Polymers (EAP) family, and are useful as active elements for electromechanical transducers [1]. They

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can be used either as actuators capable of high strains (of >100%) when applying an electric field [2], but also as soft capacitors able to harvest energy difference resulting from pumping charges from a low to a higher electrical potential under the action of a mechanical force [3]. Different forms of mechanical energy (human motion [4–8], ocean waves [9,10], etc.) can be converted into electrical energy with such systems. The performance criteria required for such applications are: low Young's modulus, low plastic deformation, high tensile elongation, high breakdown voltage and dielectric permittivity and low manufacturing costs. Among the large number of elastomers tested for such applications, three classes have proven to be the most promising: acrylic, polyurethanes and silicones [11–16] but none of them meets all the requirements listed above. Thus, acrylic elastomers show high actuation strains, high energy density, coupling coefficient and efficiency [17,18] but also high viscoelastic losses. Polyurethanes have high values for dielectric permittivity but cannot develop large strains and show high sensitivity towards humidity [17,19]. Silicones meet most of these requirements, having high energy density and deformation capacity, low viscoelastic loss, high coupling efficiency. In addition, their great advantage consists in that they are able to operate in a wide range of temperature and humidity without significant alteration of the properties. Thus, silicones have become serious candidates for energy harvesting applications, one of the main commercially available soft capacitor material so far, being PolyPower™ Silicone from Danfoss and consists in silicone elastomer sheet with compliant metal electrodes [3]. A generator based on such silicone film covered with silver electrodes harvests 94.5 mJ for a 15% strain and at a constant charge test carried out on a simple rectangular corrugated sample of 20 cm long [20]; on the same material, another study reports the generation of 6.52 mJ/cm^3 with 0.986% efficiency [4]. However, silicones have low dielectric permittivity requiring relatively large voltages to operate as soft capacitor actuators [3]. Therefore, new formulations are constantly developed based on modified silicones, or commercially available elastomers with different additions, combining required performances in a single material and limiting their disadvantages. Among other aspects, it has been studied the effect of various fillers such as metal oxides, ceramic materials or conductive polymers, metal complexes in form of nanoparticles [21]. However, although incorporation of the fillers leads to increase in dielectric permittivity, reasonable values are sometime obtained near the percolation threshold, when these are accompanied by large current losses and decrease in breakdown strength [22,23]. Therefore, solutions to minimize these undesirable effects are an important challenge under intense research. In fact, improving properties for such elastomer formulations depends on multiple factors, namely the filler nature, concentration, particle size and shape, as well as the degree of compatibility, dispersion and orientation within the matrix. One of the fillers used in this purpose is titanium dioxide, which has been reported to successfully enhance the dielectric permittivity of the resulted materials [24].

There are relatively few studies about silicones filled with titanium dioxide (commercially available powder [25–28], *in situ* generated by sol-gel [29,30], or nanotubes synthesised by hydrothermal technique [31,32]), most of which are intended for applications as antibacterial agents [26], UV-ray attenuator [29] or dental flowable composites [32] and even less focused on electromechanical applications. The first report on the incorporation of rutile-type titanium dioxide powder within a silicone matrix (a room temperature three-component system, Cine-Skin), aiming to increase the electromechanical response for dielectric elastomer actuation, showed traverse strain and stress values more than eight and four times, respectively, higher than the corresponding values generated with the pure polymer matrix for analogous electrical stimuli [28]. A recent study reported how a commercial silicone, POWERSIL® XLR LSR, filled with high loading (35%) of nano-sized titanium dioxide (TiO_2) particles showed improved actuation response (10% strain for a 50 V·μm^{-1} electric field) as compared with neat matrix [25]. In a previous approach, we incorporated TiO_2 powder in increasing percentages, between 0 and 50 wt%, into a high molecular mass polydimethylsiloxane (PDMS) already mixed with 28 wt% silica, the resulted materials being cured by heating in the presence of peroxide. An increase of dielectric permittivity with the amount of TiO_2 added was achieved, but also a stiffening of the materials was observed. However, the flexibility still remained within the limits that allowed obtaining reasonable electromechanical (both actuation and harvesting) responses [27]. Among the above-mentioned features required, the particle geometry has an important role. Thus, a geometry such as plate or sphere, sheet-like, nanotubes, or polyhedral nanoparticles can have a large impact on the properties of the resulted material, since it can affect both surface energy and surface to volume ratio [33]. It has been proved that the orientation of the titanium dioxide nanotubes in a chain structure by dielectrophoretic effect using an alternative electric field within the raw polymeric matrix (Sylgard 184 - silicone elastomer), followed by cross-linking, boosted the dielectric permittivity and reduced the dielectric loss in the orientation direction.

In this paper, we prepared and thoroughly characterized TiO_2-based nanotubes. These were incorporated within a silicone matrix consisting in a high molecular weight polydimethylsiloxane-α,ω-diol curable at room temperature. The morphology, mechanical and dielectric properties, as well as electromechanical response of the cross-linked materials processed in films were measured.

2. Experimental

2.1. Materials

Titanium(IV) dioxide nanoparticles (TiO_2), rutile crystal structure, 99% purity (dried in vacuum at 100 °C before any further use) and hexamethyldisilazane (HMDS), $d = 0.774$ g/mL (25 °C), ≥98% assay (GC) were supplied by Fluka. Polydimethylsiloxane-α,ω-diol (PDMS) with the average numerical molecular weight of 350,000 g·mol^{-1}, as was estimated by GPC, was synthesised according to the procedure described in Ref. [34], by bulk polymerization of octamethylcyclotetrasiloxane catalysed by H_2SO_4 at room temperature. Dibutyltindilaurate, DBTDL, (95%) and triethoxymethylsilane, TEMS, (≥97%) were purchased from Sigma Aldrich and used as received. Carbon Black Super P Conductive (CB-P), 99+% (metal basis), was purchased from Alfa Aesar, dried overnight in vacuum at 100 °C and hydrophobized by surface treatment with a silane (TEMS) in vapour state to ensure compatibility and good dispersion within the silicone polymeric matrix. CB-P was used as filler for PDMS, the same used as matrix for dielectric composites, to make by an own, original approach, electrodes for energy harvesting experiments. 3 M VHB 4910 acrylic tape (AR – acrylic rubber) with 1 mm in thickness is commercially available. Elastosil silicone film (EL FILM 2030) with 100 μm thickness was acquired from Wacker Chemie, Germany.

2.2. Procedure

2.2.1. Preparation of TiO_2 nanotubes

Of the methods presented over time in the literature [35–40], three of them have been noted as the most used for preparation of titania-based nanotubes: anodic oxidation [41], template method [42] and wet chemical method [43]. In this work, we synthesised TiO_2-derived nanotubes by adapting the Kasuga method [44], which consists in hydrothermal treatment of commercial TiO_2 nanoparticles at elevated temperatures with 10 M NaOH concentration. This is a chemical method based on self-assembly, without using a template that allows obtaining TiO_2 with nano-sized tubular morphology at low temperatures. Most of the other methods require a post heat treatment to obtain crystalline nanoparticles [43,45,46]. The parameters that we used were the same as described in Ref. [44] (150 °C, 72 h and the volume occupied in autoclaves was 70%), except the NaOH concentrations (5 M and 10 M) and starting oxide (rutile-type structure instead of anatase). Thus, in two