INTERNSHIP REPORT

CONDUCTIVE POLYMERS

JULY 2019 – SEPTEMBER 2019

Place : Polytechnique Montréal & McGill University

Montréal, Canada

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Acronym

OFET – Organic Field-Effect Transistor

PEO – Poly(oxyethylene)

OECT – Organic Electrochemical Transistor

PDMS – Polydiméthylsiloxane

PEDOT:PSS – Poly(3,4-ethylenedioxythiophene) : Polystyrene sulfonate

EG – Ethylene glycol

DMSO – Dimethyl sulfoxide

PET – Polyethylene terephthalate

Introduction

As part of my engineering physics formation in INSA Toulouse, this summer I complete a research internship in Canada. It takes place at Polytechnique Montréal, from July 2nd to September 27th, with a view to broaden my spectrum of expertise and to have international research experience.

I was in the Laboratory of Organic Iontronics in the research group of Prof. Fabio Cicoira. This group is composed of postdoctoral fellows, PHD students, master students and interns working on organic electronic materials and more precisely conductive polymers. I have taken part in various projects developing this theme, including one in partnership with research group of Prof. Noémie-Manuelle Dorval Courchesne from McGill University.

Projects, I was part in, were mostly rotating around chemistry and biology, and thus permit me to learn new methods and theories about conductive polymers, an emerging domain in relation with nowadays environmental matters. In fact, Prof. Cicoira's group use conductive polymers as flexible, stretchable and biocompatible electronics (sensors, implantable electrodes, transistors…). Prof. Dorval's group focuses on the association of biological structures (proteins, micro-organisms…) and organic material (conductive polymers) to get functional new devices with novel physical properties.

First, this report will review the contexts and objectives of conductive polymers and then develop chronologically each of the projects studied.

Context and objectives

As said before, this internship focuses on conductive polymers. Conductive polymers associate polymers properties such as strength, flexibility, mouldability and good electrical conductivity.

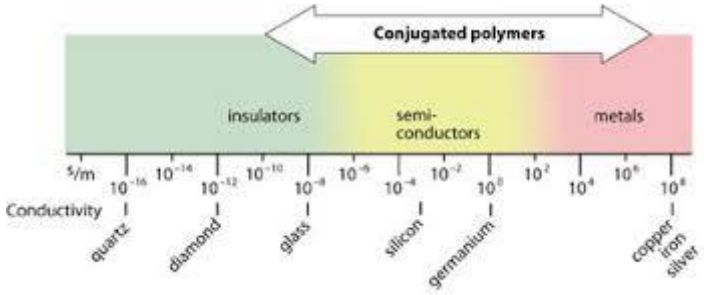


Figure 1 - Conductive Polymers [3]

Conductive polymers alone show low conductivity. They need to be doped (n or p) and behave like semiconductors: doping generates charge carriers which can move in an electric field. They are called conjugated polymers.

From this, we can imagine using biocompatible and biodegradable conductive polymers to revolutionize the microelectronic industry, with new possibility for transistors and for technologies interconnection with biology (electrodes, wiring).

During this internship, I have been involved in 3 projects following this direction.

The first one was about electrospinning of PEO fibers, with different concentrations, additives and electrospinning parameters, to obtain and optimize OECT's channel.

I worked also on the association of PDMS and PEDOT:PSS, to link good mechanical properties and high conductivity in structures like Kirigami (bi-stable structure).

My last project was about the mixing of PEDOT:PSS and Curli protein fiber to get new functional device capable of self-healing properties and conductivity.

A. Electrospinning Project

I/ Presentation

This project consisted in helping a PhD student working on his electrospinning thesis with another trainee. This allowed me to practice in the chemistry laboratory while working on an interesting starter project. The project is not yet completed, the following will be just an overview of my participation without results.

Electrospinning is the technique used to obtain nanofibers with very interesting properties for nanotechnologies. This allows to obtain fibers with a very high surface / weight ratio, a control of the pore size...

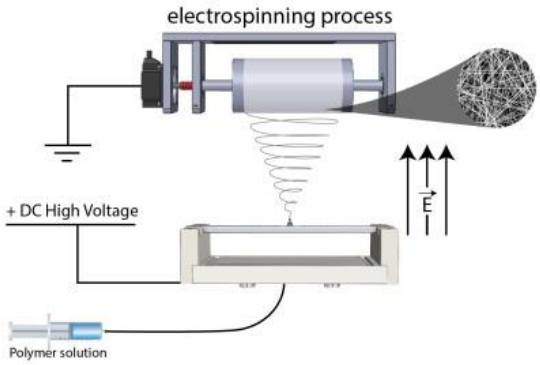


Figure 2 - Electrospinning setup [4]

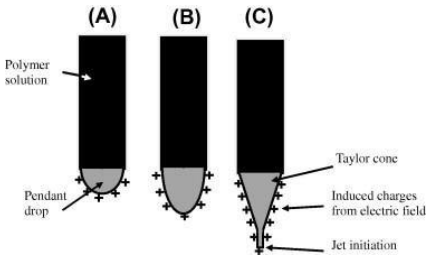


Figure 3 - Taylor cone [5]

The electrospinning setup consist in a syringe with polymer (liquid state or melt), a power supply capable of deliver high voltage (kV) and a conductive cylinder (collector).

The principle is to apply a sufficiently high voltage between the syringe and the collector. The droplet at the outlet of the syringe will therefore be subjected to an electrostatic force that will oppose the surface tension, and the surface tension will stretch. As soon as the surface tension is lower than the electrostatic force, a jet of charged particles will form (from the Taylor cone) between the collector (ground) and the syringe (high potential) allowing the formation of controlled fibers on the cylinder [6].

The project was to study different electrospinning parameters in order to optimize the conductivity and therefore the OECT's channel.

II/ Data handling

For our various tests, we decided to set a certain number of parameters from the beginning. The electrospinning tests are carried out in a chamber with humidity and temperature control (33 °C and 23 - 27% humidity). The syringe-cylinder distance is also set at 17 cm and time of spinning fixed at 300 seconds.

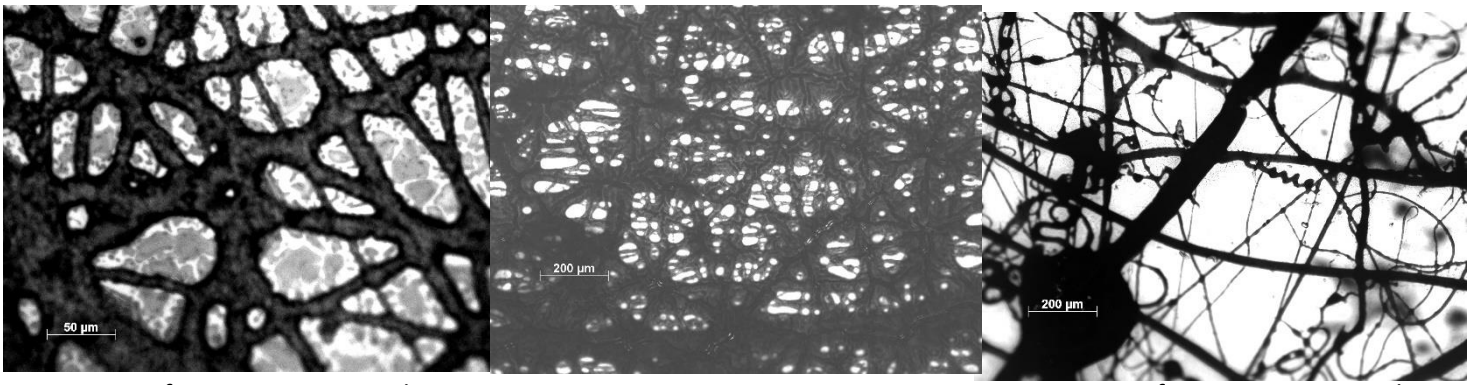
The variable parameters that we have chosen to study are :

- Voltage applied (15, 25 or 35 kV)
- Concentration of PEO (7, 15, 45, 75 & 150 mg)
- Additives used (EG, DMSO, Glycerol)
- Fibers substrate (PET films, PDMS films or Carbon paper)

This leads us to a long sample preparation with almost 45 PET films to prepare.

1) Fibers aspect control

Once prepared, in order to compare and control the fibers, we used transmitted optical microscopy and got this :



45 mg of PEO in DMSO – 15 kV | 45 mg of PEO in Glycerol– 25 kV | 15 mg of PEO in DMSO – 35 kV

Figure 4 - Fibers with transmission microscopy

Here, fibers are different according to electrospinning parameters. With a view to handle all these pictures and get key parameters (fibers diameter distribution, porosity…) we used ImageJ software, which is useful for image processing, and more precisely DiameterJ add on.

Figure 5 - Radius distribution histogram

Combined histograms are generated by the software showing porosity, diameters, orientation…

2) Conductivity measurements

We also want to know the conductivity of our different films and to measure it we used a 4-point probe (see appendix for operating principle). The 4-point probe gives us a sheet resistance in Ω/sq. For the thickness, we use a profilometer and do triplicates at different places (also with 4-point probe).

If we approximate and consider a uniform thickness for our films, we obtain the resistivity and respectively conductivity :

$$\rho = R_S . e \qquad\qquad \sigma = \frac{1}{\rho}$$

With ρ resistivity in Ω.cm, R_S the sheet resistance in Ω/sq, e thickness in cm and σ in S/cm.

Conductivity and different aspect parameters will allow the PhD student to conclude. However, they are a lot of parameters to study which needs to prepare precise set of experiments (design of experiments).

B. Kirigami Project (PDMS & PEDOT:PSS)

I/ Presentation

Kirigami can be defined as Bistable Auxetic Metamaterials (BAMs). It is a monolithic perforated periodic structure with a negative Poisson's ratio. In fact, auxetic materials, because of the microstructure, show stretch perpendicular to stress as show below:

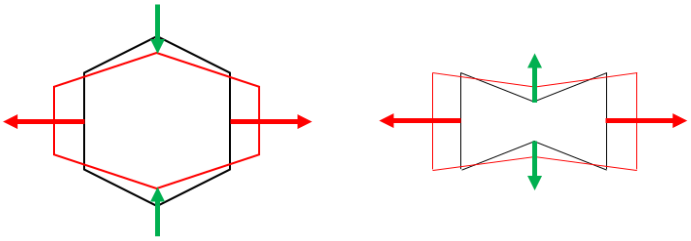


Figure 6 - Auxetic material [7]

With kirigami, we can obtain auxetic properties on substrate such as PDMS. It can be stretched under tension which leads to a second state of equilibrium through a complete shape transformation that is ensured by the stretch ability of the substrate material (bi-stable structure) [8].

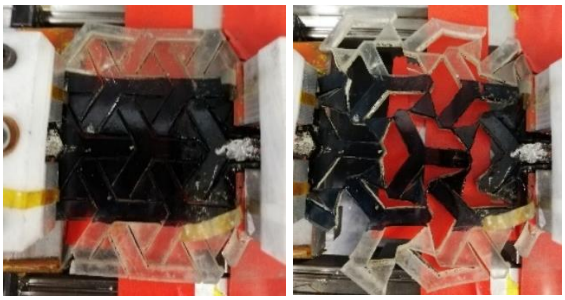


Figure 7 - Open/ closed form

Our group is trying to use kirigami structure as a substrate for conductive polymer such as PEDOT:PSS. As you can see above, the PEDOT:PSS is applied on the top of the kirigami structures and with eutectic metal or silver paste we wired it to make our study.

II/ Fatigue of the samples

The difficulty of this project is about the sample gesture. The Kirigami cut is perform by another university (McGill) and thus having new samples can be long. Furthermore, with optical microscopy we can see that old samples (from previous intern) show signs of fatigue:

Breaks perpendicular to the stress direction can be seen and in general PDMS starts to crack.

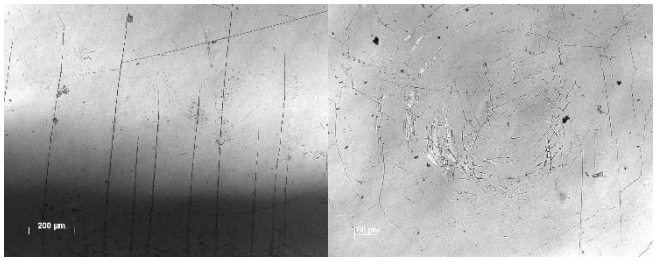


Figure 8 - PDMS with optical microscopy

It is very difficult to remove the conductive polymer layer from the PDMS substrate and samples show resistance increasing according to time (see III) Durability).

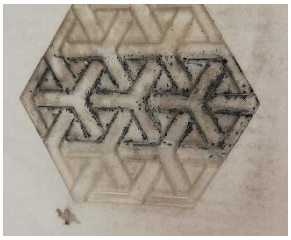


Figure 9 - Old sample

All this led us to anticipate the need for samples and prepare several s
for cutting (see Appendix for list and protocol for PDMS substrate).

III/ Durability of PEDOT:PSS

After analysis of the resistance of the PEDOT:PSS on top of PDMS on old samples, we noticed an increase in the resistance compared to the measurements made by the previous trainee. This may be a problem for future applications. We had therefore decided to study the longevity of the samples in terms of resistance.

Purpose: Show effect of time on sample resistance and compare protected samples (top layer PDMS) with unprotected ones.

Our PDMS substrate can be spin-coated with a solution of PEDOT:PSS or manually smeared with a glass slide and a more viscous solution of PEDOT:PSS (INK) on its top.

We protect 2 samples with a top layer of PDMS (P3 samples) and others were left out in the open (P2 samples), and each of them got triplicates of both INK and spin-coated PEDOT:PSS, as you can see below) :

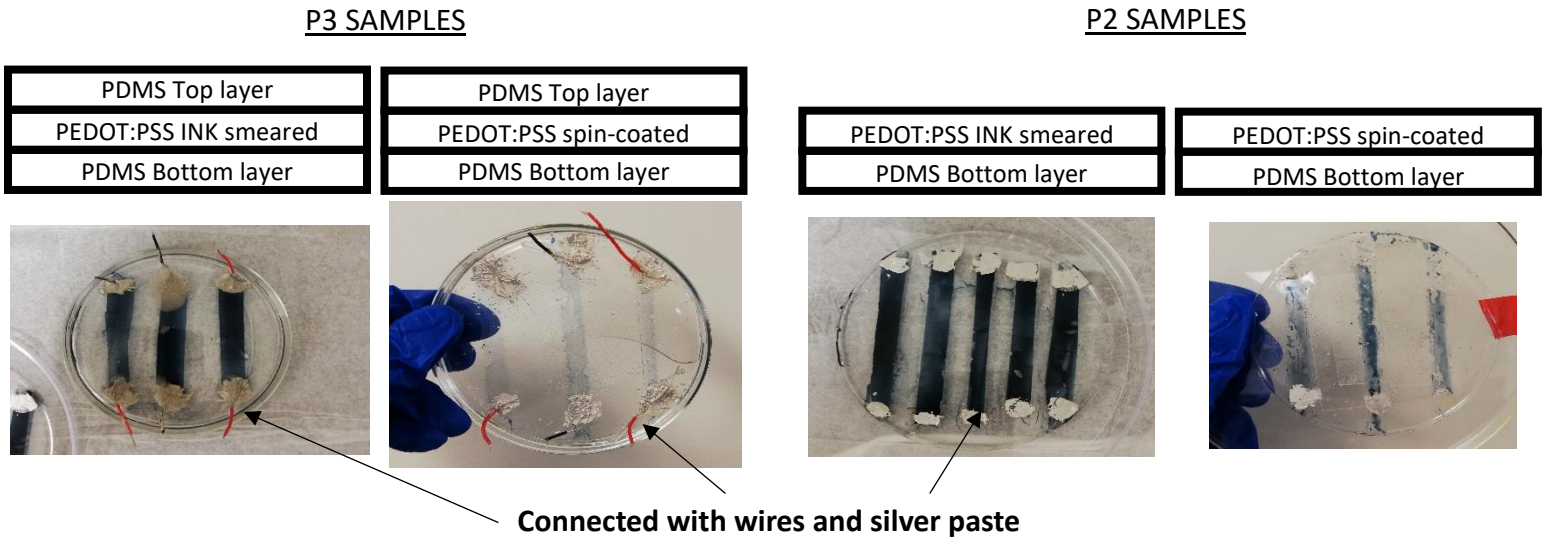


Figure 10 - Samples description

Method : Measure Resistance of Sample with 2 points probe every ≈ 5 days. To get resistance, apply a range of current (10 nA – 1 mA) each time and look for the voltage response to obtain the slope.

The wire and the silver paste are through the PDMS top layer for P3 samples, for P2 samples we just need to connect a wire to the silver paste.

Results :

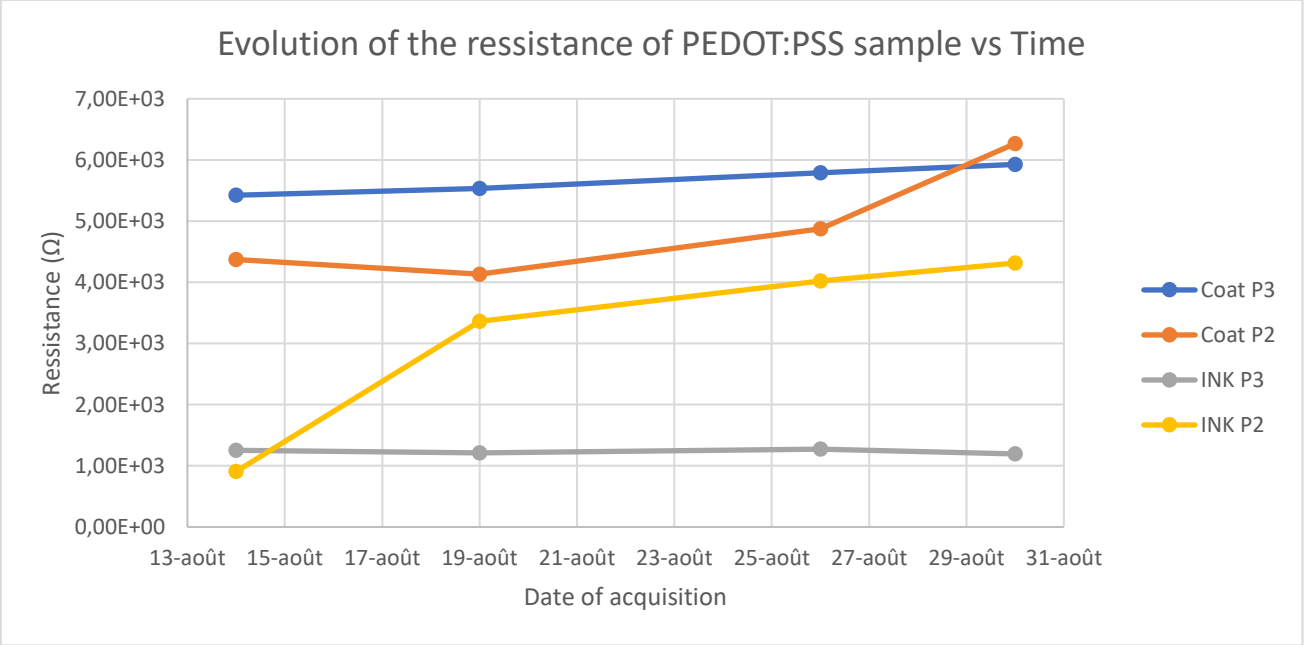


Figure 11 - Sample's resistance vs Time

Initially spin-coated samples have higher resistance because they are thinner than INK ones.

We can see that P3 encapsulation show stability, indeed if we look the maximum resistance variation for each sample :

Δ P3 Coat = 500 Ω **Δ P3 INK = 100 Ω**

Δ P2 Coat = 2,14 KΩ **Δ P2 INK = 3,41 KΩ**

P3 samples show a much lower order of magnitude for resistance variation. This trend is confirmed by the curve, almost plain for P3 while P2 show significant increase.

In addition to this, encapsulation of the PEDOT:PSS brings better repeatability for measurements : wires are stuck in the PDMS.

In the end, P3 INK sample show the best results for stability and the lowest resistance value.

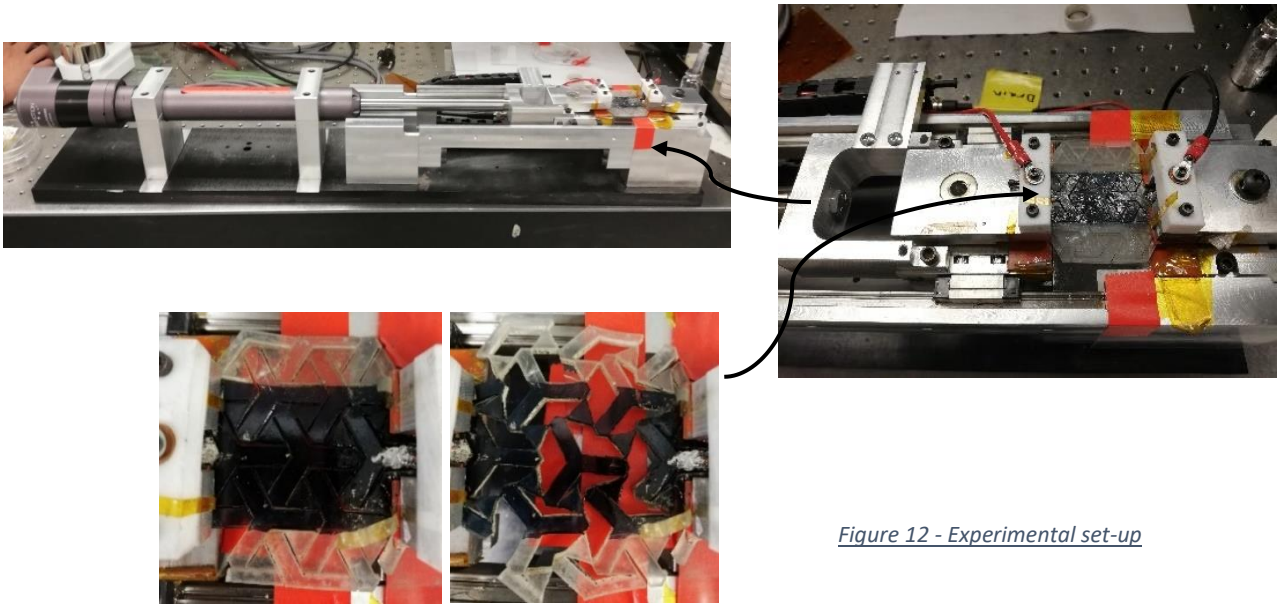
We know now that times can impact measurements for unprotected samples, new samples with a top-layer of protection are ready for kirigami cut (see appendix).

IV/ Kirigami's resistance open-closed study

Purpose: Prove that kirigami structure cover with conductive polymer (PEDOT:PSS) keep same ressistance after several open-closed cycling.

Method : We apply a constant voltage to our kirigami structure and look for the current according to the time I(t) with a 2 points probe (connected with silver paste on the PEDOT:PSS). The structure is opened and closed to its bi-stable forms with different numbers of cycles during measurements.

We use the following bench to perform tests :



Closed form Open form

Figure 12 - Experimental set-up

To get consistent results we use our sample when I(V) curve is linear (10mV as constant voltage applied) :

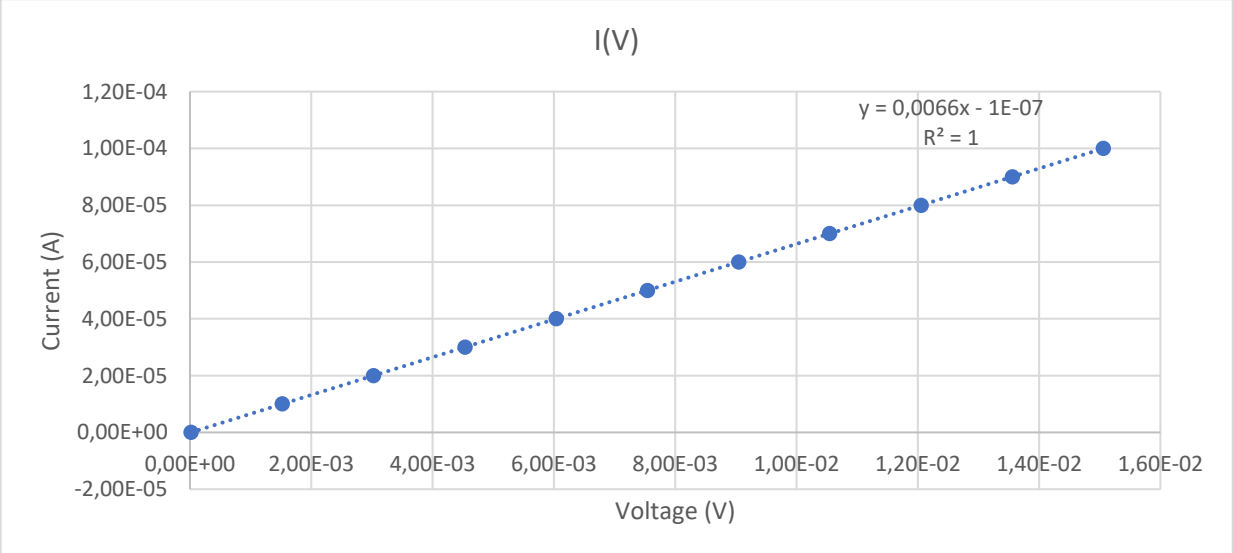


Figure 13 - I(V) curve linear regime

1) Prelimenary Results

With one kirigami structure already made (3mm thickness), we applied an ink layer of PEDOT:PSS and using the tensile/2 points probe bench we check for the resistance (current respond to constant voltage applied). With good amount of sampling points, we got these results for 10, 20 and 100 cycles :

Parameters of the test :

Number of cycle : 10, 20, 100 *Initial / Final Position : 4,15 cm / 5,8 cm*

Open / Closed holding : 5 s / 5 s *Vitesse / Acceleration : 1 m.s^{-1} / 10 m.s^{-2}*

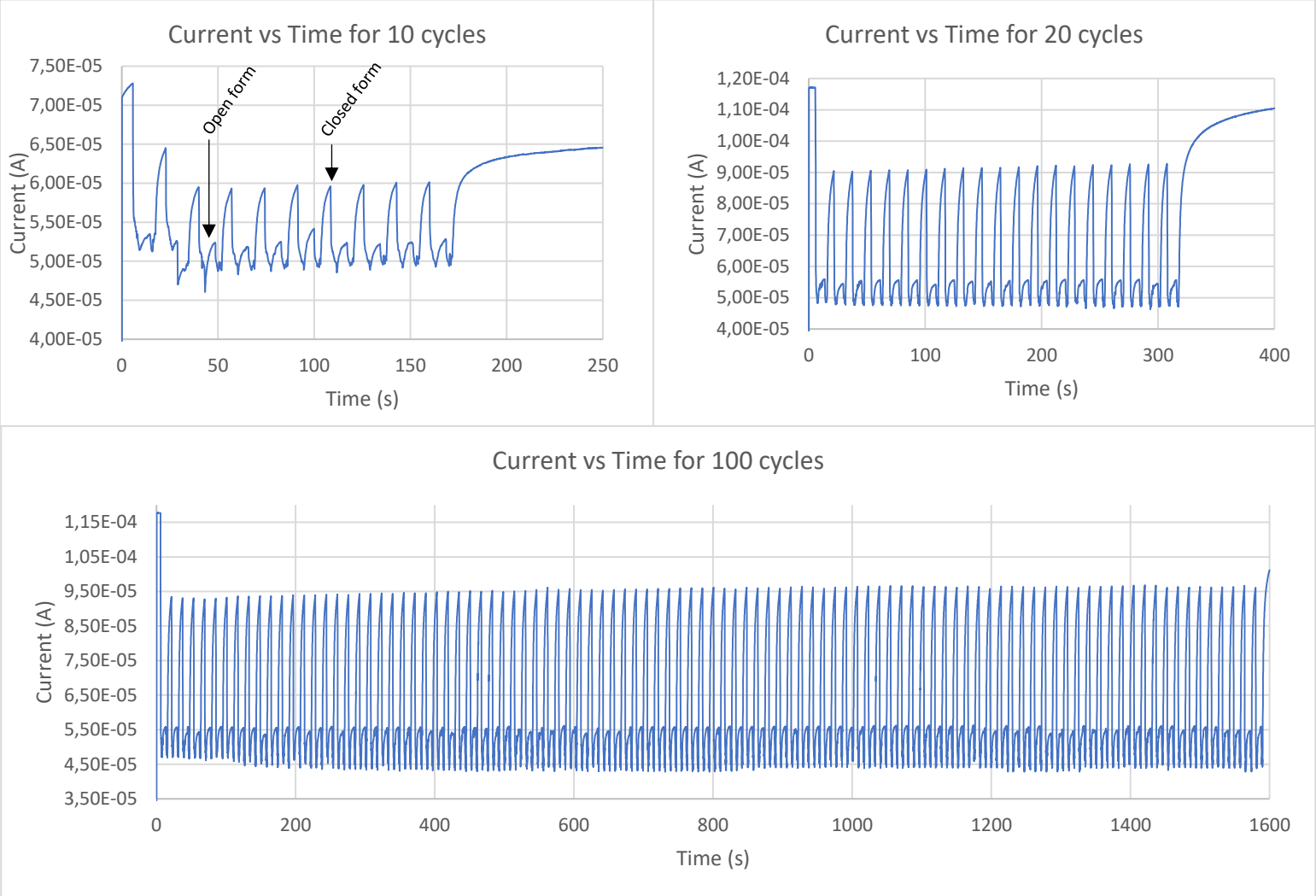


Figure 14 - Current vs Time for 10, 20 and 100 cyles

We are looking for the current amplitude between open and closed form (initial value change with positioning of the probe).

We can see that the current amplitude is not decreasing for even 100 cycles, variating between 4,5.10^{-5} and 9,5.10^{-5} A : $\Delta \mathbf{I_{total}} = \mathbf{5.10^{-5}}$ **A** (respectively **R = 105 Ω** when **closed** and **222 Ω** when **open**).

If we look carefully values, we got a current value variation in closed form of ΔI_{closed} = **4.10^{-6} A**

The ratio $\Delta I_{closed}/\Delta I_{total}$ **= 8 %** gives us the maximum fluctuation of current between each cycle. This value is low so we will not considerate it in the following.

2) Reach the limit of the kirigami

We decided to increase the number of cycling to reach the limit and see significative decreasing of the current.

After some changes in the Labview code of the tensile bench we could obtain the number of cycles we wanted.

For 1000 cycles :

Parameters of the test :

Number of cycle : 1000 *Initial / Final Position : 4,15 cm / 5,8 cm*

Open / Closed holding : 5 s / 5 s *Vitesse / Acceleration : 1 $m.s^{-1}$ / 10 $m.s^{-2}$*

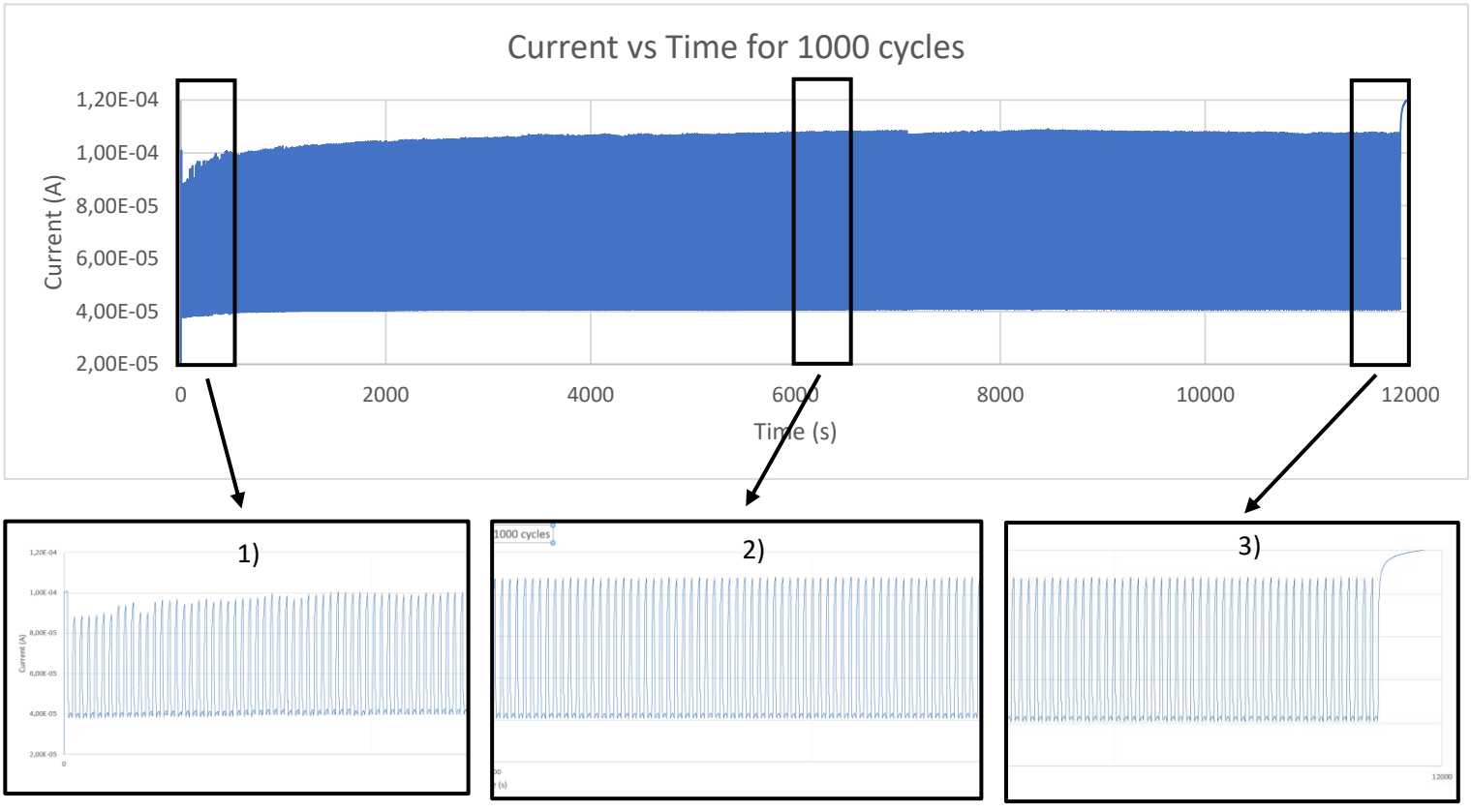


Figure 15 - Current vs Time for 1000 cycles

For this trial, we can see a sort of transitory behavior during 1) phase. If we don't considerate it, we can see that the current amplitude stays stable even during 1000 cycles (according to 2), 3) and general view of the curve).

We still need to increase the number of cycles.

For 5000 cycles :

Parameters of the test :

Number of cycle : 5000 *Initial / Final Position : 4,15 cm / 5,8 cm*

Open / Closed holding : 2 s / 2 s *Vitesse / Acceleration : 1 $m.s^{-1}$ / 10 $m.s^{-2}$*

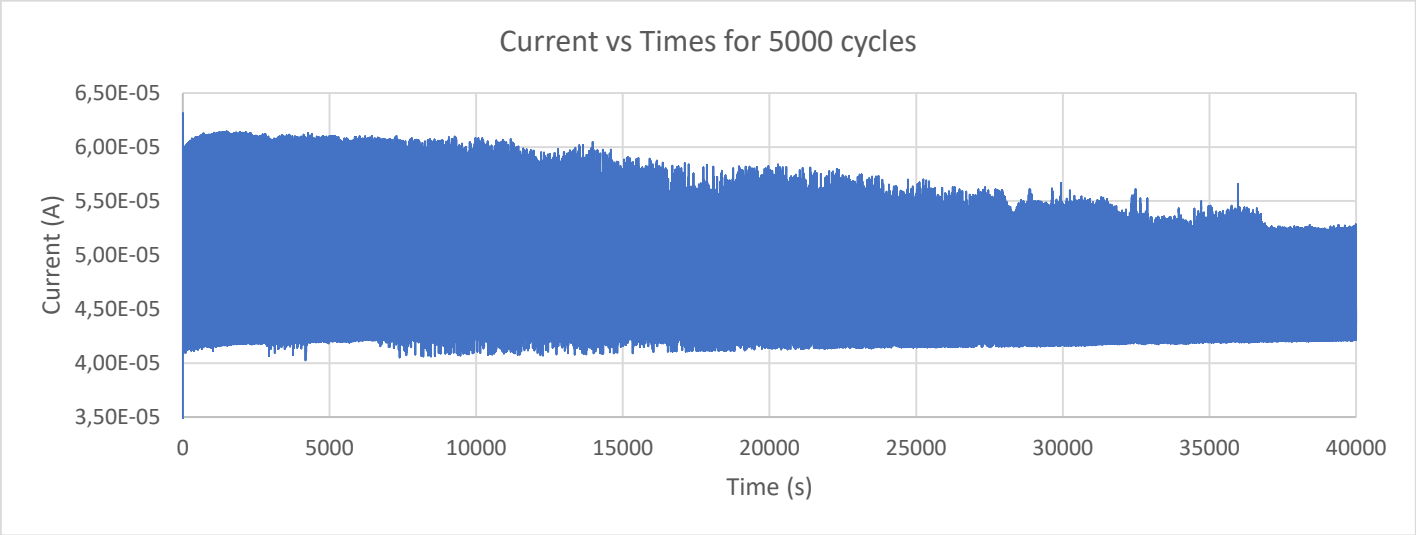


Figure 16 - Current vs Time for 5000 cyles

This time we can see a significative decreasing. It appears after 10000 s (almost after 1000 cycles).

If we look the current amplitude between open and closed form at 0 s and at 40000 s, we got this :

$\Delta I_{0s} = 1{,}8.10^{-5}$ and $\Delta I_{40000s} = 9{,}8.10^{-6}$

The ratio $\Delta I_{40000s}/\Delta I_{0s} = 54\ \%$.

After 37 200 seconds ≈ 10 hours (4650 cycles) the kirigami structure show a decrease of 54 % from its initial current in closed form (increase of the resistance in closed form **556 Ω -> 1029 Ω**).

At 15 000 seconds ≈ 4,1 hours (1875 cycles) the decrease is about 90 % from its initial current in closed form (increase of the resistance in closed form **556 Ω -> 617 Ω**).

In the end, after 10 hours of intense testing we multiply by 2 the resistance, these results are good and confirm potential use of kirigami structures for furthers application (see V) Outlook).

Remark : We observe a strange behavior during this trial. We tried to explain it without success. The current seems to increase constantly during all the test we perform (at a lower order of magnitude than the kirigami opening and closing so it can be neglected) :

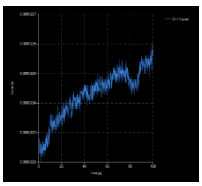


Figure 17 - Strange increasing behaviour

As we can see here and at the beginning and the end of measurements on each previous curve.

V/ Outlooks

We have proven the possibility of using the mechanical properties of Kirigami structures as a support for polymer conductors. This study revealed some disadvantages inherent to PEDOT:PSS (P3 encapsulation, use of INK...).

We now need to consider the prospects and possible applications of this technology :

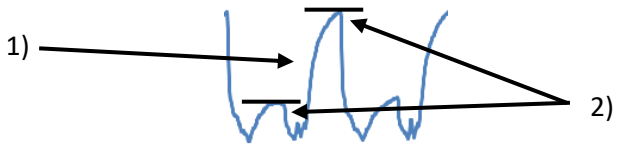


Figure 18 - 2 period of Current vs Time

If we look at one period of the current of our kirigami and at the same time the kirigami structure, we notice 2 potential use :

1) During “almost closing” phasis

When the sample is almost returned to closed postion, the behavior can be assimilated as a 2nd order and we can get with a simple curve fitting on Matlab the link between stretch and current/conductivity of the sample.

$$f(x) = a.\exp(b.x) + c.\exp(d.x)$$

With the sample studied, we obtain this :

Results

General model Exp2:
f(x) = a*exp(b*x) + c*exp(d*x)
Coefficients (with 95% confidence bounds):
a = 5.754e-05 (4.918e-05, 6.59e-05)
b = 0.02122 (0.01409, 0.02835)
c = -119.9 (-376.8, 137)
d = -0.9742 (-1.116, -0.8321)

Goodness of fit:
SSE: 6.185e-11
R-square: 0.9923
Adjusted R-square: 0.9919

Figure 19 - Matlab fitting

Fit is good with $R^2 = 0.99$, the model seems consistent.

Applications : According the fact that the current show the quality of the contact at the interface of the different parts of the kirigami, we can imagine a hermetic sensor able to detect the leakage of very small quantities of gases or liquids in containers by looking current change and knowing exactly the amount lost.

2) Two bistable state

The kirigami show two stable current form (2 current trays), so it’s a two-resistance component and we showed that this property can long during time.

Applications : Mechanical transistor, heart break tracking with a device shaped for heart breaks of a certain person and the kirigami will be around the heart, so this device will know heart rate, pulse amplitude and could alert emergency in case.

C. Curli protein Project

I/ Presentation

Curli proteins can play an important role in revolutionizing electronics and microelectronics. They have the advantage of being biocompatible, biodegradable, easy to produce and provide many innovative properties to components made of conductive polymer [9].

Prof. Dorval's laboratory specializes in the production of aggregated protein nanofibers expressed from E. Coli bacteria.

They are obtained by vacuum filtration, as shown below :

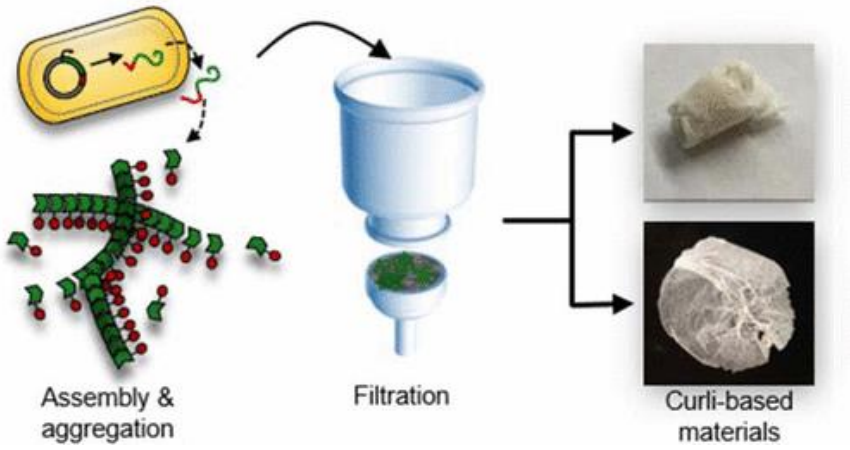


Figure 20 - Protein procurement [9]

This study is used to determine the possible benefits of protein combination in controlled quantities in PEDOT:PSS solutions. The drop-casting process was used to obtain free standing films.

II/ Concentration and Conductivity

Purpose : Obtain Conductivity vs Protein Concentration on free standing film of PEDOT:PSS and curli fiber (more ratio)

Method :

It is tested different proteins mass ratios into PEDOT:PSS.

For all the following tests, the same mold was used to make free standing films (see appendix for the protocol) :

Figure 21 - 2 X 2 inches mold

Once the free-standing film is ready, it must be carefully unmolded. Then using a razor blade, it is cut into 6 equal pieces (see III/ Re-healing properties).

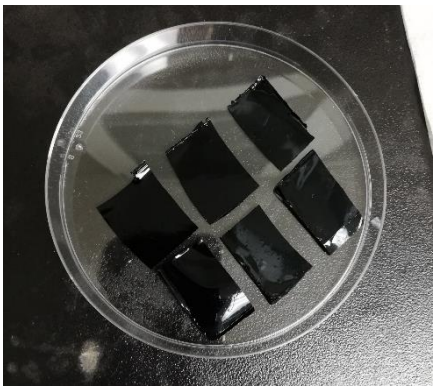


Figure 22 - 6 pieces from the film

The different parts are numbered and with three of them, resistance measurements are carried out with the help of 4-point probe (see Appendix for principle).

The probe gives us the sheet resistance R_S :

$$\rho = R_S . e \qquad \sigma = \frac{1}{\rho}$$

We obtain the conductivity with the thickness.

For the thickness, we use profilometry. The film is glued to a glass slide with tape at the edges. The measurement is taken in such a way that it is as close as possible to the area glued with the tape (avoid air underneath the sample).

This method is not very precise but, in any case, it allows to obtain an order of magnitude for the conductivity, which varies strongly according to the concentration of PEDOT:PSS.

Samples preparation

3 different films were made. Protein filtration takes time for McGill students, we could only test one ratio including 5% protein by weight (10 mg of protein in total).

1	2	3
PEDOT:PSS 95% vol. Glycerol 5% vol. 7,5 mL	PEDOT:PSS 95% weight Curli protein 5% weight 7,5 mL	PEDOT:PSS with 5% vol. Glycerol 95% weight Curli protein 5% weight 7,5 mL

Figure 23 - 3 free-standing films

We try to make a free-standing film with 5% vol. of glycerol in order to increase the conductivity of the film. In fact, with 100% PEDOT:PSS free standing film, we obtain an approximate value (with the method describe above) of 60 mS/cm.

PEDOT:PSS should be more conductive on glass substrate (1000 S/cm). However, here we are studying free standing films and I have values that are in the same order of magnitude than previous person on this project.

For film 2, At first, we thought that the proteins were not dispersed homogeneously on the film (white spot at the bottom left of the first picture), but on the second picture we can see that the distribution is almost homogeneous.

Results :

1	2	3	100 % PEDOT :PSS
92 mS/cm	51 mS/cm	Not dry	60 mS/cm

As mentioned above, the results agree with the previous trainee.

The addition of Glycerol in film 1 increases the conductivity by 50%, which can be interesting for various applications.

The problem with glycerol is that it affects the mechanical properties of the film: the film is much more flexible, fragile and sticky, which makes it difficult to handle.

Continuity of the previous project by adding a ratio (film 2):

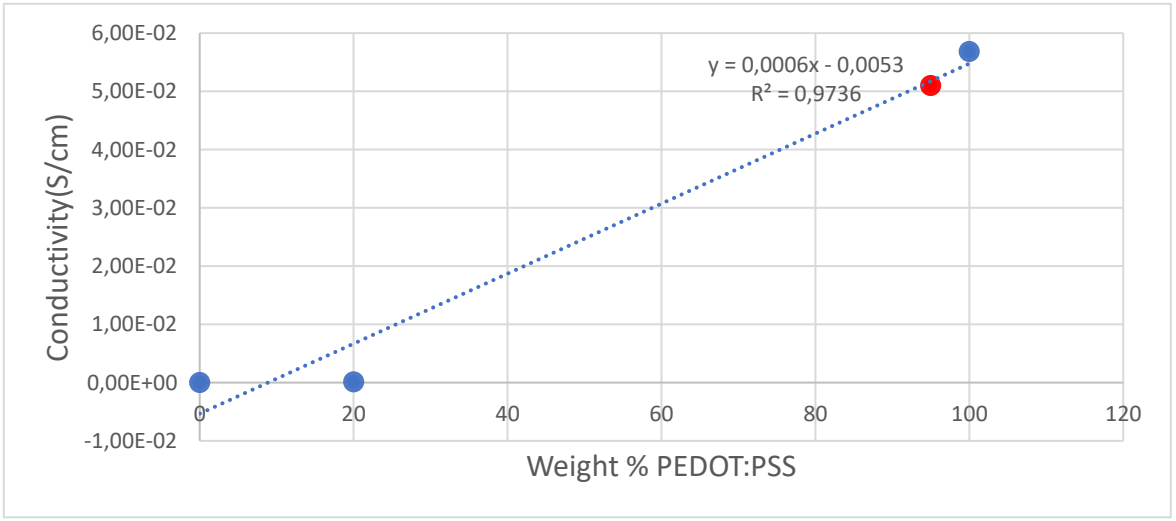


Figure 24 - Conductivity vs Concentration of PEDOT:PSS

Sample 3 was not usable before I left (not dry).

It can be interesting to investigate why free-standing films show low conductivity value, because even if the method described above can be questioned, especially in terms of thickness measurement, this cannot explain going from 1000 S/cm to 60 mS/cm.

III/ Self-healing properties

For all the following, we used film 2 : 95% PEDOT:PSS / 5% Curli protein weight

Purpose : Obtain conductance value on free standing film of PEDOT:PSS and curli fiber (more ratio and healing)

Method :

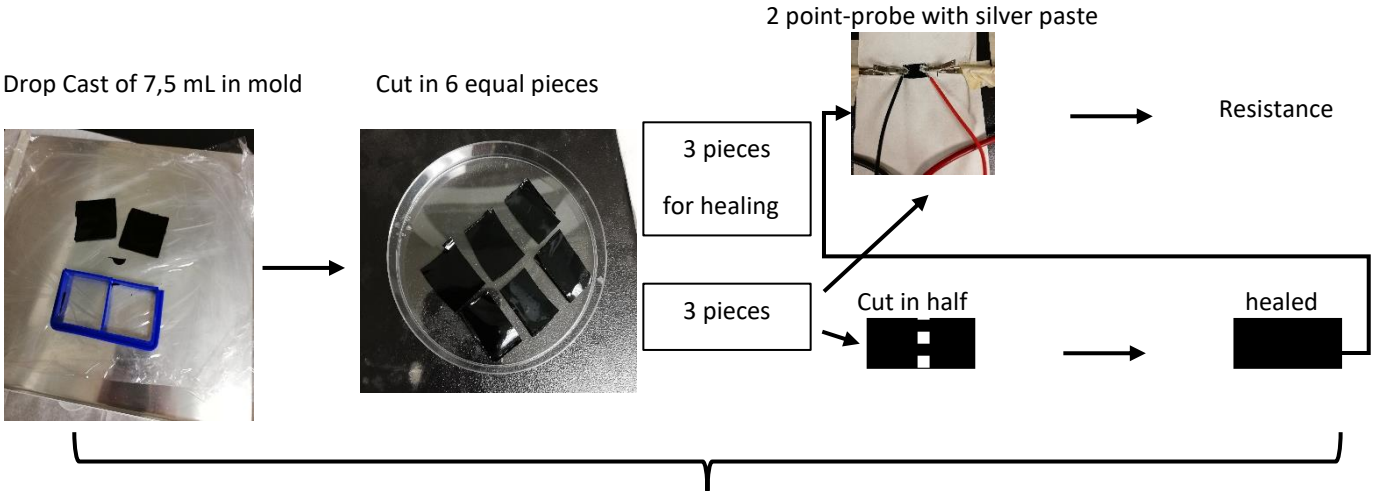


Figure 25 - Method for characterizing self-healing properties

We use 3 pieces for resistance value : before being cut in 2, their conductance is measured on the 2-point probe and then cut in 2 using a razor blade (always connected to the probe). By adding a few drops of water at the cut-off point, the sample will heal itself and a resistance measurement can be taken again.

Results :

PEDOT:PSS 95% weight
Curli protein 5% weight

Ressitance value :

Sample 1	Sample 2	Sample 3
Resistance before cut : **3,11 kΩ**	Resistance before cut : **4,62 kΩ**	Resistance before cut : **3,74 kΩ**
Resistance after cut : **4,64 kΩ**	Resistance after cut : **3,18 kΩ**	Resistance after cut : **3,70 kΩ**
Healing ratio **67 %**	Healing ratio **145 %**	Healing ratio 101 %

$$Healing\ ratio\ (electrical) = \frac{before}{after}$$

Average **104 %** → More test need to be run

In the end, we obtain a restoration of electrical properties (healing ratio) close to 100% on average. Contact after self-healing is better than before cutting for 2 samples. Many more tests must be carried out to confirm this trend.

For 100% PEDOT:PSS, there is also restoration of electrical properties by adding water, however this restoration does not last in time and is not accompanied by a recovery of mechanical properties, so proteins provide this self-healing capacity that can be very interesting for bioelectronics.

Technological demonstration :

Healing in a circuit

Experimental setup :

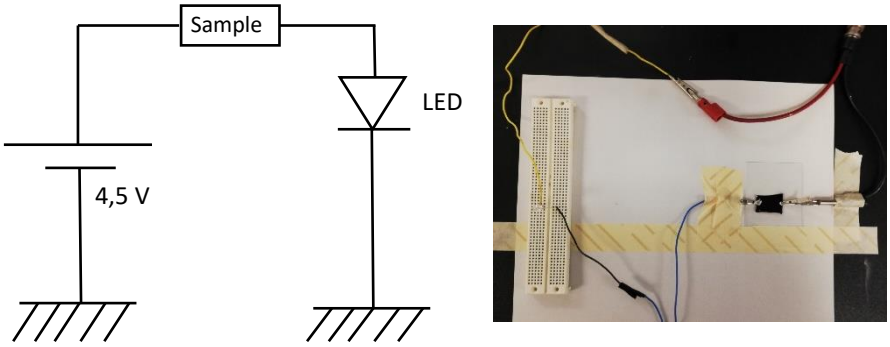


Figure 26 - Experimental setup

The interest here is to supercharge a serial diode with 2 crocodile clips and PEDOT:PSS samples with 5% curli protein. Two samples must be placed so that one circuit remains open. With the help of a 3rd sample (previously hydrated), the circuit is closed and the LED lights up.

Video : https://drive.google.com/open?id=1szaBv0WgOukmw2Z7sBhMgQ0vaOozPjAV

Advantage of protein instead of only PEDOT:PSS

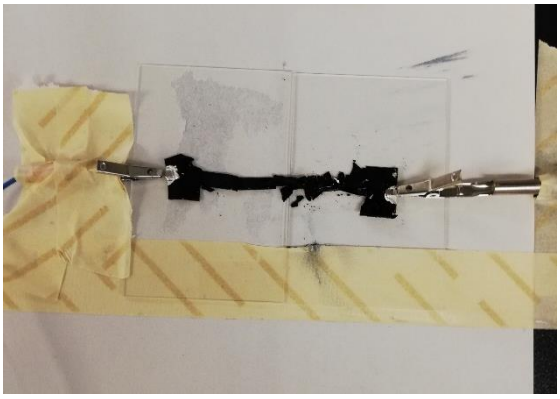


Figure 27 - Multiple healing

Proteins make it very easy to connect film pieces together. The video above shows a multiple healing made with many small pieces of film of different shapes and which allow to light the LED after adding a few drops of water.

When the last piece of film is removed, the LED lights up briefly before water is added.

Video : https://drive.google.com/open?id=1rOEJNpqLycuMcZy3fUFxmGRLquOhu7Zu

This last video below shows what is not possible for PEDOT:PSS film only, mechanical rehealing. We cut a piece of film in 2 using razor blade and with water we re-healed it and by abusing it, we are seeing a restoration of mechanical properties.

Video :

https://drive.google.com/open?id=17ah-Hp2p_lmf-pOVlXIiO_lNd3qF0Ini

Appendix

4-point probe

The principle of this method is to align the 4 points on the sample away from the edges. The sample is then subjected to a current (between 1 and 4) and the voltage between 2 and 3 is measured. This voltage divided by the current sent gives the resistance between peaks 2 and 3. Then by integration it is necessary to add the remaining infinitesimal resistances. In our geometry this corresponds to :

$$R = \frac{\pi}{\ln(2)} \cdot \frac{U}{I}$$

For all the measurements presented above, a current ramp setpoint is sent to the sample.

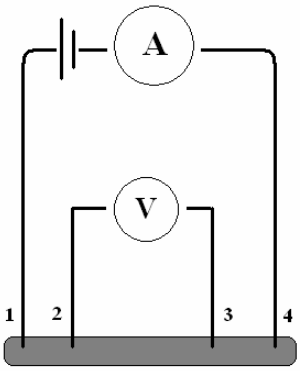


Figure 28 - 4-point probe

List of new samples

Those are ready for being cut into Kirigami structure :

- 5 round PDMS mold 4" (thickness : 1 X 3,3mm ; 3 X 3,5mm ; 1 X 3,8mm)
- 3 P3 Samples 4" :

PDMS Top layer
PEDOT:PSS INK spin-coated
PDMS Bottom layer

We used the viscous PEDOT:PSS (INK) easier to spin-coat and because of its performance (see III) Durability of PEDOT:PSS) and add encapsulation P3 method.

Protocols

1) Protocol PDMS mold

Substrate used is Polydimethylsiloxane (PDMS). It is prepared by mixing the monomer Dimethysiloxane and its crosslinker in the ratio 10:1. Here, 25 grams of monomer is added with 2,5 grams of crosslinker in a plastic container (average thickness 3,5 mm with these parameters in 10 cm mold). Then it is mixed in a centrifuge at 2000 rpm for 3 minutes. The mixture is desiccated to release any bubbles.

The mixture is then poured into a suitable mold. The mold used here is a circular shaped glass container of diameter 10 cm. It is thoroughly cleaned with acetone, Isopropanol (IPA), distilled water and it is dried using air gun. Then the mold is treated with UV\Ozone for 20 minutes. A solution of 5 mM of cetyl trimethylammonium bromide (CTAB) in deionized water is used to wash the glass mold which acts as a mold releasing agent for easy removal of the substrate.

Now, the desiccated mixture is carefully poured into the cleaned mold. The thickness could be varied between 3 to 4 cm which is the most suitable for kirigami structure cuts.

For curing process, the mixture is covered with suitable cap to keep it away from contaminants. It is cured by keeping it on hot plate at 100 °C for 1 hour.

After an hour the sample is removed and allowed to cool for 10 minutes. Using a thin cutter, the edges are carefully cut from the glass mold and the substrate is peeled off the glass container.

2) Protocol smeared INK on PDMS

To do that, we put our sample (PDMS mold) during 20 minutes under UV/ozone to clean it and increase adhesion of its surface.

INK is the viscous PEDOT:PSS. It is smeared onto PDMS with the help of a glass side. To have uniform line of PEDOT:PSS, it is smeared with a PET film mask (cut into line).

Once smeared, it is cured by keeping it on hot plate at 100 °C for 1 hour with the PET film mask.

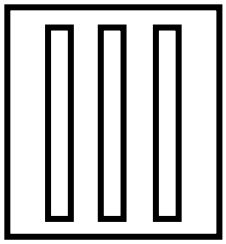


Figure 29 - PET film mask (lines are perforated)

3) Protocol spin-coated INK

To do that, we put our sample (PDMS mold) during 20 minutes under UV/ozone to clean it and increase adhesion of its surface.

The PDMS mold is stuck with double tape on a glass slide and stick with vacuum on the spin-coater. INK is added in the middle and spred out a little bit.

Because of the viscosity, it requires a rather high rotation speed to distribute the solution well and a rather low acceleration to avoid losing everything when launching the spin-coater.

Spin-coateing parameters :

- Speed : 1000 RPM
- Acceleration : 200 RPM
- Time : 35

4) Protocol top-layer PDMS (P3 encapsulation)

Use the same mold and add on the PEDOT:PSS PDMS (15 g monomer and 1,5 g crosslinker).

It is cured during 1 hour at 100 °C on hot plate.

5) Protocol free standing films of PEDOT:PSS & Curli proteins

The final solution for the mold is 7,5 mL : Calculate according to the weight ratio you want. Use the scale for more accurate measurements using mass rather than volume.

Proteins tend to aggregate together, they should be delicately separated as much as possible and added to the PEDOT:PSS solution piece by piece. Then we place the whole thing in the mixer for 3 minutes at 2000 RPM. The mold must be placed on a perfectly flat surface on tightly stretched food paper. The solution is then gently poured into the mold, distributing it evenly. Allow to dry at room temperature for at least 60 hours and check thoroughly before demolding. To remove the molds, simply cut the edges with a cutter.

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