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RAPID PROTOTYPING OF ELASTOMERIC MEMS FOR WEARABLE COMPUTING

Dissertação de Mestrado Integrado em Engenharia Física

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Rapid Prototyping of Elastomeric MEMS for Wearable Computing

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Abstract

Wearable technologies are receiving an increasing attention, and they intend to change the way we interact with machines. Stretchable Electronics are the building blocks of the human machine interfaces of future. Such systems should not only be flexible and bendable, but they should also be stretchable, matching the properties of the human organs, such as skin. Integrated electronics system with a Young’s modulus between (0.1-10MPa) are the target of this research field. Challenges are mainly on materials and fabrication methods that allow reliable application of such systems.

In this dissertation, it is studied fabrication methods, materials and measurement methods for stretchable sensors that are able to measure pressure. The intended application might be a soft bionic hand, a tactile sensor mesh, or a stretchable touchpad. The focus of this dissertation, however, is not to fully develop and characterize any of these systems. Instead, the objective is to work around the triangle of fabrication methods, measurements and materials and evaluate each of them in terms of reliability of the sensors, and acceptability of the fabrication method (cost, required equipment, production time). This, however, enforces not only studying deeply the state of the art on fabrication and materials, but also to prototype and evaluate several sensors with different methods and evaluate their performance.

Materials that were evaluated include the base polymer for the stretchable insulating material, the conductive measuring probes and interconnects (such as conductive polymers, liquid metal). Additionally, fabrication methods include different concepts, such as stencil lithography and lifting, using different technologies such as 3D printing and laser cutting, and measurement methods include resistive and capacitive sensing.
Furthermore, it is briefly discussed an anisotropic z-axis film that are able to interface stretchable electronics with rigid electronics microchips and also enable multi-layer stretchable electronics circuit.

In summary, this dissertation should be a useful guideline for future researchers to rapidly gain an overview of materials and methods for stretchable and flexible electronics. Therefore on the last 2 chapters, beyond a demonstration of two case studies, this dissertation concludes with some guiding flowchart, that will help researchers to chose the fabrication method, based on their intended application.

**Keywords:** Wearable Devices; Soft Sensors; Stretchable Sensors; Pressure Sensors; Strain Sensors; EGaIn; cPDMS;
Resumo

A forma como o ser humano interage com dispositivos eletrônicos tem vindo a mudar devido a um crescente interesse na tecnologia vestível. Componentes eletrônicos flexíveis e extensíveis são a base para a interface humanos - robots do futuro. Estes sistemas, para além de flexíveis, devem ainda ser extensíveis para serem condizentes com as propriedades de certos órgãos humanos, como a pele. Assim, sistemas eletrônicos integrados com um módulo de Young entre (0.1 - 10 MPa) são o alvo deste campo de pesquisa. Os principais desafios prendem-se com o estudo de materiais e métodos de fabrico que permitam uma aplicação fidedigna destes sistemas.

Nesta dissertação, são estudados e abordados métodos de fabrico, materiais e métodos de medida para sensores extensíveis capazes de medir forças de pressão. O objetivo passa por criar sensores capazes de integrar numa mão protética ou num "touchpad" flexível. Contudo, o principal foco desta dissertação não é o desenvolvimento e caracterização destas aplicações diretamente, mas sim, trabalhar em torno do triângulo de métodos de fabrico, métodos de medição e materiais e assim, avaliar cada um deles em termos de confiabilidade dos sensores e aceitabilidade do método de fabrico (custo, equipamento necessário, tempo de produção). Contudo, isto implica não só um estudo profundo do estado da arte da fabricação e materiais, mas também uma fase de prototipagem e avaliação de diversos sensores para avaliar a sua performance.

Os materiais que foram objeto de estudo nesta dissertação, incluem os polímeros base para o material isolador e os terminais condutores e interconexões (polímeros condutores e metais líquidos). Adicionalmente, em termos de métodos de fabrico foram avaliados diferentes conceitos como stencil lithography e lifting utilizando diferentes
tecnologias como impressão 3D e máquinas de corte laser. Em termos de métodos de medição foram estudados sensores resistivos e capacitivos. Para além disso, é brevemente apresentado um filme anisotrópico que conduz apenas no eixo-z, que pode ser utilizado como interface entre eletrônica rígida e extensível e ainda permite a construção de circuitos eletrônicos extensíveis com múltiplas camadas.

Em resumo, esta dissertação deve ser um útil guia para futuros investigadores que queiram ter uma ideia geral sobre métodos e materiais para sensores extensíveis e flexíveis. Assim sendo, nos últimos dois capítulos, para além de uma demonstração de dois casos de estudo, esta dissertação é concluída com esquemas que procuram ajudar investigadores na escolha de métodos de fabrico, tendo por base a aplicação que pretendem desenvolver.

Keywords: Dispositivos Vestíveis; Sensores Flexíveis; Sensores Extensíveis; Sensores de Pressão; Sensores de alongamento; EGaIn; cPDMS;
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Acronyms

**EGaIn**  Eutectic Gallium-Indium

**cPDMS**  Carbon Polydimethylsiloxane

**PDMS**  Polydimethylsiloxane

**HMI**  Human Machine Interfaces

**MEMS**  Microelectromechanical Systems

**LMEE**  Liquid Metal Embedded Elastomers

**CNT**  Carbon Nanotubes
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Chapter 1

Introduction

These days, the progressive evolution of technology has led to a whole new concept about robots. In the past, robots were made, mainly, to help in an industrial environment and controlled by humans. However, this definition is perishing and is being replaced by a new one where a robot is something present in the human daily routine and, furthermore, there is a real interaction between humans and robots. Almost every day, a new product, either hardware or software, that somehow improves this interaction is released. Despite the firsts robots were also built to change the human life and, preferably, make it easier, this new interaction has been growing rapidly in the last decades, where it could be seen the developing of the portable devices – from laptops to mobile phones – and, even more relevant, the creation of the smart wearable devices.

The wearable technology started decades ago with the firsts and simple watches. However, the continuous growing and improvement led to new horizons, and these days a wearable device is much more than a device that provides the time. Some devices can be connected to internet and can even interact with the human user, being able to provide important information about the person who is wearing them. It is possible to obtain, for example, the precise location and speed that a person is moving.
Additionally, it is also possible to detect, measure and monitor body signs such as heart rate, EMG (Electromyography), ECG (Electrocardiography) and the glucose in the bloodstream. Although these devices do not replace professional care, some of the devices that provide these applications are starting to be used in daily routines for patient monitoring, health monitoring and professional sportsman.

![Global Wearable Device Unit Shipments Forecast](image.png)

**Figure 1.1:** Forecast for the growth of wearable devices, from Business Insider Intelligence.

In the plot from figure 1.1, a survey from *Business Insider Intelligence* based on smart-watches from Google and Apple and its impact in the society, it can be seen that the forecast for the wearable technology shows that the number of devices used is continuously growing for the next 3 years. It is estimated that the global wearable market will grow at a compound annual rate of 35% over the next three years, reaching 148 million units shipped annually in 2019. However, this evolution in the interaction between human and machines is not just due to the need to measure human events, but it is also due to an improvement in the materials used by those machines. This relation would not be possible if the device that interact with the human was uncomfortable and difficult to use.

Similarly to all sensors designed to detect, measure and/or monitoring any event or change in theirs environments, the wearable sensors must also be easily adaptable
to their host without interfering with its mechanical properties and abilities and, ob-
viously, must be reliable. To fulfill all these characteristics there is a specific field of
the electronics, the Soft Electronics, which main goal is to approximate the humans
from the robots. As can be deducted from the name, Soft Electronics are made from
soft materials, which means light, flexible and eventually stretchable materials, such
as elastomers. This is an important point in the wearable technology. As can be seen
in figure 1.2, the Young’s Modulus of the materials used to produce soft sensors are
pretty similar to the skin itself, which means that the human body will recognize these
materials and the user will not feel as using a strange object attached to him/her. Some
of these materials can bend and sustain large elongations, being able to stretch several

Figure 1.2: Young’s Modulus of various materials in nature. [1]
times their rest length, and enable a rich range of electronic and sensing functionalities. This is very important in biomechanics and also in robotics so that electronic components have good conformation to joint rotations and do not interfere with the natural mechanics of the host. Therefore, Soft Electronics are not only restricted to the wearable sensors but also to robotics in general. They can replace the actual and rigid electronics in every situation, minimizing the impact of the electronics in the operation of the host. Moreover, due to theirs ability of being stretched or bended without damage, it is possible to adapt them in round objects easily. Additionally, there are also some applications of soft technology in rehabilitation, and also to help in the tactile sensing in minimal invasive surgery.

Figure 1.3: a) Soft strain sensors placed at lower limb joint, knee and ankle. b) A wearable device designed to measure strain and transmit data to a bluetooth enabled device. c) EMG sensor developed in ISR & SML

In order to produce this type of electronics, researchers have a wide quantity of...
materials and fabrication methods available. Although the fact that this demonstrates the extensibility of this field, it also makes evident that there is no specific fabrication method neither material that ensures complete quality, reliability or repeatability.

The Human Machine Interfaces (HMI) of today are rigid, brittle and hard. They are not adequately conformable to soft human tissue and organs. This conspicuous mismatch has been an inspiration for the novel field of stretchable electronics to enable development of HMIs that highly match the mechanics of human organs, such as skin. Flexible MEMS and electronics are not fully conformable to the skin and human organs, i.e. they bend but they do not stretch along with the skin. It is desired to develop ultrathin and stretchable MEMS that can attach to the skin and can follow the dynamic morphology of the skin. Examples of achievements for the medical application includes a thin, flexible device that produces electrical power when mounted on the surface of the heart or lung [14], or a skin mount stretchable electronics device for blood oximetry with wireless power and data transmission [14].

Figure 1.4: Contributions of John Rogers Research Group, a) Thin, Battery free, Skin-like devices for blood oximetry, [15], b) 3D Electronic Pericardium

Beyond Rogers Research Group, there is the Integrated Soft Materials Lab from Carmel Majidi group at CMU, that made excellent progress on fabrication methods of
A sensor is a type of transducer, which means that is a device that is able to convert one form of energy to another. Specifically, a sensor is an object whose purpose is to detect events and changes in its environment, without causing any interference, and then provide a corresponding output using a different form of energy. A soft and wearable sensor, may be used to detect or measure, depending on the desired application, pressure forces, bending angles of the joints, electrical activity of the body, slippage, among others properties that may interest.
1.1 Motivation and Goals

Despite the potentials of stretchable electronics as the building blocks of the future wearable HMIs, they face several challenges on their fabrication and reliable application. As explained, this dissertation does not focus on a single application. Instead, it focuses on fabrication methods and materials for their reliable application.

In any case, as a reference of application & case study, we consider soft pressure sensors that can be applied for instance on a soft prosthetic hand.

![Figure 1.5: Picture of the ISR Hand, A and B, with the soft sensors integrated, C.]

In general, the goal of this thesis is to study the following aspects of stretchable electronics in general and soft pressure sensors in particular.

1. Materials;
2. Fabrication Methods;

It can be said that these aspects are related to each other because a specific material may correspond to a specific fabrication method and therefore to a different measurement method, or vice-versa.

Furthermore, the vast diversity of soft materials, either conductive or nonconductive, that can be used to produce soft sensors, makes impossible to work with all the products that are commercially available. However, some polymers and conductive materials were carefully tested in different ways. In order to build a reliable pressure sensor, two
different types of sensing were tested, resistive and capacitive based sensing, which also implicates specific fabrication and measurement methods.
1.2 Thesis Overview

This dissertation is divided into seven chapters. For the sake of better readability, some of the results and takehomes are discussed at the end of each chapter, excluding the Introduction, Triangle of Fabrication & Case Study and General Conclusions.

The first chapter, Introduction, presents the framework, motivation and thesis organization. The second chapter, Materials and Fabrication Methods, introduces a summary of the conductive and nonconductive materials utilized in stretchable electronics field as well as the fabrication methods for different materials. This chapter is based on a simple exposition of different materials and fabrication methods, and there is no comparison neither analysis in detail of each element - which will be performed in the following chapters.

The third chapter, Resistive Sensing, includes the theory behind the use and applications of resistive sensing and also the firsts tests performed with soft sensors. It describes how the type of sensing works, the patterns that were used and why and makes an analysis of the results. Furthermore, it explains the issues of conductivity of the conductive polymers, and also presents a possible approach to get better conductivities with conductive polymers.

The fourth chapter, Capacitive Sensing, analyses another type of sensing, discussing the theory behind different topologies and analysing the results for this type of sensing.

In the fifth chapter, it is explored a hypothesis of diffusion of the uncured polymer in the conductive polymer, analysing different effects to prove this hypothesis, and drawing a conclusion.

In the sixth chapter, Triangle of Fabrication & Case Study, it is analysed the triangle of fabrication presented in the Introduction, making a more detailed examination about the measurement methods, materials and fabrication methods utilized. More-
over, based on conclusions drawn in the previous chapters, this chapter demonstrates the fabrication of a multi-layer hybrid capacitive-resistive sensor as a case study.

In the seventh and last chapter, the general conclusions are summarized and future work is discussed.
Chapter 2

Materials and Fabrication Methods

2.1 Materials

The main requirement for fabrication of stretchable electronics circuits and sensors are stretchability similar to human organs (e.g. a Young’s modulus between 0.1-10 MPa). Materials for these systems should be either an elastic insulator as a base material, and an elastic conductor for the interconnects or sensors.

2.1.1 Nonconductive Materials

Since soft sensing is a relatively new field of research, none of the materials commercially available used to produce these sensors were specifically fabricated or focused to fulfill the requirements of this type of sensing. However, in order to produce soft sensors, it can be used many materials relatively inexpensive that are reliable to act as soft sensors. As nonconductive materials, it has been used polymers, which are desired to be flexible and stretchable. A polymer is a large molecule or macromolecule that is synthesized in a process of combining many small molecules known as monomers - polymerization. There are synthetic and natural polymers that have a broad range of properties, including toughness and viscoelasticity, that can be explored depending the
application. Furthermore, depending on the molecular arrangement of the monomers the resultant polymer can be glassy, crystalline or rubbery.

\[ \sigma = \frac{F}{A_0} \]  

\[ \epsilon = \frac{\Delta L}{L_0} \]  

This differentiation is due to the behaviour of the materials when subjected to deformations. Different materials have different ways to react to external forces. When deformed, a solid body has an internal reactive force called stress that resists to the deformation. Stress, \( \sigma \), can be defined as force, F, per unit of area, A, applied on a given material.

\[ \sigma = \frac{F}{A_0} \]  

On the other hand, strain, \( \epsilon \), is the amount of elongation or compression, due to an external force, relative to the original dimensions in the axis of the strain.

\[ \epsilon = \frac{\Delta L}{L_0} \]  

Having the strain and stress, it is possible to calculate the Young’s Modulus, the modulus of elasticity of a given material, which is defined as the ratio between stress
2.1. MATERIALS

and strain. This modulus is a mechanical property of linear elastic solid materials and as high is the modulus, more rigid is the material. A solid body deforms when a load is applied on it. If the material is in the elastic zone, the body returns to its original shape after the load is removed, if the material is in the plastic, some of the deformation remains in the material and it cannot restore its original shape. Moreover, if the deformation is large enough, it can lead to a rupture or fracture in the material.

According to figure 2.1 it can be verified that the desirable polymers for soft sensing should be rubbery. The glassy polymers are hard and have no ability to suffer any major extensions, breaking at a low extension ratio. In contrast, the crystalline polymers go through successive changes. They deform elastically, yield, deform plastically and fracture at last. Although they can sustain more extension ratio than glassy polymers, some of that extension is in a plastic behaviour, which is not desired. Finally, the rubbery polymers are unique, showing highly extensive elastic abilities. Their wide response to external influences such as pressure or strain and also their ability to change their shape under these conditions, turn silicone-rubbers into great engineering materials. These rubbery polymers are also known as elastomers. Therefore, an elastomer is a rubbery amorphous polymer with high viscoelasticity and very weak inter-molecular forces, generally having low Young’s modulus and high failure strain, when compared to other materials, which means that they can be expanded or contracted easily upon application of external forces. They have numerous cross-links that pull them back into their original form when the stress is removed. The cohesive interactions between the chains of an elastomer are weak. Specifically, the weakness in the silicon-oxygen bonds, is what makes this amorphous polymer into a silicone with high elasticity.

The most common type of elastomers used by research groups in the area of stretchable and wearable electronics are silicone elastomers. \[21,22\]. They are basically polymers with low glass transition temperatures, which means that in room temperature they benefit from an elastic behaviour \[23\]. The most common silicon-based elastomer are the polydimethylsiloxane (PDMS) and EcoFlex 0030since they are commercially
available and have great mechanical properties \cite{24, 25}.

\section*{2.1.1.1 Polydimethylsiloxane (PDMS)}

Polydimethysiloxane (PDMS) is a silicone elastomer that can be purchased from Dow Corning. It is a low cost polymer and in its pure state - without any conductive dopant - it is not conductive, which means that can be used as an insulator, as a stamp or mold to produce Micro Electro Mechanical Systems (MEMS) in methods such as micro-contact printing and replica molding, or can even be used as dielectric for a capacitor. PDMS is a transparent silicon that is chemically inert, thermally stable, permeable to gases, simple to handle and manipulate and also simple to produce. Additionally, it can be also used as a biomaterial in catheters, drainage tubing and insulation for pacemakers due to its biocompability - Young’s Modulus of human skin vary between 420 MPa to 850 \cite{26} - and non-toxicity.

Furthermore, there are other properties of PDMS that are useful to produce soft sensors. It has a mass density of 0.97$kg/m^3$ and Young’s Modulus between 360 and 870 KPa. Additionally it has a tensile or fracture strength of 2.24MPa and a dielectric constant of 2.5. \cite{27}

The procedure to produce PDMS is incredibly simple, it is just needed to hand mix the polymer with the curing agent, during 5 minutes, in a ratio of 10:1 by weight, respectively, and then cast it in the desired pattern and cure it either at room temperature, which can take up to 12 hours, or curing it in the oven or on a hot plate at 130°C for 10 minutes. In order to obtain thin films, it can be used either a Thin Film Applicator or a Spin Coater \cite{28}. The ratio of PDMS to curing agent can also be modified resulting in a polymer with different viscoelastic properties. For instance, if it is added more curing agent, in a ratio of 5 of PDMS to 1 of curing agent, the film will become stiffer. On the other hand, if the ratio is 20 to 1, the resulting film will be smoother and more stretchable. Instead of hand mix the PDMS and curing agent,
2.1. MATERIALS

it can be used a centrifuge optimized to mix polymers (Thinky Planetary Mixer), to ensure a proper mixing and also to defoaming the sample.

Sylgard 184 and Sylgard 186 (commercial name: Dow corning) are the most used PDMS silicones in the area of stretchable MEMS

2.1.1.2 EcoFlex

EcoFlex is a platinum-catalyzed silicone from Smooth On, a company that offers a wide range of polymers to make masks and molds of everything that may interest. Along with Sylgard, Ecoflex is one of the most used material for stretchable MEMS due to its low viscosity, softness, high stretchability - can be stretched up to 600% its original size fully recovering its original shape - and it also has a fast curing time when compared to PDMS. Figure 2.2 shows an example of a sensor that was easily stretched to twice its original size.

![Figure 2.2: Stretchability of a sample made with Liquid Metal and EcoFlex in SML, CMU. The white scale bar refers to 5cm](image)

Ecoflex is commercialized in 5 different hardness level (Ecoflex 10, 20, 30, 40 and 50). The most commonly used is the EcoFlex 00-30, and it is also what was used during
Chapter 2. Materials and Fabrication Methods

this project, both in ISR and in SML. Although the normal siliconeecoflex has a foggy colour. The colour can be modified with specific pigments to it without interfering with its mechanical properties.

Figure 2.3: Examples of possible applications of EcoFlex 00-30. From left to right, a cushioning for orthotics, prosthetic appliance and an example of colored material

This material is suitable for example for making prosthetic appliances, cushioning for orthotics and special effects. Furthermore, it is certified to be used in direct contact with skin, since it was tested for irritation and skin sensitization. The material itself is not conductive, and it has a Young’s Modulus of 80kPa. Since the dielectric value of Ecoflex was not found in the literature, we tested the material in a parallel plane capacitor to measure the dielectric constant.

Knowing that the capacitance of a parallel plate is given by:

\[ C = \frac{k \cdot \epsilon_0 \cdot A}{d} \]  

(2.3)

where k is the dielectric constant of the material, \( \epsilon_0 \) the vacuum permittivity, A the area of the plates and d the distance between plates. Thus, 4 different parallel plate capacitors, with \( A = 1cm^2 \) and a dielectric layer made with EcoFlex with a thickness of
200 ± 5\( \mu \text{m} \). The capacitance was measured with a LCR meter which allows to calculate the dielectric constant \( k \). Table 2.1 shows the measured capacitance and the calculated dielectric constant of the ecoflex on each of the capacitors.

**Table 2.1: Dielectric Constant of EcoFlex**

<table>
<thead>
<tr>
<th>Sample</th>
<th>C(pF)</th>
<th>( \sigma_C )</th>
<th>( k )</th>
<th>( \sigma_k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.168</td>
<td>0.5</td>
<td>2.97</td>
<td>0.14</td>
</tr>
<tr>
<td>2</td>
<td>13.576</td>
<td>0.5</td>
<td>3.07</td>
<td>0.14</td>
</tr>
<tr>
<td>3</td>
<td>13.424</td>
<td>0.5</td>
<td>3.03</td>
<td>0.14</td>
</tr>
<tr>
<td>4</td>
<td>13.036</td>
<td>0.5</td>
<td>2.94</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Furthermore, there is also the associated error for these two values. While the error of the measured capacitance is due to the variations during the measuring, the error of the dielectric constant is calculated by the propagation of errors.

\[
\sigma_k = \sqrt{\left( \frac{C}{\epsilon_0 \cdot A} \times \sigma_d \right)^2 + \left( \frac{d}{\epsilon_0 \cdot A} \times \sigma_C \right)^2}
\]  \hspace{1cm} (2.4)

Calculating the average of the results it can be concluded that the dielectric constant for the EcoFlex is 3.00 ± 0.14.

To prepare a sample of EcoFlex, part A to part B should be mixed in equal proportions, either by weight or volume. After that the viscous solution has to be hand-mixed for 5-10 minutes, which allows the curing of the polymer. Then the desired pattern should be casted and either put in the oven or on a hot plate at 130\( ^{\circ} \text{C} \) for 10 minutes or left at room temperature for one hour to cure. For better results, if possible, the use of a centrifuge (Thinky Planetary Mixer) to ensure a proper mixing and also to defoaming the sample, is recommended.

### 2.1.2 Conductive Materials

Rigid PCBs use copper wires as interconnects between electronics chips and components. However, copper has a very high Young’s modulus and the elasticity of the
copper does not afford the required stretchability.

Three main methods have been used for creation of interconnects within the stretchable electronics.

1. Deterministic structures In this method rigid conductors such as copper are used to create stretchable geometries. That is, the material itself is not a very elastic material (e.g. copper), but in plane and out of plane geometries are created to afford the stretchability. This approach is not easy to prototype, and limits the possible fabrication methods. For instance it is not possible to cast the conductive material with this method. Since we are looking for truly stretchable materials that can be processed easily, this is not our focus. 2. Liquid metals 3. Conductive Polymers.

For instance, a copper wire or copper foil is reasonably flexible. However, it is not stretchable, which means that when embedded in a elastomer such as EcoFlex 00-30 or PDMS that are both flexible and stretchable, if the sample is stretched it will cause a displacement of the copper wire because it cannot follow the stretchy behaviour of the elastomer, causing the damage of the circuit. Moreover, the rigidity of the copper can cause the tear of the elastomer and, consequently the damage of the sample. 29

Therefore, some alternatives to rigid metals have been being tested in order to produce reliable and longstanding soft electronics. These materials are based on liquid metals and on conductive polymers.

2.1.2.1 cPDMS and AgPDMS

cPDMS is a term created at SML that has two possible meanings. On the one hand it can stand for conductive PDMS, which is the composite resultant from the mixing of PDMS with conductive particles. On the other hand, it can also be used in a more restrictive meaning that is the conductive PDMS produced with Carbon Black particles. The first one includes the latter. However, in this essay every time that
2.1. MATERIALS

is referred to conductive polymers made with Carbon Black, it is used the acronym cPDMS and when referred to particles different than carbon it is used other acronyms such as AgPDMS - composites embedded with silver coated nickel particles – to make it clear which is the meaning of the acronym.

![Example of a patterned cPDMS on PDMS.](image)

Ecoflex cannot be used as the base material for making a conductive polymer, since Carbon Particles devastates the curing process of the Ecoflex, which means that if EcoFlex is mixed with conductive particles, it will stay at liquid state forever.

As conductive particles, it was utilized Carbon Black Powder (CB) and Silver Coated Nickel (AgPDMS). The latter has its percolation threshold - concentration needed to become conductive (properly explained in section ) for concentrations as high as 80wt%. On the other hand, it is much better conductor that the composites made with CB. However, the high concentration makes the composite too viscous and hard to mix. Usually, a solvent as Hexane (ACS Hexane, Sigma-Aldrich) is used to help in the mixture and to ensure that the particles become well mixed in the polymer because without the solvent it is not possible to have a uniform paste. Furthermore, the viscosity is also important concerning the fabrication methods and the cast of some patterns, the composite should not be neither too viscous that makes it difficult to cast,
neither too liquid, preventing the polymer to drain. Figure 2.5 shows the percolation threshold for both cPDMS and AgPDMS.

![Figure 2.5: Conductivity of cPDMS and AgPDMS for different concentrations.](image)

As expected, due to the better conductivity of silver ($6.30 \times 10^7 S/m$ at $20^\circ C$) compared to carbon ($1.25 \times 10^3$ to $2 \times 10^3 S/m$ at $20^\circ C$), which makes it an interesting composite. However, the percolation of Carbon particles inside PDMS happens at much lower percentage (0.5wt%) compared to the silver. In addition carbon particles have a much lower cost compared to the silver. Therefore, CB based PDMS is usually preferred by most of the research groups.

By analysing the figure 2.5 it can be deducted that although those values are, in fact, from the percolation threshold, as can be seen the increase on conductivity for concentrations higher than 15wt%, it is not possible to see if the 26wt% is the maximum of this threshold. However, the use of concentrations higher than 22wt% makes the sample very difficult to use since makes it more difficult to mix and to cast.

To better understanding the conductivity of the cPDMS, the resistivity for different weight total concentrations was calculated. Therefore, applying the Ohm’s Second law, which says that the electrical resistance (R) of a homogeneous conductor of constant
transversal section is directly proportional to its length (l) and is inversely proportional to the area of its transversal section (A).

\[ R = \frac{\rho l}{A} \]  

(2.5)

Where \( \rho \) stands for resistivity. Despite the cPDMS is not a homogeneous conductor, as was already explained this test served either to prove the Ohm’s law for this material and to obtain a value for the resistivity.

Therefore, ten traces of cPDMS were patterned with a weight total concentration of 15%, 17%, 19%, 21% and 23%, with length from 5mm to 50mm, width of 2mm and thickness of 0.5mm to expect a linear behaviour. To ensure this thickness, it was used a Thin Film Applicator that can be used to make layers of polymers as thin as 50 \( \mu m \) with improved accuracy.

By analysing the graphics from figure 2.6 it can be verified that the worst case, either for linear behaviour and resistivity, is the 15wt%. Probably, this unexpected behaviour is related with the percolation threshold, since the 15% is very close to the point where a composite starts to be conductive. Furthermore, all the remaining graphics show a \( R^2 \), which despite is not ideal, is acceptable.

Concerning the resistivity values, it is obvious that increasing the concentration of particles means an increase of conductance. However, even the best case, at a concentration of 23wt%, the calculated resistivity is 0,068k\( \Omega \)m, which is much worse than the resistivity of some liquid metals ( 29.4 x 10^{-6} \( \Omega \)cm). This poor conductivity must be carefully evaluated when patterning soft circuits. It should be noted that while a good conductivity is desired for the wiring on a circuit, it is less important in the sensing element, for example.
Figure 2.6: Second Ohm’s law for different concentrations of carbon. a) 15%; b) 17%; c) 19%; d) 21%; e) 23% and f) the legend of the graphics and also the calculated resistivity for each concentration.

Also in figure 2.6, each linear regression should have a $b$ value – intersection with y axis – equal to 0. This deviation from the theoretical model is due to the contact resistance between rigid and soft electronics. One of the challenges which is not addressed so far in soft electronics is the interface with rigid electronics, as will be discussed in detail in chapter 6. As interface between the cPDMS traces and the multimeter probes it was used a commercial conductive tap from 3M and copper foil, with better results for the latter. Even though, the measured contact resistance was as high as $10\,k\Omega$ for the 15wt% and around $1\,k\Omega$ for the remaining samples.
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2.1.2.2 Liquid Metals - EGaIn

Liquid metals is an alternative to conductive polymeric composites. The liquid state of these metals, at room temperature, allows to include them in the requirements to soft electronics. However, it is important to note that, although the liquid metals are not stretchable, when a sample is stretched the liquid metal can flow within the microchannels and change their form, guaranteeing always a conductive path. The most used liquid metal is mercury. However, the mercury is also known as a toxic material and therefore its use should be avoided. An alternative to Mercury is Gallium alloys that are not as toxic as mercury and are generally considered safe to interact with [36].

Therefore, the use of liquid metals to produce soft sensors is restricted to gallium based alloys, such as Galistan (68%Ga – 22%In – 10%Sn) with a melting point of 19°C and Eutectic Gallium Indium (EGaIn) (75.5% Ga – 24.5% In) with a melting point of 15°C [37].

The electrical properties of the liquid metals are similar to the rigid metals, which signifies that are much better conductors than the elastomers filled with conductive particles. However, the cost of the liquid metal is also much more expensive than the carbon microparticles used.

The liquid metal more commonly used is the Eutectic Gallium Indium (EgaIn), a gallium-based alloy. The components of EGaIn have low orders of toxicity since the Indium has been used as dental fillings and Ga is a trace nutrient. Furthermore, EGaIn is a moldable material with low viscosity, $1.99 \times 10^{-3} \text{P.a.s}$, in the absence of the oxide skin that forms on the surface and has a resistivity of $29.4 \times 10^{-6} \Omega \text{cm}$ [38].

To compare the resistivity of EGaIn with cPDMS, the same test regarding the second Ohm’s law was made. Therefore, ten traces similar to the ones used to obtain the graphics from figure [2.6]. With this test, it was not possible to calculate the re-
sistivity since all electrical resistance measured were the same. This can be explained by the small value of resistivity found on literature, which means that for these traces the resistance is constant, taking into account the minimum resolution of the digital multimeter.

![Figure 2.7](image.png)

**Figure 2.7**: Test made to compare the change of resistance with length for EGaIn

Therefore, comparing the figures 2.7 and 2.6 it can be verified that the conductivity of the liquid metal is much better than the conductivity of cPDMS.

Despite the expensive cost of the EGaIn, it is possible to produce it in lab by alloying gallium and Indium. To do so, it just consists on weight in the right proportion 75.5% of Ga and 24.5% of In, which are solids at room temperature and then put it on a hot plate at 195°C, which causes the melting of Indium and Gallium, for 24 hours.

### 2.2 Fabrication Methods

#### 2.2.1 cPDMS

##### 2.2.1.1 Stencil Lithography

Stencil Lithography is a fabrication method commonly utilized to produce Micro Electro Mechanical Systems, that utilizes masks to pattern the desired material. The material is casted over the stencil and when the stencil is removed, it is obtained the
2.2. FABRICATION METHODS

desired pattern. This concept can be easily transferred to production of soft sensors, since it is a reliable and low cost method.

As can be seen in figure 2.8, this method consist in firstly pour a silicone layer on a glass substrate, it can be either PDMS or EcoFlex, and cure it. When the silicone is cured, the stencil should be placed on top of the polymer and the magnet below. At that moment, using a blade or a spatula the uncured cPDMS can be casted to fill the stencil. The excess can be easily removed using a blade to ensure that the cPDMS layer is as thick as the stencil. Then, the magnet and the stencil can be removed and the cPDMS cured in an oven at 120°C for 10 minutes. When the cPDMS is cured, the sample can either be removed from the glass or covered with silicone elastomer. For a multi-layer sensor, such as a capacitive sensor, this process is repeated on top of the last layer of the elastomer.

**Figure 2.8:** Illustration of the stencil lithography method

Basically, everything can be used as a mask to pattern the conductive polymers. The only concern is to fix the mask properly to avoid some displacement. Therefore, to ensure a proper attachment of the stencil it was used a 0.1mm thick steel stencil,
patterned with a laser cutter. Consequently, using the magnetic properties of the stencil, it can be used a magnet, that can be placed below the substrate or the work desk (depending on the magnetic force) to fix the stencil. This way, a thin film of cPDMS can be successfully patterned.

Similarly to steel stencil, and with the growing of the 3D printing technology, a 3D printed molds can be used instead of the steel stencil, \[2.9\] In a prototype phase, where the patterns are still being tested, it is easier to use a 3D printer than a laser cutter. The mold should be well fixed, using tape for example, to ensure that the casting is done properly. Furthermore, the 3D printed molds can be also used to control the thickness of the entire sensor. The minimum thickness achievable in the available 3D printers (Prusa I3 and TAS 5, LulzBot) is 200$\mu m$. Therefore, it is possible to print some frames with that thickness and then use them to cast the polymer. After the pouring of the uncured polymer on a glass substrate, in a surface limited for the frame, the excess of material is removed using a roller or a spatula.

![Figure 2.9: a) Picture of the 3D printer Prusa I3, and b) a 3D printed mold.](image)
2.2. FABRICATION METHODS

For instance, knowing the thickness of the molds used to pattern the cPDMS and using the 3D printed molds to control the thickness of the elastomer, is possible to make a soft, flexible and stretchable sensor with a known overall thickness.

2.2.1.2 Lifting

Another method to produce soft sensors consists on creating structures on the surface of a mold. The molds works as a 3D mask since it can be patterned either on $x$ and $y$ axis but also on the $z$ axis, which allows to control length, width and thickness of the samples. Furthermore, one sample can be patterned with different thicknesses if it is desired.

![Fabrication method of soft sensors using laser patterned acrylic molds](image)

**Figure 2.10:** Fabrication method of soft sensors using laser patterned acrylic molds

Figure 2.10 shows the lifting process. As it can be seen, a 3D pattern is created in a mold. The mold can be created for instance by 3D printing or by laser engraving on an acrylic sheet. The pattern is then filled first with the cPDMS and then a layer of PDMS is constituted over the cPDMS by pouring the uncured PDMS over it. PDMS is then fused into cPDMS and when removing the PDMS layer, it lifts the cPDMS.
pattern with itself.

Therefore, it was used acrylic to make these masks. The acrylic was patterned in a $CO_2$ laser with different power and speed to achieve different thickness. However, there are some issues of using $CO_2$ lasers to pattern these molds. It is not possible to select the desired depth of cutting, it has to be controlled by changing the power and the speed of the laser. Furthermore, using a laser cutter to engrave the acrylic, the cut is not strictly vertical due to the movement of the laser nozzle.

To produce soft sensors using this method, the uncured cPDMS should be casted in the acrylic molds and the excess removed. If the concentration of particles in cPDMS is not too high this process is simple and fast. Then the cPDMS should be cured in the oven at a temperature below 80$^\circ$C to avoid the damage of the acrylic mold. When the cPDMS is cured, the pure PDMS can be deposited in the acrylic mold, which can be patterned with a specific thickness for PDMS also, and then cured. Finally, it is just needed to extract the sample from the acrylic mold, figure 2.10.

Figure 2.11: Picture of the acrylic molds utilized in this fabrication method and (top left) a sample of a pressure sensor

Usually the sample is not damaged during the extraction step due to the bonding
between the PDMS from the pure PDMS layer and the PDMS from the cPDMS. As is discussed in detail in chapter 4, there is some diffusion from the pure PDMS in the cPDMS that helps to bond the two different polymers. In figure 2.11 there are two examples of different acrylic molds that were cut using a laser cutter.

These two previous methods, sometimes present some defects during the fabrication procedures, as can be seen in figure 2.12. These defects are the discontinuity of the conductive traces – more common in the lifting method - and shortening of traces – more common in the stencil method.

![Figure 2.12](image1.png)  ![Figure 2.12](image2.png)

**Figure 2.12:** Common defects during fabrication procedure.

### 2.2.1.3 Laser patterning

Another fabrication method to produce soft sensors based on conductive polymers is the laser patterning.

Contrarily to the previous method, in this method, the laser cutter is used to pattern directly a film of cPDMS. Therefore, a thin film of cPDMS should be applied on a metal substrate, either using a spin coater or a thin film applicator (ZUA 2000; Zehntner Testing Instruments), and cured. Then, the cured cPDMS is patterned on a CO$_2$ laser (VLS 3.50; Universal Laser System, Inc.) with 3W of power (10%), 10 mm/s (20%) speed and 1000 PPI. The patterning is repeated three times to make sure that the cuts are all the way through and clean, figure 2.13 i. After that, the excess is manually removed, figure 2.13 ii, and a layer of pure PDMS is used to seal the cPDMS, figure 2.13 iii. As already described, the PDMS bonds to cPDMS which allows to peel the
sample from the substrate when the silicone cures.

To produce multiple layers, the previous steps must be repeated and a film of PDMS should be cured in a metal substrate. Then, a layer of cPDMS is applied and cured, and the sample is patterned in the laser cutter, figure 2.13 v. Then the excess material is removed and the uncured PDMS add to the sample, figures 2.13 vi and vii. Then, the previous made layer is placed on the uncured PDMS, figure 2.13 viii and finally the sample is cured, figure 2.13 ix.

Some tests were then made to find which is the minimum width achievable with the CO$_2$ laser. Therefore, different traces were tried and its integrity was verified using a stereo microscope. The minimum width that performs clean cuts was observed to be 400$\mu$m. As can be seen in 2.14a the laser cut is wavy and the risk of having a hole in the trace is very high. On the other hand, in figure 2.14b it can be seen that the width is very constant and regular.
2.2. FABRICATION METHODS

![Image](image1.png)

(a) ![Image](image2.png) (b)

Figure 2.14: Figure of a) a trace of 0.1mm wide cPDMS and b) 0.4 mm wide

2.2.2 EGaIn

Up to now, Liquid metals are the most interesting and promising material for application on stretchable electronics. They benefit from an excellent conductivity and can change their shape to afford the required stretchability of the circuits. However, fabrication technology for liquid metals is more difficult than conductive polymers and they are still in their infancy. In this section some of the fabrication methods are described. A fabrication method firstly used, but not used in this project, consisted on filling microchannels patterned in the elastomer using two syringes, one to add liquid metal and another one to remove the air from the microchannels, figure ?? [39,40].

However, this method had a high rate of failure due some leaks in the elastomer, which increased the cost of production, since the price of the EGaIn. For this reason, the liquid metals were replaced by conductive polymers. However, because of the recent advances on the fabrication methods, LMs are regaining an attention in the community of soft electronics.

2.2.2.1 Laser Ablation

Similar to the laser patterning on cPDMS, it is also possible to use a $CO_2$ laser to pattern liquid metals. Therefore, a layer of silicone should be applied in a substrate and cured. After that, a drop of EGaIn can be placed in the center of the substrate. The surface tension of the liquid metal avoids that the liquid metal disperses naturally on the substrate. Therefore, a roller or a rod have to be used to spread the liquid metal.
on the substrate. Figure 2.16j. When the EGaIn is spread all over the surface, it can be used a spin coater to remove the excess of EGaIn and to ensure a more uniform layer. After that, a final thin layer of elastomer is applied over the liquid metal. Then, the sample can be patterned in the CO$_2$ laser. Finally, the excess from the laser cut is removed, and another layer of silicone is deposited to fill the holes between the patterned EGaIn traces and cured, respectively.

However, the cut made by the laser is not equal to the one made with cPDMS. In fact, since EGaIn is a metal alloy, it means that it does not ablate at 10.6$\mu$m wavelength and will not vaporize at a range of 1 to 30 W (maximum power of the laser). Therefore, it is postulated that the laser beam heats the bottom layer of polymer (the top layer is cut by the laser) which vaporizes the polymer. The vaporized polymer is believed to exert sufficient pressure on the EGaIn film to displace it and penetrate through it.
2.2.2.2 Roller Deposition

This method consist on applying and curing a silicone layer. Then then a mask is used to pattern the liquid metal over the silicone layer. The mask can be produced in the $CO_2$ laser, and it can be made from paper, tape or another material that is possible to pattern in the laser cutter. Then the mask must be carefully placed and fixed on the silicone substrate. Then a drop of EGaIn is placed in the mask and a roller is used to disperse the material in the patterned surface. It was found that the best materials to use as roller is either EcoFlex or PDMS. Therefore, some rollers of these materials were made in order to produce soft sensors using this method. Finally, the mask is removed and a seal layer of silicone is applied to the patterned EGaIn.

2.2.2.3 Spray Deposition

The EGaIn Spray method also consist on using stencils to produce the desired pattern. However, this method showed some improvements in terms of uniformity and dispersity of the EGaIn particles and also consumes less material than the other methods.
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**Figure 2.17:** Schematic explaining the Roller (left) and Spray (right) deposition of EGaIn. The stencil is patterned in a laser cutter and then applied in the silicone substrate where the EGaIn is deposited.

Therefore, a silicone layer is cured on a substrate and a stencil of tape is patterned in the CO$_2$ laser, similarly to the previous method. However, instead of drop EGaIn and then disperse it using a roller it is used an airbrush to spray the liquid metal over the stencil, figure 2.17. For the compressed gas, Nitrogen, Argon or similar gases can be used - but not oxygen, since it creates the oxide layer over the egaln - which helps to break the oxide skin of EGaIn and then have a more uniform spraying. Although using the airbrush is possible to control the flow of spraying and is possible to pattern traces as small as 200$\mu$m wide, a drawback of this method is that the thickness of the patterned EGaIn may not be constant.

### 2.3 Conclusion

The main requirement to produce soft sensors is the flexibility and, eventually, the stretchability of the materials. Therefore, it is desired that both conductive and nonconductive materials are flexible and stretchable. The nonconductive materials that
2.3. CONCLUSION

Figure 2.18: Pictures of spray deposition a) Laser patterning the mask. b) Result of the patterning. c) Spray EGaIn in a specialized structure to avoid inhalation of EGaIn particles. d) Removal of the stencil and the result of the spraying

are mainly being used are:

- PDMS

- EcoFlex.

These elastomers are soft materials that can easily be bended and stretched, recovering the initial state, unless the material is stretched beyond the rupture point.

Concerning the conductive materials there are two possibilities that are both flexible and stretchable.

- Liquid Metals

- Conductive Polymers.

Regarding the liquid metals, it is important to notice that, in fact, they are not stretchable. However, when a sample of PDMS filled with Liquid metal is stretched, the liquid rearranges itself allowing the conductive path. Liquid Metal, such as EGaIn, can be used either as sensing element or as wiring since it has good conductivity. Despite all the existing fabrication methods to pattern EGaIn, during this project it was utilized
three:

- Laser Ablation
- Roller Deposition
- Spray Deposition

The conductive polymers consist on doping polymers with conductive particles, such as silver and carbon black particles. Although the conductivity of the conductive polymers is much worse than the conductivity of the EGaIn, the materials are cheaper and easier to process and pattern. Utilizing Carbon Black, it is possible to ensure a rapid prototyping, using low cost and repeatable methods. However, using some specialized equipments, such as centrifuge mixers and laser cutters, the quality and reliability of the sensors are improved. Therefore, the fabrication methods described were:

- Stencil Lithography
- Lifting
- Laser Patterning
Chapter 3

Resistive Sensing

3.1 Theory

One possible way to detect and measure an external stimuli is the resistive sensing. As the name implies, this type of sensing is based in the electrical resistance and the eventual changes result in variations in the electrical resistance.

Knowing that the electrical resistance for a simple uniform conductor is given by:

$$R = \frac{\rho l}{A}$$ (3.1)

Where $\rho$ is the resistivity, $l$ the length and $A$ the cross sectional area through which the current flows. This equation can be used to understand the possible changes in the electrical resistance. Considering the conductive material as uniform conductor, which is not completely true for the cPDMS since there are a distribution of particles in a polymer matrix and it is unlikely that the particles are perfectly distributed, it can be concluded that the resistivity is constant and therefore the changes in resistance are just due to the geometrical parameters.

Since all the materials that are used in soft sensors are flexible and stretchable, it means that these sensors have an improved sensitivity because when a small force is
applied to the sensor it leads easily in a deformation of the sample.

The electrical resistance is defined by the change of the length, the area or the resistivity. This means that to obtain an optimal result, one needs to optimize the shape of the sensor. For instance a spiral sensor, figure 3.1 right, is more sensitive to normal forces, since a normal force affects several traces of the spiral. However, a serpentine sensor, figure 3.1 left, is a better geometry for a strain sensor, since a strain changes the geometry of all conductive traces.

Figure 3.1: Designs prepared to measure stretch (left) and pressure (right) forces

A bend sensor on a soft finger is actually a strain sensor, and what makes the bending "measureable" is the actual strain that is happening to the upper layer of the bent beam.

All the sensors produced in this section were made with cPDMS as conductive material and using the stencil lithography and lifting as fabrication methods. In the schematic from figure 3.2

The stencil used during the fabrication of resistive sensors was the steel stencil. Therefore, a thin layer of silicone was casted and cured on a glass support - using a 3D printed frame to control the thickness - and the steel stencil was fixed over the elastomer using a magnet below the glass support. The cPDMS was then deposited on the stencil, removing the excess carefully, and cured in the oven. Finally, a final layer of silicone, with a thickness controlled by a 3D printed mold, sealed the conductive layer.
3.1. THEORY

Figure 3.2: Schematic of fabrication steps of resistive sensors, based on stencil lithography.

Furthermore, and despite the integration of a sensor in an application is not part of this work, the goal for these sensors was to be integrated in the fingers of ISR Prosthetic hand to measure pressure forces [41] and strain forces [42]. The sensors to detect pressure forces were made to be integrated into the fingerprint to know if the hand is holding an object and how much force is being applied, and the latter were made to integer in the back of the finger to know the angle that the finger is bended.

Figure 3.3: a) Strain sensor integrated in a finger to measure the bended angle. b) Pressure sensor integrated in the fingerprint to measure pressure forces
Therefore, a different model was designed for each specification. To detect pressure, it was made a spiral sensor in order to increase the traces that are more likely of being touched and, thus, increase the sensitivity. To measure the bended angle of the finger, which actually is strain, a linear shape was used, as can be seen in figure 3.1.

The spiral sensor is expected to change the width and the thickness of the traces when is pressed. There is an increase in width and a decrease in thickness. On the other hand, the strain sensor, when is stretched leads to a change in length but also small changes in the thickness and even in the cross sectional area. Therefore, it was expected a linear behaviour for the latter and a rational behaviour for the first one.

3.2 Results

3.2.1 Pressure Sensor

In order to follow the idea to have a rapid prototyping and low cost fabrication method, in this chapter it was only utilized cPDMS as conductive material.

To test the pressure sensors it was developed an experimental setup that permits to control the force that is applied and measure it. Therefore, as can be seen in figure 3.4, the system consisted in a roller that was controlled by a screw and a digital scale. The sensor that is being tested is put in the digital scale and then the roller presses the sensor.

To perform the measurements, the mass that pressed the sensor was increased from 0g to 2000g and then from 2000g to 0g in steps of 100g and the resistance was measured with a multimeter. However, while performing the tests it was observed that the value of resistance was very unstable and despite the changes when the pressure was increased or decreased, it was difficult to understand when the resistance became stable. Therefore, after each step of pressure it was made an interval of 50 seconds before
3.2. RESULTS

Figure 3.4: Experimental setup to test pressure forces

measure the resistance.

Figure 3.5: Plot of change in resistance with increasing and decreasing pressure, for a sensor with 25wt% of CB and EcoFlex as elastomer

In figure 3.5 can be verified that the change of resistance is not linear. This behaviour proves that when a pressure force is applied, the most relevant factor that changes is the cross sectional area. Furthermore, it can be seen that the unloading of pressure has some hysteresis from the loading cycle. In fact, the sensor can restore its original value, but it took around 15 minutes to restore it.
3.2.2 Strain Sensor

The system to measure the effect of strain forces developed consisted in a micrometer screw gauge that permits to stretch the sensor with 0.5 mm of precision. The sensor is fixed in the device using needles, as can be seen in figure 3.6.

Analysing the results, figure 3.7 of this test it can be concluded that in these sensors the major changes are due to increase of length since the resistance increases in a linear behaviour.

However, and as can be seen in the figure 3.7 it was not measured the resistance for the unloading cycle. The response time was very long and it took over 50 minutes for the sensors to restore their original value. This is not optimal for reliable application of these sensors. Despite all the results from the pressure and strain sensors, a sensor cannot be used in an application if its response to a stimulus and its recovering time is more than milliseconds.

The reason behind the high recovery times in these sensors is that after stretching, some of the percolating networks will lose their connection to adjacent particles. After the stimuli is removed, such percolating network require a long time to rearrange themselves exactly as they were before the stimuli is applied. In the next section, this problem further discussed. That means that we study the electrical conductivity of the
3.3. ELECTRICAL CONDUCTIVITY OF CONDUCTIVE POLYMERS

percolating networks of doped PDMS and discuss the problems.

![Figure 3.7: Plot of change in resistance with increasing and decreasing pressure, for a linear sensor with 25wt% of CB and EcoFlex as elastomer](image)

3.3 Electrical Conductivity of Conductive Polymers

Due to the issues found in testing strain and pressure sensors, it was made some research to learn about the cause of this problem and also the conductivity in general of conductive polymers.

By synthetizing conductive polymers, it is ensured almost the same mechanical properties of a polymer itself, since the synthetises of conductive polymers consists on mixing conductive particles with a pure polymer. There is a wide range of particles that can be used to produce conductive composites, some microparticles, such as Carbon Black (CB), Silver coated Nickel ($69.5\%Ni - 30.5\%Ag$), and also some nanoparticles Single-Wall and Multi-Wall Carbon Nanotubes (SW and MW CNT) [43][45] and Silver Nanowires (AgNWs) [46]. However, the electrical properties from a conductive polymer cannot be explained by the same rules that are applied to metals, which are more commonly used.

Firstly, to ensure the electrical conductivity of the polymers it may exist a path that allows the electrons to flow from one end to the opposite end that is desired to
use. The conductive paths in a composite are due to the connections between particles. Therefore, a sample is conductive only if, from one end to another, an electrical signal can find a path of particles \cite{47}. If some particles are too separated from each other the sample may not be conductive, since the matrix where the conductive particles are distributed is one of the polymers described previously, which means that the material between two separated particles is insulator. This fact could lead to an assumption that increasing the concentration of particles dispersed in the polymer matrix results in better conductivity. However, this statement is just partially correct.

### 3.3.1 Percolation Theory

The relation between concentration of particles in a composite and its conductance can be explained by the Percolation Theory \cite{48}. This theory is, for example, the same used to predict the propagation of a fire in a forest. Considering a wild forest that is not uniformly distributed with trees, a fire will propagate towards the zone with higher density of vegetation and, obviously, if there is a relatively large area without vegetation the fire will not be able to pass through it. This analogy can be applied to conductive polymers, where the particles are the trees and the fire the electrical signal that needs to be passed through the composite.

![Figure 3.8: An illustration of the Percolation Threshold and its effect on conductivity.](image)

However, the increase of conductivity with concentration of particles is not a linear
behaviour has can be seen in figure 3.8 that can be added to a polymer must be controlled. On the one hand if the concentration of particles is too low, the sample is not conductive. However, when a certain concentration of particles is achieved the sample suddenly becomes conductive. Then, the increase of concentration of particles will result in an abrupt increase of conductivity until a point from which the conductivity is almost constant. This steep slope, marked in figure 3.8 is called Percolation Threshold because it means that if the concentration of particles is lesser than the threshold the sample is not conductive, but if it is bigger than it does not have a significant influence on the conductance. On the other hand, increasing the concentration of particles means an increase in the viscosity of the pre-cured conductive polymer making it more difficult to mix properly and cast with the desired pattern. Moreover, it also results in a degradation of the mechanical particles of the polymer making it more stiff and breakable.

### 3.3.2 Size of particles

Hitherto, it was only referred the concentration of particles. However, considering different size of particles, the number of particles for a same concentration in a same volume is considerably different. Bearing in mind that there are micro and nano particles commercially available, it can be analysed the number of particles in a reference volume with the same concentration but for different particles. The figure 3.9 illustrates an ideal and uniform distribution of different particles in a volume of $1mm^3$, having the same concentration.

As can be easily anticipated, smaller particles will result in more number of particles, which reduces the concentration needed to achieve the percolation threshold. Although the use of nanoparticles leads to better conductance, the cost of this type of conductive material is much more expensive than micro particles. Furthermore, to use this particles it must be used some equipment that is not necessary for micro particles because
Figure 3.9: Distribution of micro and nano scale particles, a) Al₂O₃, b) carbon fiber, c) graphene nanoparticles and d) carbon nanotubes, of the same 0.1vol% in a reference volume of 1mm³. [49]

the distribution of nanoparticles is not as uniform as illustrated in figure 3.9. Due to the huge number of particles, it must be considered the electrostatic interactions and van der Waals forces, which leads to agglomeration of particles, Figure 3.10b). When particles become agglomerated, instead of the distribution is like the one of the figure, it will have spaces with a big concentration of particles and other spaces without any particle. The agglomerations reduce the electrical conductivity, because of the empty spaces between them just filled with polymer matrix, and the fracture toughness, because they act as a stress concentrator when the samples are stretched.

Figure 3.10: Different levels of agglomeration. a) particles perfectly dispersed, b) particles completely agglomerated and c) a mixture of dispersed and agglomerated particles. [50]

Therefore, in order to use these particles, they must be very well dispersed to eliminate all the agglomerations and entanglements. Several methods were already designed to perform this dispersion such as Ball Milling, Stir and Extrusion and the Three Roll Mills [51–54]. The latter is believed to be the most effective method and it is a machine tool that employs the shear force created by the three rollers to mix, disperse and
homogenize viscous materials. By using this machine, the particles could be previously mixed with polymer and then poured in the machine that will disperse the particles within the polymer, as can be observed in Figure 3.11.

![Figure 3.11: Schematic showing the working mechanism of the three roll mills machine](image)

The first and the third rollers from the figure 3.11 called, respectively, feeding and apron rollers, rotate in the same direction, while the centre roller rotate in the opposite direction. The dispersion occurs by adding pre-dispersed mixtures into the machine. The opposite rotation of the rollers n1 and n2, will transport the material to the bottom of the centre roller, which transports it to the second gap, between centre and apron roller. In this gap, the material is dispersed to the desired degree of fineness, due to the narrow distance and shear force between rollers. There are some machines, where the velocity of each roller and the distance between rollers could be controlled for the desired purpose. This process could be repeated several times to maximize the dispersion and it is probably the best approach to disperse the entangled particles.

However, even considering all these aspects and ensuring that all of them are well adjusted, the conductivity of a conductive polymer is not as good as a metal. As was already written the conductivity of the polymers is dependent of the number of contacts between particles. In spite of it depends on the properties of the conductive
material, it can be assumed that, when the electrons flow inside the particles, the resistance is negligible. However, when the electric signal has to cross the junction between two particles there are an intrinsic resistance. This resistance is called Contact Resistance (CR) and has a significant role to analyse the conductivity of the polymers. It must be considered that, even if the particles are perfectly dispersed, they are randomly oriented. Consequently, the junctions between particles could occur at the ends of each particle - perfect situation - but it could also occur that one overlaps the other, figure 3.12. This means that it may have more junctions than it was expected, which leads to an increase of the overall resistance.

![Figure 3.12: An illustration of a) the distribution of nano particles in a polymer matrix, b) the Tunneling Effect and the c) Contact Resistance.](image)

Furthermore, when the effects of the CR in the conductivity was analysed it was concluded that it cannot be the only responsible for the loss of conductivity because the results showed that the conductivity is lower than it should be, if this was the only factor that increase the resistance. In fact, in some cases the conductivity is much lower than it should be.

It was found that this increase in electrical resistance is due to some particles that, despite are close to each other are not in touch. This means that the electric signal has to cross the polymer matrix, which has a high electrical resistance. When this occurs it is called as Tunnelling Effect (TE) and refers to situations when there is a gap in the path of particles responsible to ensure the percolation but still, the signal is able to cross the polymer matrix. Although the high resistance, the TE could help to maintain the conductivity when the gap is very small.
3.3. ELECTRICAL CONDUCTIVITY OF CONDUCTIVE POLYMERS

Figure 3.13: The increasing resistance of TE with the distance between carbon nanotubes with different tube diameter. [55]

As can be seen in Figure 3.13, the resistance due to TE has a great dependence with the distance that has to be crossed in the insulator material. Adding this effect to the CR it could be written:

$$R_{\text{film}} = R_{\text{contact}} + R_{\text{tunnel}}$$  \hspace{1cm} (3.2)

where $R_{\text{contact}}$ is the Contact Resistance and is assumed to be constant, $R_{\text{tunnel}}$ is the Tunnelling Resistance and is dependent from the distribution of the particles and can vary when the sensor is stretched, and $R_{\text{film}}$ corresponds to the total resistance of the film. It is desirable that $R_{\text{film}}$ is the lowest possible and for that the tunnelling distance should be small. If the distance is around 1.0 nm the tunnelling resistances are in the order of 100 $G\Omega$, which is several order of magnitude larger than the CR and, in a practical view, can be considered as nonconductive.

Lastly, another factor relevant in the conductivity of a sample is the aspect ratio of the particles embedded in an elastomer. The aspect ratio is the ratio between the length and the diameter of the particles. The higher the aspect ratio is the bigger is the path that the electric signal can travel with a negligible resistance.

Therefore, the electrical resistance of a sensor, either to measure pressure or strain, is not just based on equation 3.1 but also on the distribution of the conductive particles.
When some forces are applied to a sensor, it will change the distribution of particles in the polymer, which can lead to ruptures of some junctions between particles. In some cases, when the sensors are relieved from the forces, they show some hysteresis due to the new connecting path that has to be formed due to the irredeemably ruptures caused by the applied forces and eventually, will increase the $R_{tunnel}$.

### 3.3.3 Nano Composites

Despite the reported issues about using conductive polymers to resistive sensing, there are some improvements when it is used nanoparticles instead of micro particles.

*Morteza Amjadi et al.*,[35] investigated characteristics such as linearity, hysteresis performance, stretchability and overshoot behaviour using Carbon Nanotubes – EcoFlex composites. The CNTs used were Multi-Wall CNTs with an average length and diameter of $5 \pm 20 \mu m$ and $16 \pm 3.6 \mu m$, which is relevant to note since the aspect ratio is important to conductivity effects and also the Multi-Wall or Single-Wall have different properties. The fabrication method for these sensors is different from the ones described in this essay. The CNTs particles were added into isopropyl-alcohol and sonicated for an hour - to disperse the particles. Then, the solution was drop-casted on patterned polymide (PI) substrate in a rectangular shape, and the solution was dried under light heating. When the thin film of CNT was formed, it was embedded in EcoFlex, which penetrates into the porous network of the CNT thin film due to its low viscosity.

After the production of the sensors it was made some strain tests. Therefore, different strain levels were applied – 30%, 60% and 90% - to the strain sensor and the response in the electrical resistance was measured for both, stretching and releasing cycles. As can be seen in figure 3.15a, the sample showed a good linear response and the resistance recovered very well after the releasing cycle, with just a small hysteresis.
3.3. ELECTRICAL CONDUCTIVITY OF CONDUCTIVE POLYMERS

Figure 3.14: a-f) Fabrication steps of the CNT-EcoFlex strain sensor. g) image of the produced sample and h) Cross-sectional images

Figure 3.15: a) Resistance-strain dependent for a CNT-EcoFlex sample. b) Response of the sensor to a loading and unloading cycle to strain up to 510%

To evaluate the response time of the sample, Amjadi et al, also tested a loading and unloading cycle, where the sample was stretched to 510% strain and then released at the same rate and the resistance measured simultaneously. From figure 3.15b can be seen that the behaviour of the resistance is practically similar to the loading and unloading cycles, which means that the sensor responds well and fast to deformations.

Furthermore, it was made a failure strain test where strain was continuously applied to the strain sensor while the resistance was being measured, until the failure of the sensor. As can be verified in figure 3.16a the sample shows a linear response for a strain as large as 800% where it starts a non-linear behaviour. Even though, the failure was
Figure 3.16: a) Failure strain measurement with an illustration of the re-positioning and re-orientation of CNTs upon stretching. b) Overshoot behaviour of the strain sensor just verified for strain at 1380% due to the elasticity of EcoFlex.

Finally, it was also measured an overshoot peak when the applying strain is stopped. The sensor was subjected to an increasing strain from 0% to 250% and then it remained at that strain. As can be analysed in figure 3.16b there is an overshoot peak when the strain becomes constant. This overshoot peak is believed to be related with the viscoelastic properties from the silicone base, which means that the sensor adjusts to a more conformal position when the sensor reaches a steady state.

By analysing all the data from Amjadi et al research it can be concluded that it is possible to use conductive polymers in a resistive based sensing. However, to have a working sensor, it must be used Carbon Nanotubes which are expensive and require some treatment to disperse the nanoparticles, which usually means some specialized equipment.

3.4 Conclusion

The resistive sensing is based on the Second Ohm’s Law, in which the electrical resistance is only dependent of geometric factors, length and area. Therefore, the changes in the electrical resistance is due to changes caused in the geometry of the
3.4. CONCLUSION

sensors. Based on the desired application, two optimized patterns were designed:

- spiral sensor to detect pressure forces
- linear sensor to detect strain forces.

Although the good results obtained when tested the sensors - the sensors were exclusively made with cPDMS -, it was verified that when a perturbation is made, the recovering time of the sensor is in the order of dozens of minutes, which is too long to be used in an application. Therefore, the percolation theory was studied for conductive polymers and it was found that the changes on the electrical resistance are also due to changes on the distribution of the conductive particles in the polymer matrix and sometimes the initial distribution is not fully recovered due to some ruptures on the conductive path.

Furthermore, the difference between the size of particles was analysed and it was verified that nanoparticles are better conductors for lower percolation thresholds, and can be used in a resistive-based sensing. However, the nanoparticles are expensive and need some pre-processing in order to obtain a dispersed sample.
Chapter 4

Capacitive Sensing

4.1 Theory and Topologies of Capacitive Sensing

Beyond the resistive sensing, that was proven not to be the best approach to produce soft sensors, at least in a low cost perspective, avoiding the use of nanoparticles and liquid metals, there is another possible approach that is based on capacitive sensing. Capacitive sensing is becoming a popular technology and has already replaced some optical detection methods and mechanical designs due to its improved sensitivity. In fact, when comparing capacitive sensing with resistive, the first one is more sensitive and accurate. However, the measuring of capacitance is not as straightforward as measuring the electrical resistance.

Figure 4.1: Image of a Parallel Plate capacitor. W and L are the width and length of each electrode, respectively, and d the distance between electrodes
4.1.1 Parallel Plate Capacitor

Generally, a capacitor is an electrical component that consists of two conductors separated by a nonconductive medium. Each conductor is charged with opposite charges, which creates an electric field between them. The nonconductive medium can be either vacuum or any other electrical insulator material, which is known as a dielectric.

The simplest capacitor is the parallel plate capacitor that consists in two parallel conductors that are separated by the dielectric, where the capacitance, \( C \), the ability of a capacitor to store an electrical charge, is given by:

\[
C = \frac{\epsilon_r \times \epsilon_0 \times A}{d}
\]  

(4.1)

Where \( \epsilon_r \) is the dielectric constant of the material between the plates, \( \epsilon_0 \) the permittivity of free space \((8.85 \times 10^{-12} F/m)\), \( A \), the surface area of the conductive plates and \( d \) is the separation between plates, which means the thickness of the dielectric. This equation, is an approximation that assumes that the electric field between the two electrodes of the capacitor ends abruptly at the edges of the plates. Therefore, the changes caused in the capacitance are just due to the dielectric properties of the insulator material and the geometric shape of the capacitor. This is an advantage compared to the resistive sensing when is used cPDMS as conductive material. As was described in [2] the conductivity of the cPDMS is poor, which can be a problem when used as resistive sensor. However, in the capacitive sensing the conductivity of each electrode does not affect the capacitance and, therefore, using cPDMS or for example composites made with nanoparticles is the same. Furthermore, it also means that the problems with the recovering time, measured for resistive sensing, is not a problem here.

Considering the capacitance just dependent on geometrical factors, the use of capacitive sensing in soft sensors is facilitated due to the viscoelasticity of the materials.
4.1. THEORY AND TOPOLOGIES OF CAPACITIVE SENSING

Despite either EcoFlex and PDMS are hyperelastic and incompressible materials and its behaviour cannot be predicted by the Hooke’s Law, $E = \frac{\sigma(\epsilon)}{\epsilon}$, its viscoelastic characteristics allows to use them in this type of sensing for small systems with few sensing elements.

![Figure 4.2: Schematic showing the steps to produce parallel plate capacitors with PDMS and cPDMS](image)

When a soft sensor is stretched or pressed either the size of the electrodes and mainly the distance between them changes, which implicates changes in capacitance. For pressure sensors, some researchers used air or foam as dielectric to avoid the high hydrostatic pressure due to the incompressibility of the elastomers. [56–58]

Despite the accuracy of the equation 4.1 that assumes that there is no electric field in the edges of a parallel plate capacitor, in fact, there is some field outside the plates which can affect the measurement. These effect is known as Fringe Effect and its represented in figure 4.3

The fringe effect can also be used to as a type of sensing, [59]. When there is a conductive material that gets close to the capacitor, it changes the outside electric field, which results in a change of capacitance. Therefore, this effect can be used to, among others possibilities, measure proximity of a conductive object to a sensor.
4.1.2 In Plane Capacitors

This topology of capacitors works under the principle of fringing capacitance. Instead of having the two parallel plates, the electrodes are placed side by side, increasing the electric field lines at the edges between electrodes. Therefore, when an object approximates to the sensor, it changes the electric field which can be measured.

In fact, this topology is common in touchscreen technology. However, instead of just two electrodes it is used a grid of electrodes, and instead of placing them side by side, they are placed in different layers, figure 4.4a. This way, the bottom layer corresponds to the $y$ axis while the other layer of electrodes corresponds to $x$ axis. Therefore, by analysing which element from the $x$ axis and which element from the $y$ axis has changed its capacitance, it is possible to understand the exact location of the object, either if it is pressing the sensor or just close to it.
4.1. THEORY AND TOPOLOGIES OF CAPACITIVE SENSING

![Image](a) Figure 4.4: a) Illustration of a grid of electrodes that allows to detect position of a touch, for example. b) Grid of electrodes made to test proximity and pressure.

4.1.3 Shielding

A drawback of using a capacitive sensor is the interferences in the signal. For instance, as was verified in the previous cases, the capacitance is in order of some dozens of pF, which means that is difficult to separate the noise interferences from the actual signal. To remove these interferences, it can be used an active shield, that consists in an extra charged electrode that can be placed underneath the sensor. An active shield coupling with the sensor helps to filter interference and parasitic capacitances.

![Image](b) Figure 4.5: Schematic of the possible shields that may be used to remove the interferences from the signal

Depending on its size the shield can be:

1. A shield the same size as the electrodes placed directly underneath the sensor
2. A shield larger than the sensor electrode placed directly underneath the sensor
3. A shield ring wrapped around the top side adjacent to the sensor with a shield underneath the sensor.

As the shield size increases, the effect from interference decreases but the sensitivity and dynamic range of the capacitance measurements also decreases.

4.2 Results

4.2.1 Parallel Plate Capacitor

In order to replace the resistive sensors, it was tested the capacitive sensing. The capacitance of a parallel plate capacitor is determined only by the geometric parameters and the material used as dielectric. The relative permittivity of the EcoFlex and PDMS is, respectively, 2.5 and 3, which means that concerning the dielectric material the difference on capacitance using these materials is not relevant. Moreover, the capacitance can either be measured in a LCR Meter or using a Cypress Board.

These sensors were made with cPDMS using all the three described fabrication methods. However, to produce a capacitor, it must be done a multilayer construction, which means that for Laser Patterning and Lifting the sample has to be peeled from the substrate to make the second conductive layer. Furthermore, it is important to control the distance between electrodes, given its importance to calculate the capacitance.

In order to test a pressure sensor based on the parallel plate capacitor, we made a sensor of $9 \times 9 \text{mm}^2$ with a dielectric thickness of $400 \mu m$. The material used for the dielectric was PDMS. The sensor was then placed on a digital scale and pressure was applied in steps of 200g from 0g to 2000g. As can be seen in figure 4.6 the change in capacitance shows a linear response with a $R^2$ of 0.99341, which proves the accuracy of the fit. The values were measured using a LCR Meter with a frequency of $40kHz$. Despite the good linear behaviour the range between the maximum and minimum force
4.2. RESULTS

The applied is just 9\( pF \).

Additionally, and similarly to tests made with resistive sensing, it was also made a strain sensor to measure the bending of the finger. The sensor, made with cPDMS, has a rectangular shape, 65 \( \times \) 6\( mm^2 \), and a dielectric thickness of 400\( \mu m \). The dielectric used was also PDMS. The sensor was then stretched in steps of 1mm. As the sensor was made with PDMS, the stretchability of the material is less than if it was used EcoFlex and, consequently the sensor was just stretched up to 180\% its initial dimension. As can be seen in the plot from figure 4.7 the response is linear with a \( R^2 = 0.9997 \), which shows the quality of the fit. However, the changes in capacitance are just 3\( pF \) when compared the maximum and the minimum value. Here, and in contrary to the resistive sensors with cPDMS, the recovery time is immediate.

4.2.2 In-Plane Capacitors

The electrodes of the sensor were made from EGaIn while the nonconductive material used was EcoFlex. This sensor was built to, eventually, be integrated in the fingerprint of the prosthetic hand, and detect the proximity of a conductive object, pressure and also slipping. The idea is to use an EcoFlex based sensor due to its elas-
Figure 4.7: Change in capacitance with increasing of strain.

The Cypress board uses a switched capacitor circuit, figure 4.8a on the front end of the system to convert the sensor capacitance ($C_p$) to an equivalent resistor, $R_{eq}$, figure 4.8b. A Sigma-Delta modulator then converts the current measured through the equivalent resistor into a digital count. When a finger ($C_f$) is on the sensor, the capacitance increases and the equivalent resistance decreases. This causes an increase in current through the resistor, which the Sigma-Delta modulator balances by controlling the Modulation IDAC, resulting in an increase in the digital count. The Sigma Delta converter maintains the voltage of Analog Mux Bus (AMUXBUS) at a constant $V_{REF}$, which is typically 1.2V, with the help of a CMOD capacitor. An external resistor ($R_s$) in-series with the sensor along with the AMUXBUS resistance ($R_{bus}$) helps to improve noise immunity. [60]

The continuous switching of SW1 and SW2 forms an equivalent resistance, $R_{eq}$, as...
Figure 4.8: a) CSD Block diagram and b) Equivalent Resistor model

Figure 4.8b shows, that is given by:

\[ R_{eq} = \frac{1}{C_s F_{SW}} \]  \hspace{1cm} (4.2)

Where:

1. \( C_s \) = Total sensor capacitance = Parasitic capacitance \( (C_p) \) + Finger capacitance \( (C_p) \)
2. $F_{sw} = \text{Frequency of the switching clock or Sense Clock Frequency}$

Furthermore, the average current taken by the sensor capacitor from the AMUXBUS is given by:

$$I_{CS} = C_s F_{SW} V_{REF} \quad (4.3)$$

Equation 4.4 shows the raw count equation when only the Modulation IDAC (single IDAC mode) is used while Equation 4.5 shows the raw count when both Modulation IDAC and Compensation IDAC (Dual IDAC mode) are used. The dual IDAC mode gives more sensitivity and produces more count for a specific finger capacitance compared to the single IDAC mode.

$$Raw\ count = (2^N - 1) \frac{V_{REF} F_{SW}}{I_{MOD}} C_s \quad (4.4)$$

$$Raw\ count = (2^N - 1) \frac{V_{REF} F_{SW}}{I_{MOD}} C_s - (2^N - 1) \frac{I_{COMP}}{I_{MOD}} \quad (4.5)$$

Where N is the scan resolution of the Sigma-Delta modulator in bits.

As can be seen from figure 4.9, it was tested the accuracy to measure proximity. Therefore, a finger was approached and then removed, decreasing the distance in each step. The finger started at 4cm above the sensor and then approximated to 2cm – when the sensor detected its presence – recovering its original position. After that the distance was shortened step by step until the finger slightly touch the sensor.

The Cypress board communicates the data at a rate of 47 packets per second. The x-axis corresponds to time and can be converted to an interval of $[0 : 13]$s. Once more, the y-axis does not corresponds to the real capacitance. However, the real value of
4.3. RANGE AND SENSITIVITY

Figure 4.9: Test of proximity. Peaks for a finger when in at a distance of: 2cm; 1cm; 0.5cm and in touch

the capacitance does not matter for this application, since the goal is just to detect changes on capacitance.

4.3 Range and Sensitivity

It is known that the sensitivity of a capacitive sensing system is better than a resistive sensing. However, it is important to have an idea of what can be done to increase the sensitivity. To get the best sensitivity, it may be used EcoFlex due to its viscoelastic properties. However, its dielectric constant is small, which means that the capacitance is also small, and therefore it can be affected by small interferences that are surrounding the sensor. Thus, it is also desired to increase the capacitance, which can be done by:
1. decreasing the thickness of dielectric, which implicates some specialized equipment, such as spin coater or thin film applicator

2. increasing the area of electrodes, which is not desired since the goal is to reduce them and not to increase.

3. using a material with higher dielectric constant.

The dielectric thickness is the main parameter in a parallel plate capacitor, for instance. Decreasing the thickness results in an increase of capacitance, which does not signify an increase on range of sensitivity. If the dielectric material used are the elastomers introduced in chapter 2, it must be recalled that they are both incompressible materials with high hydrostatic pressures. When the thickness of dielectric is too thin, it is not possible to compress the sensor and then change the capacitance. Therefore, either the range and sensitivity can be deteriorated with the use of thinner dielectrics.

By increasing the area of electrodes, the range of operation may increase, since for the same force and contact area, the pressure applied in the sensor in smaller. Therefore, to have the same pressure than a smaller sensor, it can be applied more pressure force. However, it may be loosen some sensitivity for the same reason. For small pressure forces, the change in the capacitance may be insignificant.

Therefore, the approach to increase capacitance is to change the dielectric material. The dielectric material can be every insulator since it is soft and flexible. All the polymers commercially available have its dielectric constant similar to the EcoFlex and PDMS. However, based on Nayak et al. [61] it is possible to increase the dielectric constant of an elastomer by doping it with conductive particles. In his work, he embedded barium titane \( (\text{BaTiO}_3) \) in PDMS enhancing the electrical, thermal, barrier and other properties.

Similar to this research, Bartlett et al from SML, CMU, tested what was called Liquid Metal Embedded Elastomers (LMEE), embedding liquid metal, such as EGaIn,
in silicone increasing its dielectric constant.

![Figure 4.10: Illustration of the liquid metal embedded in an elastomer.](image)

Depending on the elastomer, the final result is different. If it is chosen EcoFlex 00-30 as base material, it becomes nonconductive but enhances the dielectric constant four times when compared to the unembedded elastomer. On the other hand, if it is used PDMS, although the sample becomes also nonconductive, it is possible to make it conductive by applying pressure on it. The applied pressure, breaks the insulator layer between particles and creates a conductive. However, this does not happen in EcoFlex due to its viscoelastic properties.

The fabrication of these LMEE composites consists on hand mixing the elastomer with the liquid metal in the desired volume percentage vigorously for 10 minutes, which creates a viscous emulsion and reduces the size of the liquid metal droplets to $30\mu$m. Then a film should be casted on a substrate and cured at 100°C for an hour. An illustration can be seen in figure 4.10.

Depending on the volume percentage of EGaIn that is added to the elastomer it results in different dielectric constant, figure 4.11. However, for a volume percentage of 50% the dielectric constant is $18.9 \pm 1.1$.

Nevertheless, even using the LMEE composite, there are some loss of sensitivity. To get the best sensitivity, the elastomer that must be utilized is the EcoFlex.
4.4 Conclusion

The capacitive sensing is a good alternative to resistive sensing since the variables that change the capacitance are all geometric. Therefore, there is no difference in using conductive polymers (with micro and nano particles) or liquid metals, which means that the issues related with cPDMS that was identified in the previous chapter is now solved. However, the values measured for the capacitance are in the order of a few pF which means that any conductive object close to the sensor interferes with the signal. To prevent these interferences it can be used some shielding.

Thus, the topologies available and tested were:

- Parallel Plate Capacitors
- In-Plane Capacitors

The changes in the capacitance of the Parallel Plate Capacitors is due to changes in the dielectric thickness. Therefore, the dielectric material should be as viscoelastic as possible in order to increase the sensitivity of the sensor.

Regarding the In-Plane Capacitors, they can be used to measure and detect the proximity of conductive objects due to the Fringe effect.
Furthermore, there is the possibility to increase the capacitance about 50 times by embedding liquid metal particles in a silicone elastomer, LMEE, losing some sensitivity.
Chapter 5

Stability Analysis for Carbon Doped PDMS Conductive Polymer

An interesting goal for the soft and stretchable sensors is to produce the sensors easily without the need for a fully equipped lab. Therefore, one of the goals of the soft technology is to be possible for everyone make sensors based on a rapid prototyping and low cost process. As was already introduced, the different conductive materials available are:

- Liquid Metals
- Conductive Polymers
  - Nano particles - Carbon Nanotubes, Silver Nanowires.
  - Silver particles
  - Carbon Black particles

Using liquid metals, it is guaranteed the best conductivity values and also the flexibility and stretchability that is required. However, beyond the cost of the liquid metal, the fabrication is not accessible. Firstly, the EGaIn is corrosive to some metals,
which implies some cares regarding the material that is surrounding the workspace. Furthermore, it requires expensive equipment, which impedes its use outside a lab environment.

Despite nano particles seem a promising material due to its high conductance at a low percolation threshold, the cost of these particles is very expensive, and to use them properly, it should be done some pre-processing, such as dispersion of particles and functionalization. Although some methods to disperse the nano particles are not so expensive, it is something avoidable for someone who wants to produce sensors at home and, additionally the time of production is increased.

Concerning the micro particles, there are silver and carbon based polymers. Regarding the silver doped particles, the conductivity is better than carbon doped polymers, but the stiffness of the uncured polymer prevents the correct patterning of the samples. On the other hand, the Carbon Black based polymers have worse conductivity but the viscosity of sample is ideal to pattern the samples, making it easy to process. Furthermore, the fabrication can be accessible since it is not needed any specialized equipment to treat or pattern the material, despite the use of some specialized equipment guarantee better results, and it is possible to have a rapid prototyping. However, when analysed the samples used with cPDMS, either in chapters 3 and 4 it was verified a loss of conductivity throughout the fabrication steps. Therefore, it was made a careful analysis of the stability of the carbon doped PDMS

5.1 Experimental Method

The purpose of this study is to understand the reason behind the changes on the conductance of the cPDMS over time and, based on that, suggest methods to minimize the conductance loss. We observed that the changes on conductance happen after curing the cPDMS and after integrating the cPDMS on the PDMS. In some cases,
5.1. EXPERIMENTAL METHOD

the resistance of a pattern became stable after a couple of hours. However, in some other cases, the resistance increased over the course of several days, up to the point of sometimes the sensor becoming non-conductive. The goal of this study is to understand the effect of materials and fabrication process parameters on the conductance of the cPDMS over time and to suggest a fabrication process that results in stable conductivity over time.

5.1.1 Materials

The cPDMS was produced by mixing PDMS (Sylgard 184; 10:1 base-to-catalyst ratio; Dow Corning) with acetylene CB. The minimum weight percentage of CB necessary for conductivity was found to be around %12wt. In the experiments, we tried two compositions based on 16% and 25% weight of carbon black. For concentrations larger than 25%wt, the material becomes too viscous to be manually mixed and fill the molds. Thus, 25%wt was the highest concentration considered in this study. Even so, we added acetone to the silicone and CB mixture to make it less viscous. EcoFlex 00-30 and PMC Urethane (Smooth On) were both produced by mixing part A and part B in equal amounts by volume or weight.

5.1.2 Fabrication

The general fabrication method for every sensor is based on integration of patterned cPDMS with an insulating polymer (PDMS, ecoflex, Urethane). This was done either by surface printing through a stencil, or by lifting from a laser patterned mold. For the lifting process molds were produced by engraving an acrylic sheet (figure 5.2a. and figure 5.2c., molds A and B, respectively). For the surface printing (figure 5.2b.), a stainless steel stencil was produced by a laser cutter(mold C).

We fabricated stretchable strain and pressure sensors with different dimensions,
insulating materials and process. All sensors are fabricated either by first creating a layer of an insulating polymer and then depositing the cPDMS using the patterned molds, or by first filling the molds with cPDMS and then pouring the insulating pre-polymer over it.

Figure 5.1: Schematics depicting each of the fabrication methods: a.) Curing PDMS first; b.) Curing cPDMS first; c.) Curing PDMS and cPDMS at the same time.

In summary, sensors were produced using three different techniques in order to reflect the differences in the curing order, i.e. PDMS first, cPDMS first, or both cured together:

- Stencil lithography in which PDMS is cured first (130°C for 25 min.) and then uncured cPDMS is deposited using a stainless steel stencil. The excess cPDMS is cleaned in such a way that when the stencil is removed, only the desired pattern remains over the PDMS layer. Both layers are then cured at 130°C for 25 minutes or at room temperature for 48 hours. (Fig. 5.1a).

- Referring to Fig. 5.1b, acrylic mold is first filled with cPDMS. After the excess is removed, the cPDMS is cured at 130°C for 25 minutes. Lastly, a PDMS layer with a thickness of 0.5mm is added on top of the cPDMS and is cured at room
temperature for 48h or again in the oven under the same conditions.

- Referring to Fig. 5.1c, the mold is first filled with cPDMS and the excess is carefully removed. In this method, it is impossible to clean the mold afterwards, meaning that it is imperative to clear all the material that may create shortcuts between the paths before pouring the final layer of PDMS. The sample is then either cured in the oven at 130°C for 25 minutes or placed at room temperature to cure for 48h.

The width \times thickness dimensions (in mm) of the cPDMS channels for each developed sensor are: 

\[(0.6, 1.5, 3) \times (0.25, 0.3, 0.4)\] and 
\[(1.5, 3) \times (0.35, 0.4, 0.6, 0.9)\]

**Figure 5.2:** Molds used to make the cPDMS patterns: a.) Acrylic mold made using a laser-cutting machine (“S” refers to the laser speed and “P” to its power) to engrave patterns with dimensions \(1.5 \times 3 \times (0.35, 0.4, 0.6, 0.9)\) mm; b.) Mold made in the back of a PCB using a CNC to engrave the patterns; c.) Acrylic mold made using a laser-cutting machine to engrave patterns with dimensions \(0.6 \times (0.25, 0.3, 0.4)\) mm; d.) Close-up of a spiral pattern; e.) Mold made from a 0.1mm stainless steel sheet (stencil).

### 5.1.3 cPDMS and PDMS integration

Fig. 5.3a shows a close-up picture of some of the sensors. Using the molds from Fig. 5.2 148 different sensors were built and extensive tests concerning their resistance
were performed. Most of the sensors were made with PDMS and cPDMS and using the lifting and stencil fabrication method. The resistance of the sensors was measured at specific instances (fresh, cured and integrated) and over time, at 24h intervals over a 10 days period.

- Fresh - right after mixing the composition and casting it into the mold (uncured cPDMS);
- Cured - right after curing the cPDMS (not applicable if PDMS and cPDMS are cured together);
- Integrated - right after integration and curing of the PDMS layer (if cured in the oven, a waiting period of 30 minutes is given for the sensor to cool down);
- Over time - every 24 hours after integration.

In these tests, it was tested different CB concentrations, different thicknesses and also different curing methods, table 5.1

1. Method 1 - first cure a layer of cPDMS alone in the oven for 25 mins at 130°C and then add on top of it a layer of uncured PDMS. Cure the two layers in the oven for 25 mins at 130°C ;
5.2. ANALYSIS OF RESULTS

2. Method 2 - first cure a layer of cPDMS alone in the oven for 25 mins at 130°C and then add on top of it a layer of uncured PDMS. Cure the two layers at room temperature for 48h;

3. Method 3 - cure cPDMS and PDMS at the same time in the oven for 25 mins at 130°C;

4. Method 4 - cure cPDMS and PDMS at the same time at room temperature for 48h;

5. Method 5 - first cure a sheet of PDMS and then use the steel stencil molds to print the cPDMS sensors on top of it. Take everything to cure in the oven for 25 mins at 130°C;

6. Method 6 - first cure a sheet of PDMS and then use the steel stencil molds to print the cPDMS sensors on top of it. Take it to cure at room temperature for 48h.

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<th>Table 5.1: Parameters</th>
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<tr>
<td>Parameter</td>
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<tr>
<td>cPDMS layer (Width × Thickness)</td>
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<tr>
<td>(mm)</td>
</tr>
<tr>
<td>Carbon Percentage</td>
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<td></td>
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5.2 Analysis of Results

To be able to compare the changes on the electrical resistance, all the lines in the plots were normalized either to their corresponding fresh or cured value, depending
Chapter 5. Stability Analysis for Carbon Doped PDMS Conductive Polymer

on the situation. Due to the nature of methods 3, 4, 5 and 6, where the curing and integration develop at the same time, it was impossible to measure the cured resistance values of the cPDMS, and thus it was given the same value for cured and integration step in the respective plots.

5.2.1 Changes in resistance

Whenever it was possible to obtain the cured value (method 1 and 2), it became apparent that the resistance of the cPDMS pattern always decreased after curing in relation to the freshly made uncured cPDMS, as is exemplified in figure 5.4. In this plot the resistance was normalized to the fresh value because it was the first measured value. The increase on conductivity between the Fresh and Cured state may be due to the evaporation of some of the chemicals in the composition during the curing process which causes an increase in concentration of carbon microparticles. To track the changes on the resistance of the traces, the actual comparison should be between the resistance value of the traces right after curing and then over time. As can be seen in figure 5.4 it is actually the integration stage that causes an increase in the resistance from the cured value (this is when cPDMS and PDMS are put in contact). If the claimed hypothesis exists in fact, it must be seen in between these two steps – right after curing and when integrated with the pure polymer. However other factors are going to be analysed in order to explore all the possibilities.

5.2.2 Influence of Thickness

Firstly, it must be noted that the increase of thickness results in better conductivity. By increasing the thickness of the sample it is also increasing the number of particles and therefore increasing the number of conductive paths, as discussed in chapter 3.

Furthermore, Figure 5.3 shows the effect of the thickness of the traces on the change
5.2. ANALYSIS OF RESULTS

Figure 5.4: Plot of resistance for different states of cPDMS of the conductivity over time. The thinner the cPDMS track is, the higher is the rate of the increase of the resistance, after integration with the PDMS. This is probably because the material exchange between PDMS and cPDMS happens mostly at the boundary between both polymers and the neighbouring regions. As the thickness increases the region affected by the eventual diffusion is smaller, when compared to the entire thickness. If the region not affected by the diffusion is much larger than the one that is, the influence of the diffusion is lessened. Therefore, thinner sensors are more prone to loss of the conductivity than the thicker ones. Furthermore, small thicknesses and low concentrations, at times, may introduce some instability in the sensor conductance as can be seen in figure 5.5a where the 0.35mm thickness does not exhibit a well-defined plateau. However, in 5.5b with a higher concentration of particles this effect is not verified.

5.2.3 Influence of Concentration Gradient

As was already seen in figure 5.5, the concentration gradient seems to be an important factor in the electrical resistance of the samples. Therefore, and despite this behaviour has been verified in all methods, it was chosen just one method to best understand the plot. Thus, the figure 5.6 shows that the deterioration of conductivity for the sample with lower concentration is much more evident when the polymer is added
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Figure 5.5: Resistance over time for different thicknesses. a) samples with 16wt% and b) 25wt% to the cPDMS, when compared to the higher concentration sample. Furthermore, the sample with 25wt% of Carbon Black seems to be much more stable over time than the sample with 16wt%. The argument to explain this behaviour is that the lower concentration of CB in cPDMS, and when the percolation threshold is passed only slightly, a small material migration between cPDMS and PDMS, can immediately drop the CB percentage below the percolation threshold. However, for higher concentration of CB, the molecules migration has a smaller impact on conductivity. Nevertheless, increasing the percentage of the CB is not always desired, since it changes the mechanical properties of the cPDMS and the viscosity of the paste. It is normally desired to reach the percolation threshold with the lowest amount of added particles.

Figure 5.6: Plot of resistance for different concentrations of CB by weight
5.2.4 Influence of Curing Temperature, Order, & Time

These three factors also have a significant effect on the overall conductance of the sensors. Starting with the temperature of curing, it was analysed the curing methods 1 and 2 and the curing methods 5 and 6. The methods 3 and 4 are not analysed since the polymer and the conductive composite are cured at the same time. Each of those two methods are the similar expect for the curing temperature. The methods 1 and 5 cures the last layer in the oven while the methods 2 and 6 cures the respective last layer at room temperature.

Concerning the diffusion hypothesis, it is expected that curing in the oven is better than curing at room temperature because the polymers will cure faster and consequently the eventual time of diffusion will be reduced.

As can be seen in figure 5.7a, the curing method in the oven 1 is better than the curing at room temperature. For figure 5.7b it can be seen that there is practically no difference between curing methods. This may indicate that there is no diffusion from the cPDMS to the PDMS.

![Normalized resistance for different temperatures of curing](image1)

![Normalized resistance for different temperatures of curing](image2)

**Figure 5.7:** Resistance over time for different temperatures of curing. a) curing methods 1 and 2 and b) curing methods 3 and 4

Analysing now all the curing methods in a same plot, figure 5.8b to compare them it can be seen that, for instance, adding uncured PDMS on top of cured cPDMS
methods 1 and 2) has a worse effect when compared to the situation in which uncured cPDMS is deposited over cured PDMS (methods 5 and 6). The fact that adding the uncured PDMS over cPDMS has a worse effect than the opposite method, suggests that either the uncured PDMS is able to creep into the CB aggregation of cPDMS, or the CB aggregations of cPDMS can move into the lower viscosity PDMS. The effect of the curing order can be studied by comparing only the methods in 5.8b that share the same curing temperature and time, that is, methods 1, 3 and 5 (in which the samples are cured at overn), and methods 2, 4 and 6 (in which the samples are cured at room temperature). In the first set, sensors built by curing the PDMS and the cPDMS (method 3) together always performed the best. Considering the second set, figure 5.8a, the worst case scenario since it is when where all materials are cured at room temperature, method 6 (cure first PDMS and then pour cPDMS over it), was the one that exhibited the best results. In its uncured form, cPDMS is essentially carbon particles in suspension within uncured PDMS. When uncured PDMS and uncured cPDMS are integrated together, they are still in liquid phase and the diffusion that occurs is mostly of PDMS going back and forth between the uncured polymers. The carbon particles, which are much larger than the pre-polymers PDMS molecules, remain relatively unmoved, causing the net effect of the diffusion to be reduced and thus limiting it. For short curing periods, this is the main reason why method 3 is also the best method among all six methods.

Figure 5.8: Comparison of different curing methods, a) worst case of each pair of methods and b) all methods
5.3 Diffusion analysis

In this section it is discussed a bit further the diffusion hypothesis as a possible reason for the change of the resistance of the cPDMS sensors and discuss how these results can be used in order to improve the fabrication process of the cPDMS based traces, for reliable and long lasting conductive traces whose resistance stays constant during a long time.

The variations observed in the electrical conductivity of cPDMS samples suggest that a material migration or diffusion is the most convincing hypothesis as the reason for loss of the conductivity. Such diffusion at the boundary between the PDMS and cPDMS is responsible for increasing resistance of the cPDMS over time. In order to investigate other factors, such as the effect of environmental factors such as oxidization, solvent effects, etc., it was performed another test. A sample consisting on one trace of cPDMS (0.5mm × 2mm × 45mm) for different CB concentration without combining them with any insulator polymer and measured the resistance for 220 hours. As can be seen in figure 5.9 results show that the resistance did not change over 220 hours, expect for the 15% sample, in which the resistance slightly decreased. This shows that other environmental factors do not change the resistance of the samples, and such changes happens only when the cPDMS gets in touch with PDMS.

![Figure 5.9: Plot of the variation of the resistance over 220 hours.](image)
Chapter 5. Stability Analysis for Carbon Doped PDMS Conductive Polymer

The variations over time observed in the resistance values are indicative of changes in carbon concentration within the cPDMS which, in turn, may be a product of the way diffusion develops. A drop in conductivity implies that either PDMS is creeping into the cPDMS or that conductive material (CB aggregations) is leaving the cPDMS. Also, it should be mentioned that most of the parameters in table 5.1 have an effect in the way diffusion interacts with sensor conductance: a large thickness provides more robustness against the carbon loss/PDMS gain; when the curing order is changed, it changes the diffusion couple which means the curing order gives rise to different $D$ coefficients. Curing temperature and time have a direct impact in the $D$ parameter and Fick’s Second Law, respectively.

Then, it was tested addition of two different insulating flexible polymers to evaluate the results. In addition to PDMS, it was tested PMC Urethane and EcoFlex 0030 (both for smooth-on). cPDMS was cured first and uncured PDMS, Uretheane, and EcoFlex was added to it. The samples were either let to cure at room temperature and on a hot plate and the resistance measured while the silicones were curing. As can be seen in figure 5.10e when combined by urethane, the conductivity of the cPDMS remains constant. The reason behind this is that the bonding between PDMS and Urethane is generally poor. Therefore, the test on a hot plate was not made because it is also constant.

Furthermore, EcoFlex presents the worst results and conductivity of the cPDMS in contact with EcoFlex decreases substantially. The plot of the EcoFlex cured on a hot plate, 5.10d, the reason of the variation of the resistance is either due to is was used an handheld digital multimeter that is not precise for values above 10MΩ and also the effect of temperature on the probes, since that when the sample was removed from the hot plate, it is possible to see that the resistance became constant.

Finally, for PDMS it can be seen that the diffusion prolongs to more time because the curing time of the PDMS is much longer than the other silicones. However, even
if the diffusion is longer than when using EcoFlex, the loss of conductivity is smaller.

Furthermore, to prove that the temperature and consequently the time of curing, has an effect in diffusion. It can be seen that either for PDMS and EcoFlex the results were better when the samples were cured on a hot plate. For the PDMS is was not made a continuously measuring while the temperature was decreasing, however it can be seen that after the sample cool down, the final value of resistance is just 200% higher than the cured state. Once more this shows that the bonding stage between the polymers (conductive and nonconductive) is the reason behind the loss of the conductivity.

![Image](a)

![Image](b)

![Image](c)

![Image](d)

![Image](e)

**Figure 5.10**: Changes in resistance while the sealing polymer is curing, either on a hot plate or at room temperature.
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A previous study on morphology of the carbon black doped polymers [63] compared the aggregation of CB in polymers with different viscosities, and suggested that in a lower-viscosity matrix, CB aggregates diffuse and form an agglomerate-network. While in a higher viscosity the aggregate diffusion slows down significantly. This also fortifies the diffusion hypothesis, since as uncured PDMS gets in touch with the cured cPDMS, the CB aggregate can diffuse into the lower viscosity network.

Independent from the reason behind the loss of conductivity over time, it is shown that it is possible to minimize this effect in order to fabricate conductive traces that are reliable over a long period.

5.3.1 The Diffusion depth

Since cPDMS and PDMS bond together strongly, it will be difficult to unbound them and examine the cross section with microscopy. However, it was tried to estimate the diffusion depth by a comparative study.

**Figure 5.11:** $t$ shows the overall thickness of the patterned cPDMS and $t_d$ shows the diffusion depth after integration of the PDMS, impairing thus the the percolation of CB in the border layers.

Considering samples with only 16% of CB, it can be assumed that small amounts of the diffusion on layers of cPDMS drops the CB percentage below the conductivity threshold and become nonconductive. Here it is defined $t_d$ as the effective depth of the diffusion. That is, if is possible to calculate $t_d$ based on change of the resistance for each of the samples, it can be estimated $t_d$ for all samples. It should be mentioned that the effective diffusion depth is different with the actual diffusion depth. The effective diffusion depth, is defined for being able to compare the results. To do so, it was compared the resistance of the samples with different thickness before and after curing.
5.3. DIFFUSION ANALYSIS

the PDMS. The calculations were performed to methods 1 and 2.

As may be known:

\[ R = \frac{\rho l}{w t} \]  

(5.1)

So, making a relation with the initial resistance, \( R_0 \), and the final resistance \( R_f \), assuming an initial thickness \( t_0 \), a constant length, \( l \), and width, \( w \), and a final thickness \( t_f \), it can be calculated the \( t_d \) as \( t_d = t_0 - t_f \), or:

\[ t_d = t_0 - R_0 \times t_0/R_f \]  

(5.2)

| Table 5.2: Depth of diffusion, \( t_d \), for method 1 |
|---|---|---|---|---|
| \( t_0 (mm) \) | \( R_{cured} \) | \( R_{72h} \) | \( t_f (mm) \) | \( t_d (mm) \) |
| 0.25 | 2.97 | 31.2 | 0.02 | 0.23 |
| 0.3  | 0.927 | 3.76 | 0.74 | 0.23 |
| 0.4  | 0.574 | 1.44 | 0.16 | 0.24 |

| Table 5.3: Depth of diffusion, \( t_d \), for method 2 |
|---|---|---|---|---|
| \( t_0 (mm) \) | \( R_{cured} \) | \( R_{72h} \) | \( t_f (mm) \) | \( t_d (mm) \) |
| 0.35 | 0.108 | 1.16 | 0.03 | 0.32 |
| 0.4  | 0.091 | 0.271 | 0.13 | 0.27 |
| 0.6  | 0.044 | 0.0891 | 0.30 | 0.30 |

As can be seen from table 5.2 and 5.3, for each method, the \( t_d \) is almost equal for all samples. That is, for method 1, samples with different thickness (0.35, 0.4 and 0.6) have all an equal effective diffusion depth of 0.23mm. and for the method 2, this is 0.29mm. This means the actual resistance of each sample produced by each method, can be calculated by

\[ R = \frac{\rho l}{w \times (t - t_d)} \]  

(5.3)
while the $t_d$ of each fabrication method can be estimated by one experiment. Also, as it was expected the $t_d$ for the method 1, in which the samples are cured in the oven, is lower than the $t_d$ of the samples with method 2.

5.4 Conclusion

It is shown that the durability of the conductivity of the cPDMS depends on several factors. First of all, when possible, a higher concentration of CB on PDMS (e.g. over 20% weight) is recommended. The higher concentration proved to be less prone to loss of the conductivity, since even a small diffusion cannot damage the percolating CB network. Second, since the diffusion happens up to a limited depth, when possible thicker cPDMS is preferred. In any case, the first two recommendation have disadvantages, and both of them are undesired for many applications.

Then, when possible, the cPDMS and PDMS should be cured together (and not one of them before the other or, if the previous method is not possible, PDMS should be cured before cPDMS and not vice versa. Finally, in all cases curing in the oven results better than curing at room temperature. Finally, a urethane insulator may replace the PDMS. Even though the bonding between cPDMS and Urethane is not very good, it is possible to sandwich a cPDMS pattern between two films of urethane.
Chapter 6

Triangle of Fabrication & Case Study

6.1 Triangle of Fabrication

As was being described in the previous chapters, all the materials and procedures to produce soft and flexible sensors were sufficiently explored and tested, which means that the production of reliable sensors is not an issue anymore.

Regarding the triangle of fabrication, that was already introduced in the Introduction, a more detailed analyses is going to be made in this chapter. The triangle of fabrication is the base that orientated this dissertation, and knowing that each element of the triangle is correlated with the others, every step during this project was always related to this schematic.

All the vertices of these triangle were already, at least, slightly mentioned and detailed in the previous chapters, especially the Fabrication Methods and Materials. However, even these elements are going to more properly detailed. In each element, it is always possible to find a better approach but also more expensive. In this analyse, it will be discussed the pros and against but for two different points of view: the best
approach possible and also a reliable and “low cost” approach.

6.1.1 Materials

6.1.1.1 Conductive

When comparing the electrical properties of the two conductive materials more utilized in this dissertation it is obvious that the Eutectic Gallium Indium is much better than cPDMS. However, the use of EGaIn leads to a more expensive cost of production and therefore, the fabrication method and the design should be wisely chosen to avoid possible mistakes and waste of material. Furthermore, the handling of EGaIn is very messy and hard to clean, which can contaminate an entire workspace if not handled with care. Moreover, the EGaIn is considered a hazardous material since it may be corrosive to some metals – but safe for human interaction.

On the other hand, the use of cPDMS can also be reliable enough to produce sensors. However, it is important to know and try to produce the best samples taking into account the conductivity issues and also the diffusion problems. Therefore, it cannot be used when the conductivity is a fundamental factor of an application, but it works well enough in a capacitive based sensing. To better compare the materials utilized in this dissertation, conductive polymers and liquid metal, it can be analysed the table 6.1.
6.1. TRIANGLE OF FABRICATION

**Table 6.1:** Table of comparison between conductive polymers and liquid metals.

<table>
<thead>
<tr>
<th></th>
<th>Conductivity</th>
<th>Cost</th>
<th>Safety</th>
<th>Processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid Metals</td>
<td>↑</td>
<td>↓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conductive Polymers</td>
<td>↓</td>
<td>↑</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

By analysing each column of the table is possible to understand which material, liquid metals or conductive polymers, is better on that specific aspect. Therefore, it can be seen that the liquid metals have more conductivity than the conductive polymers but are more expensive. In terms of safety, the conductive polymers, while in the powder can be problematic to the lungs to the small size of the particles. On the other hand, the liquid metal is corrosive to some metals, such as aluminum. In the last column it is analysed the time, the equipment and the complexity that is needed to produce soft sensors with these materials, and the conclusion is that using conductive polymers is better than liquid metals - ignoring the nanocomposites in this column.

Additionally, in table 6.2 and since conductive polymers refer to multiple conductive materials, it is analysed the different conductive polymers - cPDMS, AgPMDS and Nano Composites.

**Table 6.2:** Table of comparison between cPDMS, AgPMDS and Nano Composites.

<table>
<thead>
<tr>
<th></th>
<th>Percolation Threshold</th>
<th>Processing</th>
<th>Cost</th>
<th>Accessibility</th>
<th>Rapid Prototyping</th>
</tr>
</thead>
<tbody>
<tr>
<td>cPDMS</td>
<td>⭐⭐⭐</td>
<td>⭐⭐⭐</td>
<td>⭐⭐⭐</td>
<td>⭐⭐⭐</td>
<td>⭐⭐⭐</td>
</tr>
<tr>
<td>AgPMDS</td>
<td>⭐⭐⭐</td>
<td>⭐⭐⭐</td>
<td>⭐⭐⭐</td>
<td>⭐⭐⭐</td>
<td>⭐⭐⭐</td>
</tr>
<tr>
<td>Nanocomposites</td>
<td>⭐⭐⭐⭐</td>
<td>⭐⭐⭐⭐</td>
<td>⭐⭐⭐</td>
<td>⭐⭐⭐</td>
<td>⭐⭐⭐</td>
</tr>
</tbody>
</table>

The method of comparison in this table is different. Therefore, in each aspect it is attributed 1 star to the worst case scenario and 3 stars to the best case scenario. The cases where were attributed 2 star are in an intermediary situation.

In terms of percolation threshold, the best case scenario is the nano composites since
Chapter 6. Triangle of Fabrication & Case Study

it is the material that requires less concentration to become conductive. Additionally, regarding the processing and cost, the cPDMS is the best case because it is the less expensive - the Acetylene Carbon Black is cheap and easy to find - and is the one that is easier to pattern (the AgPDMS mixture is too stiff to pattern and the nanocomposites require pre-processing). Concerning the accessibility, it is analysed the equipment needed to produce, pattern and process the conductive polymers, and can be concluded that despite cPDMS and AgPDMS use laser patterned molds or 3D printed molds, the molds can be used several times without being damaged. The time of prototyping is also similar between cPDMS and AgPDMS but better than the nanocomposites.

6.1.1.2 Nonconductive

The choice of the elastomer is strongly dependent on the desired application. If an application is designed to be discreet and easily camouflaged in the host environment, the PDMS is better than EcoFlex due to its transparency. On the other hand, if the sensor needs to be more stretched than 200% its original dimension, it is not advised to use PDMS but EcoFlex. However, consulting the table 6.3 it is possible to see a comparison between these two elastomers.

<table>
<thead>
<tr>
<th></th>
<th>Transparency</th>
<th>Curing Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td>EcoFlex</td>
<td>↓</td>
<td>↑</td>
</tr>
</tbody>
</table>

In the table, it can be seen that the PDMS is more transparent than the EcoFlex. On the other hand, EcoFlex can sustain more strain (it can be stretched up to 600% its initial dimension) and it cures faster than PDMS. However, the use of EcoFlex should be avoided or produced with certain cautions when the conductive material is cPDMS due to the diffusion effect.

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6.1.2 Fabrication Methods

From the fabrication methods described to produce cPDMS, all of them use a laser cutter or a 3D printer to pattern the sample or to make the mold. However, for the methods described as stencil lithography and lifting, the use of laser cutters or 3D printer may be residual since the methods are possible to be replicated using the same molds. Although with a higher failure rate than the laser patterning, these two methods are low cost methods with reliable results. In a prototype stage, trying new approaches and new designs, these methods are suitable for the purpose. On the other hand, the method that ensures better results is the laser patterning. In this method it is easy to design the desired pattern and, using the right power and speed of the laser cutter, the rate of success is very high. However, it requires a CO$_2$ laser. To better resume and compare these methods it can be observed the following schematic.

![Schematic to compare the fabrication methods using cPDMS. The + and – refer to advantages and disadvantages, respectively](image)

Figure 6.2: Schematic to compare the fabrication methods using cPDMS. The + and – refer to advantages and disadvantages, respectively.

Regarding the Liquid Metals patterning, there is a drawback in all fabrication methods. Since the EGaIn is corrosive to metals, it cannot be patterned using a thin film
applicator. Therefore, the thickness of the EGaIn layer is impossible to predict during the fabrication processes. Comparing now the different methods, it can be analyzed the following schematic.

**Figure 6.3:** Schematic to compare the fabrication methods of LM. The + and − refer to advantages and disadvantages, respectively

To analyse the fabrication methods using liquid metal it was divided into two main categories, that were then divided into two smaller categories:

- **Deposition**
  - Spraying
  - Rolling

- **Patterning**
  - Stencil Lithography
  - Laser Ablation
6.1. TRIANGLE OF FABRICATION

Remembering that the different fabrication methods described were Laser Ablation, Rolling Deposition and Spraying Deposition, it can be said that in terms of deposition the laser ablation and rolling are both equal, using a roller to deposit EGaIn. In terms of patterning either the spraying method and rolling use stencil lithography while the laser ablation direct patterns the sample.

Regarding the schematic from [6.3] it is important to note that the spraying deposition is more reliable than the rolling, since in the rolling deposition sometimes there is some gaps in the layer due to the cohesion forces and surface tension. Furthermore if the spraying is done at a constant rate is possible to have a relatively uniform layer, while in the rolling deposition it should be used a spin coater to remove the excess and eventually have a uniform layer. On the other hand, in terms of patterning, the stencil lithography allows to pattern smaller traces than the laser ablation. However, the laser ablation consists on direct patterning the sample reducing mistakes of placing stencil, for example.

6.1.3 Measurements

Regarding this vertex of the Triangle of Fabrication, this is the point that still has more topics of discussion and, therefore, more work to be developed. During the previous chapters, it was discussed either the resistive and capacitive sensing as different types of measurements and some conclusions drawn. However, more than the type of sensing, there is a real issue in the interface between soft and rigid electronics.

6.1.4 Capacitive vs Resistive Sensing

Considering all the work developed during this project, it can be concluded that the capacitive sensing is better than the resistive. The capacitive sensing is more sensitive and does not need a good conductor to work properly. Furthermore, it is
more responsive than the resistive sensing and it is possible to build different designs that corresponds to different measurements, which means that the capacitive sensing is also adaptable depending on the desired application. However, the capacitive sensors are more propitious to interferences of external electric field, effect that is not detected in the resistive sensing and the measurement is not as straightforward as it is for the resistive sensing.

On the other hand, despite it was proven that the resistive sensing cannot be used with cPDMS, it works with liquid metal and even with conductive nanoparticles. The fabrication method of these sensors is easier and less expensive, since it uses less material and just consists on one layer of conductive material.

6.1.5 Interface

Currently, there is no electronic components available that permits to build an entirely soft system. Therefore, it is needed at some point to interface the soft conductive material with some rigid electronics that can be embedded in the polymer matrix or with some rigid interfaces to connect with external boards. Actually, this is the biggest issue in the production of the soft sensors and is the step that shows more failures, because even the material that is relatively flexible is not as flexible as the elastomers used, which usually results in breaking of the conductive traces, damaging the sensor irremediably. However, some approaches are still being used in order to find the best approach.

6.1.5.1 Copper foil and conductive paper

The conductive paper is product commercially available from 3M with tape on one of the sides that can be used to attach to a substrate. The difference of conductivity between sides is considerably and therefore it must always be used the uncovered side for better results.
6.1. TRIANGLE OF FABRICATION

The conductive paper can be patterned in the CO\textsubscript{2} laser cutter and then be attached to the silicone substrate where will be patterned the terminals of the conductive material. The conductive material is then casted over the polymer substrate, being the terminals casted over the conductive paper. The sample can then be sealed with a polymer layer, which seals the conductive material but also the conductive paper. The flexibility of the conductive paper allows to bend the sensor without damaging it – the stretchability is reduced.

However, although the conductive paper has a very good conductivity and is as flexible as the polymers, it cannot be used in soldering to solder copper wires, for example, since the temperature destroys the conductive paper. Therefore, if the traces need to be extended with copper wires it has to be used a specific connector, figure 6.4. Therefore, the traces of conductive paper should be exactly patterned to match the different connections of the connector.

![Figure 6.4: Example of connector that should be used with conductive paper.](image)

Regarding the conductive foil and comparing it to the conductive paper, the advantage is that is possible to solder external electronics to it without needing a connector. However, the copper cannot be patterned in the CO\textsubscript{2} laser cutter and due to its hardness, the sensors become more fragile. Furthermore, the different rigidity between the silicones and elastomers means that when the sample has to be peeled from the substrate it must be peeled with care, since it is during this step that happens the most of the damages in the sensors.
6.1.5.2 zPDMS

Although use of AgPDMS is limited due to the difficulty to produce a uniform and liquid enough paste, another approach was found useful for the composites made with polymer and silver coated nickel particles. Instead of making an isotropic conductive composite, that is conductive in all directions, it was found that reducing the concentration of particles, and this way make it easier to mix and use, but orientate those particles using a magnet, is possible to obtain an anisotropic conductive sample, being conductive just in one direction – z-axis, figure 6.5a.

This concept is not new. In fact, it was first reported in 1988 by researchers at AT&T [64].

Figure 6.5: a) illustration of PDMS embedded with an array of vertically aligned columns of Ag-Ni microparticles. b) Microscope side view of the aligned columns of 20% and 40% by weight. c) zPDMS resistance for composites with different volume fraction, $A = 9mm^2$ and thickness $t = 90\mu m$ [65].
To produce an anisotropic zPDMS it must be filled the PDMS (Sylgard 184, 10:1 base-to-catalyst ratio; Dow Corning) with 15µm diameter silver coated nickel microparticles in a weigh total % from 10 to 40. It must be noted that this values are lower than the percolation threshold and then the composite is not conductive. Then, a film as thin as 45µm of the uncured composite can be casted and then the sample is placed on top of a flat magnet, which aligns the microparticles as the elastomer cures at 100°C in oven.

As can be seen from figure 6.5b the increase of particles results in an increase of columns, which means that more conductive channels through the z-axis are created. Furthermore, analysing the figure 6.5c can be verified that even for a mass fraction of 10%, a sample with 90µm of thickness, has a resistivity of 0.3Ω·m.

Since the zPDMS is just conductive through the z-axis, it is very useful to use as interface because it can seal properly a conductive trace made either of cPDMS or liquid metal, and it avoids shortening between traces. By increasing the concentration of particles is also increasing the contact points between different interfaces. Furthermore, antagonistically to cPDMS, for a more stretchable film, it can be used EcoFlex 00-30 since the EcoFlex filled with the Ag-Ni microparticles is able to cure.

Using zPDMS is possible to attach copper or conductive paper without damaging the conductive traces. To attach the conductive paper/copper foil to zPDMS it can be either cure the zPDMS over them or place the conductive paper/copper over the zPDMS in the exact place. In figure 6.6 can be seen an image from a stereo microscope that shows clearly the zPDMS columns over an EGaIn trace.
6.2 Case Study

In order to show that soft sensors are a technology that fits in nowadays requirements, it is demonstrated that it is possible to design a circuit that integrates either soft and rigid components. Firstly, to show in a simple circuit the workability of soft technology it was patterned a design for a LED circuit. This circuit is composed by a small lithium battery with 3V, a MosFet, a resistor and a LED. One of the terminals of the LED is directly connected to the battery while the other one is connected to the gate of the MosFet. The drain is directly connected to the MosFet but is also connected to the source through a resistor. To light the LED it is needed to connect the source to the opposite terminal of the battery, which is made only using a finger or another conductive object, since the circuit is designed with a gap, which means that the LED is normally off. In figure 6.7 are represented the two circuits produced using liquid metal, a) and b) and cPDMS. c) and d). In figure 6.7a is possible to see the small battery and two external wires that can be used to recharge the battery. Then, from the top to the bottom is placed the LED, the MosFet, the 10 $\Omega$ resistor and the interface with the user. To make the interface it was used cPDMS instead of EgaIn since the first one is possible to cure and become rigid. Similarly, it could be used zPDMS to seal all the circuit ant then the finger could interface directly with zPDMS. Furthermore, the LED from the EGaIn circuit is much more brighter than the circuit.
made with cPDMS due to the high resistance of the cPDMS.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{led_circuits.png}
\caption{LED circuits with EGaIn a) and b), and cPDMS c) and d) }
\end{figure}

The major issue regarding the interface between rigid and soft materials is overtaken by placing the rigid components in the soft material. Therefore, it was used a stereo microscope to precisely place the components on uncured cPDMS and on the liquid metal. Using conductive polymers, the rigid components become fixed to the cPDMS when it become cured. On the other hand, when it is used liquid metals, the components just become attached when the circuit is completely cured. Another possible approach to integrate rigid components on EGaIn is using copper on the terminals of each component. The liquid metal in contact with the copper forms an alloy which facilitates the integration of the rigid electronics. Furthermore, it can be used HCl to automatically orientate the rigid components in the EGaIn traces.

Additionally it is proposed a different sensor. Most applications that utilises capacitive sensing, as touch screens for example, does not use the ability to detect and measure proximity, filtering these changes, just considering the bigger changes that are due to pressure. Therefore, it is proposed a multi-layer hybrid liquid metal based sensor, composed by a resistive and capacitive sensing.

Using this proposed design, it can be detected multiple changes in a single sensor element. With the capacitive element it can be detected the following:

1. which object is approaching the sensor (conductive or non conductive);
2. proximity of the object (three axis).

It is known that by approaching a conductor from a capacitive sensor based on the fringe effect it changes the capacitance of the sensor. However, depending on the conductor the changes on the capacitance provoked by the object is different. For instance, using the capacitive element is possible to understand if the object is a metal object or a human finger. The human finger has its own charges, which causes a different response on the capacitance when compared to a metal object. Furthermore, it is also relevant to note that a nonconductive object, as plastic, is not detected by the sensor. Therefore, based on the behaviour of the changes, it can be concluded if it is a finger that is approaching or another conductive object.

On the other hand, the resistive element is used to evaluate the pressure that is applied on the sensor. Combining the two different measurements, from either the capacitive and resistive element it is possible to make another conclusion. In any change is detected in the capacitance, but there is a change in the resistance of the resistive element, it means that the object in not conductive. Therefore, combining the two elements it can be concluded if the external object is a human finger, a conductive object or a nonconductive object, beyond the pressure and proximity, already explained.

### 6.2.1 Fabrication Method

The fabrication method used for this sensor is slightly different from the ones described before. This sensor is composed by a capacitive element in a grid shape, which means that the rows and columns are in a different layer. The idea of using a grid is to increase the elements that reads the proximity and therefore be able to understand not just the proximity (z axis) but the actual position – x, y and z coordinates. Adding the resistive element, it means that the sensor is produced with three layers of conductive materials. Due to the resistive element, and in order to have the best results, the conductive material used is EGaIn, which allows to use EcoFlex as polymer matrix
and make use of its improved viscoelastic properties. In figure, 6.8 it can be seen the designs used to produce this hybrid sensor.

![Figure 6.8: a) and b) designs of the capacitive element c) design of the resistive element](image)

To interface the soft elements with an external board it was used copper. However, instead of a normal copper foil, it was used a flexible substrate that better conforms to the flexibility of the soft sensor, and consists on copper and kapton. Therefore, it was patterned some traces in the flexible substrate. Since it is not possible to pattern copper in a CO\(_2\) laser cutter, the traces were patterned in a UV Laser (LPKF ProtoLaser U3), figure 6.9.

![Figure 6.9: Result of the UV laser patterning on the Copper.](image)

However, to use this patterned copper the three different layers of the sensor must converge in a single layer. Therefore, there are two different ways to make this possible. One way consists on using zPDMS or zEcoFlex and multiple traces of EGaIn through all the layers. In a step by step description, the first layer, 6.8a is patterned using the
spray method. After that, the sensor itself is covered with EcoFlex and the EGaIn traces are covered with zEcoFlex. Then, the second layer of EGaIn is patterned, \[6.8b\] but additionally to the design of the image, the traces from the previous layer are also patterned. Once more, the zEcoFlex and EcoFlex cover the traces and the sensor, respectively, and the final layer, \[6.8c\] and the traces from the previous layers are patterned. This way, it is possible to have a connection path through all the thickness. Finally, the last layer of zEcoFlex is added to seal the sensor and the patterned copper is applied correctly on top of the EGaIn traces.

On the other hand, the other method consists in a novel fabrication method that seems to be reliable and also fast. In figure \[6.10\] are represented all the 5 steps that resumes this fabrication method.

\[\text{Figure 6.10: Fabrication method of multi-layer sensors converging in a single layer.}\]

The first step consists on applying a 500\(\mu m\) of EcoFlex and place on top of the uncured polymer, the patterned copper. After that, using the spray method and a mask patterned in the \(CO_2\) laser cutter, the EGaIn is sprayed on the EcoFlex and on the copper traces, figure \[6.10a\]. After this first step a second layer of the uncured silicon is applied all over the EGaIn, except for the EGaIn on top of the copper, \[6.10b\]. When the EcoFlex is cured, the second conductive layer is sprayed. Due to the different
height of the layers, the placing of the mask does not damage the pre patterned and still exposed EGaIn trace, image 6.10c. Then, the process is repeated for the following conductive layer, 6.10d, and finally, all the sample is covered in EcoFlex, including the copper traces, 6.10e.

The figure 6.11 shows a side view where is possible to see the slope of the EGaIn but also the successfulness of this method. This prototype is composed of 7 layers with an overall thickness of 1.4nm. This includes conductive electrodes of the capacitive sensor (2 layers), the spiral resistive sensor (one layer), and the intermediate and external PDMS films (4 layers).

Unfortunately, this sensor was not properly characterized in this project. Despite it was tested all the different measurements that can be performed with the sensor, a complete characterization of the sensor must still be done, testing the response for different materials, distances and angles. However, some work on programming has to be done in order to facilitates the characterization.
Chapter 7

General Conclusions

The work developed in this project managed to study and evaluate different fabrication methods, materials and types of sensing regarding the production of soft sensors. Some conclusions regarding conductivity issues, mainly in cPDMS were drawn, and the path to produce reliable sensors is now more defined.

Having written about all the proposed subjects, it is now interesting to discuss which are the main contributions of this dissertation. First of all, I believe that my principal contributions are related to cPMDS. Therefore, I think that all the study and work developed, is a great contribution to better understand all the procedures to produce soft and stretchable sensors. Furthermore, the results obtained with the Stability Analysis for Carbon Doped PDMS is a novelty and it might be very important in this field. From the results, it can be concluded that the loss of conductivity is due to diffusion between the silicone and the cPDMS, which deteriorates the conductive layer, reducing the conductivity of the sample. Eventually, it can be tested if this hypothesis is also verified with other conductive polymers, beyond cPDMS. Finally, the last great contribution is the last Case Study presented. For the first time it is proposed a multi-layer hybrid sensor made with EGaIn. This hybrid sensor uses either Resistive and Capacitive Sensing to not only measure pressure, but also to distinguish
if an object in the proximity is conductive or nonconductive, and if conductive estimate the approximation angle.

The main goal of this project was based on how to produce soft sensors, explore different approaches and then be able to decide how should a sensor be built based on the desired application. Therefore, based on this project, it is possible to understand the pros and against of each characteristic that composes a soft sensor. Arguments for and against for each material, either conductive or nonconductive, were presented, which means that is possible for any future researcher who want to fabricate soft sensors, to choose the more proper material based on the desired requirements of the application.

Furthermore, different fabrication methods were also presented, and all of them proved to be reliable, even though some of them require some training to expertise on the fabrication. This means that, depending on the available equipment, it is possible to use the fabrication method that is more convenient. Additionally, the theory behind Resistive and Capacitive sensing was explored and some conclusions drawn. In general, the capacitive sensing has been growing in the last years and has been replacing the resistive sensing, in some cases. This is applied for the technology in general, and it is not different to soft sensors. However, the capacitive sensing is also more expensive than the resistive, since it requires more material and the measurement of its values is not as straightforward as the resistive sensing.

Additionally, some ways to interface the soft sensors with rigid electronics were also suggested. However, this is definitely the aspect that still needs more research and more improvements. The anisotropic conductors such as zPDMS and zEcoFlex, seem to be promising and the improvements in the interface are going to be related with these kind of z-films.

Since the wearable technologies are growing, it is expected that some soft sensors, based on similar materials and fabrication methods presented in this dissertation, are
going to be commercially available in a near future. However, and in a perspective of resuming the topics approached in this dissertation, it was made the following tree diagram, based on a goal of this dissertation that is to produce soft sensors based on a rapid prototyping and low cost method. Therefore, in order to follow this thesis goal, the left side of the previous schematic, related to cPDMS sensors, is the one that is more indicated since the cPDMS is much cheaper than nanocomposites or liquid metal. Otherwise, to ensure better results and knowing that the price is higher than cPMDS, it can be chosen liquid metal.

Taking into account the diffusion effect that was discussed in chapter the elastomer chosen for the sensors made with cPDMS must be Urethane or, eventually, PDMS (in certain circumstances), while for the EGaIn it can be used either PDMS or EcoFlex (better mechanical properties than Urethane). Therefore, having decided which con-
ductive material and which elastomer is desired to be used, it must be decided the type of sensing, either capacitive or resistive. As was explained in chapter 3, it cannot be used resistive sensing with cPDMS due to the recovering time. Finally, it is advised which fabrication method is more convenient for both cases. For the stencils that need to be patterned for the Stencil lithography, either for cPMDS and EGaIn, it is also used a laser cutter. However, if the stencil is made with a rigid material that allows to be used several times without damaging, there is no need of a laser cutter to make new stencils every time that a sensor needs to be produced. Furthermore, in the branch of cPDMS, it is proposed the laser patterning. However, this is just considered as a “low-cost” method if a laser cutter is already available in the laboratory. Otherwise, the stencil or even the lifting method are the less expensive methods.

Furthermore, it was also made a different tree diagram, 7.2 with the objective to help in the decision-making for anyone who wants to produce soft sensors. Therefore, the user must choose which type of sensing wants for his application. After that the user can consult this tree-diagram in order to produce the desired sensor. In the bottom of the tree diagram, in the capacitive branch, there is a topology that was not introduced neither tested during this dissertation, Interdigital Capacitors. This type of capacitors consists on having the electrodes in the same plane but with more surface area between electrodes, image 7.3, where \( G_E \) and \( G \) are the gaps between conductors and \( L \) and \( W \) the length and width, respectively, [66].
Figure 7.2: Guide for the decision-making to produce soft sensors.

Figure 7.3: Interdigital Capacitor Geometry
7.1 Future Work

The presented work is an important contribution for the soft sensing technology and as was proven with the Case Study, it is possible to have a functional soft sensor. Therefore, the first next step would be to integrate a soft sensor in a real application. It can be either the Prosthetic Hand from the ISR or another application totally different as, for instance, a gamepad that can interact with the user in 3 dimensions and not just by touch. This gamepad or even a touchscreen, can interpret some gestures made in a reasonable distance, and responds to that gestures. However, to have one of this applications working it is required some work either on the electronics and mainly on the programming. Furthermore, a more complete characterization of the sensor is also needed.

Furthermore, further tests may be done to prove the Diffusion Hypothesis. Some samples concerning the different approaches suggested in this project may be prepared with a high purity and then analysed using a microscope.

Additionally, the search for an optimized material specific for the soft technology is also important. Therefore, some research should be done in order to find a transparent polymer. The ideal polymer would have an Young’s Modulus in order of $0.1\, 1\, MPa$, a strain limit up to $300\%$, an electrical conductivity of $10^3 S/m$ and a dielectric constant in order of $10$.

Another possible future approach can be using soft elements to build soft electronic components. Despite it was not tested yet, it can be used, for example liquid crystals in the soft technology. Liquid crystals are particles that can be orientated when a voltage is applied and, therefore, it might be possible to produce a soft transistor based on liquid crystals.
7.2 Publications

The work developed in this dissertation resulted in the following publications:

- Published:


- Prepared:

  1. Stretchable Conductive Polymers based on Sliver/Carbon, Micro/Nano, Particles/Tubes: A review Rui Rocha, M. Tavakoli

  2. Soft Bionic hand: capacitive all-elastomer pressure sensors M. Tavakoli, Rui Rocha, Eduardo Sportelli, Pedro Lopes
Chapter 7. General Conclusions
Bibliography


ing with ultra-high stretchability,” MEMS.


Appendices
Soft Bionics Hands with a Sense of Touch
Through an Electronic Skin

Mahmoud Tavakoli, Rui Pedro Rocha, João Lourenço,
Tong Lu and Carmel Majidi

Abstract Integration of compliance into the Robotics hands proved to enhance the functionality of under-actuated hands for prosthetic or industrial applications. An appropriate design of the finger geometry with compliant joints allows the fingers to adapt to the shape of the object, and the soft and compliant skin allows for a higher contact area and contact friction. In this article, we describe how these properties were exploited for the development of compliant hands that are simple, efficient and easy to control. We also discuss integration of soft pressure and bending sensors into the digits of these hands.

1 Introduction

About a quarter of the motor cortex in the human brain (the part of the brain which controls all movement in the body) is devoted to the muscles of the hands. This shows the complexity of the human hand, which is composed of 34 muscles. It is clear that individual control of many of the hands joints and thus muscles requires considerable effort from the brain. However many of the tasks, such as grasping, is pretty instinctive for humans and does not involve a considerable brain effort.

Neuroscientists research shows that to control the complicated hand mechanism for a grasping action, the human brain does not control each joint and muscle individually, but utilizes some predefined motion pattern or synergies [1]. Therefore, as stated by Bicchi et al., all joint configurations belong to the s-dimensional manifold, where s expresses the number of synergies” [2]. This means that only a limited number of the vast possible joint configurations are used by humans.

The term synergy comes from the Attic Greek word synergia from synergos, meaning “working together”. A grasping synergy, thus makes the control of the hand “easier” for the brain. On the other hand, if we consider the human hand as a rigid
mechanical system, the limited number of predefined synergies will result in a limited number of contact points which does not comply with the range of the objects that one grasps each day. When the size and shape of the objects slightly change, using the same synergy cannot result in a stable grasp. But the key point here is that the human hand is not a rigid system. Compliance of the musculoskeletal system, of the skin and of the object combine in an overall grasp stiffness. This results in a new definition of synergy, called soft synergy [3], since the hand compliance allows several possible contact point posture with the same joint posture. Thus, the integration of compliance into the anthropomorphic hands will help in increasing the range of the objects which can be grasped.

2 Compliance in “Soft-Hands”

Compliance allows several possible contact point posture with the same joint posture. One approach for integrating compliance into the hands, is to integrate compliant joints and soft skin into the hand. Pisa-IIT Softhand [4], ISR-Softhand [5], Flexirigid [6], SDM hands [7] and the UB hand [8] are examples of recent development of soft hands that directly integrate the compliance into the joints. In Pisa-IIT Softhand several elements are interconnected with elastic elements, while in UB hand the joint compliance is achieved by integration of springs into the joints.

One development of our group was ISR-Softhand. ISR-Softhand is a low cost and highly adaptive hand system that embeds elastic joints and soft elements. For more information, readers are invited to see [5].

Figure 1 shows the first prototype of the ISR-Softhand. Except the thumb palmar abduction joint (actuated manually), all other joints are composed of elastic materials. Each finger has a single tendon, which drives the MCP and PIP joints simultaneously in order to perform the finger flexion. The PIP joint is designed with a higher stiffness compared to the MCP joint. In this way, if the MCP joint is blocked (meaning that the first contact with the object is established) the tendon force is applied to the PIP joint and thereby the PIP closes until surrounding the object. With only 3 actuators for flexion of the thumb, the index finger and the other 3 fingers, ISR-Softhand can imitate 21 out of the 33 grasp forms that humans perform in their daily activity (from the feix taxonomy [9], and for more 10 grasp posture, ISR-Softhand can perform an approximate posture to the one of the human (Fig. 1)[10].

Another example of a soft anthropomorphic hand is the UC-Soft hand (Figs. 2 and 3) [11]. The UC-Softhand is also composed of soft digits, but also benefits from an innovative twisted string actuator, which is low-cost, light weight and non-backdrivable. We modelled and developed a novel twisted string actuation scheme that can fit into the palm of a human [12]. While the number of actuators is same as the ISR-Softhand, the actuation strategy is different. Here, the thumb’s Palmar abduction is actuated by sacrificing the independent flexion of the thumb and index finger (coupled together).
In fact, this decision was the result of two independent and comprehensive analyses: on the actuation strategy of an anthropomorphic hand for a better anthropomorphism [13], and the other one on the actuation strategy for better functionality [10]. Selection of the actuation strategy for prosthetic hands is indeed one of the most important stages of optimization for the design of prosthetic hands. Therefore, in these two comprehensive analyses [10, 13], we showed how different actuation strategies can affect the functionality and anthropomorphism of the hand (in terms of grasping postures). These two benchmarks and the related analysis (anthropomorphism and functionality), helps a designer to choose the best actuation strategy for a prosthetic hand. For instance, both analysis showed the importance of the Palmar abduction in increasing both indices of anthropomorphism and functionality.

3 Soft Electronic Skin for Prosthetic Hands

For three main reasons we are interested in integration of an electronic skin into the hand.

- First, since a sense of touch is an important, but a missing factor in the today’s prosthetic hands. The sense of touch, brings the feeling that the prosthetic terminal is a part of the body and not an external machine.
Fig. 2 UC-Softhand is composed of a twisted string actuator scheme, making it very low cost, simple and light-weight.

Fig. 3 UC-Softhand has an independent actuator dedicated for rotation of the thumb.

Fig. 4 Body-actuated hand with soft digits.

- Second, because sensing the contact pressure, allows us to make a closed-loop control of the hand, thus we reduce the control effort from the amputee, and facilitate its usage.
- Third, since the bending profile of a soft and under-actuated finger, does not always correspond to the position of its tendon/ pulley, and depends on the shape of the object. Therefore, an encoder installed on the pulley does not provide the control system, precise information regarding the bending profile of the digits. Therefore a bend sensor integrated directly into the joints of the soft fingers is very beneficial (Fig. 4).

Details of the design and implementation of the electronic skin is out of focus of this article. But as can be seen in Fig. 5, the skin is composed of pressure sensors embedded in the finger tips and bend sensors that are embedded in the joints. The sensors are made from Ecoflex-30 (smooth-on) which is a biomedical grade silicone with mechanical properties similar to those of the human skin. The conductive layers of the sensors can be made by a stretchable silicone (e.g. Sylgard 184 or Ecoflex) dopped with conductive particles (usually silver or carbon). To pattern the specific
shape of the sensor, several methods can be used, including screen printing, Laser patterning and lifting [14]. Integration of these sensors helps to make the hand more autonomous and less dependant to the amputee. For instance, closing the control loop of the hand with the force feedback feature, makes the hand more autonomous. Furthermore, the sense of touch can be transmitted to the amputee. Finally, this is a low-cost method that does not require integration of expensive pressure sensors.

4 Conclusions

Integration of compliance into robotic hands for prosthetic applications brings many advantages which were not possible with rigid hands. First, a better adaptability to objects on underactuated digits of the hand is possible, simply by an appropriate design of the elastic properties of each of the joints. Second, a soft skin can improve highly the quality of the contact between the object and the fingers (bigger contact area and higher contact friction). Third, with the recent advances on soft and stretchable electronics, it is possible to embed low cost pressure and bend sensors into the fingers. As a result of these sensors, the sense of touch can be transferred to the amputees and the control of the hand can be simpler for them.

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References


Analysis on the conductance of Carbon based cPDMS and implications on additive manufacturing of stretchable electronics

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Abstract

Carbon dopped PDMS (cPDMS), have been used as a conductive polymer for stretchable electronics. Compared to liquid metals, cPDMS is low cost and it is easier to process or to print with an additive manufacturing process. However, changes on the conductance of the carbon based conductive PDMS (cPDMS) were observed overtime and specially after integration of cPDMS and the insulating polymer. In this article we investigate the process parameters that leads to improved stability over conductance of the cPDMS over time. Slight modifications on the fabrication process parameters were conducted and changes on the conductance of the samples for each method were monitored. Results suggested that change of the conductance happens mostly after integration of a pre-polymer over a cured cPDMS, and not after integration of the cPDMS over a cured insulating polymer. We show that such changes can be eliminated by adjusting the integration priority between the conductive and insulating polymers, by selecting the right curing temperature, changing the concentration of the carbon particles and the thickness of the conductive traces, and when possible by changing the insulating polymer material. In this way, we obtained important conclusions regarding the effect of these parameters on the change of the conductance over time, that should be considered for additive manufacturing of soft electronics. Also, we show that these changes can be possibly due to the diffusion from PDMS into cPDMS.

I. Introduction

Electronics that are intrinsically soft and stretchable have the potential to revolutionize the way in which humans physically interact with machines. By matching the compliance, elasticity, and density of human tissue, soft electronics could adhere to the skin or be incorporated into clothing without causing discomfort or constraining natural motion. In recent years, a broad range of materials, composites, and so-called “deterministic” micropatterned architectures have been introduced to support soft and stretchable electronic functionality [1]. These include conductive textiles composed of Ag-coated elastane fabrics (e.g. MedTex P-130; Statex), spray-deposited films of SWCNT on an elastomer substrate [2], microfluidic channels of liquid-phase metal embedded in polydimethylsiloxane (PDMS) [3], and wavy circuits composed of pre-buckled or serpentine Au and Cu wiring [4]. Another common approach is to use conductive rubber composites composed of elastomers filled with percolating networks of conductive microparticles, ranging from Ag microflakes in a fluoropolymer [5] to acetylene carbon black (CB) in Polymethylsiloxane (PDMS) [6], [7].

Among these existing soft electronic materials, CB-filled conductive PDMS (cPDMS) elastomers are particularly attractive for their intrinsic mechanical properties – soft (elastic modulus ∼1 MPa), highly stretchability (above 100% strain), and low density (∼1 g/cm³) – low cost, and ease of manufacturability through laser patterning [8], screen printing, and additive manufacturing (e.g. syringe-based 3D printing). However, in spite of their promise as an inexpensive and versatile material for wearable electronics, cPDMS can suffer from poor electronic performance depending on the method for rapid prototyping. In particular, using screen printing, stencil lithography, or 3D printing to combine uncured cPDMS and insulating PDMS can lead to significant loss of conductance in the embedded cPDMS traces. This particularly happens after integration of insulating polymers into the cPDMS. Such processes can occur for several days and in some cases, the reduction in the conductance of the composite continues until it drops below the percolation threshold.
and loses conductance.

Figure 1 shows one of the applications of the all-elastomer stretchable sensors which are embedded in the fingers of the new versions of ISR-Softhand and the UC-Softhand [7], [8]. Patterned geometries of cPDMS are embedded inside an elastomeric skin in order to measure the pressure on the finger tip and bending of the joints.

In this manuscript, we examine the change in conductance of cPDMS traces embedded in insulating PDMS. We produce samples with stencil lithography and casting as these are among the most popular, rapid, and inexpensive ways of producing cPDMS-based electronics. Specifically, we created custom masks and molds to produce several sensing elements with different combinations of insulating polymers, curing methods, CB concentration, and geometry. We show that by appropriate selection of these parameters, it is possible to produce reliable and long lasting cPDMS that would keep their conductance constant for long periods. These findings are useful for different fabrication methods including soft lithography, screen printing, 3D printing, and other methods in which conductive and insulating elastomer are deposited while still in their uncured state.

II. Experimental Method

The purpose of this study is to understand the reason behind the changes on the conductance of the cPDMS and, based on that, suggest methods to minimize the conductance loss. We observed that the changes on conductance happen after curing the cPDMS and after integrating the cPDMS on the PDMS. In some cases, the resistance of a pattern became stable after a couple of hours. However, in some other cases, the resistance increased over the course of several days, up to the point of sometimes the sensor becoming non-conductive. The goal of this study is to understand the effect of materials and fabrication process parameters on the conductance of the cPDMS over time and to suggest a fabrication process that results in stable conductivity over time.

A. Materials

The cPDMS was produced by mixing PDMS (Sylgard 184; 10:1 base-to-catalyst ratio; Dow Corning) with acetylene CB. The minimum weight percentage of CB necessary for conductivity was found to be around 12 wt%. In the experiments, we tried two compositions based on 16% and 25% weight of carbon black. For concentrations larger than 25 wt%, the material becomes too viscous to be manually mixed and fill the molds. Thus, 25 wt% was the highest concentration considered in this study. Even so, we added acetone to the silicone and CB mixture to make it less viscous. EcoFlex 00-30 and PMC Urethane (Smooth On) were both produced by mixing part A and part B in equal amounts by volume or weight.

B. Fabrication

The general fabrication method for every sensor is based on integration of patterned cPDMS with an insulating polymer (PDMS, ecoflex, Urethane). This was done either by surface printing through a stencil, or by lifting from a laser patterned mold. For the lifting process molds were produced by engraving an acrylic sheet (figure 3a. and figure 3c., molds A and B, respectively). For the surface printing (figure 3e.), a stainless steel stencil was produced by a laser cutter (mold C). We fabricated stretchable strain and pressure sensors with different dimensions, insulating materials and process. All sensors are fabricated either by first creating a layer of an insulating polymer and then depositing the cPDMS using the patterned molds, or by first filling the molds with cPDMS and then pouring the insulating prepolymer over it.

In summary, sensors were produced using three different techniques in order to reflect the differences in the curing order, i.e. PDMS first, cPDMS first, or both cured together:

- Stencil lithography in which PDMS is cured first (130°C for 25 min.) and then uncured cPDMS is deposited using a stainless steel stencil. The excess cPDMS is cleaned in such a way that when the stencil is removed, only the desired pattern remains over the PDMS layer. Both layers are then cured at 130°C for 25 minutes or at room temperature for 48 hours. (Fig. 2a).
- Referring to Fig. 2b, acrylic mold is first filled with cPDMS. After the excess is removed, the cPDMS is cured at 130°C for 25 minutes. Lastly, a PDMS layer with a thickness of 0.5mm is added on top of the cPDMS and is cured at room temperature for 48h or again in the oven under the same conditions.
- Referring to Fig. 2c, the mold is first filled with cPDMS and the excess is carefully removed. In this method, it is impossible to clean the mold afterwards, meaning that it is imperative to clean all the material that may create shortcuts between the paths before pouring the final layer of PDMS. The sample is then either cured in the oven at 130°C for 25 minutes or placed at room temperature to cure for 48h.

The width×thickness dimensions (in mm) of the cPDMS channels for each developed sensor are: (0.6, 1.5, 3) × (0.25, 0.3, 0.4) and (1.5, 3) × (0.35, 0.4, 0.6, 0.9)

C. cPDMS and PDMS integration

Fig. 4a shows a close-up picture of some of the sensors. Using the molds from Fig. 3, 148 different sensors were built and extensive tests concerning their resistance were performed. The resistance of the sensors
**Figure 1:** a.) The new version of the ISR-Softhand with embedded pressure sensors b.) Soft elastomeric fingers with all elastomer pressure and bending sensors c.) An example of a pressure sensor before integration into the hand d.) the sensor is composed on patterned cPDMS sandwiched between layers of PDMS and is then embedded in an ecoflex substrate e.) Percolating networks of CB inside the PDMS assures conductivity of the cPDMS traces.

**Figure 2:** Schematics depicting each of the fabrication methods: a.) Curing PDMS first; b.) Curing cPDMS first; c.) Curing PDMS and cPDMS at the same time.

was measured at specific instances (fresh, cured and integrated) and over time, at 24h intervals over a six days period, and then the test was repeated after one year!!!!!

- **Fresh** - right after mixing the composition and casting it into the mold;
- **Cured** - right after curing the cPDMS (not applicable if PDMS and cPDMS are cured together);
- **Integrated** - right after integration and curing of the PDMS layer (if cured in the oven, a waiting period of 30 minutes is given for the sensor to cool down);
- **Over time** - every 24 hours after integration.

Sensor measurements are presented in Figs. 5 and 6 and demonstrate the influence of CB concentration, sample thickness, and curing method for linear sensor
Figure 3: Molds used to make the cPDMS patterns: a.) Acrylic mold made using a laser-cutting machine (“S” refers to the laser speed and “P” to its power) to engrave patterns with dimensions (1.5, 3) × (0.35, 0.4, 0.6, 0.9) mm; b.) Mold made in the back of a PCB using a CNC to engrave the patterns; c.) Acrylic mold made using a laser-cutting machine to engrave patterns with dimensions (0.6) × (0.25, 0.3, 0.4) mm; d.) Close-up of a spiral pattern; e.) Mold made from a 0.1mm stainless steel sheet (stencil).

Table 1: Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>cPDMS layer</td>
<td>0.6 × (0.25, 0.30, 0.40)</td>
</tr>
<tr>
<td>(Width × Thickness)</td>
<td>1.5 × (0.25, 0.35, 0.40, 0.60, 0.90)</td>
</tr>
<tr>
<td>(mm)</td>
<td>3 × (0.25, 0.35, 0.40, 0.60, 0.90)</td>
</tr>
<tr>
<td>Carbon Percentage</td>
<td>16%wt</td>
</tr>
<tr>
<td>Curing Order</td>
<td>cPDMS first</td>
</tr>
<tr>
<td></td>
<td>PDMS first</td>
</tr>
<tr>
<td></td>
<td>Both together</td>
</tr>
<tr>
<td>Temperature</td>
<td>At 130°C for 25 minutes</td>
</tr>
<tr>
<td></td>
<td>At room temperature for 48h</td>
</tr>
</tbody>
</table>

designs. The curing methods are defined as the following:

1) Method 1 - first cure a layer of cPDMS alone in the oven for 25 mins at 130°C and then add on top of it a layer of uncured PDMS. Cure the two layers in the oven for 25 mins at 130°C;

2) Method 2 - first cure a layer of cPDMS alone in the oven for 25 mins at 130°C and then add on top of it a layer of uncured PDMS. Cure the two layers at room temperature for 48h;

3) Method 3 - cure cPDMS and PDMS at the same time in the oven for 25 mins at 130°C;

4) Method 4 - cure cPDMS and PDMS at the same time at room temperature for 48h;

5) Method 5 - first cure a sheet of PDMS and then use the steel stencil molds to print the cPDMS sensors on top of it. Take everything to cure in the oven for 25 mins at 130°C;

6) Method 6 - first cure a sheet of PDMS and then use the steel stencil molds to print the cPDMS sensors on top of it. Take it to cure at room temperature for 48h.

Figure 4: Samples of the produced sensors: (a.) Close-up of the two types of sensors; (b.) Sensors developed in acrylic molds; (c.) Measuring the resistance of a spiral sensor using a pair of acupuncture needles; (d.) Sensors made using the CNC-milled PCB (notice the irregularities on the cPDMS tracks).
To be able to compare the changes on the resistance, all the lines in the plots were normalized by their corresponding fresh value. Due to the nature of methods 3, 4, 5 and 6, where the curing and integration develop at the same time, it was impossible to measure the cured resistance values of the cPDMS, and thus these values were omitted in the respective plots.

III. Results and Discussion

In this section we discuss the obtained results in details.

A. Sensor Resistance

Whenever it was possible to obtain the cured value, it became apparent that the resistance of the cPDMS pattern always decreased after curing in relation to the freshly made uncured cPDMS, as is exemplified in figure 5. This is due to the evaporation of some of the chemicals in the composition during the curing process which causes an increase in concentration of carbon microparticules. To track the changes on the resistance of the traces, the actual comparison should be between the resistance value of the traces right after curing and then over time. As can be seen in figure 5, it is actually the integration stage that causes an increase in the resistance from the cured value (This is when cPDMS and PDMS are put in contact). This is probably because the cPDMS becomes less concentrated in carbon particles, when it get in touch with PDMS.

1) Influence of Thickness: Figure 5 shows the effect of the thickness of the traces on the change of the conductivity over time. The thinner the cPDMS track is, the higher is the rate of the increase of the resistance, after integration with the PDMS. This is probably because the material exchange between PDMS and cPDMS happens mostly at the boundary between both polymers and the neighbouring regions. As the distance grows from the contacting surfaces, the carbon concentration of the corresponding layers is less affected. If the region not affected by the diffusion is much larger than the one that is, the influence of the diffusion is lessened. Therefore, thinner sensors are more prone to loss of the conductivity than the thicker ones. This can be further observed across both tables IV and V. Furthermore, small thicknesses, at times, may introduce some instability in the sensor conductance as can be seen in the left plot of figure 5 where the 0.35mm thickness does not exhibit a well-defined plateau.

2) Influence of Concentration Gradient: By comparing the same lines between the left and right plots in figures 5 and 6, and specially by looking at the thinnest sample (0.35mm), it can be seen that the loss of conductivity is more visible in the sample with lower carbon concentration. On the lower concentration of Cb in cPDMS, and when the percolation threshold is passed only slightly, a small material migration between cPDMS and PDMS, can immediatly drop the CB percentage below the percolation threshold. However for higher concentration of CB, the molecules migration has a smaller impact on conductivity. But increasing the percentage of the CB is not always desired, since it changes the mechanical properties of the cPDMS. It is normally desired to reach the percolation threshold with the lowest amount of added particles.

3) Influence of Curing Temperature, Order, & Time:

These three factors also have a significant effect on the overall conductance of the sensors (see figure 6). For instance, it can be seen that adding uncured PDMS on top of cured cPDMS (methods 1 and 2) has a worse effect when compared to the situation in which uncured cPDMS is deposited over cured PDMS (methods 5 and 6). This situation is not limited to the particular conditions of figure 6 since careful examination of tables IV and V reveals the trend repeats itself for different sensor parameters. The fact that adding the uncured PDMS over cPDMS has a worse effect than the converse method, suggests that either the uncured PDMS is able to creep into the CB aggregation of cPDMS, or the CB aggregations of cPDMS can move into the lower viscosity PDMS. The effect of the curing order can be studied by comparing only the methods in 6 that share the same curing temperature and time, that is, methods 1, 3 and 5 (in which the samples are cured at overn), and methods 2, 4 and 6 (in which the samples are cured at room temperature). In the first set, sensors built by curing the PDMS and the cPDMS (method 3) together always performed the best. In the second set, where all materials are cured at room temperature, method 6 (cure first PDMS and then pour cPDMS over it), was the one that exhibited the best results. In its uncured form, cPDMS is essentially carbon particles in suspension within uncured PDMS. When uncured PDMS and uncured cPDMS are integrated together, they are still in liquid phase and the diffusion that occurs is mostly of PDMS going back and forth between the uncured polymers. The carbon particles, which are much larger than the pre-polymers PDMS molecules, remain relatively unmoved, causing the net effect of the diffusion to be reduced and thus limiting it. For short curing periods, this is the main reason why method 3 is also the best method among all six methods. However, if the duration increases, the net effect starts to become more noticeable and the resistance of the sensor begins increasing relatively to the corresponding fresh value. That is why method 6 actually becomes the best approach in the second set of methods.

In order to correctly analyze the effect of curing temperature and time on the sensors, we should only compare method pairs that share the same curing order: methods 1 and 2 (first cure cPDMS and then cure PDMS), methods 3 and 4 (cure PDMS and cPDMS at the same time), and methods 5 and 6 (first cure PDMS and then cure cPDMS). As seen in the right plot from figure 6, methods 1, 3 and 6 were always better than methods...
Figure 5: Left Plot: Dependence of the Normalized Resistance (to the Fresh Value) on the Thickness of the Sensor (Linear with 1.5mm Width) for the Curing Method 2 and 16% Carbon Case. Right Plot: Dependence of the Normalized Resistance (to the Fresh Value) on the Thickness of the Sensor (Linear with 1.5mm Width) for the Curing Method 2 and 25% Carbon Case. The resistance drop from the fresh to cured value is due to the evaporation of the solvents. After cPDMS is cured in all cases the resistance increases compared to the cured value. It can be seen in both plots that when the sample is thinner the change of the resistance is higher. Also by comparing the two plots, one can see that the resistance of the cPDMS with lower carbon concentration is increasing more than the same geometry of sensor with more carbon concentration on PDMS.

Figure 6: Left Plot: Dependence of the Normalized Resistance (to the Fresh Value) on Curing Method for a 16% Carbon 0.6 × 0.25mm Linear Sensor. Right Plot: Dependence of the Normalized Resistance (to the Fresh Value) on Curing Method for a 25% Carbon 0.6 × 0.25mm Linear Sensor.

Figure 7: Left Plot: Comparison between linear and spiral shapes for different thicknesses (Method 1, 0.6mm Width, 16% Carbon). Right Plot: Comparison between linear and spiral shapes for different thicknesses (Method 1, 0.6mm Width, 25% Carbon)

2, 4 and 5, respectively. By increasing the temperature and reducing the curing time, we are actually limiting the diffusion time. This is the main reason why methods 1 and 3 are better than methods 2 and 4. Methods 5 and 6, are not different, and in both cases the change of the resistance is minimum. This shows that curing PDMS before integration of the cPDMS, is a good practice.

IV. Analysis of the results and Discussion

In this section we further analyze the results. We first discuss a bit further the diffusion hypothesis as a possible reason for the change of the resistance of the cPDMS
sensors and discuss how these results can be used in order to improve the fabrication process of the cPDMS based traces, for reliable and long lasting conductive traces whose resistance stays constant during a long time.

The variations observed in the electrical conductivity of cPDMS samples suggest that a material migration or diffusion is the most convincing hypothesis as the reason for loss of the conductivity. Such diffusion at the boundary between the PDMS and cPDMS is responsible for increasing resistance of the cPDMS over time. In order to investigate other factors, such as the effect of environmental factors such as oxidation, solvent effects, etc., we performed another test. We fabricated one trace of cPDMS (0.5 mm × 2 mm × 45 mm) for different CB concentration without combining them with any insulator polymer and measured the resistance for 220 hours. As can be seen in figure 8 results show that the resistance did not change over 220 hours, expect for the 15% sample, in which the resistance slightly decreased. This shows that other environmental factors do not change the resistance of the samples, and such changes happens only when the cPDMS gets in touch with PDMS.

Figure 8: Plot of the variation of the resistance over 220 hours.

The variations over time observed in the resistance values are indicative of changes in carbon concentration within the cPDMS which, in turn, may be a product of the way diffusion develops. A drop in conductivity implies that either PDMS is creeping into the cPDMS or that conductive material (CB aggregations) is leaving the cPDMS. Also, it should be mentioned that most of the parameters in table I have an effect in the way diffusion interacts with sensor conductance: a large thickness provides more robustness against the carbon loss/PDMS gain; when we change the curing order, we are actually changing the diffusion couple which means the curing order gives rise to different $D$ coefficients. Curing temperature and time have a direct impact in the $D$ parameter and Fick’s Second Law, respectively.

We then tested addition of two different insulating stretchable polymers to evaluate the results. In addition to PDMS, we opted for PMC Urethane and Ecoflex 30 (both for smooth-on). cPDMS was cured first and uncured PDMS, Uretheane, and Ecoflex was added to it. We let the samples to cure in the room temperature. As can be seen in figure 9, and as we expected, when combined by urethane, the conductivity of the cPDMS remains constant. The reason behind this is that the bonding between PDMS and Urethane is generally poor. But ecoflex presents the most poor results and conductivity of the cPDMS in contact with ecoflex decreases substantially. Ecoflex bonds well with PDMS, but in addition, the curing process of ecoflex is affected by CB. That is when ecoflex is mixed with CB, it does not cure. For this reason, when adding ecoflex to cPDMS, the ecoflex in touch with cPDMS stays liquid and can diffuse for a longer time, compared to PDMS. Once more this shows that the bonding stage between the polymers is the reason behind the loss of the conductivity.

A previous study on morphology of the carbon black doped polymers [7] compared the aggregation of CB in polymers with different viscosities, and suggested that in a lower-viscosity matrix, CB aggregates diffuse and form an agglomerate-network. While in a higher viscosity the aggregate diffusion slows down significantly. This also fortifies the diffusion hypothesis, since as uncured PDMS gets in touch with the cured cPDMS, the CB aggregate can diffuse into the lower viscosity network.

Independent from the reason behind the loss of conductivity over time, it is shown that it is possible to minimize this effect in order to fabricate conductive traces that are reliable over a long period.

V. Effect of other factors

As mentioned, it seems that the change of the conductance on the samples is due to some kind of material exchange between the conductive and insulating polymers.

A. The Diffusion depth

We first evaluate if the second Ohm’s law is valid for the cPDMS tracks. To do so it was patterned 10 traces of cPDMS (19 wt%) with length from 5 to 50 mm and with constant width and thickness, 2 mm and 0.5 mm respectively. As expected, the increase of length led to a linear increase of resistance, figure 10.

Figure 11 shows how diffusion impairs the percolation in the cPDMS layers that are joined to PDMS. Since cPDMS and PDMS bond together strongly, it will be difficult to unbound them and examine the cross section with microscopy. However, we try to estimate the diffusion depth by a comparative study.

If we consider samples with 16% of CB, we can assume that small amounts of the diffusion on layers of cPDMS drops the CB percentage below the conductivity threshold and become non conductive. Here we define $t_d$ as the effective depth of the diffusion. That is, if we are...
Figure 9: From left to right: Changes in electrical resistance when the uncured Urethane, PDMS and EcoFlex respectively, are added to previously cured cPDMS.

Figure 10: Validation of second Ohm’s law for cPDMS.

Figure 11: $t$ shows the overall thickness of the patterned cPDMS and $t_d$ shows the diffusion depth after integration of the PDMS, impairing the percolation of CB in the border layers.

Table II: Depth of diffusion, $t_d$, for method 1

<table>
<thead>
<tr>
<th>$t_0$ (mm)</th>
<th>$R_{cured}$</th>
<th>$R_{72h}$</th>
<th>$t_f$ (mm)</th>
<th>$t_d$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>2.97</td>
<td>31.2</td>
<td>0.02</td>
<td>0.23</td>
</tr>
<tr>
<td>0.3</td>
<td>0.927</td>
<td>3.76</td>
<td>0.74</td>
<td>0.23</td>
</tr>
<tr>
<td>0.4</td>
<td>0.574</td>
<td>1.44</td>
<td>0.16</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table III: Depth of diffusion, $t_d$, for method 2

<table>
<thead>
<tr>
<th>$t_0$ (mm)</th>
<th>$R_{cured}$</th>
<th>$R_{72h}$</th>
<th>$t_f$ (mm)</th>
<th>$t_d$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>0.108</td>
<td>1.16</td>
<td>0.03</td>
<td>0.32</td>
</tr>
<tr>
<td>0.4</td>
<td>0.091</td>
<td>0.271</td>
<td>0.13</td>
<td>0.27</td>
</tr>
<tr>
<td>0.6</td>
<td>0.044</td>
<td>0.0891</td>
<td>0.30</td>
<td>0.30</td>
</tr>
</tbody>
</table>

This means the actual resistance of each sample produced by each method, can be calculated by

$$R = \frac{\rho l}{w} \times (t - t_d)$$

while the $t_d$ of each fabrication method can be estimated by one experiment. Also, as it was expected the $t_d$ for the method 1, in which the samples are cured in the oven, is lower than the $t_d$ of the samples with method 2.

B. Improved durability for cPDMS

It is shown that the durability of the conductivity of the cPDMS depends on several factors. First of all, when possible, a higher concentration of CB on PDMS (e.g. over 20% weight) is recommended. The higher concentration proved to be less prone to loss of the conductivity, since even a small diffusion cannot devast the percolating CB network. Second, Since the diffusion happens up to a limited depth, when possible thicker cPDMS is preferred. In any case, the first two recommendation have disadvantages, and both of them are undesired for many applications. Third, if possible, the cPDMS and PDMS should cure together (and not one of them before the other). Forth, if the previous method is not possible, PDMS should be cured before cPDMS and not vice versa. Fifth, In all cases curing at the oven results better than curing in the room temperature. Finally, an urethane insulator may replace the PDMS. Even though the bonding between PDMS and Urethane is not very good, it is possible to sandwich a cPDMS pattern between two films of urethane.
C. Implication for fabrication techniques and 3D Printing

Based on these analysis, we can draw some conclusions that will be useful for the operation of the SML soft electronics additive manufacturing machine. An example of a 3D printer for producing cPDMS-based electronics and sample prints of soft electronics with this machine are presented in Fig. 12 and Fig. 13. The printer relies on a motorized syringe extrusion-based technique: two different syringes, one carrying PDMS and another cPDMS, act in conjunction with a heated printing bed in order to produce the desired patterns. The hardware interfaces with the computer host through an Arduino Mega and a specialized motherboard (Ramps 1.4). First of all, recall that because the operating principle is based in extrusion syringes, the materials on their inside are necessarily in an uncured stage. This causes a general technical difficulty in additive manufacturing due to the polymers having a low viscosity which causes them to spread when deposited on the printing table. Consequently, we are interested in curing each layer before adding a new one. However, this is not always a good idea due to the negative effects on the conductance.

When depositing the first layer of PDMS, the machine should wait until this layer cures before pouring the uncured cPDMS on top, effectively mimicking methods 5 and 6 depending on the curing temperature used. However, quickly after adding the cPDMS pattern and without waiting for the cPDMS to cure, an additional top layer of PDMS must be deposited over the cPDMS for them to cure together (similarly to methods 3 and 4). This is possible because cPDMS has a higher viscosity and does not lose its integrity after adding the top PDMS layer. In short, methods 5/6 would develop between the bottom layer and the cPDMS, and methods 3/4 between the cPDMS and the top PDMS layer. This is the procedure that guarantees long lasting cPDMS tracks, considering the technical limitations imposed by the viscosity of the uncured polymers.

Based on this fact, we enhanced the early version of the printer with a heating bed (Fig. 13). In this way, the layers are cured based on the priority order explained above.

VI. Conclusion

In this article, we evaluated the effect of composition, layer thickness, curing order and curing temperature, and some insulating materials on the change of the conductivity on soft and stretchable electronics that are composed of PDMS and cPDMS layers. We found out that the change on the conductivity is happening due to the diffusion process between the PDMS and cPDMS layers. We also show that by calculating the effective diffusion depth for each fabrication method, the eventual resistance of the tracks can be calculated. From the interpretation of the results we suggested that such diffusion can make the cPDMS less populated with conductive particles, thus resulting in the loss of conductance. However, by careful selection of the diffusion parameters one can limit the effective diffusion depth, and thus limit the changes on the conductance. Conductive cPDMS tracks with lower changes on their resistance are obtained when curing cPDMS and PDMS layers together at high temperatures, or if the PDMS is cured before integration of the cPDMS. In all cases, deposition of an uncured PDMS over cured cPDMS should be avoided as much as possible. These findings can help in the design of the fabrication process both by manual or additive manufacturing methods, so that the conductivity of the cPDMS layer can be maintained fix for long time.

Acknowledgment

This work was supported by the Portuguese Foundation of Science and Technology and the CMU-Portugal program, under the contract numbers CMUP-EPB/TIC/0036/2013 and CMUP-ERI/TIC/0021/2014.
References


VII. Support Material
Table IV: Resistance of the sensors produced with cPDMS with 16% of carbon. (in MΩ)

<table>
<thead>
<tr>
<th>Mold</th>
<th>Cure method</th>
<th>0.168</th>
<th>0.196</th>
<th>1.35</th>
<th>1.36</th>
<th>3.01</th>
<th>14.48</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Linear</td>
<td>0.62</td>
<td>0.6</td>
<td>0.25</td>
<td>0.27</td>
<td>0.37</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Linear</td>
<td>0.36</td>
<td>0.37</td>
<td>0.12</td>
<td>0.14</td>
<td>0.2</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>N.A.</td>
<td>0.2</td>
<td>0.21</td>
<td>0.13</td>
<td>0.15</td>
<td>0.18</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>N.A.</td>
<td>0.1</td>
<td>0.11</td>
<td>0.06</td>
<td>0.07</td>
<td>0.09</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>N.A.</td>
<td>0.05</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>2</td>
<td>Linear</td>
<td>0.22</td>
<td>0.22</td>
<td>0.12</td>
<td>0.14</td>
<td>0.2</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Linear</td>
<td>0.13</td>
<td>0.13</td>
<td>0.09</td>
<td>0.11</td>
<td>0.13</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>N.A.</td>
<td>0.09</td>
<td>0.09</td>
<td>0.06</td>
<td>0.07</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>N.A.</td>
<td>0.06</td>
<td>0.06</td>
<td>0.04</td>
<td>0.05</td>
<td>0.06</td>
<td>0.03</td>
</tr>
</tbody>
</table>

* Cure method:
1 - first cure a layer of cPDMS alone in the oven for 25 mins at 130°C and then add on top of it a layer of uncured PDMS. Cure the two layers in the oven for 25 mins at 130°C; 2 - first cure a layer of cPDMS alone in the oven for 25 mins at 130°C and then add on top of it a layer of uncured PDMS. Cure the two layers at room temperature for 48h; 3 - cure cPDMS and PDMS at the same time in the oven for 25 mins at 130°C; 4 - cure cPDMS and PDMS at the same time at 130°C; 5 - first cure a sheet of PDMS and then use the steel stencil molds to print the cPDMS sensors on top of it. Take everything to cure in the oven for 25 mins at 130°C; 6 - first cure a sheet of PDMS and then use the steel stencil molds to print the cPDMS sensors on top of it. Take it to cure at room temperature for 48h;
Table V: Resistance of the sensors produced with cPDMS with 25% of carbon. (in MΩ)

| Mold | Cure method | Pattern | W x T (mm) | 25% of weight in carbon | Cure method | Dimensions | 0,6 x 0,25 | 0,6 x 0,4 | 0,6 x 0,3 | 0,6 x 0,25 | 0,6 x 0,4 | 0,6 x 0,3 | 0,6 x 0,25 | 0,6 x 0,4 | 0,6 x 0,3 |
|------|-------------|---------|-------------|------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| 1    | linear      | spiral  | 0,0066      | 0,0122                | linear      | 0,0349     | 0,172       | 0,181       | 0,161       | 0,156       | 0,157       | 0,197       | 0,197       | 0,197       | 0,197       |
|      | linear      | spiral  | 0,0066      | 0,0122                | linear      | 0,0349     | 0,172       | 0,181       | 0,161       | 0,156       | 0,157       | 0,197       | 0,197       | 0,197       | 0,197       |
|      | spiral      | linear  | 0,0066      | 0,0122                | spiral      | 0,0349     | 0,172       | 0,181       | 0,161       | 0,156       | 0,157       | 0,197       | 0,197       | 0,197       | 0,197       |
|      | spiral      | linear  | 0,0066      | 0,0122                | spiral      | 0,0349     | 0,172       | 0,181       | 0,161       | 0,156       | 0,157       | 0,197       | 0,197       | 0,197       | 0,197       |
| 2    | linear      | spiral  | 0,0066      | 0,0122                | linear      | 0,0349     | 0,172       | 0,181       | 0,161       | 0,156       | 0,157       | 0,197       | 0,197       | 0,197       | 0,197       |
|      | linear      | spiral  | 0,0066      | 0,0122                | linear      | 0,0349     | 0,172       | 0,181       | 0,161       | 0,156       | 0,157       | 0,197       | 0,197       | 0,197       | 0,197       |
|      | spiral      | linear  | 0,0066      | 0,0122                | spiral      | 0,0349     | 0,172       | 0,181       | 0,161       | 0,156       | 0,157       | 0,197       | 0,197       | 0,197       | 0,197       |
|      | spiral      | linear  | 0,0066      | 0,0122                | spiral      | 0,0349     | 0,172       | 0,181       | 0,161       | 0,156       | 0,157       | 0,197       | 0,197       | 0,197       | 0,197       |
|      | linear      | spiral  | 0,0066      | 0,0122                | linear      | 0,0349     | 0,172       | 0,181       | 0,161       | 0,156       | 0,157       | 0,197       | 0,197       | 0,197       | 0,197       |
|      | linear      | spiral  | 0,0066      | 0,0122                | linear      | 0,0349     | 0,172       | 0,181       | 0,161       | 0,156       | 0,157       | 0,197       | 0,197       | 0,197       | 0,197       |
|      | spiral      | linear  | 0,0066      | 0,0122                | spiral      | 0,0349     | 0,172       | 0,181       | 0,161       | 0,156       | 0,157       | 0,197       | 0,197       | 0,197       | 0,197       |
|      | spiral      | linear  | 0,0066      | 0,0122                | spiral      | 0,0349     | 0,172       | 0,181       | 0,161       | 0,156       | 0,157       | 0,197       | 0,197       | 0,197       | 0,197       |

Note: The table continues with similar entries for different conditions and measurements.
Stretchable Conductive Polymers based on Sliver/Carbon, Micro/Nano, Particles/Tubes : A review

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Abstract—Stretchable Conductive Polymers are an important building block for stretchable sensors. The composition of polymer composites and their fabrication method determines their electro-mechanical properties. This article provides a review of fabrication methods and composition of carbon and silver based conductive polymeric composites, with nano/micro sized particles/tubes. It also provides a review on resistive and capacitive measurement methods for sensors made out of these composites, namely on their response time, repeatability, and recovery time. Finally it summarizes the advantages and disadvantages of each composition for fabrication of stretchable sensors.

I. INTRODUCTION

Stretchable sensors are an important building block of the wearables. Various fabrication methods have been studied by investigators for development of stretchable sensors. This includes liquid metals embedded on micro-channels of a stretchable material, and composites based on micro/nano particles/tubes of Carbon, Graphene, Silver, Copper, etc [1]–[5]. Liquid metals are good conductives and when embedded in a soft matter to form a sensor, they provide a fast response to the external stimuli such as strain, in form of a change of resistance. However, these

In spite of composites have worse conductivity than liquid metals, they have the advantages of easy shaping, low density and a wide range of electrical conductivities, which strongly depends on the particle that is used. There are many different composites that can be used to produce stretchable sensors, such as nano or micro size composites, silver, carbon or other conductive particles. The focus in silver and carbon particles is even better conductor than the carbon particles, and is not discussed in any other article found, there is a factor that leads to an increase of viscosity when the composition of poly + conductive particles should not be too viscous neither too liquid. In fact, either the polymer and the particles should be carefully chosen to ensure a good viscosity. An important factor that leads to an increase of viscosity is the concentration of conductive particles. As will be discussed in this article and is not discussed in any other article found, there is a strong dependence on the size of particles and its effect on the properties of the mixture.

Nano particles, such as Carbon Nanotubes (CNTs) [6] or Silver Nanowires (AgNWs) [7], which has different properties when compared with micro size particles, have became an interesting object of research due to their improved mechanical and electrical properties when embedded in a polymer - such as polydimethylsiloxane (PDMS). Since the smaller particle size, it is possible to have much more particles in a same volume fraction, comparing with micro particles. This effect helps to ensure that each particle is close to each others, producing a reliable path for the electrons flow. For this reason, these kind of particles are being considered to produce soft and wearable sensors, capable of detect and measure stretch and pressure forces, once they allow the producing of sensors, which also has good viscosity levels when in liquid state. By achieving a desired viscosity level that permits a good handling, it is possible to idealize future fabrication methods, such as a 3D printer that previous makes the mixture and is capable of cast the result of the mixture in a PDMS layer. This will ensure a reliable and repetitious method to fabricate sensors. However, it is important to have a viscosity level that is liquid enough that the solution could flow through the syringes of the 3D printer but is viscous enough to avoid the draining of the dropped fluid.

 Depending on many factors, such as type of conductive material used, the particle size, the fabrication methods [8]–[15], the polymer matrix that coats the conductive part, the electrical and mechanical properties as well as the sensitivity, the precision, the restore time, the linear range, the accuracy and the resolution of each sensor could be a lot different, which leads to researches to find the properties of the sensor that ensures which is the most reliable for the desired application [16], [17]. This article includes descriptions about some of these factors and explanations about the lost of conductivity.

II. PARTICLE SIZE

As was already written the size of particle is a major factor for producing conductive polymers. Although there are many types of nano particles - Single-Wall Carbon Nanotubes (SWCNT), Multi-Wall Carbon Nanotubes (MWCNT) Graphene NanoParticles (GNP) Silver NanoWires( AgNW) - the maximum diameter and length of these examples are around 200nm and 20µm, respectively, to the AgNWs [7]. While the dimensions of a carbon fiber (micro particle) are around 5µm in diameter and 200µm in length [18], which means that each micro particle occupies 250 times more volume than a nano particle. This also means that in multiple
samples with the same volume, the number of nano particles is much more bigger than the number of micro particles, for the same volume fraction.

The distribution of particles from Figure 1 assumes a uniform distribution. However, in the case of nano particles, this is not what happens in a real situation. Due to the huge number of particles, it must be considered the electrostatic interactions and van der Waals forces, which leads to agglomeration of particles, Figure 2b). When particles become agglomerated, instead of the distribution is like the one of the figure, it will have spaces with a big concentration of particles and other spaces without any particle. The agglomerations reduce the electrical conductivity, because of the empty spaces just filled with polymer matrix - which could be considered as an insulator -, and the fracture toughness, because they act as a stress concentrator when the sensors are stretched. To avoid the effects of electrostatic and van der Waals interaction it must be considered a method to ensure the good dispersion of the particles.

Furthermore, another relevant factor is the aspect ratio of each particle. The aspect ratio is the ratio between the length and the diameter of the particles. With the values mentioned before, it is possible to verify that a nano particle has a higher aspect ratio than a micro particle. In fact, the nano particles could have more than 100 times the aspect ratio of the micro particles. The importance of the aspect ratio is related with the internal resistance of the conductive layer of the sensors and means that, for the same volume fraction, the nano particles have much more surface area than the micro particles.

Comparing sensors made with liquid metal and nano or micro composites, it could be verified that the later has lower electrical conductivity level because does not have the behaviour of a metal. Despite this fact, one other reason of the reduced conductivity could be explained by the use of a polymer matrix that is not a conductor. When the sensors are fabricated, the insulator material fills the gaps between each particle of the conductive material. Despite the large number of nano particles, there is also some gaps between particles that are filled with polymer, decreasing the conductivity of the sample. Although the polymer is the responsible for the decreasing of the electrical conductivity, it ensures some mechanical properties, e.g. the stretch ability, that were not possible without it.

III. PERCOLATION THEORY

To ensure the electrical conductivity of the polymers it may exist a path that allows the electrons to flow from one side to the opposite side. As was already explained, the flow of the
electrons is not uniform owing to the gaps between particles, which are filled with insulator material. Therefore, to exist electrical conductivity each particle should be in contact with other particles. If there are a considerable distance between particles the sensor does not conduct electricity. This concept is explained by the Percolation Theory [20].

A. Tunneling Effect and Contact Resistance

The conductivity of the polymers is dependent of the number of contacts between particles. In spite of it depends on the properties of the conductive material, it can be assumed that, when the electrons flow inside the particles, the resistance is negligible. However, when the electric signal has to cross the junction between two particles there is an intrinsic resistance. This resistance is called Contact Resistance (CR) and has a significant role to analyse the conductivity of the polymers. It must be considered that, even if the particles are perfectly dispersed, they are randomly oriented. Consequently, the junctions between particles could occur at the ends of each particle - perfect situation - but it could also occur that one overlap the other. This means that it may have more junctions than it was expected, which leads to an increase of the overall resistance.

When the effects of the CR in the conductivity was analysed it was concluded that it cannot be the only responsible for the loss of conductivity because the results showed that the conductivity is lower than it should be, if this was the only factor that increase the resistance. In fact, in some cases the conductivity is much lower than it should be [21].

It was found that this increase in electrical resistance is because some particles are close to each other but they are not in touch. This means that the electric signal has to cross the polymer matrix, which has an high electrical resistance. When this occurs it is called as Tunneling Effect (TE) and refers to situations when there are a gap in the path of particles responsible to ensure the percolation. Although the high resistance, the TE could help to maintain the conductivity when the gap is very small.

As can be seen in Figure 3, the resistance due to TE has a great dependence with the distance that has to be crossed in the insulator material. Adding this effect to the CR it could be written:

$$ R_{film} = R_{contact} + R_{tunnel} \quad (1) $$

where \(R_{contact}\) is the Contact Resistance and is assumed to be constant, \(R_{tunnel}\) is the Tunneling Resistance and is dependent from the distribution of the particles and can vary when the sensor is stretched, and \(R_{film}\) corresponds to the total resistance of the film. It is desirable that \(R_{film}\) is the lowest possible and for that the tunneling distance should be small. If the distance is around 1.0 nm the tunneling resistances are in the order of 100 GΩ, which is several order of magnitude larger than the CR. Above this distance, the film could be considered as non-conductive. Figure 3 also illustrates the effect of the diameter of the tubes. It could be verified that the larger the tube diameter is, the lower the tunneling resistance is. However, it is not a significant difference, which means that it is not a major factor to concern about.

Figure 4 shows how the nano particles are distributed in a polymer matrix and examples of the effects described before. According these facts described before, it could be explained the importance of the aspect ratio and the large number of particles. The higher the aspect ratio is, the bigger is the path that the electric signal could travel without resistance. Furthermore, a large number of particles correlated with a good dispersion, where the particles are uniformly distributed, means that the distance between particles is small. If the distance between particles is small the Tunneling Effect is low and, consequently, the conductivity is acceptable.

B. Concentration of particles

The Percolation Theory can only be applied if the concentration of particles in the sample is enough to ensure the conductive path [22]. By increasing the concentration, the number of particles and the viscosity also increase. It is not desired that the concentration is as high that it becomes hard to mixture with PDMS because the sample become to viscous to mixture, [23], [24]. To avoid too high concentration, a compromise between number of particles and viscosity should be made. Considering the Percolation Theory there is a Percolation Threshold, which means that, when the concentration of particles is below that threshold, the film has small conductivity but by gradually increase the concentration of particles, when the concentration is close to this threshold the composite undergoes an insulator-to-conductor transition. Above the Percolation Threshold the conductivity is almost constant, even if the concentration is much higher than this threshold [25], [26]. The Figure 5 shows an illustration of this explanation.

Once more, the particles size has an effect on the conductivity. As was already explained, for the same concentration the number of particles is very different. For example, in Figure
1 there are only 2 Al₂O₃ particles but there are 442 millions of CNT, for the same volume fraction. This permits to predict that the threshold for nano composites is lower than the one for micro composites. In fact, despite the threshold is different from each polymer, Figure 6, the micro filler content needs to be as high as 10⁻⁵⁰ wt.%. On the other hand, the nano filler content just has to be as low as 0.5 wt.%. The concentration threshold is very important for those who needs to produce some sensors to ensure that they use the correct quantity of conductive material.

Bauhofer et al., [27], summarized the effect of experimental parameters on the percolation threshold of CNT/polymer nanocomposites and determined that the critical factors for the percolation threshold are:

1) aspect ratio.
2) disentanglement of CNT agglomerates.
3) uniform distribution of CNTs.

IV. DISPERSION AND FUNCTIONALIZATION

Most of the Carbon Nanotubes that are commercially available, are supplied in the form of heavily entangled bundles, mainly due to the strong van der Waals interactions. In this state, the CNT are not ready to use because it means that they will not be distributed uniformly in the polymer, which leads to the creation of some gaps in the matrix and in a decrease of the electrical and mechanical properties.

Therefore, to properly use nano particles, such as CNT, some methods are used to ensure a good dispersion of the entangled bundles, [28], and, consequently, a uniform distribution in the polymer matrix.

A. Dispersion

In this section, some methods to disperse the CNT will be briefly described. Some of these methods could lead to the damage of the particles, which is not desirable, but necessary. These methods consist in break the bundles into small pieces. However, sometimes the pieces became too small, decreasing the aspect ratio, which makes the sample as a non-conductor.
1) Ultrasonication: This is an effective method to disperse particles in liquids having a low viscosity, such as water, acetone or ethanol. This means that it should be used when the particles are suspended in a solution and the solution is dropped on the polymer. After that, the solution is dried by light heating. It also means that it cannot be used in those fabrication methods which nano particles are mixed with viscous polymers, such as PDMS, and the mixture is then poured above a polymer layer.

The method consists in applying ultrasound energy to the solution. The ultrasound waves will agitate the particles in the solution with the purpose of separate the bundles of particles. However, if it is used high energy, or even if the particles are subjected to the treatment for too long, the nano particles can be easily and seriously damaged - some defects are generated on their surface.

2) Ball milling: Ball milling is a type of grinding method used to grind materials into extremely fine powder. It consists in a cylinder container with tiny and rigid balls inside. During the milling, a high pressure is generated locally due to the collision between the rigid balls. The balls could be made of different materials, but they should be rigid enough to sustain the impact forces of the collisions.

Inside of the container it could also be added some chemicals to enhance the dispersion and to introduce some functional groups to the surface of nano particles, as will be described below.

3) Stir and extrusion: Stir is a common technique to disperse particles in liquid systems and can also be used to disperse the nano particles when they were already mixed in a polymer matrix. The dispersion is achieved by intensive stirring the particles using a propeller. The size and the shape of the propeller and the mixing speed control the dispersion results.

On the other hand, extrusion is a popular method to disperse material into solid polymers. It consists in twin screws, which rotates at high speed, creating high shear flow. It will lead to the dispersion of the agglomerated particles.

4) Calendering process: More commonly known as three roll mills, is a machine tool that employs the shear force created by the three rollers to mix, disperse and homogenize viscous materials. By using this machine, the particles could be previously mixed with polymer and then the result is poured in the machine, as can be observed in Figure 8.

The first and the third rollers from the figure 8, called, respectively, feeding and apron rollers, rotate in the same direction, while the centre roller rotate in the opposite direction.

The dispersion occurs by adding pre-dispersed mixtures into the machine. The opposite rotation of the rollers n1 and n2, will transport the material to the bottom of the centre roller, which transports it to the second gap, between centre and apron roller. In this gap, the material is dispersed to the desired degree of fineness, due to the narrow distance and shear force between rollers. There are some machines, where the velocity of each roller and the distance between rollers could be controlled for the desired purpose.

This process could be repeated several times to maximize the dispersion and it is probably the best approach to disperse the entangled particles.

Peng-Cheng et al resumed all these methods in a table, Table I, that could be used to compare each method. [18]

B. Functionalization

As was already introduced, it is possible to add chemical groups to the walls of the nano particles, for example in the CNTs. By adding some chemical groups, the load transfer across the CNT/matrix interface are enhanced. This transformation in the surface of nanotubes is called functionalization.

There are two different types of functionalization: chemical and physical functionalization. The chemical is based on the covalent linkage of functional entities onto carbon scaffold of CNTs. Due to the aromatic nature of the bonds in CNTs, they are chemically stable. Therefore, the chemical functionalization is based in a change of hybridization from $sp^2$ to $sp^3$ and a simultaneous loss of $\pi$ - conjugated system. This process can be made by react some molecules of a high chemical reactivity with the original CNTs.

Furthermore, the physical functionalization is based on a non-covalent method. For this method, some polymers are added to the suspension of CNTs, which leads to the wrapping of polymer around CNTs to form supermolecular complexes.
Table I: Resume of all dispersion methods described [18]

<table>
<thead>
<tr>
<th>Technique</th>
<th>Factor</th>
<th>Suitable polymer matrix</th>
<th>Governing factors</th>
<th>Availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrasound</td>
<td>Yes</td>
<td>Soluble polymer, low viscous polymer or oligomer, monomer</td>
<td>Power and mode of sonicator, sonication time</td>
<td>Commonly used in lab, easy operation and cleaning after use</td>
</tr>
<tr>
<td>Calendering</td>
<td>No</td>
<td>Liquid polymer or oligomer, monomer</td>
<td>Rotation speed, distance between adjacent rolls</td>
<td>Operation training is necessary, hard to clean after use</td>
</tr>
<tr>
<td>Ball milling</td>
<td>Yes</td>
<td>Powder (polymer or monomer)</td>
<td>Milling time, rotation speed, size of balls, balls/CNT ratio</td>
<td>Easy operation, need to clean after use</td>
</tr>
<tr>
<td>Shear mixing</td>
<td>No</td>
<td>Soluble polymer, low viscous polymer or oligomer, monomer</td>
<td>Size and shape of the propeller, mixing speed and time</td>
<td>Commonly used in lab, easy operation and cleaning after use</td>
</tr>
<tr>
<td>Extrusion</td>
<td>No</td>
<td>Thermoplastics</td>
<td>Temperature, configuration and rotation speed of the screw</td>
<td>Large-scale production, operation training is necessary, hard to clean after use</td>
</tr>
</tbody>
</table>

The polymer wrapping process is obtained through the van der Waals interactions and $\pi - \pi$ stacking between CNTs and polymer chains containing aromatic rings.

Once more, Peng-Cheng et al resumed all the chemical and physical functionalization methods in a table, II, that is reproduced below.

The chemical functionalization could damage the surface of the CNT. However, if the particles in use are Multi-Wall CNT the damage is less than if it was Single-Wall CNT, because the boundary layer of MWCNT is affected but the intern layers are not affected, while the SWCNT just have one layer, so if it is affected all the composite is affected.

V. CARBON NANOTUBES/SILVER NANOWIRES EMBEDDED IN A POLYMER MATRIX

As described previously, nano particles, such as CNT or AgNW, seem to have an high potential to be embedded in polymers in order to fabricate soft and stretchable sensors. For this purpose, most of the fabrication methods consist, basically, in to apply the conductive layer - as a solution of conductive material or a mixture of polymer and conductive material - above a polymer layer already cured. After that the conductive layer is cured and then another polymer layer is poured above the conductive material. Despite some differences between each method, these steps are almost the same for every fabrication method. The final result is a polymer that is an insulator in its external layers but has a conductive film embedded, where, for example, the electrical resistance can be measured. These polymers can be used as sensors due to the changes in electrical resistance when the film is subjected to external forces. Another approach is to prepare CNT films known as buckypaper, made only of CNTs, no matrix, and put them in a polymer or composite at the site where is needed for local strain measurement. [29]

There are two different types of sensors, based on its fabrication - resistive and capacitive [30]–[32]. While the resistive sensors are a continuous path of conductive material in a serpentine form, capacitive sensors are like a capacitor, which means that they have two conductive and parallel plates separated by a dielectric layer, such as PDMS. Despite both of them could detect and measure external forces with a linear response, there are some differences in terms of sensitivity, hysteresis, time of response, etc. The lasts tests showed that the capacitive sensors could be better than resistive sensors in most of these aspects. For example, a resistive sensor takes a lot of time to recover its original resistance when a defect in the morphology of the sensor is applied. By contrast, a capacitive sensor could recover its capacitance much faster than the resistive one. Despite the differences both types can detect and measure stretch and pressure forces. In the resistive sensor, every change that is promoted to the sensor means a rearrangement in the particles distribution, which signifies variations in the electrical resistance. On the other hand, when a capacitive sensor is stretched or pressed, there is a decrease in the thickness of the dielectric layer, which means that the conductive plates became closer to each other and leads to a change in the capacitance of the sensor.

In a micro scale, it could be assumed that the distribution of nano particles is like the one in Figure 4a). As the sensors are made by stretchable and malleable polymer, when they are stretched it leads to an rearrangement of the distribution of the composites. Along the stretching of the polymer, the nano-composites follow this behaviour, which could break some junctions between particles, or increase the distance between them. This will increase the Tunneling Effect and, consequently, the Contact Resistance, which results in a lower conductivity. When the stretch are released, the particles resume its original position and almost all of the junctions are recovered. It means that the sensors show a good repeatability, with just a small level of hysteresis. Comparing CNTs and AgNWs, it could be said that the results are better for the first ones. For the AgNWs it was verified that the nanowires just assume a stable position after 5 or 6 stretching and releasing cycles [7]. This effect could be seen in figure 9

By analysing the graphic from Figure 9a) it could be verified that after the first stretch some junctions are broken and did not recover after the releasing cycle. It is explained by the increase of the resistance at 0% strain after the first cycle. However, from the fifth cycle, the values of the resistance are constant, which means that the position of the CNT at 0% strain is also constant. This effect signify that the sensor shows repeateability after the fifth cycle. However it also signify that the sensor has a small range of response - between 50% and 80% of tensile strain. Nevertheless, beyond 50% strain, the resistance increase linearly with the strain, following the same path of the first stretching. Even if this effect is less visible in
CNTs, it is possible to avoid this behaviour. For doing that, the conductive layer of CNTs should be poured in a pre-stretched polymer. However, this strategy cannot be followed to produce AgNW due to the weak adhesion between AgNWs film and the pre-stretched PDMS surface.

The CNT/polymer composites also shows a linear response with strain, [33], [34] . Furthermore, they could be subjected to tensile strains much higher than AgNWs/polymer due to better mechanical properties of the CNT and its better ability to hold stretch forces. Another comparison between AgNWs and CNTs that should be made is the percolation threshold. Both particles need much less concentration to achieve the percolation threshold than micro particles. While for micro particles the percolation threshold is around $15 - 50\text{wt}\%$, for CNTs, for example, it is possible to find thresholds as low as $0.1\text{wt}\%$ [27].

REFERENCES


