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Manufacture of electrodes entirely made of modified PDMS

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Abstract:
Materials with different mechanical characteristics are used for common flexible electrodes. These differences limit their long term usability as interface to biological tissue. In this paper a manufacturing process for structural compatible PDMS electrodes is described. Issues like the adhesion between the components, the Young's moduli of the materials as well as the contacting process were addressed. Direct cell contact tests provided the evidence of cell compatibility. By recording electromyograms (EMG) and the evaluation of the charge injection capacity (CIC) the functionality of the electrodes could be shown. The used material for the electrode contact was investigated regarding its phase boundary. For the description of impedance spectra of the polymeric electrode an equivalent circuit is described.

Key words: PDMS electrodes, soft lithography, contacting, characterization, equivalent circuit

Introduction

Electrodes are used as conductive interface to biological tissue, both transcutaneous and implanted. Flexibility is achieved by using polymeric substrates. The conductive structures usually are metallic or made of intrinsic conductive polymers [1]. Differences in the Young's moduli of tissue and the used materials cause mechanical stress within the structure as well as at its borderline. This limits the long-term stability of micro electrodes used in a moving environment. In short, structure compatibility of flexible, implantable electrodes is still challenging.

The aim of the presented work is the development of structure compatible electrodes based on modified polydimethylsiloxane (PDMS) as monomorphic material. A process for fabrication of electrodes should be developed. Addressed applications are the recording of biological potentials and electrical stimulation. The charge transition between the polymeric electrode and a surrounding electrolytic solution should be modeled.

Methods

The Young's modulus of PDMS (MED-6015, Nusil) was reduced by adding silicone thinner (ST, Smooth-ON). Based on former research [3] PDMS filled with carbon nanotubes (CNT, Sigma-Aldrich) was used as conducting paths. For the electrode contact an established [2] PDMS composite, based on conductive glimmer particles, was adapted. The particles were dispersed into the silicone matrix with a dual asymmetric centrifuge (SpeedMixer, Hauschild). Two metallic stirring balls were used to increase the mixing effect.

Regarding the connection of all materials as different components of a PDMS electrode, two soft lithographic assembling methods were compared. On the one hand a replica molding technic [4] was adapted to particular needs and present conditions. On the other hand a new method, based on a screen printing process, was designed. For the latter 3D-printed (Objet Connex500 3D-printer, Stratasys) stencils were used. To connect the conductive silicone to metallic compounds different contacting methods were compared regarding electrical and mechanical characteristics.

The Young's moduli of the PDMS composites were evaluated by using tensile tests. With peeling tests the adhesion between all components could be analyzed. To stress the assembled electrodes biochemically, they were stored in Ringer's solution at 37 °C for 25 days. Mechanical stress was applied by cyclic stretching. The effects of the accelerated aging were evaluated with the help of electrochemical impedance spectroscopy. Applying the electrodes for EMG recordings demonstrated the functionality in terms of acquisition of biological signals. The signals were recorded from the M. abductor pollicis brevis of

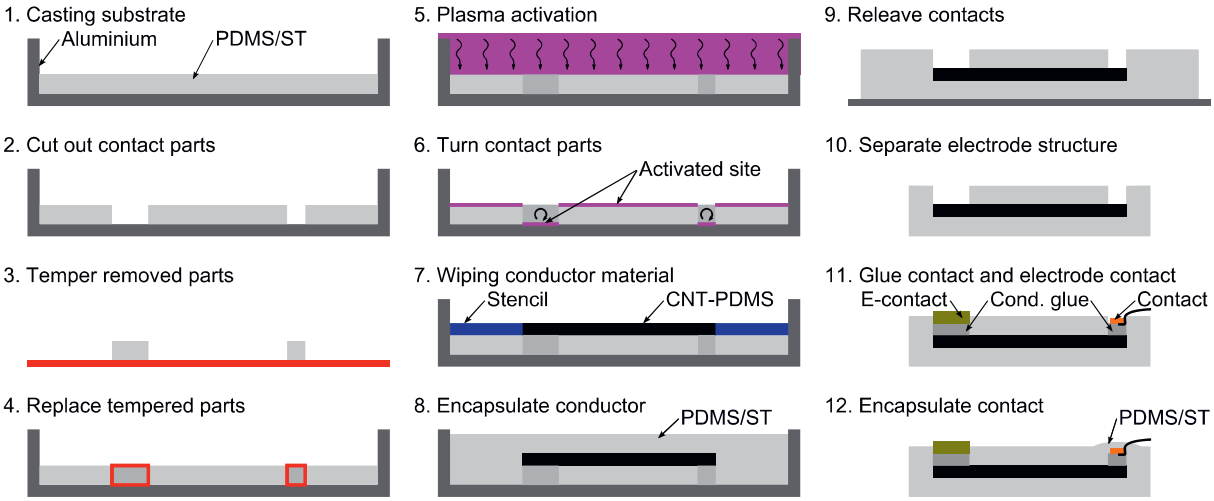

Fig. 1. Manufacturing Process for PDMS electrodes.

the right hand, simultaneously with the developed and standard Ag/AgCl electrodes (filter: 10 Hz - 5 kHz, 50 Hz notch). For stimulation purposes the CIC was evaluated with pulse tests. The cell compatibility was investigated by direct cell contact tests with human lung fibroblasts and human cardiomyocytes.

Based on the conduction mechanisms within the electrode material a current transition model for its interface to sodium chloride solution, as model electrolyte, was developed. It was used to fit impedance spectra, which were acquired using test structures out of the conductive PDMS.

Results - Fabrication

The CNT were dispersed in the PDMS by mixing them 5 times 2 min with 2200 rpm. Due to friction the CNT-PMDS-composite was slightly heated. To prevent it from premature curing, cooling steps were inserted. This way the temperature of the material was kept below 40 °C. The glimmer particles caused a high viscosity of the uncured electrode material. After mixing it with 1600 rpm over 60 sec using the SpeedMixer an additionally stirring process was needed. Therefor a rod agitator was used (80 rpm, 5 min). Afterwards the composite was pressed with 110 kg/cm². Under maintenance of the pressure the material was cured for 24 h at 80 °C. From the resulting block slices were cut off. Out of these, the electrode contacts were stamped out, finally.

The adapted replica molding technic made it necessary to remove the casted foil from the mold. It has to be turned to the flip side to fill its cavities. This process caused the relaxation of internal stress, which was induced by the curing

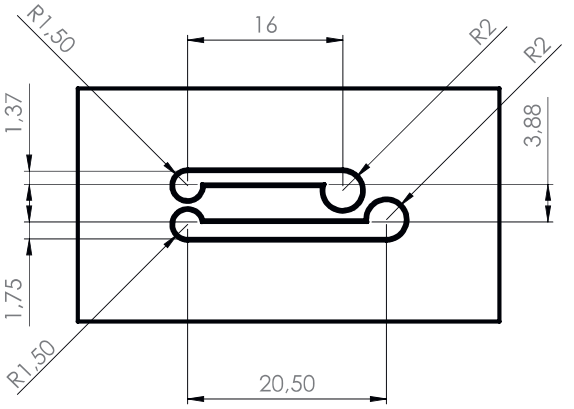

Fig. 2. Sketch of a stencil, dimensions in mm

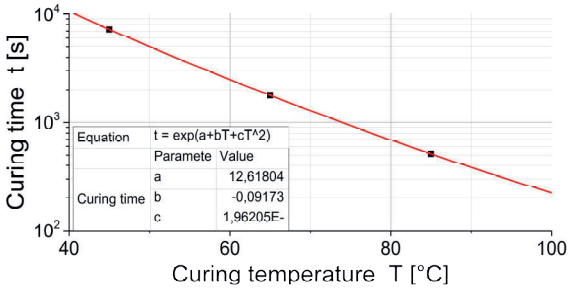

Fig. 3. Polymerization time of PDMS beginning at 0.02 % for reaching a degree of vulcanization of 62 % (gel point); data from [5]

process [5]. The vulcanization of the conductor material and the encapsulating layer led to the same shrinking effect. This caused internal stress between the relaxed substrate and the topping layers applied later. As result delamination occurred after a few months. For this reason the method, based on screen printing (depicted in Fig. 1), was preferred.

This process involves fife basic steps. At first the desired shape of the electrode was designed computer aided (see Fig. 2). Using rapid prototyping this design was printed in form

of a stencil of the thickness of 0.3 mm, which was needed for the conducting paths.

In the second step a basis substrate foil was casted (Fig. 1.1). The material was cured dynamically. Literature data [5] were fitted to calculate the time PDMS needs for reaching its gel point (Fig. 3). At a temperature of 80 °C the time was determined to be 11:28 min. Based on this, a 5 min initialization phase at 80 °C was used to start the vulcanization process. Crossing the PDMS gel point was performed at a temperature of 60 °C. This temperature was applied for a period of 2 h.

In step 3 the slab had to be prepared to achieve adhesion where it was needed and to inhibit it at the places where the contacts should be. To be able to expose the contacts after curing, parts of the foil were cut out, tempered, and removed into the foil (Fig. 1.2-4). At the rest of the surface, adhesion should be enhanced by activation with an oxygen plasma (effective pressure: ~1.4 mbar, O2 flow: 10 sccm, RF power: 90 W, duration: 180 sec; Fig. 1.5). Afterwards, the prepared contact parts were turned around for the desired reduction of the adhesion, mentioned above (Fig. 1.6).

For printing the CNT-PDMS-composite on the PDMS/ST substrate in step 4 the stencils were placed on the foil. The conductive PDMS was manually wiped into the stencil by applying low pressure and using a small angle between the scraper and the foil (Fig. 1.7). Subsequently, the stencil was lifted up from the foil. To close the backside of the conductive paths, they were coated with a layer of substrate material (Fig. 1.8). Both, conductor and encapsulation layer were cured simultaneously for 2 h at a temperature of 60 °C.

Step 5 started with the removal of the contact parts and the separation of the electrode structures (Fig. 1.9-10). For mounting the electrode contact as well as the contact pad on the CNT-PDMS a conductive silicone adhesive (R-1505, Nusil) was used (Fig. 1.11). Alternatively used conductive tape and a direct press contact were found to be mechanically or electrically unstable. Afterwards, the metallic contact pads were sealed with PDMS/ST material, which was cured 2 h at 60 °C (Fig. 1.12). To finalize the vulcanization a final tempering step of 30 min at 110 °C was added.

Due to the high surface energy of the metallic contact pad (coper, γ = 1862 ± 100 mN/m [6]) the silicone phase in the conductive glue perfectly wets the metal. Because of this, an insulating layer between the conductive particles and the metal was formed. Especially

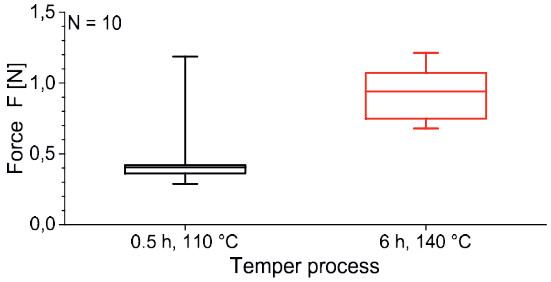

Fig. 4. Adhesion force after two different tempering processes

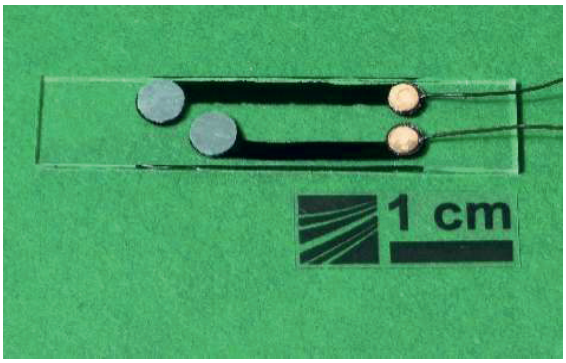

Fig. 5. PDMS electrode [8]

for small contact pads this layer could cover the entire surface. To reduce this effect, the metallic contact pads were coated with the intrinsically conductive Polymer PEDOT:PSS (γ = 73 ± 1 mN/m [7]).

Finally intensive tempering for 6 h at 140 °C could further increase the inter-compound adhesion. Using test structures of a width of about 1 cm the adhesion force after intensive curing could be measured to be twice as large as before (Fig. 4).

A bipolar electrode produced by the introduced process is shown in Fig. 5.

Results - Characterization

The Young's moduli of the different materials were measured to be 1.00 ± 0.10 MPa for the conductor, 0.99 ± 0.02 MPa for the substrate, and 4.57 ± 0.17 MPa for the electrode contact (also presented in [8]). For comparison: tetanic and non-active muscle tissue have moduli of 20 MPa and 10^{-3} Pa, respectively [9].

Biochemical stress, applied to the structures did not cause any visual changes of the electrodes. For three different frequencies the impedance to NaCl over a period of 25 days is shown in Fig. 6. Cyclic elongation of the electrodes resulted in a singular increase of the impedance mean value by factor 10.

The cell compatibility tests on the materials and the whole electrode structure showed no cytotoxic effects of the polymers. Although, the pure copper had a cytotoxic effect to the cells, it

was totally extincted in the complete structure. Tab. 1 shows the results of the direct cell contact test using lung fibroblasts. The cardiomyocytes show rhythmic beating for over 10 days (also presented in [8]).

Tab. 1. Results of direct cell contact test with human lung fibroblasts, negative control: in culture medium, positive control: 0.2 % 2-hydroxyethylmethacrylate (HEMA); Reactivity scale: none, little, light, medium, heavy; Grade: 0 - 4 (acc. USP 23)

Material	Morphology	Reactivity	Grade
negative control	typical	none	0
positive control	changed	little	1
substrate	typical	none	0
conductor	typical	none	0
electrode contact	typical	none	0
copper contact	destroyed	heavy	4
whole structure	typical	none	0

The acquired EMG signals were of same quality for the compared electrodes (Fig. 7).

The electrodes possess a CIC of 1.40 ± 0.34 µC/cm² (also presented in [8]).

Results - Modelling

Fitting the impedance spectra of polymer electrodes with standard models (i.e. Geddes-Baker) provided unsatisfying results. Hence, a new model was needed.

The conductivity arises due to percolation of flat glimmer particles. Their concentration was chosen to lead to a complete percolation network with a complex percolation path. This causes inductive effects [10], which could be shown in impedance spectra of the bulk material (Fig. 8).

Parallel to this, the flat particle geometry cause capacitive effects. The particles used to achieve conductivity in the electrode material possesses a semiconducting coating. Thus, a semiconductor-electrolyte boundary exists. An equivalent circuit of this interface was proposed by Tomkiewicz et al. [13]. A current-voltage plot of the electrodes (Fig. 9) show a typical shape as it was described for the presence of surface states at the electrode [12]. The modified PDMS had a heterogeneous and rough surface as can be seen in Fig. 10. This result in a distribution of time constants, which can be expressed by the use of constant phase elements (CPE) instead of ideal capacitors [14].

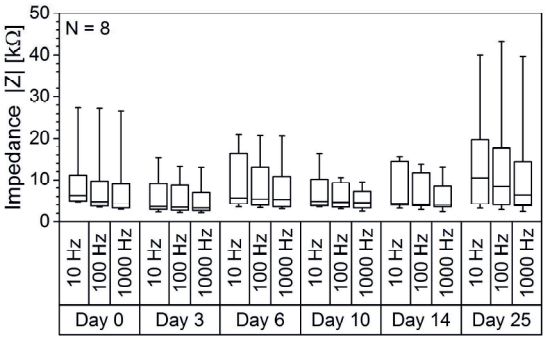

Fig. 6. Impedance to NaCl measured by a three point method over 25 days for 3 frequencies; visualization as box plot (25th percentile, median, 75th percentile and min/max whiskers)

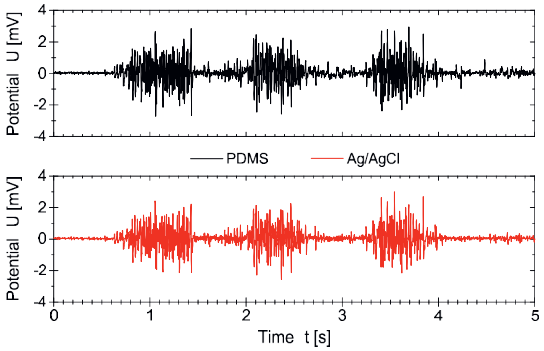

Fig. 7. EMG comparison between PDMS (top) and standard Ag/AgCl (bottom) electrodes

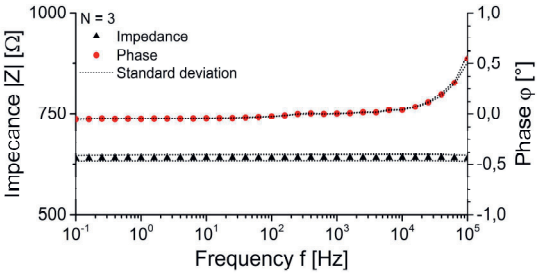

Fig. 8. Impedance spectra of filled PDMS [11]; inductive effect at high frequencies.

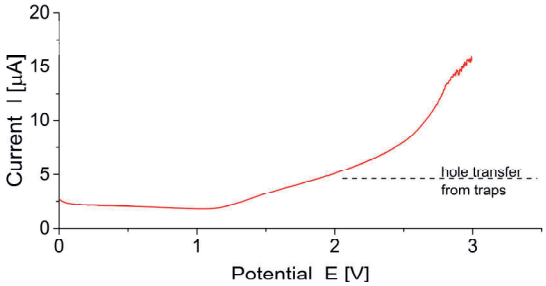

Fig. 9. Current voltage plot of PDMS electrodes; the plateau (dashed line) indicates the maximum achievable current from the surface states [12]

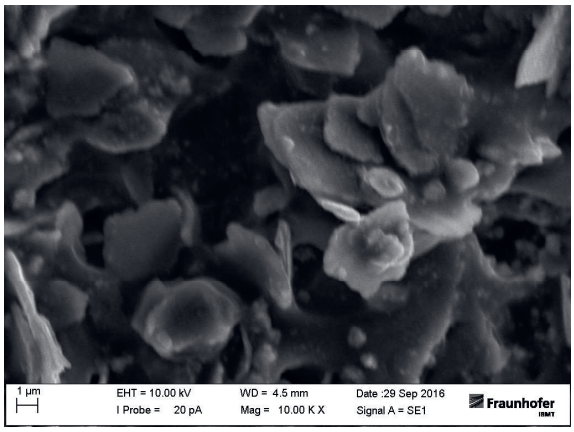

Fig. 10. REM of the electrode surface

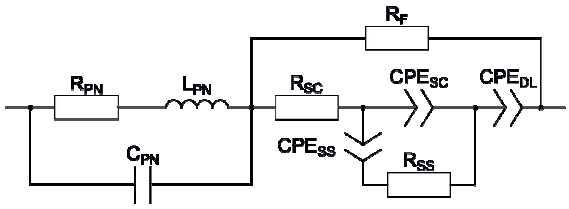

Fig. 11. Equivalent circuit of the PDMS electrode; R_{PN}, L_{PN}, and C_{PN} are the resistance, the inductivity, and the capacity associated with the particle network. R_F is associated to the faraday charge transfer. R_{SC} and CPE_{SC} are the resistance and the constant phase element of the space charges. CPE_{SS} and R_{SS} are associated to the surface states and CPE_{DL} to the double layer.

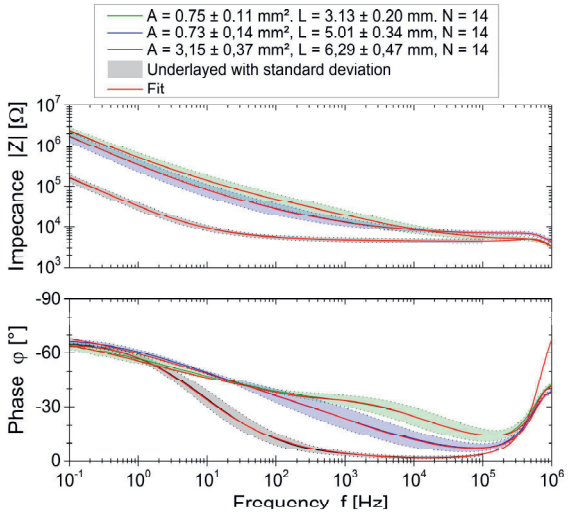

Fig. 12. Impedance spectra of the electrode material in NaCl solution, 2 different electrode sizes (A) and 3 lengths (L); data fitted with the developed model.

By combining all of these points, a model was developed (Fig. 11). Faradayic charge transition was found to be not relevant. The corresponding resistance thus could be removed in this special case.

This model was able to fit impedance spectra of test structures of different geometric dimensions (Fig. 12).

Conclusions

A technology to fabricate PDMS electrodes was developed. Filled silicone was used as conductor and electrode contact. The adhesion was maximized by using: (1) surface activation with oxygen plasma; (2) partial curing combined with a temper process; (3) preservation of internal stress within the substrate foil.

The Young's moduli of the compounds were in same range as that of muscle tissue. Cell compatibility was shown by direct cell contact tests using different human cell lines. Recording EMG has shown the functionality of these structural compatible electrodes. Furthermore the charge injection capacity was determined.

The equivalent circuit of the interface between the electrode material and NaCl solution provide a possible description of the charge transfer to a PDMS electrode. The calculated model fits impedance spectra that were acquired at test structures. The effect of the polymeric electrode material could not be neglected as it would be the case for metals. The bulk electrode material is explicitly included in the model and could not be mixed with the resistance of the electrolyte solution. The semiconducting coating of the glimmer particles in the PDMS resulted in an unusual and special case model.

Main advantage of PDMS is its capability for additional functionalization. With it structural compatible sensors for simultaneous recording of mechanical and electrical signals are possible to realize.

Acknowledgement

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