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Silicone dielectric elastomers based on radical crosslinked high molecular weight polydimethylsiloxane co-filled with silica and barium titanate --Manuscript Draft--

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Silicone dielectric elastomers based on radical crosslinked high molecular weight polydimethylsiloxane co-filled with silica and barium titanate

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4 **Abstract**
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6 A strategy, consisting in the use in tandem of two active fillers in different ratios with
7
8 complementary effects: silica mainly as a reinforcing agent and barium titanate as dielectric
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10 permittivity enhancer, was approached to optimize the electromechanical properties of the
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12 silicone elastomers. A high molecular mass polydimethylsiloxane- α,ω -diol ($M_w=642000 \text{ g}\cdot\text{mol}^{-1}$)
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14 ¹) was used as a matrix to prepare silicone composites, which further were processed as films and
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16 crosslinked at high temperature. The morphology, thermal and moisture behaviour of the films
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18 were studied by adequate techniques. The mechanical properties were estimated on the basis of
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20 normal and cyclic stress-strain curves. Dielectric spectra were recorded in the frequency range 1-
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22 10^6 Hz at normal temperature. The voltages generated by a mechanical impulse created by
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24 falling of a metal ball of 7.1 g from a height of one hundred millimetres on the surface of the
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26 films placed between two electrodes ranged between 28.4 and 157.3 V/mm.
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37 **Keywords:** dielectric elastomers; silicones; composites; barium titanate; silica; energy
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4 **1. Introduction**
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6 Energy harvesting technologies aiming the conversion of different energy forms (light, thermal,
7 mechanical, etc.) [1] from the natural sources such as wind, waves, or animal movements into
8 electrical energy is attracting a high interest in the scientific community in special in the last
9 twenty years [2, 3]. One way to convert the mechanical energy into electrical one is to use high
10 reversible deformability of the dielectric elastomers. Among this class of materials, silicones
11 attract great interest because of their high elasticity and weather resistance [4–8]. A drawback of
12 silicones is their low dielectric permittivity (in the range 2.5-3.0), many studies thus aiming to
13 improve this parameter and maintaining good mechanical properties. The unique molecular
14 structure and chemistry of the silicone polymers permit their formulations that meet to a specific
15 application. Different strategies have been used to improve the dielectric properties [9], but the
16 most promising one is incorporation of filler particles with high dielectric permittivity, such as
17 ceramic fillers (e.g., barium titanate, titanium dioxide, calcium copper titanium oxide, lead
18 zirconate, etc.) [10–14]. The dielectric relaxation of the crystallites embedded into the polymer
19 matrices was studied [15, 16] and it was established the principal role of the interface states on
20 the border polymer-crystallites in defining the corresponding dielectric features. Barium titanate,
21 a ferroelectric crystal with high dielectric strength, is widely used for this purpose [17–20]. The
22 effect of BaTiO₃ nanoparticles on electrical and mechanical properties are extensively studied
23 and found that dielectric constant of nanocomposites significantly increases with the increase in
24 BaTiO₃ concentration whereas volume resistivity decreases continuously [21]. However, while
25 the thermal stability of the composites in which it is incorporated increases, the mechanical
26 properties, i.e. tensile strength and elongation at break are worsened as BT content increase due
27 to no reinforcing nature of BT [22]. On the other hand, the effective reinforcing effect
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4 (increasing in tensile strength, tear resistance, compression set, and good dynamic properties
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6 besides anti-aging and anti-friction) of the nano-silica on the silicone rubber is well-known [23,
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8 24]. Depending on the silica content, the silicones strength could be significantly increased.
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10 However, by the addition of silica as filler, an increase in stiffness, undesired in electro-
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12 mechanical application, occurs simultaneous with resistance to fracture. Therefore, a
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14 compromise must be made between these two features.
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19 Continuing our efforts to obtain silicone elastomers with optimized electro-mechanical properties
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21 [11, 25–28], in this paper we addressed the working strategy consisting in the original
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23 combination of two active fillers with complementary effects: silica, as a reinforcing filler and
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25 barium titanate, both from commercial sources, to increase the dielectric permittivity of the
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27 composites obtained. In addition, the originality of our approach consists in the using as a matrix
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29 of a polydimethylsiloxane of high molecular weight ($M_w = 642000 \text{ g}\cdot\text{mol}^{-1}$) and its curing by
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31 radical mechanism, which takes place at high temperature and pressure. The cross-linking pattern
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33 is different from that used in the majority of cases reported in the literature to stabilize the
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35 dielectric silicone elastomers for which, in general commercial silicone kits with vulcanization
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37 by condensation of the chain ends with a tri- or tetrafunctional crosslinking agent are used [5, 25,
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39 29, 30]. The system reported here rather resembles the curing by hydrosilylation but which is
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41 applicable only in case of relatively low molecular weight polysiloxanes, more flexible, to ensure
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43 access to each other functional groups (Si-H and Si-CH=CH₂) [27, 31, 32]. The films obtained
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45 by us are robust, easy to handle and use in tougher conditions. Also, an original setup was used
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47 to roughly evaluate energy output capacity based on direct piezoelectric effect without previous
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49 polarization. The effect of filler`s presence and their amounts embedded within a polysiloxane
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51 matrix of high molecular weight on the mechanical properties and dielectric behavior were
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4 studied. Also, preliminary estimations of the ability of the resulted materials to convert
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6 mechanical energy into electric one were made on a homemade set up.
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10 11 **2. Materials and Methods**

12 13 14 **2.1. Materials**

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16 The polymeric matrix, polydimethylsiloxane- α,ω -diol (PDMS), was obtained by bulk
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18 polymerization of octamethylcyclotetrasiloxane catalyzed by H_2SO_4 , at room temperature,
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20 according to procedure described in ref. [33]. A small percent of vinyl-substituted cycle (3 wt%
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22 heptamethylvinylcyclotetrasiloxane, $[(CH_3)_2SiO]_3[C_2H_3(CH_3)SiO]$), was added. The polymer
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24 was purified by repeated washing with slight alkaline solution and then with water, until a
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26 neutral pH. Then, the polymer was devolatilized in vacuum at 180 °C to remove water and low
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28 molecular weight siloxanes. The molecular mass, as was evaluated by Gel Permeation
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30 Chromatography by using chloroform as eluent, was $M_w=642000 \text{ g}\cdot\text{mol}^{-1}$ ($M_n=438000 \text{ g}\cdot\text{mol}^{-1}$),
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32 $d=1.00 \text{ g}\cdot\text{cm}^{-3}$, dielectric permittivity $\epsilon'=2.9$. Fumed silica, Aerosil 380 (Degussa), with 100%
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34 purity, specific surface area 380 m^2/g , particle diameter 3 - 15 nm, $d=2.2 \text{ g}\cdot\text{cm}^{-3}$, tapped density
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36 around 50 $\text{g}\cdot\text{l}^{-1}$, dielectric permittivity $\epsilon'=3.9$ and barium titanate, $BaTiO_3$, (Fluka AG), BT, with
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38 m.p. 1625 °C, particle size $<3 \mu\text{m}$, $d=6.08 \text{ g}\cdot\text{cm}^{-3}$, dielectric permittivity $\epsilon'=1700$ at room
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40 temperature were dried in vacuum at 100 °C and hydrophobized by treatment with
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42 dimethylcyclosiloxanes mixture in vapour state. 2,4-Dichlorobenzoyl peroxide, paste 50% in
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44 silicone oil, having a critical temperature: 60 -70 °C and set-cure temperature in the range 115 –
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2.2. Measurements

Gel permeation chromatographic analysis, GPC, was carried out on a PL-EMD 950 Evaporative Mass Detector instrument by using CHCl_3 as eluent, after calibration with standard polystyrene samples. The obtained thick films were cryo-fractured and the cross-section surface was examined with an Environmental Scanning Electron Microscope (ESEM) type Quanta 200, operating at 30 kV with secondary electrons in low vacuum mode. Stress-strain measurements were performed on TIRA test 2161 apparatus, Maschinenbau GmbH Ravenstein, Germany, on dumbbell-shaped cut samples with dimensions of 50x8.5x4 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 5 s. Novocontrol setup (Broadband dielectric spectrometer Concept 40, 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 thickness in the 0.5-1 mm range were placed between gold plated round electrodes, the upper electrode having a 20 mm diameter. Differential Scanning Calorimetry measurements, DSC, were conducted on a DSC 200 F3 Maia (Netzsch, Germany). A mass of 10 mg from each sample was heated in pressed and pierced aluminum crucibles from -150 to 50 °C at a heating rate/cooling rate of $10/-10$ °C min^{-1} and in nitrogen as inert atmosphere at a flow rate of 50 mL min^{-1} . The temperature against heat

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4 flow was recorded. The baseline was obtained by scanning the temperature domain of the
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6 experiments with an empty pan. The enthalpy was calibrated with indium according to standard
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8 procedures. Water vapors sorption capacity of the film samples was measured by using the fully
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10 automated gravimetric analyzer IGAsorp supplied by Hiden Analytical, Warrington (UK). The
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12 measurements were performed at room temperature (~25 °C) in the 0 - 90 % relative humidity
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14 range (Figure 3S). A step of humidity change of 10 wt% and pre-established equilibrium time
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16 between 10 and 30 minutes were used. The samples were dried previously in flowing nitrogen
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18 (250 mL/min) until a constant weight was achieved. An ultrasensitive microbalance measures the
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20 weight change as the humidity is modified in the sample chamber at a constant regulated
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22 temperature. The measurement system is controlled by a IGASORP Windows™ based software
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24 package. Harvesting experiments (voltage recording) were performed by using a memory
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26 oscilloscope Tektronix DPO 4032 (350MHz, 2.5GS/s), as we already described in ref. [11, 23].
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36 **2.3. Preparation of the composites and films formation**

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38 Previously hydrophobized silica nanoparticles and barium titanate were stepwise incorporated in
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40 small portions within the PDMS by mechanical mixing in a Yanke - Kunkel laboratory mixer
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42 equipped with double palettes and cooling mantle in different percentages, according to Table 1.
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44 The homogenization was finalized on a rampart, where the crosslinking catalyst (2 wt% 2,4-
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46 dichlorobenzoyl peroxide) was also added [33]. To obtain crosslinked films, small amounts of
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48 each mixture (~10 g) were put as a round blob of material inside frame (1x70x70 mm) mounted
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50 between two stainless steel plates (1x100x100 mm) and pressed with a manual press, after that
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52 this assembly was heated at 120 °C for 1 h when crosslinking occurs. Then, the films peeled off
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54 from the substrate were post-cured by maintaining for 10 h at 150 °C in air stream for
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4 devolatilization. These films were used to investigate some of the properties of interest for the
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6 target application.
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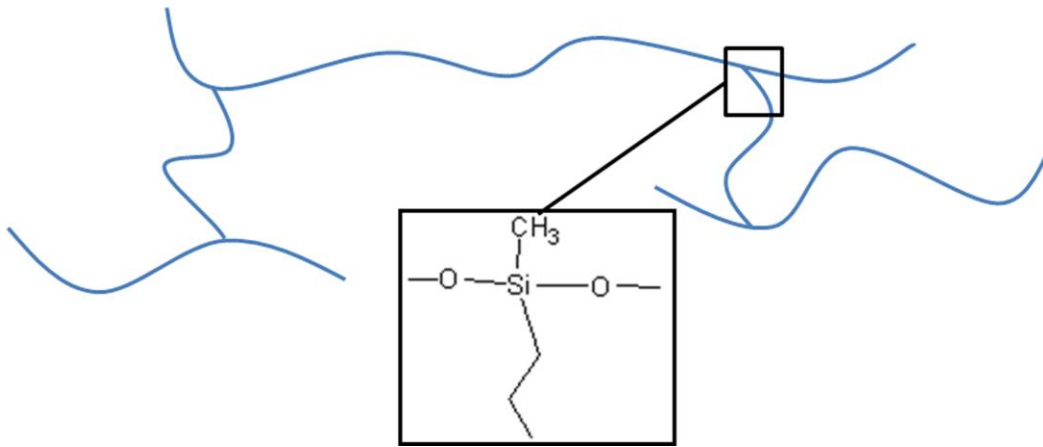
10
11 **Table 1. Recipes to obtain desired elastomers** (added catalyst: 2 wt% 2,4-dichlorobenzoyl
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13 peroxide)
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Sample	Silica, wt%	Barium Titanate, wt%
S0B0	0%	0
S10 B0		0
S10 B5	10%	5
S10 B15		15
S15 B0		0
S15 B5	15%	5
S15 B15		15
S30 B0		0
S30 B5	30%	5
S30 B15		15

39 40 **3. Results and discussion**

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43 A polydimethylsiloxane- α,ω -diol of high molecular mass ($M_w=642000 \text{ g}\cdot\text{mol}^{-1}$) was used as a
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45 matrix to prepare silicone composites. Two fillers, silica and barium titanate, were incorporated
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47 in different ratios (Table 1) within the polymer to improve its properties, each of them having a
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49 specific role. Thus, while the silica adding aims to improve the mechanical properties, the
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51 ceramic material should lead to increased dielectric permittivity. Both fillers were previously
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53 surface hydrophobized by treating with dimethylcyclosiloxanes mixture in vapour state. The
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55 composites formulated with different percentages of each filler were processed as films with
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4 dimensions of 70x70x1 mm, and stabilized by radical curing initiated by 2,4-dichlorobenzoyl
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6 peroxide at 120 °C in a press. At high temperature, the peroxide decomposes to form free
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8 radicals that attack preferably vinyl groups, these continuing free radical chain reactions. In such
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10 conditions, the crosslinking occurs by the formation of the alkylene (ethylene, propylene)
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12 interchain bridges along the siloxane backbone [34] (Figure 1).
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35 **Figure 1.** Chain crosslinking pattern.
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39 40 **3.1. Morphology**

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43 The distribution of the fillers within the polymeric matrix was appreciated by SEM examination
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45 of the cryo-fractured cross-section surface. The SEM images of the samples filled with silica
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47 only, taken with the resolution according to Figure 2, reveal a good dispersion of these
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49 nanoparticles not being identified individual or agglomerated silica nanoparticles neither at 10
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51 nor at 30 wt% content (sample S10B0 - Figure 2d, S15B0 - Figure 2g and S30B0 - Figure 2j).
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53 Instead, in the samples in which barium titanate was incorporated, aggregates thereof with large
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55 dimensional dispersion from a few micrometres corresponding to *ex situ* dimensions of the
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57 barium titanate (Figure 2a,b) to 50-60 µm (Figure 2f-1) can be seen. It is presumed that the
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4 aggregation occurs during the hydrophobization treatment due to the high incompatibility
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6 between the strong hydrophobic dimethylcyclosiloxane and hydrophilic barium titanate, which is
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8 not soluble in water but disperses well in it. As a result, there is a natural tendency of the
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10 particles to agglomerate at the expense of their coverage with a hydrophobic coating. It seems
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12 that this method is not optimal for the hydrophobization of barium titanate. It is assumed that the
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14 use of a silane coupling agent such as alkyltrialkoxysilane or hexamethyldisilazane would be
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16 more appropriate in order to maintain a good dispersion of the polar filler within a nonpolar
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18 matrix.
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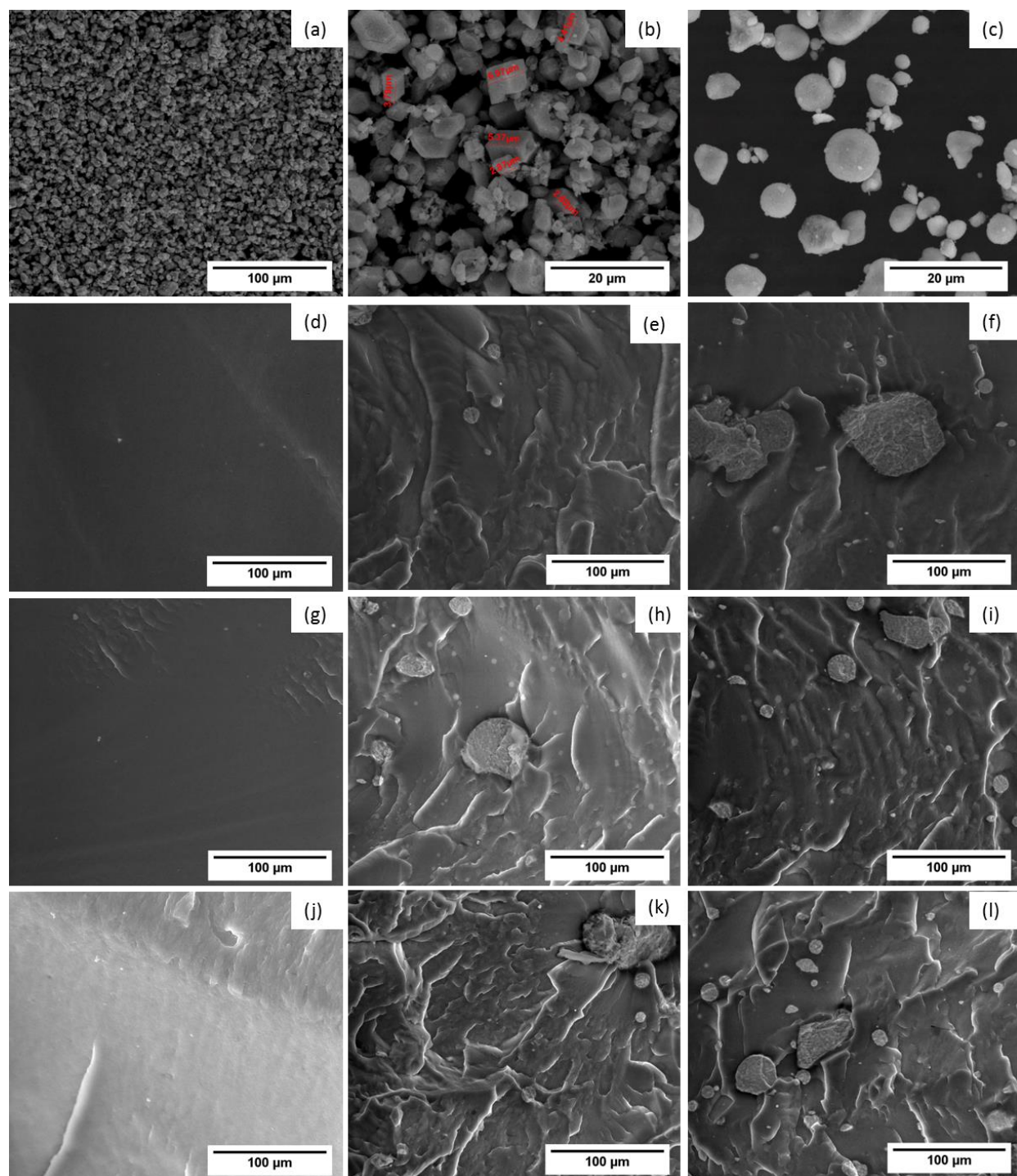


Figure 2. SEM images of: a, b - raw commercial barium titanate, c - surface treated commercial barium titanate, and d - S10B0, e - S10B5, f - S10B15, g - S15B0, h - S15B5, i - S15B15, j - S30B0, k - S30B5, l - S30B15 in cryo-fractured cross-section surface.

3.2. Mechanical behavior

Stress-strain curves were recorded (Figure 3a) at room temperature and atmospheric humidity.

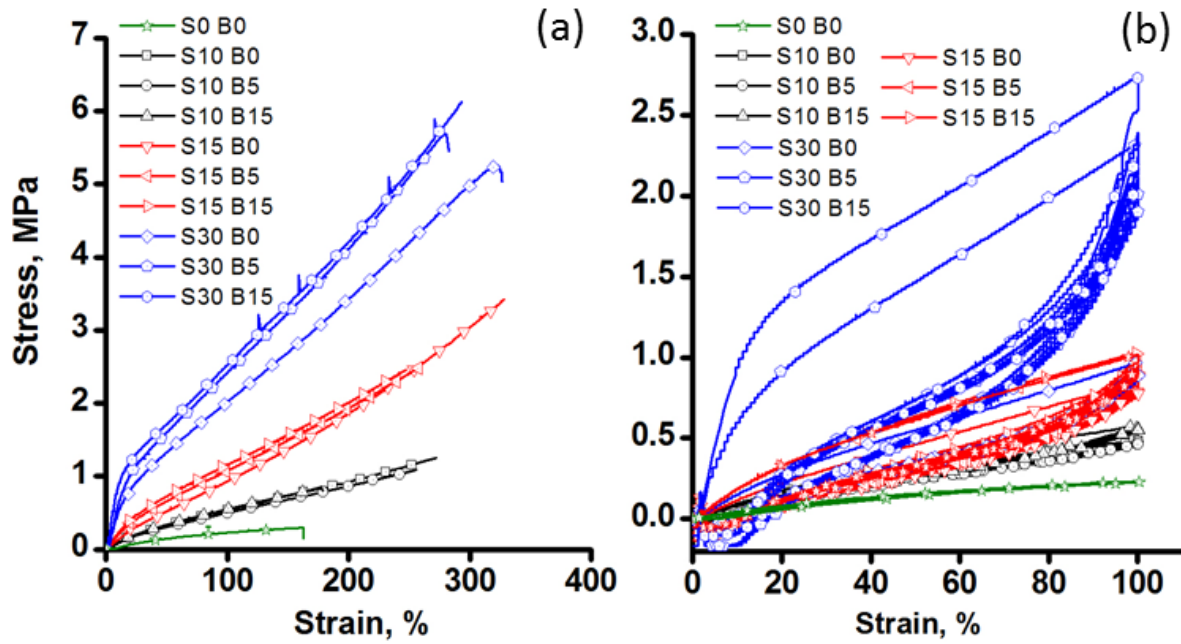


Figure 3. Normal (a) and cyclic (b) stress-strain curves recorded at RT and atmospheric humidity.

The main parameters estimated on the basis of these curves are centralized in Table 2.

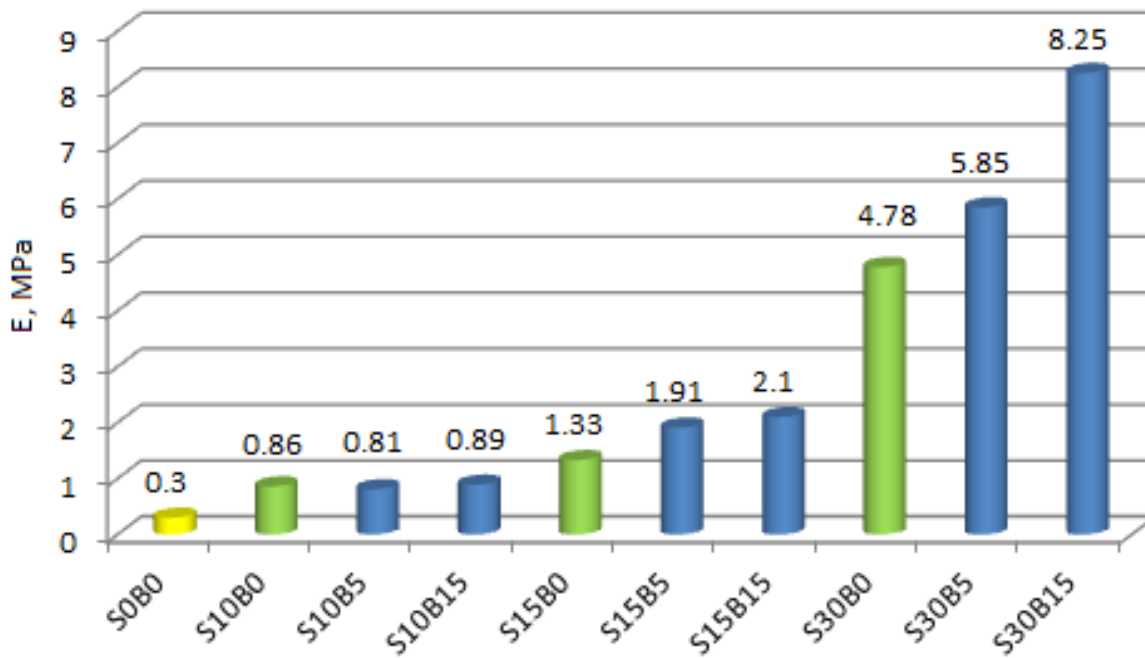
Table 2. Relevant mechanical, dielectric and electromechanical data for prepared silicone composites

Sample	d,^a	σ,^b	ϵ,^c	σ_{el},^d	ϵ_{el},^e	E,^f	ϵ'^g	ϵ''^h	U_{vv},ⁱ	U_{vv}/d,^j
	mm	MPa	%	MPa	%	MPa			V	V·mm⁻¹
S0B0	1.60	0.15	162	0.1021	32.6	0.30	3.02	0.01	8	5.0
S10B0	0.88	1.25	272	0.1707	19.4	0.86	3.41	0.01	25	28.4
S10B5	0.89	1.09	255	0.0439	5.4	0.81	3.67	0.01	140	157.3
S10B15	0.91	0.81	178	0.1340	14.6	0.89	3.95	0.01	90	98.9
S15B0	0.84	3.41	328	0.2140	15.6	1.33	3.48	0.01	70	83.3
S15B5	0.91	2.50	259	0.2639	13.7	1.91	3.66	0.02	49	53.8
S15B15	0.96	2.45	247	0.2337	10.6	2.10	4.09	0.02	98	104.1
S30B0	0.82	5.03	326	0.5030	12.1	4.78	3.45	0.01	76	92.7
S30B5	1.01	5.44	282	0.7445	12.1	5.85	3.89	0.01	61	60.4
S30B15	0.93	6.13	292	0.9690	9.9	8.25	4.26	0.01	37	39.8

^aFilm thickness; ^bstress at break; ^celongation at break; ^dstress at the upper limit of elasticity; ^estrain at the upper limit of elasticity; ^fYoung's modulus (calculated at 15% strain); ^gdielectric permittivity at 10 Hz; ^hdielectric loss at 10 Hz; ⁱharvested energy, expressed as a peak to peak voltage; ^jharvested energy reported to the film thickness, expressed as a peak to peak voltage/mm.

Due to the compatibility and reinforcing effects of silica nanoparticles, the mechanical properties were enhanced as its incorporated amount rises. Thus, the ultimate tensile strength increases from 0.15 MPa for pure crosslinked silicone to 5.03 MPa when 30 wt% silica was incorporated (Table 2). However, the increase in elongation is modest one, from 162 % for S0B0 to 272, 328 and 326 % for the elastomers containing 10, 15 and 30 wt% SiO₂, respectively. As a result, the

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4 Young's modulus significantly increased, from 0.30 MPa for pure crosslinked silicone to 4.78
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6 MPa for elastomer filled with 30 wt% silica. When the second filler, barium titanate, was added,
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8 due to its lower compatibility with silicone matrix and aggregates formation during the
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10 hydrophobization and incorporation procedures in polymeric matrix by mechanical mixing, a
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12 worsening is registered both in ultimate tensile stress and elongation values in the case of the
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14 series S10 and S15 containing less silica, while the Young's modulus continues to increase. This
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16 growth is not just of the same magnitude as that induced by incorporating increasing amounts of
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18 silica but generally occurs systematically in all three series, S10, S15, S30, as BT content
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20 increases from 0 to 15%, from 0.86 to 0.89, from 1.33 to 2.10 and from 4.78 to 8.25 MPa,
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22 respectively, as is suggested by graphical presentation in Figure 4.
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52 **Figure 4.** Evolution of elastic modulus (determined at 15% strain) with the filler's content.
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4 In order to evaluate mechanical fatigue resistance, cyclic stress-strain tests were performed, five
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6 cycles being made for each sample until 100 % elongation from the initial length, at room
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8 temperature and atmospheric humidity (Figure 3b). After the first cycle, all samples show a big
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10 hysteresis loop which disappears, due to the rearrangements of polymeric chains when undergo
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12 elongation, also known as Mullins effect [35]. The shape of the cyclic stress-strain curves reveals
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14 that the incorporation of small percent of silica does not significantly affect the elastic properties
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16 of silicones. These are also not drastically affected by adding barium titanate to the composites
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18 containing 10 and 15 wt% silica. Instead, in the case of the composites containing 30 wt% silica
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20 and different percentages of barium titanate, the viscoelastic loss is manifested by the presence
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22 of visible hysteresis loops on the stress-strain curves. By the incorporation of the silica only (i.e.,
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24 samples S10B0, S15B0, S30B0), the elastic region (where Hook's law can be applied)
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26 significantly decreases from 32.6 % in pure crosslinked PDMS to 19.4, 15.6 and 12 % when 10,
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28 15 and 30 wt% silica, respectively, was added (Table 2). This is a consequence of the limitations
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30 in the polymer chains movement due to the physical bond changes occurred within the strained
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32 material [36]. The contribution of the barium titanate to the viscoelastic loss is more reduced.
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34 The maximum limit of pure elastic strain decreases from 19.4 to 14.6, from 15.6 to 10.6 and
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36 from 12.1 to 9.9 %, when 15 wt% barium titanate was incorporated into the samples of the three
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38 series, already containing 10, 15 and 30 % silica, respectively.
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51 **3.3. Dielectric spectroscopy**

52 Dielectric spectra were also recorded at room temperature in the frequency range $1 - 10^6$ Hz
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54 (Figure 5) the desire being to have increased dielectric permittivity values while the dielectric
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loss to be at low level, which creates prerequisites for applying a low voltage for actuation or for more energy that could be harvested.

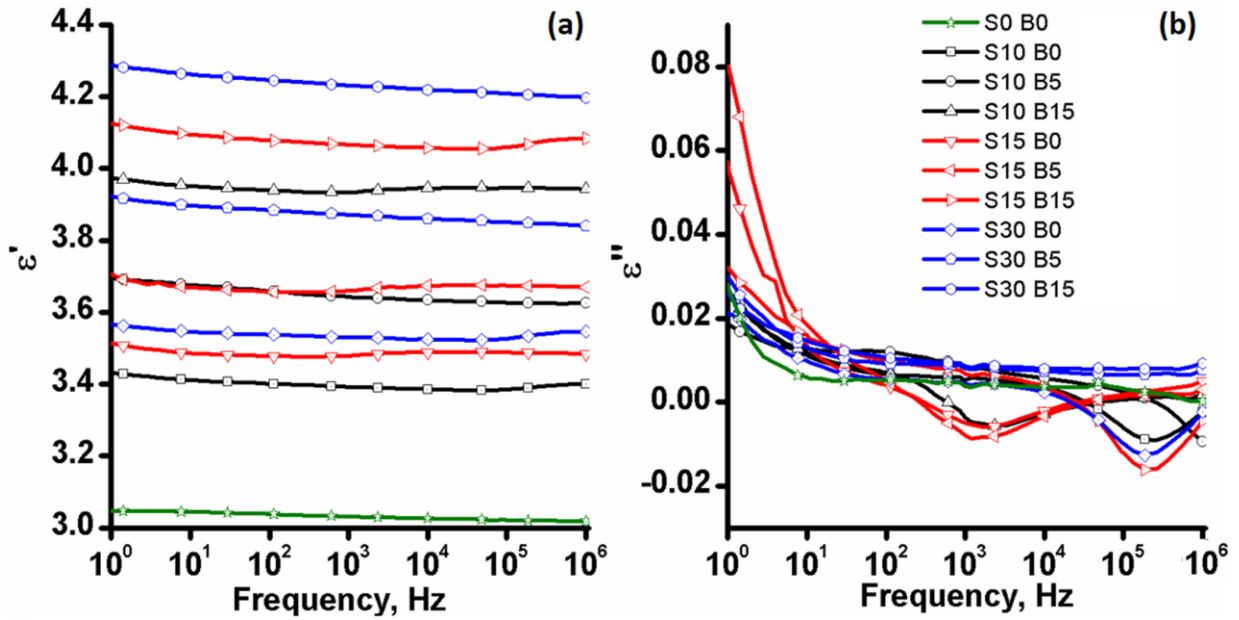


Figure 5. Dielectric measurements: (a) - Dielectric permittivity; (b) - Dielectric loss; the symbols have the same meaning for both graphs.

As can be seen, even adding silica only lead to a slight increase of the dielectric permittivity from 3.02 for pure matrix to 3.45, 3.48 by adding 15 and 30 wt% silica, respectively. When barium titanate was added, the dielectric permittivity increases as the filler content rises from 5 to 15 wt% (Table 2, Figure 6). The highest value, 4.26, was registered for the sample S30B15 with the highest amounts of the two fillers.

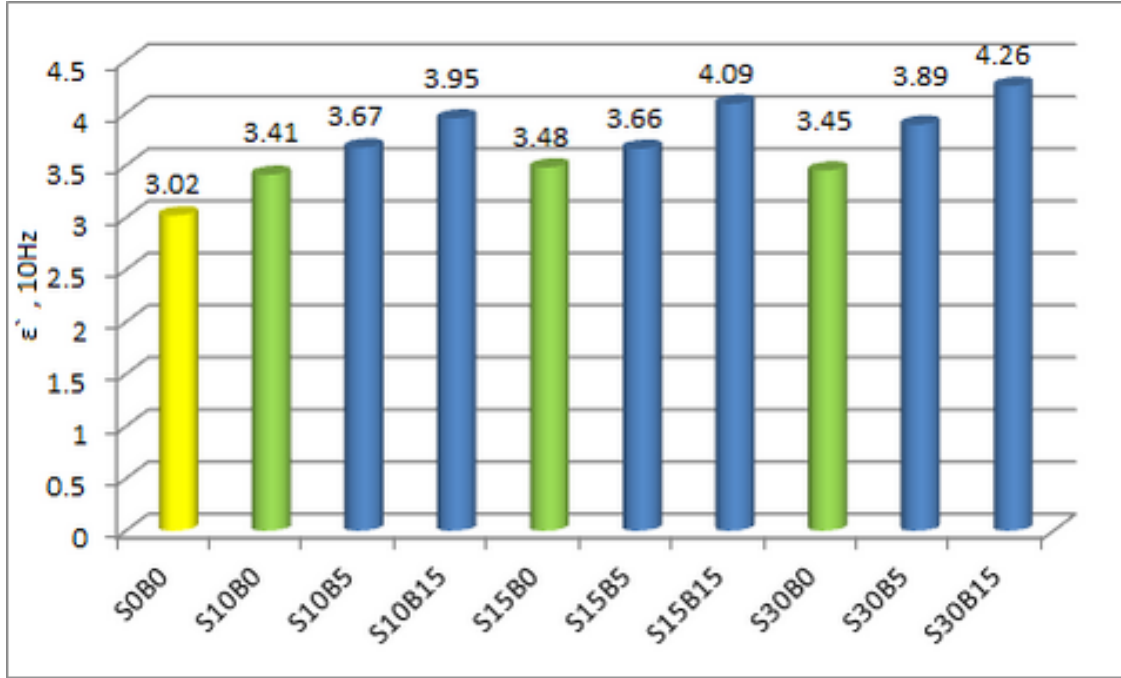


Figure 6. Comparative values of the dielectric permittivity at 10 Hz for the samples containing the two co-fillers in different ratios.

The increasing in the dielectric permittivity of the composite, as the amount of barium titanate added increases, is expected one at least from the perspective of volume-fraction average model:

$$\epsilon_{ff} = \varphi_p \epsilon_p + \varphi_c \epsilon_c + \varphi_s \epsilon_s \quad (1)$$

where the subscripts p, c and s are the polymer, the ceramic phase and silica, respectively, and φ is the volume fraction of the constituents. When an electric voltage is applied, positive and negative charges appear at the surface of the polar particles dispersed within continuous phase. Thus, the particles behave as dipoles, which align head-to-tail in the direction of the electric field and polarization leads to increased capability of the prepared dielectric materials to store energy [37]. Logic, increasing the volume fraction of the component with the highest dielectric constant ($\epsilon'_{BT} = 1700$ at room temperature), the dielectric permittivity of the composite should increase.

However, the values obtained by this theoretical approach are more higher than experimental

ones (Table 1S, Figure 2S). In fact the prediction of dielectric permittivity value by this way has been already disproved by other theoretical [38] and experimental studies [39]. Instead, the experimental values better fit theoretical ones obtained using other models, i.e., Maxwell-Garnett [40], Bruggeman [40, 41] and Lichtenecker-Rother [41–48] (see SI) as can be seen in Figure 7.

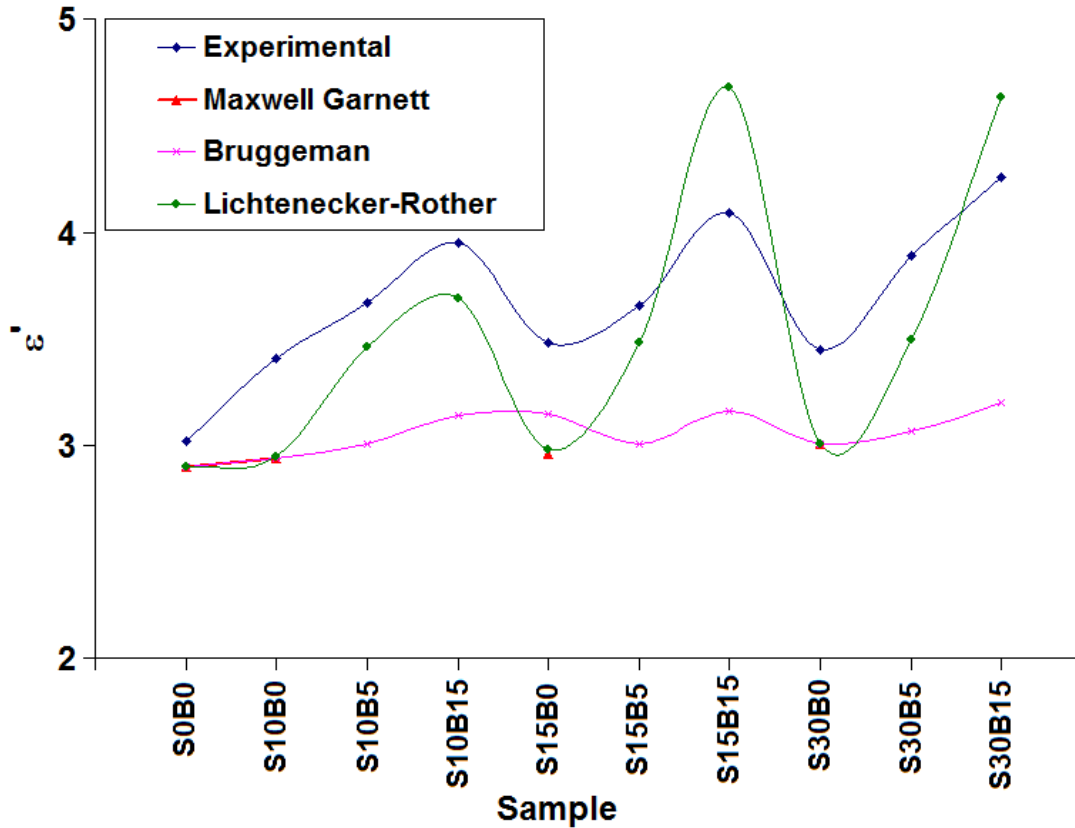


Figure 7. Plotting experimental dielectric permittivity values as compared with those theoretical estimated by using different models.

An interesting aspect is that, the dielectric permittivity remains almost stable over the entire range of frequencies. This might be ascribed to high stiffness matrix limiting pole orientation even at low frequencies. Dielectric loss values are low for all samples, thus the used fillers do not affect the insulating properties of PDMS based elastomers. The dropping below 0.00 value on

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4 some of dielectric loss curves recorded around 10^3 and over 10^5 Hz frequencies are due to
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6 resolution limits of the dielectric spectrometer.
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10 11 **3.4. DSC analysis** 12

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14 In order to see how the incorporation of the fillers affects the thermal transitions of the PDMS in
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16 composites, DSC curves were recorded in the range $-150 \dots +50$ °C. It was observed (Figure 4S)
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18 that these do not vary significantly, only a few degrees with plus or minus from the reference
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20 sample values. Thus, the operating temperature window for composites do not change from that
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22 known for the silicones. Absolute heat capacity values determined on the basis of DSC curves
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24 (Figure 4S, Table 3) were used to estimate the crosslinking density according to procedure
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26 described in the literature [49–51]. The following equation was used:
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$$30 \quad \rho_c = (C_p^i - C_p^0) / C_p^0 \quad (2)$$

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32 with C_p^i being the heat capacity of the polymer network at a given crosslinking density [1, 52]
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34 and C_p^0 the heat capacity of the non-crosslinked polymer. The heat capacity is a measure which
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36 energetically characterizes only segmental chain mobility in the polymer matrix.
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40 Polydimethylsiloxanes have T_g around -123 °C, while data from DSC analysis for the
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42 crosslinked samples show T_g values around this same temperature (-123 °C) (Figure 3S).
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46 Therefore, the heat capacity for this transition is used for calculating the crosslinking density
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48 value, with equation (2), for each of the prepared samples, the results being centralized in Table
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Table 3. Thermal and moisture sorption data

Sample	DSC data		Weight, ^b % d.b.
	Heat capacity, ^a C_p (J g ⁻¹ K ⁻¹)	Crosslinking density, ρ_c' (mol cm ⁻³)	
PDMS	0.073	–	-
S0B0	0.097	0.328	0.57
S10B0	0.058	0.205	0.70
S10B5	0.061	0.164	0.36
S10B15	0.092	0.260	0.52
S15B0	0.091	0.246	0.66
S15B5	0.088	0.205	0.82
S15B15	0.052	0.287	0.33
S30B0	0.066	0.096	0.75
S30B5	0.087	0.191	0.89
S30B15	0.054	0.260	0.86

^aCrosslinking density; ^bmaximum vapour water sorption capacity reported to the dry mass.

The crosslinking degree decreases when silica particles are introduced in the composition of the silicone elastomers (from 0.328 mol·cm⁻³ for S0B0 to 0.196-0.246 mol·cm⁻³ by incorporating silica), and this leads to a small decrease of T_g, with 1-3 °C in comparison with the pure crosslinked PDMS, S0B0. The surface of the silica particles is treated with octamethylcyclotetrasiloxane and therefore these particles are not acting as crosslinking centers but occupy the free volume between the siloxane polymer chains and interact with these only by physical interactions. However, the introduction of 15 wt% barium titanate nanoparticles in the formulation of the elastomers seems to lead to a small increase of crosslinking density (0.260,

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4 0.287, 0.260 mol·cm⁻³ for the samples S10B15, S15B15 and S30B15, respectively) as compared
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6 with samples containing silica only, but not up to the level of pure siloxane polymer.
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9 Unfortunately, it can not establish a correlation between the crosslinking degree and mechanical
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11 or dielectric characteristics due to the complexity of the material induced by the presence of the
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13 two fillers.
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15 16 17 18 19 **3.5. Vapor sorption capacity**

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21 The amount of humidity adsorbed by the dielectric can lead to failure when a voltage is applied;
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23 conductive pathways can form and dielectric breakdown suddenly appears. For this reason, the
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25 moisture behavior of the samples was investigated by recording water sorption isotherms at room
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27 temperature (~25 °C) in the 0 - 90 % relative humidity range (Figure 3S). The maximum sorption
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29 values range between 0.33 and 0.89 wt% indicating hydrophobic materials. A maximum sorption
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31 capacity of 0.57 wt% was recorded for the pure crosslinked silicone matrix while a very slight
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33 increase only can be noticed for some of the samples filled with silica (0.7, 0.66, and 0.75 wt%)
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35 or silica and barium titanate (most of them around 0.8 wt%) but without a logical variation.
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40 (Table 3).
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45 46 **3.6. Energy harvesting measurements**

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48 The capacity of the sample to convert the mechanical energy into electrical one, sought as a
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50 ultimate features, was estimated by using a set up similar to that described by us in ref. [11] and
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52 consisting in measuring peak to peak voltages generated by a mechanical impulse created by
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54 falling of a metal ball of 7.1 g from a height of 100 mm on the surface of the elastomeric films
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56 placed between two electrodes (Figure 8).
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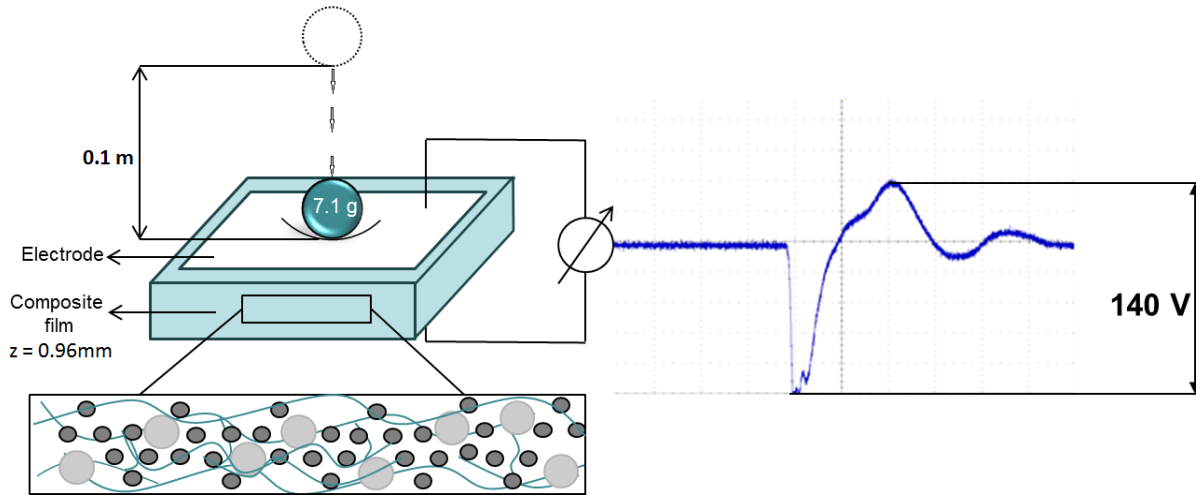


Figure 8. Setup for the energy harvesting measurements and an illustrative signal registered for the sample S10B5 (See Figure 5S for the other samples).

The dynamic parameters used for these experiments were:

- speed at contact with the elastomeric membrane, v :

$$v = \sqrt{2gh} = \sqrt{2 \cdot 9.8 \cdot 0.1} = 1.4 \text{ [m/s]} \quad (3)$$

- mechanical impulse, p :

$$p = mv = 9.94 \cdot 10^{-3} \text{ [Ns]} \quad (4)$$

- kinetic energy in contact, E :

$$E = \frac{mv^2}{2} = 6.96 \cdot 10^{-3} \text{ [J]} \quad (5)$$

- the micro-force, F :

$$F = \frac{E}{h} = 0.0696 \text{ [N]} \quad (6)$$

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4 Compared with existing results [29, 53–55], the amounts of energy harvested, expressed as a
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6 peak to peak voltage for all samples (Table 2), indicate good values ranging between 25 and 140
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8 V. As films of different thicknesses were measured, the peak to peak voltages have been
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10 reported to the film thickness in order to better compare the samples to each other. It seems like,
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12 along with dielectric permittivity value induced by the silica and barium titanate content,
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14 Young's modulus has a great influence. Thus, sample S10B5 (10 wt% silica and 5 wt% barium
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16 titanate) having the lowest value for Young's modulus (0.81 MPa) among all composites showed
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18 the biggest harvested energy value, 157.3 V/mm, although the dielectric permittivity is 3.67 only.
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26 **4. Conclusions**

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28 A series of silicone elastomer samples have been prepared by incorporation of two fillers, silica
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30 and barium titanate, each of them having different roles, within a high molecular mass
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32 polydimethylsiloxane- α,ω -diol followed by a peroxide crosslinking. By incorporating silica,
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34 Young's modulus strongly increased, as expected, but there was also a very slightly increasing in
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36 the dielectric permittivity value. Instead, by the addition of the second filler, barium titanate,
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38 while the dielectric permittivity more significantly increases, as expected, reaching 4.28 value (at
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40 15 wt% barium titanate and 30 wt% silica loading), and the obtained values reasonably fit those
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42 estimated on the basis of several theoretical models, a worsening is registered both in tensile
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44 stress and elongation values in the series with less silica (S10 and S15), due to lower
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46 compatibility of ceramic filler with silicone matrix and the aggregates formation. Cyclic stress-
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48 strain tests revealed that the elastic properties of resulted elastomers are not significantly affected
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50 by incorporation of barium titanate but they are rather influenced by the silica content. The
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52 dielectric permittivities of all prepared samples remain almost stable over the entire range of
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4 frequencies. Dielectric loss values are low for all samples. The incorporation of the silica and
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6 barium titanate not significantly affects the thermal transitions and moisture sorption of the
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8 composites. Instead, by incorporating silica, the crosslinking degree decreases as was estimated
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10 on the basis of DSC curves, while by co-adding barium titanate some of this loss is recovered but
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12 not to the level found in pure crosslinked silicones. The preliminary harvesting tests reveal
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14 promising results, the best value, 157 V/mm, being obtained in the case of the sample, which has
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16 lowest Young's modulus among prepared composites, 0.81 MPa and dielectric permittivity 3.67.
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18 Thus, starting from the chosen polymer matrix and crosslinking system and considering output
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20 energy as an ultimate features sought, the optimum formulation seems to be S10B5, filled with
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22 10 wt% silica and 5 wt% barium titanate.
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31 **Supporting Information:** Figures 1S shows film formation procedure; Figure 2S- Plotting
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33 experimental dielectric permittivity values as compared with those theoretical estimated by using
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35 different models; Figure 3S - DSC curves for all samples; Figure 4S- water vapor sorption
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37 isotherms; Figure 5S - The electric responses at an applied mechanical impulse; Table 1S-
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39 Dielectric permittivity values predicted by using different models; Theoretical estimation of
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41 dielectric permittivity. This material is available free of charge via the Internet at
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45 <http://pubs.acs.org>.
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