



Dielectric silicone elastomers with mixed ceramic nanoparticles



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ABSTRACT

A ceramic material consisting in a zirconium dioxide-lead zirconate mixture has been obtained by precipitation method, its composition being proved by wide angle X-ray powder diffraction and energy-dispersive X-ray spectroscopy. The average diameter of the ceramic particles ranged between 50 and 100 nm, as revealed by transmission electron microscopy images. These were surface treated and used as filler for a high molecular mass polydimethylsiloxane- α,ω -diol (Mn = 450,000) prepared in laboratory, the resulted composites being further processed as films and crosslinked. A condensation procedure, unusual for polydimethylsiloxane having such high molecular mass, with a trifunctional silane was approached for the crosslinking. The effect of filler content on electrical and mechanical properties of the resulted materials was studied and it was found that the dielectric permittivity of nanocomposites increased in line with the concentration of ceramic nanoparticles.

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1. Introduction

Silicone rubber is a well-known dielectric elastomer, which can be used for applications such as actuation and for devices able to convert electrical energy into mechanical energy and vice versa [1]. For such applications it is necessary to have a material with low stiffness (low Young's modulus), high breakdown strength and good values for dielectric permittivity [2].

Silicones manifest highly elastic behavior due to the high flexibility of the siloxane bond [3]. While the polarizability of the Si–O bond in polydimethylsiloxane (PDMS) is higher than that of organic nonpolar polymers (e.g., polyethylene), the side methyl groups prevent Si–O dipoles from approaching each other too closely [4], thus the dielectric permittivity of PDMS is very low (ca. 3). Therefore, the siloxanes are chemically modified by attaching polar groups to the silicon atoms, such as *N*-allyl-*N*-methyl-4-nitroaniline [5] or cyanoalkyl [6,7], for the purpose of obtaining large values for the dielectric permittivity.

The incorporation of inorganic fillers with high dielectric permittivity in a polymer matrix is a well-known technique to improve the dielectric constant of the material [8–11] and the use of such fillers sometimes also leads to increasing in mechanical strength. Depending on its type and proportion, the filler can lead to visible changes of the permittivity values of the final material [12].

There are different types of fillers that are generally used for improving the permittivity of the dielectric elastomer: (i) ceramic particles with a high dielectric constant—most used are titanium dioxide, barium titanate, magnesium niobate, lead magnesium niobate-lead titanate, and strontium titanate nanoparticles [13–15]; (ii) conductive particles, such as carbon nanotubes, carbon black, copper-phthalocyanine/polyaniline [16]; (iii) highly polarizable conjugated polymers—undoped poly(3-hexylthiophene), polyaniline, or polythiophene incorporated by blending [10,14,17–21].

In general, commercially available room temperature vulcanization silicone formulations are used to design elastomers for actuators. These are based on low molecular weight polydimethylsiloxane fluid compounds which are converted into silicone elastomers by addition (hydrosilylation) or condensation reactions. Besides siloxanes, there is also a large variety of commercial dielectric elastomer materials available: acrylic VHB foil, polyurethanes, polystyrene/polybutadiene copolymers [22], acrylics and acrylonitrile butadiene rubber [18–21].

In this paper a custom made high molecular weight PDMS was used as polymeric matrix in which different percentages of surface-treated mixed ceramic nanoparticles (MCN) were incorporated. We opted for an interesting ceramic mixture of zirconium dioxide and lead zirconate and used it as filler for the PDMS matrix in order to obtain materials with larger dielectric permittivity. The lead zirconate crystals are orthorhombic antiferroelectric [23,24] with no apparent transitions in the dielectric spectra at low

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temperatures ($<100^\circ\text{C}$) and lead zirconate has a value of $\epsilon_r \sim 160$ at such temperatures. The zirconium dioxide crystals at usual temperatures ($<1170^\circ\text{C}$) are monoclinic, such as in baddeleyite [25] also with no apparent transitions in the dielectric spectra at low temperatures ($<100^\circ\text{C}$) and with ϵ_r value of ~ 20 at such temperatures. Also zirconium dioxide has the property of stabilizing the permittivity response and it can lower the loss factor value of ceramics [26]. After the incorporation of the MCN filler, the resulted composite materials were processed as films and crosslinked by condensation at room temperature with a trifunctional silane. After the step of aging, the surface, thermal, mechanical and dielectric properties were investigated.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

The reagents for the synthesis of MCN nanoparticles: lead(II) chloride (PbCl_2), $>99\%$ (Aldrich); zirconium(IV) chloride (ZrCl_4), $>99.5\%$ (Aldrich); sodium hydroxide (NaOH), pellets, $>99\%$ (Fluka AG); urea, $>99.0\%$ (Aldrich), all were used as received. Octamethylcyclotetrasiloxane, $[(\text{CH}_3)_2\text{SiO}]_4$, (D_4), $>99\%$ (GC) (Fluka AG) and Pluronic L-31, HO-poly(ethyleneglycol)-block-poly(propyleneglycol)-block-poly(ethyleneglycol)-OH, $M = 1100$, $d_{25}^{25} = 1.02$, viscosity (25°C) = 175 cps (Sigma-Aldrich) were used as received. Methyltriacetoxysilane (MTS) was prepared and purified in house using a technique adapted from literature [27] ($>98\%$, b.p. = $94\text{--}95^\circ\text{C}$, $d_4^{20} = 1.20$).

2.1.2. Equipments

Gel permeation chromatography (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.

Dielectric spectroscopy was performed using the Novocontrol "Concept 40" broadband dielectric spectrometer (Hundsangen, Germany) at 25°C in the frequency range $1\text{--}100000\text{Hz}$. Water vapors sorption isotherms of the film samples were recorded in dynamic regime by using the fully automated gravimetric analyzer IGA sorp supplied by Hiden Analytical, Warrington (UK). An ultrasensitive microbalance measures the weight change as the humidity is modified in the sample chamber at a constant regulated temperature. The measurement system is controlled by a software package.

Wide angle X-rays diffraction (WAXD) analysis on MCN powder was performed on a Bruker-AXS D8 ADVANCE diffractometer, with Bragg Brentano parafocusing goniometer. Scans were recorded in step mode using Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.1541\text{ nm}$). The working conditions were 40 kV and 30 mA tube power, room temperature. The Bruker computer softwares Eva 11 and Topaz 3.1 were used to plot and process the data.

Differential scanning calorimetry (DSC) measurements were conducted with a DSC 200 F3 Maia (Netzsch, Germany). About 10 mg of sample was heated in pressed and punched aluminum crucibles at a heating rate of $10^\circ\text{C min}^{-1}$, in nitrogen inert atmosphere. The temperature range for TG-DTG measurements performed with the same instrument was $25\text{--}750^\circ\text{C}$ with a heating rate of $10^\circ\text{C min}^{-1}$.

An Energy Dispersive X-Ray system (EDX) available on environmental scanning electron microscope (ESEM) type Quanta 200 was used for qualitative analysis and elemental mapping. The transmission electron microscopy (TEM) images were taken using a dedicated HITACHI HT7700 microscope operated in high contrast mode at 100 kV accelerating voltage. The samples have been prepared by placing small droplets of the diluted dispersion (1 g/L)

of ceramic powder on 300 mesh carbon coated copper grids and dried in vacuum at 50°C .

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. 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 previous test. Five stretch/recovery cycles were registered. The stationary time at minimum and maximum applied stress was 2 s.

Dielectric strength measurements were made on a home-made installation (PERCRO Laboratory-TeCIP Institute-Scuola Superiore Sant'Anna, Pisa, Italy) consisting in high-speed high-voltage power amplifier, function generator, and an oscilloscope. The brass electrodes were applied on the film samples and the measurements were performed at 60 Hz , and a voltage increase rate of 2000 V s^{-1} at room temperature (25°C). The samples were previously brought into equilibrium with the humidity of the environment in which the measurements were made. Three samples were analyzed for each composite formulation and the lowest value was taken into consideration.

A home-made set-up was used for performing energy harvesting tests with the new dielectric elastomers (Fig. 1 ESI). In this set-up electrodes ($20 \times 20\text{ mm}$) made of copper plated textolite were placed on each side of the sample and the voltage was recorded with a memory oscilloscope Tektronix DPO 4032 with two channels, at frequency of 100 MHz . The kinetics consists in a steel ball ($m = 7.1\text{ g}$) falling freely from a height of 100 mm in the center of the upper electrode surface. The signal wave shape 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. 2 ESI). Three measurements were performed for each sample and the average values were taken into account.

2.2. Procedure

2.2.1. Preparation of mixed ceramics nanoparticles, MCN

The MCN nanoparticles were prepared by using the procedure described by Oren et al. [28], namely a homogeneous precipitation, modified as follows. First a mixture of 100 mL of cation stock solutions was prepared by mixing lead and zirconium chlorides (0.556 g PbCl_2 and 4.66 g ZrCl_4) in a glass beaker at room temperature (RT) (Fig. 1). Then a solution of urea (15.5 g urea in

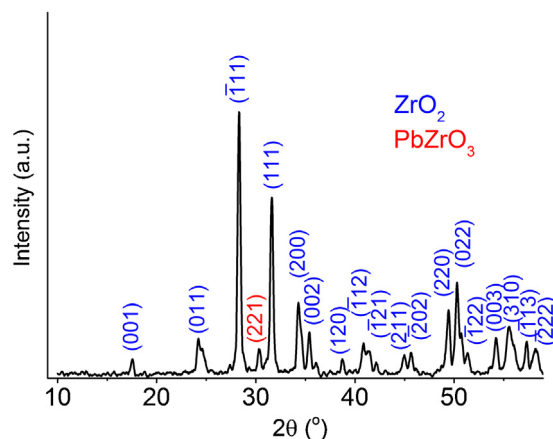


Fig. 1. XRD patterns of the MCN powder (2-column fitting image).

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