ROMANIAN ACADEMY

„PETRU PONI” INSTITUTE OF MACROMOLECULAR CHEMISTRY, IAȘI

SMART SILICONE MATERIALS

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Iași, 2017

ROMANIAN ACADEMY

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Nr. 6479 / 29 IX 2017

To Mr/Mrs ______________________________

We would like to inform you that on **25.10.2017**, at **12:00 p.m.**, in the library of the „Petru Poni" Institute of Macromolecular Chemistry, Iași, will be the public presentation of the doctoral thesis entitled **„Smart Silicone Materials"** elaborated by **Eng. Adrian Bele,** in order to confer the scientific title of doctor.

The doctoral commission has the following members:

PRESIDENT: **PhD. Anton Airinei**, senior researcher (CSI)
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In accordance with the Regulation regarding the organization and conducting the doctorate for awarding the scientific titles within the Romanian Academy, we are sending you the summary of the doctoral thesis with the request to communicate in writing your appreciations and remarks.

On this occasion, we invite you to participate to the public defence of the doctoral thesis.

DIRECTOR,

PhD. Anton Airinei

INSTITUTUL DE CHIMIE MACROMOLECULARĂ "PETRU PONI" IAȘI

Acknowledgments

At the end of the PhD, I like to give my sincere thanks to **Dr. Maria Cazacu**, scientific coordinator, for the exceptional guidance, patience and advices offered during the scientific research period.

To Dr. Carmen Racleș, grateful gratitude and deep respect for the support, help, guidance, advices and ideas offered generously, trust and patience for the entire period of scientific research.

Thanks to the **Romanian Academy** for the financial support along the PhD period.

Thanks to the teams that led the projects **PolyWEC** (New mechanisms and concepts for exploiting electroactive Polymers for Wave Energy Conversion, 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 Romanian National Authority for Scientific Research CNCS-UEFISCDI (Contract 205EU), ***Energy harvesting by dielectric elastomer generators*** – Swiss-Romanian cooperation programme (IZERZO_142215/1; 10/RO-CH/RSRP/01.01.2013) and **GreENergy** (Silicone-based conversion units obtained by "green" chemistry, PN-III-P2-2.1-PED-2016-0188).

Many thanks to all the members of the **Inorganic Polymers Laboratory** for help and advices, and to all my colleagues that helped me characterize the materials and for their scientific advices.

Thanks to my family for the graceful support granted throughout the research period and not just.

Part I: Introduction

Part II: Original Contributions

This thesis is structured in six chapters with annexes and references. Chapter 1 is dedicated to literature survey, emphasising generalities about smart materials, electroactive polymers in particular, and fundamentals about actuation and energy harvesting. Chapter 2 emphasizes results regarding the chemical modification of polysiloxanes by hydrosilylation reactions and co-crosslinking of the synthesized copolymers with high molecular weight polydimethylsiloxane, thus obtaining polar-non-polar interconnected networks. Chapter 3 presents the thiol-one addition and its application in the chemical modification of polysiloxanes containing vinyl groups with allyl chloride thus attaching polar groups. It presents the synthesis and characterization of the co-polymers and the evaluation of the electromechanical behaviour of the elastomeric films obtained based on them. Chapter 4 is dedicated to composites based on poly(dimethyl)siloxane-α,ω-diols of different molecular weights and ceramic particles (barium titanate and titanium dioxide) as fillers. Protocols for obtaining polymers, ceramic nanoparticles and elastomeric films, as well as their characterization and evaluation of the electromechanical response, are presented. Chapter 5 describes the production of polar silicone elastomers in which different polar organic groups have been attached to the silicone network nodes by the crosslinking agent used. Several crosslinkers have been used that differ by the organic group attached to the silicon atom. The networks were fully characterized and a comparative assessment of the final properties was made. The crosslinking agent that offered the best results, the one containing the chloropropyl groups, was used in increasing amounts to generate silsesquioxane structures in the silicone matrix as polar fillers. This research is extensively presented in Chapter 6. The thesis ends by centralizing the main conclusions on the results obtained in the thesis and emphasizing the original contributions, future work and the scientific activity in which the results were disseminated. The published articles are attached.

Part I (Chapter 1): Theoretical and historical landmarks

The first official definitions of "**Smart Materials**" were established at a meeting organized by the American Army Research Office (1988) where it was established that "smart materials are materials that have the ability to change their physical properties in a specific way under the influence of a specific stimulus."[1] External stimuli can be: pressure, temperature, electric field, magnetic field, chemical or nuclear radiation. The physical properties that can be changed are: shape, stiffness, viscosity, etc.

Dielectric elastomers are a class of smart materials that can respond to an electrical stimulus, converting electrical energy into mechanical energy, or to an mechanical stimulus, converting mechanical energy into electrical energy.[2,3]

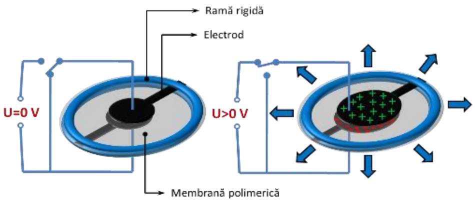

Figure 1. Actuator operating principle

Such an actuator/generator is generally formed of an elastic polymeric membrane having on both sides compliant electrodes (Figure 1). In case of actuators, after applying a voltage, most of the charges are accumulated on the electrodes, while part of them are "flowing" through the membrane due to impurities or defects. Charges accumulated induce an electric field polarizing the polymer membrane that in turn induces electrostatic attraction forces. Thus, the thickness of the membrane decreases and the membrane area between the electrodes increases. In accordance with the polarization effect, the actuation mechanism is also favoured by the attraction of opposing charges on the electrodes with the rejection of the same charges on each electrode. Due to the dielectric membrane elasticity, the actuator returns to the initial form after the voltage is interrupted and the short circuit of the electrodes. The pressure **p**, exerted when the actuation takes place, is given by equation 1, where **E** is the applied electric field, **ε_r** is the dielectric constant of the material, **ε_0** is the vacuum permittivity ($8.8 \cdot 10^{-12}$ F/m), **V** is the applied voltage and **z** is the thickness of the material.[4]

$$p=\varepsilon_r\varepsilon_o E^2=\varepsilon\varepsilon_o\left(\frac{V}{z}\right)^2 \quad (1) \qquad\qquad S_z=-\frac{p}{Y}=-\frac{\varepsilon_r\varepsilon_o\left(V/z\right)^2}{Y} \quad (2)$$

The mechanical response from the actuation (S_z) is given by equation 2, where Y is the Young's modulus (modulus of elasticity). The mathematical equations for large stretches, given real-life boundary conditions such as directing a weight, are much more complex. This simplified model, assuming that the elastomer is incompressible and has a Poisson ratio of 0.5, reveals the influence of the mechanical and dielectric properties of the material on actuation performance.[4]

An energy conversion cycle (from mechanical energy into electrical one) shown in Figure 2 depends on the change in the geometry of the elastomer and on an initial electric field applied to the generator. In step 1 the elastomer is relaxed (no mechanical deformation) and no electric field is applied. When the elastomer is elongated by an external ambient force (step 2), the mechanical deformation is converted into potential elastic energy and the capacitance increases to a maximum (step 3) determined by the mechanical properties of the elastomer. Upon reaching the maximum elongation (step 3), an electric field is applied until an experimentally predetermined breakdown strength (less than the dielectric strength of the dielectric elastomer is reached. The elastomer relaxation (step 4) reduces the active surface of the capacitor and the elastic strain is opposed to Maxwell's effort, increasing the distance between the opposite charges and the same charges approach. From an electrical point of view, these changes increase the voltage of charges. After the polymer returns to the initial elongation (step 5), some of the potential elastic energy is converted into electrical energy in the form of voltage.[5–7] In order to highlight the parameters of the material that can be optimized for efficient conversion, it can be considered a simple mathematical model considering that the generator is a capacitor whose electric capacity varies with elongation, so the electrical capacitance, **C**, is given by equation 3, in which: **A** – the active area of the capacitor, **z** – the elastomer thickness, **v** – the membrane volume. If we consider that the membrane is incompressible and the volume is constant, then Az=v, the electrical capacity can be written in the form (equation 3):

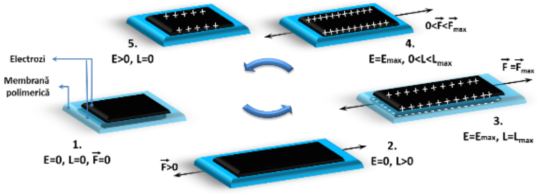

Figure 2. Energy conversion operating cycle[5–7]

$$C=\varepsilon_r\varepsilon_0\frac{A}{z}=\varepsilon_r\varepsilon_0\frac{v}{z^2}(3);\ \ V_2=Q/C_2=\left(C_1/C_2\right)\left(Q/C_1\right)=\left(C_1/C_2\right)V_1(4);\ \ E=0.5C_1V_1^2(C_1/C_2-1)(5)$$

Considering variable voltages, **V**, we can consider a system with electric charge, **Q**, constant in the generator for a short period of time. Considering that V= Q/C, for the elongated and relaxed voltages **V1** and **V2**, equation 4 can be obtained, where **C1** and **C2** are elongated and relaxed electrical capacities respectively. If C2<C1, the voltage in relaxed state is greater than the voltage in elongated state, fact demonstrated both practically and theoretically.[7] The energy harvested by the polymer generator for an elongation-relaxation cycle is given by the difference of the electrical capacities in elongated and relaxed states, according to equation 5. Consequently, the energy converted by a polymer generator is given by as much elongation as possible, a high dielectric constant and breaking strength of the elastomer. Using acrylic or silicone polymers to obtain the dielectric membrane, energy densities as high as one order of magnitude larger than piezoelectric or electromagnetic were obtain.[8]

There are three main classes of polymers in the literature that can be processed as dielectric polymeric membranes for generators or actuators: silicone polymers, acrylic polymers or polyurethanes.[9,10] Silicone elastomers offer the best properties, consisting of large elongations, high breakdown strength, low Young's modulus, high electrical resistivity, can be processed as very thin films in any shape, low viscoelastic creep, very low glass transition temperature, but also a low dielectric permittivity. In general, two methods are used to optimize the properties of the silicone elastomers in order to improve dielectric permittivity without compromising the properties of interest such as the breakdown strength or the Young's modulus: attaching the polar groups, either on the polymer backbone or in the network nodes, or the introduction of high dielectric permittivity fillers of different morphologies, sizes and/or functionalities. Taking into account the achievements reported so far in the field of dielectric elastomers and still insufficiently explored possibilities to optimize them, identified based on the study of literature, this thesis has the main purpose to contribute to the development of the field through approaches that meet the challenges still open: increasing the dielectric permittivity of silicones, one of the highest potential polymer classes, without significantly damaging the other useful properties (mechanical, electrical, thermal or surface) so as to obtain smart materials with the best electromechanical response.

To achieve this goal, the following objectives were proposed:

- chemical modification of silicones by attaching polar groups (on chain or in network nodes) approaching original synthetic strategies: **a.** attaching by hydrosilylation of both cyanopropyl polar groups and long alkyl groups for fine adjustment of the polar/non-polar balance and crosslinking the resulted polar polymers to non-polar networks in optimal ratios to provide good mechanical properties to the resulting materials; attaching by thiol-ene "click" chemistry of chloropropyl groups and crosslinking the resulted copolymers; **b.** using crosslinkers with different polar groups attached to the silicon atom to obtain polar elastomers;
- development of new silicone formulations (composites) having pre-established characteristics (structure and molecular weight of polymers, composition, morphology and nanoparticle size) and crosslinking patterns;
- theoretical and experimental evaluation by specific techniques of developed materials and the comparing the results to those obtained with dielectric elastomers already recognised for electromechanical applications.

Part II: Original contributions

In a first approach (Chapter 2) on chemical modification of siloxane polymers, cyanopropyl as polar groups were attached by hydrosilylation reactions to a homopolymer, α,ω-bis(trimethylsiloxy)poly(methylhydro) siloxane (Figure 3) in order to evaluate the influence of the number of polar groups on the properties of the resulting silicone elastomers. By using a homopolymer, the same length of the macromolecular chain is maintained, the variation in chain structure is eliminated and by using a co-reactant, 1-hexene, the number of attached polar groups can be controlled. A series of copolymers, B1-B7, with a molar polar group (n2) ranging from 87.8 to 0%, have been synthesized. Due to the low molecular weight, the elastomers obtained from B1 - B6 copolymers have poor mechanical properties; therefore, a strategy for interconnecting the copolymers with a larger, non-polar molecular weight polymer such as polydimethylsiloxane-α,ω-diol has been

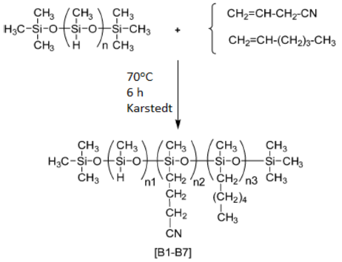

Figure 3. General hydrosilylation reactions

approached, which allows a subsequent cross-linking of the network. The crosslinking process takes place in three steps (Figure 4): **A.** Hydrolysis of the Si-H groups present in the main chain of the Bx copolymers; **B.** Hydrolysis of the crosslinking agent, tetraethylorthosilicate (TEOS), condensation of the Si-OH groups formed and anchoring the polar copolymers; **C.** Condensation of the Si-OH groups at the ends of the polymer chains with those on the main chain of the polar copolymers formed in step A.

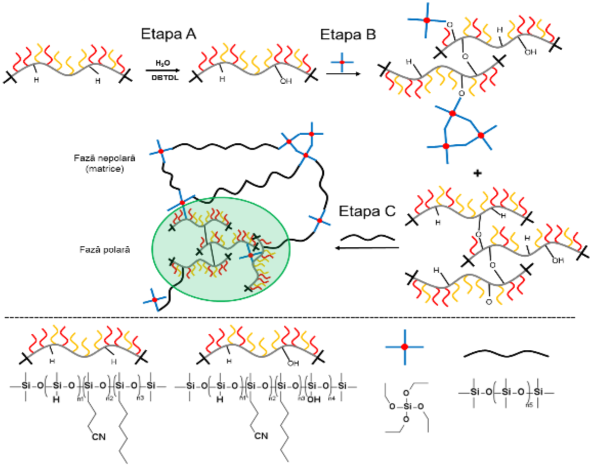

Figure 4. Schematical illustration of the crosslinking pathway

The interconnected networks between the polar component (Bx) and the nonpolar component (PDMS) were prepared in three ratios in order to obtain elastomers with a percentage of polar groups ranging from 5.33 to 0 %, Px (y/z) (y/z is the ratio between polar and non-polar). Using this method, phase separation at the macroscopic level was avoided and materials with high dielectric permittivity and breakdown strength were obtained, and mechanical properties significantly improved compared to the reference sample used or other results published in the literature. The electromechanical actuation values (Figure 5) are approximately 13 times higher than the reference sample, values that can be varied slightly with the amount of Bx used. The materials obtained are suitable for use both in actuation and in energy harvesting.

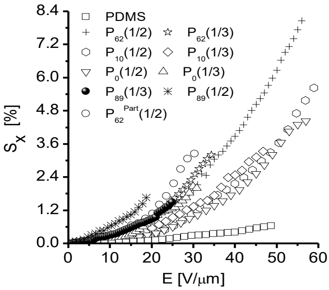

Figure 5. Actuation curve of the obtained interconnected networks

In another approach (Chapter 3), the study of the influence of the chloropropyl dipole on a series of polar copolymers obtained by a two-step method (Figure 6) was carried out: **A.** heterogeneous cationic ring opening copolymerization of octamethylcyclotetrasiloxane (D4) and 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (V4) monomers to obtain copolymers of 1.5% (V1.5), 5.5 (V5.5), 10 (V10), 45 (V45) and 100% (Hp) methyl-vinylsiloxane units; **B.** addition of 3-

chloro-1-propanethiol by "click" thiol-ene reactions under UV radiation in the presence of 2,2-dimethoxy-2-phenylacetophenone as photoinitiator.

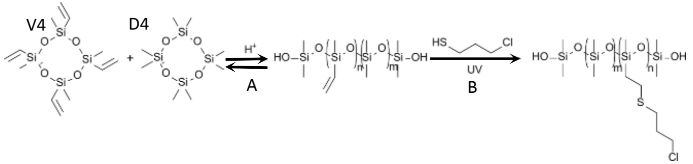

Figure 6. General scheme of the reactions used to obtain chloropropyl substituted copolymers

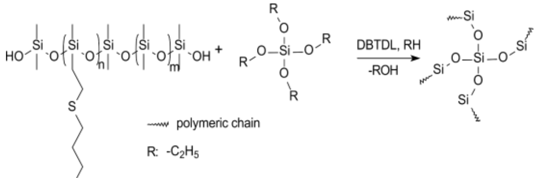

Figure 7. General crosslinking reaction

The resulted polar copolymers (Clx; x = 1.5, 5.5, 10) were stabilized as elastomer films by crosslinking reactions (hydrolysis-condensation) occurring at the ends of the polymeric chains (Figure 7). The presence of polar groups influences both the Young's modulus and the breakdown strength that are determinant in the subsequent electro-mechanical behaviour of the dielectric elastomers. Thus, compared to the series of non-functional copolymers having lower Ebd from actuation and high Y, after functionalization high Ebd values were obtained (three times), a decrease of Y with one order of magnitude and an improvement of the ε_r values. The films obtained from non-functional copolymers have low electromechanical properties, maximum lateral actuations reaching 4.7% for V1.5, 0.8 % for V5.5 and 0.4% for V10, due to the low breakdown strength from actuation, 13, 10, and 5 V/µm, respectively. The values of the lateral actuation are in correlation with the Young’s modulus, which increases with the cross-linking density. After the chemical modification of the copolymers, significant increases in lateral actuation were recorded, according to the number of attached polar groups and Young’s modulus values, with a maximum lateral actuation of 53% for the Cl5.5 and 85 % for sample Cl10 (Figure 8), high values compared to literature: 7.1% for PDMS-polyurethane interconnected networks (at 20 V/µm and 10% polyurethane solution in DMF), 15 % for PDMS grafted with 7.1 % mol azobenzene (at 65 V/µm), 12 % for a PDMS stabilized by crosslinking with TEOS (65 V/µm), 35% for an n-butyl acrylate copolymer matrix elastomer that contains maleimide-furan moieties (at 45 V/µm) and 20% at 10 V/µm.[11–15]

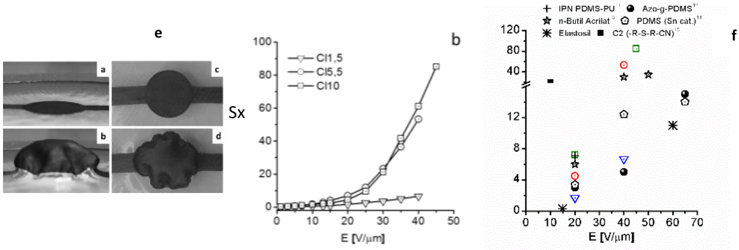

Figure 8. Images obtained during electromechanical tests on sample Cl10; a, b - side view; c, d - top view; e - the actuation curves for the series of polar elastomers; f – obtained actuation values in comparison with the reported data for different systems

Another approach to improving the properties of silicone elastomers was the use of ceramic nanoparticles (Chapter 4) as fillers. Due to its high permittivity, barium titanate (BT) is an active dispersion material for the silicone matrix leading even at a relatively small addition to the significant increase in dielectric permittivity without adversely affecting the mechanical properties of interest for electromechanical applications. To see how this effect can be maximized, the influence of particle morphology has been studied. Therefore, along with the commercial one, barium titanate with different morphologies (cubic and nanorod) was synthesized using a hydrothermal reaction procedure and incorporated into a high molecular weight silicone matrix. Cubes with sides between 350 nm and 450 nm were obtained, while the nanorods had a diameter of about 200 nm and 2-3 µm in length, as could be estimated from transmission electron microscopy images (TEM). For commercial BT, although scanning electron microscopy (SEM) images indicate large prisms with high polydispersity (1-7 µm), TEM images reveal smaller sizes (less than 50 nm) and uniform. Large macromolecular chains and the applied crosslinking system (like that shown in Figure 7) have yielded large elongations to the resulting composites (~ 890, ~ 2190%). The incorporation of these ceramic particles led, depending on morphology, to dielectric properties superior to those corresponding to the polymeric matrix (C-R sample). Thus, particles with a large size ratio (nanorods) led to an improvement of ε_r by about three times compared to the measured value for the silicone matrix, a decrease of the Young's modulus (by an order of magnitude, Figure 9, C-NR composite) and an elongation of approximately 900%. Electromechanical sensitivity and actuation, calculated from mechanical and dielectric data, have been found to be highest in the case of sample C-NR (composite with nanorods as filler) and are also large compared to those in the literature (β ~ 400 MPa-1 and Sx ~ 23%). At the same time, the obtained composites have high thermal stability and reduced water vapor sorption capacity.

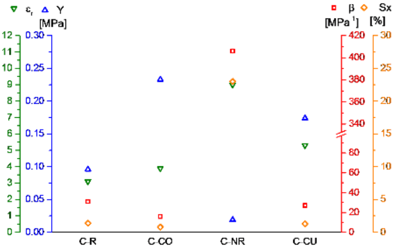

Figure 9. Comparative presentation of the defining parameters and their influence on the electromechanical properties

In the next subchapter is presented the detailed study of high molecular weight polydimethylsiloxane (Mn=350 000 g / mol) based nanocomposites and titanium dioxide nanotubes as dispersed phase, both materials being synthesized in the laboratory. The nanotubes used in this study were obtained following a hydrothermal method described in the literature, the Kasuga method.[16] Protocol A1 (5 M NaOH solution) led to pyramidal particles with sides averaging approximately 127 nm. Using the A2 protocol (10 M NaOH solution) resulted in multi-tubular nanoparticles with an average inner diameter of 4 nm, an average external diameter of 10 nm and an average length of 67 nm, dimensions comparable to those reported in the literature.[16] For a better compatibility with the siloxane matrix, the ceramic nanotubes were surface treated with hexamethyldisilazane. They were introduced into the siloxane matrix in two percentages, 2 wt% (TO2 sample) and 5 wt% (TO5 sample), the nanocomposites being stabilized by a crosslinking reaction similar to the one shown above (Figure 7). The surface treatment of the filler particles has been shown to be effective by allowing good dispersion of them within polymer matrix, and resulting in a reinforcing effect. This has been demonstrated by increasing the modulus of elasticity due to the incorporation of nanotubes (0.4 and 0.5 MPa by incorporating 2 and 5 wt% of TiO_2 based nanotubes compared to 0.26 MPa for PDMS). In addition, the presence of inorganic nanotubes, as expected, has led to significant increases in dielectric permittivity values at low frequencies (7.75 and 11.6 at 0.1 Hz for samples containing 2 to 5 wt% of nanotubes), but modest values at high frequencies (3.23 and 4 at 10^3 Hz). As a result of surface treatment chosen for nanoparticles, breakdown strength has high values (i.e. 60 V/µm). The reasonable modulus and the high dielectric permittivity values are reflected in better electromechanical performances of TO2 sample, which has an actuation value of 4.2%, but in particular a high mechanical energy conversion efficiency of 8.84% at 400 V and at a 150% elongation (Figure 9).

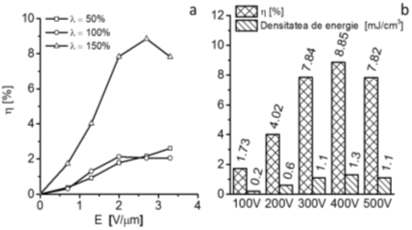

Figure 10. Graphic representation of the efficiency of the device based on the TO2 elastomer film as a function of the applied electric field and elongation (a) and the comparative histogram of the calculated energy densities at λ = 150% and the conversion efficiency (b)

A less approached strategy to improve the electromechanical properties of silicone elastomers is the use of polar crosslinkers. In order to study the influence of the crosslinking agent (Chapter 5) on the properties of the silicone elastomers, two poly(dimethyl)siloxane-α,ω-diols with molecular weights of 34 500 g/mol (A) and 125 000 g/mol (B) were synthesized by ring opening polymerization of octamethylcyclotetrasiloxane and cross-linked by hydrolysis-condensation using five organosilanes, which differ by the nature of the organic group attached to the silicon atom (Figure 11), namely methyl (M), 3-chloropropyl (C) 3-aminopropyl (A), 3-cyanopropyl (Cy) and phenyl (Ph).

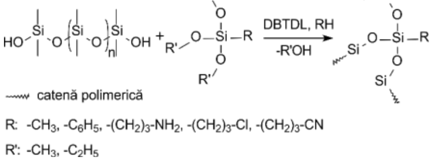

Figure 11. Crosslinking reaction with different silanes through which the silicone elastomers were obtained

While the presence of polar groups leads mainly to the increase in dielectric permittivity (from 2.5 in the case of methyltrialcoxysilane to 3.7 when the cyano-derivate was used as a crosslinker), the higher molecular weight polymeric matrix has an opposite effect, decreasing it. Long chains also led to a decrease of the elastic modulus of 1.6 to

7.7 times, depending on the nature of the crosslinking agent. The electromechanical behaviour (Figure 12) depends in a complex manner on these parameters. The best results were obtained for the PDMS with a lower molecular weight crosslinked with chlorpropyltrialcoxysilane and for PDMS with a higher molecular weight crosslinked with cyanopropyltrialcoxysilane, i.e. the lateral actuation values of 1.45 % and 0.25 %, respectively, for E=0.63 V/μm. All samples exhibited high thermostability, up to 300 and even 500 °C for samples containing chloropropyl groups. Humidity absorption values are slightly increased in samples containing polar groups, but they remain, however, at a low level; the highest values were measured for samples containing aminopropyl groups, 1.86 and 1.56 % in A and B series respectively.

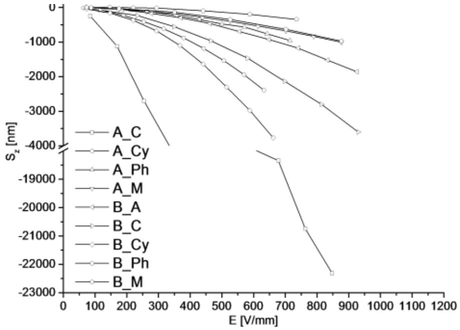

Figure 12. Electromechanical behavior of A and B series

This study has been deeply elaborated (Chapter 6) by studying the effects of the presence of the chloropropyl dipoles attached to the silicon atoms, in both network nodes and *in situ* generated nanoparticles, on the electromechanical properties. For this study, the same polymers presented in the previous study, two polydimethylsiloxane-α,ω-diols, A and B, with different molecular weights (Mn_A=34 500 g/mol, PDI = 1.5 and Mn_B = 125 000 g/mol, PDI = 1.38, respectively) were used and stabilized by cross-linking with (3-chloropropyl)trimethoxysilane (CPTMS). CPTMS was added in quantities close to those calculated according to the stoichiometry of the crosslinking reaction (samples A0 and B0) or in different excesses: 5, 10, 15 and 50 wt% relative to the mass of the mixture (Ax and Bx series, x = 5, 10, 15 and 50). It can be assumed that in the first stage, due to the presence of the tin catalyst, the condensation of the $\equiv$Si-O-C_2H_5 with the Si-OH groups on the polymeric chain ends takes place with the formation of ethanol as side-product, resulting in crosslinking (Figure 13). As the humidity from the atmosphere diffuses into the material, hydrolysis of $\equiv$Si-O-C_2H_5 groups in excess occurs with triol formation. The resulting triol is unstable and participates in intramolecular and intermolecular condensation reactions (with other methoxy groups) with the formation of fully or partially condensated silsesquioxane structures: closed polyhedral silsesquioxane (POSS), open (OPOSS), ladder (LSSQ) or random-type (RSSQ).[17] It is also possible to simultaneously develop the two processes that led to the connection of PDMS chains with silsesquioxane structures acting as crosslinking nodes (Figure 13). Conversion of the excess of CPTMS into silsesquioxane structures was confirmed by FT-IR spectroscopy which revealed the presence of characteristic absorption bands, while their ordering degree and aggregation in the silicon matrix were evidenced by TEM, WAXD and SAXS. The effects of the dipole content brought by the addition of CPTMS, as well as the molecular weight of the matrix, were evaluated in terms of mechanical, dielectric and electromechanical characteristics. The results showed that, with the increase in polar group content (linear with the amount of CPTMS used) slightly increase in dielectric permittivity (from 3.17 to 3.48 in the A series and from 2.75 to 3.52 in the B series) and a more pronounced increase of the Young's modulus (from 0.32 to 2.54 in the A series and from 0.19 to 1.83 in the B series) occurs. The increase in the molecular weight of the

PDMS used is mainly reflected in the decrease of the Young's modulus. The breakdown strength varies between 35 and 62 V/µm, the highest values being for the A series, while the lateral actuation value (Figure 14) varies between 1.39 and 7.29 %, the highest values being recorded for samples A15 (7.08 %) and B5 (7.29 %). Although these values are not spectacular, it can be appreciated that, using CPTMS as a crosslinker and as a precursor for polar fillers, the electromechanical performance of polydimethylsiloxane is improved without the involvement of a complex chemistry.

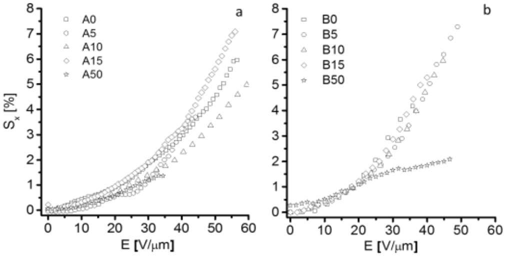

Figure 14. Electromechanical response of elastomers of series A (a) and B (b)

General Conclusions

Polysiloxanes represent a solid, easily accessible and versatile platform to produce efficient dielectric elastomers for electromechanical devices.

The thesis presents three ways that have been approached to improve the electromechanical properties of silicone elastomers:

1. Chemical modification of polysiloxanes by attaching polar groups to the silicon atom on the main chain;
2. Incorporation of high dielectric permittivity ceramic nanoparticles (barium titanate or titanium dioxide);
3. A mixed pathway consisting of attaching polar groups to the polysiloxane crosslinking nodes and on *in situ* generated silsesquioxane nanostructures;

In all cases, both the substrate polymers (polysiloxanes with varying Si-H or Si-$CH=CH_2$ groups along the chain), modified polymers (polysiloxanes with cyanopropyl or chloropropyl polar groups), matrix polymers (polydimethylsiloxane-α,ω-diols in a wide range of molecular masses) and ceramic nanoparticles (barium titanate and titanium dioxide) as dielectric enhancers were synthesized in the laboratory and completely structurally and morphologically characterized.

For the **chemical modification of polysiloxanes** by the attachment of polar groups, two types of reactions were used, each of which required specific groups and catalysts, with their advantages and disadvantages:

- **Hydrosilylation** - a classical reaction in silicone chemistry was used to attach strong polar cyanopropyl groups. This reaction, which requires a polymer substrate containing Si-H groups (in proportion and with the desired distribution) and suitable reactants containing vinyl groups, proceeds at a reasonable rate at temperatures generally higher than room temperature in the presence of a platinum catalyst. This type of reaction has the disadvantage that the catalyst contaminates the final product and is extremely difficult to be removed. In addition, it is possible to form isomers.
- **The thiol-ene addition**, a newly-referenced "click" reaction, has been proven to be a particularly effective way of chemically modifying the silicone polymers. The reaction proceeds quantitatively, thermal or photochemical, even in the absence

of a photocatalyst, thus avoiding the purification step for the removal of unconsumed reactants or catalyst residues. The presence of the vinyl and thiol groups which are easy to assure is required to carry out the reaction. In our case, the vinyl groups are present on the main polysiloxane backbone, while the thiol group is contained by the (3-chloropropyl)-1-thiol reactant, which also contains the polar group to be attached. The reaction was carried out photochemically in the presence of a photoinitiator, at room temperature. The disadvantage of this reaction is that, as it is known, thiol compounds are difficult to handle due to unpleasant odour. By using this technique, ethylthiochloropropyl groups have been successfully attached on the backbone of the siloxane copolymers.

Nanocomposites based on polydimethylsiloxane-α,ω-diols with different molecular weights as matrices with ceramic nanoparticles (titanium dioxide and barium titanate) and silsesquioxane (having attached polar groups as dispersed phases) with well-defined morphologies as fillers have been prepared. Ceramic nanoparticles were prepared in the laboratory by adapting literature techniques and optimizing them to obtain the desired morphology. It has been found that particles with high dimensional ratio (nanorods or nanotubes) are most effective to obtain maximum effects at minimum amounts added due to their large contact surface with the matrix.

Based on the foregoing precursors, elastomeric crosslinked structures were prepared. In order not to increase the number of parameters influencing the properties of the final product, the crosslinking has always been based on the condensation of the Si-OH ends of the siloxane chains with a tri- or tetrafunctional silane or with the OH groups on the polar polymers chains formed following the hydrolysis of the residual Si-H groups in case of interconnected networks. The elastomeric films were characterized in terms of structural (by IR spectroscopy), morphological, thermal, mechanical, dielectric and electromechanical (electromechanical sensitivity, electromechanical actuation, energy harvesting capability, etc.) aspects.

When the crosslinking agent was a trifunctional silane having attached a polar organic group, it represented a vehicle for the introduction of polar groups into the network nodes and its excessive use allowed, in conjunction with the crosslinking, *in situ* generation of nanoscale silsesquioxane structures functionalized with polar groups that helped to modify the properties of silicone elastomers.

Based on the literature study and the theoretical foundations, it has been established that, in order to be used as active elements in electromechanical devices, the materials obtained have to meet several conditions: easy to handle and mechanically resistant to environmental conditions (thermal and humidity), to be easily deformable and highly elastic, to have high dielectric constant and breakdown strength.

The evaluation of the materials obtained from these points of view led to the following conclusions:

- Dielectric elastomers based on polydimethylsiloxanes modified with polar groups have as their main advantage the high value of dielectric permittivity, reasonable values for Young’s modulus and elongation at break, but low values of the breakdown strength. In addition, the presence of polar groups induces phase separation and increased humidity absorption capacity that may impair dielectric properties;
- Nanocomposites prepared in optimal conditions with adequate surface treatment and good dispersion of the fillers led to a simpler pathway to more robust, reliable materials with more stable and easy to control properties, but dielectric permeability values cannot be magnified spectacularly without affecting their mechanical properties. An important role in obtaining the desired effects is the morphology and surface treatment of the dispersed phase.

The evaluation of the electromechanical behaviour of the materials obtained directly in the actuation and energy harvesting devices shows outstanding performance in the following cases:

1. Polysiloxane-based silicone elastomers having cyanopropyl and ethylthiochloropropyl dipoles are performant in actuation. Copolymers with ethylthiochloropropyl dipoles showed maximum lateral actuation strain values of 85 % at an electric field of 45 MV/m;
2. Silicone based nanocomposites with hydrophobized titanium dioxide nanotubes as filler have been shown to be capable of converting mechanical energy into electricity with 8.84 % efficiency for equiaxial stretches of 150 % and an input voltage of 400 V.

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Scientific Activity:

Articles reported to the PhD thesis:

1. Carmen Racleș, Mihaela Alexandru, **Adrian Bele**, Valentina E. Musteață, Maria Cazacu, Dorina M. Opris: *Chemical modification of polysiloxanes with polar pendant groups by co-hydrosilylation*. RSC Advances 08/2014; 4(71). DOI:10.1039/C4RA06955B (**IF: 3.108; SRI: 1.826**).
2. Carmen Racleș, **Adrian Bele**, Mihaela Dascalu, Valentina Elena Musteață, Cristian-Dragoș Varganici, Daniela Ioniță, Stelian Vlad, Maria Cazacu, Simon J. Dünki, Dorina M. Opris: *Polar-nonpolar interconnected elastic networks with increased permittivity and high breakdown fields for dielectric elastomer transducers*. RSC Advances 06/2015; DOI:10.1039/C5RA06865G (**IF: 3.108; SRI: 1.826**).
3. **Adrian Bele,** Mihaela Dascalu, Codrin Țugui, Carmen Racleș, Cristian-Dragoș Varganici, Mihai Iacob, Maria Cazacu: *Polar silicones exhibiting giant actuation stains* – **unpublish results.**
4. **Adrian Bele**, Maria Cazacu, George Știubianu, Stelian Vlad: *Silicone - barium titanate composites with increased electromechanical sensitivity. The effects of the filler morphology*. RSC Advances 10/2014; 4(102). DOI:10.1039/C4RA09903F (**IF: 3.108; SRI: 1.826**).
5. **Adrian Bele,** Codrin Țugui, Liviu Săcărescu, Mihail Iacob, George Știubianu, Mihaela Dascalu, Carmen Racleș, Maria Cazacu: *Materials of inorganic origin engineered for applications in transducers* **– trimis către publicare.**
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Total IF: 20.72; Total SRI: 12.049

Articles related to the subject of the PhD thesis:

1. Carmen Racleș, Mihaela Dascalu, **Adrian Bele**, Vasile Tiron, Mihai Asăndulesă, Codrin Țugui, Ana-Lavinia Vasiliu, Maria Cazacu: *All-Silicone Elastic Composites with Counter-Intuitive Piezoelectric response, designed for electromechanical Applications. J. Mater. Chem. C***,** 2017. DOI:10.1039/c7tc02201h (**IF: 5.256; SRI: 2.756**).
2. Mihail Iacob**, Adrian Bele**, Anton Airinei, Maria Cazacu: *The effects of incorporating fluorinated polyhedral oligomericsilsesquioxane, $[F_3C(CH_2)_2SiO_{1.5}]_n$ on the properties of the*

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9. George Știubianu, Ana-Maria Corina Dumitriu, Cristian-Dragoș Varganici, Codrin Țugui, Mihail Iacob, **Adrian Bele**, Maria Cazacu: *Changes induced in the properties of dielectric silicone elastomers by the incorporation of transition metal complexes*. High Performance Polymers 09/2015; DOI:10.1177/0954008315610393 (**IF: 1.142; SRI: 0.629**).
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Other articles:

1. Iuliana Rotaru, Carmen Bujoreanu, **Adrian Bele**, Maria Cazacu, Dumitru Olaru: *Experimental testing on free vibration behaviour for silicone rubbers proposed within lumbar disc prosthesis*. Materials Science and Engineering C 09/2014; 42:192-198. DOI:10.1016/j.msec.2014.05.021 **(IF: 4.16; SRI: 0.94).**
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1. Iuliana Rotaru, Carmen Bujoreanu, Dumitru Olaru, **Adrian Bele**, Maria Cazacu: *Preliminary experimental testing on fatigue resistance for silicone rubbers proposed within lumbar disc prosthesis*. E-Health and Bioengineering Conference (EHB), 2013; 11/2013.

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Patents:

1. Dorina M. Opris, Simon Dunki, Carmen Racleș, Adrian Bele, Maria Cazacu: *High permittivity polymers based on functionalized silicones.* I.P.N. WO 2015/135086 A1.

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3. **Adrian Bele,** Mihai Iacob, Xenia Patraș, Maria Cazacu, *Prepararea unor noi composite siliconice Electroactive și testarea lor ca mușchi artificiali*, **Appolonia 2014,** 27.02–01.03, Congres internaţional “Pregătim Viitorul Promovând Excelenţa“, Iași, Romania.

Short oral communications and posters:

1. **Adrian Bele**, Codrin Țugui, Mihaela Dascalu, Carmen Racleș, Maria Cazacu: Functionalized silicones showing giant actuation strains, EuroEAP 7th international conference on Electromechanically Active Polymer (EAP) transducers & artificial muscles, 6 -7.06.2017, Cartagena, Spain.
2. **Adrian Bele**, Codrin Țugui, Carmen Racleș, Maria Cazacu: High breakdown strength composites based on silicone and ceramic nanotubes, EuroEAP 6th international conference on Electromechanically Active Polymer (EAP) transducers & artificial muscles, 14 -15.06.2016, Helsingor, Denmark.
3. **Adrian Bele**, Mihai Gabriel Asăndulesă, George Știubianu, Maria Cazacu: Highly stretchable and compliant PDMS/carbon-based electrodes for artificial muscles applications**,** EuroEAP 5th international conference on Electromechanically Active Polymer (EAP) transducers & artificial muscles, 09 -10.06.2015, Tallinn, Estonia.
4. **Adrian Bele**, Maria Cazacu, Mihaela Alexandru, Valentina Musteață, Dorina M. Opris, Carmen Racleș: A dual strategy for improving the electromechanical properties of silicones, EuroEAP 4th international conference on Electromechanically Active Polymer (EAP) transducers & artificial muscles, 10 -11.06.2014, Linkoping, Sweden.
5. **Adrian Bele**, Maria Cazacu, George Theodor Știubianu: Effects of shape and size of the ceramic filler particles on the electromechanical properties of the silicone composites, EuroEAP 4th international conference on Electromechanically Active Polymer (EAP) transducers & artificial muscles, 10 -11.06.2014, Linkoping, Sweden.
6. **Adrian Bele**, Maria Cazacu, Carmen Racleș, Dorina Opris, Mircea Ignat, George Știubianu, Valentina Musteață, Effect of crosslinking agents on the electromechanical properties of silicones, EuroEAP 3th international conference on Electromechanically Active Polymer (EAP) transducers & artificial muscles, 25 -26.06.2014, Duebendorf (Zurich), Switzerland.

Internships abroad:

1. **EuroEAP - Scientific mission grand (SMG)**: *Green silicone based interpenetrating polymer networks as dielectric elastomers for electro-mechanical applications.,* 27.06.-12.08.2017; Department: Danish Polymer Center, Technical University of Denmark, Copenhagen, Denmark.
2. **Inter-academic research exchange**: *Preparation and complex investigation of polymeric composites materials.,* 29.06.2015 - 5.07.2015; Department: Polymer Institute, Bratislava, Slovak Republic.
3. **ESNAM Training School***: Dielectric Elastomer Transducers,* 25 – 27.03.2014, Darmstadt, Germania.
4. **ESNAM Training School***: Ionic Artificial Muscles,* 29 – 31.10.2013, Cartagena, Spain.
5. **EuroEAP Short Term Scientific Mission (STSM):** *Testing new materials with improved dielectric breakdown strength and reduced current leakage,* 27.09 – 12.10.2013, Department: PERCO laboratory for soft robotics, Scuola Superiore Sant'Anna, Pisa, Italy.