

# Dielectric elastomers based on silicones filled with transitional metal complexes

George Ştiubianu<sup>1</sup>, Alina Soroceanu<sup>\*1</sup>, Cristian-Dragos Varganici<sup>2</sup>, Codrin Tugui<sup>1</sup>, Maria Cazacu<sup>1</sup>

<sup>1</sup>*“Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania*

<sup>2</sup>*Centre of Advanced Research in Bionanoconjugates and Biopolymers, “Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania*

## Abstract

New composite dielectric elastomers with improved dielectric properties were prepared on the basis of polydimethylsiloxane rubber filled with new types of metal (Mn, Fe, Cr) complexes of the bis-azomethine derived from the condensation of a siloxane diamine, 1,3-bis(aminopropyl)tetramethyldisiloxane, with 3,5-di-bromo-2-hydroxybenzaldehyde. The tetramethyldisiloxane fragment from the structure of the complexes creates the premise for a good compatibility with the silicone matrix without the need for other surface treatments while the complexed metal unit through its polar character changes the dielectric properties of the material. The resulted composites crosslinked at room temperature as dielectric elastomer films were investigated in order to establish if such materials are suitable for use in the structure of electromechanical devices. The introduction of metal complexes in the polymer matrix has led to a slight decrease of the elastic domain but increased the relative dielectric permittivity with up to 100% and the electromechanical sensitivity of the materials, with negligible changes of the thermal behavior and overall moisture sorption capacity, thus preserving the chemical stability and hydrophobic character of siloxanes.

*Keywords:* dielectric elastomers, metal complexes, Schiff base, silicones.

## 1. Introduction

Among the classes of polymers that respond to external stimuli such as pH changes, light, temperature, magnetic or electric field, the electroactive polymers are very interesting for use as active elements in actuation and energy harvesting devices. This class of polymers is characterized by the

---

\* Corresponding author. Tel. + 4 0232-217454.  
Email address: [lazar.alina@icmpp.ro](mailto:lazar.alina@icmpp.ro) (A. Soroceanu).

capacity to be actuated almost instantaneously when an electric field is applied and therefore can convert electrical energy into mechanical work or vice versa.

The actuation strain is determined by the mechanical and electric properties of the dielectric elastomers, as shown by the equation of Pelrine [3]:

$$s = p/Y = (\epsilon' \epsilon_0 / Y) \cdot E^2 = \beta \cdot E^2 \quad (1)$$

where  $Y$  – the compression modulus in the thickness direction,  $\epsilon'$  – the dielectric constant,  $\epsilon_0$  – the permittivity of free space,  $E$  – the electric field.

From this equation results that it is desirable for a dielectric elastomer to have high  $\epsilon'$  and very low conductivity and low modulus of elasticity: materials with high  $\epsilon'$  values will generate more output stress and materials with low  $Y$  will produce more strain for the same value of the applied electric field.

In the field of the electroactive polymers, dielectric elastomer actuators are of special interest due to the intrinsic simplicity and the large achievable strains [1]. There are various categories of elastomers that were tested for use as dielectric elastomers in devices, among them being polydimethylsiloxane, [4] polyurethane, [5] and acrylate adhesive films [6].

Silicone rubber is a well-known dielectric elastomer tested for use in actuators [7]. Some of the properties that make it desirable for use in actuation devices are: large displacement with high precision and speed, durability and reliability, low stiffness (low Young's modulus), high breakdown strength [8]. Silicones have highly desired elastic behaviour [9] but suffer from low values of dielectric constant, thus requiring high driving voltages to induce mechanical work [10].

Various materials were incorporated in silicone polymers for achieving large dielectric constant values: phthalocyanines [11], ferroelectric ceramics [12,13], conductive particles [14], and ceramic . The composites of polymers with phthalocyanines are influenced by the humidity in the air [15], the composites with ceramics require a large volume fraction of ceramic, which increases too much the value of the Young modulus [16] and in the composites with conductive fillers as the filler concentration approaches the percolation threshold the conductivity and loss factor values increase very much, affecting the behaviour of the membrane [17]. Conductive metal particle fillers have some other unwanted characteristics: high values of Young modulus, thus stiffening the membrane in which they are used, and the high density of metal nanoparticles reduces the weight saving advantage of dielectric elastomers in comparison with mechanical actuation and energy harvesting [18].

In this work, we chose instead of the solutions presented above to use *3d* transition metal complexes with bis-azomethine ligands containing siloxane spacers as fillers for a polydimethylsiloxane matrix with medium molecular weight ( $M_n = 60000 \text{ g}\cdot\text{mol}^{-1}$ ). The composite

elastomer materials were processed as films and crosslinked by condensation at room temperature by using methyltriacetoxysilane as a well-known crosslinking agent leading to silicone films with good flexibility and excellent strain. We made a comparative study of PDMS-metallic clusters composite versus pure PDMS elastomer and highlighted the benefits of such fillers for the mechanical and dielectric properties of the prepared materials.

## 2. Experimental

### 2.1. Materials

Three metal complexes containing siloxane bond and manganese ( $M_1L$ ), iron ( $M_2L$ ), and chromium ( $M_3L$ ) in their structure, were used as fillers and have been prepared according to procedure reported in [19] and described in Supplementary Information (ESI).

Octamethylcyclotetrasiloxane,  $[(CH_3)_2SiO]_4$ , ( $D_4$ ), supplied by Fluka AG, with the characteristics: b.p. = 175 °C;  $n_D^{20} = 1.396$ ;  $d_4^{20} = 0.955$ , purity > 99 % (GC), was dried over sodium wire and freshly distilled before use.

Purolite CT-175, a styrene-divinylbenzene ion exchanger with  $-SO_3H$  groups (4.1 mequiv./g) was dehydrated by azeotrope distillation with toluene and vacuumation at 110 °C/10 mm Hg before use.

The used polydimethylsiloxane- $\alpha,\omega$ -diol (PDMS) matrix, with molecular  $M_n = 60000$  as estimated on the basis of GPC analysis, was synthesized according to the already described procedure [20,21]: cationic ring-opening polymerization of octamethylcyclotetrasiloxane in the presence of a cation exchanger as catalyst.

Dibutyltin dilaurate (DBTDL) from Sigma-Aldrich, f.p. = 113 °C,  $d_4^{20} = 1.066$ , was used as received.

Methyltriacetoxysilane (MTS) (yield ~75%, b.p.<sub>10</sub> = 95-97 °C,  $d^{20} = 1.17$ , freezing point ~ 40 °C) was prepared and purified in house by a procedure adapted from the literature [22] and described in ref. [23].

### 2.2. Equipments

*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.

*SEM images* on film surfaces fractured in liquid nitrogen were taken with Electron Microscope (ESEM) type Quanta 200 operating until 30 kV with secondary and backscattering electrons in low or high vacuum mode.

The presence and ratio of metals were evidenced using an *Energy-Dispersive X-ray Fluorescence* (EDXRF) system EX-2600 X-Calibur SDD, as fast and non-destructive method, able to use very small amounts of the sample. The measurements were done in the same conditions for all the samples, i.e. current 30  $\mu\text{A}$ , voltage 15 kV, time 200 s, range 10 keV in vacuum. The  $\text{K}\alpha_1$  peak for elements and its intensity (in Counts) was identified. The samples were measured at least twice on each side.

*DSC measurements* were conducted with a DSC 200 F3 Maia (Netzsch, Germany). About 10 mg of each sample was heated in pressed and punched aluminium crucibles at a heating/cooling rate of 10/-10  $^{\circ}\text{C}\cdot\text{min}^{-1}$ . Nitrogen was used as inert atmosphere at a flow rate of 100  $\text{mL min}^{-1}$ . The temperature range for the measurements performed with this instrument was (-150) – (+150)  $^{\circ}\text{C}$ , using a heating rate of 10  $^{\circ}\text{C}\cdot\text{min}^{-1}$ . The temperature against heat flow was recorded. The baseline was obtained by scanning the temperature domain of the experiments with an empty pan. The enthalpy was calibrated with indium according to standard procedures.

The measurements for *Dynamic Vapour Sorption* were performed with an IGAcorp Dynamic Vapour Sorption apparatus with resolution of 0.1  $\mu\text{g}$  for 100 mg and the sample containers are made out of stainless steel micron size mesh. Before measurements, the samples are dried in a flow of dry nitrogen (250  $\text{mL}/\text{min}$ ) at room temperature until the weight of the sample was in equilibrium, with a relative humidity  $\text{RH}<1\%$ . The measurements involve step increases of 10% for the relative humidity of the controlled flow of nitrogen and recording the mass change of the tested sample for each step, after the sample is first dried with a current of dry nitrogen.

*Stress-strain measurements* were performed on a 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  $\text{mm}/\text{min}$ , at room temperature. All samples were measured three times and the averages of the obtained values were taken into consideration.

*Dielectric spectroscopy* was performed using the Novocontrol “Concept 40” broadband dielectric spectrometer (Hundsangen, Germany). The samples were mounted between gold platens and positioned in the Novocontrol Quatro Cryosystem. The dielectric experiment was carried out keeping the temperature fixed but sweeping the frequency. The temperature during testing of samples was 25  $^{\circ}\text{C}$  and six decades (log scale) of frequency, i.e. 1–100000 Hz, were scanned, with the dielectric constant ( $\epsilon'$ ) and loss ( $\epsilon''$ ) were recorded in the frequency domain (1 Hz–1 MHz). The metal complexes were each grounded to a fine powder and then pressed with a 10-ton force press into a pill with 13 mm diameter and 1 mm thickness for dielectric properties tests, in the range of  $10^0 - 10^6$  Hz. The samples of dielectric elastomers (each with thickness <1 mm) were placed between gold plated round electrodes, the upper electrode having a 20 mm diameter.

The measurements for *electric breakdown strength* (EBD) were performed on a Trek installation consisting of: high-speed high-voltage power amplifier, function generator, and oscilloscope. All the samples were allowed to reach equilibrium with the environmental humidity by keeping for 24 hours in the equipment room before measurements. The electrodes made of aluminum discs with 2.5 cm diameter were applied on the film samples and the measurements were performed with a voltage increase rate of  $500 \text{ V}\cdot\text{s}^{-1}$  at room temperature ( $20 \text{ }^\circ\text{C}$ ) and relative humidity  $\text{RH}\sim 70\%$  and three tests were made for each sample, with the smallest value taken into account.

### 2.3. Procedure

#### *Preparation of composite materials and film formation*

Each metal complex (Supporting Information, **Figure 1 ESI**) was dissolved in chloroform as 10 wt% solution. For the preparation of each film of dielectric elastomer, in a Berzelius glass beaker a weighted amount of siloxane polymer was mixed with precise amounts of metal complex solution, the crosslinking agent methyltriacetoxysilane (MTS) (8% wt ratio to siloxane polymer) and the catalyst DBTDL (1% wt ratio to siloxane polymer). Three different metal complexes were used for the preparation of samples:  $\text{M}_1\text{L}$ ,  $\text{M}_2\text{L}$ ,  $\text{M}_3\text{L}$ , where  $\text{M}_1$  – manganese,  $\text{M}_2$  – iron,  $\text{M}_3$  – chromium and L is the ligand (Schiff base derived from 3,5-dibromosalicylaldehyde and 1,3-bis(3-aminopropyl)tetramethyldisiloxane) (*ESI 1.1, 1.2, 1.3*). For each of the three metal complexes used in tests ( $\text{M}_1\text{L}$ ,  $\text{M}_2\text{L}$ ,  $\text{M}_3\text{L}$ ), there were prepared films with different contents of these: with 2 wt % ratio to siloxane polymer ( $\text{M}_1\text{L}$  2%,  $\text{M}_2\text{L}$  2%,  $\text{M}_3\text{L}$  2%), and with high content of complex - 15 wt% ratio to siloxane polymer:  $\text{M}_1\text{L}$  15%  $\text{M}_2\text{L}$  15%,  $\text{M}_3\text{L}$  15% (**Table 1**). One reference sample (RS) was prepared only with polydimethylsiloxane, crosslinker MTS and catalyst DBTDL.

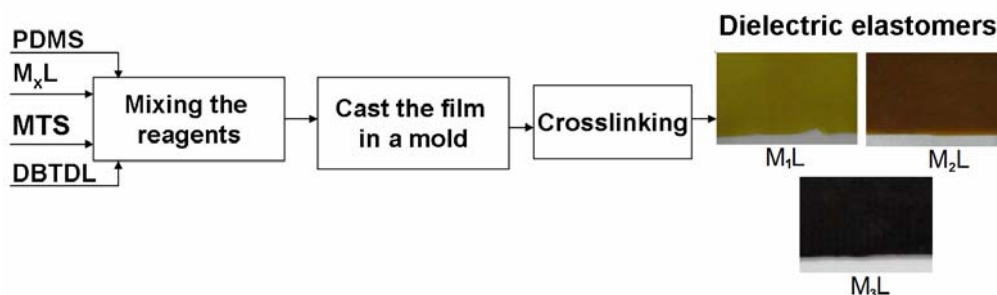
**Table 1.** The composition of the prepared films

Sample	Composition, % w	
	PDMS	$\text{M}_x\text{L}^{**}$ complex
RS*	100	0
$\text{M}_1\text{L}$ 2%	100	2
$\text{M}_2\text{L}$ 2%	100	2
$\text{M}_3\text{L}$ 2%	100	2
$\text{M}_1\text{L}$ 15%	100	15
$\text{M}_2\text{L}$ 15%	100	15
$\text{M}_3\text{L}$ 15%	100	15

\* RS – reference sample.

\*\*  $\text{M}_x\text{L}$  – the metal (1 – manganese, 2 – iron, 3 – chromium) and the ligand (bis-azomethine derived from 3,5-dibromosalicylaldehyde and 1,3-bis(3-aminopropyl)tetramethyldisiloxane).

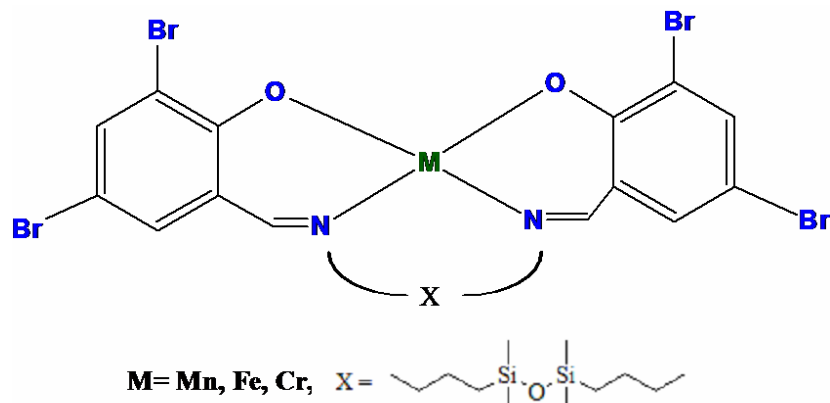
The uniform mixture was cast in teflon mold where it crosslinked for two weeks by room temperature hydrolysis of MTS with the water vapours in atmosphere and condensation of resulted silanol with the siloxane matrix polymer (**Scheme 1**). The films were manually peeled off from the surface of the mold. The sequence of the steps from the initial components to the elastomer in the form of a film is shown graphically in **Scheme 1**.



**Scheme 1.** Preparation of composites with metal complexes and film formation

### 3. Results and discussion

A polydimethylsiloxane- $\alpha,\omega$ -diol of molecular mass,  $M_n = 60000$  was prepared and used as a matrix for composites. Three complexes (**Scheme 2**) of Mn, Fe, Cr with ligands of bis-Schiff base type obtained by condensation reaction between 1,3-bis(3-aminopropyl)tetramethyldisiloxane ( $AP_0$ ) and 3,5-dibromosalicylaldehyde were considered for this study as filler for the silicone matrix taking into account their mixed nature conferred by the co-existence of highly hydrophobic bis(propyl)tetramethyldisiloxane moiety and more polar azomethine-metal complex group.



**Scheme 2.** General structure of the synthesized metal complexes

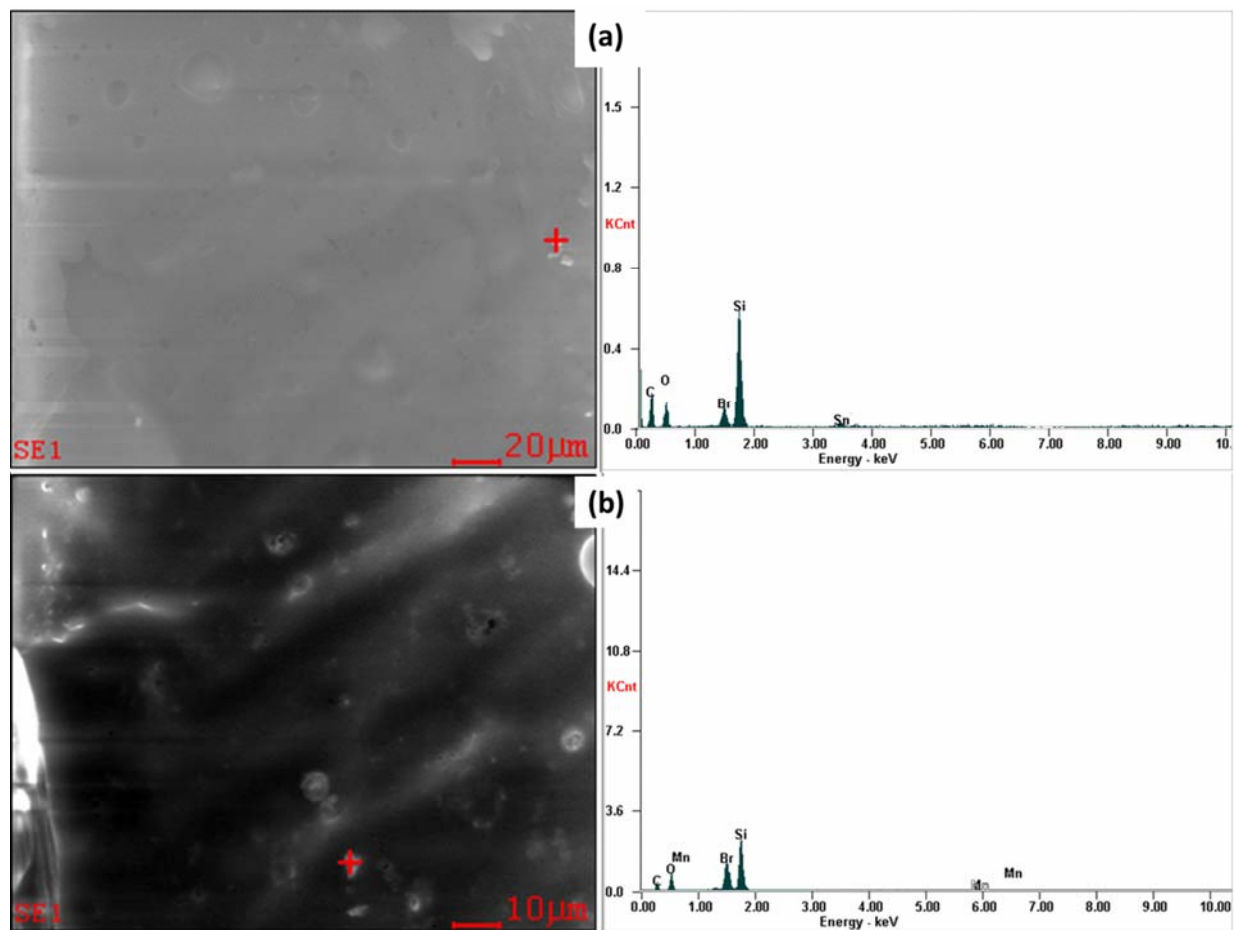
We started from the premise that the siloxane moiety in the complex will ensure its compatibility with silicone matrix while the block consisting of complexed metallic core is the polar component that will help increase the dielectric constant of the resulted composite material.

Therefore, the dielectric permittivity of the complexes was first determined. For this, each of the metal complexes was pressed as pills with 9 mm diameter and ~1 mm thickness and in this form each material was tested for dielectric properties.

Thus the complex with iron ( $M_2L$ ) has the maximum value of dielectric constant ( $\epsilon'$ ) at  $10^0$  Hz of  $7.52 \times 10^6$ , loss factor,  $\epsilon'' = 2 \times 10^7$ , and a conductivity of  $2 \times 10^{-5}$  S/cm, in the range for semiconductor materials. The complex with chromium ( $M_3L$ ) has  $\epsilon' = 7$  at  $10^0$  Hz, the value for the loss factor of  $\epsilon'' = 0.42$  and a conductivity that varies in the range  $10^{-13} - 10^{-8}$  S/cm when sweeping the current in the range  $10^0 - 10^6$  Hz, such values for conductivity being met in insulator materials. All metal complexes show a gentle slope of decreasing dielectric constant value with increasing frequency, but still have values that are larger than that of siloxane ( $\epsilon' \sim 3$ ) at large frequencies ( $10^6$  Hz). The dielectric loss factor ( $\epsilon''$ ) has large values for  $M_2L$  ( $\epsilon'' \gg 1$ ) but  $M_3L$  has small desirable values for this parameter ( $\epsilon'' \sim 4 \times 10^{-1}$  at  $10^0$  Hz). The large values for the dielectric constant make these metallic complexes interesting for use in preparation of dielectric elastomers composites, in order to increase the value of  $\epsilon'$  for such materials. From our knowledge, this is the second time that transitional metal complexes are used to enhance the properties of dielectric elastomers after our recently published first one [24] no one else reporting such approach. These were incorporated in the silicone polymer as solution in chloroform that is also a solvent for polydimethylsiloxane, thus permitting their mixing at molecular level. After incorporation of the crosslinker agent and catalyst, the mixtures were processed as films by pouring in appropriate form and crosslinked in order to obtain a dimensional stability. For this, a classical procedure consisting in condensation of the polydimethylsiloxane- $\alpha,\omega$ -diol with a trifunctional silane, methyltriacetoxysilane was performed in presence of an organometallic catalyst (dibutyltindilaureate). Coloured films in dependence of the metallic ion type were obtained, that were further analyzed (**Scheme 1**).

Due to their low surface energy, siloxane molecular chains migrate at the surface of elastomer films and form a cover layer of hundred nanometers thickness on the surface [25]. This makes it necessary to freeze the samples in liquid nitrogen and immediately fracture them when trying to analyze the morphology of the film. The SEM images (**Figure 1**) taken on cryofractured section of the films reveal presence of the roughly spherical aggregates with diameter of 2-4 micrometers dispersed within the continuum phase. These could consist in silsesquioxane generated by the hydrolysis and condensation of methyltriacetoxysilane, which was added in high excess to assure an effective

crosslinking. The samples containing metal complexes also contain micrometer size particles made of agglomerates of silica and metal complex, as evidenced by EDX (**Figure 1**) and XRF measurements for all three types of complexes, with manganese, iron and chromium respectively (**Figures 1 ESI** and **Figure 2 ESI**). The agglomerates have different sizes and are almost homogeneously dispersed throughout the siloxane elastomer. Thus, it is expected that the introduction of the metal complexes in the formulation of siloxane elastomers would change the properties of the materials in a homogeneous manner for all the surface of the elastomer film.



**Figure 1.** SEM and EDX data for two samples: (a) RS; (b) M<sub>1</sub>L 15%.

From DSC analysis (**Figure 3 ESI**) it is visible all samples have classical transitions for silicones: glass transition ( $T_g$ ) in the range  $-121 \dots -123 \text{ }^\circ\text{C}$ , with the value slightly decreasing when there is larger content of metal complex, as the particles occupy the free volume between the siloxane chains and are physically embedded in the network. DSC curves show one exothermic peak at about  $-70/-74 \text{ }^\circ\text{C}$  assigned to the phenomenon of cold crystallization and an endothermic peak at  $-38/-42 \text{ }^\circ\text{C}$  attributed to melting of crystalline phase. The area of the peak for melting ( $-42 \text{ }^\circ\text{C}$ ) is similar to the



area of the one corresponding for crystallization (-70 °C). With the increase in the content of metal complex, the temperature of the peak increases from around -42 to around -40 (M<sub>x</sub>L 2%) and then to around -39 °C (M<sub>x</sub>L 15%) (**Figures 3 ESI a,b,c** and **3 ESI a,d,e**). The different sizes of the areas of the melting and crystallization peaks demonstrate that the nature of the metal complex also influences the thermal behavior of the elastomer samples, but the influence of the degree of crosslinking (influenced by the percentage of metal complex in the sample), as seen from DSC results, is more significant than the influence of the type of metal complex used. Thus, the heat capacities associated with the melting transition vary from 21.6 J/g for reference RS to 19.7 J/g for M<sub>1</sub>L 15%, 19.1 J/g for M<sub>2</sub>L 15% and 19.5 J/g for M<sub>3</sub>L15%. Also the heat capacities associated with the crystallization transition vary from 24.2 J/g for reference RS to 20.3 J/g for M<sub>1</sub>L 15%, 19.3 J/g for M<sub>2</sub>L 15% and 18.5 J/g for M<sub>3</sub>L15%.

It is possible to use DSC data for calculation of the crosslinking density, according to equation:

$$\rho_c = (C_p^i - C_p^0) / C_p^0 \quad (2)$$

where  $C_p^i$  and  $C_p^0$  are the heat capacities of the polymer network at a given crosslinking density and of the non-crosslinked polymer, respectively [26,27]. For this purpose, DSC curves were recorded in the range -150 up to +150 °C. Polydimethylsiloxanes have  $T_g$  around -122 °C. The data obtained from DSC analysis (**Figure 3 ESI**) show that samples have  $T_g$  values in the range -121 ... -123 °C and for calculating the crosslinking density values according to equation 2 was used the heat capacity value of this transition. The degree of crosslinking has specific values for each metal complex, but there is an increase of the crosslinking degree with increasing content of metal complex in the sample (**Table 2**).

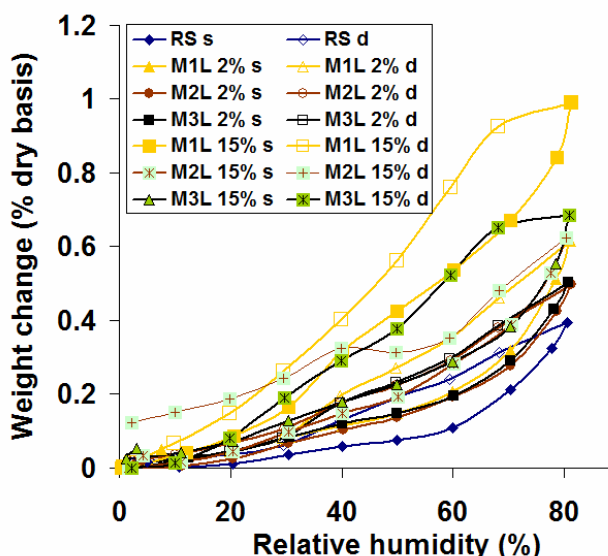
**Table 2.** Data for crosslinking degree of siloxane-metal complexes as estimated from DSC tests

Sample	Heat capacity, $C_p$ (J·g <sup>-1</sup> ·K <sup>-1</sup> )	Crosslinking density, $\rho_c$ (mol·cm <sup>-3</sup> ) <sup>a</sup>
PDMS <sup>b</sup>	0.100	0
RS*	0.095	0.05
M <sub>1</sub> L 2%	0.076	0.24
M <sub>2</sub> L 2%	0.068	0.32
M <sub>3</sub> L 2%	0.067	0.33
M <sub>1</sub> L 15%	0.075	0.25
M <sub>2</sub> L 15%	0.073	0.27
M <sub>3</sub> L 15%	0.060	0.40

<sup>a</sup>Determined using equation (2).

<sup>b</sup>PDMS – non-crosslinked polydimethylsiloxane.

**Figure 2** shows the sorption/desorption isotherms at 25 °C, as the total water uptake per sample mass in relation to the environmental relative humidity for the samples containing the metal complexes. For constructing various devices using dielectric elastomers it is important to know the way these materials behave in the presence of water vapours. The shape of the isotherms is similar for the reference samples and samples containing metal complexes. Although insignificant, the sorption capacity increases with increasing weight percentage of complex added in the siloxane, with specific values for each metal used, going from 0.39 wt% for reference sample up to 0.99 wt% in the case of the composite with highest amount of complex M<sub>1</sub>L 15%.

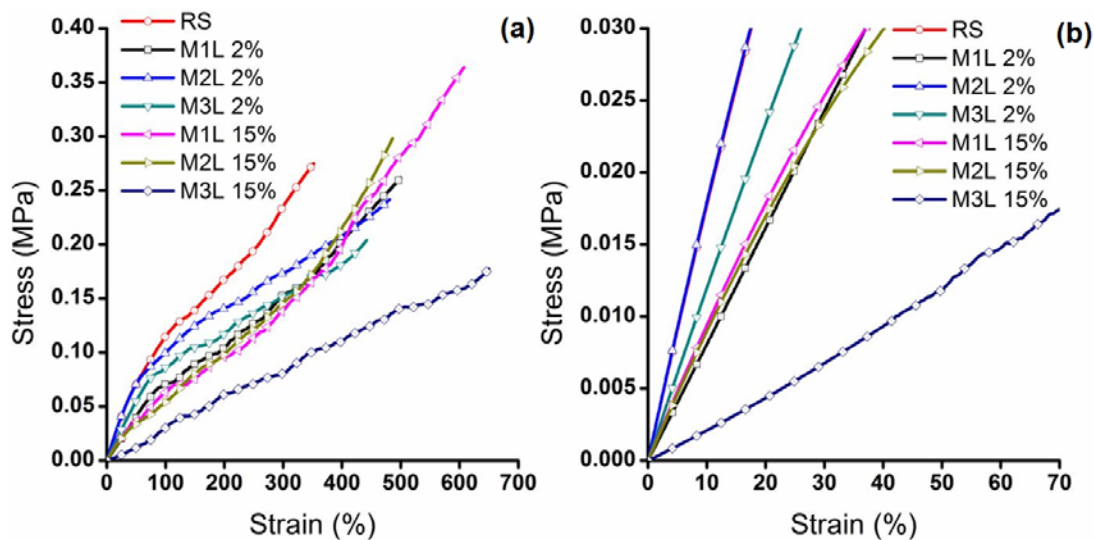


**Figure 2.** Water vapor sorption isotherms of the prepared composites: s - sorption isotherm, d - desorption isotherm

The weight change of the samples is inversely correlated with the degree of crosslinking, with the largest weight change for sample M<sub>1</sub>L 15% (0.99% dry basis) where both the effect of lower degree of crosslinking and the hydrophilic character of the metal complex particles act to increase the water vapour sorption. This is due to more polar character of the complexes able to form hydrogen bonds with water molecules. The amphiphile character of the metal complexes, that has been demonstrated for similar structures [28], permits their assembling into an aggregate which in a nonpolar environment (e.g., chloroform and silicone matrix) is oriented with the polar sides to the inside of the formation, thus hindering their contact with water. This structure of the materials leads to appearance of hysteresis loop between the sorption and desorption isotherms. Overall samples show water sorption below 1% weight dry basis, therefore the hydrophobic character specific for siloxanes is preserved. The shapes of the moisture sorption isotherms are type IV (IUPAC classification). The adsorption process shows a

type H3 hysteresis loop (along with pore condensation) and it is characteristic for mesoporous materials with slit-shaped pores [29].

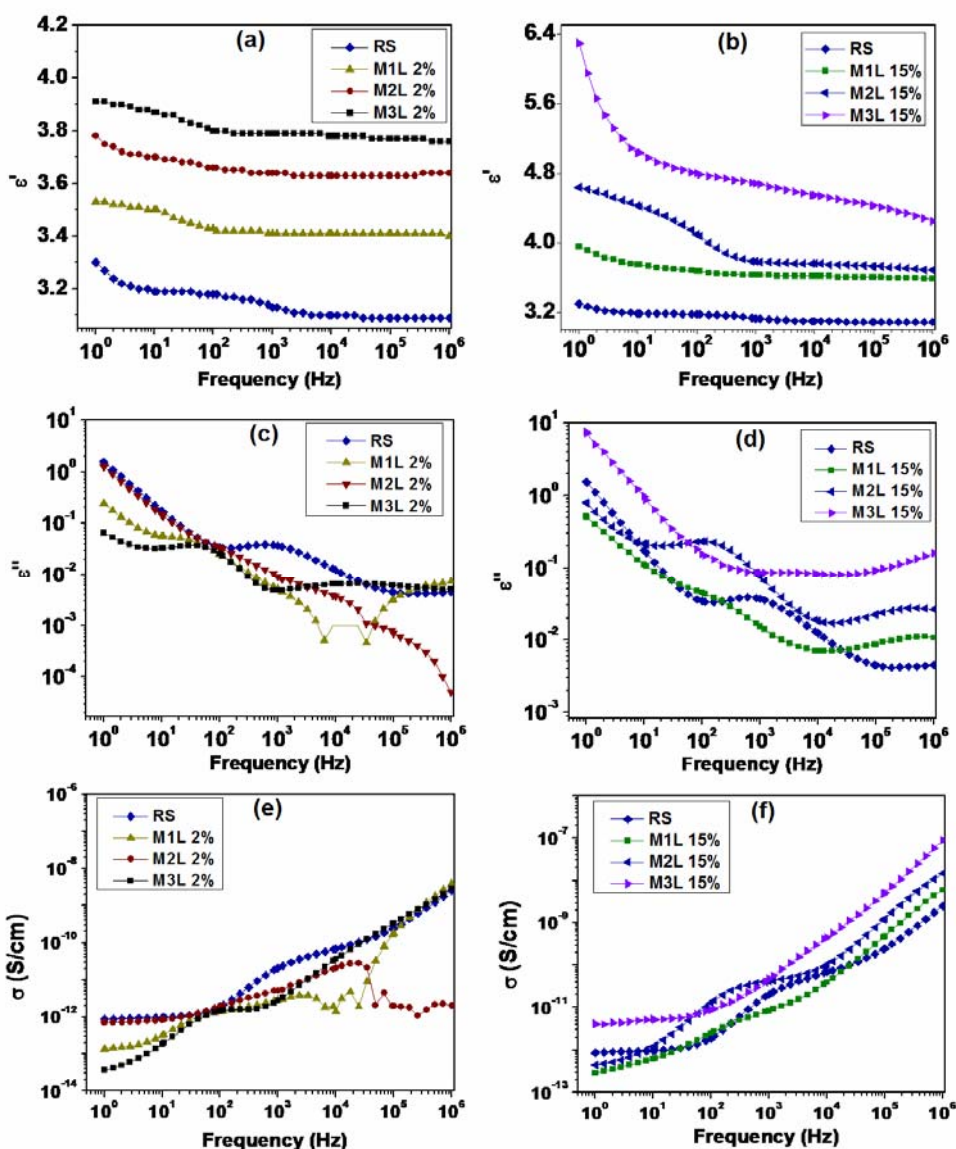
Tensile strength tests were performed at room temperature. The samples with low content of metal complex (2 wt%) show an elastic behaviour up to 50% strain (**Figure 3a**), similar to pure siloxane elastomer. At larger values of strain, above 50%, a plastic component is visible on the stress-strain curve due to crystallization processes. The samples with increased content of metal complex show a much reduced elastic domain at the beginning of the strain curve, due to plasticization effect of metal complex particles (**Figure 3b**).



**Figure 3.** (a) Stress-strain results for the tested samples; (b) elastic part of the stress-strain curves (the curve of sample M<sub>2</sub>L 2% is almost perfectly over imposed on that of sample RS up to 40% strain)

In comparison with the reference sample RS, the other samples possess increased values for breaking strain and for samples with manganese and iron also larger values for breaking stress. The values for breaking strain increase with the content of metal complex from 2 to 15 wt%, as the particles of metal complex and silica act as reinforcing filler for the siloxane matrix. The dielectric properties are the most important for dielectric elastomers that would be used in actuation and energy harvesting. Therefore these properties were determined using a dielectric spectrometer at room temperature. As a general characteristic, the samples prepared with metal complexes possess increased values of the dielectric constant in comparison with the reference sample RS. The dielectric properties at low frequencies (~1 Hz) are important both for energy harvesting and low frequency actuation. At such frequencies and also in the whole range of frequencies tested ( $10^0$  -  $10^6$  Hz) the largest values for the dielectric permittivity were recorded for samples with chromium complex.

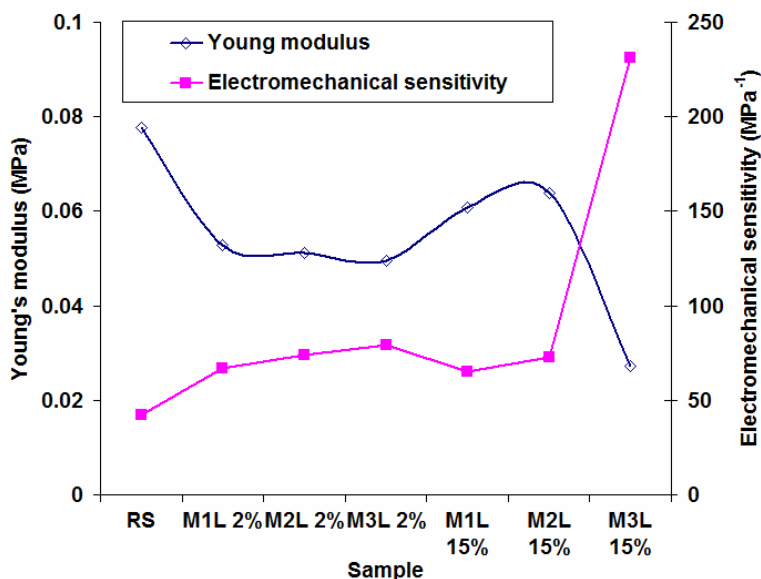
The value for the dielectric constant ( $\epsilon'$ ) increases for each type of metal with the content of it added in the elastomer from 2% to 15% weight (Figure 4 a,b). Also the values for  $\epsilon'$  correlate with the degree of crosslinking of the samples determined from the DSC measurements. On the other hand the loss factor ( $\epsilon''$ ) (Figure 4 c,d) presents a reverse evolution, with the samples containing low percentage of metal complexes (2%) having a reduced value of this parameter in comparison with the reference sample. However the increase of metal complex content in samples to 15% leads to a significant increase of the loss factor, and this is visible especially for the sample with chromium complex at low frequencies ( $<10^3$  Hz).



**Figure 4.** Dielectric data for the dielectric elastomers tested: (a),(b) dielectric constant for samples with low (2%) and high (15%) content of metal complex; (c),(d) loss factor for samples with low (2%) and high (15%) content of metal complex; (e),(f) conductivity for samples with low (2%) and high (15%) content of metal complex

The samples with iron and manganese maintain acceptable values for  $\epsilon''$  ( $<0.5$ ) at low frequencies. From the conductivity values graphs (**Figure 4 e,f**) it is visible that samples are dielectric and the electrically non-conducting character of siloxane is preserved. These values demonstrate that the samples, especially the ones with manganese and iron, are a good alternative for pure siloxane and other dielectric polymers for use in wave energy harvesting and in actuation.

An important parameter for the mechanical behaviour of a material is the Young's modulus ( $Y$ ) which was determined from the results of the stress-strain tests. Since for every material the variation of values for a series of 5 samples was less than 5%, no error bars are presented in the chart of the Young's modulus (**Figure 5**). The electromechanical sensitivity ( $\beta$ ) is the main variable of the elastic energy density (for a said electric field, the elastic energy density is proportional to the main variable  $\epsilon' \epsilon_0 / Y$  from equation (1)) [30,31] and was calculated using data recorded under the following conditions:  $\epsilon'$  was measured at 1 Hz, and  $Y$  was measured at breaking strain for each sample. The values for  $\beta$  calculated in the elastic area of deformation (at 15% strain) would result in an even larger difference between the reference sample and the samples containing metal complexes. Leaving aside the large value for sample  $M_3L$  15% which also has very large loss factor ( $>1$ ), the other samples presented values of  $\beta$  almost twice as good as the pure siloxane reference sample.



**Figure 5.** Electromechanical sensitivity of the samples compared with the Young's modulus values

The dielectric elastomer films have thicknesses of  $\sim 350 \mu\text{m}$ . The tests performed in order to determine the EBD value of each sample (**Table 3**) show there is an increase of this value at small content of metal complex filler and the best value was recorded for the samples with manganese

(M<sub>1</sub>L). The introduction of a larger amount of metal complex in the sample (15%) leads to a decrease of the EBD values for samples of all the metal complexes used. The recorded variation of the values for EBD both for multiple tests on each sample and for tests on different samples show that this is also a problem of elastomer homogeneity, and one of the goals for future works is to try to solve this by formation of elastomer films in chambers with controlled atmosphere.

**Table 3.** Mechanical and dielectric properties of the prepared composites

<b>Sample</b>	<b>Breaking stress (MPa)</b>	<b>Stress at 15% elongation (MPa)</b>	<b>Elongation at break (% initial length)</b>	<b>Young's modulus at 15% elongation<sup>a</sup></b>	<b>ε'</b> <b>(10 Hz)</b>	<b>ε''</b> <b>(10 Hz)</b>	<b>EBD<sup>b</sup></b> <b>(MV/m)</b>
<b>RS</b>	0.275	0.0135	352	0.0117	3.18	0.162	21
<b>M<sub>1</sub>L 2%</b>	0.262	0.0111	500	0.0096	3.49	0.059	30
<b>M<sub>2</sub>L 2%</b>	0.246	0.0103	481	0.0089	3.70	0.148	22
<b>M<sub>3</sub>L 2%</b>	0.208	0.0125	442	0.0108	3.86	0.032	22
<b>M<sub>1</sub>L 15%</b>	0.369	0.0154	608	0.0134	3.73	0.095	29
<b>M<sub>2</sub>L 15%</b>	0.310	0.0098	486	0.0085	4.42	0.160	11
<b>M<sub>3</sub>L 15%</b>	0.177	0.0025	650	0.0022	5.04	0.980	15

<sup>a</sup>A 15% elongation is in the range of perfectly elastic deformation of the dielectric elastomer membranes, therefore the value of Young modulus was calculated at this value of elongation

<sup>b</sup>Electric breakdown strength (EBD) values were determined from measurements performed according to the procedure mentioned in Equipments paragraph.

#### 4. Conclusions

Dielectric elastomers materials with transition metal complexes were prepared using mechanical mixing of the components followed by crosslinking using well known siloxane chemistry. The metal complexes form nano- and microaggregate particles together with the silica generated from the hydrolysis and condensation of crosslinking agent methyltriacetoxysilane, these particles being spread evenly throughout the siloxane matrix, leading to elastomer films with thermal behaviour similar with the pure crosslinked siloxane, as determined by DSC tests. The samples with metal complexes possess

improved breaking strain values in comparison with the siloxane reference sample and the hydrophobic character of the siloxane elastomer is preserved, with low values for water uptake determined from sorption isotherms.

The dielectric properties of the elastomers containing metal complexes are also improved when compared with pure siloxane (RS): dielectric constant of the films ( $\epsilon'$ ) is larger than that of the pure siloxane film, while the loss factor ( $\epsilon''$ ) remains at low values. The electromechanical sensitivity is almost twice as good for samples with metal complexes in comparison with the reference sample, which is a very good characteristic in view of using such materials for dielectric elastomer actuators.

### **Acknowledgements**

The work presented in this paper is developed in the context of the project PolyWEC ([www.polywec.org](http://www.polywec.org), prj. ref. 309139), a FET-Energy project that is partially funded by the 7th Framework Programme of European Community and co-financed by UEFISCDI (Contract 205EU).

### **References**

1. Brochu P, Pei QB. Advances in dielectric elastomers for actuators and artificial muscles. *Macromol. Rapid Commun.* 2010; 31(1): 10-36.
2. Carpi F, De Rossi D, Kornbluh R, Pelrine R, Sommer-Larsen P (Eds.). *Dielectric Elastomers as Electromechanical Transducers: Fundamentals, Materials, Devices, Models and Applications of an emerging electroactive Polymer Technology.* Elsevier Ltd. 2008; 60.
3. Pelrine R, Kornbluh R, Pei QB, Joseph J. High-speed electrically actuated elastomers with strain greater than 100%. *Science* 2000; 287(5454): 836-839.
4. Löwe C, Zhang X, Kovacs G. Dielectric Elastomers in Actuator Technology. *Adv. Eng. Mat.* 2005; 7(5): 361-367.
5. Gallone G, Carpi F, Galantini F, De Rossi D, Levita G. Enhancing the electro-mechanical response of Maxwell stress actuators. *Adv. Sci. Technol.* 2008; 61: 46–53.
6. Kofod G, Sommer-Larsen P, Kornbluh R, Pelrine R. Actuation Response of Polyacrylate Dielectric Elastomers. *J. Intell.Mater. Syst. Struct.* 2003; 14(12): 787-793.
7. Gharavi N, Razzaghi-Kashani M, Golshan-Ebrahimi N. Effect of organo-clay on the dielectric relaxation response of silicone rubber. *Smart Mater. Struct.* 2010; 19(2): 025002.
8. Enis T, Sauers I. Chapter 11. Industrial Applications Perspective of Nanodielectrics. In: Nelson J. Keith (Ed.). *Dielectric Polymer Nanocomposites.* Springer 2009; 321.

9. Koulouridis S, Kiziltas G, Zhou Y, Hansford DJ, Volakis JL. Polymer–Ceramic Composites for Microwave Applications: Fabrication and Performance Assessment. *IEEE T. MICROW. THEORY* 2006; 54(12): 4202–4208.
10. Bar-Cohen Y, Zhang Q. Electroactive Polymer Actuators and Sensors. *MRS Bull.* 2008; 33(3): 173-181.
11. Wang JW, Shen QD, Yang CZ, Zhang QM. High Dielectric Constant Composite of P(VDF–TrFE) with Grafted Copper Phthalocyanine Oligomer. *Macromolecules* 2004; 37: 2294-2298.
12. Vrejoiu I, Pedarnig JD, Dinescu M, Bauer-Gogonea S, Bäuerle D. Flexible ceramic–polymer composite films with temperature-insensitive and tunable dielectric permittivity. *Appl. Phys. A* 2002; 74(3): 407-409.
13. Iacob M, Bele A, Patras X, Pasca S, Butnaru M, Alexandru M, Ovezza D, Cazacu M. Preparation of electromechanically active silicone composites and some evaluations of their suitability for biomedical applications. *Mater. Science Eng. C* 2014; 43(1): 392-402.
14. Lu J, Moon KS, Wong CP. Silver/polymer nanocomposite as a high-k-polymer matrix for dielectric composites with improved dielectric performance. *J. Mater. Chem.* 2008; 18(40): 4821-4826.
15. Opris DM, Nüesch F, Löwe C, Molberg M, Nagel M. Synthesis, Characterization, and Dielectric Properties of Phthalocyanines with Ester and Carboxylic Acid Functionalities. *Chem. Mater.* 2008; 20: 6889-6896.
16. Brennan A, Wang B, Rodrigues DE, Wilkens GL. Structure-property behavior of novel Ti/poly(tetramethylene oxide) (PTMO) and Zr/PTMO hybrid CERAMER materials prepared by the sol gel method. *J. Inorg. Organomet. Polym.* 1991; 1: 167-187.
17. Choi HW, Heo YW, Lee JH, Park ET, Chung YK. Effects of BaTiO<sub>3</sub> on dielectric behavior of BaTiO<sub>3</sub>-Ni-polymethyl methacrylate composites. *Appl. Phys. Lett.* 2006; 89: 132910.
18. Molberg M, Crespy D, Rupper P, Nüesch F, Månson JAE, Löwe C, Opris DM. High Breakdown Field Dielectric Elastomer Actuators Using Encapsulated Polyaniline as High Dielectric Constant Filler. *Adv. Funct. Mater.* 2010; 20: 3280–3291.
19. Soroceanu A, Cazacu M, Shova S, Turta C, Kožíšek J, Gall M, Breza M, Rapta P, MacLeod TCO, Pombeiro AJL, Telser J, Dobrov AA, Arion VB. Copper(II) Complexes with Schiff Bases Containing a Disiloxane Unit: Synthesis, Structure, Bonding Features and Catalytic Activity for Aerobic Oxidation of Benzyl Alcohol. *Eur. J. Inorg. Chem.* 2013; 9: 1458–1474.



20. Cazacu M, Marcu M. Silicone Rubbers IX. Contributions to Polydimethylsiloxanes- $\alpha,\omega$ -diols. Synthesis by Heterogeneous Catalysis. *J. Macromol. Sci. Part A* 1995; 32: 1019-1025.
21. Marcu M, Simionescu M, Cazacu M, Lazarescu S, Ibanescu C. Obtaining poly(dimethylsiloxane) $\alpha,\omega$ -diols using the heterogeneous catalysis. The optimization of the reaction conditions. *Iran. J. Polym. Sci.* 1994; 3: 95–104.
22. Andrianov KA, Zhdanov AA, Bogdanova AA. *Dokl. Akad. Nauk. SSSR, Proceedings of the Academy of Sciences of the USSR.* 1954; 9: 697-699.
23. Bele A, Cazacu M, Stiubianu G, Vlad S. Silicone - barium titanate composites with increased electromechanical sensitivity. The effects of the filler morphology. *RSC Adv.* 2014; 4: 58522-58529.
24. Cazacu M, Racles C, Zaltariov MF, Dumitriu AMC, Ignat M, Ovezea D, Stiubianu G. Electroactive composites based on polydimethylsiloxane and some new metal complexes. *Smart Mater. Struct.* 2013; 22(10): 104008.
25. Twomey B, Dowling D, Byrne G, O'Neill L, O'Hare LA. Properties of Siloxane Coatings Deposited in a Reel-to-Reel Atmospheric Pressure Plasma System. *Plasma Process. Polym.* 2007; 4: S450–S454.
26. Vera-Graziano R, Hernandez-Sanchez F, Cauch-Rodriguez JV. Study of crosslinking density in polydimethylsiloxane networks by DSC. *J. Appl. Polym. Sci.* 1995; 55: 1317–1327.
27. Flory PJ, Rehner JJr. Statistical Mechanics of Cross-Linked Polymer Networks II. Swelling. *J. Chem. Phys.* 1943; 11: 521-526.
28. Soroceanu A, Cazacu M, Racles C, Stoica I. Supramolecular aggregation in organic solvents of discrete copper complexes formed with organo-siloxane ligands. *Soft Materials* 2015; 13(2): 93-105.
29. Ng EP, Mintova S. Nanoporous materials with enhanced hydrophilicity and high water sorption capacity. *Micropor. Mesopor. Mater.* 2008; 114: 1–26.
30. Hang Z, Dong-Rui W, Jun-Wei Z, Jun Z, Zhi-Min D. Increased electroaction through a molecular flexibility tuning process in TiO<sub>2</sub>-polydimethylsilicone nanocomposites. *J. Mater. Chem. A* 2013; 1: 3140-3145.
31. Kussmaul B, Risse S, Wegener M, Bluemke M, Krause J, Wagner J, Feller T, Clauberg K, Hitzbleck J, Gerhard R, Krueger H. New DEA materials by organic modification of silicone and polyurethane networks. In: *Electroactive Polymer Actuators and Devices (EAPAD)*. Proc. of SPIE 2013; 8687: 86872S.

