



Polydimethylsiloxane–barium titanate composites: Preparation and evaluation of the morphology, moisture, thermal, mechanical and dielectric behavior



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ABSTRACT

Polydimethylsiloxane- α,ω -diols were used as matrix for barium titanate particles to obtain electroactive elastomeric composites. Filler particles were previously treated with a surfactant to improve the compatibility with and dispersibility in the matrix. The composites, processed as films and crosslinked with methyltriacetoxysilane, were investigated from point of view of the morphology, moisture sorption and thermal properties, as well as mechanical and dielectric behavior. Maximum strain value of 850% at 0.32 MPa and dielectric permittivity of 4.41 at 10 Hz and 20 °C were obtained. Two parameters of interest for potential future application of such materials in electromechanical devices (actuation or harvesting), electromechanical sensitivity and harvesting energy capacity, were estimated and discussed in correlation with the molecular mass of the polymeric matrix and the content of the active filler.

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1. Introduction

Silicone rubber is a well-known dielectric elastomer which is used in electromechanical transducers, devices able to convert electrical energy into mechanical one and vice versa [1]. A promising application of these materials, which is currently being investigated, is the generation of electricity from ocean waves energy [2,3]. For such applications, large displacement with high precision and speed are required, together with durability and reliability. In order to obtain high actuation strain, a material with low stiffness (low Young's modulus), high breakdown strength, and high permittivity is desired [4]. Silicones have highly desired elastic behavior, their representative polydimethylsiloxane (PDMS) being known for its unusual rheological/flow properties [5]. The polarizability of the Si–O bond that constitutes a premise for a high dielectric constant is higher as compared to organic nonpolar polymers (e.g., polyethylene), but in reality, this is not so much due to the side methyl groups (in the case of PDMS), which prevent Si–O dipoles from approaching each other too closely) [6]. In order to increase the dielectric constant, the polysiloxanes are chemically modified by attaching polar groups, such as N-allyl-N-methyl-4-nitroaniline [7] and cyanalkyl [8] to the silicon atoms. Fillers are often used to

enhance the dielectric as well as the mechanical properties of the silicones [9]. The use of high permittivity inorganic fillers is a well-established technique to improve the dielectric constant of a polymer matrix. Various permittivity values can be achieved by changing the type and percentage of the filler in the substrate. Based on the literature data, it can be identified mainly three types of fillers used to improve the permittivity of the dielectric elastomer actuator: ceramic particles with a high dielectric constant, such as titanium dioxide, barium titanate, magnesium niobate, lead magnesium niobate–lead titanate, and strontium titanate [9–13]; conductive particles, such as carbon nanotube, carbon black, copper–phthalocyanine/polyaniline [14] and short fibers [11]; highly polarizable conjugated polymer, such as undoped poly(3-hexylthiophene), polyaniline, polythiophene incorporated by blending or as nanoparticles [9,11]. BaTiO₃, a ferroelectric crystal which exhibits spontaneous polarization and high electrical breakdown strength is often used in this aim [15]. Thus, it has been incorporated in different polymeric matrix [12], like epoxides, polystyrenes [16], polyimides, polyetherimides [17], poly-ethylene-glycol-diacrylate (PEGDA) [18], polyurethane [19], acrylics [20,21], etc. This was also used as filler for PDMS [22]. The effect of BaTiO₃ nanoparticles on electrical and mechanical properties were extensively studied and found that dielectric constant of nanocomposites increases significantly with the increase in BaTiO₃ concentration where as the volume resistivity decreases continuously [22].

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Commercially available barium titanate with particles of different shape and size or prepared by certain procedure to obtain a certain size and shape were used [23,24]. There are a few commercial dielectric elastomer materials available, these mainly including acrylic VHB (Very High Bond – a 3M tape) foil, silicones, polyurethanes, and some polystyrene/polybutadiene copolymers, acrylics and acrylonitrile butadiene rubber [13,25]. In general, commercially available room temperature vulcanization formulations based on low molecular weight polydimethylsiloxane were used as matrix in such cases and either addition (hydrosilylation) or condensation (with tetrafunctional silanes) mechanisms were used to convert the fluid compounds in silicone elastomers.

Different from the literature, in this paper, home prepared PDMSs of different molecular masses, higher as compared with those used in other studies, were used as polymeric matrix in which surface-treated barium titanate was incorporated in different percents. The composites were processed as films and cross-linked by condensation at room temperature with a trifunctional silane, methyltriacetoxysilane. The morphology, moisture sorption, thermal, mechanical and dielectric properties were investigated.

2. Experimental

2.1. Materials

The polydimethylsiloxane- α,ω -diols, PDMSs, were synthesized according to the already described procedure [26]: cationic ring-opening polymerization of octamethylcyclotetrasiloxane in the presence of a cation exchanger as catalyst. Molecular masses were estimated on the basis of GPC analysis as being those presented in Table 1. Barium titanate (BaTiO_3), CO, with particle size $<3 \mu\text{m}$ according to supplier (Fluka AG) was investigated through SEM and TEM to determine the particle size and shape (Fig. 1ESI), while BET area ($11.419 \text{ m}^2/\text{g}$) we estimated on the basis of water vapor sorption isotherms registered in dynamic regime (Fig. 2ESI). This and PLURONIC L-31, HO-poly(ethyleneglycol)-*block*-poly(propyleneglycol)-*block*-poly(ethyleneglycol)-OH ($M = 1100$, $d_{25}^{25} = 1.02$, PEG, 10 wt%) were purchased from Fluka AG. Methyltriacetoxysilane (MTAS) was prepared and purified in house (b.p. = $94\text{--}95 \text{ }^\circ\text{C}$, $d_4^{20} = 1.20$).

2.2. Equipments

GPC measurements were made in CHCl_3 on a PL-EMD 950 Chromatograph – Evaporative Mass Detector. The calibration was performed with polystyrene standards.

For SEM studies, the as obtained thick films (foils) were cryo-fractured and the cross-section surface was examined with an

Table 1
Feed compositions in pph used for the preparation of the dielectric elastomers (100 pph PDMS, 8 pph crosslinker, MTAS)0.

Sample	PDMS/100 pph			BaTiO_3 (pph)	Surfactant (pph)
	Polymer code	M_n	$I = M_w/M_n$		
ABI MB0	ABI	84,000	1.4	0	0
ABI MB1	ABI			1	1
ABI MB2	ABI			2	2
ABI MB5	ABI			5	5
ABII MB0	ABII	55,000	1.4	0	0
ABII MB1	ABII			1	1
ABII MB2	ABII			2	2
ABII MB5	ABII			5	5
ABIV MB0	ABIV	142,000	1.7	0	0
ABIV MB1	ABIV			1	1
ABIV MB2	ABIV			2	2
ABIV MB5	ABIV			5	5

Environmental Scanning Electron Microscope (ESEM) type Quanta 200, operating at 30 kV with secondary electrons in low vacuum mode. Dynamic water vapor sorption (DVS) capacity of the samples was determined in the relative humidity (RH) range 0–90% by using the fully automated gravimetric analyzer IGAsorp produced by Hiden Analytical, Warrington (UK). Thermogravimetric (TG) measurements were conducted on a STA 449 F1 Jupiter device (Netzsch, Germany) in nitrogen atmosphere, in the temperature range $25\text{--}700 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. DSC measurements were conducted with a DSC 200 F3 Maia (Netzsch, Germany) in nitrogen atmosphere at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. Stress-strain measurements were performed on 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. The acquired data were processed with MatLab software. Cyclic tensile stress tests were performed on the similar samples between 2% and 100% strain. The maximum force applied was tensile stress value as determined by previously test. Five stretch-recovery cycles were registered. The stationary time at minimum and maximum applied stress was 5 s. Dielectric spectra were registered on a Novocontrol “Concept 40” broadband dielectric spectrometer (Hundsangen, Germany), at room temperature in the frequency domain 1 Hz–1 MHz. Dielectric strength measurements were made at PERCRO Laboratory – TeCIP Institute – Scuola Superiore Sant’Anna, Pisa, Italy, on a home-made installation consisting in an USB-based oscilloscope, a signal generator and a direct current (DC) four-quadrant high-speed HV power amplifier with $\pm 10 \text{ kV}$ and $\pm 10 \text{ mA}$ voltage and current ratings. Brass electrodes were used to obtain breakdown voltage. The tests were made at 60 Hz and a 2000 V/s rate of voltage increase. The experiments were performed at room temperature and the surrounding medium was air. All the tested samples were brought into equilibrium with the atmospheric humidity. The harvesting tests were performed on a home-made set-up (Fig. 3ESI) [27]. Electrodes of dimensions $20 \times 20 \text{ mm}$ made of simple sticlotextolit (glass fibers impregnated with formaldehyde resin) plated with copper were placed on both sides of the sample. The connecting wires were attached to the electrodes by soldering and were connected to the measurement terminals of an oscilloscope Tektronix DPO4032 (350 MHz, 2.5GS/s). A steel ball ($m = 7.1 \text{ g}$) was left to fall freely from a height of 100 mm in the center of the upper electrode surface. The signal wave form and the voltage levels corresponding for the peaks at the impact of the ball on contact surface of the sensor were monitored and were acquired (Fig. 4ESI). More sets of measurements there have been done for each sample, finally being considered more representative three results for each.

2.3. Procedure

Pre-established amounts of barium titanate microparticles were mixed with surfactant PLURONIC L-31 then chloroform was added to obtain a less viscous mixture which was transferred over PDMS. Then MTAS, as crosslinker (Table 1), was added and stirred thoroughly until the components formed a homogenous mixture. The resulted mixture was sonicated for 10 min in order to remove all the air bubbles trapped in the mixture and then was used to obtain thin films (of about 0.5–1 mm thickness) by pouring in a Teflon mold ($15 \times 5 \text{ cm}$). The samples were maintained in air at room temperature for 24 h and subsequently the formed films were easily peeled off from the substrate. The films were then kept in the laboratory environment about two weeks for aging before characterization by different techniques.

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