



**Politecnico
di Torino**

Politecnico di Torino

Master's degree in Nanotechnologies for ICTs

A.a. 2025/2026

July 2026

Fabrication of flexible devices for wearable sensing based on materials derived from natural sources

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Abstract

The demand for flexible devices is rapidly increasing due to their ability to overcome the limitations of conventional bulk electronics in wearable technologies. Nowadays, the highest-performance flexible devices still rely predominantly on synthetic polymers that have significant environmental impact. Consequently, a wide interest has emerged in developing alternatives to these materials that are both biodegradable and biocompatible.

Gelatin is a natural polymer derived from animal skin that intrinsically possesses both properties, making it a promising candidate for flexible sensing. Upon methacrylation, gelatin becomes photoresponsive, enabling photopolymerization a process capable of creating specialized three dimensional geometries improving the device performance. Based on this approach a Gelatin Methacrylated (GelMA) hydrogel was investigated and demonstrated high sensibilities as a tensile sensor, exhibiting a gauge factor of approximately 2.1.

Alternative, Laser Induced Graphene (LIG) technology enables the fabrication of conductive structure directly from non-conductive precursor materials. Lignin is a biopolymer derived from plant biomass and represents a sustainable precursor for the graphene production through LIG processing. By combining gelatin, lignin and LIG process an electronic skin (e-skin) was fabricated with patterned strain gauges structures. The resulting device functioned as a bending sensor capable of detecting finger-joint motion when attached to the human body.

Table of Contents

1	Introduction.....	1
1.1	Hydrogel.....	2
1.2	Hydrogel Sensor.....	4
1.2.1	Electronic conductive hydrogels (ECH)	4
1.2.2	Ion conductive hydrogels (ICH).....	5
1.2.3	Composite Conductive Hydrogels	6
1.3	Hydrogel from natural materials	6
1.4	GelMA.....	7
1.5	Long-term stable gels.....	8
1.5.1	Eutectogels	9
1.6	Flexible Sensor.....	12
1.6.1	Mechanical sensors	12
1.7	3D printing	17
1.7.1	Light based 3D printing	17
1.7.2	Estrusion-based 3D printing.....	20
2	Laser Induced Graphene	24
2.1	Graphene	25
2.1.1	3D Porous Graphene	27
2.2	Laser Induced Graphene	28
2.2.1	Laser Parameters	29
2.2.2	Chamber atmosphere.....	32
2.2.3	LIG from ligneous materials	33
2.2.4	LIG-Hydrogel application.....	34
3	Materials and methods	38
3.1	GelMA synthesis.....	38
3.2	Eutectogel and organogel synthesis	39
3.3	Substrate for LIG.....	40
3.4	3D printing	41
3.4.1	Material testing.....	41
3.4.2	Printing.....	42

3.5	Laser induced graphene.....	43
3.5.1	Encapsulation	43
3.6	Material characterization.....	44
3.6.1	Rheology and viscosity	44
3.6.2	FESEM.....	45
3.6.3	EDX.....	46
3.6.4	RAMAN.....	46
3.6.5	Recycle test	47
3.6.6	Biodegradability test	48
3.7	Electrical test.....	48
3.7.1	electrochemical impedance spectroscopy (EIS).....	48
3.7.2	Sheet resistance	49
3.7.3	Tensile test	50
4	Results and discussion.....	54
4.1	Hydrogel.....	54
4.1.1	Photorheology	54
4.1.2	3D printing	56
4.1.3	Mechanical Test	57
4.1.4	Electrical test.....	58
4.1.5	Conductivity.....	59
4.1.6	Laser Induced Graphene on hydrogel	60
4.2	Gelatin, PVA thin film for LIG.....	62
4.2.1	Substrate conductivity	63
4.2.2	Laser induced graphene.....	64
4.2.3	Raman	65
4.2.4	FESEM.....	66
4.2.5	Recyclability	67
4.2.6	Encapsulation	69
4.2.7	Bending test.....	70
4.2.8	Biodegradability	73
5	Conclusion.....	74
6	Bibliografia	75

List of Figures

Figure 1.1: A) stress-strain curve for the P(VDF-HFP) hydrogel with different ratio of P(VDF-HFP) and PEGDA. B) schematic illustration of the Zig-Zag structure of the P(VDF-HFP) hydrogel. [5]	3
Figure 1.2: conceptual diagram of the different approach for conductive hydrogel. [7]	4
Figure 1.3: schematic illustration of the production process of the electronically conductive PVA/PAM hydrogel using PEDOT as the conductive filler. [9]	5
Figure 1.4: methacrylation process process of gelatin. [102]	8
Figure 1.5: sensing abilities of the ionogel with 20% concentration of EMIM:DCA at A) different temperature and B) different storage time at -20 °C. [21].....	9
Figure 1.6: solid liquid phase diagram of mixture A) Highlighting the solid and liquid region. [103] B) Highlighting the difference between an ideal eutectic mixture and a “deep” eutectic mixture. [24]	10
Figure 1.7: A) classification of types of DES based on the formula Cat ⁺ X ⁻ zY. [24] B) chemical structure of some B) HBD and C) HBA [100].	10
Figure 1.8: A) and B) plot describing are loss of weight vs time of NAM eutectogel and hydrogel, respectively. In C) is carried out a torsion and bending test, D) comparison between eutectogel and hydrogel. [26]	11
Figure 1.9: physical mechanism of resistive sensors under tensile strain. [105]	13
Figure 1.10: eutectogel mixture of Polyvinylimidazole(PVI) and DES (ChCl and urea) A) example of the application as strain sensor applied to the finger joint with different angle of bending. B) stress-strain curve of the eutectogel. [30]	13
Figure 1.11: tactile sensors made from a capacitive sensor, the dielectric material is a hydrogel of P(VDF–HFP) and an ionic liquid EMIM:TFSI to improve the EDL formation and the conductive layer is a hydrogel of PVA and PEDO:PSS, A) working principle and EDL formation during external pressure. B) Sensitivity curve with the normalized C variation vs the applied pressure. [36].....	15
Figure 1.12: A) Structural diagram of the piezoelectric sensor with the Conductive PVA/Gelatin hydrogel (CPGH) sandwich between the PVDF film. B) Sensitivity of the sensor with different hydrogel thickness [40].	16
Figure 1.13: Different methods of light-based 3D: A) stereolithography(SLA), B) Digital Light Processing(DLP) and C) two-photon polymerization (TPP) [44].	18

Figure 1.14: printing tests of the P(Aam-co-AAC) hydrogel and the effect of Glycerol(Gly) and Hydroxyethylcellulose(HEC) in the printed material for 3 different geometries [46].	19
Figure 1.15: schematic illustration of the mechanism of two photon absorption [99]. Where E_1 and E_2 are the energy of the two-photon absorbed exciting the molecule to different excited state E_f .	20
Figure 1.16: example of extrusion based 3D printing: A) Fused Deposition Modeling (FDM) and B) Direct Ink Writing (DIW) [44].	21
Figure 1.17: application of DES and Carpool hydrogel: A) demonstration of the resolution writing the word Green using DIW and B) auxetic sensor to monitor the joint movement [48].	22
Figure 2.1: Example the fabrication of Laser Induced Graphene with different shape [92].	24
Figure 2.2: planar hexagonal chemical structure of carbons in graphene. [50]	25
Figure 2.3: conduction and valence bands of graphene showing the six Dirac point [93].	25
Figure 2.4: Review of different fabrication methods of graphene evaluated in 5 characteristics: quality(G), cost of production (C) cost of production, scalability (S) , purity (P) and yield (Y). [50]	26
Figure 2.5: Representation of the stacking of 2D graphene into 3D porous graphene. [56]	27
Figure 2.6: chemical structure of Kapton showing the two key component ODA and PDMA. [104].	28
Figure 2.7: Difference in the excited area for different pulse laser.	29
Figure 2.8: SEM imaging of the A)Laminar, B)porous and C)fibrous graphene. [57]	30
Figure 2.9: Schematic of the overlapping due to the High PPI values. [96]	32
Figure 2.10: A) The chemical structure of Lignin shown its aromatic ring. B) Super capacitor fabricated onto the coconut shell. [73]	33
Figure 2.11: A) fabrication of LIG-PVA B) schematic of the LIG-PVA electrode. [80]	34
Figure 2.12: LIG-hydrogel actuators working principle. [81]	35
Figure 2.13: A) Stress-strain curve and B)Resistance-strain curve of the for the LIG - and PPHP hydrogel device for different concentration of MXene. [82]...	36
Figure 3.1: Synthesis process of GelMA: A) Experimental set-up. B) Mixture after the addition of Methacrylic anhydride. C) Dialysis set-up. D) Mixture put inside various container for lyophilization.	38
Figure 3.2: Resin at different Lignin concentration from 0% to 40% respect to GelMA.	40
Figure 3.3: Chemical formula of Lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP).	40

Figure 3.4: A) First solution composed by 1g of Lignin sulfonate and 0,4g of ZnO and 10 ml of DI water. B) Second solution of 1g of PVA and 10 ml of DI water C) results of the two solution together after the dehydration.....	41
Figure 3.5: A) semilogarithmic plot of exposure energy required for each thickness. B) Circular spot of polymerized resin after the irradiation for material testing.	42
Figure 3.6: experimental set-up of the sample place onto a metal plate under the LIG laser.	43
Figure 3.7: A), B) shows the process for depositing the soybean oil onto the LIG. C) The final results after the soybean oil is polymerized.	44
Figure 3.8: functioning principle of the double parallel plate set-up for rheological test. [86].....	44
Figure 3.9: schematic illustrating the working principle of the FESEM microscope and its main components. [87]	46
Figure 3.10: Recycle process of the porcine gelatin substrate from the final LIG product to the regenerated liquid state.	48
Figure 3.11: A) Image of the sample between two plate and clamped between the probe tips of the Biologic. B) Example of Nynquist plot and its relative equivalent circuit [90].	49
Figure 3.12: Van Der pauw method for a square geometry. A) Schematic of the sample and related contact point. B) Four measurements performed in Van der Pauw. C) equation to calculate the horizontal and vertical resistance.	50
Figure 3.13: A) CAD dimensions used to print dog-bone with UV Max (Asiga). B) tensile System used for the test.	50
Figure 3.14: A) Experimental configuration of bending test. B) Strain gauge geometries used for the bending test. C) Visual representation of the trigonometrical equation used to calculate the radius.	52
Figure 4.1: Rheologies tests of the hydrogel with LS concentration of w/w relative to GelMA. A) Elastic and viscous moduli before and after lamp switching on. Lamp was switched on after 60 s. B) Amplitude sweep for the formulation with CNF. C) Amplitude sweep for only DES and GelMA dissolved in DES. D) Photorheologies of only DES and gelMA analyzing the gel transition.....	54
Figure 4.2: Rheologies of the hydrogel for different LS concentration. A) Amplitude sweep performed after the polymerization. B) Details of the photorheologies when UV lamp is turn on at 60s. C) The behavior of G' during the photopolymerization.	55
Figure 4.3: Viscosity of the eutectogel resin for each LS concentration.	55
Figure 4.4: Unsuccessful polymerization of eutectogel with LS 20% w/w relative to GelMA using an UV light.	56
Figure 4.5: resolution test with difference cylinder with decreasing diameter.	56

- Figure 4.6:** A) 3D printed dog-bone shape hydrogel. B) Experimental set-up for tensile test. C) Stress-strain curve for Hydrogel at different concentration and the obtained Young's Modulus at each concentration. 57
- Figure 4.7:** Electrical curve for different LS concentration and their relative Gauge factor obtained as the slope of the curve at low strain. 59
- Figure 4.8:** Conductivity of the A) Hydrogel and B) Organohydrogel. 60
- Figure 4.9:** Attempts of LIG onto hydrogel substrate at A) 4% LS w/w respect to GelMA and B) 40% LS respect to GelMA and 30% ZnO w/w respect to LS. 60
- Figure 4.10:** A) Raman spectrum for different laser Power. B) Ratio of the peaks ID/IG and I2D/IG in the Raman spectrum. 61
- Figure 4.11:** A) Hydrogel with silver paste to ensure correct connection with LIG. B) Current-Voltage curve for the four configuration of the Van der Pauw method. 62
- Figure 4.12:** Thin film substrate for LIG for for A), B) PVA at glycerol 20% w/w relative to LS, C), D) Fish gelatin with glycerol concentration of 20% and 60% w/w relative to LS and E), F) Porcine gelatin with glycerol concentration of 60% and 80% w/w relative to LS. 63
- Figure 4.13:** Nyquist plot for A) PVA and B) porcine gelatin substrate. C) Comparison of the conductivity for different substrates. 64
- Figure 4.14:** Sheet resistance calculated using Van der Pauw method for substrate fabricated with different polymers and glycerol concentration. 65
- Figure 4.15:** A) Raman spectra of different polymeric substrate performed in both air and inert atmosphere. B) Ratio of the peaks intensity of the Raman spectra. 66
- Figure 4.16:** Image of the LIG pattern on different sample obtained through FESEM microscope. The sample observed were A) fish gelatin with glycerol 80% in inert atmosphere, B) PVA with glycerol 60% in inert atmosphere, C) porcine gelatin with glycerol 100% in air and D) porcine gelatin with glycerol 100% in inert atmosphere. All glycerol concentration are w/w relative to LS. E) and F) are details of the LIG patterned on gel porcine in O₂ and N₂, respectively. 66
- Figure 4.17:** The patterned LIG square obtained for each recycling cycle. 67
- Figure 4.18:** A) Horizontal resistance, B) vertical resistance and C) sheet resistance after each recycling cycle. 68
- Figure 4.19:** Raman spectra of the graphene square patterns onto gelatin substrate before and after recycling. 69
- Figure 4.20:** A) Resistance value of the strain gauges before and after the water was dropped for the soybean oil and uncovered substrate. B) Behavior of the resistance for the soybean oil and uncovered pattern immediately after the water was dropped. 69
- Figure 4.21:** A) during the bending test the strain gauges was placed in 2 configuration. In the first one the strain gauges is positioned to have the longer conductive path parallel to the bending direction and in the second one they were perpendicular to the bending direction. B) and C) are the

static and dynamic working curve for the bending test of the strain gauges. Static curve was obtained measuring the resistance at specific bending angles. Electrical resistance was measured every 2 mm of way. D) is the resistance variation during bending induced by manually pressing the sensor..... 70

Figure 4.22: A) Images of the sensor applied to the finger while rested and bent. B) Signal variation during the finger movement..... 71

Figure 4.23: A) and B) are the ΔR -strain curve for the encapsulated and non-encapsulated strain gauges, respectively. C) The calculated Gauge Factor for the two configurations. 72

Figure 4.24: hysteresis test performed over 300 cycles of loading and unloading with a displacement of 0,2 mm and speeds set at A) 2 mm/min and B) 20 mm/min. 72

Figure 4.25: Picture of the four pots both used to test degradability. There is a control pot with no sample place inside, one with just gelatin sample, one with only PVA sample and the fourth with both inside. The sample were observed for 15 days. 73

Chapter 1

1 Introduction

Since the beginning of the 21st century there is an increasing adoption of flexible and stretchable electronics in medical and healthcare technologies. This trend has led to the growth of the market for these types of devices. As a consequence, in the last years remarkable developments have been achieved in this field and gained widespread attention from both academia and industrial communities.

Their growing interest sprouts from their comfortable interface with the human body. Their flexibility makes them adapt to human movement, while typical deformation during daily activity doesn't affect their performance, removing the discomfort associated with using bulky and rigid electronic devices.

The term flexibility refers to abilities of a material to undergoes repeated bending without compromising its structural integrity, preserving its mechanical and electrical properties [1].

Different materials were used to fabricate flexible devices for example polymeric elastomers are commonly implemented, among them the most common is the silicon based elastomer PDMS. Unfortunately, several elastomers are biologically and mechanically incompatible with human tissues, resulting in interface delamination between the device and the human tissue [2]. In this context, the recent developments in conductive hydrogel have gained particular attention.

Nowadays the human impact on the environment has rapidly intensified. Pollution and waste continue to represent problems to be address [3]. The adoption of natural polymers offers a possible strategy, reducing the total impact on the environment. Two approaches are studied in this thesis to fabricate natural flexible devices: the first is a GelMA Hydrogel and the second is a gelatin substrate.

In the first chapter will be present what is a hydrogel is and how they are nowadays implemented as sensors.

Hydrogels are defined as a three-dimensional elastomeric network with high water content [2]. Sensors made from hydrogel present good biocompatibility with human skin and their Young's modulus is close to human skin making them adhere better and avoiding delamination. Although polymers commonly used in hydrogel fabrication are generally non conductive, hydrogel can be easily modified with conductive fillers that make them attractive for sensing application. One main drawback is their high water content, as it makes them susceptible to environmental condition and for example causes them to freeze at sub-zero temperatures. Recent advances in the field have come up with

various methods to overcome these problems. One promising solution is represented by eutectogels.

In this thesis will be present an eutectogel based on GelMa and a Deep Eutectic Solvent (DES) prepared with Glycerol and ChCl. Cellulose nanofibers (CNF) are added to the solution to increase the mechanical properties of eutectogel and Sulfonate lignin (SF) is also added as a dye to increase the resolution of the printed hydrogel.

The second approach involves a gelatin substrate enriched with Sulfonate lignin, lignin chemical structure contains numerous aromatic rings that when heated with a laser source can be turned into graphene. This method is known as Laser Induced Graphene (LIG) and it enables the development of sensor or conductive path starting from an insulating material. In the second chapter will discuss the working principle of LIG and its application starting from natural material.

1.1 Hydrogel

One of the notable advantages of hydrogels lies in the ease with which their mechanical properties can be modulated by controlling the synthesis process, thereby enabling optimal compatibility with human tissues.

Hydrogels can be classified according to two main criteria. The first classification is based on the type of polymer employed, which may be natural, synthetic, or hybrid. The second classification depends on the nature of the crosslinking mechanism used to form the hydrogel network [4]. Hydrogels can retain a significant amount of fluid in their network thanks to the crosslinks structure of the polymeric chains. Crosslinking is the method by which polymeric chains are connected and plays a crucial role in determining the physical and electrical properties directly. Crosslinking is usually divided into two groups physical and chemical.

Physically crosslinked hydrogels are created by non-covalent bonds such as ionic/electrostatic interaction and hydrogen bonding. These kinds of interactions are inter-molecular and relatively weak; meaning they are the first to break under an external stimulus but they are also the first to be reformed when the external stimulus is removed, making them reversible. The reversibility gives the resulted hydrogel lower rigidity and the ability to self- heal.

Chemical crosslinking are covalent bonds and stronger when compared with those of the physically crosslinked hydrogels that are usually considered as permanent. They are typically created via free radical polymerization. The most common kind of polymerization is photopolymerization, as the name suggests it is activated when the hydrogel is irradiated with UV or visible light. The requirements are the presence of unsaturated groups, most commonly use are methacrylic group (MA), and a photoinitiator. Photopolymerization is becoming a popular method to create hydrogel with tunable properties and complex three dimensional structure.

Building on the distinction between physical and chemical crosslinking, Double-crosslinked hydrogels integrate both approaches. Together the two types overcame the intrinsic limitation allowing the production of materials that are simultaneously robust and reversible. For instance, a double-crosslinked ionogel reported in the literature [5] was fabricated using a physically crosslinked poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) and chemically crosslinked poly(ethylene glycol)

diacrylate (PEGDA). It was prepared combining Direct ink Writing(DIW), a 3-D printing technique, and photo-polymerization. First, the ink consisted of P(VDF-HFP), PEGDA and the photoinitiator I2959, was printed onto an ecoflex film and after was photo-

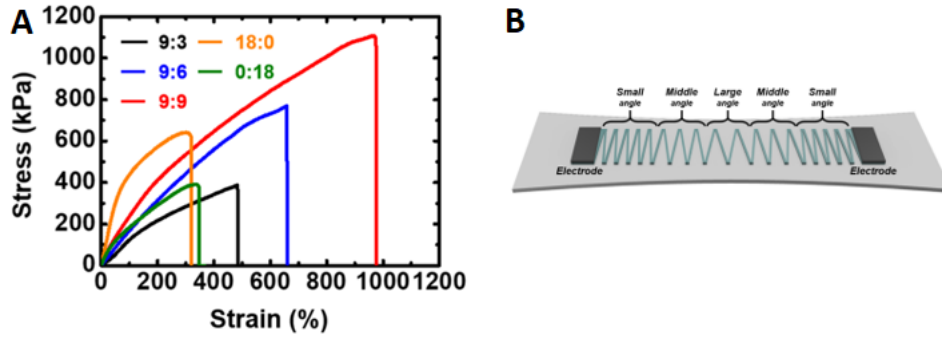


Figure 1.1: A) stress-strain curve for the P(VDF-HFP) hydrogel with different ratio of P(VDF-HFP) and PEGDA. B) schematic illustration of the Zig-Zag structure of the P(VDF-HFP) hydrogel. [5]

polymerized by exposing it to UV light (365 nm). Prior to irradiation the network only contained physical crosslinking with connected P(VDF-HFP), the final step activated the PEDGA inside the matrix, transition from single network physically crosslinked hydrogel to a double network hydrogel(DN).

The figure 1.1a shows how the hydrogel is strained under a specific external stress and how varying concentrations of P(VDF-HFP) and PEGDA change the behavior. This indirectly demonstrates how the two types of crosslinks play a role in determining hydrogel mechanical properties. The DN hydrogels is superior to both SN hydrogel (18:0 and 0:18), in particular by increasing the concentration of PEGDA from 3% to 9% the maximum stress and strain that it can support before broking increase more than double. This discussion highlights how the crosslinking strategy is closely linked to the hydrogel fabrication method, and consequently, how the physical and mechanical properties of hydrogels strongly depend on advancements in material design and processing techniques.

1.2 Hydrogel Sensor

Hydrogels have gained significant attention in flexible electronics due to their high stretchability; however, in order to be used in such applications, they must also be electrically conductive [6]. Conductive hydrogels incorporate various conductive components into the hydrogel matrix that establish conductive pathways increasing the electrical properties [7]. They are classified into different groups depending on whether

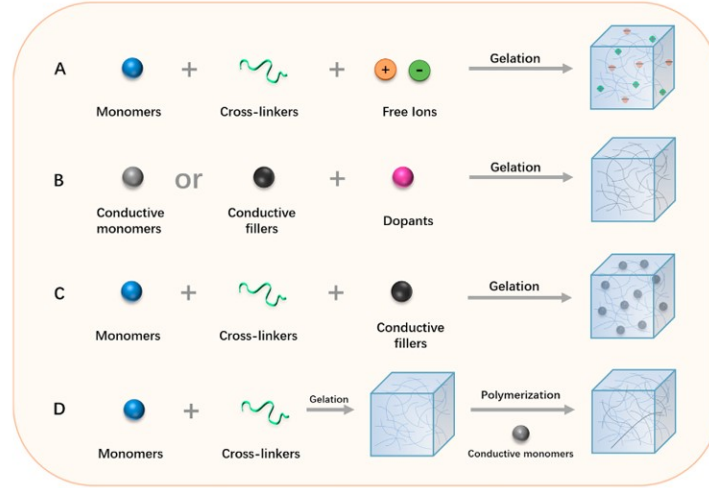


Figure 1.2: conceptual diagram of the different approach for conductive hydrogel. [7]

the conductivity arises from the transport of electrons or ions. Accordingly, they are referred to as electronic conductive hydrogels (ECH), ion conductive hydrogels (ICH), and composite conductive hydrogels (CCH) [6].

1.2.1 Electronic conductive hydrogels (ECH)

Commonly used fillers that provide electrons transport into hydrogels are carbon-based nanomaterials or metal nanoparticles or conductive polymers. [6]. A possible approach involves integrating the conductive filler or the conductive polymer directly into the hydrogel matrix, in this case the overall mechanical properties increase but the sensitivity still remains low mainly owing to poor interfacial interactions between rigid fillers and hydrogels matrix [6]. Meng et al. [8] observed with SEM a hydrogel with PANI as the conductive polymer and discovered that the filler presents itself as cluster separated from the main network, consequently the conductive filler only slightly contribute to the mechanical properties of the hydrogel. If the hydrogel has already good mechanical properties this is not a problem rather in same case avoid that their hampering. However, this configuration still presents limited sensitivity owing to poor interfacial interactions between rigid fillers and hydrogels matrix. An alternative strategy consists of incorporating polymeric conductive fillers directly into the precursor solution, allowing

both the hydrogel matrix and the conductive network to be formed during the polymerization process [6]. Rubai Luo et al. [9] designed a one-pot method that combines physically crosslinked PVA with chemically crosslinked PAM and PEDOT as the

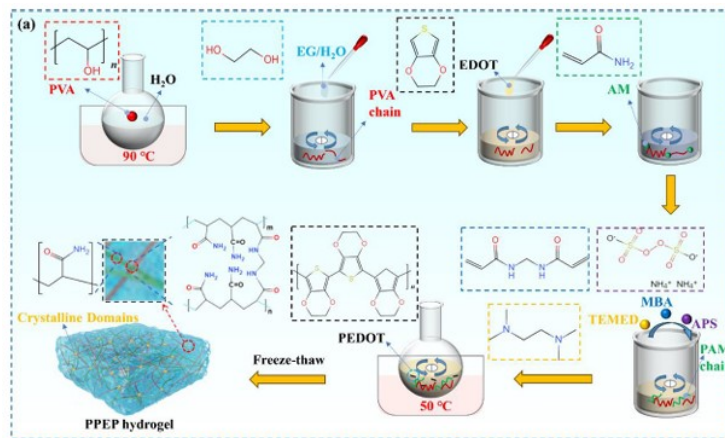


Figure 1.3: schematic illustration of the production process of the electronically conductive PVA/PAM hydrogel using PEDOT as the conductive filler. [9]

conductive filler. The synthesis is described in detail in figure 1.3. The resulting sensors demonstrated both exceptional mechanical and electrical characteristics with elongation at break up to 1050 %, conductivity of 32.39 S/m and high sensitivity across an extensive strain range of 550–1050 %. This approach avoids the phase separation between the conductive filler and the matrix resulting in more stable pathways. Overall, the design of ECH required an intrinsic trade-off between electrical conductivity and mechanical properties.

1.2.2 Ion conductive hydrogels (ICH)

Hydrogels possess a porous structure that allows water molecules to freely move inside the matrix so, by introducing water soluble ions, it is possible to obtain a conductive hydrogel [6]. Ionic conductive hydrogels (ICHs) consist of the incorporation of electrolytes (i.e. physically or chemically doped soluble inorganic salts) or ionic liquids into hydrogel matrices [6]. Inorganic salts, such as sodium chloride, lithium chloride, potassium chloride, not only increase the conductivity, but also improve the anti-freezing abilities [6]. This is shown in the work of Ge et al. [10], their polyacrylamide (PAM) hydrogel was doped with different concentration of LiCl with the highest concentration allowing the hydrogel to not freeze at -80°C . Increasing the ion concentration result to the hydrogel to became softer and the ionic conductivity to increase; a higher salts content result in more freely moving ions that contribute to the charge transport. However, there is a limit because by increasing excessively the concentration the salts form cluster that negatively impact the performance [11]. This has become the most widely used strategy for imparting conductivity to hydrogels because of their generally low impedance and simpler fabrication methods. However, a major limitation of ICHs is their higher water

content than ECH, which often results in inferior mechanical stability, poor long-term durability, and dehydration [6] [11]. A possible solution to these drawbacks is the use of a DN structure as the polymeric matrix [11].

1.2.3 Composite Conductive Hydrogels

Composite conductive hydrogels is a hybrid technique that combines the use of both conductive fillers and freely moving electrolytes or ions. They are a blend of the mechanical and electrical properties of the ICHs and ECHs for this reason they can pave the way for innovative materials with better properties.

By integrating multiple conduction mechanisms, they offer a promising pathway toward advanced applications in flexible electronics, soft sensors, and biointerfaces.

1.3 Hydrogel from natural materials

Key components in materials used for biomedical applications are biocompatibility and biodegradability, therefore researchers are constantly looking for new innovative materials that meet this requirement [12]. Natural polymers are the ideal solution, as they intrinsically possess both properties.

- **Biocompatibility**
is the property of the material to avoid adverse effect when in contact with the human body while maintaining its intended functionality during clinical therapies [13] [14].
- **Biodegradability**
According to the merriam-webster dictionary biodegradability is defined as “capable of being broken down especially into innocuous products by the action of living things (such as microorganisms)” [15]. It is a crucial properties for green engineering reducing the accumulation the material waste that can pollute soil and water.

Natural Hydrogels are hydrogels where the matrix is composed of natural polymer. They inherit biocompatibility and biodegradability from these polymers and are therefore widely used in biomedical applications. The polymers used can be divided into two main categories: polysaccharides and proteins [14].

Common polysaccharides used are cellulose, chitosan and alginate. Cellulose possesses a molecular structure stabilized by a network of intermolecular hydrogen bonds.

In order to form hydrogels, these bonds must be disrupted enhancing its ability to interact with other polymers. Unfortunately, cellulose isn't soluble in common solvent requiring extra step or personalized solvent [14].

Chitosan is derived from the partial deacetylation of chitin, which is found in fungal cell walls and exoskeleton of crustacean or insect. Chitosan-based hydrogels are known for their excellent biocompatibility. However, in the study by Pan et al. [16] its

biodegradability was observed showing that after 79 days the chitosan hydrogel retained more than 95% of its original weight. The slow degradation rate can limit its application in tissue engineering, as it may not allow proper space to the regenerated tissue to grow [14].

Alginate is obtained from brown algae extraction in an alkali solution. Hydrogel made with this polymer presents similar properties to cells natural biological networks, for this reason they are used to create synthetic extracellular matrices (ECMs) [14]. One known drawback is their poor cell adhesion, Rowley et al. [17] to overcome this problem modified the alginate with 1-ethyl-(dimethylaminopropyl) carbodiimide (EDC) enabling bonding with amine group.

Proteins include collagen and gelatin. Gelatin in contrast with other gels, like alginate, has a lower bonding energy granting reversible properties to the formed gel [18], moreover gelatin is highly soluble in water. Gelatin can be found in very different kinds of applications, it is extensively used in food industry and modern cousin, in particular for making desserts, but is also used in cosmetics and bioengineering because of its biocompatibility and degradability [18]. Gelatin is derived from collagen by breaking the covalent bonds inside with a solution of acid or alkali [18]. Collagen can be found in fish scales, pig skin and cow bones. Not all collagens are the same, as their origin determines their respective concentration of the amino acids that highly affect their final properties. [18].

Gelatin properties are mainly three Bloom, gelling point and melting point.

- Bloom is measure of the gel strength, Karim et al. defined it “as the weight in grams that is required for a specified plunger to depress the surface of a standard, thermostated gel to a defined depth under standard conditions” [18]. Fish gelatin has generally lower bloom values (between 70 and 110) than bovine or porcine gelatin, which typically ranges from 200 to 240 bloom [18].
- Gelling point and melting point are extremely dependent to the gelatin source. Porcine and Bovine gelatins have gelling and melting point between 20 to 25 °C and 28 to 31 °C, respectively [18]. For fish gelatin the range is much higher 8 to 25 °C for the gelling point and 11 to 28 °C for the melting point. According to this ranges, same type of fish gelatin is a liquid at room temperature, this can be caused by the lower imino acid reducing the structural stability of the gel [18].

1.4 GelMA

Gelatin Methacrylated (GelMA) is a three-dimensional network of hydrophilic polymers created through the substitution on amminin group (-NH) of gelatin with methacrylic group that introduce double bonds, enabling free-radical photopolymerization.

Gelatin can undergo a methacrylation process, creating GelMA, to improved mechanical properties and processability while retaining the biological features of gelatin.

In 2000, Van Den Bulcke et al. discovers that by irradiating with light and adding a photoinitiator GelMA can be crosslinked forming a GelMA hydrogel.

From then on GelMA hydrogel were widely used in drug delivery, tissue engineering and biosensor. What makes GelMA so attractive can be summarized in 4 point: biocompatibility, biodegradability, tunable properties, bioprintability.

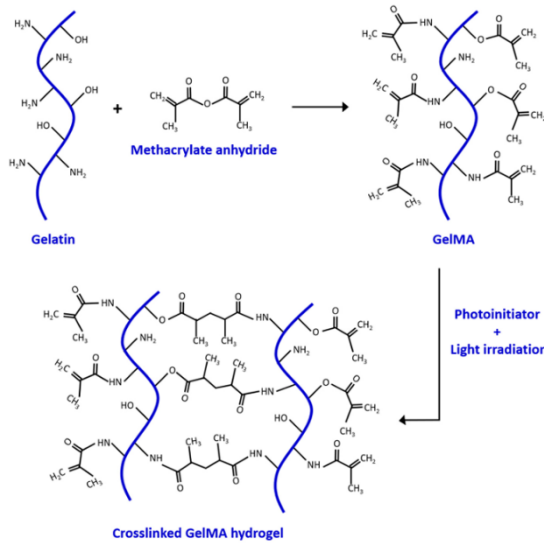


Figure 1.4: methacrylation process process of gelatin. [102]

In Yuewei Chen et al. [19] GelMA was chosen for its biocompatibility and Young Modulus similar to human tissue and great adhesion. Then incorporating Ultrafine fiber network (UFN) in the hydrogel matrix they were able to create a flexible strain sensor with tunable mechanical properties depending to the orientation of UFN. The strain sensor was attached to the cardiac surface measuring effectively both cardiac and respiratory rate. Jianpeng Gao et al. [20] developed GelMA scaffold for tissue engineering. It has been found that GelMA scaffolds promotes cell adhesion more effectively than traditional synthetic polymers the lack specific biochemical that support cell adhesion. This isn't the only interesting result, as GelMA also enchases cell proliferation.

1.5 Long-term stable gels

As described in the introduction hydrogel has two main drawbacks due to the high-water content. The first one is freezing at very low temperature resulting in a stiffer and fragile sensor, consequently leading to a decrease in sensitivity. The second one is water evaporation: The loss of water reduces conductivity, thereby worsening the electrical performance. In the past few years a lot of studies have proposed different solutions to overcame the two drawbacks. Among these solutions there is the introduction of salts, alcohols, ionic liquids, and modifications to polymer network. The addition of salts like NaCl or LiCl decrease the freezing point of the hydrogel, in particular the hydrogel [10]

with LiCl show a working range of -80 to 25 °C granted by the interaction between the water molecule and the ions inside the matrix.

The second common solution are ionic liquids (IL), they are organic salts that remain in liquid state at ambient temperature. Haibo Wang et al. [21] Reported an ionogel fabricated with Ag-lignin nanoparticle, polyurethane (ALP) and the ionic liquid EMIM:DCA with

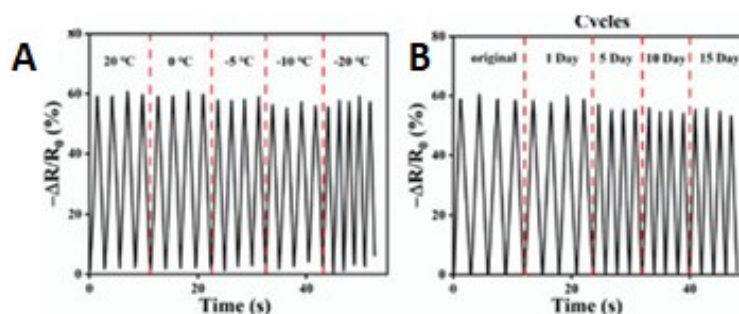


Figure 1.5: sensing abilities of the ionogel with 20% concentration of EMIM:DCA at A) different temperature and B) different storage time at -20 °C. [21]

different concentration. IL influences the mechanical properties; indeed they noted the with the increase of IL the elongation at break increases and the young modulus decreases resulting in a softer hydrogel. Regarding the conductivity the trend is unsurprising: when IL content increase from 0% to 30% the sensibility increases. The ionogel performance was then tested between -20 °C and 20 °C (Figure 1.5a, 1.5b) showing not significant change in sensitivity.

ILs increase the physical crosslinking (in particular H-bonding and ionic bonding) in the hydrogel matrix, this type of hydrogel usually presents great adhesion and self-healing. However, despite their favorable mechanical and electrical properties, the high manufactural cost and possible toxicity made the industry ask for a different solution [22]. Another possible solution is the partial or complete substitution of the water content with another solvent. When an organic solvent it use, they are referred to as organogel, interested if the solvent is a mixture of organic and water solvent they are referred as organhydrogel. Organogel can be synthesized through three main strategies: gelation in mixed solvent systems, solvent displacement, or loading of an organogel precursor with subsequent in situ polymerization. Wu et al. [23] evaluated the freezing properties of substituting the water content of a PAM/CA DN hydrogel with EG/Gly. The findings revealed that after store at -18 °C for 1 h, the hydrogel became brittle and stiff whereas the organogel still remain flexible. Moreover, the higher the water content is displaced the longer the material remain flexible.

One of the most promising recent solutions is the development of eutectogels. Eutectogels are hydrogels in which the polymeric matrix is solubilized in a Deep Eutectic solvent (DES) instead of water.

1.5.1 Eutectogels

The first recorded time when the name DES was used is in Abbott et al. in 2003 making them a recent discovery. In that study Abbott tested various eutectic mixtures of quaternary ammonium salts and hydrogen bond donor and found out that a mixture of choline chloride and urea 1:2 molar ratio presents abnormality in freezing point, it was surprisingly much lower than expected with a value of 12 °C, this behavior granted them the name “Deep” eutectic mixture. In chemistry the eutectic point is the temperature and chemical composition at which a mixture of two solids becomes fully molten at the lowest melting temperature [24].

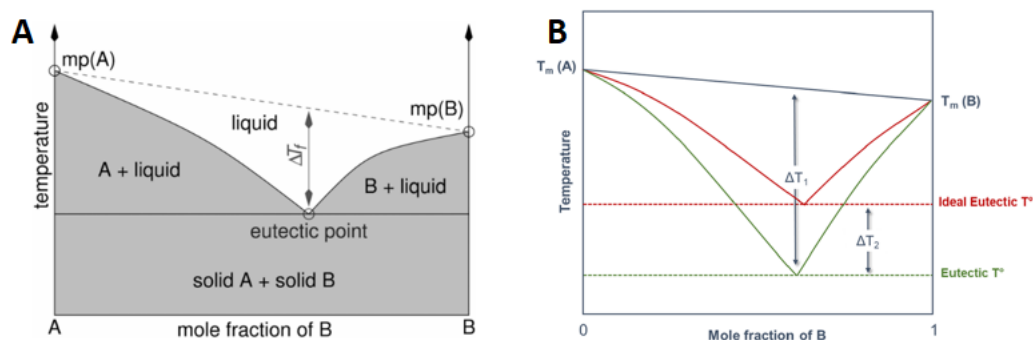


Figure 1.6: solid liquid phase diagram of mixture A) Highlighting the solid and liquid region. [103] B) Highlighting the difference between an ideal eutectic mixture and a “deep” eutectic mixture. [24]

The exact definition of DES is still a controversial subject, but the most common definition describes is a mixture of two or three compounds where some act as hydrogen bond donor (HBD) and some as hydrogen bond acceptor (HBA). This definition is controversial because all mixtures exhibit an eutectic point and having a hydrogen bond interaction is not unique to DES; in fact this definition lacks the characteristic that granted the term “Deep” in their name. Therefore, a better definition that adds one more restriction is also proposed. The added restriction stated that the difference between that of an ideal liquid mixture and the eutectic point temperature (ΔT_2) is greater than zero [25] [24].

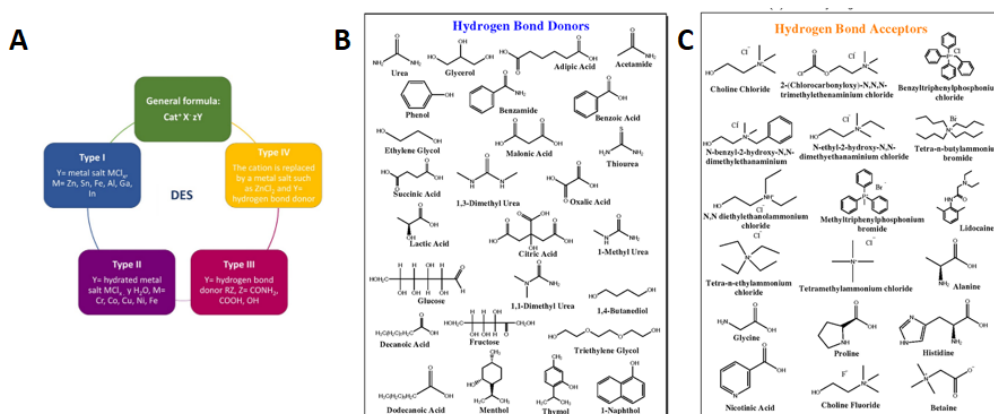


Figure 1.7: A) classification of types of DES based on the formula $Cat^+ X^- zY$. [24] B) chemical structure of some B) HBD and C) HBA [100].

DESs can be classified in 4 group by using the formula $\text{Cat}^+ \text{X}^- z\text{Y}$. In this notation, Cat^+ typically refers to an ammonium, phosphonium, or sulfonium, while X^- denotes a Lewis base, usually a halide anion. The component Y represents a Lewis or Brønsted acid and z indicates the number of Y molecules interacting with the corresponding anion [24].

Type III is the most investigated in literature and the most common HBA is Choline Chloride (ChCl). ChCl is a white salt composed of the choline cation ($\text{C}_5\text{H}_{14}\text{NO}^+$) and chloride anion (Cl^-). This widespread interest is due to its relative cheapness, non-toxicity and biodegradability and making ideal for a promising green solvent.

Together with ChCl the most used HBD are amides, alcohols, and carboxylic acids.

For instance, Xiaomin Zhang et al. [26] design an eutectogel with N-hydroxy methyl acrylamide (NAM), hydroxyethyl methacrylate (HEMA). The DES was a mixture of Choline chloride (ChCl) and ethylene glycol (EG) at a molar ratio of 1:2. The effect of DES on the mechanical properties were analyze, results indicate that increasing the DES content makes the eutectogel softer and slightly less stretchable. The performance of the eutectogel and the hydrogel, made with only NAM/ HEMA, were compared under extreme working environments conditions.

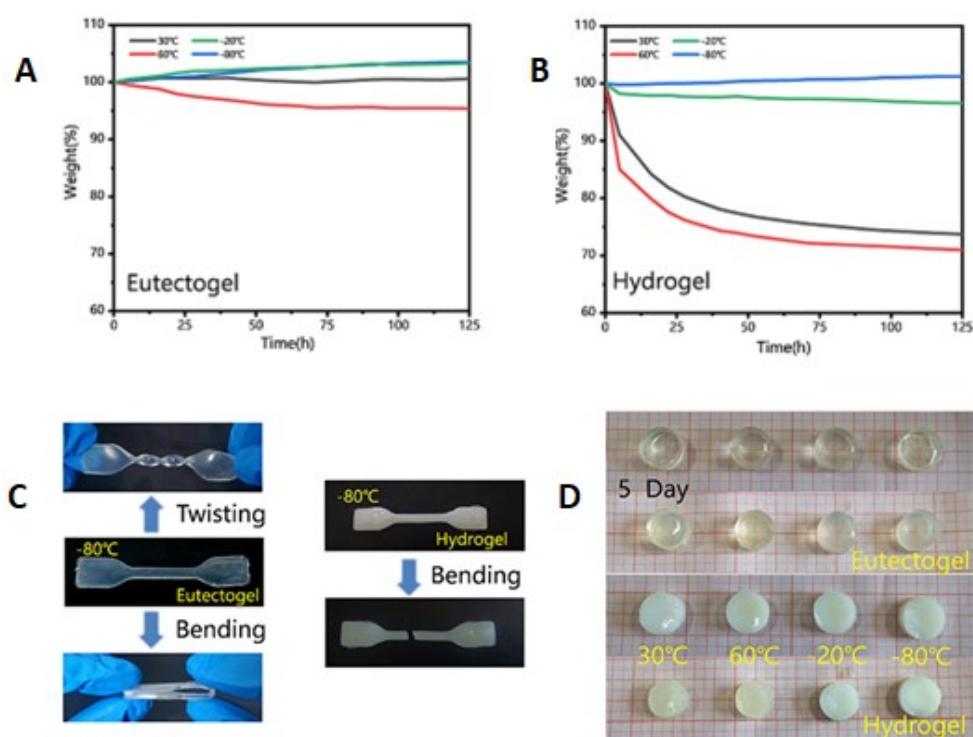


Figure 1.8: A) and B) plot describing are loss of weight vs time of NAM eutectogel and hydrogel, respectively. In C) is carried out a torsion and bending test, D) comparison between eutectogel and hydrogel. [26]

The primary notable difference between the two is visual, the eutectogel appears clearer and transparent. Regarding the performance, the hydrogel and eutectogel were left for 5 days at four different temperatures: 30 °C, 60 °C, -20 °C and -80°C. In the figures 1.8a 1.6b are shown the results. After 5 days at 60 °C, the eutectogel lost only the 10% of its total weight, it's a large number but is still better than the hydrogel losing 30% of its total weight. Regarding below zero temperature, in particular -80°C, the eutectogel is still flexible as shown in figure 1.8c it could be twisted and bent without any damages, whereas the hydrogel fractured upon the first bending attempt.

Eutectogels have a lot of freedom when designing it, by adjusting the ratio between the DES and the polymers the mechanical properties can be fine-tuned to the person's need. Compared to the previous suggested strategies, this approach doesn't raise any significant Cytocompatibility concerns as for IL and provide better conductivity than organogels.

1.6 Flexible Sensor

Nowadays, Sensors are found in almost all electronic devices as a way to connect the real world to the electronic world. They operate by converting external stimuli into electrical signals. This conversion is achieved through specific transduction mechanisms.

When flexible substrates, like hydrogel, are implemented as sensors they are referred to as flexible sensors. The recent interest in this kind of sensor is born for a search for an alternative to bulky sensors that can create discomfort when used in applications requiring contact with the human body [27] [1]. These sensors are typically used in real-time monitoring of human movement and bio-signal. Because they can remain in contact with the skin or biological tissues for an extended period, they must be extremely flexible, light weight, biocompatible, adhesive and nontoxic to ensure safer use [1]. The sensitivity of the sensor is defined by the quantity Gauge Factor (GF). GF is the ratio between the change in electrical signals to the strain.

1.6.1 Mechanical sensors

When the external stimulus is a force that emerges from torsion, strain or pressure, they are referred to as mechanical sensors.

Mechanical sensors can be classified based on which type of transduction mechanisms they use [28]. The transduction mechanism represents which physical quantities is used to detect Mechanical changes. In the following paragraphs will be described in details several of the most common transduction mechanisms.

- **Piezoresistive sensors**

Resistive sensors operate by detecting the changes in electrical resistance resulting from deformation upon an external force. The simplest resistive sensor can be described as a strip of sensing material connected to electrodes, typically made of electrode, generally made with copper, gold or titanium.

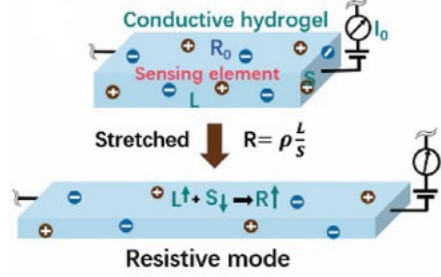


Figure 1.9: physical mechanism of resistive sensors under tensile strain. [105]

The change in resistance of the material is calculated by the equation below

$$\bullet \quad \Delta R = \frac{\Delta \rho \Delta l}{\Delta A}$$

Where ρ is the resistivity of the material, l is the length and A is the area of the section [28]. Under positive strain the material elongates, increasing its length. and the cross-sectional area decrease, resulting in an overall increase in resistance. This relationship applies to both electrical and ions conductive hydrogel, although with some difference. For ICH the deformation mainly alters the polymeric matrix and water molecules changing the path the ions follow, altering the conductivity. Therefore, ICH resistance change depends only to its shape deformation. Instead for ECH the resistance variation is also influenced by the modification of polymeric structure [29].

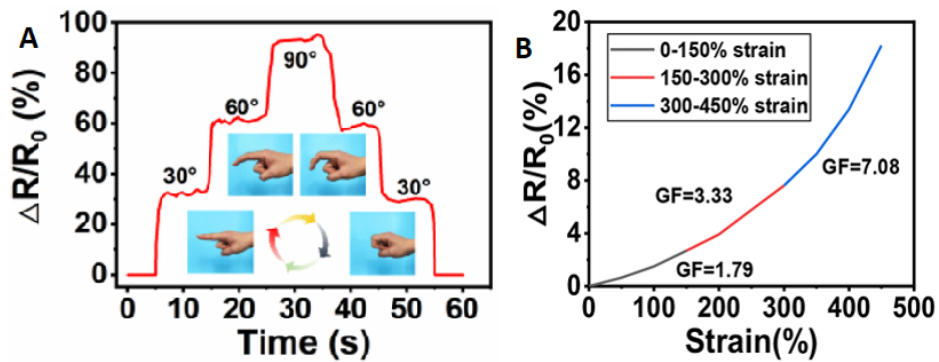


Figure 1.10: eutectogel mixture of Polyvinylimidazole(PVI) and DES (ChCl and urea) A) example of the application as strain sensor applied to the finger joint with different angle of bending. B) stress-strain curve of the eutectogel. [30]

An example of resistive sensor for human-motion sensing based on hydrogel is found in Kaiqi Fan et al. [30]. Figure 1.10b shows that when their hydrogel is stretched to twice its original length, its resistance is also almost double. This response makes it suitable for wearable sensing like the movement detection of the finger joint.

An alternative approach to fabricate a resistive sensor is to take advantage of an external pressure to create a change in resistance. As shown in the article by Xiaomin Zhang et al. [26] a hydrogel sandwiched between two electrodes can sense the pressure applied and including the air pressure generated by blowing. Moreover the sensibility sensor can be improved with better structural design, in the same article by Zhang et al. [26] a cone was tested against a thin film structure, the results shows an 8 times increase in sensitivity. Why this happens is described in Yun Xia Zhang et al. [31], where they implemented a PAAm/PVA hydrogel with micropyramid structure. A Sharper structure is subject to a greater deformation under stress leading to a greater change in resistance.

Finally, combining different types of resistive sensors, it is possible to fabricate more complex sensors, Li et al. [32] developed a three-dimensional motion detector sensor, the device measures z movement by a pressure resistive sensor with micropyramid, while X and Y axis are monitored by two strain sensors. Since conventional strain sensors lack directional sensitivity detecting strain in both direction, the solution was to print short carbon fibers (SCF) printed along specific axes enabling a selective detection of the desire axis.

To conclude, Resistive sensors advantages are low fabrication cost and simple design. Nevertheless, they present same disadvantages as poor linearity and large hysteresis [28]. Moreover, Resistance is dependent on atmosphere ambient like temperature and humidity and this is also true for the sensors possibly reducing its sensitivity [33].

- **Piezocapacitive sensors**

Capacitive sensors are primarily employed as pressure sensors with a parallel plane configuration, in which the hydrogel is sandwiched between two conductive electrodes. The capacitance is calculated as

$$\Delta C = \epsilon_0 \epsilon_r \frac{\Delta A}{\Delta d}$$

Where ϵ_0 and ϵ_r are the permittivity of free space and the relative permittivity, A is still the area of the section and d is the distance between the plates. When an external pressure is applied the dielectric material is compressed, reducing the distance d , while the area remains almost constant. This results in an increase in capacitance of the dielectric.

Capacitive sensors display a more linear characteristic and have in general a better response time than resistive sensors. [34] However, due to the small working

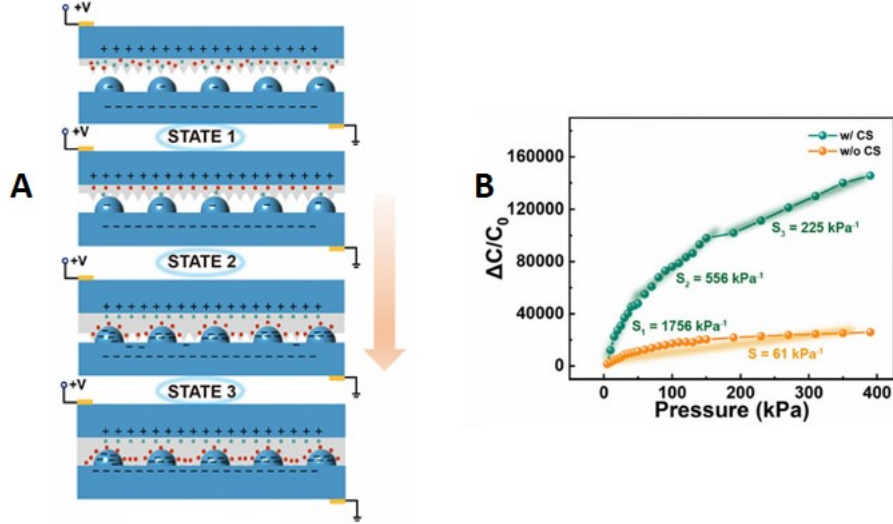


Figure 1.11: tactile sensors made from a capacitive sensor, the dielectric material is a hydrogel of P(VDF–HFP) and an ionic liquid EMIM:TFSI to improve the EDL formation and the conductive layer is a hydrogel of PVA and PEDO:PSS, A) working principle and EDL formation during external pressure. B) Sensitivity curve with the normalized C variation vs the applied pressure. [36]

capacitance values, most capacitive sensors are susceptible to signal cross talk, such as parasitic capacitance [35]. To mitigate this limitation Ao Yin et al. [36], exploited the electrical double layer (EDL) at the interface between the dielectric and conductive material. The sensitivity of the device is proportional to the contact area. Microdome and micropyramide were printed onto the conductive layer and dielectric layer, respectively. This configuration increases the total contact area, and also the EDL formed on the interface, improving the linearity and the working range as shown in figure 1.11b.

Compared with resistive sensors, capacitive sensors advantages are temperature independent, low power consumption, low detection limit and fast response [33]. These characteristics make them suitable for a wide range of applications, including robotic, e-skin, wearable sensors, health-monitoring, touchscreen, keyboards, object detection [37] [33].

- **Piezoelectric sensors**

Piezoelectricity refers to the properties of the material to become polarized under an external mechanical stress, generating electric charge on their surface. The

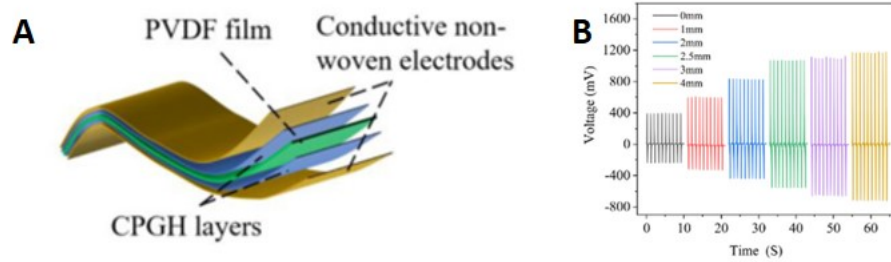


Figure 1.12: A) Structural diagram of the piezoelectric sensor with the Conductive PVA/Gelatin hydrogel (CPGH) sandwich between the PVDF film. B) Sensitivity of the sensor with different hydrogel thickness [40].

amount of charge generated is directly proportional to the amount of deformation and can be measured as the potential difference at the ends [38]. After the deformation, the material returns to the original neutral state, indicating that the piezoelectric effect is reversible. Piezoelectricity was first observed in crystalline materials such as quartz, but other material, including Lead Zirconate Titanate (PZT), Barium Titanate and PVDF, have been discovered to exhibit piezoelectric properties [39]. Regarding wearable flexible sensors, the polymer PVDF is particularly promising, however its piezoelectric output is lower respect to ceramic material. To enhance its sensibility Wang et al. [40] sandwich a PDVDF film inside two Conductive PVA/Gelatin hydrogel (CPGH) layers. The sensitivity of the device increases with the thickness of the hydrogel layer, proving that the hydrogel enhances both the deformation degree and stress concentration in the PVDF film. Piezoelectricity doesn't required external power source to function making them self-powered sensor. Disadvantages are the restrictive possible flexible piezoelectric material , and the generated charge decrease with time making them unable to sense a static signal.

- **Triboelectric**

Triboelectricity is based on contact electrification, a commonly phenomenon that occurs when two materials came in contact and became oppositely charged at the interface. In typical triboelectric sensors, the two materials initially separated, when the pressure is applied they come into contact and become charged. The triboelectric generation is retained for a relatively long time, meaning that even after separation the materials remain charged [41]. Due to electronic induction charge accumulate at the electrode, while at the surface with the air the charge isn't neutralized resulting in a voltage difference [38]. A common application of triboelectric devices are nanogenerators (TEGs). Li et al [42] fabricated a flexible TENG using a composite of PDMS and PTFE, both of which are frequently used in TENGs. PTFE is favored for its strong abilities to attract

electron and PDMS for its flexibility. As for piezoelectric, these are self-powered sensor and they are able to detect only dynamic signals.

1.7 3D printing

3D printing refers to a group of additive manufacturing (AM) techniques that build three-dimensional objects by depositing material layer by layer. Unlike traditional subtractive methods, AM reduces the material waste to create complex structure. The 3D structures are directly printed starting from a digital design. The design is then sent to the selected 3D printer for fabrication and then 3D printed. 3D printing technologies exploit different physical properties of materials to fabricate three-dimensional structures. For example some technologies exploit photosensitivity to induce Photopolymerization, but this is not the only method. In general, these techniques can be roughly classified in two categories light and estrusion-based printing.

1.7.1 *Light based 3D printing*

Light based printing exploits photoreactive resins, the photopolymerization is started by scanning the resin using a laser or projecting light using digital micromirror device (DMD).

Photopolymerization is a technique in which polymers in presence of photoinitiator can be polymerized when irradiated with UV or visible light.

Photoinitiator are compound that when irradiate generate species that initiate the photopolymerization. This species can be free radical or protonic acids, for methacrylate, as implemented in this theses, free radical photoinitiator are more commonly used [43]. In particular, the chosen photoinitiator is Lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP). LAP is a free radical photoinitiator commonly used for GelMA and PEGDA proven to have high biocompatibility and water. [citazione]

The light wavelength that can start the process is specific to the material and photoinitiator and typically falls in the UV or visible spectrum. Performance parameters, including

resolution and speed, are strongly influenced by the characteristics of the laser system. The most common techniques include stereolithography (SLA), Digital Light Processing (DLP), and two-photon polymerization (TPP) [44].

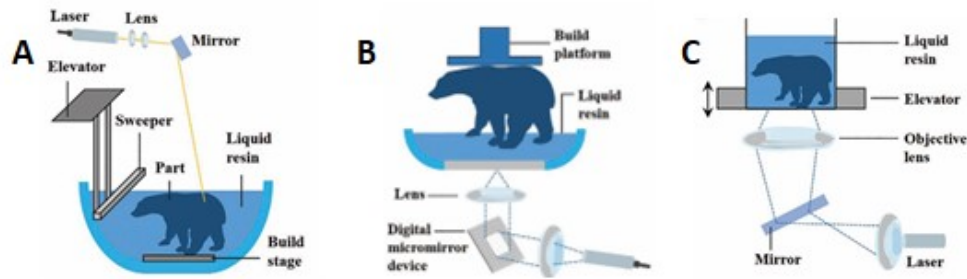


Figure 1.13: Different methods of light-based 3D: A) stereolithography(SLA), B) Digital Light Processing(DLP) and C) two-photon polymerization (TPP) [44].

(DLP), and two-photon polymerization (TPP) [44].

- **SLA**

In this technique a laser beam scans the surface of the resin. The laser passes through a series of galvanometric mirrors that direction the laser inducing a point-by-point polymerization in the wanted area creating the 2D section of the structure. Once the 2D structure is created, the structure descends and creates the next layer directly to already formed one. The layer thickness is limited by cure depth (C_d), that is the maximum depth the light can penetrate the resin. SLA has optimal resolution enabling the printing of complex 3D structure with micrometer features. However, the technique presents certain limitations: the process is relatively slow, as the laser polymerizes the material point by point, and the range of compatible materials is restricted, since the resin must exhibit low viscosity, transparency and Newtonian rheological behavior [44].

- **DLP**

DLP The principle of digital light printing is similar to SLA but instead of scanning the resin it project the 2D section simultaneously, by employing a digital micromirror device (DMD) or a liquid crystal display (LCD), after the resin is polymerized onto the build platform, the platform is elevated allowing the creation next layer below [45] [44]. Because each layer is patterned simultaneously it accelerates the printing process without compromising high resolution. A DLP 3D printed hydrogel was obtained by Guo et al [46]., where the hydrogel polymeric precursors included Acrylamide (AAm) and acrylic acid (AAc),

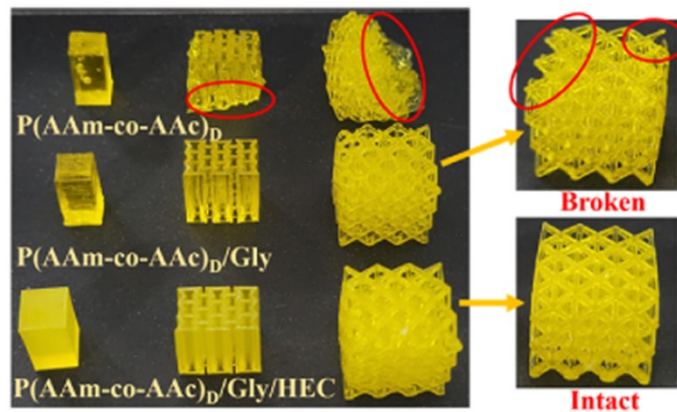


Figure 1.14: printing tests of the P(AAm-co-AAc) hydrogel and the effect of Glycerol(Gly) and Hydroxyethylcellulose(HEC) in the printed material for 3 different geometries [46].

PEGDA a crosslink agent to improves the mechanical properties, NaCl to increase the conductivity, tartrazine as the dye and TPO as the photoinitiator. diphenyl (2,4,6-trimethylbenzoyl)phosphine oxide (TPO) is a free radical photoinitiator derived from Phosphine, was widely use for its thermal stability and lack of colour and odour however suffers from pour water solubility [43]. This formulation resulted in an efficient hydrogel resin that required approximately 6s to undergo photopolymerization. The hydrogel precursor was irradiated with a projector that emits light with wavelength 405 nm and 3 different structures with different complexity were 3d printed. The results are shown in figure 1.14, the initial hydrogel exhibit limited printability, only succefully fabricating simple structure like solid cubes, instead when more complex geometries are printed they presents visible defects. To improve the printability glycerol and hydroxyethyl cellulose(HEC) were incorporated. They enhanced the viscosity and the young modulus allowing more complex structure to be printed without damages. This concludes that hydrogel printing requires a fine tune of the mechanical properties of the precursor resin to achieved a defect free self-sustaining structure.

- **TPP**

In Two-Photon Polymerization, free radical polymerization is initiated after two-photon absorption (TPA). TPA is an optical phenomenon in which two photons are simultaneously absorbed (E_1 , E_2 , Figure 1.15), this allows highly localized polymerization improving the resolution. To achieve this, the apparatus consists

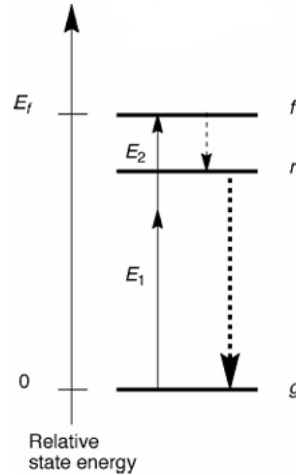


Figure 1.15: schematic illustration of the mechanism of two photon absorption [99]. Where E_1 and E_2 are the energy of the two-photon absorbed exciting the molecule to different excited state E_f .

of an ultrashort laser (emits pulse of light with very short duration around few femto or picosecond) operating in the near infrared spectra. The printing process is slower than both DLP and SLA, with the speed ranging between 80 nm/s to 2 cm/s, making TPP unsuitable for the fabrication of large-scale objects [44]. However, the slow process is counterbalanced by the high resolution capable to making structure with nanosize features. The choice of photoinitiator is even more critical for TPP, as it must be extremely sensitive to be able to absorb 2 photons simultaneously, which further restricts the range of material. [44] [6]. For example, Liao et al. [47] used Irgacure 369 as the photoinitiator to create cantilever only few nanometers long. Irgacure 369 is a highly efficient photoinitiator. However, it can be used in bioengineering for its cytotoxicity, and moreover, its considered to be highly toxic to aquatic organisms.

1.7.2 Estrusion-based 3D printing

Extrusion-based printing encompasses a versatile family of techniques that enable the use of a wide range of precursor materials, for this reason it has become one of the most frequently employed printing technique. There are numerous type of ink-based techniques in particular we will discuss two of the most utilized: Fused Deposition Modeling (FDM) and Direct Ink Writing (DIW) [44].

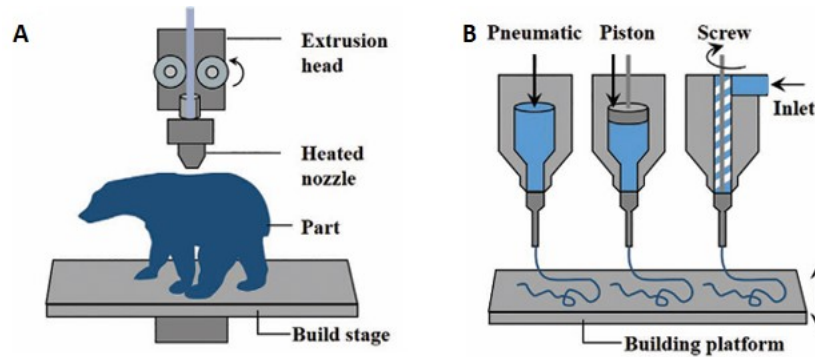


Figure 1.16: example of extrusion based 3D printing: A) Fused Deposition Modeling (FDM) and B) Direct Ink Writing (DIW) [44].

- **FDM**

In FDM a thermoplastic polymer filament is extruded from a heated nozzle where it is melted and then collected onto the building platform. The printer nozzle moves in a planar motion according to the section profile of the object geometry, once extruded the polymer rapidly cools, when solidified the next layer is deposited onto the previous one to form the 3D object. The only type of polymers that can be chosen for FDM are thermoplastic, which limits the range of possible available materials. FDM is a fast and low-cost method to create large 3D structure; however, printed components often exhibit rough surface and the limited physical interaction between adjacent filaments could weaken the structural strength along the deposition direction [27].

- **DIW**

DIW printing technology could be an alternative for solving the limitations associated with FDM. The working principle is similar; however, instead of a

filament, a precursor ink is used and extruded typically at room temperature through the application of an external force.

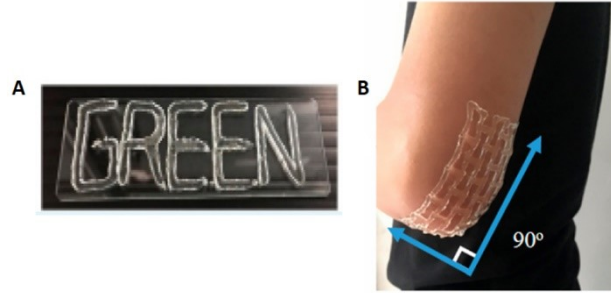


Figure 1.17: application of DES and Carpool hydrogel: A) demonstration of the resolution writing the word Green using DIW and B) auxetic sensor to monitor the joint movement [48].

These techniques enable the implementation of a wide range of materials; nevertheless, the primary constraint is that the ink must exhibit shear-thinning rheological behavior to ensure proper flow during extrudable [44]. The less constraints regarding the precursor material led various research to favor DIW over techniques such as DLP in certain applications. For instance, Trung Hieu Vo et al. [48] 3D printed using an ink composed of deep eutectic solvents (DES) and Carbopol, resulting in an eutectogel that is highly stretchable, transparent and highly sensible to strain. Cellulose nanocrystals (CNCs) have been utilized with DES to tailor rheological properties and increasing the machinal properties, in this article Carbopol is implemented instead of the usual cellulose nanocrystals (CNCs) as a low-cost alternative.

The capabilities of DIW are shown in Figure 1.17a where complex planar structures are easily printed. In Figure 1.17b we can see an example of an auxetic strain sensor. Auxetic structures are geometries that possess negative Poisson's ratio defined as the negative ratio of the transversal strain to the longitudinal strain. This kind of configuration exhibits a higher sensitivity than conventional thin-film sensors. Furthermore, the negative Poisson's ratio makes it conformed and attached better to human skin. Regarding application, the study demonstrates real-time human motion monitoring. When the eutectogel was attached to human joints (knee and elbow and) a measurable difference in resistance was detected when they are bended or relaxed.

Chapter 2

2 Laser Induced Graphene

For many years, significant research effort has been devoted to commercializing Graphene, traditional graphene synthesis methods faces several limitations for large scale

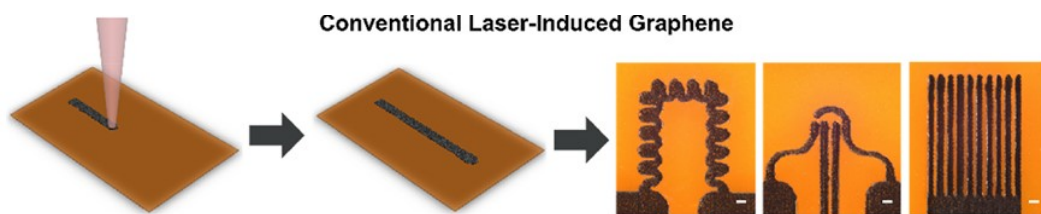


Figure 2.1: Example the fabrication of Laser Induced Graphene with different shape [92].

production. Fortunately, in 2014 [49] a new way to produce graphene was found. By irradiating, with an infrared CO₂ laser, a polyimide substrate porous graphene is obtained. Laser Induced Graphene (LIG) is a promising method to obtain conductive graphene-like structure. The implementation of a laser system avoids the requirement of high temperatures, chemical reagents, or complex fabrication found in traditional synthesis

methods. Resulting in a fast, eco-friendly and low-cost, that has generated a rapid interest in research and wide range of applications.

2.1 Graphene

Graphene is an intriguing new material recently discovered. Indeed, the first time it was

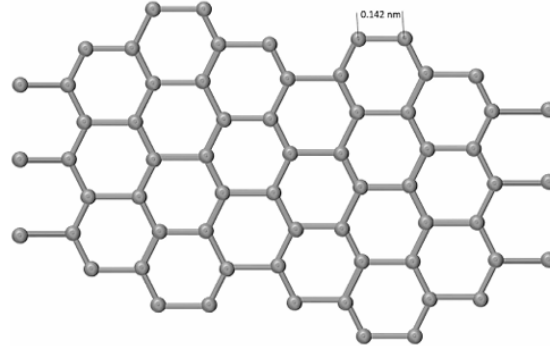


Figure 2.2: planar hexagonal chemical structure of carbons in graphene. [50]

successfully exfoliated was in 2004 by Andre Geim and Konstantin Novoselov that granted them the noble prize in 2010 [50].

Graphene itself can be described as a single atomic layer of sp^2 -hybridized carbon atoms organized in a honeycomb lattice, with an interatomic spacing of approximately 0.142 nm and it represents the fundamental the foundational component of all graphitic structures [50]. Graphene is used in a broad variety of applications particularly in electronics, bioengineering and energy storage because is seen as a candidate for next-generation devices. For example, its high surface-to-volume ratio and excellent electron

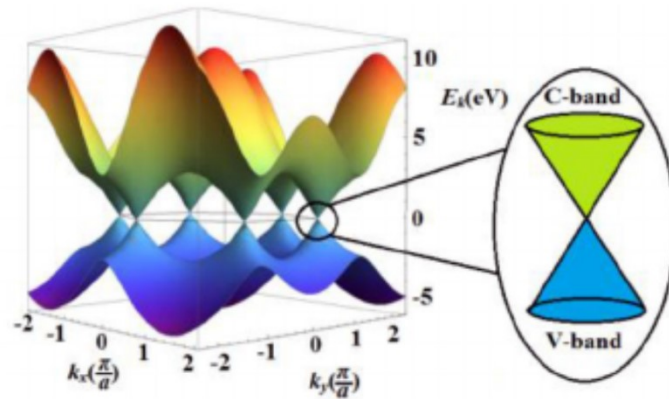


Figure 2.3: conduction and valence bands of graphene showing the six Dirac point [93].

mobility makes graphene detect low concentration of gasses [51] and molecules.

Graphene hexagonal structure has an excellent breaking strength of more than 200 times that of steel (42 N/m), tensile strength of 130 GPa, a Young's modulus of approximately 1 TPa [50] [52]. This hexagonal lattice is formed because each carbon atom in graphene is sp^2 -hybridized, forming three in-plane σ bonds. Moreover, the electrons in the p_z orbitals can tunnel between neighboring carbon atoms [53], these delocalized π electrons are responsible for graphene's exceptional electrical, thermal, and mechanical properties. This electronic structure results in the characteristic band dispersion shown in Figure 2.3, where the conduction band (E_c) and valence band (E_v) meet at six corners of the Brillouin zone, known as the Dirac points. As a consequence, graphene exhibits a zero band gap, exceptionally high in-plane thermal conductivity, of 5300 W/m·K, that is more than double of diamond and excellent electrical conductivity with extreme fast carrier velocity [51].

However, its properties are highly sensitive to the presents of defect, edge states, and functional groups. In particular, deviations from the ideal crystalline structure greatly affect the electrical properties. For this reason, the type of synthesis is important to determining the final properties.

Significant progress has been made in graphene synthesis over the years, and different fabrication techniques were developed; however, achieving optimal balance between quality, cost, scalability, purity and yield remains a challenge. The first implemented method was mechanical exfoliation [50] and from then various new approaches were studied. Graphene-based materials can be synthesized through six main approaches:

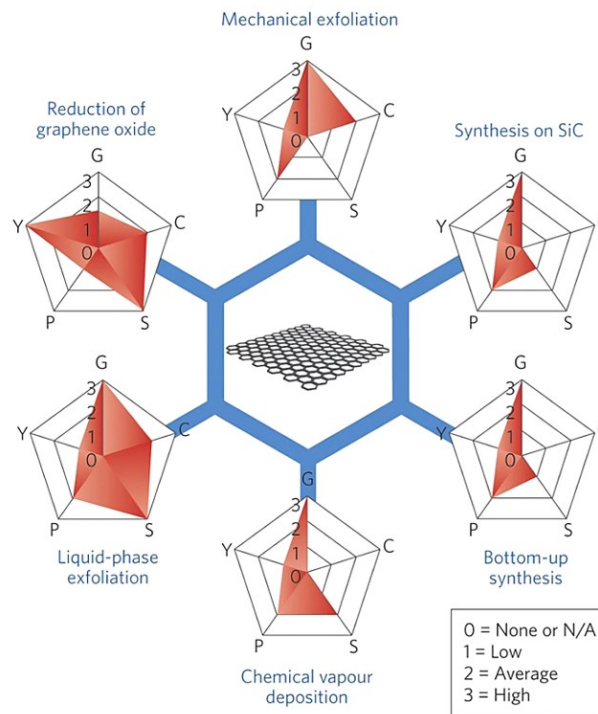


Figure 2.4: Review of different fabrication methods of graphene evaluated in 5 characteristics: quality(G), cost of production (C) cost of production, scalability (S) , purity (P) and yield (Y). [50]

Mechanical exfoliation, Liquid-phase exfoliation, reduction of graphite oxide chemical vapor deposition (CVD), epitaxial growth on SiC [54].

Mechanical exfoliation, Liquid-phase exfoliation, reduction of graphite oxide chemical are top-down processing, in which bulk graphite is progressively delaminated into thinner structures or single atomic layers [54]. While these approaches are attractive for their relatively low cost and operational simplicity, they often suffer from limited control over layer number. Furthermore, the graphite oxidation process can introduce structural defects that cannot be fully removed. As a result, many researchers prefer to distinguish the final material from pristine graphene by referring to it as reduced graphene oxide (rGO) [55].

If greater control over the number of graphene layers is desired, one may opt for bottom-up synthesis techniques [54]. Bottom-up synthesis is a layer-by-layer approach based on chemical processes that build graphene structures from molecular or atomic precursors through controlled chemical reactions. State-of-the-art bottom-up techniques include chemical vapor deposition (CVD), epitaxial growth on SiC. However, these methods use harmful solvents rendering bottom-up synthesis not eco-friendly. The epitaxial growth process requires advanced manufacturing systems that significantly increases the cost of production. Among the conventional graphene production CVD is considered the more promising for large scale production of graphene due to its abilities to create high qualities graphene at low-cost production however it is still difficult to create large amount of graphene with this technique [55].

2.1.1 3D Porous Graphene

As discussed above, graphene exhibits exceptional properties due to its unique two-dimensional structure; however, this is also one of its limitations. A single sheet of graphene is only 0,35 nm thick limiting its practical applications in 3D devices. For this reason the question of how to pack a two dimensional graphene in a three-dimensional structure must be addressed. The resulting three dimensional structure must retain the

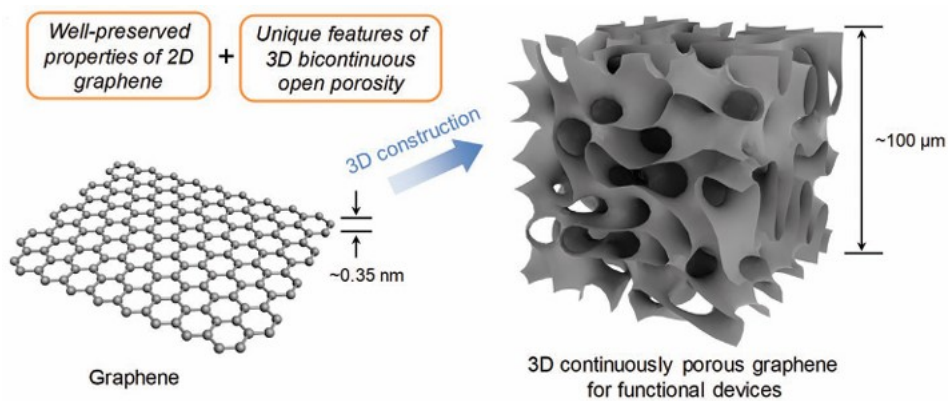


Figure 2.5: Representation of the stacking of 2D graphene into 3D porous graphene. [56]

outstanding mechanical and electrical properties of individual graphene layers and for many application is essential to have a highly accessible surface. [56]

One possible solution is to fold the graphene layer creating a porous structure as shown in figure 2.5. Porous graphene can be obtained through various method, subsequently one of this method will be described: the LIG process. Each fabrication method leads to a different porous structure, in particular the pores size directly impacting the mechanical properties of the material. For Example, structures with smaller pores exhibit a higher young modulus.

2.2 Laser Induced Graphene

Traditional top-down and bottom-up synthesis methods each present their own strengths and weaknesses, however neither of them are not suitable for large scale production. In 2014 researchers discovered that three-dimensional porous graphene can be synthesis using CO₂ infrared laser ablation of commercial polymer films [57].

Among various polymeric substrate, the most implemented polymeric film is the commercial Polyimide (PI) known as Kapton.

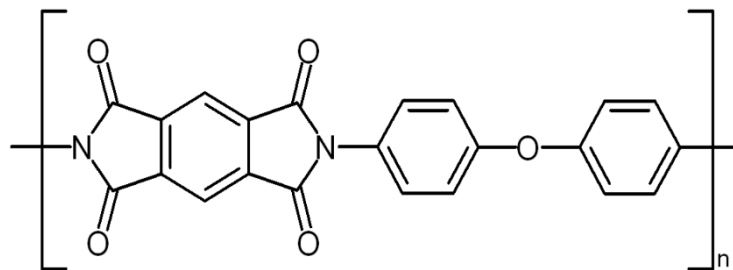


Figure 2.6: chemical structure of Kapton showing the two key component ODA and PDMA. [104]

Polyimide was first used in automotive and aircraft industry where fabrication of thin insulating layers that remained stable at 220 °C for 10 years were a requirement for powerful traction motors. Only after it was adopted for applications in flexible printed circuits for their insulating properties [58].

Polyimide is synthesized from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA), figure 2.6. For this reason its chemical structure contains a high density of fused aromatic rings and, consequently, a large carbon content, making polyimide an ideal precursor for laser-induced graphene (LIG).

LIG is becoming increasingly attractive in the wearable technologies, as it enables non-conductive, flexible, carbon-rich materials to be directly patterned into conductive structures, making them suitable for sensing applications.

In the LIG process the printed pattern is designed using dedicated software, than the CO₂ laser irradiates the polymeric film in the desired location, locally heating the substrate to temperature above 2500 °C, leading to graphene formation on the substrate [59].

The two main processes that occur during the interaction between the laser and the substrate are the photothermal and photochemical reaction.

The photothermal effect is the absorption by the substrate of the photon causing the temperature increase and breaking the bonds between the carbon atoms, rearranging them in carbon sp^2 . The photochemical effect occurs when the photon itself, without the heating, breaks the bonds, for this reason it requires a high energy photon [60]. The carbonization process is easily confirmed visually by the blackening of the heated area.

2.2.1 Laser Parameters

Several parameters are to be considered during the laser process, including: laser wavelength, pulse duration, fluence, and scanning speed. All of them together determine the magnitude and spatial distribution of deposited energy and the temporal dynamics of thermal accumulation [61]. Consequently, they influence the morphology, electrical conductivity and structural ordering of the graphene. In this next paragraph these parameters will be described in detail.

- **Laser wavelength**

Carbon precursors absorb light in the UV(200-400 nm), visible(400-700nm) and Mid Infrared(MIR, between 2.5 μm and 25 μm) [62]. Consequently, laser operating in this region was implemented in the LIG process. The main difference is the energy of the incident photon. For example, it has been found that when using an IR laser, the carbon bonds are mainly broken through the photothermal process since the photon doesn't possess enough energy to directly break the carbon bond, in contrast for the UV laser the photochemical process plays a large role in the LIG formation. As a result, different laser wavelengths produce LIG with different structures and properties. For example, the LIG formed by a 10.6 μm CO₂ IR laser and a 355 nm UV laser were compared [57] [63]. The results showed that the UV laser graphene has nanoscale pore morphology while the IR one exhibits pores with micron size and fewer lamellar structures. This indicates that the CO₂ IR laser creates higher quality graphene and for this reason is the most used in literature.

- **Pulse duration**

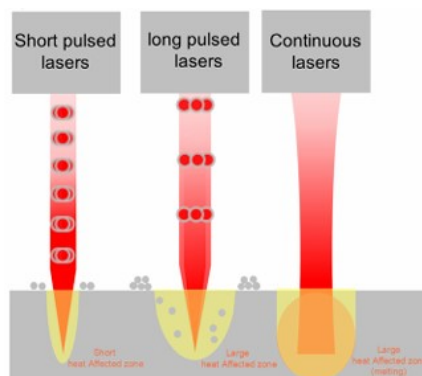


Figure 2.7: Difference in the excited area for different pulse laser.

The temporal mode of the laser can be divided into two groups: continuous-wave (CW) and pulsed regimes [61].

CW lasers provide an uninterrupted energy flux that continuously heats the substrate, leading to sustained high temperatures maintained over extended time. It's not surprising that photothermal effects are dominant during the process [61]. In pulsed lasers, the pulse duration determines the balance between photothermal and photochemical effects, shifting the process toward one mechanism or the other according to the pulse duration [61]. For relatively long pulse, the material is exposed to energy over extended period of time that the process could resemble CW, favoring the thermal process, when the duration decreases to a faster pulse the interaction becomes increasingly non-thermal and the absorption of the laser photon directly breaks the carbon precursor bond. The transition from thermal to nonthermal interactions generally occurs around the picosecond timescale, where the pulse duration matches the intrinsic electron–phonon coupling time [61].

- **Fluence**

In laser processing, fluence describes the amount of optical energy delivered per unit area measured in J/cm². It represents the combined contribution of several laser parameters that govern the graphitization. The way they are connected to one another is described by the equation [64]:

$$Fluence = P \cdot v = P \cdot \frac{t}{A}$$

Where P is the source power, t is the exposure time, and A is the irradiated area. Accordingly, fluence can be tuned by adjusting the laser power, scanning speed, laser stacking density (pulse per inch, PPI), and printing resolution (dot per inch, DPI) [62].

For each type of carbon precursor, these parameters must be fine-tuned to obtain the optimal results. Primarily, Graphene formation occurs only when the supplied energy surpasses a minimum process-dependent threshold. Furthermore, the quality and typology of LIG synthesized by lasers are significantly affected by the

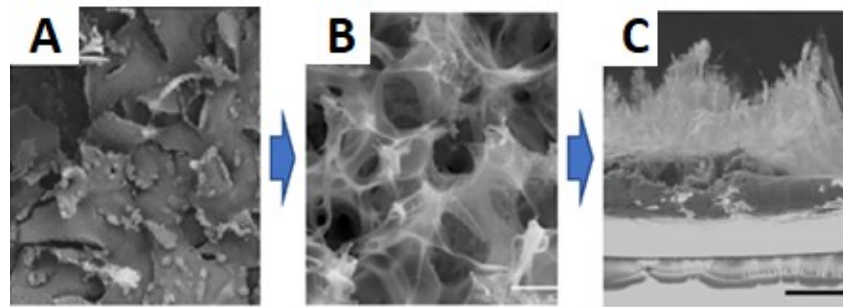


Figure 2.8: SEM imaging of the A)Laminar, B)porous and C)fibrous graphene. [57]

amount of energy provided to the substrate [57]. In order of increasing energy input, laminar graphene is formed first then porous graphene, and finally fibrous graphene forms [65]. This progression it's shown in figure 2.8. Laminar graphene is unusable for sensors applications since it is fragile even under tiny pressure. Porous graphene is the most commonly used in wearable electronics for it better stability respect the other two forms [57]. Fibrous graphene has the higher electrical response among the three, making it has the potential to be implemented as temperature, humidity or strain sensor. This can also be observed in the Raman spectra at difference fluency [66], which shows that the quality of the graphene, represented by the ratio between the D and G peaks, has a gaussian-like behavior. This indicates the existence of an optimal fluence; above which the precursor is overheated, leading to damage of the Porous Graphene.

- **Laser power e Scanning speed**

These two parameters are the main contribution to the Fluence.

Laser power is the optical power of the laser beam, measured in watts (W) [62]. It represents the optical energy emitted E delivered per unit time t :

$$P = \frac{E}{t}$$

Fluency is directly proportional to the laser power; therefore, higher power values correspond to higher temperatures reached by the substrate, significantly affecting the morphology and electrical properties of the resulting graphene. For simplicity, in continuous-wave laser regimes laser power is often preferred over fluence as a process parameter. Consequently, a power threshold is used instead of a fluence threshold. For example, for the PI substrate is found that the threshold power is 2.4 W [62].

Scanning speed refers to the linear velocity of the laser beam during the patterning process. The laser scanning speed is inversely proportional to the laser exposure time, and, according to the equation above, also inversely proportional to the fluence [62]. In Zonov et al. [67] was analyzed the effect of laser scanning speed from 10 to 400 mm/s. The results show that the better graphene was obtained at lowest velocity of 10 mm/s showing the highest areal capacitance. However, when using a scanning speed is below a critical value the laser can damage the substrate producing defective LIG.

- **pulse stacking density and printing resolution**

The pulse stacking density is commonly expressed as pulses per inch (PPI). PPI is defined as the number of laser pulses delivered along a unit length during scanning. A higher value of PPI results in an overlapping of the laser-irradiated zones [68]

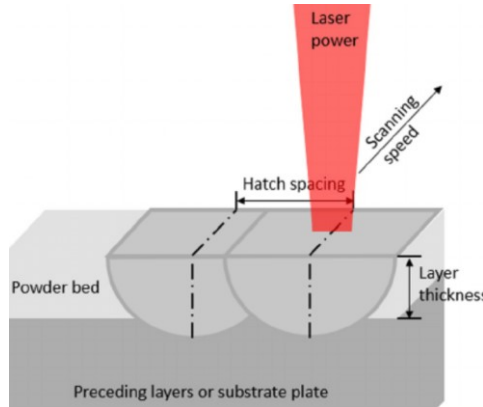


Figure 2.9: Schematic of the overlapping due to the High PPI values. [96]

and an increase of local heating, resulting in higher energy accumulating and consequently higher fluence.

Instead, the printing resolution typically expressed in dots per inch (DPI), describes the spatial resolution of the laser patterning process. Similarly, a higher DPI result in overlap of the heated area and a better graphitization [65]. Together with PPI allow the creation of unique LIG structure like sheet-like and fiber-like LIGs [62].

- **Laser passage**

The idea of using multiple laser passes was born as a solution to the limitation of the narrow possible material that can be graphenized via laser [69]. Multiple lasing lead to more efficient graphene structure that improves the electrical properties. Moreover, this technique expands the range of carbon precursors usable for LIG, and researchers were even able even to fabricate carbon structure on food [69].

This process can be achieved through two main strategies. The first method is simply making the laser go over the same spot previously heated. The second method involves increasing the spot size of the laser while keeping the density of the dots consistent, which can be achieved by defocusing the laser [69].

2.2.2 Chamber atmosphere

The laser parameters aren't the only thing to take in consideration during the LIG lasing process that influences the resulting graphene. The atmospheric condition during plays a crucial role in determining the structural composition and electrical properties of the obtained graphene [70] [71]. Yilun Li et al. [70] discovered that it possible to create superhydrophilic LIG when using O₂ or air or superhydrophobic LIG when using Ar or H₂.

2.2.3 LIG from ligneous materials

Lignin is a chemical compound found in plants. Its role is to provide them with structural integrity and mechanical strength. [72]. It is the second most abundant polymer in plant

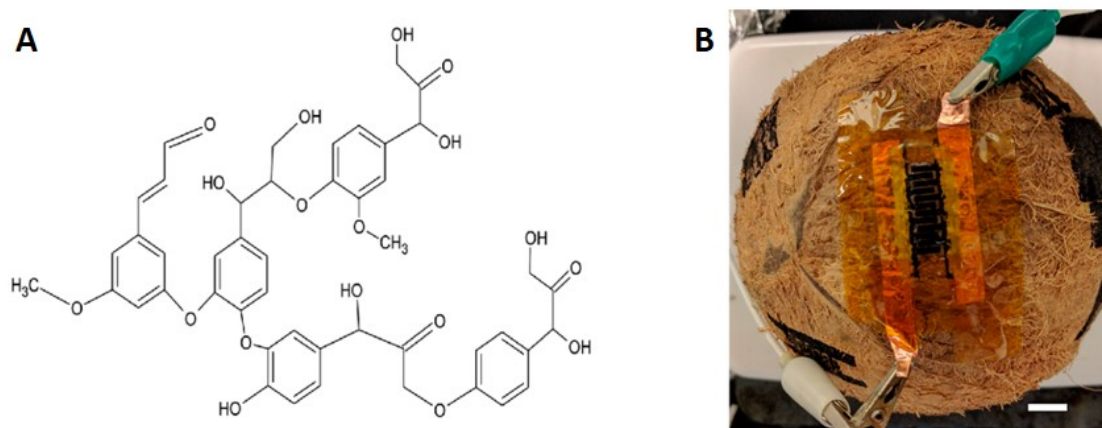


Figure 2.10: A) The chemical structure of Lignin shown its aromatic ring. B) Super capacitor fabricated onto the coconut shell. [73]

biomass after cellulose accounting for approximately 15–30% of plant dry weight [72]. The chemical structure of Lignin is a three-dimensional aromatic biopolymer mainly constituted of three phenylpropanoid units each called hydroxyphenyl (H, from coumaryl alcohol), guaiacyl (G, from coniferyl alcohol) and syringyl (S, from sinapyl alcohol) [73] [72].

It represents one of the largest renewable sources of aromatic carbons [74]. In recent years, it has gained increasing attention in the electronic field, especially in hydrogel as an environmentally friendly material. Lignin is rich in aromatic subunits that are easily converted into graphene by thermal treatment making it a promising precursor for LIG. Researchers have been able to obtain graphene from various lignin rich material like: coconut shells, potato skin, bread, almond shell, wood and cork [69] [75]. Yieu Chyan et al. [69] fabricate a microsupercapacitor on the coconut shell with an area capacitance greater than a supercapacitor made with PI substrate, however writing on this material is more challenging requiring extra step like multiple passage, pre-treatment and N₂ atmosphere.

Regarding hydrogel, Rikuto Miyakoshi et al. [76] were also able to obtained LIG from an agarose Hydrogel by adding lignin as the carbon precursor, they noted that the lignin concentration must be higher than 5% of the total weigh to observed a visible black graphene structure, and that the addition of salt, in their case NaCl, improves the quality of the graphene.

To improve the graphene quality a pre-treatment of the substrate is usually implemented. One of this treatment is incorporating the precursors with a fire retardant. For instance, Anna Lurchenkova et al. [77] used boric acid as a fire-retardant agent together with lignin. Their results show a LIG that exhibit low sheet resistance values of $6.7 \Omega \cdot \text{sq}^{-1}$ and, even if the lasing was perform in air, very few creations of oxygen-containing functional groups that can potentially hinder the quality of the graphene.

The implementation of fire retardants in the carbon precursor can improve the quality of the printed graphene even for synthetic material. ZnO nanoparticle [78] were used by Do Hoon Lee et al as fire retardant for PI. The fire retardant enhanced the photothermal process reducing the threshold fluence needed to convert PI into graphene.

2.2.4 LIG-Hydrogel application

What makes graphene interesting in electrical applications is his high electrical conductivity, in the already cited article by Do Hoon Lee et al. [78] they fabricated a stretchable strain sensor with ultrahigh sensitivity with a gauge factor of 1214 at 10% strain. LIG has also the ability to create patterned structure with different functionalities. In the next paragraph will be discussed same example of LIG application in concurrence with hydrogel.

2.2.4.1 LIG-Hydrogel Electrode

Graphene is an ideal choice to create flexible electrodes. Compared to their metallic counterpart possesses a much lower contact impedance in contact with human skin enabling highly stable electrophysiological signals recording [79]. Lei Zhaoa et al. [80] develop an electrode for electrocardiogram signal recording and electrical pacing of

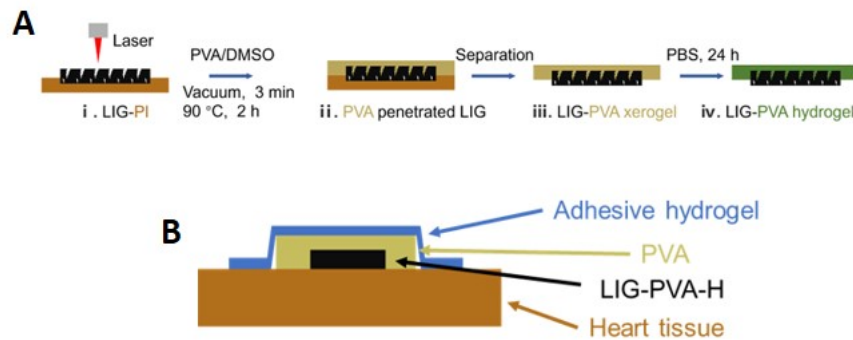


Figure 2.11: A) fabrication of LIG-PVA B) schematic of the LIG-PVA electrode. [80]

hearts. LIG was firstly printed onto the PI film then transferred onto the PVA hydrogel as described in figure 2.11. The performance of two electrodes, LIG-PI and LIG-PVA-H, were compared; the LIG-PI shows a lower impedance but after 15 minutes wasn't anymore able to effectively read the heart, in contrast LIG-PVA-H doesn't show any significant change after 15 minutes.

2.2.4.2 *LIG-Hydrogel actuators*

Actuators are fundamental devices used in automotive and mechatronic systems; their function is to transform an input signal (electrical fields, heat, pH) into motion. Soft actuators are a subclass that change their size and shape in response to the signal [81]. With the combine help of LIG and hydrogel Alexander Dallinger et al. design a multiresponse soft actuator. The device consists of three layers: LIG, PDMS and pNVCL.

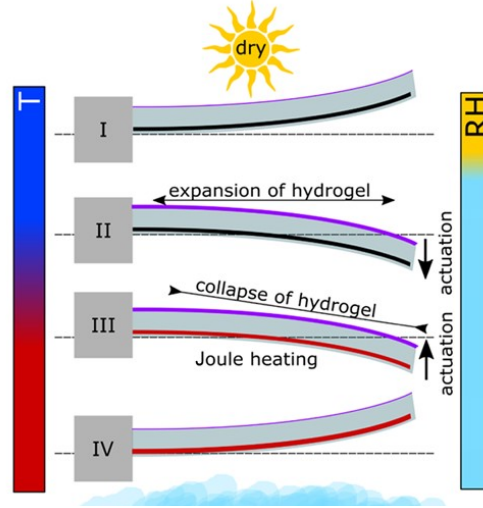


Figure 2.12: LIG-hydrogel actuators working principle. [81]

The mechanism is illustrated in figure 2.12. The PDMS and pNVCL together act as a humidity actuator. In a humid environment the pNVCL swell while the PDMS remains unchanged causing them to bend downwards. Meanwhile, the PDMS and LIG layers form a thermoresponsive actuator. When an electric current passes through the LIG path, Joule heating increases the temperature of the PDMS. As the PDMS heats up it expands, bending upward the structure. The combination of these three layers creates a multiresponse soft actuator. Both the electrode presented before and the actuators in order to obtain a high quality LIG the Laser marking was first performed onto the PI substrate and then with different method deposited onto the hydrogel, in this thesis we present a strategy to directly scribing the hydrogel.

2.2.4.3 *LIG-hydrogel sensors*

LIG pattern can be scribed onto strain sensor hydrogels to improve the sensitivity of the sensor. However, the graphene generated using the LIG process is fragile and may detach from the hydrogel during large strains.

Wang et al. [82] resolved this drawback by treating the substrate with a MXene solution. In their work, the graphene was first scribed onto PI substrate and then transferred to onto

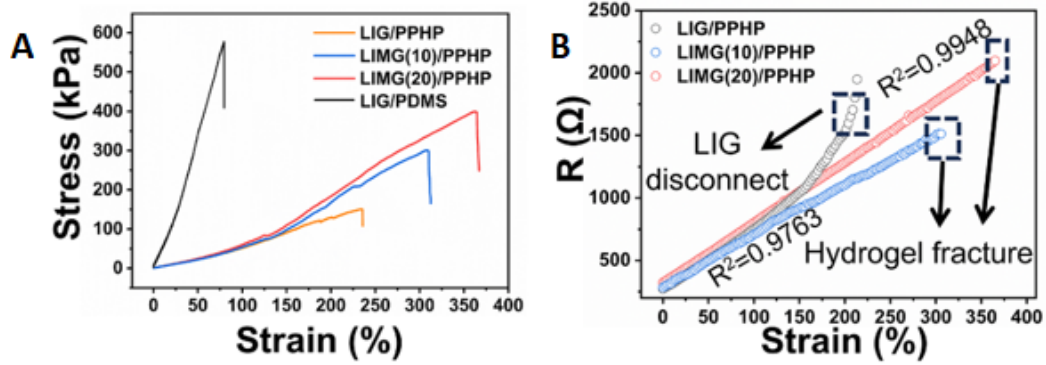


Figure 2.13: A) Stress-strain curve and B) Resistance-strain curve of the for the LIG -and PPHP hydrogel device for different concentration of MXene. [82]

a polyvinyl alcohol-phytic acid- honey-propylene glycol (PHPP) hydrogel.

The final device demonstrated an highly liner electrical characteristic and a maximum elongation of approximately 370% of its original length causing by the hydrogel fracturing. Instead, the device without the treatment has a maximum elongation of only about 250%. In this case the failure isn't caused by the fracture of the hydrogel but the LIG layer disconnecting from the hydrogel. This demonstrate the effect of the MXene solution to improve the adhesion of the LIG.

Chapter 3

3 Materials and methods

3.1 GelMA synthesis

Gelatin methacrylate was synthesis following the protocol reported by Loessner et al [83].

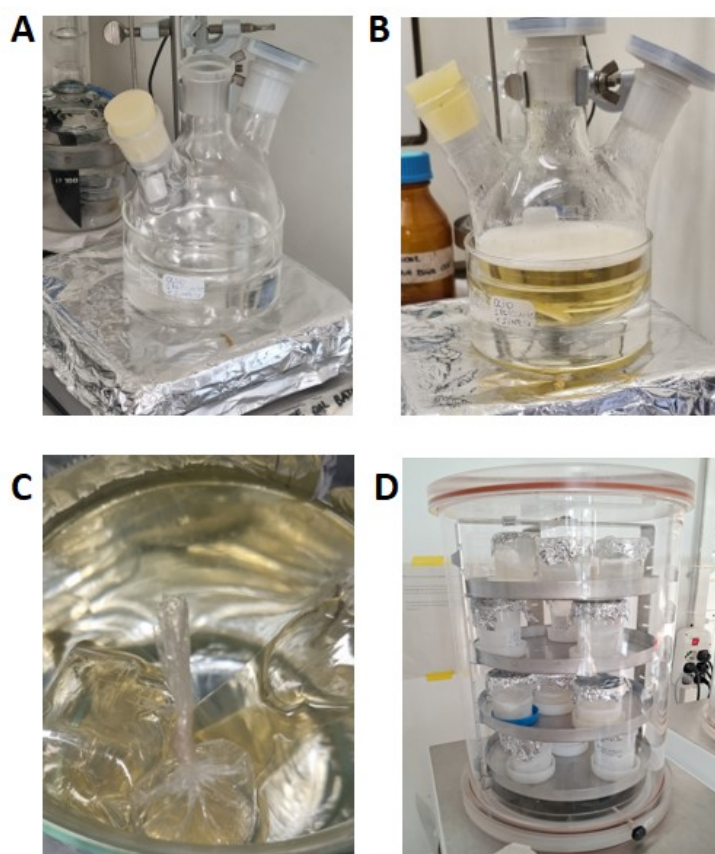


Figure 3.1: Synthesis process of GelMA: A) Experimental set-up. B) Mixture after the addition of Methacrylic anhydride. C) Dialysis set-up. D) Mixture put inside various container for lyophilization.

20 g of Gelatin derived from cold-water fish skin (from Sigma-Aldrich) were dissolved in 200 ml of distilled water inside a three-neck round-bottom flask. The solution was stirred using a magnetic stirrer while heated on a hot plate (VWR Advance VMS-C7) maintained at 55 °C until a clear solution was obtained (Figure 3.1a)

After, Methacrylic anhydride (MA) was slowly dropped with a dropping funnel over 20 min at a ratio of 5.8 ml every 10g of Gelatin. For the present synthesis, 11.6 ml of MA

was added over 40 min. For this step the temperature was lowered at 45 °C while rising the stirring speed was increased to create a vortex, ensuring homogeneous mixing and controlled methacrylation.

The reaction mixture was then allowed to rest for 2 h under continuous stirring. During the entire process the experimental set-up was covered with aluminum foil to prevent unwanted polymerization. Successful methacrylation was indicated by a visible color change of the solution from transparent to yellow (figure 3.1b).

Since not all the MA reacted with the gelatin, the solution was transferred to a Falcon vial and centrifugated, using a thermos Scientific IEC CL10, at 3500 rpm for 3 min. The unreacted MA precipitate at the bottom of the vial as a white solid substance and was removed. The supernatant solution is poured inside a beaker and diluted with 200 ml of distilled water.

The GelMA solution was transferred into Dialysis tubing cellulose membrane (from Sigma-Aldrich and molecular weight cut-off 14000) and place inside a large beaker filled with distilled water. The distilled water was replaced daily during the first four day and after a total of one week the dialyses should be completed, this can also be visually confirmed by the solution becoming clearer.

Following dialysis, the pH of the solution was adjusted to 7.5 by adding a saturated sodium bicarbonate (NaHCO_3 from Sigma-Aldrich) solution.

The solution was distributed inside several container, frozen at -80 °C, and then lyophilized for 1 week. After the lyophilization the solution becomes a porous white sponge.

3.2 Eutectogel and organogel synthesis

Once the GelMA was obtained, the hydrogel formulations were prepared.

As Deep Eutectic Solvent (DES) the common mixture of ChCl (from Tokyo Chemical Industry) and Glycerol (from Sigma-Aldrich, Germany, Darmstadt) with a molar ration of 1:2 was implemented. The mixture is heated at 50 °C and the stirrer until it becomes clear and homogeneous solution, typically about 10/15 minute.

After GelMA was gradually added at a concentration corresponding to 20% w/w with respect to the DES. To facilitate dissolution and avoiding bubbles formation, GelMA is previously broken in smaller piece and added progressively every 5 minute while the stirrer is kept at the lower stirring speed, under 100 rpm. Each 5 minute same GelMA pieces are added. Once fully incorporated, the solution should become yellow.

Subsequently, Cellulose nanofibrils (CNF) were incorporated at a concentration equal to 50% w/w with respect to the total of GelMA and DES content. Cellulose and his derivatives are frequently used in hydrogel to increase the mechanical and rheological properties of the materials[].

To reduce overpolymerization during UV exposure, a dye was added to the formulation. In this work, A natural dye, lignin sulfonate (LS), was used for this purpose. Since the hydrogel precursor is highly transparent, UV light can reach unwanted areas and polymerized them, using a dye can absorb part of the incident light and reduce the overpolymerization effect. The implementation of LS as a second advantages, the aromatic carbon ring in LS could promote the graphenization via LIG of the hydrogel. For this work Sodium-LS was implemented at different concentration varying from 2% to 40% w/w respect to GelMA, as shown in figure 3.2.

For improving the quality of the LIG structure created ZnO nanoparticle (with a diameter lower than 40nm) were added with a concentration of 30% w/w of S-LS.

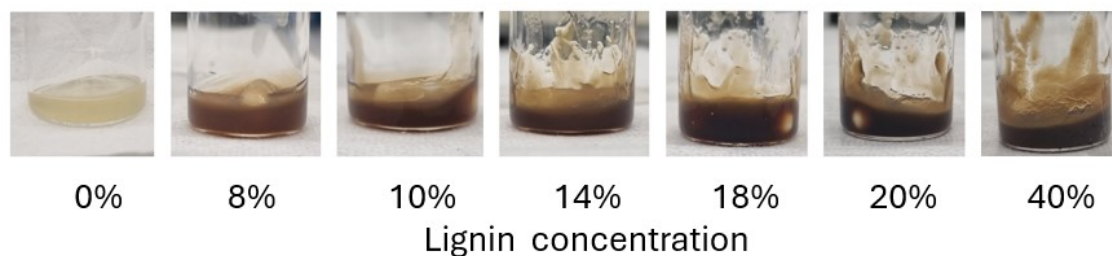


Figure 3.2: Resin at different Lignin concentration from 0% to 40% respect to GelMA.

Finally, the photoinitiator Lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP obtained from Sigma-Aldrich, USA, St. Louis) was added with a concentration of 1% w/w of GelMA. LAP is commonly employed in hydrogel for its high water solubility and lower toxicity compared to other photoinitiators like TPO. For LAP, the photopolymerization can be initiated under both UV light (365 nm) and visible light (400 nm) even if showing the highest polymerization rate with the UV light [84].

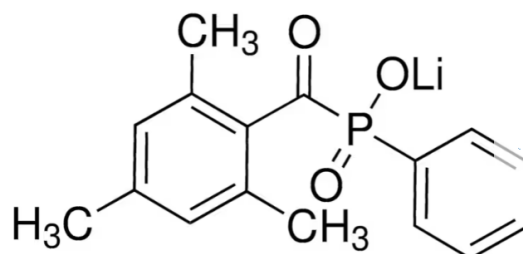


Figure 3.3: Chemical formula of Lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP).

For the organogel formulation the procedure was identical, with the only difference being the type of solvent employed. Instead of a solution of glycerol and CHCl_3 , pure glycerol was used as solvent. As for the eutectogel different concentrations of LS were tested.

3.3 Substrate for LIG

The synthesis required the polymers and the Sulfonate-Lignin to be prepared in two separate solutions. In the first vial, 1g Sulfonate-Lignin (obtained from Sigma-Aldrich Co. St. Louis, USA) was dispersed in a solution of 10 ml DI water and NaOH (2M). The solution was stirred for 30 min, after which 0.4 g of ZnO nanoparticles (diameters less than 40 nm, obtained from Sigma-Aldrich St. Louis, USA) were added and stirred for 24h, their effect during the LIG process has already been discussed previously.

In the second vial, 1g of polymer is dissolved in 10 ml of DI water. Three polymers were investigated: PVA, Gelatin from Fish, Gelatin from Pork (all obtained from Sigma-Aldrich, Canada).

The two solutions were then mixed in a 1:1 (v/v) ratio for 15 minutes. Glycerol (obtained from Panreac Quimica Sau) was added to improve the elasticity of the membrane, to evaluate the changes in material properties and the effects during the LIG process, different concentrations of glycerol, ranging from 60% to 100% w/w respect to the LS, were investigated.

To further increase the conductivity, was tried adding salts such as NaCl in the formulation.

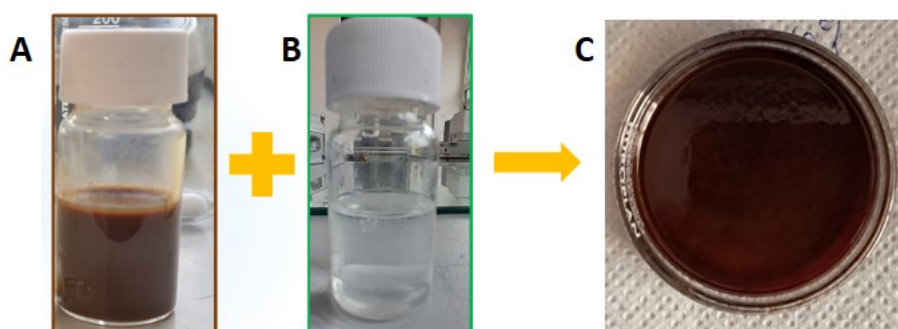


Figure 3.4: A) First solution composed by 1g of Lignin sulfonate and 0,4g of ZnO and 10 ml of DI water. B) Second solution of 1g of PVA and 10 ml of DI water C) results of the two solution together after the dehydration.

3.4 3D printing

Before printing, it is necessary to optimize the printer parameters. The Asiga UV Max DLP allows fine tuning of several parameter, like approach or separation velocity of the support, the waiting time after the exposure, the temperature of the Chamber and ecc. Among these three are the most valuable: layer thickness, light intensity and exposure time. Without prior knowledge of the resin, identifying the best combination can require several trial and error. Therefore, a screening of the parameters was performed through material testing.

3.4.1 Material testing

The DLP printer UV Max (Asiga, Australia) has a build-in material test function. The resin was poured into the tray, and the printer projects a circular spot with a diameter of 5 mm. The light intensity was kept constant at 72 mW/cm^2 while the exposure time was varied. The cured resin was then transferred to a microscopice slice and its high was measured using a caliper.

The relationship between the depth of cure C_d (thickness of the cured layer), light intensity and exposure time is defined by Jacobs [85]:

$$C_d = D_p \ln \left(\frac{E}{E_c} \right)$$

Where E is the exposure energy, defined as the product of intensity and time, E_c is the critical exposure energy required to cure a layer and D_p is the depth of light penetration. Both E_c and D_p can be determined from the semilogarithmic plot between the thickness of the cure layer and the exposure energy. In particular D_p is the slope of the plot and E_c is the intercept with the x axis.

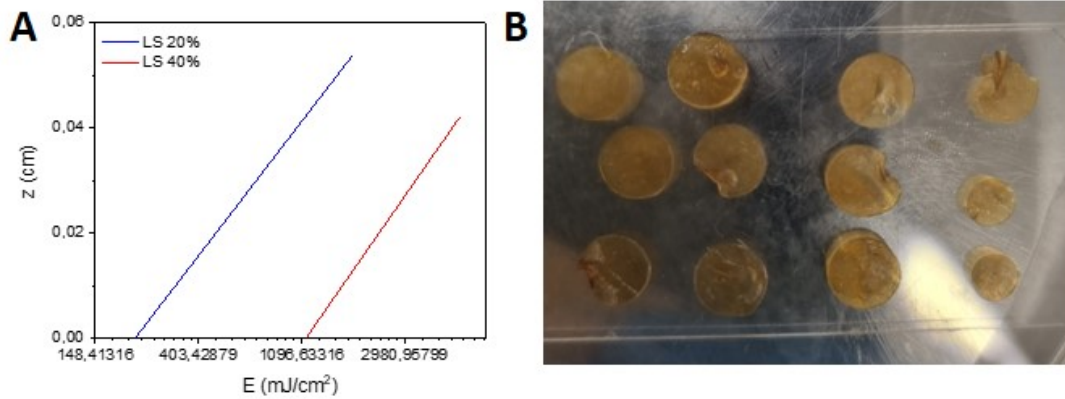


Figure 3.5: A) semilogarithmic plot of exposure energy required for each thickness. B) Circular spot of polymerized resin after the irradiation for material testing.

3.4.2 Printing

The final parameters used for a layer of 0,05 mm are summarized in the table below.

Resin	LS	Zinc oxide	Light Intensity [mW/cm ²]	Exposure Time [s]
Eutectogel	2%	No	12	10
	20%	No	20	18
	40%	No	52	36
	40%	Yes	62	50
Organogel	2%	No	20	15
	20%	No	30	22
	40%	No	62	26
	40%	Yes	62	56

The geometry of the hydrogel was designed using the Asiga composer, its proprietary software, and loaded into the printer. After the printing, the gel was separated from the support using a metal blade and placed inside a UV oven (Robotfactory, Italy, Mirano) for 7 min to complete the post curing the post-curing.

3.5 Laser induced graphene

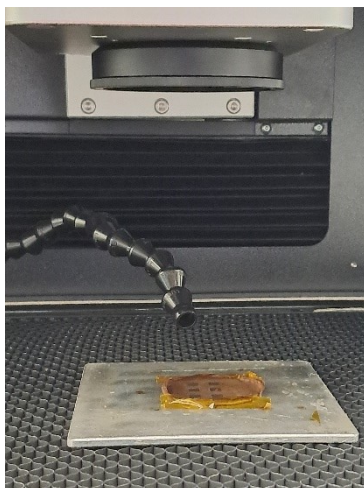


Figure 3.6: experimental set-up of the sample place onto a metal plate under the LIG laser.

LIG was employed to render the surface of hydrogel and the gelatin substrate conductive. The samples were placed onto a metal plate height 4,1 mm. The CO₂ laser system used was Colibri-Laser Veronese (Italy) with $\lambda = 10.6 \mu\text{m}$ and $P_{\text{max}} = 10\text{W}$.

For hydrogel sample 2 laser passes were performed. The first with 8W power and the scanning speed at 40 mm/s, the second with scanning speed at 100 mm/s and the power ranging from 2 to 6W.

For the gelatine substrate the speed was set at 60 mm/s, the pulse frequency at 1 kHz and the laser power was adjusted depending on the printed geometry. A 3W power was used when printing squares and 2W when printing crosses geometries. To improve the graphitization a continue flow of N₂ was introduced in the chamber through a tube pumping granting an inert atmosphere.

3.5.1 Encapsulation

To protect the graphene formation from damage during the test protective polymer were deposited. Two polymers were compared: shellac and acrylate epoxydised soybean oil (Sigma Aldrich). Liquid shellac is directly dropped onto the surface of the substrate placed inside a petri after one day the shellac should become a solid flexible gel. For the soybean oil it is prepared with 0.1wt% BAPO (Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, from Sigma Aldrich), then a small amount is poured on the patterned and thinned using a metallic bar coater and then polymerized under UV light for 2 min.

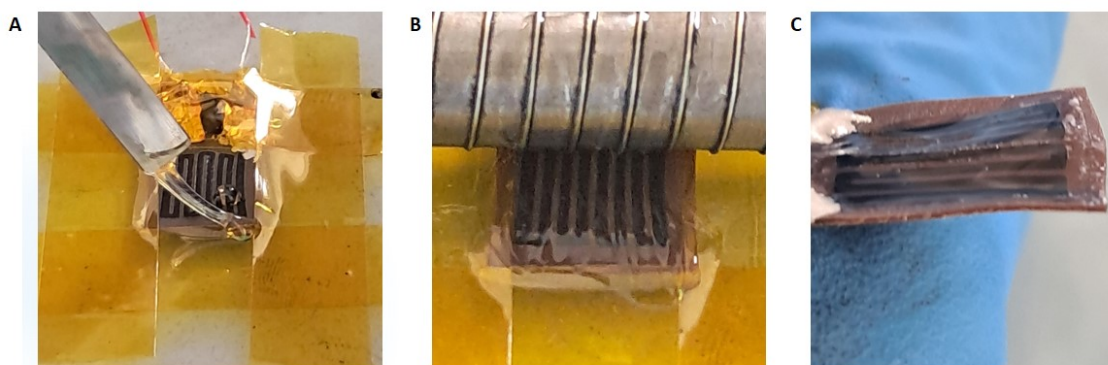


Figure 3.7: A), B) shows the process for depositing the soybean oil onto the LIG. C) The final results after the soybean oil is polymerized.

3.6 Material characterization

3.6.1 Rheology and viscosity

Hydrogels are neither fully elastic nor fully viscous materials, therefore, they are defined as viscoelastic materials. To characterize this intermediate mechanical behaviour is usually performed the rheological test.

Rheology is the study of deformation or Flow of the material under an applied external stress. Flow is defined as the continuous deformation of the material during a period of

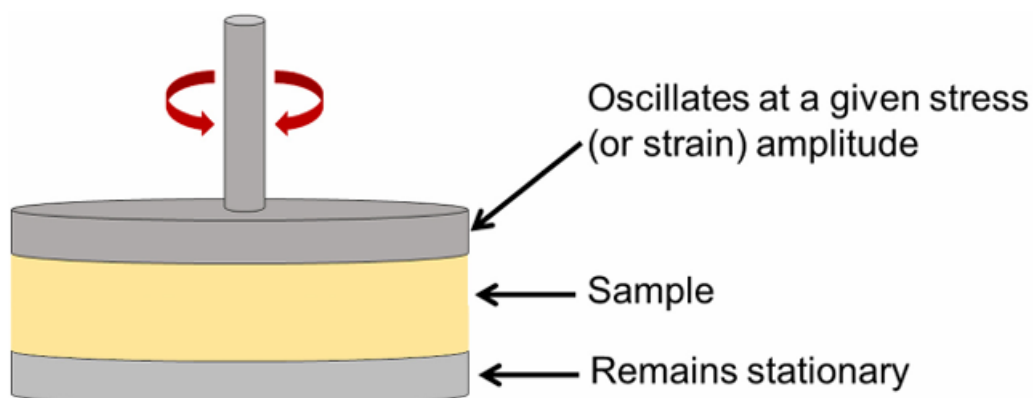


Figure 3.8: functioning principle of the double parallel plate set-up for rheological test. [86]

time. Understanding the flow behavior of the material is important in several fields because its study allows the characterization of the viscoelastic properties of the material. The most common rheological set up is small amplitude oscillatory shear (SAOS), it is a two parallel plate model in which the upper plate oscillated at a fixed frequency and the lower plate remain stationary [86]. Both plates are equipped with sensors, the upper plate

sense the strain γ , instead the lower plate measure the shear stress σ . The two physical quantities are plotted as a function of time, and, for this set up, they exhibit sinusoidal behavior. The phase difference provides information about the material viscoelastic behavior. If their phase difference δ is 0° behave as a purely elastic material, instead for a purely viscous material the phase difference is 90° . The ratio of the applied strain (or stress) to the measured stress (or strain) yields the complex dynamic modulus G [86].

$$\begin{aligned} |G| &= \frac{\gamma_{max}}{\sigma_{max}} \\ G' &= |G| \cos \delta \\ G'' &= |G| \sin \delta \\ G &= G' + iG'' \end{aligned}$$

Where G' is the real part of the dynamic modulus and represents the elastic component instead G'' is the imaginary part and describes the viscous behavior.

In this thesis, 2 types of rheological test were performed: amplitude sweep and photorheology.

- **Amplitude sweep** is a test in which the subject dynamic modulus is analyzed as a function of strain (strain applied ranges from 0,01% to 1000% of its starting length) while maintaining the oscillation frequency constant (at 1 Hz).
- In **Photorheology** the rheometer is equipped with a UV or visible lamp position under the lower plate which is made of a transparent material (For UV radiation the ideal material is quartz). In this set-up is monitored the change in G after exposed to the light, the test is started 60 second before the light is turn while the Frequency and the strain kept constant (1 Hz and 1% respectively). For hydrogel the typical response is to initially see $G' < G''$, indicating a liquid behavior. Then after light exposure both modulus increasing with G' raising faster reaching the gelling point where $G' = G''$. Both moduli will continue rising until the material is fully polymerized and the modulus became constant.

The rheometer employed in this work is the Anton Paar rheometer (Physica MCR 302) with the metallic upper plate with a diameter of 25 mm and a quartz lower separated by a gap of 0.2 mm, the sample was irradiated through the lower plate with a Hamamatsu LC8 UV lamp.

3.6.2 FESEM

The surface morphology and topography of the sample can be investigated by Field Emission Scanning electron microscopy (FESEM).

FESEM is an advanced version of Scanning electron microscopy (SEM) that improves the resolution of the image by replacing the thermionic emitter with a field emission gun as the electrons source. This modification significantly improves image resolution

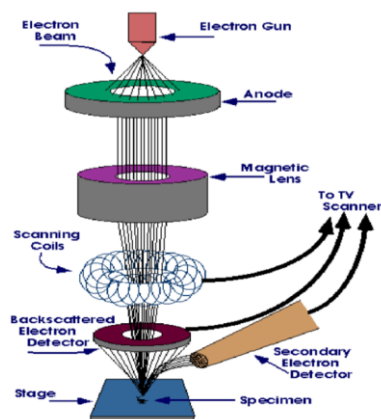


Figure 3.9: schematic illustrating the working principle of the FESEM microscope and its main components. [87]

because the generated electron beam is smaller, brighter, and more coherent. Moreover, the acceleration voltage can be lowered by increasing the ability to see finer details [87]. The samples are placed inside a vacuum Chamber to ensure that the electron beam remains stable and focused. The interaction between the sample and the beam generates secondary and back-scattered electrons that are collected by dedicated detectors to produce 3D images of the sample morphologies.

In this work, FESEM was employed to attest to the quality of the graphene formed during LIG. LIG typically exhibits a porous structure, which dimension and numbers affect the electromechanical properties. Furthermore, by mounting the sample at an angle of 45° can also be evaluated the thickness of the graphene film. The samples were prepared by sputtering with Q150T 20 nm platinum layer onto their surface.

3.6.3 EDX

Energy dispersive X-ray spectroscopy (EDX) is a technique used the microscope used for SEM/FESEM spectroscopy to characterize the chemical composition of the material [88]. The interaction between the incident electron beam interacts with the sample not only produce secondary electrons and backscattered electrons, but, iIn addition, X-rays are also emitted. These emitted X-ray are unique for each element in the periodic table because their energy depends on the atomic number. So, the EDX spectrum exhibits peaks corresponding to the elements present in the material.

3.6.4 RAMAN

Raman spectroscopy is a characterization technique used to investigate the chemical composition and structural properties of the materials. This technique uses the interaction between monochromatic light and the sample to provide information about chemical bonds, crystalline phases and molecular structure.

Some of the incident lights pass through the specimen, while another is scattered due to the interaction with the sample [89]. The scattered radiation can be either elastic, Rayleigh scattering or inelastic. Raman spectroscopy focuses on inelastic scattering, in which the energy of the scattered electron differentiates from the incident electron. There are two types of inelastic scattering:

- Stokes in which the scattered photons have a lower energy than the incident photons:

$$E = h\nu$$

$$h\nu_s < h\nu_i$$

- Anti-Stokes in which the scattered photons have an higher energy than incident photons:

$$h\nu_s > h\nu_i$$

The energy of a photon is equal to the product of the Plank constant h and the frequency of the phonon ν . ν_s and ν_i are the frequency of the scattered and incident photons respectively. Since frequency and wavelength are related by $\nu = \frac{1}{\lambda}$, means that the interaction with the vibrating atoms produces a wavelength shift called Raman shift. The magnitude of this shift is characteristic of the specific atomic vibration. Therefore, Raman spectra give a closer look to the chemical and structural composition of the material. Regarding LIG samples there are 3 characteristic peaks:

- **G Peak**

This peak originates from the in-plane vibration of sp^2 -hybridized carbon atoms. Its presence indicates the formation of an ordered graphitic/graphene structure within the matrix. Its center is usually around 1580 cm^{-1} .

- **D Peak**

This is the disorder peak and originates from the vibration of disorderly sp^2 -hybridized carbon atoms. For this reason, in literature, the quality of the graphene is evaluated through the ratio between the peaks. The I_D/I_G ratio evaluate the quantity of defects in the crystalline structure and the quality of the graphitization. The D peak is usually positioned around 1350 cm^{-1}

- **2D Peak**

The 2D peak is the second order harmonic of the D peak. The ratio I_{2D}/I_G estimates the quantity of graphene layer formed.

3.6.5 Recycle test

The LIG substrate, being primarily composed of gelatin and lignin, can be recycled and returned to the liquid state even after evaporation. To recycle the substrate a few milliliters of water was added and place on a heated plate at 60°C , after a few minutes under continuous stirring the substrate return to the liquid state. To evaluate the quality of the recycled substrate 6 $5 \times 5 \text{ mm}$ square were printed by LIG after each cycle and their sheet resistance evaluated and compared.



Figure 3.10: Recycle process of the porcine gelatin substrate from the final LIG product to the regenerated liquid state.

3.6.6 Biodegradability test

The test is performed to analyze the ability of the LIG substrate to decompose when placed into soil and, secondly, if it releases toxic chemicals during the process. The first goal is obtained by placing the substrate into a vase full of soil. Four vases were utilized, one functioned as a control with no material placed inside. In two of them, the PVA and Porcine Gelatin substrate with the parsley seeds, with gelatin concentrations of 20% and 100% w/w of LS respectively, were placed. And the fourth one with both inside.

To analyze the toxicity of the released chemical, parsley seeds are placed inside the vases. If no dangerous chemical for their growth is present in the soil, they should grow in 2-4 weeks. The soil was kept wet during the process by adding water every 2 days.

3.7 Electrical test

3.7.1 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is the most common technique to calculate the impedance. Impedance is defined as $Z = \frac{V}{I}$, it represents a generalized resistance more suitable for Alternating Current (AC) measurement. In AC the ratio results in a complex number, where the real part is the resistive contribution and the imaginary part is the reactive contribution.

In EIS measurement the material can be stimulated with either a current (GEIS) or a potential (PEIS), in this work PEIS was the preferred choice. A sinusoidal voltage centered around the Open Circuit Potential (OCP) was applied to the sample, while the current is

measured. The impedance was calculated over a broad range of frequency, by changing the frequency of the applied voltage.

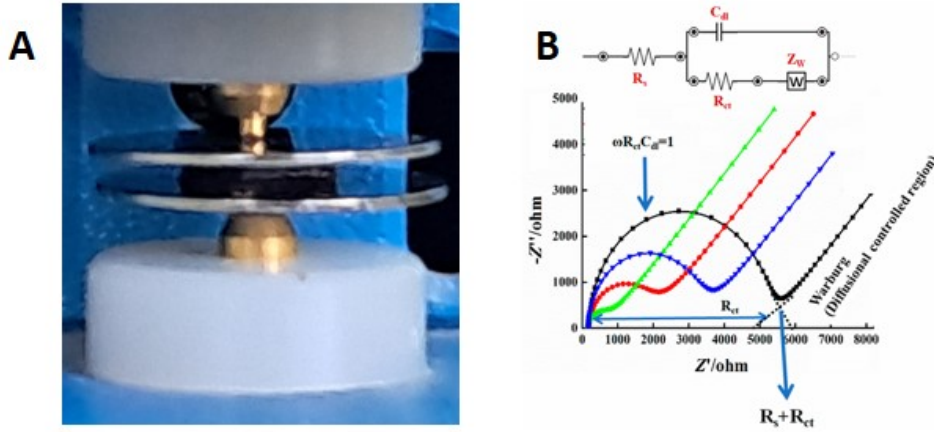


Figure 3.11: A) Image of the sample between two plate and clamped between the probe tips of the Biologic. B) Example of Nyquist plot and its relative equivalent circuit [90].

The material is cut in a disk with a puncher of 6 mm diameter and their thickness measure with a caliber, then is pressed between two titanium plates acting as electrode. The Biologic BH-11 sent the information to the computer that analyzed the data.

Usually, the impedance is plotted using the Bode diagram (Z amplitude vs Z phase) or Nyquist diagram (Z real vs Z imaginary). The shape of the generated Nyquist plot depends on the electrochemical properties of the system and can be interpreted using an equivalent circuit. In Figure 3.10b shown an example of Nyquist plot for the described circuit where R_s is the resistance of the material and R_{ct} is the charge transfer resistance [90]. Typically, the Nyquist plot shape is a semicircle in which the intersection with the real axis at high frequency is the R_s . Knowing the resistance calculating the conductivity only required

$$\rho = \frac{L}{A R_s}$$

Where L is the thickness of the sample and A is its area.

3.7.2 Sheet resistance

Sheet resistance is used to evaluate the electrical properties of thin film. It defined as

$$R_s = \frac{\rho}{t}$$

Where ρ is the resistivity of the material and t the film thickness. Sheet resistance is expressed in ohms per square ($\Omega/\square$) and represents the resistance of a square of the material independent of its dimensions.

In this work, the sheet resistance is calculated using the Van der Pauw method. Both square and cross geometries were printed onto the substrate. A current was applied between two vertices and the resulting voltage difference was measured. According to the ohm law the resistance was then calculated. Four resistance measurements were performed according to the diagram in figure 3.11b obtaining a horizontal resistance R_H and a vertical resistance R_V are obtained. In Van der Pauw method R_S is related to R_H and R_V by the equation:

$$R_s = \frac{\pi}{\ln(2)} \frac{R_H + R_V}{2}$$

To improve the electrical contact with LIG silver paste was placed at the measuring point. Four micromanipulators were connected to an SMU 4201 that supplied a current sweeps between $-1 \mu A$ and $1 \mu A$ and simultaneously reading the Voltage difference.

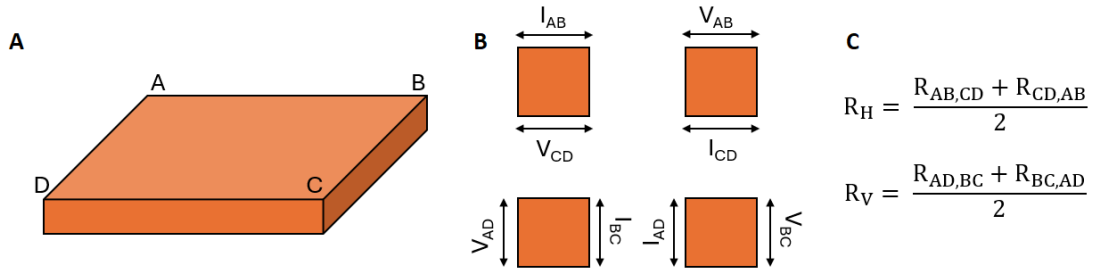


Figure 3.12: Van Der pauw method for a square geometry. A) Schematic of the sample and related contact point. B) Four measurements performed in Van der Pauw. C) equation to calculate the horizontal and vertical resistance.

3.7.3 Tensile test

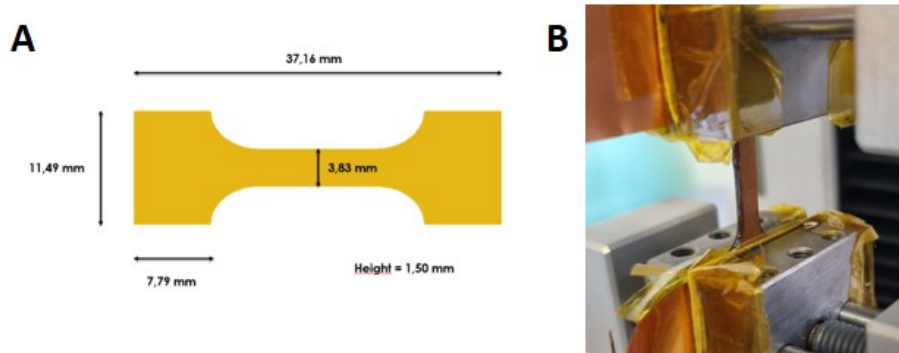


Figure 3.13: A) CAD dimensions used to print dog-bone with UV Max (Asiga). B) tensile System used for the test.

Mechanical sensors detect electrical variations in electrical properties due to external stimuli. The main mechanical properties of the sensors evaluated in this work are: Young Modulus, maximum break length and yield stress. All of these quantities can be derived from the strain stress curve obtained during tensile testing. The samples were clamped at the extremities and stretched while the applied load is measured. The universal testing machine FZ3-X500 (Test Engineering) was set to move at constant speed of 5mm/min. stress σ and strain ε were derived from the equations:

$$\sigma = \frac{Load}{Area}$$

$$\varepsilon = \frac{L - L_0}{L_0} \times 100$$

Where L_0 is the initial sample length and L the sample length after the deformation and A is the area of the sample section. Young modulus is defined as the ratio $E = \frac{\sigma}{\varepsilon}$, for this reason it can be derived from the slope of the initial region of the stress- strain curve. During the test, the resistance of the sample was simultaneously calculated with BK precision 894 LCR meter. An alternating voltage of ± 0.5 V at a frequency of 1000 Hz was applied to the sample. The resulting impedance was interpreted with a parallel resistor–capacitor (RC) equivalent. The sensitivity was evaluated through the Gauge Factor GF:

$$GF = \frac{\frac{R - R_0}{R_0}}{\varepsilon}$$

Where R_0 is the starting resistance and R is the resistance after strain.

The test sample were printed using DLP. As the shape was chosen the typical dogbone geometry that allows for better anchorage at the extremities reducing slippage during the test.

3.7.3.1 Hysteresis test

To evaluate the stability of the electrical response, the material was subjected to multiple loading–unloading cycles with a speed of 2 mm/min and 20 mm/min. During the loading phase, the sample was strained to a fixed displacement, while during the unloading phase it was returned to its initial position. These tests were performed using the same universal testing machine (FZ3-X500) employed for the strain measurements. The stability of the sensor was assessed by monitoring changes in amplitude of resistance cycles normalized to the average resistance, over the course of the cycling test.

3.7.3.2 Bending Test

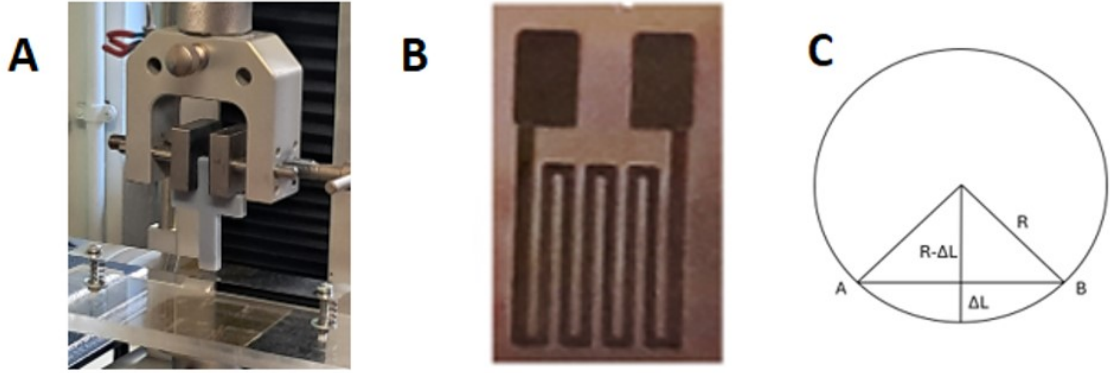


Figure 3.14: A) Experimental configuration of bending test. B) Strain gauge geometries used for the bending test. C) Visual representation of the trigonometrical equation used to calculate the radius.

To induced bending, the sample is not clamped but fixed to a metallic support, while an indenter is slowly lowered, bending the metallic support and consequently the sample. The curvature is defined as the reciprocal of the radius of the imaginary circumference formed by the bent sample. To obtain the radius R, the Pythagorean theorem can be applied to the triangle described in figure 3.13c.

$$R^2 = \left(\frac{L_{AB}}{2}\right)^2 + (R - \Delta L)^2$$

Where ΔL is the vertical displacement, and L_{AB} is the distance between the anchor point of the metallic support.

This test was performed on the LIG printed strain gauges, three different geometries were printed, as shown in figure 3.13b, in order to evaluate which configuration exhibits the greater sensitivity. Copper stripes were used as electrode and connected to BK precision 894 LCR meter, using the same parameters as tensile test, to evaluated the impedance.

Chapter 4

4 Results and discussion

4.1 Hydrogel

4.1.1 Photorheology

Photorheologies were performed to understand the behavior of the hydrogel when it polymerized. From the Graph in figure 4.1a a rapid polymerization occurs immediately after the UV irradiation for plain and 2% dyes filled (tannin, LS) inks. However, the gel transition, indicated by the crossover point between G' and G'' , was never observed because the elastic modulus G' remained greater than the viscous modulus even when the resin was not polymerized. However, the eutectogel inks, both in their neat form and with different fillers, underwent photopolymerization, forming stable gels, as demonstrated by the plateau reached by G' approximately 20 seconds after lamp activation. To understand

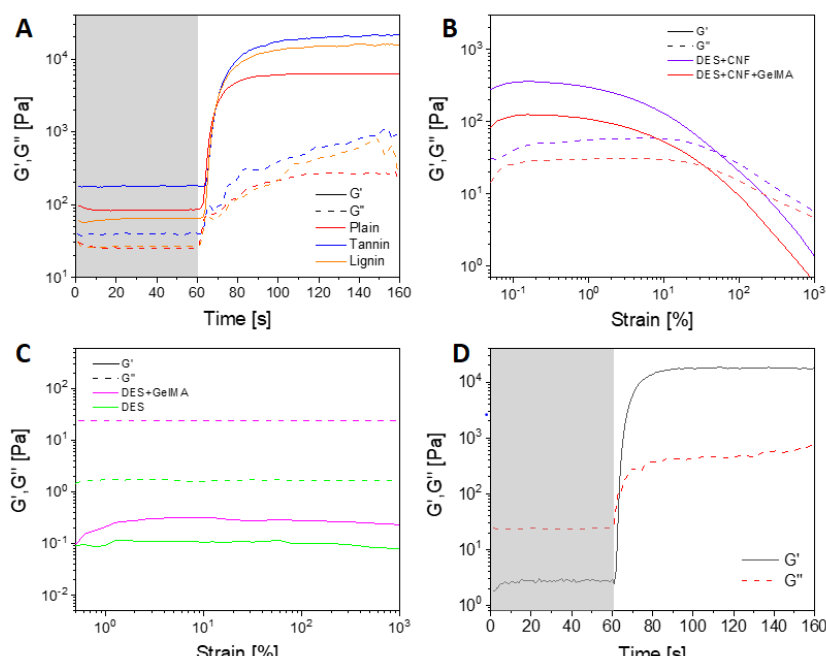


Figure 4.1: Rheologies tests of the hydrogel with LS concentration of w/w relative to GelMA. A) Elastic and viscous moduli before and after lamp switching on. Lamp was switched on after 60 s. B) Amplitude sweep for the formulation with CNF. C) Amplitude sweep for only DES and GelMA dissolved in DES. D) Photorheologies of only DES and gelMA analyzing the gel transition.

the origin of this behavior, rheological analysis were conducted on each component of the resin. The figures 4.1b, 4.1c show the only the presence of CNFs is sufficient for the resin to behave like a gel. One explanation is that CNFs already provide abundant physical crosslinking in the matrix to jellify the resin matrix. In fact, in the classical configuration, consisting only of the chemical network with GelMA dissolved in DES, the gel point was reached after 4 s, and photopolymerization occurred rapidly.

Increasing the lignin-sulfonate (LS) content drastically prolonged the polymerization process requiring nearly 6 minutes for the mixture with 40% w/w LS content respect to GelMA as shown in figures 4.2b, 4.2c. Furthermore, the addition of ZnO further delays the polymerization almost requiring 20 minutes (figure 4.2c).

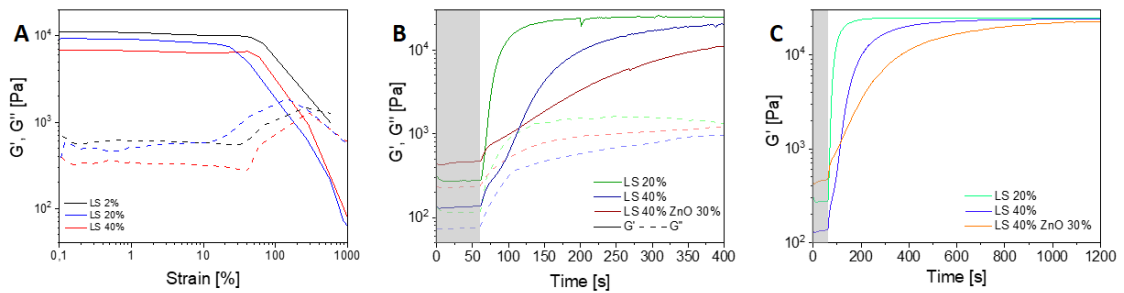


Figure 4.2: Rheologies of the hydrogel for different LS concentration. A) Amplitude sweep performed after the polymerization. B) Details of the photorheologies when UV lamp is turn on at 60s. C) The behavior of G' during the photopolymerization.

4.1.1.1 Viscosity

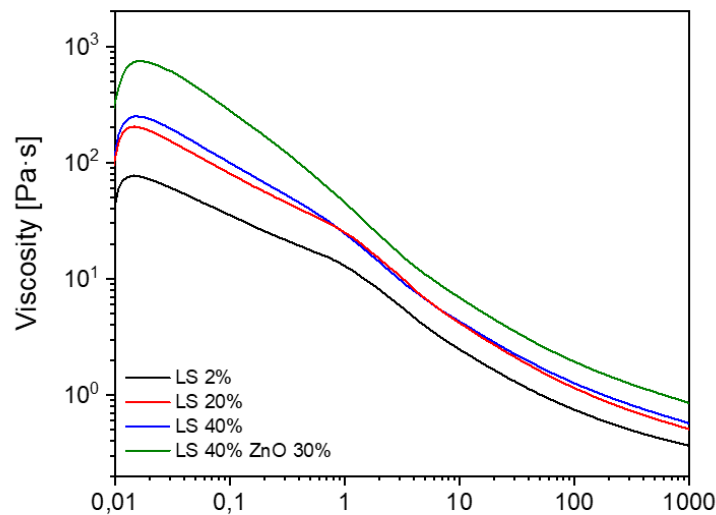


Figure 4.3: Viscosity of the eutectogel resin for each LS concentration.

The viscosity of the resin was also obtained using the rheometer, and the results are presented in figure 4.3. As expected, increasing the filler content led to a more viscous solution but is between the suitable range for DLP printing, highlighting their

compatibility with this fabrication approach. Furthermore, the viscosity linearly decreases with the increase in shear rate, typical of shear-thinning behavior.

4.1.2 3D printing

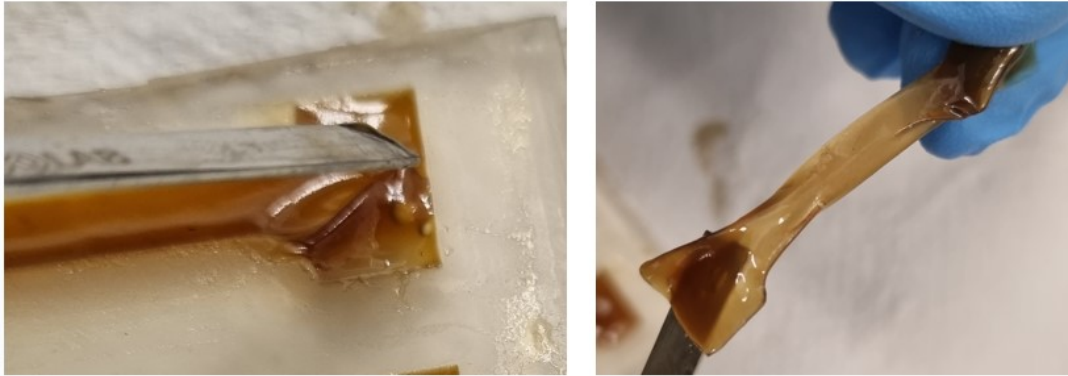


Figure 4.4: Unsuccessful polymerization of eutectogel with LS 20% w/w relative to GelMA using an UV light.

Although increasing the LS content negatively affected the photopolymerization process due to the excessive light scattering effect, the hydrogel was still able to be photopolymerized. However, because of the dark color the light cannot easily penetrate inside the resin. As shown in figure 4.4, when the resin was poured inside a mold and irradiated with an UV light, the results was that only the first layer underwent polymerization while the underlying material remained liquid.

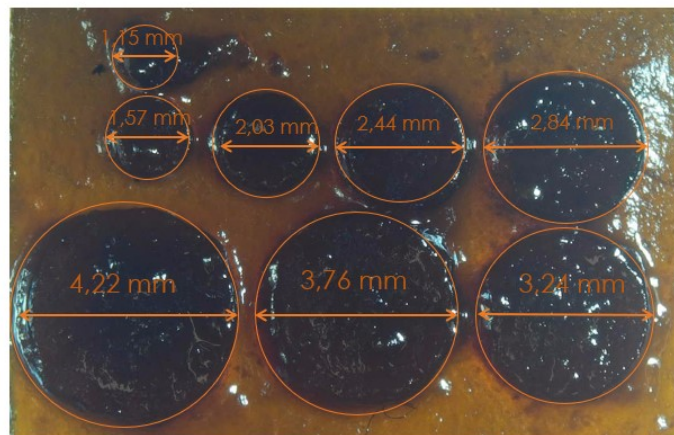


Figure 4.5: resolution test with difference cylinder with decreasing diameter.

The solution was to adopt the DLP printing technology that can polymerized small layer stack one on the other to print the hydrogel. The parameters used are described in the

material and method section. The 3D printed hydrogel shows good flexibility and high resolution able to create features with dimensions as small as 1 mm.

4.1.3 Mechanical Test

The response of the material was evaluated through tensile test. Dog-bone shapes samples were successfully printed using DLP.

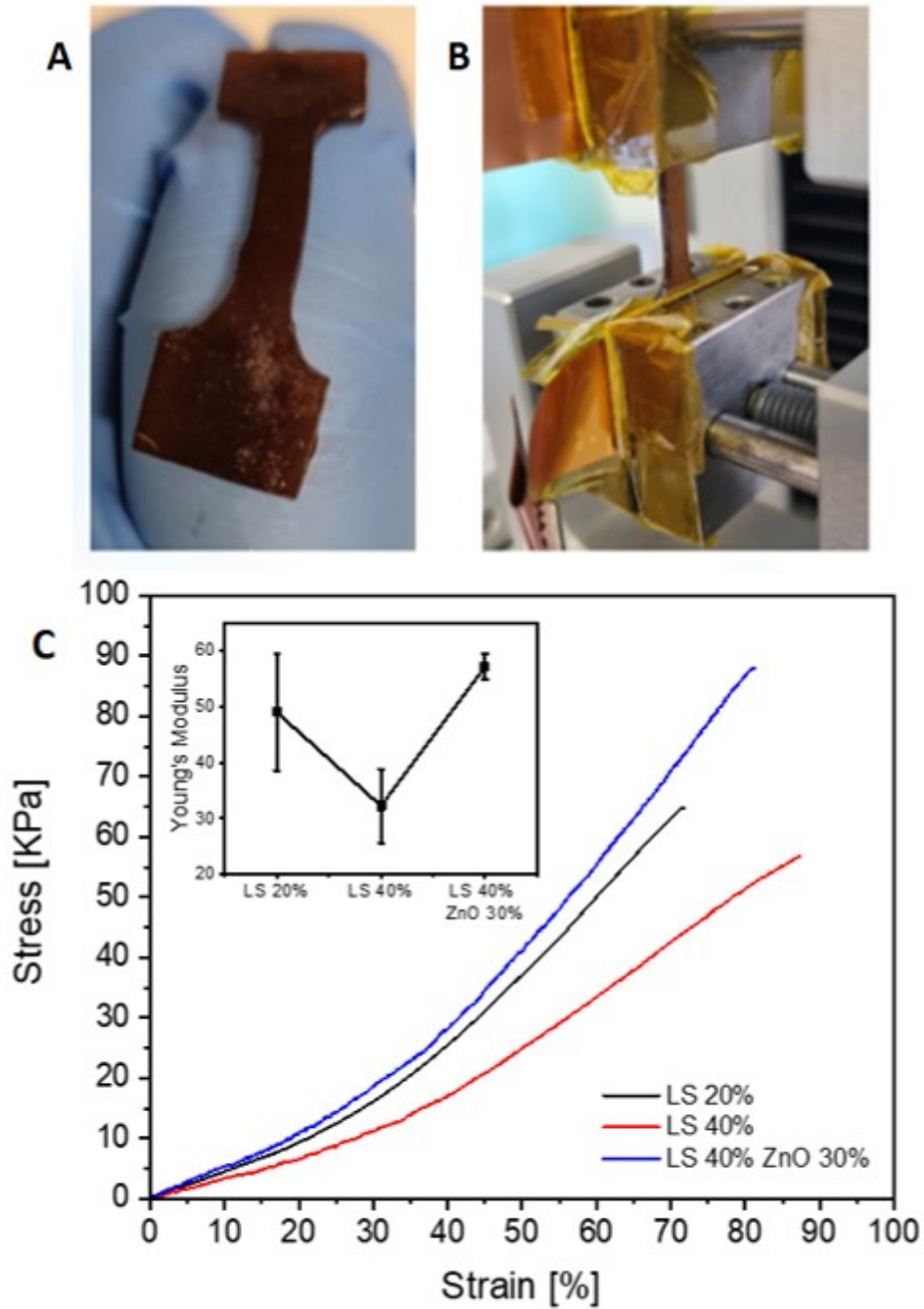


Figure 4.6: A) 3D printed dog-bone shape hydrogel. B) Experimental set-up for tensile test. C) Stress-strain curve for Hydrogel at different concentration and the obtained Young's Modulus at each concentration.

The derived Strain stress curves are presented in figure 4.6. Increasing Lignin from 20% to 40% w/w relative to GelMA led to a decrease in the Young's Modulus from 58,5 to 34,74 KPa. Usually, with the increase of polymeric filler content inside the resin it is expected to increase the material stiffness because of the increased amount of physical interaction with the main polymer networks, however, as demonstrated in the photorheology, high lignin content worsen the polymerization, resulting in incomplete polymerization of the resin reducing the young modulus.

The incorporation of ZnO increase the Young Modulus to 57,20 , as the addition of additional filler eventually led to an increase of Young's modulus, reaching values similar to those of LS20% relative to GelMA..

On the contrary, the elongation at break increase with the LS content rising from 67,7 % to 84,32 % and remains almost unchanged when the nanoparticles are added, with a value of 81,93 %.

4.1.4 Electrical test

Simultaneously with the tensile test, the change in resistance of the samples was detected through BK precision LCR meter. The initial resistance R_0 , was firstly measured for 60s while the sample was at rest. Upon loading, a rapid increase in resistance was observed owing to the high sensitivity of the strain sensor. As observed in figure 4.7, the electrical behavior is linear, optimal for sensing application avoiding abrupt changes in resistance and facilitating signal interpretation.

The sensitivity is evaluated by calculating the gauge factor (GF) obtained by the slope of the graph in figure 4.7. The GF factor showed only minor changes between the different concentration of LS, with value of 2.19, 2.20, 2.42. There is only a slightly increase for

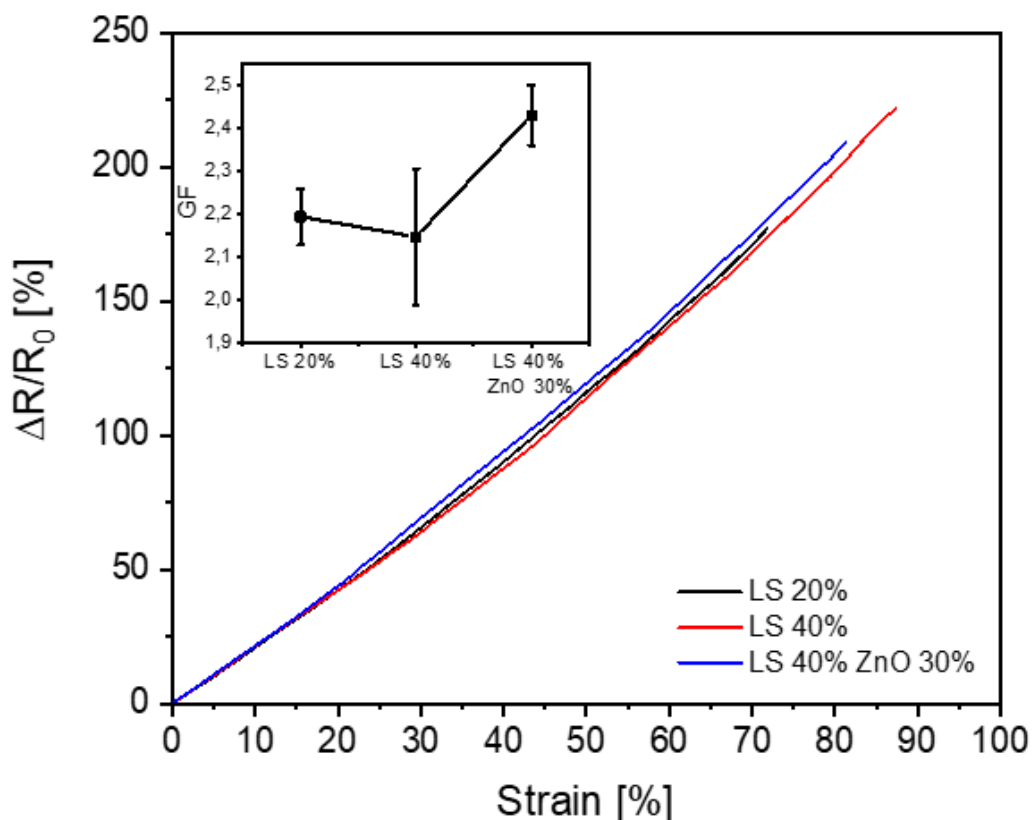


Figure 4.7: Electrical curve for different LS concentration and their relative Gauge factor obtained as the slope of the curve at low strain.

the hydrogel containing ZnO nanoparticle. Overall, the result is favorable the high concentration of lignin doesn't reduce the sensing capabilities of the device.

4.1.5 Conductivity

The Conductivity of the substrate was evaluated using electrochemical Impedance Spectroscopy (EIS). Hydrogel with different lignin concentration were cut in circular specimen using a puncher and placed between 2 metallic plate.

For the Hydrogel samples there is not substantial change in conductivity when increasing the LS content, this is consistent with the results during the tensile test and also the primarily provider of the ionic conduction is choline chloride (ChCl) presents in DES.

In contrast, for the organohydrogel the effect of LS is more pronounced. As the LS concentration increase the conductivity decrease. This behavior may be related to the reduction in photopolymerization efficiency discussed in the rheological characterization. The presence of not fully polymerized region inside the matrix create structural heterogeneities affecting the conductivity.

To conclude its positive that the LS doesn't affect the electrical properties hydrogel however probably higher LS concentration, if possible to polymerized, will reduce the conductivity of the samples. Moreover, the mainly contribution to the conductivity is the Choline Chloride present inside the deep eutectic solvent, indeed, the organohydrogel conductivity is reduced by a order of magnitude

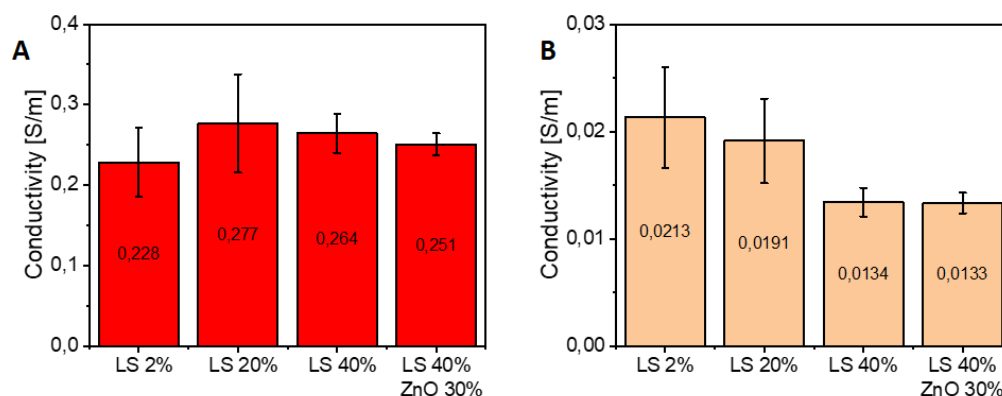


Figure 4.8: Conductivity of the A) Hydrogel and B) Organohydrogel.

4.1.6 Laser Induced Graphene on hydrogel

The high lignin content fills the hydrogel matrix with aromatic carbon rings making it an ideal precursor for laser induce graphene. The initial attempts were performed with the hydrogel with LS concentration of 4% w/w relative to GelMA. However, regardless of the laser parameters the attempts only result in the substrate melting and no graphene formation was observed (Figure 4.9a). The reason is the insufficient carbon content in the hydrogel and the high concentration of liquid content.

To address these limitations, hydrogel with higher lignin concentration where studied. Samples with 20% concentration present some graphene formation, however, the results were still not optimal. The most promising results were reached with hydrogel with 40% LS and 30% ZnO w/w relative to LS. The ZnO nanoparticles act as fire retardant, reducing the fluence required to the graphenization.

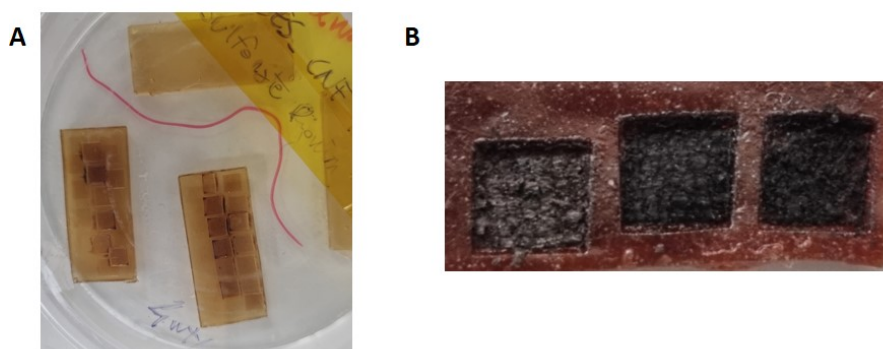


Figure 4.9: Attempts of LIG onto hydrogel substate at A) 4% LS w/w respect to GelMA and B) 40% LS respect to GelMA and 30% ZnO w/w respect to LS.

As shown in figure 4.9b, three squares patterns were printed the described substrate using two passes. The first pass was identical for all the sample with scanning speed at 40 mm/s and power 8. For the second pass the speed was kept constant at 100 mm/s, instead three different laser power were used 2, 4 and 6 W. Because of the high water content of the hydrogel the laser burns the substrate piercing it, for this the graphene structure recessed below the substrate level. Visually the squares presented continuous graphene region without any interruption. However, to evaluate the quality of the graphene Raman spectra and Sheet Resistance were performed.

4.1.6.1 Raman

The raman spectra of three patterned squares is shown in figure 4.10. Among them, only two

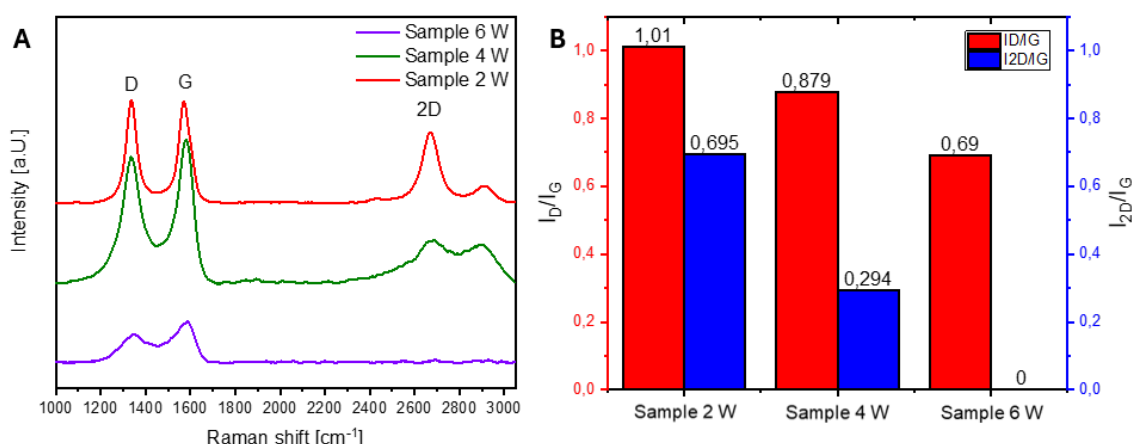


Figure 4.10: A) Raman spectrum for different laser Power. B) Ratio of the peaks ID/IG and I2D/IG in the Raman spectrum.

samples shows all the typical graphene peaks (D, G and 2D). The sample with the laser at 6 W Power present only the D and G peaks, moreover the peaks are very broad indicating the formation of very disordered carbon structure rather than graphene. A noticeable improvement is observed for the sample processed 4 W. However, the peaks remains relative broad and the 2D peak is only slightly visible, indicating highly structural disorders. The best spectra was obtained for the sample fabricate at 2 W because the peaks are narrower, similar to the Polyimide spectra, and the a pronounced 2D peaks. However, the intensity of the disorder peak (D) is quite high because this can be attribute at the presence of defects in the graphene.

This concludes that the laser parameters affect the quality of the graphene.

4.1.6.2 Sheet resistance

The sheet resistance is evaluated through the Van der Pauw method.

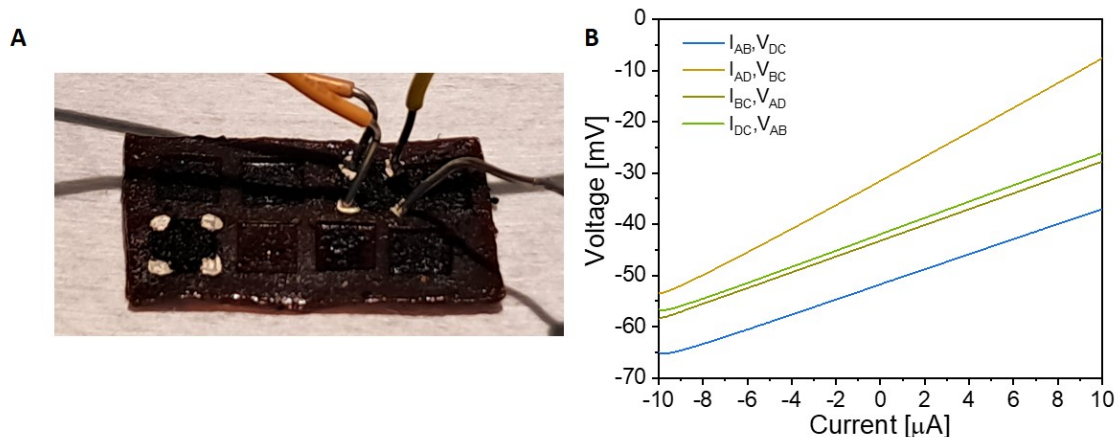


Figure 4.11: A) Hydrogel with silver paste to ensure correct connection with LIG. B) Current-Voltage curve for the four configuration of the Van der Pauw method.

To ensure an optimal connection between LIG and the micromanipulator, silver paste was applied at the four vertices of the sample. Firstly, the sheet resistance was measured for the 3 square patterned LIG used for Raman spectra. However, the resistance exhibited significant variability, consequently, making it impossible to obtain reliable resistance values. For this reason, another hydrogel substrate was written with the LIG laser using speed 100 mm/s and power 4W.

To optimize the measurement, the resistance was evaluated by applying a current sweep. Despite this approach, the results still remained variable, meaning further work is required to improve the electrode-LIG contact. Four Current-Voltage curve were acquired accordingly to the Van der Pauw method and their respective resistances were calculated. The hydrogel exhibited an open circuit voltage around 20/60 mV that offset the curves as shown in figure 4.11b.

Using the Van der Pauw formula, a sheet resistance of $7826,19 \Omega/\square$ was calculated. The sheet resistance value is relatively high for electrode application. Ideally to be used as electrode the sheet resistance should have been around few ohm to ensure adequate electrical response of the hydrogel sensor.

4.2 Gelatin, PVA thin film for LIG

Consequently, to the high sheet resistance obtained with the hydrogel, a new substrate formulation was investigated for electrical circuit LIG scribing. Unlike the previous one, the new substrate was not an hydrogel, avoiding the recessing problem due to the high liquid phase. This substrate was prepared by evaporating a mixture of water, lignin and a polymer. In particular, three type of polymer were evaluated: poly(vinyl alcohol) (PVA), Fish Gelatin and Porcine Gelatin. Glycerol was added to improve the flexibility the results are shown in figure 4.12.

The PVA substrate is flexible even at low glycerol concentration (20% w/w respect to LS), furthermore increasing the glycerol content became led to a more flexible substarte. For Fish Gelatin a concentration of 20% is not enough because the material remains stiff brittle and breaking when tried to remove from the petri. Good flexibility was achieved

only at glycerol concentration above 60%. Lastly for Porcine Gelatin, due to higher bloom value, a concentration of at least 80% is required for achieving flexibility.

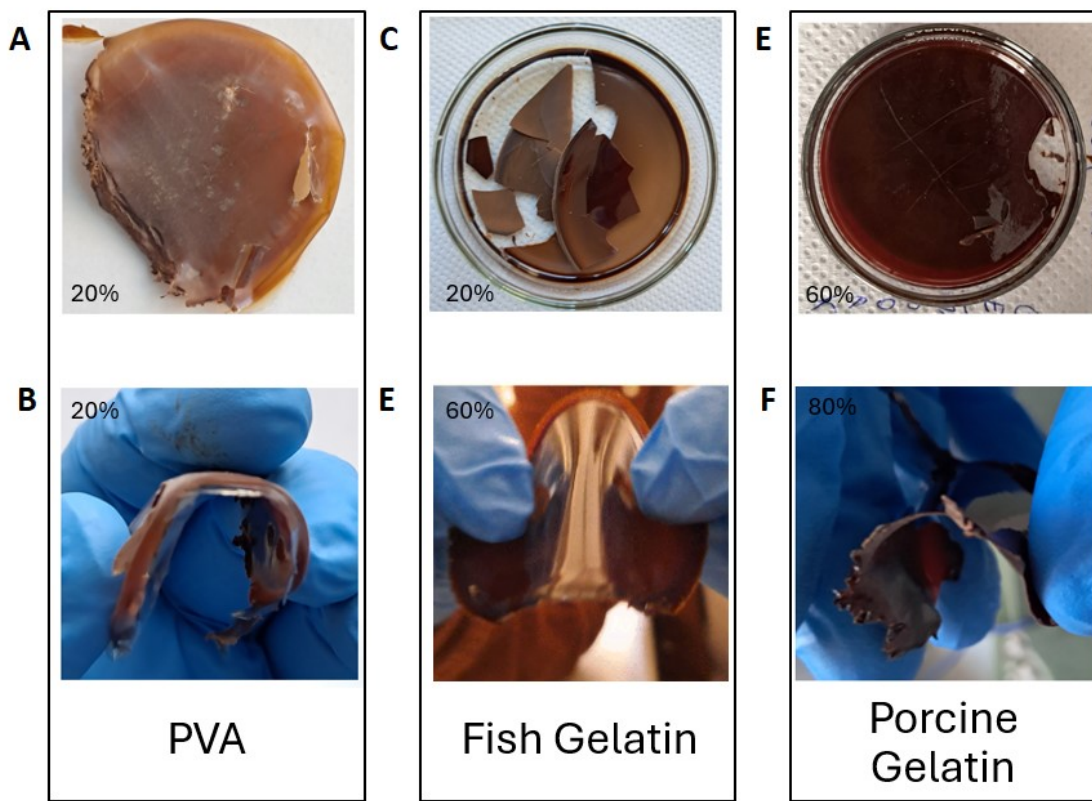


Figure 4.12: Thin film substrate for LIG for for A), B) PVA at glycerol 20% w/w relative to LS, C), D) Fish gelatin with glycerol concentration of 20% and 60% w/w relative to LS and E), F) Porcine gelatin with glycerol concentration of 60% and 80% w/w relative to LS

4.2.1 Substrate conductivity

Conductivity of the substrates was compared with that of the hydrogel using the same experimental set up. The PVA and porcine gelatin substrates exhibited conductivity values of 1.71 mS/m and 0.639 mS/m, respectively. The findings highlight that the conductivity decrease by more than an order of magnitude compared to both hydrogel and organohydrogel. This result is expected since, apart from the polymer, the formulation mainly consists of LS and glycerol, with only small amount of NaOH and ZnO. Consequently these components limited contribution to the overall conductivity.

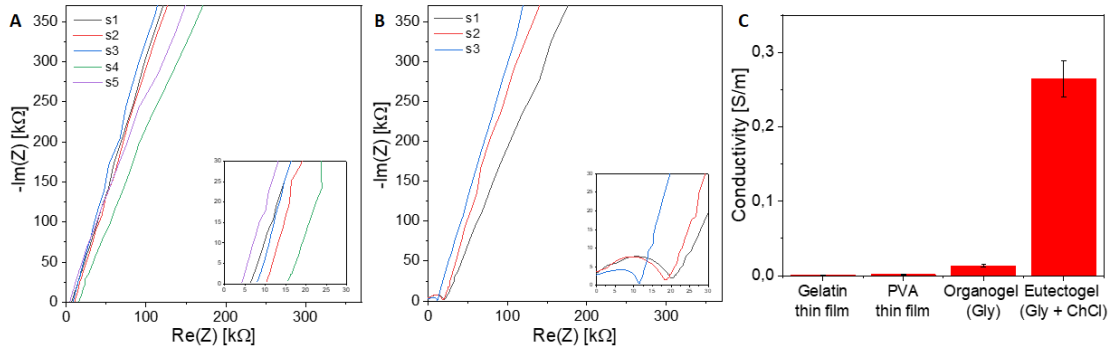


Figure 4.13: Nyquist plot for A) PVA and B) porcine gelatin substrate. C) Comparison of the conductivity for different substrates.

4.2.2 Laser induced graphene

Both square and cross geometries were fabricated using LIG on the substrate. The scanning speed were kept at 60 mm/s for all samples, the power intensity was optimized accordingly to the geometries, 3W for the squares patterns and 2W for the crosses patterns.

Overall, the results were better improved compared to those obtained with hydrogel. The graphene layer grows outwards without penetrating the substrate and the LIG structure is more uniform and homogeneous. For these substrates was also investigated the effect of the chamber atmosphere during the LIG process, in details, the samples were written in both in air and N₂ enviroment. Firstly, a difference was already observed during the lasering process. Using the parameters previously described in inert atmosphere the LIG was correctly obtained without notable damage. On the contrary, with the same parameters in O₂ the substrate is overheated resulting in poor quality LIG, for this reason the square in oxygen were fabricated at 2W laser power.

To compare the LIG structure the sheet resistance was evaluated for each type of substrate using the Van der Pauw method at the cross geometry. In figure 4.14 are shown the results, different substrates have sheet resistance value lower than those obtained with hydrogel. However, compared LIG on polyimide substrates the sheet resistance is relatively high that usually exhibit values around 2-100 Ω/□.

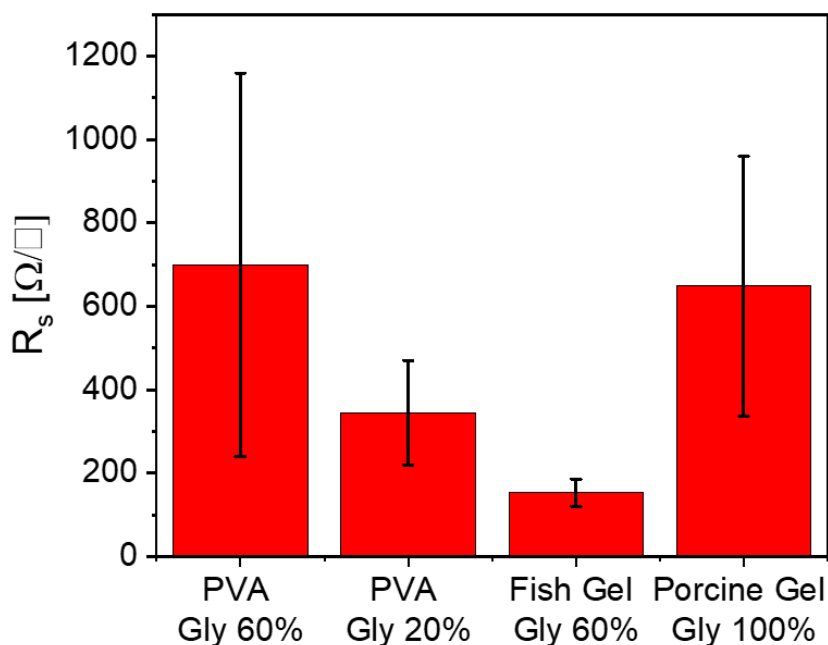


Figure 4.14: Sheet resistance calculated using Van der Pauw method for substrate fabricated with different polymers and glycerol concentration.

Among the tested substrates, the Porcine Gelatin with glycerol concentration of 100% w/w respect to LS was chosen for the sensing application. Fish gelatin, even if showed the lower resistance value, when heated at 40/30 °C within presence of water begin to melt, instead, the substrate with PVA goes against the aim of this thesis to create sensors starting from natural polymers, reducing the environmental impact. The glycerol concentration of 100% was selected for its superior flexibility without compromising mechanical and electrical properties. Nevertheless, this formulation presents some complication during the synthesis; the lower Gellin point of porcine gelatin can lead to a premature gellification before the water is fully evaporated. The structure formed this way presents the same problems of hydrogel making it unsuitable for LIG fabrication.

4.2.3 Raman

Also, the Raman spectroscopy was performed following the procedure used for hydrogels. The results are shown in figure 4.15a. The obtained results are extremely promising, For all the sample, the three characteristic peaks are narrow and the intensity of the 2D peak is relatively high, indicating the formation of a “thick” graphene layer. The only negative observation is the presence of high intensity D peaks, meaning that the LIG is quite disordered and presents a large number of defects. However, this last remark doesn’t apply for the LIG onto the PVA substrate that presents an I_D/I_G ration around 0,5 that is coherent with graphene obtain on material other than polyimide.

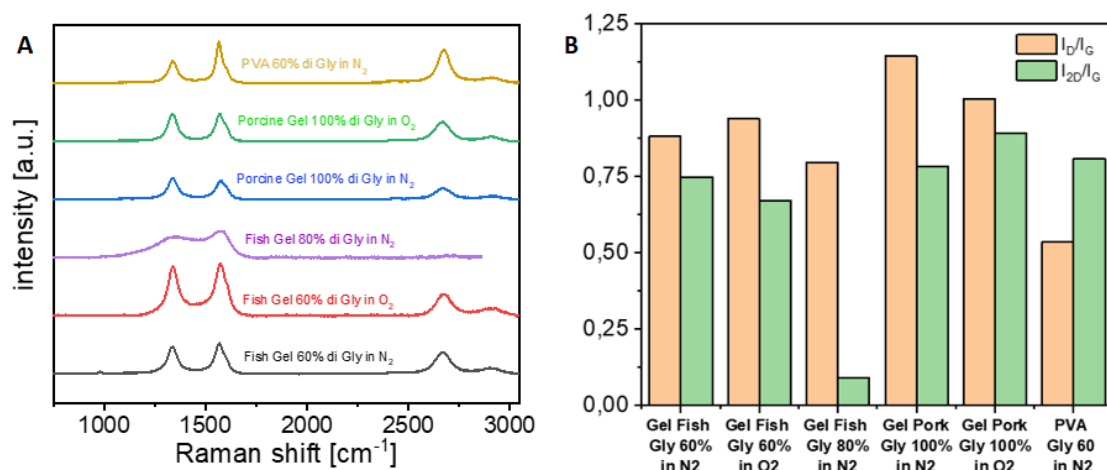


Figure 4.15: A) Raman spectra of different polymeric substrate performed in both air and inert atmosphere. B) Ratio of the peaks intensity of the Raman spectra.

Furthermore, the gas atmosphere presented during the graphenization does not appear to affect the Raman spectrum. In particular, both Gel Fish and Gel porcine spectra for the LiG fabricated in different environmental conditions show no significant changes.

4.2.4 FESEM

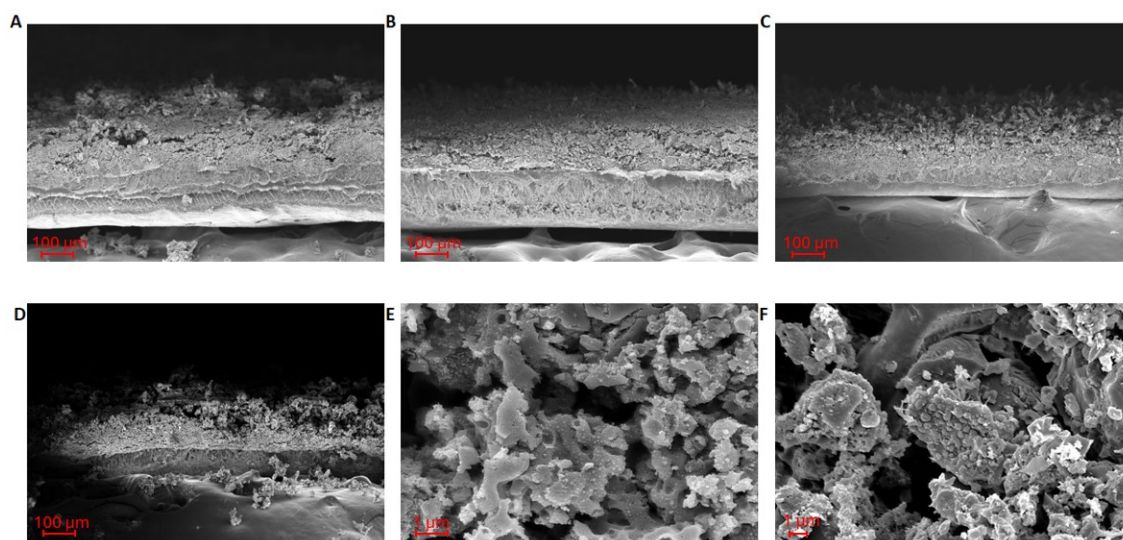


Figure 4.16: Image of the LiG pattern on different sample obtained through FESEM microscope. The sample observed were A) fish gelatin with glycerol 80% in inert atmosphere, B) PVA with glycerol 60% in inert atmosphere, C) porcine gelatin with glycerol 100% in air and D) porcine gelatin with glycerol 100% in inert atmosphere. All glycerol concentration are w/w relative to LS. E) and F) are details of the LiG patterned on gel porcine in O₂ and N₂, respectively.

The same samples analyzed by Raman spectroscopy were also characterized through a FESEM microscope. The substrates were placed onto an oblique support in order to observe their cross section. The FESEM images, in figures 4.16, show a clear separation between the substrate and the LIG, allowing the direct measurement of the LIG layer thickness.

For the PVA and fish gelatin, processed under inert atmosphere, a LIG thickness of 136,2 μm and 135 μm were measured, respectively. For porcine gelatin in inert and air environment exhibited comparable LIG thickness with value of 122,7 μm and 149,86 μm , respectively. Overall, for all the samples thickness are around the same order of magnitude, and, as suggested by the Raman spectra, a thick LIG layer of more than 100 μm was formed.

The details in figure 4.16e show the porous structure of the LIG but can also be observed little dots with diameters of less than 40 nm probably representing the ZnO nanoparticle added during the formulation.

4.2.5 Recyclability

With water and a temperature of 50 $^{\circ}\text{C}$ the substrate easily returns to the state previous to dehydration and therefore can be recycled. The idea is not to simply recycle the substrate but to investigate whether it is possible to write with LIG even on the material after has already been used a sensing device.

The chosen substrate was the Porcine Gel with 100% glycerol concentration respect to LS for reasons previously discussed. Six 5x5 mm LIG squares were patterned onto the substrate covering 10% of the total area ($d = 50\text{mm}$). The substrate was recycled for five times, notably each recycling cycle requires longer time and higher temperature to be fully recover to its initial state. For the last cycle a temperature of 80 $^{\circ}\text{C}$ and 2h were required. The results will be discussed in the next section.

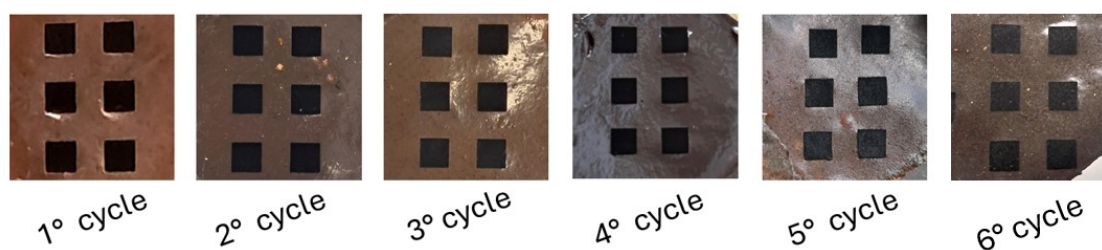


Figure 4.17: The patterned LIG square obtain for each recycling cycle.

4.2.5.1 Sheet Resistance

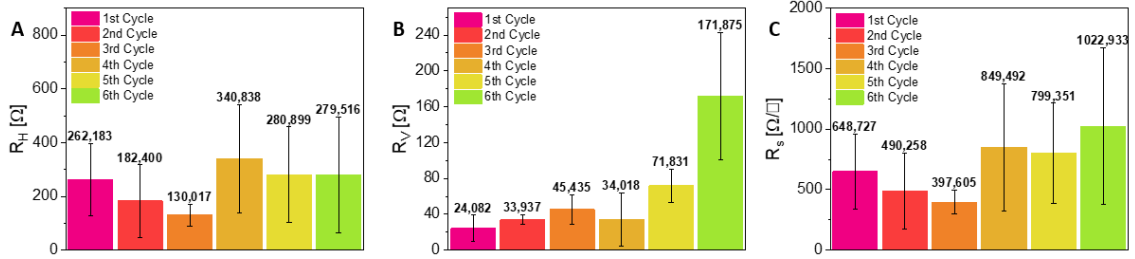


Figure 4.18: A) Horizontal resistance, B) vertical resistance and C) sheet resistance after each recycling cycle.

The sheet resistance of the square geometries was calculated after each recycling cycle. The horizontal resistance R_H , perpendicular to the writing direction, doesn't exhibit a clear trend but in general presents similar value throughout the cycles. Instead, for R_V , parallel to the writing direction, shows a slight increase with each cycle. Moreover, their value are lower than R_H but this is to be expected, LIG is more continuous along the writing direction reducing the resistance. Because of R_H higher value, the calculated sheet resistance R_s follows a trend similar to R_H .

To conclude the sheet resistance, of the substrate after 4 recycle, goes from 648.7 $\Omega/\square$ to 799.3 $\Omega/\square$, an increase of 151 $\Omega/\square$, approximately 23% of the original value. However, taking into account the error bar, one can conclude that the sheet resistance presents no significant change and the substrate is almost unchanged for sensing application after 4 recycle. After 5 recycle the sheet resistance goes to 1022.9 $\Omega/\square$ an increase of 57,7%, this cycle show a pronounced increase, with the vertical resistance more than doubling its value from the previous cycles, indicating a deterioration of the substrate.

4.2.5.2 Raman

The Raman spectra of the squares before and after three recycles were compared. Surprisingly, the results shown in the graph (Figure 4.19), suggest that the quality of the graphene seems to improve for the recycled substrate. In particular, the intensity of D peaks is lower relative to the G peaks for the Raman spectrum of the recycle substrate, indicating a less disordered graphene and reduced defect. However, this result its unlikely a consequence of the recycles, but can be attributed to the variability in the graphene fabrication by LIG.

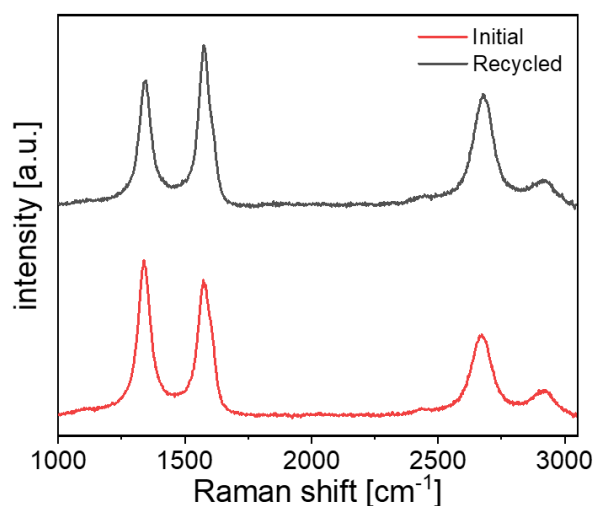


Figure 4.19: Raman spectra of the graphene square patterns onto gelatin substrate before and after recycling.

4.2.6 Encapsulation

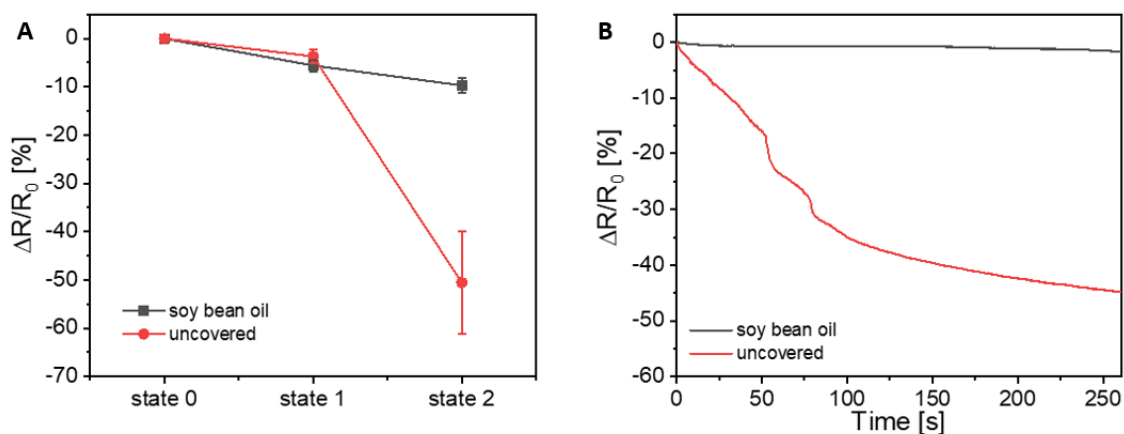


Figure 4.20: A) Resistance value of the strain gauges before and after the water was dropped for the soybean oil and uncovered substrate. B) Behavior of the resistance for the soybean oil and uncovered pattern immediately after the water was dropped.

To avoid excessive cracking of patterned structure and possibly discriminate the effect of humidity in sensors application, several encapsulation methods were studied. Traditionally, synthetic polymers like PDMS are commonly deposited to cover the substrate, reducing the environmental friendliness of the final device. Natural alternatives include soybean oil or shellac, hydrophobic polymers that could protect LIG and avoid swelling of substrate under environmental humidity. Shellac can be easily deposited; however, the presence of glycerol caused the substrate to swell, resulting in deformation of the structure.

Soybean oil can avoid this problem because it does not need to be left to dry; instead, it can be deposited and immediately photopolymerized under UV light. The resulting substrate remains flexible without damaging the graphene pattern.

To evaluate the effectiveness of the encapsulation, water droplets were placed both near and on top of the pattern while monitoring the resistance. The results are shown in figure 4.20. It can be observed that while the resistance remains almost constant for the covered substrate, whereas the resistance of the uncovered substrate changes drastically after water was dropped. These results confirm the protective effectiveness of the soybean oil.

4.2.7 Bending test

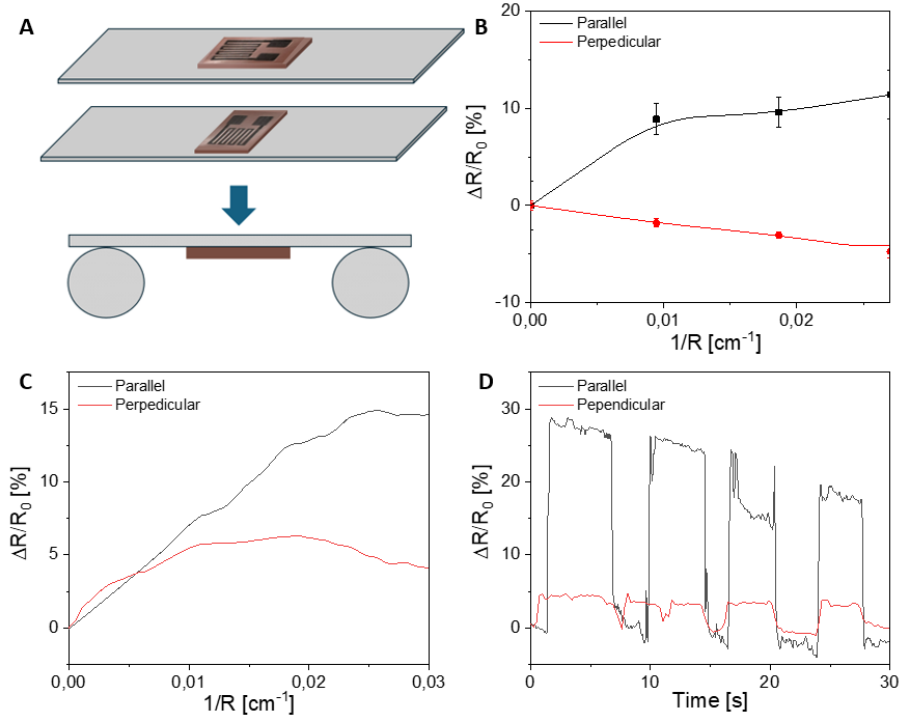


Figure 4.21: A) during the bending test the strain gauges was placed in 2 configuration. In the first one the strain gauges is positioned to have the longer conductive path parallel to the bending direction and in the second one they were perpendicular to the bending direction. B) and C) are the static and dynamic working curve for the bending test of the strain gauges. Static curve was obtained measuring the resistance at specific bending angles. Electrical resistance was measured every 2 mm of way. D) is the resistance variation during bending induced by manually pressing the sensor.

Serpentine-like patterns were scribed onto the porcine gelatin substrate to form strain gauges structure. This LIG structure ensures directional sensing; a deformation applied along the long segment of the serpentine produces a larger change in resistance than a deformation applied along the short segments, as a greater portion of the conductive path is effectively stretched.

The sensitivity of the devices was evaluated through bending tests. Initially, the devices were tested by manually pressing the metallic support with a finger to induce bending in the strain gauges.

Figure 4.21a shows the results obtained from the experiment when the bending was applied along the longer path, while in figure 4.21b presents the result for the bending applied along the shorted path.

It is evident that the sensor exhibits significant sensitivity only in the first case, indicating

that it operates as intended and demonstrates excellent directional sensitivity. Moreover, the sensor exhibits a rapid response and is able to maintain a stable signal when the bend deformation is kept for few seconds. When the load is released, the sensors can return to the initial state.

The working curve (figures 4.21b, 4.21c) was also evaluated using an indenter that slowly descended while measuring the resistance at each position. The results are consistent with those obtained for the finger test showing optimal sensitivity and confirming the monodirectional sensing behavior of the devices.

4.2.7.1 Finger bending

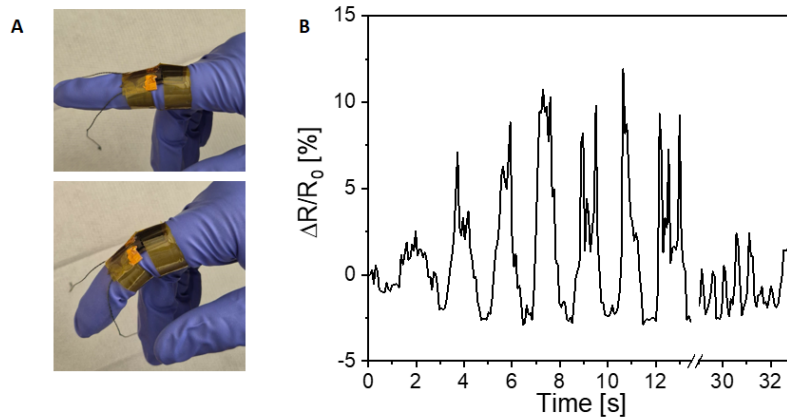


Figure 4.22: A) Images of the sensor applied to the finger while rested and bent. B) Signal variation during the finger movement.

Moreover, the device was attached to a finger joint to monitor its movement. The sensor was positioned with its longer path aligned with the direction of the finger. As shown in figure 4.22, the resistance changes rapidly in response to finger movement, demonstrating a fast response. First, the finger was repeatedly fully bent resulting in a change of resistance of 10% of its original value showing high sensitivity of the device. Secondly, the device abilities were investigated to sense smaller and faster finger movement. In this case, smaller resistance variations were observed indicating that the device is capable of detecting subtle movement.

4.2.7.2 Strain test

The strain gauges were also tested under strain using a set-up was analogous to tensile tests performed on hydrogels. The samples were clamped at the extremities and stretched; however, in this case, the material was subject to relatively small strain, 3,5% of their original length, to avoid excessive damaging the LIG. Both encapsulated and non-encapsulated strain gauges were tested.

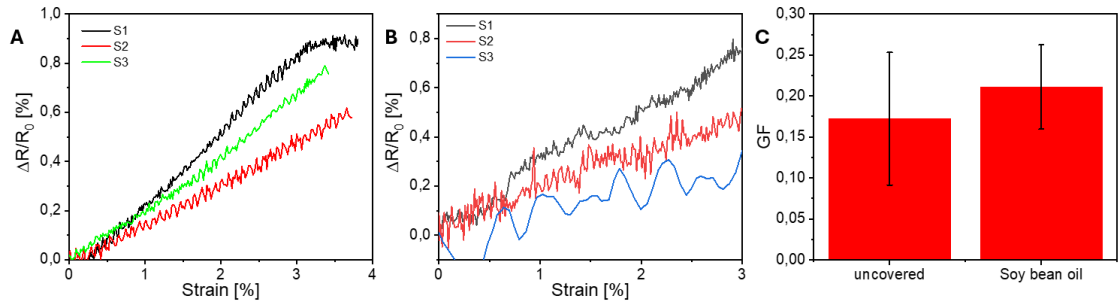


Figure 4.23: A) and B) are the ΔR -strain curve for the encapsulated and non-encapsulated strain gauges, respectively. C) The calculated Gauge Factor for the two configurations.

The resulting ΔR -strain curve (figure 4.23) demonstrates that the material is capable of detecting very small strains. However, the gauge factor has a low value approximately 0,2 for both configurations. Overall, the two configurations do not present significant changes in electrical properties, indicating that the encapsulation doesn't affect the sensor performance. The only noticeable difference is in the signal quality: the non-encapsulated strain gauges exhibit a noisier response

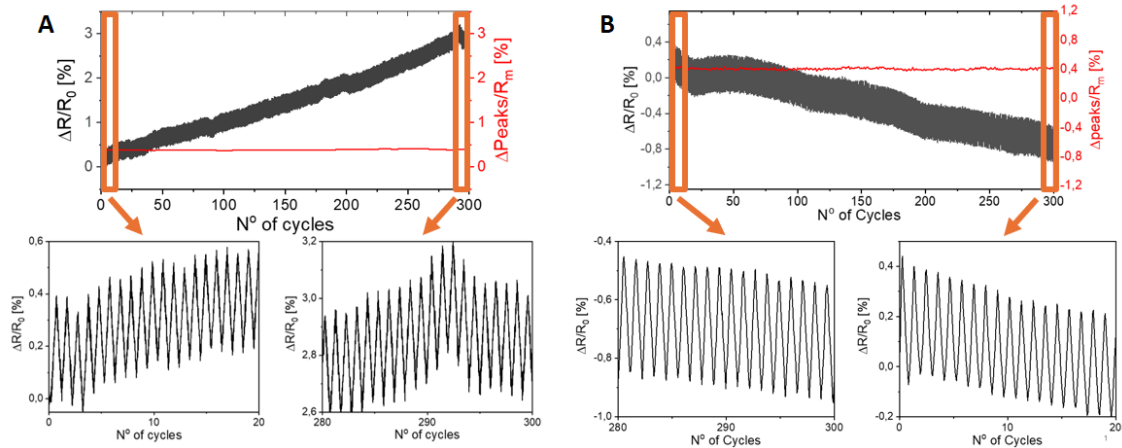


Figure 4.24: hysteresis test performed over 300 cycles of loading and unloading with a displacement of 0,2 mm and speeds set at A) 2 mm/min and B) 20 mm/min.

Also, cyclical tests were performed on the same sample. The encapsulated strain gauges were subject to a strain of 0,2 mm at speeds of 2 mm/min and 20 mm/min for 300 cycles to evaluate the stability. Even after 300 cycles of loading and unloading the material doesn't show any sign of degradation. This is evidenced by the amplitude of resistance cycles, remaining nearly constant over 300 cycles.

4.2.8 Biodegradability

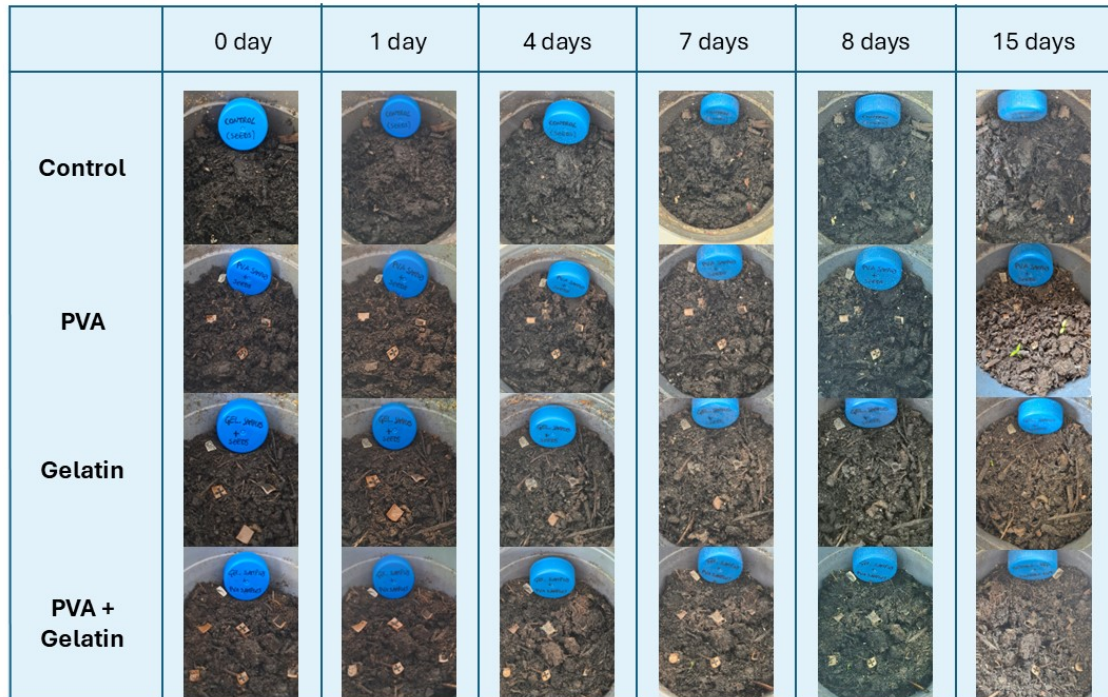


Figure 4.25: Picture of the four pots both used to test degradability. There is a control pot with no sample place inside, one with just gelatin sample, one with only PVA sample and the fourth with both inside. The sample were observed for 15 days.

As discussed during the introduction, one of the key requirements for green materials is biodegradability. To evaluate this property the samples were placed in soil and monitored over several weeks to observe their degradation.

Four different pots were prepared and observed, as described in the material and methods section. As expected, only the gelatin samples degrade over time. After just 5 days the material began to break and after 15 days only small pieces remained. Instead, for the PVA samples no noticeable changes were observed throughout the duration of the experiment. This confirms the gelatin substrate even after LIG can degrade on soil and are suitable for environmentally friendly sensing applications.

Chapter 5

5 Conclusion

In conclusion, this thesis has investigated two different approaches for fabricating wearable flexible devices based on natural the natural polymer gelatin. Moreover, the possibility of printing conductive pattern using the laser Induced Graphene (LIG) technologies was exploited.

The findings regarding the GelMA hydrogel confirmed why hydrogel are widely used in literature for wearable device applications. The hydrogel fabricated in this work results prove to be highly flexible and easily 3D printable, enabling the fabrication of complex structure. When used as a strain sensor, it exhibited a gauge factor (GF) of 2.19.

Hydrogel formulations are highly customizable, and this properties was exploited to increase the lignin sulfonate content adding large quantities of aromatic carbon rings, which can be readily transformed into graphene using a CO₂ laser. Increasing the lignin content slightly weakened the structure but had almost no effect on the sensor's sensitivity. However, when the material was scribed the results were suboptimal, sheet resistance values that were too high.

Consequently, a new formulation was developed and tested. This formulation primarily consists of porcine gelatin, lignin sulfonate and glycerol dissolved in water and subsequently left to dry for one day. This process creates a flexible substrate with high lignin concentration, resulting in more uniformed LIG patterns. Porcine gelatine was selected over other polymers because of a sheet resistance of approximately 500 $\Omega/\square$ and the ability to be recycled multiple times. The substrate was successfully recycled four times without any significant loss of electrical properties. Furthermore, its biodegradability was evaluated, and the material was found to completely degrade within 15 days.

Regarding practical application, strain gauge structures were patterned onto the substrate and encapsulated with soybean oil. he resulting strain gauge remained stable under cyclic loading for 300 cycles and was capable of detecting finger-joint movements.

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