

Towards Flexible Biocompatible Pressure Sensors: Covering Polymeric Films with a Highly Piezoresistive Organic Molecular Metal

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Abstract—The article reports a promising approach to engineering biocompatible and highly piezoresistive membrane for flexible weightless transparent pressure sensors. The developed membrane is based on a bi layer (BL) film composing a polycarbonate (PC) matrix “self-metallized” with a highly piezoresistive organic molecular metal. The key role of the matrix thickness in the enhancement of the pressure sensitivity of BL film-based membranes was shown. The presented approach permits engineering biocompatible all-organic membranes with pressure sensitivity being of 8 Ω /mmHg. To determine restrictions for BL films applications in biomedical high-tech, the effect of the body temperature on membrane piezoresistive properties was studied. The pressure tests at 26 °C, 33 °C and 40 °C showed that the body temperature does not significantly influence on the membrane pressure sensitivity. Therefore this type of membrane sensors is able to take the place of conventional metal-based strain and pressure gages in monitoring biomedical high-tech.

Keywords- piezoresistive covering; flexible, biocompatible pressure sensors; organic molecular metal; pressure testing

I. INTRODUCTION

Among the more challenging tasks undertaken in the field of sensors is design and manufacture of reliable, robust pressure sensors for plastic electronics [1-8]. There is also a continuing need to lower the cost of sensors utilized in pressure sensing applications. To lower the cost and raise efficiency of sensors, few components, less expensive materials and fewer manufacturing-processing steps are necessary. For some applications size and weight constraints may be as important as or more than cost. For example, in biomedicine, catheter-based devices must occupy small volume, or they cannot be used at all [1, 6, 8]. In order to achieve these goals pressure sensors could be made of organic materials, along with low cost processing steps. Most of all-organic pressure sensors compose of a polymeric

material surfaced with a conducting polymer layer [1, 7] The conducting polymer layers are preferably grown electrochemically [6]. Therefore, making sensitive covering layers based on conductive polymers requires both the use of specific electrochemical equipments and deposition of conventional metallic electrodes on the surface of a polymeric matrix [6, 7]. This method offers many problems that must be worked out: the adhesion between conducting layers, substrates, and electrodes, the growth of conductive polymer should be in a reproducible manner, a limited area between two electrodes applying for electrochemistry etc. Moreover, the conductive polymers tend to degrade rapidly, resulting in sensors having only a relative short lifespan.

In this context surfacing plastics with “soft” organic molecular metals [9] which have been developed in order to replace heavy-weight metals in traditional technologies, is able to overcome the above mentioned problems. Organic molecular metals are attractive for covering polymeric films for many reasons; below we will list four main ones. First, these synthetic metals demonstrate good long term stability. Second, the set of hydrogen bonds presented in the crystal structures of all organic molecular conductors [9] endows their crystallites with high elasticity and, therefore, they are able to withstand large deformation. Third, due to soft crystal structures the conducting bands of organic molecular conductors can be easily deformed and, therefore, the electrical resistance of molecular metals responds strongly to deformation [10, 11]. Fourthly, a simple single- or two-stage covering procedure has been developed to prepare such “metallized” polymeric films [12, 13] The method consists in switching on a redox reaction in the swollen surface of a polymer film that provokes the nucleation of small clusters of a molecular conductor, which are able to grow into a conductive polycrystalline layer. This covering process occurs at room or moderate (33°C) temperature.

It should be noted that the above mentioned approach to covering plastics lived up to expectations. Recently we

reported that polycarbonate films surfaced with polycrystalline layers of organic molecular metals α -, β -(ET)₂I₃, were ET=bis(ethylenedithio)tetrathiafulvalene (Fig. 1), revealed a giant tenso-resistance effect [14-16].

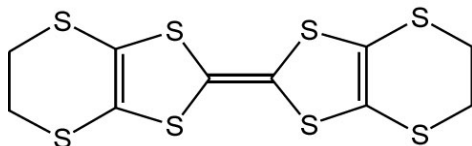


Figure 1. Skeletal formula of bis(ethylenedithio)tetrathiafulvalene (ET).

These bi-layer (BL) films are attracting large attention due to their ability to combine properties such as electrical conductivity, high sensitivity to strain (pressure), lightweight, and flexibility [12-16]. Moreover, it has been shown that BL films can be successfully integrate in textiles [17].

In order that a tenso-resistive BL film can sense pressure changes, it has to be located as a membrane. With this in mind, the first prototype of a contact sensing lens equipped with a membrane pressure sensor based on the above mentioned piezoresistive BL film has been developed for monitoring intraocular pressure (IOP) changes: a 25 μ m thick polycarbonate film covered with molecular metal β -(ET)₂I₃ was used as a flexible pressure sensor [18]. The tests showed that this BL film-based sensing membrane, being *biocompatible*, is able to control IOP changes with sensitivity of 1,4 Ω /mmHg; the pressure tests were made at room temperature (26 $^{\circ}$ C) [18, 19]. In order to adapt flexible tenso-resistive *biocompatible* BL film-based membranes for pressure monitoring in biomedical high-tech two key questions to be answered are: (1) is it possible to improve membrane sensitivity to pressure? and (2) does the body temperature significantly influence on membrane piezoresistive properties?

The goal of our study was a search for experimental data being able to answer on the above mentioned questions. We suggested that decreasing the thickness of a membrane's plastic component (polycarbonate matrix) on retention of the thickness of a membrane's piezoresistive layer has to enhance the membrane pressure sensitivity. With this in mind, we fabricated the thin membrane based on a 5 μ m thick polycarbonate film covered with the polycrystalline layer of piezo-resistive molecular metal β -(ET)₂I₃, the sensitive layer being prepared so as to be purely comparable with that of the above mentioned 25 μ m thick BL film-based sensing membrane.

Herein we show that an engendering approach based on the foregoing suggestion permitted us to fabricate a BL film-based membrane with sensitivity to pressure being five times higher than that for the previous reported one [14, 18, 19]. We also present data on electromechanical properties of this membrane showing that the body temperature does not significantly influence on membrane pressure sensitivity: pressure tests were carried out at 26 $^{\circ}$ C, 33 $^{\circ}$ C and 40 $^{\circ}$ C.

II. FABRICATING POLYCARBONATE FILM COVERED WITH A HIGHLY PIEZORESISTIVE ORGANIC MOLECULAR METAL

In line with the early reported method [12, 13] we first prepared a 5 μ m thick polycarbonate film spiced up with an 8 wt. % of ET that is a precursor for organic molecular metal (ET)₂I₃. The film was cast on a glass support at 130 $^{\circ}$ C from a 1,2-dichlorobenzene solution of a 0.5 wt.% of PC and 0.04 wt. % of ET. It should be noted that an 8 wt. % of ET embedded in this thin BL film is able to form the same amount of molecular metal (ET)₂I₃ as a 2 wt. % of ET inherent in a 25 μ m thick BL film. Therefore, the prepared composite film made possible to form the conductive covering layer of (ET)₂I₃ with the thickness being identical to that of the covering (ET)₂I₃-based layer formed at the surface of the early developed 25 μ m thick BL film [14, 18, 19].

In order to cover the film with a conducting layer of (ET)₂I₃, we exposed the film surface to the vapors of a saturated solution of iodine in dichloromethane. The covering mechanism is as follows: the surface of a polycarbonate film easily swells under its exposure to dichloromethane vapors; this swelling facilitates a migration of ET molecules from the film bulk to the swollen film surface where the part of ET molecules are oxidized to radical cations ET^{•+} by iodine, which penetrates in the film surface together with dichloromethane vapors. This redox process induces the rapid nucleation of highly insoluble [(ET)⁰(ET)^{•+}](I₃)⁻ species and a piezoresistive facing layer of molecular metal α -(ET)₂I₃ is formed. Electrical resistance of the 25 μ m thick BL film with the covering layer of α -(ET)₂I₃ responded to strain with a gage factor being 10, whereas the polycarbonate film with the same thickness but surfaced with β -(ET)₂I₃ has a gage factor being 20 [15]. The difference in gage factors between α - and β -phases of (ET)₂I₃ can be attributable to a variety of the softness of their crystal structure: β -phase has one short C-H...C and three long C-H...I hydrogen bonds whereas α -polymorphous has two short C-H...C and only two long C-H...I bonds [9]. Thanks to a larger number of the long hydrogen bonds, the crystal structure of the β -phase is significantly softer than that of the α -one and, therefore, the conducting band of β -(ET)₂I₃ can be easily deformed under load.

The 5 μ m thick BL film covered with a highly piezoresistive layer of β -(ET)₂I₃ was formed via a thermo-activated $\alpha \rightarrow \beta$ phase transition that occurs at T>100 $^{\circ}$ C [9, 13]. For this purpose the BL film covered with the layer of α -(ET)₂I₃ was annealed at 150 $^{\circ}$ C during 30 min. The formation of the covering layer of β -(ET)₂I₃ was confirmed by its X-ray diffraction pattern (Fig. 2). The figure shows only one line at $2\theta=5.8^{\circ}$ and its higher order reflections, that corresponds to "c"-oriented crystallites of organic metal β -(ET)₂I₃ [9, 13].

The surface analysis on a micro scale, performed using "Quanta FEI 200 FEG-ESEM" scanning electron microscope (SEM), showed that the crystallites of the covering layer of β -(ET)₂I₃ are of submicro size (Fig. 3). It should be noted that the sizes of the crystallites of the reported 25 μ m thick BL film were of the same scale. The calculated possible

maximal thickness of the piezoresistive covering layer is around 250 nm.

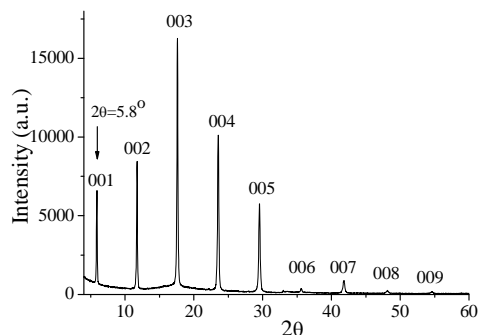


Figure 2. X ray diffraction pattern of the covering layer of the 5 μm thick BL film after its annealing. The film sample with 2.3 cm² was attached to a glass support and X-ray diffraction data were recorded on a Rigaku “Rotaflex” RU-200B diffractometer in reflection mode with monochromatic CuKα radiation (λ = 1.540598 Å); the generator was activated at 50 kV and 80 mA.

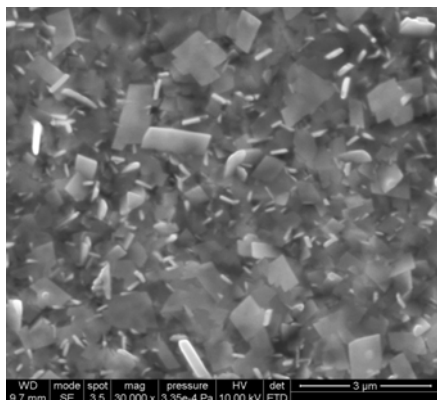


Figure 3. SEM image of the piezoresistive covering layer of β-(ET)₂I₃; the SEM image was acquired at 20 kV.

The BL film-based sensing membrane of a round configuration was cut and equipped with two electrical contacts: two 20 μm thick Pt wires were attached to the piezoresistive layer of the membrane using a linear contact configuration (Fig. 4).

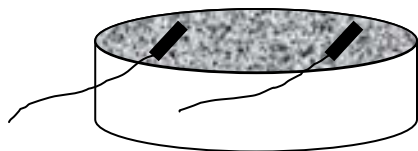


Figure 4. Schematic view of the pressure membrane sensor with two electrical contacts attached using a linear configuration

As a final remark we would like to add that the membrane temperature resistance coefficient (TRC) and membrane gage factor were found as 0.3 %/°C and 20, respectively. These values are in excellent agreement with the data reported for the 25 μm thick BL film [15]. The TRC was calculated as a relative resistance change per grade and gage factor was calculated as the ratio between the relative resistance change and the relative strain value.

The above result demonstrates that both TRC and gage factor of polycarbonate films “self-metallized” with molecular metal β-(ET)₂I₃, being independent on the thickness of a polymeric matrix, are governed by the nature of the molecular metal used for covering a polycarbonate film.

III. PRESSURE TESTS

The pressure testing experiments were performed by using a tailor-made water based column manometer that is shown in Fig. 5. To prepare pressure tests under moderated temperature a demountable home made thermostat was designed and fabricated. This mini thermostat is made up of a rigid polyurethane foam-based camera whose interior walls were faced with Cu plates. The thermostat was equipped with two commercial Kapton Flexible Heaters (KHLV - 102/10) that were arranged on the opposite camera walls. The heaters were connected with DC Power Supply E3617A. Temperature was maintained constant with an accuracy of ±0.02°C and controlled by the Pt-thermometer.

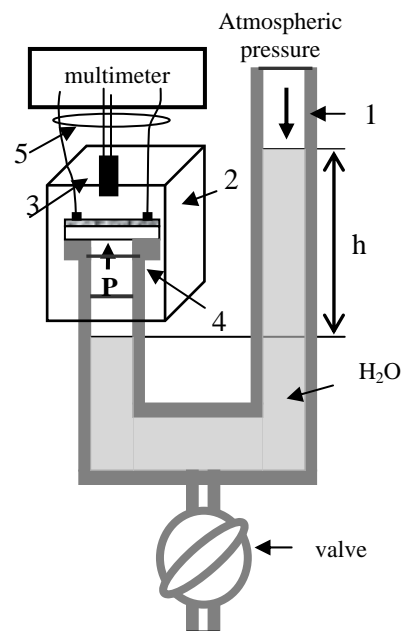


Figure 5. Schematic view of setup developed for pressure tests: 1 - water column U- tube manometer; 2 -home-made thermostat; 3 - Pt thermometer; 4 - glass holder with a BL film-based sensing membrane; 5 – electrical connections.

The pressure tests were carried out when thermostat temperature was stabilised at 26 ±0.02 °C, 33±0.02 °C and 40±0.02°C. Tests were conducted with simultaneously

temperature monitoring; for this purpose the Pt-thermometer was located very close to the tested membrane. The membrane was pasted over a ring-like top of a glass holder as shown in Fig. 6. The holder was designed and tailor-made for connecting the BL film-based membrane with one of the tube of the tailor-made U-shaped tube manometer.

In these experiments the pressure (P) of the gas that is trapped in the end of the tube closed with the tested membrane is greater than atmospheric pressure by the amount of pressure exerted by the column of water of height h. The bottom part of the manometer was equipped with a valve; the valve permits decreasing the water column height that in turn results in gas pressure decrease in the closed end of the tube. Pressure applied to a BL film-based membrane pasted over the holder can be easily measured as h mmH₂O.

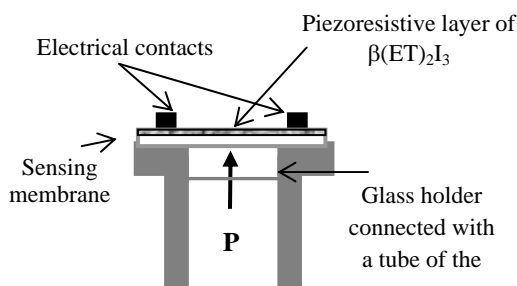


Figure 6. Schematic view of BL film-based membrane located over the tailor-made holder fabricated for pressure tests

The electrical responses of the thin sensing membrane to pressure changes were measured with a multimeter Agilent 34970A. The applied pressure was changes from 0 to 320 mmH₂O (0-32 mbar). The responses of the sensing membrane to applied pressure at 26 °C, 33 °C, and 40 °C are shown in Fig 7, 8 and 9, respectively. The pressure sensitivities (S_p) of the membrane at different temperature were calculated from the R(P) dependences shown in the bottom of the figures and summarised in Table 1.

Figs. 7, 8 and 9 demonstrate that in the studied pressure and temperature ranges the electrical resistance of the membrane linearly and reproducibly response to pressure changes with a steep-slope, which has only a weak dependence on the body temperature.

The data presented in Table 1 clearly show that the matrix thickness is a key parameter for engineering highly piezoresistive BL film-based membranes: a fivefold decrease in the thickness of a membrane plastic component on retention of the thickness of the piezoresistive layer resulted in a fivefold increasing of the membrane pressure sensitivity.

TABLE I. RELATIONSHIP BETWEEN THE THICKNESSES OF BL FILMS-BASED MEMBRANE AND ITS ELECTRICAL AND ELECTRO-MECHANICAL PROPERTIES

Membrane thickness μm	TRC, %/°C	Gage Factor	Pressure sensitivity (S _p) Ω/mmHg		
			26°C	33°C	40°C
25 (Ref. 15)	0.26	18±2	1.4	-	-
5	0.25	20.2	8.4	7.54	7.51

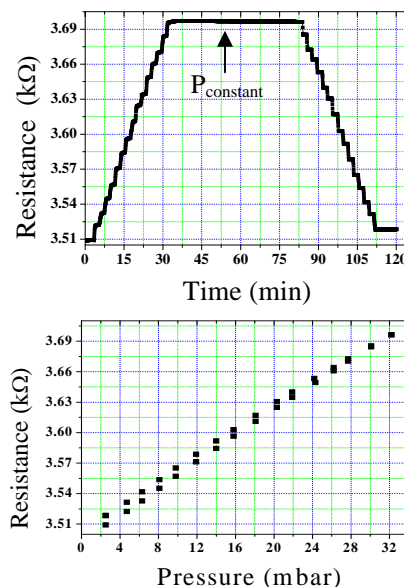


Figure 7. Loading at 26°C; Top: Electrical response of the BL film-based membrane corresponding to a variation of pressure in range 0- 32 mbar (0- 320 mmH₂O or mmHg), each step up and down being 2 mbar (20 mmH₂O or 1.5 mmHg); Bottom: R(P) dependence based on data collected for up and down sweeps from the loading graph presented at the top. Constant load of 32 mbar was applied during 65 min

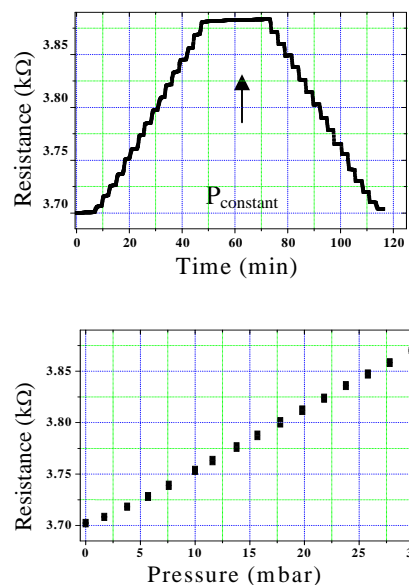


Figure 8. Loading at 33°C; Top: Electrical response of the BL film-based membrane corresponding to a variation of pressure in range 0- 32 mbar (0- 320 mmH₂O), each step up and down being 2 mbar (20 mmH₂O or 1.5 mmHg); Bottom: R(P) dependence based on data collected for up and down sweeps from the loading graph presented at the top. Constant load of 32 mbar was applied during 30 min.

Additionally, the pressure tests showed that resistance of the BL film based membrane under constant load of 32 mbar (24 mmHg) is time-independent in the studied temperature

range. Following the above pressure tests the membrane was studied anew by pressure loading at 26 °C (Fig. 10). According to data presented in Fig. 10, the sensitivity of the BL film-based membrane to pressure was found as 8,4 Ω/mmHg that is precisely the same as before it was found from the first loading experiment (Table 1). Therefore, the polycarbonate films covered with organic molecular metal β-(ET)₂I₃ are highly piezoresistive materials with a good reproducible electrical response to pressure

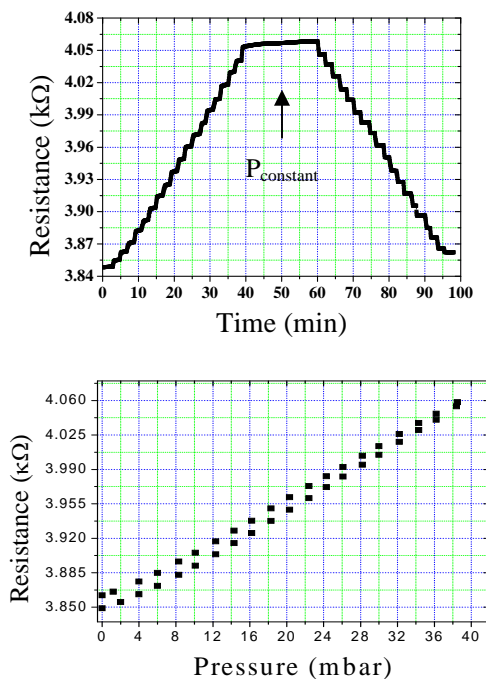


Figure 9. Loading at 40°C; Top: Electrical response of the BL film-based membrane corresponding to a variation of pressure in range 0- 32 mbar (0- 320 mmH₂O or 24 mmHg), each step up and down being 2 mbar (20 mmH₂O or 1.5 mmHg); Bottom: R(P) dependence based on data collected for up and down sweeps from the loading graph presented at the top. Constant load of 32 mbar was applied during 20 min.

IV. SUMMARY

The flexible pressure sensing membranes capable of measuring very small pressure changes have been developed. The pressure tests at different temperature showed that the body temperature does not significantly influence on the membrane pressure sensitivity.

This study also demonstrated the feasibility of a fivefold increase of the sensitivity of BL film-based membranes to pressure changes that is a very important step on the road to the development of flexible weightless miniature pressure sensors.

From the above it might be assumed that BL film-based sensors can be embedded in catheters, contact lenses and textiles for monitoring the body’s physiological processes and mechanical movements.

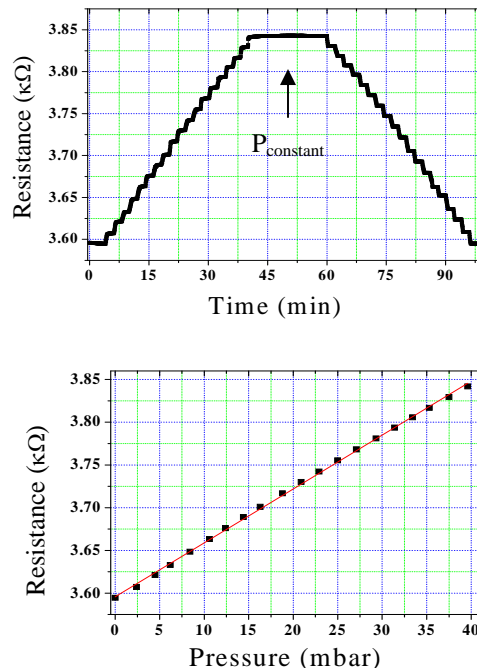


Figure 10. Replicate of loading at 26°C; Top: Electrical response of the BL film-based membrane corresponding to a variation of pressure in range 0- 32 mbar (0- 320 mmH₂O or 24 mmHg), each step up and down being 2 mbar (20 mmH₂O or 1.5 mmHg); Bottom: R(P) dependence based on data collected for up and down sweeps from the top. Constant load of 32 mbar was applied during 20 min.

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