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3D-printed flexible energy storage for soft robotics

By

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A dissertation submitted to the University of Bristol in accordance with the requirements of the degree of DOCTOR OF PHILOSOPHY in the Faculty of Science.

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Flexible and stretchable energy storage devices have attracted significant attention of industry and academia. These devices show great potential for applications in wearable electronics or soft robotics. However, the fabrication of flexible and stretchable electronic devices such as supercapacitors is challenging and requires expensive and time-demanding processes.

Additive manufacturing has become one of the most attractive techniques for building bespoke devices. In this regard, 3D-printing has emerged as an extrusion-based method for an accurate rapid prototyping. Here, we propose a combined method of 3D-printing and laser-scribing to fabricate flexible and stretchable supercapacitors.

The developed technique consists of the synthesis of the required materials, as well as the manufacturing processes of each part of a flexible supercapacitor. The components of the supercapacitor such as the conductive current collectors, electroactive material, gel electrolyte, as well as the housing encasement were successfully attained. The integration of the parts to obtain a complete flexible energy storage device was successfully achieved by investigating the interactions of the developed materials in contact.

The obtained flexible energy storage device presents an areal capacitance of 2.3 F cm\(^{-2}\), excellent cycling stability (97% retention after 10,000 cycles). Also, the developed supercapacitor prototype can deliver a high energy density of 0.21 mWh cm\(^{-2}\) and a maximum power density of 39 mW cm\(^{-2}\) making it competitive compared with similar micro-supercapacitors reported to date. In addition, the manufactured devices kept its remarkable capacitance properties while being bent and stretched. It is envisaged that these precisely controlled software processes could be easily integrated in a production line with determined manufacturing times and keeping the resulting devices with their remarkable electrochemical performance. All the rapid prototyping manufacturing processes were accomplished by affordable commercial 3D printers and laser scribes.

The attained integration results pave the way towards automated fabrication processes of flexible energy storage devices with industrial and academic applications.
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I declare that the work in this dissertation was carried out in accordance with the requirements of the University’s Regulations and Code of Practice for Research Degree Programmes and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate’s own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. Any views expressed in the dissertation are those of the author.

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LIST OF ABBREVIATIONS

- 2D: two-dimensional
- 3D: three-dimensional
- AA: ascorbic acid
- ACN: acetonitrile
- AM: additive manufacturing
- AMW: average molecular weight
- ATMP: aminotris(methylene)phosphonic
- AR-27: acid red-27
- CAD: computer-aided design
- CCC: conductive current collector
- CB: carbon black
- CNT: carbon nanotube
- CP: conductive polymer
- CSA: (1S)-(+)\textsuperscript{1}-camphorsulphonic acid
- CV: cyclic voltammetry
- DBSA: 4-dodecylbenzenesulphonic acid
- DI: de-ionised
- DIW: direct ink writing
- EB: emeraldine base
- EDLC: electric double layer capacitors
- EDX: energy-dispersive X-ray spectroscopy
- EES: electrical energy storage
- EESD: electrical energy storage devices
- ES: emeraldine salt
- ESS: energy storage systems
- FDM: fused deposition modelling
- FT-IR: Fourier-transform infrared spectroscopy
- GCD: galvanostatic charge/discharge
- GA: glutaraldehyde
- GCODE: geometric code
- GO: graphene oxide
- ICPS: intrinsically conductive polymers
- IL: ionic liquid
- LEB: leucoemeraldine base
- LED: light emitting diode
- LES: leucoemeraldine salt
- LIG: laser-induced graphene
LIST OF ABBREVIATIONS

- PANI: polyaniline
- PC: propylene carbonate
- PDMS: polydimethylsiloxane
- PEO: polyethylene oxide
- PET: polyethylene terephthalate
- PPO: polypropylene oxide
- PS: pernigraniline salt
- PVA: polyvinyl alcohol
- PWM: pulse width modulation
- RGO: reduced graphene oxide
- SC: supercapacitor
- SEM: scanning electron microscopy
- ST: surface tension
- STL: surface tessellation language
- SWCNT: single-wall carbon nanotube
- UV: ultraviolet
- WA: work of adhesion
- XRD: X-ray diffraction
Some of the work reported in this thesis forms the basis of forthcoming articles:

Most of Chapter 3 forms the basis of one forthcoming article:


Parts of Chapter 3, Chapter 4, Chapter 5, and Chapter 6 contributed towards one forthcoming article:

Generation techniques in power systems are evolving dynamically, based on the increasing demands of energy in the world moving to a low carbon economy. The conventional synchronous machines-based power generation systems driven by water, geothermal energy and fossil-based fuels are sharing the portfolio with intermittent renewable energy sources, e.g., solar photovoltaic panels, wind turbines, and microscale energy harvesting. A major challenge facing most of these alternative energy sources is that they occur intermittently, which makes them unreliable for steady energy supply. These sources require that the harvested energy is readily stored when available and retained until needed for applications in various sectors, e.g., utility, industry, building and transportation. Renewable generation suffers not only from intermittency of short bursts of several seconds of too much power or too little power, but also from frequency distortions resulting from the energy harvesting process. Therefore, short and long-term energy storage (ES) is considered one of the prominent solutions for solving these difficulties.1–3

1.1 Electrical Energy Storage

ES is the process of capturing energy produced at one time to use it at a later point of time. The energy capturing cycle is regarded as charging and the energy release cycle is known as discharging. The charging and discharging processes can be achieved using Electrical Energy Storage technology (EES). EES refers to the complete cycle of converting electrical energy to a storable form (charging) and maintaining it in various media; the stored energy can then be retrieved as electrical energy (discharging) when needed. The different methods used to convert and store the electricity determine the classification of the EESs. They can be grouped as: mechanical energy
storage, chemical energy storage, electrochemical energy storage, superconducting magnetic energy storage and thermal energy storage.\textsuperscript{4,5}

1.1.1 Electrochemical Energy Storage

Electrochemical Energy Storage refers to EES technology that converts electrical energy into chemical energy to store it and the opposite conversion cycle to release it. According to the nature of the chemical reaction, structural features, and design, there are two major branches of electrochemical energy storage technologies: electrochemical batteries and electrochemical capacitors. The latter are named supercapacitors (SC), ultracapacitors or electric double-layer capacitors. While electrochemical batteries can be used for applications requiring long charge-discharge processes such as flashlights, mobile phones, laptops and electric cars, traditional capacitors can be used for applications with very fast (fractions of seconds) charge-discharge cycles such as high-frequency systems and electronic processors. SCs can have characteristics of both traditional capacitors and electrochemical batteries. These features make them suitable for short-term storage applications where charge–discharge cycles on the order of hundreds of milliseconds or seconds are required and millions of cycles are desired such as elevators, cranes or regenerative braking systems for electric vehicles.\textsuperscript{6,7} They can store hundreds or thousands of times more charge per unit of mass compared with conventional capacitors, thus filling the gap between the latter and the electrochemical batteries.\textsuperscript{5,8,9} SCs can be applied in soft robotics where most of the electronics and actuators mimic the movements in nature. These movements need short peak power that batteries only can provide if they are heavy and bulky. On the other hand, traditional capacitors cannot supply the required constant energy because of their limited power capacity. In addition, the demanding increase in the efficiency in the electric vehicles requires kinetic energy to be stored somewhere whenever the vehicle slows down or stops, and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Ragone_Plot.png}
\caption{Ragone Plot: Charge-discharge characteristics of energy storage systems. Reproduced and adapted from reference.\textsuperscript{10}}
\end{figure}
1.2. SUPERCAPACITORS

retrieved later in the acceleration cycle. These efficiency requirements can only be achieved with the large amounts of power provided by energy storage technologies such as SCs.\(^5,11,12\)

The above-mentioned variables of energy, power and time-spans of the charge-discharge processes of energy storage systems (ESS) are conveniently represented and compared in a logarithmic plot as shown in the Figure 1.1. This diagram known as Ragone plot comprises the specific power (W kg\(^{-1}\)) and the specific energy (Wh kg\(^{-1}\)) of a large range of ESS. The parameters of specific energy and specific power of a ESS can be obtained by fully discharging the device from a fully charged condition.\(^10,13\)

1.2 Supercapacitors

SCs are high capacity capacitors with a capacitance value higher than other capacitors. SCs contain two electrodes or current collectors normally made of porous carbon or another high surface area material. The electrodes are separated by an electrolyte and a porous membrane separator, whereby ion diffusion between the two electrodes is permitted. This arrangement differs from the common design of a solid dielectric between two electrodes seen in traditional capacitors (Figure 1.2). The energy storage capability of SCs is based on their capacitance. The total capacitance is the result of two contributions: electric double-layer capacitance and pseudocapacitance.\(^14\) These two contributions are discussed in more detail in the following sections.

![Figure 1.2. Schematic representation of: a) Traditional capacitor b) Supercapacitor. Reproduced and adapted from reference\(^{15}\)](image)

1.2.1 Electric Double-Layer Capacitance

Double-layer capacitance occurs due to the potential-dependence of the surface density of charges electrostatically stored at the interfaces of the capacitor electrodes. For the latter, the accumulated
CHAPTER 1. INTRODUCTION

charge is a combination of deficit (or excess) of electrons at the near-surface region of the interface, together with accumulated cations (or anions) of the electrolyte acting as counterbalancing charge densities on the solution side of the double-layers at the electrode interfaces. Thus, we can say that an electric double-layer appears as the result of the interaction of a charged object immersed in a liquid. To balance the charge of the placed object a counter charge will form on the liquid near the surface of the object. There are various models to describe this interface between a charged solid and a liquid. One of them is the Helmholtz model (Figure 1.3(a)) where the charge of the solid electronic conductor is neutralized by opposite charged ions at a distance d, from the solid. According to this model the potential decays in a constant rate from the surface of the electrode to the ions layer. That is a simple approximation to explain the charge distribution at the double-layer interface, however, it considers rigid layers balancing the charges of the solid. This model is too simplified to fully explain what actually occurs in nature. The Helmholtz model was modified by Gouy and Chapman in 1910 and 1913, respectively. This new theory was regarded as the Gouy-Chapman model. This latter accounted for the ions mobility in the liquid electrolyte solvent, describing a distribution of ions diffused in a region of thickness much larger than a thin rigid layer (Figure 1.3(b)). The potential in this model is considered to decrease exponentially through the diffuse layer. This model fails for highly charged double-layers where the measured thickness of double-layers is greater than model prediction.

The Gouy-Chapman model has limited quantitative applications because it assumes that the ions are point charges approaching the surface with no limit, which is not correct. The shortcomings of the model were solved by Otto Stern in 1924 combining the Helmholtz model with the Gouy-Chapman model. Stern assumed that there are strongly surface-absorbed ions by the electrode within a compact layer (forming the inner Helmholtz plane) and non-specifically absorbed ions, forming the diffuse layer.

Figure 1.3. Schematic representation of: a) Helmholtz model b) Gouy-Chapman model c) Stern model. Reproduced and adapted from reference 16
absorbed counter-ions (forming the outer Helmholtz plane) in an outer diffuse layer (Figure 1.3(c)). These two layers are equivalent to two capacitors in series, and the total capacitance of an electrode is given by Equation (1.1).

\[
\frac{1}{C_S} = \frac{1}{C_H} + \frac{1}{C_{GC}} \tag{1.1}
\]

Where \(C_S\) is the Stern model capacitance, \(C_H\) is the Helmholtz model capacitance, and \(C_{GC}\) is the Gouy-Chapman model capacitance. The combined model is regarded as Stern model and has been adopted in the development of the electric double-layer capacitors (EDLC).12,16–18

The described mechanism of operation of the electric double-layer capacitance is a non-Faradaic charge storage process where no electron transfer take place across the electrode interface. This implies that the storage of electric charge and energy is electrostatic. The charge accumulation is attained by positive and negative charges electrostatically residing on the two interfaces separated by a molecular dielectric. These electrons involved in the double-layer charging process are the delocalised conduction-band electrons of a metal or carbon electrode.19–21

1.2.2 Pseudocapacitance

Pseudocapacitance is the second contribution to the total capacitance in SCs. Before understanding the significance of the term it is necessary to first explain what a Faradaic charge storage process is.

A charge storage process is Faradaic when an electron transfer produces chemical or oxidation state changes in the electroactive material of the electrode. In this process, the electrons are transferred to or from valence-electron states (orbitals) of the redox electrode producing the changes. Therefore, pseudocapacitance (PC) is a Faradaic charge storage process that involves surface or near-surface redox reactions achieving high energy densities at high charge rates. The electron charge transfer is attained by electron absorption producing the very fast reversible Faradaic redox reactions on the electrode surface. Compared with electric double-layer capacitance, PC is a completely different energy storage mechanism and it can be combined with electric double-layer capacitance in a SC. In this combined configuration the contribution of PC is about 90% to 95% of the total capacitance.20,21

From a materials point of view, the contribution of the electric double layer capacitance is obtained from the potential-dependence of the surface density of charges stored electrostatically at the interfaces of the supercapacitor electrodes. These electrodes are commonly made of metal, carbon surfaces or in general conductive porous material surfaces. On these surfaces the accumulated charge is the result of an excess of conduction-band electrons in the near-surface region of the interface and a counterbalancing charge densities of accumulated counter-ions in the electrolyte side. Alternatively, the contribution of the pseudocapacitance appears at the material electrode where a different charge-storage mechanism applies. This mechanism
includes the transfer of charges across the double layer. The charges transferred to the electrodes produce reversible redox reactions on the surface of the material electrode. The latter reactions take place in a molecular level within a material such as a redox-active polymer or a metal oxide-based electrode surface. Also, the pseudocapacitance is due to fast and reversible faradaic reactions which involve the electrochemical interconversion between reduced and oxidised species. There is an additional group of materials that show the electrochemical signature of a battery electrode coming from intercalation mechanisms but they are part of battery-like energy storage devices.21–25

PC has attracted the attention of several investigations and efforts to improve the energy densities (energy storage capacity) of EDLCs and SCs. The strategies to achieve enhanced devices include functionalizing the surface of the electrodes, changing the pore sizes to match the electrolyte ion size, applying redox-active species in the electrolyte or utilising electroactive materials with fast and reversible faradaic reactions. The most commonly studied materials include oxygen- and nitrogen-containing surface functional groups, transition metal oxides and electroactive conductive polymers.26–28

1.2.3 Architecture and flexibility

The expansion of the potential applications of SCs has been increased into a variety of fields including avionics, hybrid and electric vehicles and back-up power systems. At the same time SCs are in demand for use in portable electronics, wearable electronics, micro-electronics, printable electronics and especially flexible electronic devices. These requirements have stimulated enormous enthusiasm from both industrial and academic communities to develop highly flexible supercapacitors with integrated functions using compliant materials. To achieve the characteristics of flexibility while maintaining a good performance, it is necessary to use or design materials with intrinsic flexibility and compliance.19,29

Conventional supercapacitors are composed of collectors, electrodes, electrolytes and separators (Figure 1.4). The separators are usually made of soft-materials such as nonwoven fabric, microporous membranes or even a structurally enhanced electrolyte. The electrolytes are generally liquid or gel-like materials. The use of the latter have raised several challenges to attain long-term stability. Over long cycling usage supercapacitors are likely to suffer from electrolyte dry-out. This effect leads to a continuous degradation in the performance of the supercapacitors. The slow and constant evaporation of the electrolyte is a chronic issue resulting in capacitance retention losses greater than 20%.30,31 Alternative gel-like electrolytes are ionic liquids (IL)-based polymer electrolytes. ILs are liquid salts at room temperatures and consist of ions and counter ions being together as a liquid and without the presence of any solvent. In general IL-based polymer electrolytes present high ionic conductivity and superior thermal properties. Despite these remarkable properties, IL-based polymer electrolytes show long-term operation that generally results in a progressive release of the IL components producing an undesired
decline in the supercapacitor performance. A possible way to overcome the above-mentioned setbacks and weakness of the liquid electrolytes is the use of solid electrolytes or solid gel electrolytes. However, the use of the latter raised new challenges such as low ionic conductivity and poor processability that can lead to contact problems between these electrolytes and the electrodes.33–35 Regarding the electrode materials, the most significant and challenging task is to flexibilise the electrodes. Thus, several efforts have been made to develop flexible electrode materials. Typically, the current reported flexible electrode materials include carbon nanotubes, graphene, transitional metal oxides, conductive polymers as well as their combined composite. Among them, conductive polymers are the most promising materials to fulfil the requirements of electrochemical stability, electrical conductivity, electroactivity and desired flexibility.36–38

![Figure 1.4](image)

**Figure 1.4.** Schematic representation of a conventional supercapacitor composed of collectors, electrodes, electrolyte and separator. Reproduced and adapted from reference.39

### 1.3 Conductive Polymers

#### 1.3.1 Electrically conductive polymeric systems

In general, there are four types of electrically active polymeric systems with different degrees of conductivity. The first and the most extensively used conducting polymeric systems are the composites in which insulating polymer matrices are loaded with conductive particles or a conductive fibrous filler such as a carbon or a metal to attain high conductivity. These materials are used in different applications such as antistatic coatings and substitutes for soldering metals.

The second group is regarded as ionic conductive polymeric systems where the conductivity is the result of the movement of ions present in an organic polymer system. Examples of these composites can be found in electrolytic solutions partially solidified by adding suitable gel-forming substances.

The third group is based on redox-active polymers, which contain immobilised redox centres (electroactive centres). The centres are not necessarily in contact with one another but can
conduct charge by electron transfer from one centre to another through a hoping mechanism. This latter is only possible when the density of redox centres is high enough so that the probability of tunnelling of electrons through the insulating barrier between the centres is large enough.

The fourth group are conjugated systems. The polymers of these systems consist of alternating single and double bonds, creating an extended $\pi$-network. In this group electrons and holes are charge carriers as in redox polymers. The conductivity is less dependent on the hoping mechanism but more on the conjugated nature of the polymer molecules and the resulting mobility of $\pi$-electrons and holes in the $\pi$-band (i.e., n or p-type). The source of conductivity is the movement of these charge carriers (electrons and holes) within this $\pi$-framework.\textsuperscript{40,41} However, the structure of most conjugated polymers is semi-crystalline, with a combined morphology consisting of well-ordered crystalline aggregates surrounded by disordered amorphous regions. The mixed ordered and disordered structures are a limiting factor in the charge transport process as demonstrated by Bombile \textit{et al.}\textsuperscript{42} The latter investigation carried out by computational modeling and experimental observation supported the view that charge transport in polymers is limited by inter-chain hopping producing a rate-limiting conduction effect.\textsuperscript{43} The characteristics of strong packing and disordered polymer chains are common to many disordered materials such as amorphous semiconductors.\textsuperscript{44} The mechanism of carrier transport in conducting polymers is considered more likely amorphous semiconductors (hopping transport) than to crystalline semiconductors (band transport).\textsuperscript{45}

Following these developments, polymers with comparable characteristics of a metal, such as electrical, electronic, magnetic, and optical properties were highly investigated. In this regard, conductive polymers (CPs) have been studied for several decades and gained particular interests. Especially in the late 1970s when polyacetylene, known as the prototype conducting polymer,\textsuperscript{40} was successfully doped to the metallic state endowing it electrical and electrochemical properties comparable to those of both traditional semiconductors and metals. Since then, the development of the field has continued to accelerate at an unexpected speed and a variety of other CPs and their derivatives have been discovered. All of these efforts have been rewarded with new CPs with remarkable properties such as easy synthesis, mild processing conditions, chemical diversity, tuneable conductivity and structural flexibility. In addition, CPs are environmentally friendly and highly affordable because of their simple components (C, H, N or S).\textsuperscript{46,47}

\subsection*{1.3.2 Intrinsically Conductive Polymers (ICPS)}

ICPs refer to organic polymers that possess the electrical, electronic, magnetic, and optical properties of a metal while retaining the CP properties such as processability, structural flexibility etc. A high level of conductivity can be achieved in ICPs using redox processes or doping with an appropriate dopant. There are some ICPs that exhibit high conductivity comparable with that of copper but their stability and processability are very poor compared with typical polymers. Conversely, ICPs such as polypyrrole, polythiophene and polyaniline (PAni) exhibit a comparatively...
lower conductivity but their stability and processability are better than those ICPs with high conductivity.\textsuperscript{40,48}

### 1.3.3 Polyaniline (PAni)

PAni is an ICP with a remarkable specific capacitance due to multi-redox reactions, good electronic properties, ease of synthesis and low cost. PAni can exist in different oxidation states (Figure 1.5): fully reduced or leucoemeraldine base (LEB), half oxidised or emeraldine base (EB) and fully oxidised pernigraniline base (PB).\textsuperscript{49,50}

![Figure 1.5. Schematic representation of interconversion of PAni redox states. LEB—leucoemeraldine; EB—emeraldine base; PB—pernigraniline base. Reproduced and adapted from reference.\textsuperscript{50}](image)

Although all three base states are insulators, the EB state will exhibit conductivity after protonation to the emeraldine salt (ES). LEB and PB states can be protonated to leucoemeraldine salt (LES) and pernigraniline salt (PS), respectively. These latter are not conductive states of PAni. The PAni used in electrodes is a mixture of its states with a highest portion in emeraldine state. The overall scheme of how PAni states may be interconverted is shown in Figure 1.6 where the ES conductive state can be achieved by oxidation-reduction or protonation.\textsuperscript{51,52}

When protonation changes the EB state via protonic acid to the highly conductive ES state, the number of electrons associated with the polymer remains unchanged during the doping process.\textsuperscript{48,54} The conductive ES form can also be obtained from the LEB state via oxidative
doping where the number of electrons in the polymer are changed. Both ways to obtain the ES conductive state will promote the formation of bipolarons. The latter will change into polaron species normally represented in the ES-related literature Figure 1.7. The achieved conductivity results from both the existence of the charge carriers (bipolarons and polarons) with the ability to move along the \( \pi \)-bonded structure of the polymer.\textsuperscript{55–57}

1.3.4 Synthesis of PAni

The synthesis of PAni is generally conducted by direct oxidation of the aniline monomer utilising a chemical oxidant or by electrochemical oxidation on an electrode material, in the presence of an acid. The initial electrochemical synthesis methods yielded dark blackish precipitates when aniline was oxidised in sulfuric or hydrochloric acid medium at a platinum electrode. These methods have undergone numerous modifications.\textsuperscript{57,59}

Various chemical oxidising agents are used to polymerise the aniline monomer in acidic media. One of the most common agents is ammonium persulfate. Pan et al.\textsuperscript{60} performed in situ polymerisation obtaining doped PAni hydrogels by utilising aniline monomer, phytic acid and ammonium persulfate. Similarly Peng et al.\textsuperscript{61} carried out an identical process changing the phytic acid for aminotrismethylenephosphonic (ATMP) acid. In both cases, the selected acid acts as dopant and physical crosslinker of the polymer chain resulting in a rapidly formed PAni-based hydrogel (Figure 1.8 and Figure 1.9).

In the same way, alternative precursors can be used for the synthesis of PAni including dodecylbenzenesulfonic acid and camphorsulfonic acid as they are well known dopants utilised to achieve
1.4. GRAPHENE OXIDE

FIGURE 1.7. Schematic representation of protonation-induced spin unpairing in polyaniline. Reproduced and adapted from reference 58

The obtained nanostructured hydrogels exhibit high specific capacitance and good stability making them suitable as electroactive electrode materials. Furthermore, this synthesis method produces materials that exhibit high processability for multilayer manufacturing.62–64 The PAni-based hydrogels obtained with the described methods have been used as electroactive material in supercapacitors where repeated cycles of charge-discharge are the main processes for energy storage and energy release. The charge-discharge operations can cause swelling and shrinkage in the polymer networks leading to a possible mechanical degradation of the electrodes and fading the electrochemical performance in the time.65 One way to reinforce the stability of PAni-based hydrogels is the combination of PAni with porous carbon materials such as single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), carbon nanofibers and graphene nanosheets (GNS).66,67

1.4 Graphene Oxide

Graphene is a crystalline allotrope of carbon (Figure 1.11) with unique features, including: planar form of sp² hybridized carbon structure, large surface area (2630 m² g⁻¹), mechanical strength, excellent electronic and thermal conductivity endowed by its π–π conjugated structure, and potentially low manufacturing cost.68,69

Graphene oxide (GO) is one of the functionalised forms of graphene and consists of exfoliated...
CHAPTER 1. INTRODUCTION

**Figure 1.8.** Chemical structure of phytic acid gelled and doped polyaniline hydrogel synthesised by Pan et al. Reproduced and adapted from reference 60

**Figure 1.9.** Schematic illustration of the formation of the 3D hierarchical nanostructured PAni hydrogel and a photograph of the PAni hydrogel synthesised by Dou et al. in a glass vial. Reproduced and adapted from reference 61

sheets of graphite oxide. GO can be attained by Hummers method and modified Hummers method with low cost and easy manufacturing process. GO is electrically insulating containing functional epoxide, hydroxyl, carbonyl and carboxyl groups (Figure 1.10(b)) that can generate a homogeneous colloidal suspension in water.68,70,71 The electrical conductivity of GO can be enhanced by the removal of the oxygen-containing groups. This process is regarded as reduction of GO and can be achieved by chemical or thermal processes. The resulting reduced GO (RGO)
1.4. GRAPHENE OXIDE

![Schematic representation of graphene materials: a) Graphene, b) Graphene oxide, c) Reduced graphene oxide. Reproduced and adapted from reference 72 and reference 73.](image)

inevitably contains lattice defects (Figure 1.10(c)) that affect its electrical properties compared with pure graphene. However, RGO and GO have good processability, making them suitable and attractive materials to reinforce PANi-based hydrogels and promote their use in 3D printing. 74,75

1.4.1 Reduction of Graphene Oxide

One of the most attractive properties of GO is that it can be partially reduced to graphene-like sheets by removing the oxygen-containing groups and recovering the sp² conjugated structure. The latter process of deoxygenation of GO offers partial recovery of the graphene-conjugated structure, which gains original properties of electrical and thermal conductivity in the obtained RGO. 76,77

The reduction of GO can be carried out through various processes. The most common methods include thermal treatment, chemical reagent reduction, and microwave or laser irradiation. Thermal treatment is performed with high temperatures (900 °C to 1100 °C) limiting the practicality of this method. On the other hand, microwave irradiation requires complicated and additional equipment for their application in GO reduction. The obtained reduced GO (RGO) exhibits increased stiffness impeding their practical use in flexible devices. Reduction by chemical reagents
can be realised at room temperature or by moderate heating, which decrease the required equipment compared with thermal reduction making chemical reduction a cheaper and easily available way for the mass production of RGO.\textsuperscript{77,78} Chemical reduction has been carried out with a large number of reductants. Among these, hydrazine and its derivatives are the best-known reducing agents to achieve RGO with electrical and structural properties resembling pristine graphene. However, the main drawbacks of hydrazine are its very high reactivity and toxic nature.

Metal hydrides, e.g. sodium hydride, sodium borohydride and lithium aluminium hydride, are widely used as strong reducing reagents in organic chemistry, but unfortunately, these reductants exhibit very high reactivity with water, which is the main solvent used for the exfoliation and dispersion of GO.\textsuperscript{78,80}

The environmental and chemical disadvantages of the reducing agents have led to the introduction of “green reduction” with alternative environmentally friendly reducing agents with qualities comparable to hydrazine. One alternative green reductant is ascorbic acid (Vitamin C) because of its nontoxicity and higher chemical stability in water, making it a promising material for 3D and extrusion printing. Furthermore, the reduction of aqueous colloidal suspensions does not result in the aggregation of RGO sheets as produced by hydrazine, which is beneficial for further applications.\textsuperscript{77,81}

Additional practical methods of reduction such as laser-induced reduction have been developed with the use of cheap engineered devices like adapted 3D-printers endowed with customised laser-engravers and computer-aided design (CAD) systems. These methods have been developed because of the increasing demand of bespoke and precise electronic devices. The laser-patterning technologies are simple, scalable, and cost-effective and can provide versatile designs, functions,
1.5 ELECTROLYTES

and aesthetics.\textsuperscript{82,83}

1.4.2 Conductive current collectors

The conductive current collectors are important constituent parts of a supercapacitor as they mechanically support the electrode material and also electronically bridge the internal electrochemical circuit with the external source/load circuit. Graphene-based materials are commonly employed as current collectors for supercapacitors because of their good conductivity, high chemical stability, and high mechanical strength. With the development and improvement of the GO reduction methods such as computer-controlled laser-engraving, many laser-induced graphene electronic materials for sensors and supercapacitors have been achieved. This technique thermally removes the oxygen-containing groups from GO-based materials and re-establishes the sp\textsuperscript{2}-carbon atoms into a graphene-like lattice. The process is a one-step approach to obtain conductive current collectors to be used in the fabrication of high-performance graphene-based supercapacitors.\textsuperscript{84–86}

1.5 Electrolytes

The electrolyte material in supercapacitors not only plays a fundamental role in the electronic double-layer formation (in EDLCs) and the reversible redox process for charge storage (in pseudocapacitors) but also determines the accessibility of pores to the electrolyte ions and the supercapacitors’ performance. Electrolytes that exhibit high chemical and electrochemical stabilities allow extended supercapacitor life-cycles.\textsuperscript{19,87}

Various types of electrolytes have been developed. These are mainly classified as liquid electrolytes, and solid/quasi-solid-state electrolytes. Liquid electrolytes with high ionic conductivity have been used and reported to have good performance for supercapacitors.\textsuperscript{19} Similarly, their quasi-solid-state counterparts have shown comparable performance when utilised in the fabrication of flexible energy storage devices.\textsuperscript{88}

1.5.1 Gel electrolytes

In terms of the manufacture of flexible supercapacitors a liquid electrolyte can cause undesired leakages. This drawback can be solved with the use of quasi-solid electrolytes. These are used to combine the function of the electrolyte and separator into a single component to reduce the number of parts in a supercapacitor.\textsuperscript{89}

In this group of quasi-solid electrolytes, the hydrogel polymer electrolytes have been extensively studied and used for flexible supercapacitors. This preference for the hydrogel polymer electrolytes could be attributed to their ease of preparation, high hydrophilicity, good film forming properties, non-toxic characteristics and low cost. Polyethylene oxide (PEO) and polypropylene oxide (PPO)-based solid polymer electrolytes are normally considered because of their strong thermal conduction and electrochemical properties over a wide operating temperature range.\textsuperscript{90}
However, at room temperature PEO and PPO solid state polymer electrolytes exhibit low ionic conductivities that prevent successful application in supercapacitors. Pandey et al. incorporated PEO and PPO into a gel electrolyte to boost conductivity, the result indicated that they are actually inferior compared with poly(vinyl alcohol) (PVA) and polyvinylidene fluoride (PVdF) as gel electrolytes because the oxygen atoms in the polymer backbone limit ion mobility. One of the most used polymers in hydrogel polymer electrolytes synthesis is PVA. PVA can be used in combination with aqueous solutions of strong acids such as H$_2$SO$_4$ to obtain PVA/H$_2$SO$_4$-based gel electrolytes, appropriate for flexible supercapacitors and suitable for 3D printing and extrusion printing processes.

The mechanical and structural properties of the PVA/H$_2$SO$_4$-based gel electrolyte can be enhanced to obtain a material that can act not only as an electrolyte but also as a separator, preventing the need for additional separators between the electrodes. In terms of 3D and extrusion printing, this enhancement reduces the number of materials to be printed, thus reducing the required nozzles or extruders in a 3D-printer. The structural enhancement can be achieved by the method reported by Wang et al. and Su et al. consisting of crosslinking of PVA chains with glutaraldehyde (GA) (Figure 1.12) in acidic medium.

### 1.6 Materials and 3D-printing

The manufacture of individual components (such as electrode materials, electrolytes and structures) is relatively easy. However, the possible interactions between them must be considered to achieve the highest synergetic effect in an assembled device. These interactions can be found between materials such as the water based PVA/H$_2$SO$_4$/GA gel electrolyte and the electroactive polymer-based material, and between the latter and the conductive current collectors. Furthermore, additional factors must be taken into account for the manufacturing process to secure the best results. Among them the electrolyte penetration capacity into the electrode material and the match between the latter and the current collector material must be considered carefully.
1.6. MATERIALS AND 3D-PRINTING

This compatibility makes the materials easy to assemble in a supercapacitor using a layer-by-layer architecture to obtain a multilayer device (Figure 1.13). A multilayer design can be constructed with additive manufacturing (AM) (often referred to 3D-printing). This is a method in which a model designed by a computational package is captured and transformed into a 3D-printer-compatible file and then constructed on a layer-by-layer basis. 3D-printing technology is becoming increasingly capable and affordable, making it a promising tool for rapid production of bespoke 3D objects and devices.\textsuperscript{94,95}

1.6.1 Additive manufacturing methods

AM is a technological development defined as a process of joining materials to obtain objects from 3D-model data, usually in a layer by layer fashion, i.e., creating physical objects by successive addition of material. The 3D-models are designed with the support of a computer-aided design (CAD) software and sliced into individual layers, which then supply the toolpath code for a 3D printer.\textsuperscript{96,97}

Following the standard ISO/ASTM52900-15 of AM process classification, there are seven types of AM techniques of:
Figure 1.14. Schematic representation of additive manufacturing methods: a) binder jetting. Reproduced and adapted from reference 98 b) directed energy deposition. Reproduced and adapted from reference 97

• Binder jetting: AM process by which a liquid bonding agent is deposited onto a bed of powder. Used with glass, sand, metal, gypsum, and several others (Figure 1.14(a)).

• Directed Energy Deposition: In which a metal powder or wire feedstock is fed in front of an energy source, such as an electron or laser beam, mounted on a multiaxis robotic arm. The material is melted onto a substrate layer-by-layer. Used with metals such as titanium and cobalt-chrome. (Figure 1.14(b)).

Figure 1.15. Schematic representation of additive manufacturing methods: a) material extrusion. Reproduced and adapted from reference 99 b) material jetting. Reproduced and adapted from reference 100

• Material extrusion: process in which material is selectively dispensed from an extruder onto a substrate. Used with a melted thermoplastic filament or a viscous materials such as concrete, clay, organic tissue, polymer blends, and even food (Figure 1.15(a)).

• Material jetting: process in which droplets of build material are selectively deposited using piezoelectric print-heads similar to those found in 2D inkjet printers. Most often, this material is wax or a photosensitive plastic resin (photopolymer) hardened by UV-light (Figure 1.15(b)).
1.6. MATERIALS AND 3D-PRINTING

- **Powder bed fusion**: process in which thermal energy (such as a laser or electron beam) selectively fuses regions of a powder bed. This technology is associated with metals such as titanium or plastics such as nylon (Figure 1.16(a)).

- **Sheet lamination**: In this process, sheets of material are fused together to form a part. This method is used mostly with paper, and also with metal and plastics (Figure 1.16(b)).

- **Vat photopolymerisation**: AM process by which a vat photopolymer resin is exposed to an energy source, such as a laser beam or a digital light projector, which hardens or cures the resin layer-by-layer (Figure 1.17(a)).

1.6.2 Direct-Ink Writing (DIW)

The term “direct-ink writing” describes fabrication methods that employ a computer-controlled translation stage, which moves a pattern-generating device, that is, an ink-deposition nozzle, to create materials with controlled architecture and composition. The different direct-ink writing techniques have been developed for patterning materials in three dimensions. They can be
CHAPTER 1. INTRODUCTION

FIGURE 1.18. Schematic illustration of the different printheads and nozzles used in DIW of viscoelastic materials. Reproduced and adapted from reference.\textsuperscript{104}

classified into robocasting or robotic deposition, micropen writing, fused deposition, droplet-based approaches, and hot-melt printing. Most of these techniques aim to conduct a fabrication process with visco-elastic materials under ambient conditions.\textsuperscript{104,105}

The ink material to perform a DIW fabrication process should be carefully selected. Several designs and formulations of these inks have been developed to attain the required fluid properties towards the printing of accurate patterns and shapes. The outcome of these efforts is a plethora of inks that include products such as colloidal suspensions and fluids, waxes, concentrated polyelectrolyte complexes, colloidal gels, and polymer blends. One of the most important characteristics of these inks is that they can be categorised as yield-stress fluids and are described by the Herschel–Bulkley model:

$$\tau = \tau_y + K\dot{\gamma}^n$$

(1.2)

Where $\tau$ is the shear stress, $K$ is the consistency, $\dot{\gamma}$ is the shear rate and $n$ is the flow index ($n<1$ for shear-thinning fluids). However, for the purposes of this research and in accordance with the shear profile of the instrument used to carry out the rheology characterisation of the inks, the following expression will be used:

$$Viscosity(\eta) = \frac{Shear Stress}{Shear Rate} = \frac{\tau}{\dot{\gamma}}$$

(1.3)

Equation (1.3) can be used to calculate the related fabrication parameters such as the diameter of the nozzles, the required stress in the printhead to induce flow and the amount of dispensed material. Additional treatment could be required after the 3D-printing process, such as photopolymerisation or UV-curing to harden or fully solidify the printed parts. The enhanced and precise automated control of the DIW technique is the starting point to obtain an standard procedure of rapid prototyping. This latter grants the reproducibility of engineered pieces or bespoke parts with precise shapes and patterns required in electronic and energy storage devices.\textsuperscript{104,106,107}
1.7 Electrochemical Measurement of Capacitance

The capacitance in supercapacitors can be characterised with electrochemical techniques such as cyclic voltammetry (CV). CV is widely used studying electrode processes and consists of the application of a continuously time-varying potential to the studied electrode. The result of

![Figure 1.19. Applied potential as a function of time for a cyclic voltammetry experiment.](image)

the potential $E$ applied is a current $i(E)$. The latter is caused by the formation of EDLC (Section 1.2.1) and the occurrence of oxidation or reduction processes (faradaic reactions) of electroactive materials in solutions or electrolytes. The potential is carefully changed with a controlled sweep rate. The sweep experiment is performed in one direction and then inverted at a certain chosen potential (Figure 1.19). The resulting voltammetric waveshape (voltammogram) is the current passed by the electrodes related to the potential applied. These current values are analysed to characterise the electrode features.

The potential to invert the direction of the sweep experiment is chosen depending on the analysed electroactive material. In the case of PAni, the sweep potential considered starts from $-0.2$ V to $0.8$ V (forward scan or oxidising wave) then from $0.8$ V to $-0.2$ V (reverse scan or reducing wave) and the resulting current density ($A g^{-1}$) shows the redox reactions produced in the electroactive material (Figure 1.20) during the sweep experiment. The oxidation/reduction peaks found in the voltammograms show the transitions between oxidation states of PAni-based materials when they are analysed as electrode. By definition, when an interface sees a single redox half-reaction occurring, the electrode where oxidation takes place is called the anode, and the electrode where reduction takes place is called the cathode. The first peak in Figure 1.20 shows the transition between the fully reduced state LE to the half-oxidised state EB, then the second peak denotes the transition from the EB state to the fully oxidised state PE. The same shape but inverted is expected when the sweep experiment is reversed as the reduction processes occur. The presence of PAni salts instead of PAni bases or a combination of them can be obtained
Figure 1.20. Cyclic voltammogram (voltammetric waveshape) for the oxidation and reduction processes of PANi. Reproduced and adapted from reference.\textsuperscript{52}

during the electrochemical analysis depending on the pH of the electrolyte used.\textsuperscript{52,109,111}

The obtained voltammograms can be used to calculate the capacitance of the electrodes. The charge accumulated in the electrodes can be calculated using the current density curve. The capacitance can then be obtained from the total charge, the potential window (from the initial potential to the final potential value of the sweep experiment) and the sweep rate:

\[
C = \frac{dQ}{dE} = \frac{dQ}{dt} \frac{dt}{dE} = \frac{i}{dE/dt} = \frac{i}{v}
\]  

(1.4)

where \( i \) is the instantaneous current in the voltammograms, \( Q \) is the charge in the electrode, and \( dE/dt \) is the scan rate. The calculation of the capacitance is made using all the current points obtained during the potential sweep. In this regard, the average current \( \bar{i} \) is needed. The latter can be obtained integrating the instantaneous current along the whole potential sweep and dividing it by the scan rate:

\[
\bar{i} = \frac{\int_{E_1}^{E_2} i(E) \, dE}{(E_2 - E_1)}
\]

(1.5)

Substituting Equation (1.5) into Equation (1.4), the capacitance \( C \) becomes:

\[
C = \frac{\bar{i}}{v} = \frac{\int_{E_1}^{E_2} i(E) \, dE}{v(E_2 - E_1)}
\]

(1.6)
1.8 Aim and objectives

The overall aim of this project is to develop fully 3D-printable flexible and stretchable energy storage devices.

To fulfil this aim the following objectives have been accomplished:

- **Synthesise and characterise the required materials for soft supercapacitors**: Electroactive materials for energy storage such as PAni, PAni/GO, and PAni/RGO have been successfully synthesised. In this regard, it is worth incorporating new approaches and architectures to produce PAni-based electroactive materials for enhanced energy storage devices. This effort has been conducted to achieve a proper combination of the synergistic contributions of electrical double-layer capacitance and pseudocapacitance of graphene-based materials and PAni respectively, to increase the total capacitance in a supercapacitor prototype. The supercapacitor assembling process includes careful consideration to combine an appropriate gel electrolyte with the electroactive material and the latter with the current collector. Further optimisation of these three components were investigated to obtain a desired enhancement on the supercapacitor device capabilities.

- **Test the suitability of the synthesised materials for the construction of flexible supercapacitor prototypes**: This part of the work was performed to construct not only rigid supercapacitors but also flexible supercapacitor devices, once the produced PAni/GO-based materials and gel electrolytes have been synthesised and optimised into enhanced structures. The flexibility of the electroactive materials, gel electrolytes and current collectors are tested through bending/stretching tests whilst maintaining the desired capacitive performance. This aspect is noteworthy considering that this project aimed to obtain a flexible energy storage device.

- **Test and optimise the materials for 3D-printing the supercapacitors**: The synthesised electroactive material, gel electrolyte and current collectors are combined and tested in constructed flexible devices. These devices are manufactured by 3D printers and laser scribers, considering different architectures to create complex shapes and patterns with different materials with a highly precise conformal process. This has been achieved using a Computer

---

\[
C_S = \frac{C}{m} = \frac{\int_{E_1}^{E_2} i(E) dE}{m v (E_2 - E_1)}
\] (1.7)

The specific capacitance can also be calculated considering not only the mass \( m \), but also, the surface \( s \), or the volume \( v \) of the electroactive material or the electrode evaluated.
Aided Design (CAD) packages and customised 3D printers with extruding systems and a laser-scriber.

1.9 Thesis Summary

The work required to accomplish the objectives towards the completion of the aim of this research project has been distributed in this thesis as follows:

In Chapter 2 there is a detail of the experimental methods used in the fabrication of the supercapacitor prototype device and each one of its parts. Additional to that, the methods of characterisation used in this research are included.

In Chapter 3 the synthesis of 3D-printable GO-based extrudable inks are investigated and a laser-engraving reduction process of the GO extruded material is described. The conductive properties of the obtained laser reduced RGO-based material are evaluated and its possible use as conductive current collector in supercapacitor prototypes is demonstrated.

In Chapter 4 the synthesis of various PAni-based materials are investigated. The electroactive and capacitive properties of the obtained PAni-based materials are demonstrated with their use in the construction of the supercapacitor prototypes. A fully 3D-printable ink is developed and its successful use in flexible supercapacitor prototypes is evidenced.

In Chapter 5 a suitable electrolyte material to fulfil the requirements of a supercapacitor prototype is developed and its properties are investigated. The possibility of transferring the electrolyte properties to a 3D-printable gel electrolyte is demonstrated.

In Chapter 6 the investigation focuses on the fabrication and testing of a supercapacitor prototype device. The integration of the enhanced parts is investigated and the construction of a 3D-printed flexible energy storage device is demonstrated.

In Chapter 7 the conclusions of the research are reported. Additional in the future aspects of this investigation that can be continued, and projects that can be derived from this work are also presented.

1.10 References


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CHAPTER 1. INTRODUCTION


2.1 Device Fabrication

Supercapacitor prototype devices have been manufactured by the combination of the construction processes of the conductive current collectors, electroactive material and gel electrolyte. Here the methods of synthesis, characterisation and manufacture are detailed for each one of the constituent parts of the supercapacitor. In addition, any supplementary methods used in the performed research is reported in this chapter.

2.1.1 Conductive current collectors

The conductive current collectors were manufactured by the combination of the construction processes of the CCCs, electroactive material and gel electrolyte.

2.1.1.1 3D printing of current collectors

The CCCs have been extruded by a customised software controlled 3D printer Prusa i3 with a RAMPS 1.4 controller board. The 3D printer was previously modified in the Faul Research Group into a 2-extruder multimaterial configuration. The controller firmware of the RAMPS 1.4 card used is Marlin 1.1.9. The G-CODE files were developed using Simplify3D® as a suitable G-code generator. The volumes, shapes and patterns of the models were designed using Autodesk® Inventor® Professional Software and Blender Software.

Polyethylene oxide / graphene oxide-based ink preparation  The polyethylene oxide reagents with different molecular weights were purchased from Sigma-Aldrich and used directly with no further treatment. The Graphene Oxide (GO) was purchased in different batches from
CHAPTER 2. EXPERIMENTAL METHODS

Graphenea Inc. (USA) and Graphitene Ltd. (UK). In addition, a 3\textsuperscript{rd} batch of GO synthesised at the Faul Research Group lab was used (for the elemental analysis results of the GO samples, please refer to Section A.1.3). The PEO/GO extrudable ink was prepared by mixing PEO powder in a 10 mg ml\textsuperscript{-1} GO suspension. The concentration of the polymer was calculated in wt\% in the overall blend for all samples. Fast drying inks were prepared by replacing the GO suspension with a solvent blend of 20\% of ethanol and 80\% of the GO suspension.

![Syringe-based mixing set](image)

**Figure 2.1. Syringe-based mixing set.**

The blends were transferred into a mixing set prepared with two 10ml luer slip syringes (Terumo, UK) connected by a plastic three-way tap T connector as shown in Figure 2.1. The mixing process of the precursors are performed by repeatedly transferring the ink from one syringe to the other for 10 min. The mixing sets are left 24 h at ambient conditions. The mixing process is repeated for 10 min and left for another 24 h to ensure the PEO in the blend is totally and smoothly dissolved. The mixing process is repeated for a final 10 min. The syringes with the inks are then centrifuged for 5 min at 2300 rpm and placed under vacuum to remove bubbles. The centrifuge/vacuum cycle is repeated 5 times to obtain a smooth and bubble-free blend. The syringe with the ink is installed in the customised supports of the 3D printer and left ready for extrusion as shown in the Figure 2.2. The patterns and models were extruded on a glass substrate.

![Syringe attached to the 3D-printer](image)

**Figure 2.2. Syringe attached to the 3D-printer.**

After each extruded layer, the 3D-printed models were left to evaporate the ethanol/water-based solvent. The extrusion process is repeated as many times as needed by the requirements of
the layer-thickness for laser-scribing. To ensure a safe laser-scribing process, 6 layers of the PEO/GO-blend are extruded in each sample. The final model is dried at 40\(^\circ\) Celsius in an oven for 1h.

The control samples of PEO-based inks were produced replacing the GO with a red dye AR-27 (Amaranth Red) and following the same preparation procedures. The concentrations of AR-27 were kept consistent with those of the GO.

**Controlled pressure assistance**

The controlled pressure system provides a constant pressure to the extrusion system by a regulated nitrogen gas support. The nitrogen gas line available in the Faul Research Group lab has a pressure close to 6 bar (600 kPa). This line is connected to a Shako URPL4-02 manual pressure regulator valve (SHAKO Co., Ltd., Taiwan) that can be precisely adjusted to produce a regulated output pressure between 10 kPa and 400 kPa with a sensitivity and repeatability of \(\pm 0.5\%\). The regulated pressure line is connected to the syringe-based container previously mounted to the 3D-printer as shown in the Figure 2.3. The required pressure at the nozzle entrance is provided by the contributions of the cylinder with an auger-like screw mechanical extruder and a compressed nitrogen line. The material flow is not directly controlled by the pressurised nitrogen line. Instead, the flow control is provided by the auger extruder allowing a fully software-controlled 3D-printing process.

![Diagram of controlled pressure assistance](image)

**Figure 2.3.** Syringe attached to the 3D-printer.

### 2.1.1.2 Laser Scribing of current collectors

For the laser-engraving system a DuetWiFi (Think3DPrint3D Ltd., UK) 3D printer was endowed with a 455 nm / 1600 mW laser diode. The laser was mounted as part of the printing head. The laser signal is controlled by a pulse width modulation (PWM)-based waveform. The waveform
consists of complementary on and off cycles repeating several times per second depending on the power and frequency required.

The laser scribing parameters of power, speed and frequency can be set in the laser software previously developed in the Faul Research Group. The laser-scribing process is software-controlled following the instructions of a GCODE file. The latter is generated based on a model previously designed on Autodesk® Inventor® Professional Software or Blender Software and processed by Simplify3D®.

The laser-scribing of the PEO/GO-based models is performed after moving the models to the customised laser-engraving system bed. The distance from the laser to the models is adjusted to focus the beam on the model surface prior the laser-scribing procedure.

**Power and wavelength**

The laser-scribing system delivers power by repeated pulses of on time and off time several times or cycles per second. The power value of the laser is controlled by changing the percentage distribution of the complementary on and off states of the laser per cycle. The power expressed in percentage is directly related to the portion of the on-state per cycle or repeated interval as shown in the Figure 2.4.

![Figure 2.4. PWM power of the laser scriber](image)

The wavelength of the laser diode is located in the band of 400 to 460 nm. Most of the radiation is located in the band of 445 to 455 nm wavelength blue colour. The colour does not have a particular reason more than being an affordable laser diode to build the laser-scribing system.

**Frequency**

The frequency of the laser can be changed from 0 to 65.5 kHz (65535 Hz). The parameter
of frequency of the laser can be changed before starting a laser-engraving process. The laser frequency can be easily set in the command line used to switch the Duet3d 3D-printer to laser mode (M452 command) within the GCODE command lines.

**Speed**

The speed of the laser can be modified on Simplify3D® or any slicer used to generate the GCODE file. This file is then loaded in the customised 3D printer with the attached laser-engraver system. In addition, the speed of the laser head and the 3D-printing heads can be further modified by the controller application software of the 3D-printers. This additional alternative offers sliding controls and virtual knobs that allow the user to change the 3D-printing and laser-engraving speeds. With these controls the parameter of laser speed can be modified before and also (if required) during the 3D-printing or laser-engraving processes.

### 2.1.2 Flexible substrate preparation and attachment to the conductive current collectors

The flexible substrate and encasement of the supercapacitor prototype are constructed using UV-curable silicone rubber UV Electro 225-1 (Momentive Performance Materials, USA). The silicone rubber was received as two components: a base and a catalyst. The two components were mixed in a ratio of 100:2. The blend was normally prepared in batches of 10 g since this is the capacity of the disposable syringes used as material containers. The syringes were centrifuged at 2700 rpm for 5 min, then transferred into a vacuum oven at ambient temperature to remove bubbles. The centrifuge/vacuum cycles were repeated 5 times to ensure a smooth and bubble free extrudable blend. A layer of the obtained silicone rubber was 3D-printed on the surface of the previously laser-scribed CCCs. The thickness of the extruded layer was carefully set in the design of the model or STL file on Autodesk® Inventor® Professional Software or Blender Software. To cure the 3D-printed silicone rubber, the area of the extruded silicone rubber was irradiated with a 3.8 W UV LED with a speed 50 mm min\(^{-1}\) and from a distance of 5mm from the surface. The process was repeated 3 times to ensure the silicone rubber was properly cured. The irradiated models were left to cool at ambient temperature because the UV-supported curing process produces heat on the irradiated model. The cured silicone rubber was peeled off from the CCC-based models, holding attached to it the laser-scribed porous graphene patterns. The peeled off CCCs attached to the silicone rubber became the new substrate for the next 3D-printed layer of electroactive material.

#### 2.1.2.1 Extrudable silicon rubber

The UV-curable silicone rubber UV Electro 225-1 (Momentive Performance Materials, USA) extrudable blend was prepared by the combination of the base and catalyst and degassed by
cycles of centrifuge/vacuum treatment. The resulting material was directly extruded by the customised 3D printers with no further treatment. Neither a plasticiser nor a solvent were used to change the attained viscosity of the blend.

2.1.2.2 UV-curable silicon rubber

The UV-curable silicone rubber UV Electro 225-1 (Momentive Performance Materials, USA) was found to have a remarkable chemical and mechanical stability. These characteristics made it suitable for 3D printing and no other UV-curable silicone rubber were tested. In addition, the use of a UV-activated catalyst delays the activation of the curing process until the blend is exposed to a UV light source. This featured mechanism ensures a long pot life of the prepared material whilst allowing a fast curing process after UV-irradiation.

2.1.3 Electroactive material

2.1.3.1 PAni synthesis

The PAni-based electroactive material was prepared using different methods and dopants. The phytic acid-doped PAni was prepared following the method reported by Pan et al.,\(^1\) where a solution A and a solution B were prepared separately. Solution A was obtained by dissolving 0.286 g (1.25 mmol) in 1 mL of deionised water. Solution B was prepared by combining 0.921 mL (1 mmol) phytic acid (50%, wt/wt in water) with 0.458 mL (5 mmol) of aniline monomer and 2 mL deionised water. Solutions A and B were combined to produce an in-situ polymerisation in about 3 to 5 min. In addition, conductive carbon cloths were immersed sequentially in the A and B solutions, respectively, to obtain a fully PAni-coated conductive fabric. As an alternative, the A and B solutions were cooled to 4°C and mixed. Before the polymerisation process takes place, the conductive carbon cloths were immersed and soaked in the mixed solution so the polymerisation was produced on the surface of the conductive fabric. To obtain an ice-templated version of the phytic acid-doped PAni the A and B precursors were cooled to 4°C and mixed and immediately poured into a customised polydimethylsiloxane (PDMS) mould with an aluminium base. After the polymerisation process took place the mould was transferred to a container with liquid nitrogen at -196 °C. The aluminium base was put directly in contact with the liquid nitrogen as shown in

![Figure 2.5. PDMS mould and setting for vertical ice-templating](image)
Figure 2.5 so that the PAni-based blend was vertically ice-templated by the frozen water in the polymer hydrogel.

To obtain the phytic acid-doped PAni/GO-based material the deionised water of the precursor A was replaced by a GO aqueous suspension (5 mg ml\(^{-1}\)). The precursor B was not modified and the mixing method was the same as the one used in the synthesis of the phytic acid-doped PAni.

The reduced GO (rGO)/PAni-based material was attained by adding ascorbic acid with a ratio of 1:5 (AA:GO) by weight to the phytic acid-doped PAni/GO-based blend and stirring it overnight. The resulting suspension was drop-cast on carbon cloths and allowed to dry in a vacuum oven at 40 °C overnight.

The (1S)-(+) -10-camphorsulphonic acid/4-dodecylbenzenesulphonic acid (CSA/DBSA)-doped PAni was synthesised by combining CSA (1.16 g, 5 mmol) with aniline monomer (0.91 mL, 10 mmol) and DBSA (0.77 mL 2.5 mmol). The resultant paste was constantly stirred and cooled to 5° C, whilst a solution of (2.28 g, 10 mmol) of ammonium persulfate in deionised water (5 mL) was added drop-wise during 20 min keeping the stirring and the low temperature. The blend changed colour from a yellow/white to a dark blue/green. The blend was then heated to 60° C and left under reflux for 4h keeping the constant stirring and the temperature. The attained blend was left to cool overnight under constant stirring ensuring that no aggregates were left insulated from the blend. The constant stirring eliminates bubbles from the synthesised electroactive ink. The obtained ink was collected the next day and transferred to a syringe container for the 3D-printing process.

### 3D-printing of PAni-based inks

Once prepared the CSA/DBSA-doped PAni obtained above was ready to be 3D-printed. To perform the extrusion process a syringe filled with the CSA/DBSA-doped PAni blend is mounted to the 3D-printer and attached to the controlled pressure assistance system. The extrusion process is performed according a GCODE based on a pattern or a model previously developed in the CAD packages Autodesk® Inventor® Professional Software or Blender Software. The controlled pressure assistance system is adjusted to obtain a constant and smooth extrusion. After this calibration, the system does not require further adjustments.

#### Polyethylene oxide (PEO)/ PAni-based ink preparation

The PEO/PAni-based ink was prepared using phytic acid-doped PAni powder and PEO. The PEO powder with a molecular weight of 1'000,000 Da was purchased from Sigma-Aldrich and used directly with no further treatment. The PAni-based powder was obtained by drying phytic acid-doped PAni in a vacuum oven at 40° C for 48 h. The dried samples were ball milled in a Retsch Mixer Mill MM 200 (Retsch, Germany) for 2 hours at 33 Hz. The obtained powder was mixed with a PEO 6 wt% aqueous solution. The concentration of the PAni powder was 6 wt%
in the overall polymer aqueous blend. The mixture was transferred to the mixing set prepared with two 10ml luer slip syringes (Terumo, UK) connected by a plastic three-way tap T connector previously detailed in Section 2.1.1.1.

The blend was kept in one of the syringes then degassed and centrifuged for 5 min at 2300 rpm to eliminate bubbles. The syringe was placed in the 3D-printer for the extrusion process.

**Controlled pressure assistance**

The syringe placed in the 3D-printer was connected to the 6 bar nitrogen line of the laboratory through a Shako URPL4-02 manual pressure regulator valve (SHAKO Co., Ltd., Taiwan). The regulator was calibrated to attain a constant extrusion process free of discontinuities or bubbles. The calibration allowed a smooth 3D-printing process and compensates a possible depletion of pressure when the auger-screw mechanism pushes the blend to the printing nozzle.

### 2.1.4 Electrolyte material inks

#### 2.1.4.1 Polyvinyl alcohol/\(\text{H}_2\text{SO}_4\)-based electrolyte synthesis

Polyvinyl alcohol (PVA) was purchased from Sigma-Aldrich and was used directly with no further treatment. The synthesis of the PVA/\(\text{H}_2\text{SO}_4\)-based electrolyte was attained by mixing 1 g of acid, 1 g of PVA and 10 mL of deionised water. The resulting slurry was heated to 90°C and kept for 2 h under continuous stirring until a clear solution was obtained. The attained aqueous solution was left to cool to room temperature and under continuous stirring. The obtained blend is centrifuged to eliminate bubbles. The standard 1M aqueous solution \(\text{H}_2\text{SO}_4\) was prepared by dissolving 1 mol of the acid in deionised water. Please note: appropriate care has to be taken when diluting concentrated acids.

#### 2.1.4.2 3D-printing of PVA/\(\text{H}_2\text{SO}_4\)-based ink

**PVA/\(\text{H}_2\text{SO}_4\)-based ink preparation**

The obtained PVA/\(\text{H}_2\text{SO}_4\)-based electrolyte blend was transferred into a syringe. The syringe was centrifuged at 2300 rpm and degassed in vacuum at ambient temperature. The degassing and centrifuge cycles were repeated 5 times to eliminate bubbles. The syringe was then mounted on the 3D printer. The extrusion process was performed by the customised 3D printer following the GCODE files generated based on a CAD STL model or pattern.
2.2 Device Characterisation

2.2.1 Conductive current collectors

2.2.1.1 Characterisation of 3D printable ink for conductive current collectors

Rheology measurements of the inks

PEO/GO-based inks were directly characterised after being the degassing process. Shear rheology of the degassed inks was measured at 21 °C using a Malvern Kinexus Pro Rheometer with rSpace software, a cone geometry with a 20mm radius and 4° angle and flat base-plate. The measurements were taken at different shear rates from 0.1 to 100 s$^{-1}$.

2.2.1.2 Conductive current collectors morphology characterisation

Scanning Electron Microscopy

The morphology characterisation of the samples were performed using scanning electron microscopy. The images were taken using a Jeol IT300 SEM with an accelerating voltage of 15 kV. The conductive samples were directly put on top of a carbon-based tape on an aluminium stage. The non conductive samples were also put on an aluminium stage by sticky carbon disks. The samples were silver-coated before the characterisation process.

X-ray diffraction (XRD) characterisation

Films of GO were deposited on glass disks and dried in a vacuum oven at 40° C for 24 h. The XRD diffraction spectra was generated using a Bruker D8 ADVANCE powder diffractometer at room temperature with a Cu K-α radiation source with a wavelength of 1.5406 Å. The measurements were taken on the same day to keep the results consistent with no ambient humidity variations specially for sensitive samples such as GO-based samples.

2.2.1.3 Conductive current collectors composition characterisation

Fourier-transform infrared (FT-IR) spectroscopy of 3D printed films

3D-printed films of PEO/GO-based ink on glass were dried and scratched from the glass substrate. The obtained powder was deposited on the stage of a PerkinElmer FTIR Spectrum two Spectrometer with an ATR accessory. Each sample was individually treated with a baseline correction
CHAPTER 2. EXPERIMENTAL METHODS

FT-IR spectroscopy of the laser-scribed films

3D-printed films of PEO/GO-based ink on glass were dried and laser-scribed. The resulting laser-scribed material was removed and deposited on the stage of the same PerkinElmer FTIR Spectrum two Spectrometer with an ATR accessory. For this characterisation, also, each sample was individually treated with a baseline correction.

Raman spectroscopy of Graphene Oxide-based films

The graphene oxide samples were prepared by 3D printing the PEO/GO-based blends on glass substrates. The samples were left at ambient conditions to let the solvent evaporate. The dried samples were transferred to a vacuum oven and left at 40° C for 24 h. The samples were characterised using a Renishaw 2000 Raman spectrometer with a 514 nm wavelength laser.

Raman spectroscopy of Laser-Scribed Graphene Oxide-based films

The dried PEO/GO 3D-printed samples were laser-scribed at a speed of 300 mm min\(^{-1}\), with a frequency of 75 Hz and a laser power of 15%. The samples were similarly characterised using the same system of Renishaw 2000 Raman spectrometer with a 514 nm wavelength laser.

2.2.1.4 Conductive current collectors conductivity characterisation

The evaluation of the conductivity of the laser-scribed CCCs was performed by two methods. The fastest and simplest method was by 3D-printing and laser-engraving rectangular areas of PEO/GO-based samples. The samples were transferred onto silicone rubber following the method described in Section 2.1.2. The flexible samples were then measured with a customised 2-probes setting and a Fluke 77 IV digital multimeter (Fluke Corporation, USA). In this method two parallel plates of copper tape were put in contact with the square samples. The copper tape-based setting was placed so the parallel copper contacts touch the edges of the sample leaving a square area enclosed in between the probes. The reason to assume a parallel current flow within the sample is that the resistance of the copper is negligible compared to those of the samples. The resistance can be calculated by using the Equation 2.17.

\[
R = \frac{Rw}{l}
\]

(2.1)

In this case, for an encased area where \(w=l\), the measured resistance is equal to the sheet resistance. Figure 2.6 shows the transverse view of the two-probe measurement technique.

The measurements were repeated three times each time in a new sample. The average of the three measurements was used.
2.2. DEVICE CHARACTERISATION

A second method, similar to the previously described method but using silver paste to enhance the electrical contact between the CCCs and the two probes. The calculations of the resistance were performed using Equation 2.17 as before. The second method was selected over the first because it reduces any contact resistance that can result from the mechanical contact between the laser-carbonised porous surface and the probes. The sheet resistance values obtained with the second method were similar to the ones obtained with the first method.

4-point probe measurements

As an alternative to the previously described methods to measure the resistance of the CCCs, a 4-point probe (4PP) method was used. The 4PP method consists of four conductive probes aligned and with equal spacing in between each probe.

Figure 2.7 shows the schematic diagram of the 4PP setup. The measurements are performed by applying a current to the external probes and taking a reading of the voltage between the inner probes. The values of current and voltage are used to calculate the sheet resistance using

Figure 2.7. Four-point-probe system to measure resistance. Reproduced and adapted from reference 2
the Equation 2.2 where $C$ is a geometric correction factor.

$$R = C \frac{\pi}{\ln(2)} \frac{V}{I}$$

(2.2)

The latter is required to account for the limiting proximity of the edges of the sample that can limit the possible current paths leading to a overestimated sheet resistance. Similar results of sheet resistance were obtained with this method compared to the 2-probe methods described previously.

Once the three methods of measuring the conductivity of the CCCs were evaluate, the 2-probe method using silver paste to reduce the contact resistance was selected. The use of this method is also supported because it allows to obtain faster results compared with the 4PP method. The reliability and velocity of the method used are important factors because of the amount of samples and repeats required during this research effort.

2.2.1.5 Conductive current collectors stretching tests

Strain and conductivity measurements

The conductivity measurements of the CCCs subjected to strain tests were performed by a 2-probe method. The terminals of the Fluke 77 IV digital multimeter (Fluke Corporation, USA) were connected to an attached copper tape to the ends of CCCs. The strain tests were performed using a customised IMADA DPS-110 (Imada, Inc., USA) digital force gauge to measure the strain distance as shown in Figure 2.8.
2.2 DEVICE CHARACTERISATION

2.2.2 Electroactive material

The PANi-based electroactive material was characterised using Ultraviolet-Visible-near-IR Spectroscopy (UV-vis), XRD, FT-IR spectroscopy. The morphology of the electroactive material was characterised by SEM and the 3D-printable PANi-based inks were characterised by rheology experiments.

2.2.2.1 Characterisation of synthesised PANi (UV-vis spectroscopy, XRD, FT-IR spectroscopy)

UV-vis spectroscopy of PANi-based inks

The phytic acid-doped PANi and the CSA/DBSA-doped PANi inks were smeared and compressed between two quartz slides and put on the stage of a Shimadzu UV-2600 UV-VIS Spectrophotometer. The spectra was obtained in the wavelengths ranged from 370 to 850 nm.

FT-IR spectroscopy of PANi-based inks

The phytic acid-doped PANi and the CSA/DBSA-doped PANi were directly deposited on the stage of the Perkin Elmer FTIR Spectrum-two Spectrometer with an ATR accessory used to previously characterise the CCCs.

XRD spectroscopy of PANi-based inks

The CSA/DBSA-doped PANi was extruded on glass substrates and allowed to dry in a vacuum oven at 40°C for 48 h. The XRD diffraction spectra was generated using a Bruker D8 ADVANCE powder diffractometer at room temperature with a Cu K-α radiation source with a wavelength of 1.5406 Å.

2.2.2.2 Characterisation of 3D printable electroactive material ink

Rheology measurements of the inks

The viscosity of the CSA/DBSA-doped PANi samples were characterised by shear rheology experiments performed at 21 °C using a Malvern Kinexus Pro Rheometer with rSpace software, a cone geometry with a 20mm radius and 4° angle and flat base-plate. The measurements were taken at different shear rates from 0.1 to 100 s⁻¹.

Sessile drop and pendant drop methods

Sessile drop and pendant drop tests were performed at room temperature with a Krüss DSA30 Drop Shape Analyzer. The sessile drop experiments were carried out with 2 test liquids: deionised water and diiodomethane. 2 μL of the test liquids were deposited on top of the CCCs and gel electrolyte. The contact angle data was measured for 5 repeats for each material.
CHAPTER 2. EXPERIMENTAL METHODS

The same procedure was performed to obtain the contact angle between the CSA/DBSA-doped PANi inks and PDMS substrate. The surface tension of the inks was obtained by generating a droplet at the end of a flat edge of a 1.55 mm needle. The calculations were carried out using the Krüss ADVANCE software. The surface tension of a liquid can be calculated by combining the Young-Laplace Equation 2.3 and Pascal’s law of hydrostatic pressure Equation 2.4:

\[
\Delta P = P_{int} - P_{ext} = \sigma l \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.3)
\]

\[
\Delta P = \Delta P_0 \pm \Delta \rho g Z \quad (2.4)
\]

The resulting Equation 2.5 can be used to calculate the surface tension of the PANi-based inks:

\[
\Delta P = \rho g Z - \sigma l \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.5)
\]

where \(\Delta P\) is the equilibrium pressure difference between the internal and external pressure of the droplets, \(\rho\) is the PANi density, \(g\) is the acceleration of gravity, \(\sigma l\) is the surface tension of the liquid droplet and \(R_1\) and \(R_2\) are the principle radii of curvature, and \(Z\) is the length of the droplet as shown in the Figure 2.9.

![Figure 2.9. Sessile drop model used for surface tension calculations. Reproduced and adapted from reference 3](image)

The surface free energy (SFE) of the CCCs and the PVA-based gel electrolyte were calculated using the Young’s Equation:

\[
\sigma_s = \sigma_{sl} + \sigma l \cdot \cos \theta \quad (2.6)
\]
2.2. DEVICE CHARACTERISATION

where \( \sigma_{sl} \) is the interface energy at the solid-liquid interface, \( \sigma_s \) and \( \sigma_l \) are the surface tensions of the solid substrate and liquid droplet respectively. The contact angle formed by the liquid droplet and the solid surface is \( \theta \) as shown in Figure 2.10.

**Figure 2.10.** Contact angle associated with surface wetting at a solid-liquid interface. Reproduced and adapted from reference 3

Equation 2.6 can be applied for different liquids. By using two liquids with well known \( \sigma_l \) such as water (72.75 mN m\(^{-1}\)) and diiodomethane (50.80 mN m\(^{-1}\)), the unknown variables \( \sigma_s \) and \( \sigma_{sl} \) can be determined. The calculation of the unknown variables can be processed by including the Fowkes Method:

\[
\sigma_{sl} = \sigma_s + \sigma_l - 2 \left( \sqrt{\sigma_s^D \cdot \sigma_l^D} + \sqrt{\sigma_s^P \cdot \sigma_l^P} \right) \tag{2.7}
\]

where \( \sigma_s^D \) and \( \sigma_l^D \) are the dispersive contributions to the solid and liquid surface tensions. \( \sigma_s^P \) and \( \sigma_l^P \) are the polar contributions to the solid and liquid surface tensions. Equation 2.7 can be rearranged to give \( \sigma_s \), then this latter substituted in Equation 2.6. When characterising the surface energy of the solid with diiodomethane the polar contributions can be removed. Similarly, the dispersed contributions can be ignored when the test liquid is water with the same substrate. Thus, the individual polar or disperse contributions can be given. The combination process gives the Owens, Wendt, Rabel and Kaelble method as follows:

\[
\sigma_{sl} - \sigma_l + 2 \left( \sqrt{\sigma_s^a \cdot \sigma_l^a} \right) - \sigma_{sl} = \sigma_l \cdot \cos \theta \tag{2.8}
\]

\[
2 \left( \sqrt{\sigma_s^a \cdot \sigma_l^a} \right) - \sigma_l = \sigma_l \cdot \cos \theta \tag{2.9}
\]
\[
2\left(\frac{\sigma_s^n \cdot \sigma_n^s}{\sigma_l}\right) = \cos \theta + 1 
\]  
(2.10)

\[
\sqrt{\sigma_s^n \cdot \sigma_n^s} = \frac{\sigma_l(\cos \theta + 1)}{2} 
\]  
(2.11)

\[
\sigma_s^n \cdot \sigma_l^n = \frac{\sigma_l^2(\cos \theta + 1)^2}{4} 
\]  
(2.12)

\[
\sigma_l^n = \frac{\sigma_l^2(\cos \theta + 1)^2}{4\sigma_s^n} 
\]  
(2.13)

Then, combining the results for \(\sigma_s^D\) and \(\sigma_s^P\) the variable \(\sigma_s\) can be given for each solid substrate. This is known as the Good–van Oss–Chaudhury theory:

\[
\gamma_{tot} = \gamma^P + \gamma^D 
\]  
(2.14)

where \(\gamma_{tot}\) is the total SFE, and \(\gamma^P\) and \(\gamma^S\) are the disperse and polar contributions to the interfacial or total SFE respectively.

The previously detailed theory was applied to the extrudable PANi-based inks on a PDMS substrate which has a well known \(\sigma_s^D\). The contact angle PANi-PDMS and the surface tension of the PANi ink were obtained from the Krüss DSA30 Drop Shape Analyzer. The values were the uses in the Equation:

\[
\sigma_l^D = \frac{\sigma_l^2(\cos \theta + 1)^2}{4\sigma_s^D} 
\]  
(2.15)

The resulting \(\sigma_l^D\) can be subtracted from the \(\sigma_l\) of PANi to obtain \(\sigma_l^P\).

The work of adhesion (WA) between the materials was obtained from the calculated contributions of \(\sigma_l^P\), \(\sigma_s^D\), \(\sigma_l^P\) and \(\sigma_s^P\) of the solid substrates and all the PANi-based inks by combining them in the Equation:

\[
WA = 2\left(\sqrt{\sigma_s^P \cdot \sigma_l^P} + \sqrt{\sigma_s^D \cdot \sigma_l^D}\right) 
\]  
(2.16)

### 2.2.2.3 PANi-based electroactive material composition characterisation

### 2.2.2.4 PANi-based electrodes morphology characterisation

**Scanning Electron Microscopy (SEM)**

The morphology characterisation of the PANi-based samples were performed using scanning electron microscopy. The conductive samples were dried on vacuum oven at 40° C for 48 h. The dried samples were directly put on top of a carbon-based tape on an aluminium stage. The samples of the doped PANi are conductive and did not required further conductive coating treatment prior the SEM characterisation. The images were taken using a Jeol IT300 SEM with an accelerating
voltage of 15 kV. In the case of the ice-templated samples, the mould with the frozen sample was transferred to a vacuum container and kept at -45 °C for a week. The dry samples were collected and small sections of the material were put on an aluminium stage for SEM characterisation.

2.2.3 Electrolyte

2.2.3.1 Characterisation of synthesised polyvinyl alcohol/H$_2$SO$_4$-based electrolyte (XRD, FT-IR spectroscopy, SEM)

XRD spectroscopy of the gel electrolyte
The samples of polyvinyl alcohol/H$_2$SO$_4$-based electrolyte were extruded on glass substrates and allowed to dry at ambient conditions. The XRD diffraction spectra was generated using a Bruker D8 ADVANCE powder diffractometer at room temperature with a Cu K-α radiation source with a wavelength of 1.5406 Å.

FT-IR spectroscopy of the gel electrolyte
The samples of polyvinyl alcohol/H$_2$SO$_4$-based electrolyte were directly deposited on the stage of the Perkin Elmer FTIR Spectrum-two Spectrometer with an ATR accessory used to previously characterise the CCCs and PANi-based material.

The same procedure was followed to characterise the samples of the PVA-based gel electrolyte synthesised with different acids.

SEM characterisation of the PVA-based electrolyte samples
The PVA-based samples were frozen by immersing them in liquid nitrogen at -196. The samples were transferred to plastic centrifuge tubes. The tubes with the frozen samples in it were transferred to a vacuum container and kept at -45 °C for a week. The dry samples were collected and small pieces were put on an aluminium stage for SEM characterisation. The images were taken using a Jeol IT300 SEM with an accelerating voltage of the probe of 10kV to 15 kV. No additional conductive coating was applied to the samples. The obtained images were highly bright and the brightness levels were post-processed for presentation and report purposes.

2.2.3.2 Characterisation of 3D-printable electrolyte-based ink

Rheology measurements of the PVA/H$_2$SO$_4$-based ink
The PVA/H$_2$SO$_4$-based ink were directly characterised after being synthesised and degassed. Shear rheology of the degassed ink was measured at 21 °C using a Malvern Kinexus Pro Rheometer with rSpace software, a cone geometry with a 20mm radius and 4° angle and flat base-plate. The measurements were taken at different shear rates from 0.1 to 100 s$^{-1}$. 

47
2.2.4 Electrochemical Characterisation

2.2.4.1 Cyclic Voltammetry

The edges of the CCCs of the supercapacitor prototype devices were connected to copper conductors using silver conductive epoxy adhesive (MG Chemicals, Ontario CA). Cyclic Voltammograms were obtained using a BASi LC-Epsilon Electrochemical Analyser with BASi Epsilon E2/MF-9092 Basic software equipped with a C3 cell stand. Three repeats were performed and the average was used. One model was prepared for each repeat.

The capacitance was calculated using the Equation 2.17. The gravimetric specific capacitance was used to characterise the phytic acid doped-PAni.

\[ C_S = \frac{C}{m} = \frac{1}{m_0} \int_{E_1}^{E_2} \frac{i(E) dE}{v(E_2 - E_1)} \]  

(2.17)

where \( i(E) \) is the recorded current density as a function of the applied potential, \( E_1 \) and \( E_2 \) are the lower and upper limits of the potential window, \( v \) is the scan rate used in the CV test and \( m \) is the mass of the electroactive material in the supercapacitor prototype. For the CSA/DBSA-doped PAni supercapacitor prototype, the surface specific capacitance was calculated as an indicator of the supercapacitor functionality, thus the mass \( m \) is replaced by the surface \( s \) in the Equation 2.17. The surface \( s \) is the area covered by the electroactive material.

2.2.4.2 Galvanostatic Charge-Discharge Investigations

The galvanostatic charge-discharge curves were recorded using a potentiostat/galvanostat Model 273A, (EG&G Princeton Applied Research, USA). The edges of the CCCs of the supercapacitor prototype devices were connected to copper conductors using silver conductive epoxy adhesive (MG Chemicals, Ontario CA)

Strain tests, bending tests and capacitance measurements

To perform the bending and stretching tests the supercapacitor prototypes were mounted in a customised EleksLaser A3 (EleksMaker Smart Device Co., Ltd., China) with an EleksMana SE 2-axis control board. The supercapacitor device prototypes were gripped using wood-pole-clamps (Kytotech, Toronto CA) and a customised base mounted on the ElekLaser chassis. The bending cycles were performed by reducing the space between the gripping pieces holding the supercapacitor as shown in the Figure 2.11

The stretching tests were performed by increasing the distance between the gripping pieces holding the supercapacitor. The software controlled movements were performed by programming the required distances and movement speeds and generating the corresponding command lines. The latter were programmed in LaserGRBL free laser-engraving software.
Figure 2.11. Customised platform for bending and stretching tests based on an Elek-sLaser A3 system.

2.3 References


3.1 Abstract

Most of the research carried out in the field of supercapacitors has promoted the use of conductive carbon cloth as conductive current collector (CCC) for prototype devices. The carbon cloth-based CCC is a conductive textile with high mechanical flexibility and strength. In spite of these remarkable properties, carbon cloth-based CCCs do not reach the capacitance values and stretchability reported in their graphene-based counterparts. Previous efforts to obtain flexible and stretchable graphene-based CCCs have been performed with the use of a separated conductive material (normally a metal-based material) as a substrate. This chapter details the development of an accurate and cheap method to construct 3D-printed and laser-scribed flexible and stretchable CCCs for supercapacitor prototypes.¹–³

3.2 Introduction

3D-printing techniques are always attractive routes to the fabrication of customised parts and devices. These bespoke devices can fulfil determined properties for different specific applications in fields such as electronics, aerospace, avionics, and soft-robotics.⁴ In this regard, 3D-printing technology is an unique platform to develop, investigate and understand the processes needed to construct a fully functional CCC for a supercapacitor prototype. This chapter focuses on three important parts: first, the preparation and characterisation of GO-based 3D-printable inks as precursors to obtain laser-induced rGO-based CCCs, second, the investigation of the use of the obtained CCCs to construct supercapacitor prototypes, and third, the optimisation of the CCCs
and their construction process to achieve precise bespoke conductive shapes and patterns. The latter are used as flexible and stretchable CCCs for supercapacitor prototypes in a next stage.

The research carried out in the synthesis of the GO-based ink accounts for a facile and affordable process to obtain a suitable 3D-printable precursor in the CCC fabrication. The outcome of this approach paves the way for a versatile 3D-printing technique.

The present investigation aims for an optimised 3D-printable GO-based ink. Also the related processes have been enhanced to obtain reproducible procedures. The latter allow the manufacturing engineering variables to be tuned towards precise bespoke parts. This endeavour has been possible with the availability of affordable open-source 3D-printers. These electronic and mechanical pieces of equipment have been assembled, customised and programmed to fulfill the demands of the construction and fabrication processes during this research. Additional effort has been invested in the hardware and software of one of the 3D printers to enhance the fully-automated programmable laser scriber already implemented in this 3D printer by a former PhD student in the Faul Research Group, Dr. Djen Kuhnel. This latter mechanism allows the controlled laser system to produce laser-induced rGO from the 3D printed GO-based precursors.\(^5\)\(^-\)\(^7\) Once the 3D-printing and laser-scribing processes have been fully developed and optimised, they could be used, not only to produce a rGO-based CCC, but also to attain a construction strategy to bind the obtained CCC to a flexible and stretchable commercial silicone rubber.

Many investigations have been carried out to obtain laser-induced rGO-based electrodes and CCCs,\(^8\)\(^-\)\(^13\) most of them consider different variables of the laser-scribing process such as laser power, speed, and frequency. However, a global analysis covering the interaction of multiple laser-related variables is required. In this regard, the research carried out in this chapter considers the influence of the engineering parameters of speed, power and frequency of the laser scriber in the fabrication and optimisation of the CCC.

In addition to these activities, simultaneous efforts have been successfully realised to establish and optimise the best achievable accuracy and patterning for the CCC to be used in a flexible and stretchable supercapacitor prototype.

### 3.3 Results and discussion

#### 3.3.1 Synthesis of polymer ink

Many authors have investigated different approaches to obtain 3D-printable materials to extrude and produce CCCs.\(^14\)\(^-\)\(^16\) These efforts are parts of a natural progression towards the design and fabrication of complex structures via the utilisation of affordable 3D-printing technology. To fulfill the demand of a conductive extrudable (3D-printable) material, the printing industry has developed different commercial alternatives. Among those, the most popular composites are made of a conventional insulating polymer which is endowed with conductivity. The latter property
is achieved by filling the insulating polymer matrix with powdered conductive material such as carbon or metal particles.\textsuperscript{17}

In this regard, a suitable polymer precursor was required. The selection criteria should account for:\textsuperscript{1,5,18}

- tunable viscosity keeping the self support and stability of the 3D-printed shape.
- compatibility of the polymer with a quick-evaporating solvent.
- easy and homogeneous dispersibility of the active material.
- processability at ambient conditions.

In addition to those, bio-compatibility and low costs are desirable.\textsuperscript{19} In this project, a progressive investigation with different approaches was performed to obtain a polymer-based 3D-printable ink.

3.3.1.1 Polymer matrix

The advantage of using a construction method for rapid prototyping such as 3D printing relies on the precise control of the size and geometry of the extruded prototypes with the support of computer aided design. This control can be achieved by using polymer-based composites as extrudable inks to obtain a reinforced outcome with structural and functional properties such as flexibility and conductivity.\textsuperscript{20} In this project, the initial efforts to attain an extrudable ink were

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{biopolymers.png}
\caption{Biopolymers used as polymer matrices}
\end{figure}
performed using biopolymers dissolved in water. These aqueous polymer matrices were prepared with polysaccharides such as sodium alginate, xanthan gum, sucrose, and raffinose (Figure 3.1).

![Digital pictures of: a) Disposable material path b) Disposable material path mounted on a 3D printer Prusa-i3](image)

The resulting inks were tested for extruding arbitrary shapes and surfaces using a disposable material path (Figure 3.2(a)) attached to a Direct Ink Writing (DIW) 3D printer Prusa-i3 (Figure 3.2(b)). The raffinose-based matrix showed low viscosity even when the maximum polysaccharide concentration in water was reached (up to 203 mg mL\(^{-1}\) in ambient conditions). A similar low viscosity solution was obtained with the highest concentrated sucrose-based matrix (up to 2.1 g mL\(^{-1}\) in ambient conditions). This attribute of the sucrose and raffinose-based inks impeded their use as an extrudable 3D-printing inks. The extrusion process with these inks can not be controlled accurately. The customised 3D printers can generally work over a very large range of material viscosities from 50 Pa s to 500 Pa s. When the viscosities of the inks are out of the range supported by the 3D-printer, some extrusion issues appear such as under-extrusion or over-extrusion. The first is a deposition-associated issue that produces visible gaps and missing material in or between the printed layers. This undesired deposition issue can have several origins such as an incorrect extrusion multiplier setting, G-CODE and STL generation issues, hardware-related problems, and most commonly a poor quality material.\(^{21,22}\) On the other hand, over-extrusion is also a deposition-associated issue where the 3D printer extrudes more material than the software expects. This latter phenomena forms printed blobs affecting the dimensional accuracy and the aesthetics of the printed object. Over-extrusion phenomena can be caused by a high extrusion multiplier, printer speed set to too high. Compared with under-extrusion, over-extrusion can be beneficial for a 3D-printing process, especially to enhance the mechanical properties of the 3D-printed object. The latter process should be done carefully so the dimensional accuracy of the object is not compromised.\(^{22,23}\)

The synthesised inks are too fluid and caused unfavourable effects during the 3D-printing procedure such as undesired drops, over-extrusion and under-extrusion.

Conversely, the xanthan gum and sodium alginate-based inks, (Figures 3.4(c) and 3.4(d) respectively) reached a viscosity that allowed a controlled 3D-printing process with low concentration such as 6 wt% of the polymer solution. There was no evidence of over-extrusion or under-extrusion during the deposition process.
Additional polymer-based aqueous inks were prepared with synthetic polymers such as polyvinyl alcohol (PVA) and polyethylene oxide (PEO). Both, PEO and PVA are synthetic polymers currently used in biomedical applications. On the basis of their biocompatibility they are interesting candidates to be used to synthesise a non-toxic extrudable ink.\cite{24,25} The synthetic-polymer-based inks needed low concentrations to achieve the required viscosity for 3D-printing in a similar manner compared to their polysaccharide-based counterparts. This characteristic of the synthetic polymer-based matrix can be attained using a high molecular weight polymer. The molecular weights used in this investigation were 146,000–186,000 Da for PVA and 1,000,000 Da for PEO, the highest molecular weight available on the market at the time of these experimental efforts. The candidate synthetic-polymer-based inks were qualitatively evaluated using the 3D printer Prusa-i3 for controlled and precise extrusion.

For evaluation purposes a precision extruding deposition system can be defined as a system...
that not only performs direct printing without post-printing treatment but also demonstrates high repeatability at extruding viscous materials through small-diameter-nozzles, particularly by using nozzles with diameters of hundreds of micrometres. Following the latter definition, in the present research effort a successful precision extruding deposition investigation is evaluated and quantified by measuring the difference between the desired pattern (defined in the CAD designs) and the actual pattern of the extruded material. The distance (d) between the patterns have been taken at regular intervals (25 \( \mu m \)). The obtained data shows that the distances (\( d_n \)) do not reach 100 \( \mu m \). In fact, all the measured differences between the designed and the extruded patterns are less than 50 +/-8 \( \mu m \) (Table 3.1). The difference between the designed pattern and the extruded pattern could be attributed to a neglectable flooding effect of the ink.

<table>
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<td>42.3</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>20</td>
<td>45</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>

Any measured difference greater than 100 \( \mu m \) between the designed pattern and the extruded pattern is considered unsuccessful. The latter consideration is based on the definition of the above-mentioned precision extruding deposition process. Figure 3.5 shows the difference between a designed pattern and the 3D-printed resulting pattern. In addition, Figure 3.6 shows the distances between the desired pattern and the obtained 3D-printed patters. The resulting distances taken by ImageJ software\(^{27}\) show that all distances are close to 50 \( \mu m \) providing evidence that the resolution of the 3D-printing process is less than 100 \( \mu m \).
3.3. RESULTS AND DISCUSSION

**Figure 3.5.** Evaluation of a precision extruding deposition in the 3D-printed patterns: 
(a) Extruded model  b) SEM image of the extruded model edge.

**Figure 3.6.** Evaluation of a precision extruding deposition in the 3D-printed patterns: 
(a) difference between the desired pattern edges (yellow dotted and dashed line, as defined in the CAD designs) and the actual pattern edges of the extruded material.  
(b) Distances between the edges of the designed and extruded patterns taken at regular intervals (25µm).

The repeatability of the extruded samples was further evaluated by SEM characterisation. A successful extrusion process shows repeatability in the features of the 3D-printed models. Figure 3.7 shows the obtained thickness of 4-layers 3D-printed model. In all the cases the thickness of the patterns stays consistent (approx. 100 µm) for all the models extruded under the same conditions of design, hardware and software settings and conditions. The roughness of the surface of a 3D-printed model was also evaluated by SEM. Figure 3.8 shows the surface of different 3D-printed models where a smooth area can be observed in the extruded models. The latter morphology is common to the 3D-printed models showing the repeatability of the extrusion process (Figure 3.8). The 3D-printing operation was successfully performed in the absence of over-extrusion or under-extrusion during the deposition process after the concentration of the polymer reached the 6wt% in the polymer solution. This value is very similar compared with the one found to be suitable for the successful extrusion of biopolymer-based inks as shown in the previous sections.
CHAPTER 3. SYNTHESIS AND PREPARATION OF CONDUCTIVE CURRENT COLLECTORS

Figure 3.7. Evaluation of a precision extruding deposition: thickness of the 3D-printed patterns: a), b) Thickness (d1 and d2) of 4-layers 3D-printed models evaluated by SEM imaging.

Figure 3.8. Evaluation of a precision extruding deposition: smoothness of the surface of 3D-printed models: a) Surface of 3D-printed models evaluated by SEM imaging.

Additional factors such as the nozzle flow speed, ink flow rate, and nozzle height are related by the Hagen-Poiseuille equation:  
\[ \Delta P = \frac{8\eta LV}{r^2} \]  
(3.1)

where \( r \) is the radius of the extrusion nozzle, \( L \) the length, \( \eta \) the viscosity, and \( V \) the speed of extrusion. The analysis of the above-mentioned variables have been further detailed in Section 3.3.2.3. However, these factors are addressed in the present section to evaluate their influence towards a successful 3D-printing process. The extrusion process requires a consistent and constant viscosity. The latter must be ideally lower than the viscosity in the resting state. This characteristic of viscosity is present in shear-thinning inks. In the present study the polymer-based ink demonstrated faster printing with smaller nozzles. The evaluated nozzles had inner diameters of 0.8, 0.6, 0.4 and 0.2 mm corresponding to the Stubs Iron Wire Gauges or Birmingham gauges 18, 20, 22 and 27 respectively.  

The mechanism of rotating a threaded spindle forces the ink downwards creating a current. The nozzle with an inner diameter of 0.8 mm allowed an
extrusion process where the material presented post-extrusion issues. The identified issues were related with flooding and deformation of the extruded lines causing loss of definition. The latter undesired effect could not be solved by changing the speed of the 3D-printing neither by increasing nor by reducing it, thus discarding the 0.8 mm nozzle. The extrusion process was repeated with a 0.6 mm inner diameter nozzle demonstrating slightly better results. The extrusion with the latter required a much slower printing speed to avoid any flooding or deformation effects. However, the accuracy attained was not on the order of micrometres. In addition, the reduction in the speed resulted in a far longer manufacturing time. The results showed that the 0.6 mm nozzle was not appropriate for a rapid prototyping manufacture process and was not used in this research. The 0.4 mm inner diameter nozzle showed a smoother extrusion process. There were no flooding issues and the size of the extruded lines stayed consistent after the extrusion process. The 3D-printed patterns performed with the 0.4 mm nozzle show an accuracy of hundreds of microns as showed in Figure 3.6. In the case of the 0.2 mm nozzle the resulting patterns are accurate. There are no signs of flooding or deformation. The only setback of an extrusion process performed with a 0.2 mm nozzle was the long time required to complete the procedure. This again could be deemed a disadvantage when procuring a prototype for possible mass production.

To summarise, four 3D-printing-suitable inks were successfully produced and tested for an automatic and controlled extrusion process. The next step in this research was the endowing of the extrudable inks with conductivity towards the production of 3D-printable CCCs. This characteristic of conductivity can be achieved by a combination of a conductive powder or particles within the polymer-based ink.\textsuperscript{14,16,19} Among the potential conductive particulate fillers, carbon black (CB) and silver flakes were used to test the previously synthesised polymer-based 3D-printable matrices. The concentration of the conductive fillers was initially fixed to values as low

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3_9.png}
\caption{Digital pictures of the 3D-printed CB-based inks with different polymers as matrices:\ a) Sodium alginate \ b) Xanthan gum \ c) PVA \ d) PEO.}
\end{figure}
as 3 wt% in the polymer-based aqueous solutions. The filler concentration was then increased to 6 wt%. In both cases the resulting blends were successfully extruded to form films on different substrates, i.e., glass or polyethylene terephthalate (PET).

The 3D-printed films were left in ambient conditions so the solvent evaporated. This drying step exposed the properties of the 3D-printed composites without the presence of the solvent. This action revealed a mechanical instability of some of the polymer-based 3D-printed materials. The xanthan gum-based and sodium alginate-based patterns turned into a brittle material and cracked upon drying (Figure 3.9(a) and Figure 3.9(b)). Conversely, the PVA-based and PEO-based patterns kept structural stability (Figure 3.9(c) and Figure 3.9(d)).

Among the synthesised polymer-based 3D-printable inks, the PVA-based ink and the PEO-based ink demonstrated the highest processability. In addition, the extruded shapes showed mechanical stability upon 3D-printing. These properties of the PEO-based and PVA-based extruded models compared with those of the xanthan gum-based and sodium alginate-based models demonstrated the suitability of using the synthetic polymers over the polysaccharides as matrices for conductive inks.

### 3.3.1.2 Solvents

A key combination of design criteria is important in the development of functional inks. In particular, the timescale of the 3D-printing procedure should be consistent with that of the ink solvent evaporation. As 3D-printing has become a rapid-prototyping method, the production time has arisen as a competitive value to be considered. In this regard one effective approach to optimise this production time consist of the addition of a volatile solvent to accelerate the overall solvent evaporation immediately after the extrusion.

In this work, a volatile solvent such as ethanol was combined with the synthesised 3D-printable polymer-based inks. The addition of ethanol was performed to reach a concentration as low as 20 wt% in the solvent composition. In the case of the PEO-based ink, the incorporation of the volatile solvent increased the time of dissolution of the PEO powder in the solvent solution. The resulting ink was tested for 3D printing showing similar mechanical properties compared to that only water-based ink. There was no signs of under-extrusion or over-extrusion during the 3D-printing process. This new ink is suitable to form structurally-stable models upon 3D printing in much less time compared with the polymer-based aqueous solutions.

The content of ethanol in the solvent solution can reach up to 80 wt% without a significant change in the extrudability of the ink. These results are consistent with those reported by Zhu et al.\(^\text{19}\) where they attained a reduced printing time and improved printing fidelity using a mixture of ethanol and water as a solvent in a PEO-based extrudable ink. Conversely, a PVA-based ink could not be obtained upon the introduction of ethanol in the solvent composition. The PVA precursor was left to dissolve following the method described in Section 2.1.4.1. However, after more than 24h a slurry of undissolved PVA powder dispersed within the solvent solution.
### Table 3.2. Biological-polymer-based inks

<table>
<thead>
<tr>
<th></th>
<th>Sucrose</th>
<th>Raffinose</th>
<th>SA</th>
<th>XG</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ink synthesis conditions</strong></td>
<td>ambient conditions</td>
<td>ambient conditions</td>
<td>ambient conditions</td>
<td>ambient conditions</td>
</tr>
<tr>
<td><strong>Solubility in water</strong></td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td><strong>Problems at 3D-printing</strong></td>
<td>over-extrusion</td>
<td>over-extrusion</td>
<td>under-extrusion</td>
<td>under-extrusion</td>
</tr>
<tr>
<td><strong>3D-printed shapes accuracy</strong></td>
<td>imprecise patterns</td>
<td>imprecise patterns</td>
<td>precise patterns</td>
<td>precise patterns</td>
</tr>
<tr>
<td><strong>Shapes mechanical strength</strong></td>
<td>poor</td>
<td>poor</td>
<td>brittle</td>
<td>brittle</td>
</tr>
<tr>
<td><strong>Solubility in fast-drying solution</strong></td>
<td>poor</td>
<td>poor</td>
<td>poor</td>
<td>poor</td>
</tr>
</tbody>
</table>

was found. This outcome supports the findings previously reported by Lopes et al.\(^\text{32}\) where the solubility of PVA in ethanol is described as “practically insoluble or insoluble”. This result hinders its potential use as a precursor for the synthesis of fast-drying extrudable inks.

### Table 3.3. Synthetic-polymer-based inks

<table>
<thead>
<tr>
<th></th>
<th>PVA</th>
<th>PEO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ink synthesis conditions</strong></td>
<td>85°C during 2h</td>
<td>ambient conditions</td>
</tr>
<tr>
<td><strong>Solubility in water</strong></td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td><strong>Problems 3D printing</strong></td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td><strong>3D-printed shape accuracy</strong></td>
<td>precise patterns</td>
<td>precise patterns</td>
</tr>
<tr>
<td><strong>Shapes mechanical strength</strong></td>
<td>poor</td>
<td>poor</td>
</tr>
<tr>
<td><strong>Solubility in fast-drying solution</strong></td>
<td>very poor</td>
<td>very good</td>
</tr>
</tbody>
</table>

A summary of the results reported in the previous sections are detailed in the Table 3.2 and Table 3.3. The term precise here can be applied as defined in Section 3.3.1.1 once a 3D printed pattern has been evaluated and quantified by measuring the difference between the desired pattern (defined in the CAD designs) and the actual pattern of the extruded material. To this point, the evaluation of the different potential inks showed that the biopolymer-based inks have some disadvantages. The over-extrusion/under-extrusion effects and poor mechanical strength
of the final models temper their potential use as 3D-printable inks. Conversely, the synthetic-polymer-based inks are good candidates with no presence of over-extrusion or under-extrusion effects during 3D printing and showing enhanced mechanical strength in their extruded models upon 3D printing. The PEO/water/ethanol-based blend showed the best suitability to be used as a fast-drying and well-controllable 3D-printable ink.

### 3.3.2 3D printing of patterns and films

3D-printing technology or additive manufacturing is a rapid prototyping process to construct 3D structures in a layer-by-layer architecture. This technology allows the creation of 3D models attaining accurate geometry (in the order of hundred micrometres) and reducing waste. The initial step of the 3D-printing process is the creation of a 3D model. This latter is a 3D structure built using a CAD software package. The resulting outcome is a "Surface Tessellation Language" (STL) file. This archive is further processed into a model of 2D slices or layers and converted into a 3D-printer language commonly known as a geometric code (GCODE) file.

The GCODE file can be interpreted by the 3D printers. They can form a 3D model by depositing an extrudable material following the coordinates, directions and speeds specified in the file. This entire process allows the rapid prototyping of complex and accurate engineered surfaces and volumes.

In this investigation, these computational and sequential processes were followed to obtain the 3D-printed models from the synthetic-polymer-based inks. The structures were designed taken into consideration the requirements of a layer-by-layer supercapacitor prototype. These requirements include the shapes, distances and volumes needed to achieve specific electrical and mechanical attributes of the designed device.

#### 3.3.2.1 Computer aided design

The design of supercapacitor prototypes is performed based on the availability of accurate 3D printers. This accuracy should be carefully taken into account before the computer-assisted development and construction of 3D models. In this research a customised Prusa-i3 3D printer and a DuetWiFi-based 3D printer were used and optimised. These 3D printers were constructed in a previous investigation by Dr. Djen Kuhnel, a former PhD student in the Faul Research Group. In this investigation, the 3D printer Prusa-i3 was re-assembled and optimised so it could be used together with the DuetWiFi 3D printer to carry out the research activities. The 3D printers are designed with stepper motors, which endow the machines with a lateral positioning resolution of 50 \( \mu \)m. However, the lateral feature size will also depend on the size of the nozzle used for 3D-printing.

These parameters of lateral positioning resolution and lateral feature size are considered before starting the computer-assisted design of the shapes and 3D-models developed in this research. This consideration helps to avoid any design with features that can exceed the accuracy
of the 3D printers. In the investigation carried out, the 3D printers where equipped with nozzle sizes starting from 200 \( \mu \text{m} \) to 800 \( \mu \text{m} \). In addition, a laser-scribing process is described in Section 3.3.4, and the diameter of the laser-spot (i.e., approx 100 \( \mu \text{m} \)) is taken into account in the CAD process as well.

Once the accuracy parameters were defined, the design process started by evaluating the possible models to be used for the construction of supercapacitor prototypes. In this research, the most widely used design architectures have been explored to develop a 3D-model of a supercapacitor prototype.

First, a traditional design in a sandwich-like structure is used to create a model in a layer-by-layer architecture. This model was constructed using Autodesk® Inventor® Professional Software and Blender Software (Figure 3.10(a) and Figure 3.10(b)). These CAD packages were suitable for 3D-model construction and development. Second, a planar structure in an in-plane interdigitated electrodes architecture was built using the previously mentioned software packages (Figure 3.11(a) and Figure 3.11(b)).

The obtained 3D-models are stored as a STL file, which can be easily transferred between
CHAPTER 3. SYNTHESIS AND PREPARATION OF CONDUCTIVE CURRENT COLLECTORS

devices. This resulting STL file cannot be interpreted directly by the 3D-printer yet. An additional slicing process is required to obtain a 3D printer-compatible GCODE file. This latter process can be performed by a slicer program. In this investigation the slicing process was performed by using Cura Software, Slic3r Software and Simplify3D Software. There was not any apparent difference between the obtained GCODE files. However, Simplify3D has been reported as the best option as a slicer tool and having advantages over its competitors such as being capable of creating 3D-models with higher accuracy.34

Once the GCODE files were obtained, they were transferred and loaded into the 3D-printer for an automatically controlled extrusion of the designed 3D-models. The success of this process not only depends on the accuracy of the 3D-printers, but also on the proper viscosity of the inks. This latter characteristic is considered and evaluated in Section 3.3.2.2 of this thesis.

3.3.2.2 Rheology of the inks

The different extrudable materials can be categorised by their viscosity. Using this characteristic, the viscous materials can be classified as Newtonian or non-Newtonian. A Newtonian fluid keeps its viscosity independent of the stress state and velocity of the flow. This implies that its rheological characteristics can be described by a unique feature, its shear viscosity. One example of a Newtonian fluid is water. Conversely, a non-Newtonian fluid shows a viscosity that can change under force becoming more liquid or more solid. This viscosity can be a decreasing function of 1) shear rate or, 2) shear stress. In the first case, the material is considered a shear-thinning or pseudoplastic fluid. On the other hand, the second case corresponds to a shear-thickening or dilatant fluid. In both cases the function can be calculated to predict the behaviour of the fluid under different conditions of flow or velocity.28,29

3D printers can extrude materials depending on their viscosity. This extrusion capability of the 3D printers was studied in a previous investigation performed in the research group. The results obtained showed that any liquid or paste-like material with a viscosity between 50 Pa·s and 500 Pa·s can be dispensed by the customised 3D printers.35 Any other value of viscosity will require the support of an additional external pressure source to obtain a controlled extrusion process. In this research, the prepared fast-drying PEO-based ink was subjected to rheological testing in a cone and plate rotary rheometer described in Section 2.2.1.1. The obtained results show a decreasing function of viscosity related to the increment of the shear rate (Figure 3.12). This relation can be described using the mathematical equation:

\[
Viscosity(\eta) = \frac{Shear Stress}{Shear Rate} = \frac{\tau}{\dot{\gamma}}
\]

(3.2)

This outcome reveals a shear-thinning or pseudoplastic behaviour of the PEO-based ink. This result could be attributed to two important factors i.e., the high molecular weight of the PEO, and the concentration of the polymer in the synthesised blend. In both cases, the long molecular
3.3. RESULTS AND DISCUSSION

Polymer chains could start an entanglement effect between them. This finding is consistent with those of Ebagninin et al.\textsuperscript{36} They reported that a determined concentration of the polymer combined with its high molecular weight can produce the formation of a three-dimensional network and local polymer-polymer interactions. Both of these effects are responsible for the rheological behaviour of the aqueous PEO solution. Also, a critical concentration of 4.9 wt\% was reported as the starting point where the PEO-based blends start showing viscoelastic behaviour, becoming a "concentrated network solution" with entanglement effect. Furthermore, a molecular weight greater than $4 \times 10^5 \text{ g mol}^{-1}$ endows the polymer blend with a dominant elastic behaviour.\textsuperscript{36,37} The concentration of the synthesised PEO-based ink and the molecular weight of the polymer are 6 wt\% and $1 \times 10^6 \text{ g mol}^{-1}$, respectively. These numbers are over the cited critical values and it is a possible explanation why the synthesised PEO-based extrudable ink fits the described effects.

The rheology tests also revealed that greater concentrations or lower concentrations of the polymer in the overall blend (6 wt\%) produces thinner inks and thicker inks, respectively. They could present 3D-printing issues or post-extrusion problems. The inks were evaluated by extrusion tests performed with a 0.4 mm nozzle. In the case of a thinner ink with an initial viscosity of 300 Pa s, its application could be beneficial for a quick extrusion procedure. However, the greatest drawback of the lower viscosity is the lack of definition during application, which undermines the main intention of using 3D printing for precision. In addition, low viscosity also may imply flooding of the material upon extrusion. The latter process of flooding can produce contamination between patterns or material reaching zones beyond the edges of the design, causing greater problems such as short circuits between interdigitated electrodes in supercapacitors. Conversely, a thicker ink resulting from a higher concentration of the polymer produced a restricted flow.

**Figure 3.12.** Viscosity as a function of shear rate of PEO-based extrudable ink.
CHAPTER 3. SYNTHESIS AND PREPARATION OF CONDUCTIVE CURRENT COLLECTORS

detrimentally affecting the extrusion process. The rheology tests for a polymer-based ink with a concentration of 10 wt% showed an initial viscosity of 3023 Pa s. The resulting 3D-printing process using this thicker ink produced noncontinuous patterns. In addition, the 3D-printer required continuous adjustments to keep responsive and maintain a steady flow of deposited material.

This section has reviewed the viscosity behaviour of the PEO-based ink as an important aspect to be considered to obtain a smooth extrusion process. These outcomes will ensure an uninterrupted 3D-printing process during the fast prototyping of the CCCs.

3.3.2.3 Extrusion speed

As described in the previous section, the viscosity of the PEO-based ink has been identified as an important factor to consider for the 3D printing process. The range of viscosity of the PEO-based ink presented in the previous section (Section 3.3.2.2) can be used to obtain the corresponding extrusion pressure needed to attain a determined speed for 3D printing the synthesised PEO-based blend.

The extrusion speed and the pressure values of a fluid flowing through a tube can be calculated using the mathematical relation:

$$\Delta P = \frac{8\eta L V}{r^2}$$

(3.3)

where $r$ is the radius of the extrusion nozzle, $L$ the length, $\eta$ the viscosity, and $V$ the speed of extrusion. In the case of the 3D-printers used in this research, they have been endowed with a pressure control system based on compressed nitrogen gas. This system is based on the 6-bar-pressure nitrogen gas line of the lab where this investigation was carried out. This hardware enhancement provides to the 3D-printers a regulated extrusion operation capability and the availability of a controlled pressure set point. The pressure set point is adjusted by a Shako URPL4-02 manual pressure regulator valve (Shako Co., Ltd., Taiwan) connected to the nitrogen gas line. The calculation of the speed required depends on the shape and the expected time of extrusion. A good trade-off between these two variables can be obtained using a standard size for a CCC to be used in a supercapacitor prototype. For calculation purposes a square shape of 5 cm x 5 cm is used as an example. This surface can be covered with a single layer of the PEO-based ink by a controlled 3D-printing process achieving different thicknesses. The thickness of the extruded layer can determine the smoothness of the attained surface of this PEO-based ink layer. Undesired effects, defined as any side effects that produces a detriment in the quality and properties of the extruded model, can appear in this stage. In order to avoid the latter, the thickness optimisation of a single layer can promote or reduce the presence of these undesired effects such as bubbles, gaps between extruded lines, and nonuniform solvent drying. These effects are also influenced by two additional factors: the nozzle diameter, and the
width of extruded lines described by each sweep movement of the 3D-printer. A too small or narrow nozzle diameter increase the overall 3D-printing time per prototype whilst a too wide nozzle diameter maximises the possibilities of having undesired effects on the extruded surface. Likewise, the width of the extruded lines should keep a close relation with the nozzle diameter, ideally they should be the same so each sweep movement of the 3D-printer performs a line pattern covering the width equivalent of a nozzle diameter and the next sweep line does not overlap with the previous. A good combination between the nozzle diameter and the sweep line width was found by testing different nozzles and width line settings obtaining the best result at 0.4 mm for both variables. With this starting point, the variable of thickness can be established by considering the accuracy of the 3D-printer in the z-axis, i.e., 0.1 mm as a starting point. With all these preliminary dimensions defined, the volume $v$ of the extruded model can be worked out as follows:

$$v = \text{length} \times \text{width} \times \text{height}$$

$$v = 50 \text{ mm} \times 50 \text{ mm} \times 0.1 \text{ mm}$$

$$v = 250 \text{ mm}^3$$

With the obtained volume to be extruded and the radius of the nozzle, an alternative mathematical relation can be used to calculate the speed of extrusion:

$$Q = \frac{1}{4} \pi D^2 V$$  \hspace{1cm} (3.4)

or

$$V = \frac{Q}{\pi r^2}$$  \hspace{1cm} (3.5)

Where $Q$ is the volumetric flow rate and can be directly calculated from the extruded volume divided by the extrusion process time. The latter can be considered for calculation purposes and rapid prototyping as fast as 5 min for the proposed model size (5 cm x 5 cm x 0.1 mm).

$$Q = \frac{250 \text{ mm}^3}{600 \text{ s}} = 0.42 \text{ mm}^3 \text{ s}^{-1}$$

Replacing the obtained value of $Q$ in the Equation 3.5:

$$V = \frac{Q}{\pi r^2} = \frac{0.42 \text{ mm}^3 \text{ s}^{-1}}{\pi \times 0.2^2 \text{ mm}^2} = 3.32 \text{ mm s}^{-1}$$

With this simple calculations example, the variation of pressure $\Delta P$ can be obtained from Equation 3.3:
\[ \Delta P = \frac{8\eta LV}{r^2} = \frac{8\eta \times 11 \text{ mm}}{0.2^2 \text{ mm}^2} \times 3.32 \text{ mm s}^{-1} \]

or

\[ \Delta P = 7294.6\eta \]

At this point the pressure is still a function of the viscosity. The latter can be calculated experimentally from the viscosity vs. shear rate curve represented in the Figure 3.12. The reference point of this shear rate can be calculated considering the non-Newtonian nature of the PEO-based blend,\textsuperscript{43} using the equation:

\[ \dot{\gamma} = \frac{4Q}{\pi r^3} \]  

obtaining:

\[ \dot{\gamma} = \frac{4 \times 0.42 \text{ mm}^2 \text{ s}^{-1}}{\pi \times 0.2^3 \text{ mm}^3} = 66.84 \text{ s}^{-1} \]

The corresponding viscosity for the calculated shear rate is \( \eta = 6.3 \text{ Pa s}^{-1} \) obtained from the experimental data on Figure (3.12). Then \( \Delta P \) becomes:

\[ \Delta P = 7294.6 \times 6.3 \text{ Pa} \]

\[ \Delta P = 45956 \text{ Pa} \]

The performed calculations are relative and represent the difference of pressure between the entrance of the needle and the extruding end. This pressure should be applied at the beginning of the needle and can be attained by the synergistic combination of two contributions: the first from the mechanical screw-cylinder mechanism of the automated extrusion system (disposable material path) and a second contribution from the pressure control system.

The screw-cylinder mechanism pushes the material in an automated and controlled fashion according the lines of code in a GCODE file to extrude the material and form the engineered 3D models. This is the most important source of pressure to push the material through the extrusion nozzle at the speed set in the design and construction process of the 3D models and transformed into command lines executed sequentially by the 3D printer. Here, it can be remarked that the presence of the small but not less important contribution of the pressure control system. In fact, this mechanism keeps a constant pressure on the material so there is no any undesired depletion of pressure during the 3D-printing process. As a summary, a determined extrusion speed of the PEO-based ink can be obtained, smoothly controlled and kept during the 3D-printing process by the provision of a constant pressure at the entrance of the extrusion nozzle. This constant pressure is the result of a combined actions of a screw-cylinder-based extrusion system and a pressured-nitrogen-based pressure control system (Figure 3.13).
3.3. RESULTS AND DISCUSSION

3.3.3 Graphene oxide/PEO-based extrudable ink

The constructed 3D models of the CCCs were extruded successfully on PET and glass as substrates. This outcome was attained using the strategies described in Section (3.3.2.3). However, in this section an additional approach is used to develop a CCC firmly attached to the surface of a stretchable substrate. This approach considers the use of a PEO-based extrudable ink to prepare a 3D model in a similar fashion as it was described in the previous section. The use of a PEO-based blend as an extrudable ink was demonstrated, and this result promotes its utilisation to prepare a precursor material in the process to achieve stretchable CCCs. The PEO-based ink is prepared with different nanofillers compared with the previous version. In the previous strategy, conductive nanofillers such as silver particles or carbon black were used to endow the polymer blend with conductivity. In this new method a non-conductive nanofiller is used instead of conductive particles. The desired non-conductive nanofiller can be chemically or thermally treated to obtain a conductive material. Additional to this criterion, a non-conductive nanofiller with good processability in aqueous solutions is desirable for the preparation of a PEO-based ink. Accounting for these requirements an aqueous suspension of graphene oxide (GO) is used in combination with PEO to obtain a new 3D-printable ink.

The GO can be produced with cheap raw materials, i.e., graphite with cost-effective chemical methods and with a high yield. A second (and most important) characteristic of the GO is its high hydrophilicity facilitating the formation of stable aqueous colloids and making it a good candidate to prepare water-based blends.\textsuperscript{44,45} Also, GO can be reduced by removing the oxygen functionalities by chemical or thermal procedures and obtain reduced-GO (rGO). The latter is a conductive material that can be used in the production of CCCs. In this research a GO suspension is used as aqueous solvent for PEO powder (1x10\textsuperscript{6} g mol\textsuperscript{-1}). The preparation of the PEO/GO-based
blend is performed using the syringe-based mixing procedure detailed in Section 2.1.1.1 to ensure a smooth combination of the polymer within the GO suspension. Various polymer-based inks are prepared with a constant 10 wt% of GO and different concentrations of the PEO in the blend composition. In the following section, the obtained inks are evaluated to characterise their chemical properties. Also, the results of changing the PEO concentration in the GO-based solvent suspension are analysed.

### 3.3.3.1 Chemical properties of PEO/GO-based extrudable ink

Samples of the polymer ink were prepared with different concentrations of PEO (1 wt%, 3 wt% and 5 wt%) and identified as PEO1-GO, PEO3-GO, and PEO5-GO, respectively. Additional blends of GO-only and PEO-only were prepared as control samples and identified as "GO-0" and "PEO-0" respectively. All GO containing samples exhibit a dark brown color under optical inspection, whilst the PEO-only sample appear opaque with no particular color.

The prepared inks are characterised by Attenuated Total Reflectance (ATR)-Fourier Transformed Infrared (FTIR) spectroscopy experiments. These ATR FTIR studies reveal spectra of the samples shown in the Figure 3.14. The obtained spectrum of the sample "GO-0" (only GO) shows a broad peak at 3171 cm\(^{-1}\) that can be attributed to the stretching vibrations of the O-H groups. The peak at 1719 cm\(^{-1}\) can be related to the C=O stretching vibration, whilst the peak at 1613 cm\(^{-1}\) correspond to the aromatic C=C stretching vibration. A small peak at 1033 cm\(^{-1}\) is consistent with vibrations of the C-O groups.

The spectrum of the sample "PEO-0" (only PEO) reveals peaks at 838 cm\(^{-1}\) and 953 cm\(^{-1}\), normally assigned to the CH\(_2\) rocking vibrations and C-O-C scissor/deformation vibrations. The peak at 1093 cm\(^{-1}\) can be attributed to the C-O-C stretching vibrations. The peaks at 1279 cm\(^{-1}\) and 1240 cm\(^{-1}\) are related to the CH\(_2\) twisting vibrations. The peak at 1349 cm\(^{-1}\) is attributed to the CH\(_2\) wagging vibrations, whilst the peak at 1463 cm\(^{-1}\) corresponds to the CH\(_2\) bending and scissor/deformation vibrations. A characteristic peak at 2879 cm\(^{-1}\) is consistent with the CH\(_2\) stretching vibrations of PEO.

The spectra of the PEO/GO-based inks unveil the presence of the main peaks of PEO and GO. This outcome could be the result of the main functional groups of PEG and GO maintained in the PEO/GO-based inks. Additional to that, the FTIR spectra shows the strong intensity of the characteristic peaks of PEO compared with the peaks of GO. The latter can be noticed in the increasing trend in the peak size when the concentration of PEO increases from 1 wt% to 3 wt%, and then to 5 wt% . It implies that a greater concentration of PEO produces greater amplitude peaks in the spectra as expected. However, the sample of PEO-0 shows a smaller sharpness and amplitude of the peaks compared with the sample PEO5-GO. This result could be attributed to a possible interaction between the PEO chains and the GO sheets through hydrogen bonding that influences the C-O-C vibration related peaks and slightly changes their shape.
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Further analysis was carried out by X-ray diffraction (XRD) experiments. The XRD spectrum in Figure 3.15 shows sharp and intense peaks of the sample PEO-0 at $2\theta=19.2^\circ$ and $2\theta=23.3^\circ$. These peaks are attributed to the semi-crystalline structure of the PEO, and are related to the 120 and 112 and 032 planes of refraction, respectively. The calculations of the d-spaces for the planes 120 and 112 are 4.61 Å and 3.81 Å, respectively, and are consistent with the literature.\textsuperscript{54,55} This crystalline structure of the PEO can be associated to the polymer being ordered by the strong intermolecular interaction between its polyether chains through hydrogen bonding.\textsuperscript{55,56}

On the other hand, the registered XRD data of the GO-0 sample reveals a spectrum with a broad peak at 10.89°. The latter is attributed to the (002) planes of GO layers with a d-spacing of 8.12 Å. This result is in good agreement with the previously reported literature values and is related to the single GO layers stacked perpendicularly to the 2D GO structures. The d-spacing of the GO is much wider compared to its graphite precursor (normally 3.3 Å). The d-spacing expansion is attributed to the presence of oxygen-containing functional groups (carboxyl, hydroxyl, epoxyde, carbonyl, etc) on the carbon sheets. This interlayer spacing of the GO samples can vary depending on the different levels of oxygen-containing groups attached to the 2D carbon lattice.\textsuperscript{56–59}

The XRD spectra of the PEO-GO composites reveal a diffraction peak shift of the (002) planes to lower angles upon the incorporation of PEO. The broad peak of GO at 10.89° shifts to 6.91° with...
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**Figure 3.15.** XRD patterns of PEO, GO, and PEO/GO-based polymer composites with different PEO concentration

An initial concentration of 1 wt% of PEO in the GO-based blend. This shift in the peak position could be attributed to the GO interlayer spacing being increased with the addition of PEO. The value of 8.12 Å calculated for the d-space of the GO peak is increased to 12.78 Å. This result can be related to the presence of the PEO chains being intercalated between the GO layers. A further increase in the concentration of the PEO in the PEO/GO-based blend produces additional effects in the interlayer distance. The samples with a weight fraction of 2 wt%, 3 wt%, 4 wt%, 5 wt%, and 6 wt% identified as PEO2-GO, PEO3-GO, PEO4-GO, PEO5-GO, and PEO6-GO, respectively show a decreasing 2θ values indicating an increasing d-spacing trend. These results suggest the presence of interactions between the PEO chains and the GO oxygen-containing functionalities through hydrogen bonding.48,60 Careful consideration of the environmental conditions of the XRD characterisation were counted before the interpretation of the results. All the PEO-GO, GO and PEO samples were subjected to the XRD experiments in the same batch during the same XRD session. This procedure ensured a common environmental relative humidity during the XRD data collection to avoid any possible influence of this variable in the results.61

The observed difference between the d-spacing values of the GO-based sample and the PEO/GO-based sample is approximately 4 Å. This finding can be associated with the transverse diameter of the intercalated chains of PEO lying parallel to the GO sheets.54,62,63

A new peak appeared at 11.6°, which could be related to pristine GO not interacting with the
PEO chains or traces of not completely exfoliated graphite oxide.\textsuperscript{64,65} The results obtained after FT-IR and XRD characterisation suggest a very good combination of the GO and PEO precursors. In addition, samples with different PEO content showed the possible molecular interactions between PEO and GO within the extrudable blends.

The characterised inks were subjected to 3D-printing tests to determine their suitability for an automatically controlled extrusion process. The inks with PEO concentrations less than 4 wt\% presented poor extrusion control with noticeable under-extrusion and over-extrusion issues. These phenomena decrease when the concentration of PEO is increased and the issues are finally overcome when the PEO concentration reaches 6 wt\%. Therefore, the concentration of the PEO in the prepared inks was maintained at 6 wt\% in all the GO-based solvent suspensions. The aim of this procedure is to obtain an aqueous GO-based suspension dissolving the PEO towards an ink of similar viscosity as described in Section 3.3.2.2. The prepared PEO/GO-based blends show a similar viscoelastic behaviour compared with the previously synthesised conductive nanofillers/PEO-based blends. This result are consistent with the outcome obtained when the new PEO/GO-based blend was tested and successfully extruded in a controlled fashion by the customised 3D printers. After an initial modification in the adjustable pressure regulator valve, the 3D-printing process with the new synthesised blends will successfully proceed and will promote a smooth and precise software-controlled extrusion process.

Once the 3D-printing process was finely tuned, a rectangular shape of 6 cm x 2 cm was extruded. The thickness of the 3D-printed layer is set to 0.1 mm, the extrusion width to 0.4 mm with a 0.4 mm diameter extruding needle. The extrusion speed can be calculated using the volume to be extruded and the equations (3.4) and (3.5):

\[
v = length \times width \times height
\]

\[
v = 60 \text{ mm} \times 20 \text{ mm} \times 0.1 \text{ mm}
\]

\[
v = 120 \text{ mm}^3
\]

With this value of volume, the volumetric flow \(Q\) and the extrusion speed \(V\) are determined as 0.2 mm\(^3\) s\(^{-1}\) and 1.59 mm s\(^{-1}\).

The attained 3D model has a thickness of 0.1 mm, however, by setting the height of the extruded rectangle to 0.5 mm, the 3D-printing procedure will perform 5 layers of the PEO/GO-based ink.

After the 3D-printing procedure, the evaporation of the solvent will significantly reduce the thickness of the 3D-printed object. This decrease in the thickness of the 3D printed model was evaluated by scanning electron microscopy (SEM). Each 3D-printed layer was designed with a 100 \(\mu\text{m}\) thickness. However, the cross section SEM images (Figure 3.16) show that after
the solvent evaporation 5-layers PEO/GO-based model have a 120–125 µm thickness. These findings reveal the expected contraction of the thickness after the evaporation of the solvent in the 3D-printed models. Also, the micrographs reveal the stacked configuration of the 3D-printed PEO/GO structures.

The disparity between the thickness obtained immediately after the extrusion process and the thickness after solvent evaporation is a well-known effect in direct ink writing of polymer-based materials and hydrogels.\(^{66,67}\) This effect is noticeable in GO/polymer-based inks where the GO flakes can be aligned in the polymer-based matrix by the shear forces during the extrusion process. The resulting post-extrusion alignment of the flakes is typically arranged horizontally after the extruded GO/polymer-based ink dries on the substrate reducing the thickness of the printed layer.\(^{68}\)

The reduction of the thickness of the extruded layer upon the solvent evaporation can be easily mitigated. One mitigation strategy is by simply controlling the number of printed layers.\(^{66}\) In the present research effort the thickness of a 3D-printed layer of PEO/GO-based ink is characterised after the solvent properly evaporated. For this purpose the 3D-printer bed was heated to 40° C to ensure a fast and smooth solvent evaporation from each 3D-printed layer. This approach helped to obtain a precise repeatable height of each 3D-printed layer so the change in the Z axis can be properly set in the GCODE file.

![Figure 3.16. SEM images of a 5-layer PEO/GO 3D-printed model with the 5 printed layers (L1 - L5) indicated: a) cross-section of the 3D-printed model b) higher magnification cross-section of the model](image)

The PEO/GO-based 3D-printed model is made of a non-conductive material. However, the GO-based precursor can be easily reduced by chemical or thermal treatments to obtain a rGO conductive material. A plethora of methods are available to perform the reduction process. Some of these procedures include the use of toxic or irritant reducing agents such as hydrazine-based derivatives, concentrated sulfuric acid solutions and diluted or concentrated hydriodic acid. Other reducing methods use expensive and time consuming thermal approaches at temperatures around
1000 °C and ultra high vacuum environments.

In this research a cheap and rapid prototyping process is performed using the interaction of a laser beam directly irradiating on the GO-based precursor. The resulting material is a laser-scribed graphene with conductive properties. This obtained rGO is evaluated in the next Section (3.3.4) for practical applications such as CCCs or electrode materials for energy storage applications.

### 3.3.4 Laser Scribing

Laser scribing is a laser-assisted strategy to produce conductive rGO from GO-based precursors. This technique allows pioneering research in the direct writing of microelectronics, including conductive CCCs and electrodes for supercapacitors.\textsuperscript{13,69–71} In this research a micrometre-accuracy 465 nm laser-scriber was mounted in the customised commercial 3D-printer. The laser is endowed with software-controlled engineering parameters of speed, frequency and power to generate a plethora of shapes and patterns. The chemical and physical properties of the resulting laser-induced rGO depend on the different combinations of the controlled engineering parameters. Further analysis of these parameters, the variation of the outcome after modifying these parameters and how they affect the conductivity of the laser-induced rGO will be presented in Sections 3.3.4.3, 3.3.4.4, and 3.3.4.5, respectively.

This laser-irradiation method can generate complex laser-scribed shapes with the same accuracy of the 3D-printer, i.e., in the order of micrometres. The shapes and patterns can be designed in the same fashion as the 3D-models of PEO-based ink were generated using a CAD package. In the case of a flat pattern or a 2D-shape is required, a simple raster graphics editor such as Microsoft Paint can be used to generate the model. Additional were previously developed

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**Figure 3.17.** 3D-printed PEO/GO-based model on glass substrate located for laser-scribing process
in the Faul Research group to generate complete GCODE files for laser-scribing procedures from files with graphic formats such as JPEG. The code for this automatic generator was written by a former PhD student in the group Dr. Djen Kuhnel and it simplifies the process of creating the object in a CAD package. The developed software interprets a monochrome 2D-pixel-based image of a bitmap file and generates commands directly into a ready-to-scribe GCODE file. The file can be interpreted and implemented by the customised 3D printer. The dimensions of the bitmap can be precisely transformed into the dimensions of the model by setting the length unit per bitmap pixel. The attained GCODE file can be easily combined with other GCODE lines. This characteristic enables the laser-scribing code to be combined with a 3D-printing code to have a complete automated process. Once the laser-scribing code is generated and ready to use, a set of PEO/GO-based models were prepared with different GO concentrations (2.5 mg/ml, 5 mg/ml, and 10 mg/ml). The dry 3D-printed PEO/GO-based models on a glass substrate are 3D-printed, keeping them aligned to the x and y axis and the origin of the 3D-printer coordinates (Figure 3.17). The 3D models are then irradiated by the laser following the developed code to form designed shapes or patterns (Figure 3.18). An initial approach of speed, laser frequency and power is considered to perform the laser irradiation procedure with these values:

\[ \text{laser frequency} = 3\,000\, \text{Hz} \]

\[ \text{speed} = 1000\, \text{mm min}^{-1} \]

\[ \text{power} = \text{variable from 20 to 60%} \]

An important property of an electrode material used as a CCC is its electrical conductivity. The obtained laser-scribed surfaces were evaluated by the sheet resistance upon laser irradiation. This method was used because of the particular interest in this research of using the attained laser-scribed material as CCCs. These latter should ideally have a high surface area and electronic conductivity for use in energy storage devices such as supercapacitors and micro-supercapacitors. The sheet resistance experiments were performed using a Fluke 77 IV digital multimeter (Fluke Corporation, USA) following the procedures detailed in Section 2.2.1.4. With this method, initial sheet resistance values from 4 kΩ/sq to 60 Ω/sq were obtained, with a starting laser irradiation power of 20 % and increased up to 40 and 60 %. The progressive decrease of the sheet resistance (Figure 3.19) is directly related to the increase of the laser power during irradiation. These results could be attributed to the GO-based material being reduced upon direct exposure to the 465 nm laser irradiation. A lower sheet resistance can be attributed to a higher production of laser-scribed graphene (LSG) and the amount of the GO reduction can be controlled by the power of the laser irradiation. This outcome is consistent with the findings of Strong et al. and El-Kady et al.\(^{13,72}\)
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Figure 3.18. 3D-printed PEO/GO-based model on glass substrate under laser irradiation

Figure 3.19. Sheet resistance of the laser-scribed 3D-printed PEO/GO-based models on glass substrate, in dependence of laser power.

Further analysis on the GO reduction is presented in the next section (3.3.4.2)

3.3.4.1 Laser-Scribed Graphene Oxide

In this work, the laser-scribing system mounted onto the customised 3D-printer is equipped with a 400–460 nm commercial laser. This system performs a software controlled laser-scribing of the GO-based material into laser-induced graphene. This automated irradiation procedure transforms the PEO/GO-based insulating material into a conductive material. This conductivity
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is generated by the laser interaction over the PEO/GO-based models and can be related to the GO laser-induced reduction process. However, to qualitatively evaluate the contribution of the rGO to the overall conductivity of the laser-scribed material, a comparison between the attained material and a PEO-based control sample without GO is performed. This procedure is executed by preparing a set of PEO/GO-based models with different GO concentrations (2.5 mg/ml, 5 mg/ml, and 10 mg/ml). Also, a group of PEO-based models were produced replacing the GO with a red color dye AR-27 (Amaranth Red). The aim of the usage of this food and cosmetic colorant is to remove the characteristic transparency of the PEO-based inks and models. Without the AR-27 red dye the transparency of the PEO-based samples can cause the laser beam to pass through the samples with no scribing process taking place. With the presence of AR-27, the resulting PEO/AR-27-based material can absorb the laser energy and can be scribed in the irradiation process. Previous research carried out in the Faul Research Group showed that the material to be laser-scribed must absorb the laser wavelength to an enough degree that the temperature which the scribing process starts can be reached. Therefore an absorbent filler leads to the temperatures required when the laser is irradiated on the polymer-based material. The selection of AR-27 was carried out based on the UV-Vis absorbance spectrum of the dye. The most important aspect of using a dye is its capacity to absorb the light radiation in a wavelength range that includes the wavelengths of the laser-scribing LED. In this research a micrometre-accuracy 465 nm laser-scriber LED was mounted on the customised commercial 3D-printer for the laser-scribing process. Figure 3.20 shows the UV-Vis spectra of the AR-27 dye (1 wt% in the overall aqueous PEO-based blend). The collected UV-Vis data exhibit a broad absorbance peak in the wavelength range of 200 nm to 600 nm. This range covers the wavelength of the laser-scriber promoting the absorption of the energy produced by laser-LED during the engraving process. Additionally, for comparison purposes, we have included the UV-Vis spectra of the PEO/GO-based blend (1 wt% GO in the overall aqueous PEO-based blend) as well.

A lower sheet resistance can be attributed to a higher production of laser-scribed graphene (LSG) and the amount of the GO reduction can be controlled by the power of the laser irradiation. This outcome is consistent with the findings of Strong et al. and El-Kady et al. Further analysis on the GO reduction is performed in the next section (3.3.4.2)

3.3.4.2 Laser-Scribed Graphene Oxide

These AR-27-based control samples are prepared with similar concentrations to those prepared with GO, i.e., (0.2 wt%, 0.5 wt%, and 1 wt%). These samples and the original PEO/GO-based samples were subjected to the same laser-scribing process under the same conditions and engineering parameters of frequency, speed and power. The obtained sheet resistance of the PEO/GO-based samples is compared with the resulting sheet resistance of the control samples.

Figure (3.21(a)) and Figure (3.21(b)) show a sheet resistance decreasing trend related to an increasing laser power. This trend is common for the PEO/GO-based samples and the measurable
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**Figure 3.20.** UV-Vis spectra of the PEO/AR-27-based blend and PEO/GO-based blend (the concentrations of AR-27 and GO are 1 wt% in the overall blend, respectively)

**Figure 3.21.** Sheet resistance of the laser-scribed PEO/GO-based and AR-27-based 3D-printed models: a) 4 layers model  b) 5 layers model. Note: Some of the measured sheet resistance values were larger than $10^4$ Ohms/sq, and thus not included in the graphs (AR-27 0.2 wt% and AR-27 0.5 wt%).

AR-27-based control samples. This could be related to an increasing amount of carbon-based material produced by a higher laser power irradiation. Further analysis of the conductivity contribution of the rGO is performed ahead in this research work. The sheet resistance of the PEO/AR-27-based samples with a concentration of 0.2 wt%, 0.5 wt% of AR-27 can not be evaluated because their values are off-scale of the equipment used to characterise them (greater than hundreds of MΩ/sq). However, the control sample of PEO/AR-27-based with a
dye concentration of 1 wt% shows a measurable sheet resistance with higher values compared to its PEO/GO-based counterpart. These results could be attributed to a qualitatively higher contribution of the laser-induced graphene (rGO) to the overall conductivity of the laser-scribed samples.

To further evaluate the effects of the laser irradiation on the PEO/GO-based samples, a set of PEO/GO-based models were prepared. The concentrations of the PEO and GO precursors were maintained at 6 wt% and 10 wt% respectively. After the drying and laser-scribing steps, the morphology of the samples was investigated by SEM experiments. The preliminary results (Figure 3.22) show a mostly uniform surface in the not scribed area (Figure 3.22(a)) and a porous structure in the laser-scribed area. A higher magnification micrograph (Figure 3.22(b)) shows a porous material made of flakes-like structures with no obvious arrangement or orientation. This result could be attributed to the presence of heat expansion and gases production during the laser irradiation process. The morphology of the laser-scribed surface can significantly change with the variation of the engineering parameters of the laser. For instance, a slight change in the power of the laser can produce a different morphology in the arrangement of the laser-irradiated material. Figure 3.23 reveals the morphology of a laser-scribed PEO/GO-based sample with ordered stacked flakes parallel to the axis direction of the laser (horizontal left to right and vice-versa). This outcome is the result of a laser-irradiation process upon decreasing the power of the scribing system from 60% to 20%. The morphology can be modified as well by increasing or reducing the frequency and the speed of the laser-scribing system. In this regard, the Figure 3.24 exhibits a SEM image of a laser-scribed model with low laser-scribing frequency (25 Hz) implying a period $\tau$ with a duration of 40 ms. This latter shows laser-scribed spots of approximately 150 µm separated by non-scribed spaces. Additional to the variation on frequency, the separation

![Figure 3.22](image-url)
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Figure 3.23. SEM image of a laser-scribed PEO/GO-based 3D-printed model irradiated with lower laser power

of the laser-irradiated spots can be increased or reduced by modulating the speed of movement of the laser-scriber Figure (3.25(a)) and Figure (3.25(b)). The bigger size of 200 µm of the laser-scribed spots shown in Figure 3.25(b) could be attributed to a greater laser-irradiation dwell time per spot. All these preliminary results promoted additional studies on the effects of the speed, frequency and power of the laser on the scribed samples. Actually, the modification of the laser parameters not only changes the morphology, but can also dramatically influence the conductivity of the resulting laser-induced graphene material. Further analysis upon the variation of these parameters was carried out in this research work in Sections 3.3.4.3, 3.3.4.4, and 3.3.4.5.

In addition, the variation of the laser parameters can determine the suitability of attaching the laser-engraved material to a flexible substrate. This step is highly important to produce laser-scribed flexible and stretchable CCCs for supercapacitor prototypes.

3.3.4.3 Laser Speed

Among the engineering parameters of the laser-engraver, the speed of the laser-irradiation process is highly important to control the amount of energy delivered by the laser per unit of surface. This effect can determine the size and shape of the laser-irradiated spots on the PEO/GO-based material. The laser unit used in this research work is equipped with a pulse width modulation
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Figure 3.25. SEM images of laser-scribed PEO/GO-based samples with different laser speeds: a) sample laser-scribed at 350 mm min\(^{-1}\) b) sample laser-scribed at 300 mm min\(^{-1}\)

(PWM) power control system (See detailed information on PWM laser control in Section 2.1.1.2). This PWM-system controls the delivered power by switching the laser on and off in a very accurate fashion. The on and off periods are expressed by complementary percentages (Figure 3.26). The on percentage defines the proportion of on time to the total cycle period or repeated interval. This on percentage is called duty cycle (DC). During the laser-scribing process the DC will be noticed as scribed spots of laser-irradiated surfaces along the laser travel path. If the DC is kept constant, then the length of the scribed spots depends on the speed of the movement of the whole system during the laser-scribing process. A higher laser speed will produce longer spots (Figure 3.27(a)). Conversely, when the laser speed is decreased the laser-irradiated spots are reduced in length (Figure 3.27(b)). These latter spots have a slightly increased width. This effect could be attributed to the laser-scriber irradiating the same power (determined by the constant DC) in a reduced length.

The laser speed can be further reduced to a critical value where the laser-scribed spots start overlapping. This can only happen when the laser spot size (approx. 100 µm diameter) has

![Figure 3.26. Laser-scriber duty cycle](image-url)

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Figure 3.27. Scheme of the laser-speed effect on the laser-scribed surface: a) laser speed at 1200 mm min\(^{-1}\) b) laser speed at 300 mm min\(^{-1}\)

not been completed by the laser travel before starting a new on period (Figure 3.28 producing overlapped irradiated areas. This overlapping effect is very important because it generates connections between the conductive laser-induced graphene spots. These connections can modify the conductivity of the laser-scribed surfaces.

Figure 3.28. Overlapped laser-scribed spots

In general, a greater overlapping of laser-engraved spots will produce better conductivity. However, an excessive overlapping over the same area or surface will produce ablation and can not only sweep away the GO-based material, but also damage the substrate. A good balance between the overlapping effect and the production of conductive laser-induced graphene must be found, and is one of the main subjects evaluated in Section 3.3.4.6.

3.3.4.4 Laser frequency

In the present work, the initial laser frequency was a standard parameter fixed at 5000 Hz for any laser-scribing process. This particular value was assumed as default during the exploration of the laser-scribed GO-based surfaces towards the production of laser-induced graphene. At this very high frequency, any small change of this parameter did not produce any obvious change in the conductivity of the obtained laser-induced material. If the frequency of the laser scriber is set
to a very low value (i.e., 10 Hz), the laser-scribed spots will be separated because of the speed of the movement of the laser as shown in the Figure 3.29(a). If it is increased in a controlled fashion

![Figure 3.29](image1.png)

**Figure 3.29. Effect of the laser frequency on the laser-scribed surface: a) laser frequency set at 10 Hz  b) laser frequency set at 20 Hz**

(Figure 3.29(b)), then, a critical frequency can be reached. This critical frequency is the frequency where the produced laser-scribed spots start to overlap. This frequency controlled increase is performed keeping the laser speed as a constant. At higher frequencies than the critical frequency, the combination of the on and off periods of the laser produce a controlled overlapping effect over the laser-scribed areas (Figure 3.30). This effect is produced in a similar fashion as it was described in Section 3.3.4.3 and can be observed in the microscope image of the figure 3.31 where 4 parallel lines were irradiated at 25 Hz in a constant speed laser of 300 mm min$^{-1}$. The obtained scribed areas show intersecting laser-irradiated spots resulting from the irradiation of repeated on periods, close to each other during the laser movement. The conductivity of the

![Figure 3.30](image2.png)

**Figure 3.30. Frequency-controlled laser-scribed spots**

laser-induced surfaces can be attributed to the intersected spots of laser-induced graphene. A greater frequency can produce an increased overlapping effect with a significant improvement in
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Figure 3.31. SEM image of frequency-controlled laser-scribed spots on a GO-based surface

The overall conductivity of the irradiated surfaces. However, very high frequencies can reduce the scribing capabilities of the laser. This latter effect is produced when the on period is too short and the laser power does not reach the highest value possible, and could be related to the non-ideal behaviour of the activation signal of the laser at those high frequencies. A good trade-off between the frequency and the overlapping effect should be found. This is one of the most important aims of Section 3.3.4.6, where the frequency of the laser is varied sequentially. This controlled variation is combined with the variables of laser speed and power of the laser, not only to obtain an optimal value of conductivity, but also to find additional mechanical and morphological characteristics of the laser-induced graphene-based surfaces.

3.3.4.5 Laser power

During each cycle of the PWM-controlled laser scriber, an on period and an off period take place. This latter description implies that the percentage of the laser-active duration and the percentage of the laser-inactive duration are complementary in each total period. The percentage of the laser-active period is taken as the power value of the PWM-controlled laser scriber. The variation

Figure 3.32. Scheme of the laser power effect on the laser-scribed surface: a) laser power set to 10% b) laser power set to 20%
of this percentage is reflected in the shape of the laser-scribed surface. The resulting laser-scribed area shows shorter irradiated spots at low laser power. Conversely, higher laser power will result in longer irradiated spots on the GO-based surface. These laser power variation experiments were performed keeping a fixed laser speed and fixed laser frequency. These latter conditions guarantee that any change in the shape on the resulting irradiated spots can be attributed to the corresponding change of the laser power.

Laser-scribing experiments performed on the GO-based surface with constant laser frequency and constant laser speed can produce an initial overlapping effect. The speed and frequency of the laser must be slightly greater than the critical values to attain overlapping laser-irradiated spots. In this case, a fixed frequency of 25 Hz and a fixed speed of 300 mm min\(^{-1}\) were selected based on the previous experience of Section 3.3.4.4. Then, an initial laser power of 10 % is applied obtaining a small overlapping effect between the laser-scribed spots (Figure 3.32(a)). The overlapped areas increased when the laser power is raised to 20 %. Figure 3.32(b) shows a qualitative relationship between the laser power and the overlapping areas. Optical microscope images can be seen in Figure 3.33(a) and Figure 3.33(b), showing the different sizes of the laser-scribed areas and the overlapped laser irradiated spots when the laser power is increased from 10 % to 20 %. In addition, this modification of the laser power produces changes in the overall conductivity of the laser-scribed surfaces. In general, the laser-scribed areas at higher power have less sheet resistance compared to those scribed at lower laser power. This qualitative relationship and results are further analysed and detailed in Section 3.3.4.6.

### 3.3.4.6 Reduction of Graphene Oxide

The laser-irradiation performed on the GO-based material produces conductive laser-induced graphene. This outcome is attained by the reduction the GO as it was introduced in Section 3.3.4.2. This is further supported by additional characterisation of the laser-scribed material.
Energy-dispersive X-ray spectroscopy (EDX) images reveal a laser-irradiated product with a qualitative higher content of carbon compared with the original GO-based precursor.

The laser-scribed spots can be clearly seen as patterns in the micrographs of Figure 3.34. When the laser parameters are set to obtain separated irradiated spots, the resulting scribed sites unveil reduced-oxygen-containing surfaces (Figure 3.35(a)). Likewise, the same areas present an increased carbon content (Figure 3.35(b)) suggesting an effective oxygen-reducing process. The noticeable greater carbon content could be attributed to the removal of the oxygen functionalities from the GO-based material produced by the laser-scriber reducing effect. This effect was previously described by Deng et al., and it keeps a close relationship with the amount of energy delivered by the laser scriber per unit of surface. The irradiated surfaces reveal different effects depending on the laser parameters. In all cases, the change of the parameters of speed,

(a)  (b)

Figure 3.35. EDX micrographs of a laser-scribed surface showing: a) Oxygen content b) Carbon content

power or frequency not only influence the obtained intersected (overlapped) laser irradiated
areas, but also produce changes in the morphology of the surface of the scribed areas. This effect can be seen in Figure 3.36 where a predominantly porous surface is produced by the laser irradiation. This porosity is one of the characteristics that is explored in this work to attain a binding effect between the laser-induced graphene and a flexible substrate such as silicone rubber. This effect is detailed in Section 3.3.5. One of the most important results of the laser-scribing process performed on the GO-based material is the reduction of the GO into a conductive material. The conductivity of the attained material is evaluated by sheet resistance measurements. This characterisation technique is used to evaluate the conductivity of conductive or semi-conductive surfaces. These measurements were performed according the methods described in Section 2.2.1.4. The sheet resistance evaluation of the laser-irradiated material reveals quantitative changes of this property upon change in the laser parameters. In general, any variation of the laser parameters of speed, power or frequency attaining a higher overlapping effect will result in a lower sheet resistance.

Figure 3.37(a) shows the changes of the sheet resistance of the laser-induced graphene surfaces related to the variation of the speed of the laser. The latter reveals a reduction of the sheet resistance when the speed of the laser increases. Figure 3.37(b) illustrates the inverse relationship between the sheet resistance and the laser power. The higher the laser power, the lower the sheet resistance.

**Figure 3.36.** SEM image of porous laser irradiated areas

**Figure 3.37.** Change of the sheet resistance of the GO-based materials related to the variation of laser parameters: a) change of speed and power  b) change of power and frequency
resistance when the laser speed is increased from 1000 mm min$^{-1}$ to 2000 mm min$^{-1}$. However, at speeds higher than 2500 mm min$^{-1}$ the sheet resistance starts an increasing trend. This experiment was repeated at 80% and 90% of laser power with similar results. This experiment combined two laser parameters (speed and frequency) to find an optimal results when these two variables are modified. Similarly, Figure 3.37(b) shows the resulting variation in the sheet resistance when the laser power is incrementally increased. An increased laser power produces an expected decrease in the sheet resistance. This trend can be observed in the range of 5% to 45% of the laser power. The decreasing trend turn into an increasing variation of the sheet resistance in the laser power range of 45% to 100%. This change in the trend could be attributed to the fact that an intense radiation (resulting from a very high laser power) of the GO-based material can lead to ablation and a sweep-off process of the laser-scribed material. Experiments were conducted in different scenarios that are identified with a particular frequency. These experiments were carried out combining the variables of laser power and laser frequency with the aim of obtaining the lowest sheet resistance value.

The analysis of the resulting sheet resistance should be related not only to the variation of the laser parameters, but also to the combined interaction of those variables during the laser-irradiation process. The latter effects can be attained by a controlled change of each laser parameter and a constant evaluation of the sheet resistance of the laser irradiated areas.

![Figure 3.38](image-url)

**Figure 3.38.** Sheet resistance of laser-scribed GO-based surfaces related to variations of the laser power and frequency.

Figure 3.38 shows the resulting sheet resistance of the laser-induced graphene surfaces upon combined effects of a laser power variation from 5% to 100% performed in a defined range of
frequencies from 25 Hz to 100 Hz. This range of frequencies is not arbitrary and has been selected because in this range the overlapping effect starts to be noticeable and can be smoothly increased by changing the laser parameters. This figure reveals initial values of sheet resistance in the order of thousands $\Omega$/sq at a laser power of 5%. This result could be attributed to the presence of conductive laser-induced graphene on the irradiated surface. Then, small 5% increases in the laser power are performed and after each change the sheet resistance of the laser-scribed surface is evaluated. The variation of the sheet resistance shows a decreasing trend. This tendency could be related to the increase of the overlapped areas and a greater concentration of laser irradiation per unit of length. This effect can be seen in the Figure 3.39 where not only the intersected areas are increased but also the size of the laser scribed spots are increased.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.39}
\caption{Optical microscope images of laser-scribed surfaces and intersected spots: a) at 15\% laser power b) at 20\% laser power c) at 25\% laser power d) intersected at 15\% laser power e) intersected at 20\% laser power, and f) intersected at 25\% laser power}
\end{figure}

The described trend continues until a minimum value of sheet resistance is reached. From this point, any additional increase in the laser power produces an increase in the sheet resistance or, in other words, compromises the conductivity of the laser irradiated areas.

This result could be attributed to excessive laser irradiation of the GO-based surface. Further morphology studies of the obtained surfaces reveal the over-irradiated areas with a reduced amount of laser induced material. This decrease of the material on the laser-scribed surface is more noticeable at higher laser power values. This effect can be related to a lower availability of the conductive laser-induced graphene on the irradiated surface and it could explain the increasing trend in the sheet resistance. These results of material displacement caused by an excessive laser power can be seen in Figure 3.40 where the irradiated material has been swept off at laser powers of 90\%, 95\%, and 100\%. These outcomes are consistent with previous findings reported by Deng et al.\textsuperscript{74} The research efforts of the current investigation provide new insight
3.3. RESULTS AND DISCUSSION

FIGURE 3.40. Optical images of laser-scribed surfaces with excessive laser power: a) at 90% laser power b) at 95% laser power c) at 100% laser power

into the role of additional laser parameters to produce conductive laser-induced-graphene-based surfaces. Further analysis was carried out to find the combined influences of frequency and laser speed on the sheet resistance of the laser-scribed surfaces. Figure 3.41 reveals the obtained sheet resistance for a laser power range from 5% to 100%, a frequency range from 25Hz to 100Hz with an increasing step of 25Hz, and a speed range from 300 mm min\(^{-1}\) to 1200 mm min\(^{-1}\) with increasing steps of 300 mm min\(^{-1}\).

Figure 3.41(a) and Figure 3.41(b) show a sheet resistance variation with a similar trend as described before, i.e., with a decreasing tendency until it reaches a minimum value. From this point any additional power increase produces an increase in the sheet resistance. This behavior is common to all frequencies in these two cases. This could be explained by low and moderate laser speeds (300 mm min\(^{-1}\) and 600 mm min\(^{-1}\)) used for the laser-scribing process. At these speeds, the laser irradiation strongly depends on the laser power used. Also, at these laser speeds the irradiation becomes highly intense at higher laser power per unit of length. The latter produces ablation and material removal from the surface as was explained before.

Likewise, Figure 3.41(c) reveals a decreasing trend in the sheet resistance. The decreasing tendency found in the laser power range of 5% to 50% can be attributed to the contribution of an increasing overlapping effect and a higher irradiated power producing higher amount of laser-induced graphene. The sheet resistance seems to stay constant in the range of 50% to 100% of laser power. The behavior slightly changes for the results of the experiment carried out at a frequency of 25 Hz: the sheet resistance seems to increase for any laser power greater than 70%. The latter is a particular case that should be carefully considered before continuing with the trend analysis.

If we compare Figure 3.41(a) and Figure 3.41(b), it can be seen that in the first case (laser-scribing performed at 300 mm min\(^{-1}\)) the minimum sheet resistance value is reached at lower laser power values, i.e., close to the range of 15% to 20%. However, for the second case (Figure 3.41(b) -laser-scribing performed at 600 mm min\(^{-1}\)), the minimum sheet resistance is obtained at values of laser power in the range of 40% to 60%. So, a clear displacement of the power range with minimum values of sheet resistance can be seen. This displacement goes from lower to higher laser power ranges when the laser speed is changed from 300 mm min\(^{-1}\) to 600 mm min\(^{-1}\).
This result can be attributed to an effect produced by the interaction of the laser power and the laser speed at a fixed laser frequency. Such interaction effects are related to the number of laser on cycles performed along the laser path. At lower laser speeds such as 300 mm min⁻¹, the number of laser on cycles per unit of length of the laser-travel path is higher. This implies that less power will be needed to obtain a conductive laser-induced-graphene-based material. This effect could be attributed to a greater amount of energy density delivered per surface unit. The overlapping effect will promote a double amount of energy irradiated in the same surface. The irradiated energy density analysis is addressed in the next page of the present research effort for further details and explanation. The decreasing trend of the sheet resistance at lower laser power range is driven by the overlapping effect of the laser irradiated spots. When the minimum sheet resistance is attained, any increase of laser power will start producing ablation and sweep-off of the laser-irradiated material. The increasing trend of the sheet resistance in higher ranges of laser power is driven by the excess of the laser power (longer laser on or duty periods creating bigger and highly intersected irradiated spots at higher power per unit of length.
of the laser-travel path) on the PEO/GO-based surface producing delamination and ablation. At medium laser speeds such as 600 mm min\(^{-1}\) the number of laser on cycles per unit of length of the laser-travel path is lower and the overlapping effect increases very gently following the increase of the laser power. It implies that an optimum overlapping effect and the lowest sheet resistance are attained at higher values of laser power. Further analysis at higher laser speed support this interaction between the laser speed and the laser power. Figure 3.41(c) and Figure 3.41(d) correspond to a laser engraving process performed at 900 mm min\(^{-1}\) and 1200 mm min\(^{-1}\). They show a smoother behaviour of the sheet resistance at higher laser powers. The previous explanation about the interaction of the laser speed and the laser power applies very well to the demonstrated sheet resistance tendency. Based on the latter, a higher laser speed will produce a decreasing trend on the sheet resistance at lower laser powers. This latter effect is mostly driven by the overlapping effect of the laser scribed spots. At higher laser powers there are longer laser on or duty periods creating bigger and more intersected irradiated spots. Despite of higher laser power being irradiated, the increase in lasers speeds will impede a concentration of laser power per unit of length of the laser-travel path. The latter effect keeps a conductive laser scribed surface free of excess of laser dwell time and any possible ablation effect.

In the laser-scribing process the energy is absorbed in a thin surface layer. The absorbing surface may experience a large increase in temperature.\(^{75,76}\) One of the most popular measurements to evaluate the irradiated power of a laser is using the power density or specific power per unit of area.\(^ {77}\) In this regard, the power of the laser is assumed to be distributed in an irradiated surface. The ratio of the laser power to the scribed area will give the specific power of the laser scribe. Using the latter definition we have the power of the LED laser and we can calculate the energy per surface unit during the laser scribing process. The laser irradiation is performed at different speeds and at different duty cycles to obtain the energy deposited on the laser scribed surface.

For simplifying purposes we have kept a constant laser frequency of 25 Hz. At the selected frequency each cycle has a duration of 40 ms. Within this period of time the DC is determined by the value set in the laser-power (0% to 100%). The DC is a fraction of the cycle duration. For example, with a laser-power of 15\% the DC will be \(0.15 \times 40 \text{ ms} = 6 \text{ ms}\). On the other hand, the complementary percentage of the DC (85\%) equivalent to \(0.85 \times 40 \text{ ms} = 34 \text{ ms}\) determines the duration of the off state where the laser does not deliver any energy to the scribed surface.

During the DC the laser will deliver a power of 1.6 W. To calculate the energy delivered to the scribed surface we can multiply the delivered power by the DC duration. In the present example the delivered energy is \(1.6 \text{ W} \times 6 \text{ ms} = 9.6 \text{ mJ}\). The energy was delivered onto a well-determined surface area. This surface area can be calculated using the speed of the laser-scriber, the laser spot size, and the displacement of laser-spot during the DC duration. Currently, the laser spot is a circle with a diameter of 100 \(\mu\text{m}\). The spot moves at the laser speed in the laser direction set in the GCODE file.

During this movement the laser spot describes a surface that will increase in the direction
of the movement as shown in the Figure 3.42 a. The resulting scribed surface can be calculated adding the laser spot surface and the rectangular surface resulting from the laser movement (Figure 3.42 b). The total scribed surface is attained by combining the areas of the laser round spot (areas A1 and A2) and the area described by the movement of the laser scriber (area A3). In the present example A1 and A2 are obtained as the surface of the round spot of the laser \( \pi x r^2 \) where \( r = 50 \mu m \):

\[
A_1 = A_2 = \frac{\pi x r^2}{2} = \frac{3.1416 x (50 \mu m)^2}{2} = 3.927 \mu m^2
\]

Likewise, the area A3 in this example is given by the distance travelled by the laser at a laser speed of 300 mm min\(^{-1}\) (5.000 \( \mu m s^{-1} \)), multiplied by the laser-spot diameter (100 \( \mu m \)). The distance is \( d = \text{laser speed} \times \text{DC}, d = 5.000 \mu m s^{-1} \times 0.006 s = 30 \mu m \). Therefore, the surface A3 is:

\[
A_3 = \text{distance} \times \text{laser spot diameter} = 30 \mu m \times 100 \mu m = 3000 \mu m^2
\]

Then the total laser-scribed surface is:
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\[ A_1 + A_2 + A_3 = 3.927 \, \mu m^2 + 3927 \, \mu m^2 + 3.000 \, \mu m^2 = 10.854 \, \mu m^2 \]

Now, with the energy deposited and the radiated surface, the energy density can be calculated:

\[
\text{Energy density} = \frac{\text{energy deposited}}{\text{surface irradiated}} = \frac{9.6 \, mJ}{10.854 \, \mu m^2} = \frac{0.0096 \, J}{1.08 \times 10^{-4} \, cm^2}
\]

\[ \text{Energy density} = 88.45 \, J \, cm^{-2} \]

Following this procedure we can obtain a general expression to relate the laser speed and the DC in the total energy deposited:

The above-mentioned scribed surfaces can be calculated as a function of the laser-spot size and the laser-spot diameter:

\[ A_{\text{TOTAL}} = A_1 + A_2 + A_3 = \text{laser spot size} + 2r \times d \]

Where \( r \) is the laser-spot radius. Also, the distance \( d \) can be expressed as a function of the laser speed, the DC in seconds as follows:

\[ d = \text{laser speed} \times \text{DC} \]

Then, replacing the distance \( d \) in the surface calculations we obtain:

\[ A_{\text{TOTAL}} = A_1 + A_2 + A_3 = \text{laser spot size} + 2r \times \text{laser speed} \times \text{DC} \]

On the other hand, the laser-power irradiated during the DC will provide the total energy deposited in the laser-scribing process:

\[ \text{Energy deposited} = \text{Power} \times \text{DC} \]

With the latter, we can calculate the energy density per square unit (laser-irradiated area):

\[
\text{Energy density} = \frac{\text{Energy deposited}}{A_{\text{TOTAL}}}
\]

or:

\[
\text{Energy density} = \frac{\text{Power} \times \text{DC}}{\text{laser spot size} + 2r \times \text{laser speed} \times \text{DC}}
\]

The latter mathematical expression shows the influence of each variable on the laser energy delivered onto the irradiated surface. The power of the laser LED (1.6 W) is the leading value
of the total energy delivered. However, this energy is modified by the irradiation time (DC) and the surface irradiated. The irradiated surface shows an inverse relationship with the irradiated energy density. This effect is produced because whilst the irradiated surface increases, the energy density decreases. This latter effect could be attributed to the fact that the laser-scribed surface increases in a direct relationship with the laser speed and the DC. As a summary, if the laser speed increases the delivered energy density decreases. Conversely, if the DC increases the total energy delivered increases. However, the energy density per unit of laser-scribed surface will not be significantly modified by the DC. The latter factor is part of the numerator and part of the denominator in the mathematical expression. This effect shows that the energy deposited and the surface irradiated will be modified in a direct relationship with the DC. On the other hand, the energy density depends on both factors, energy deposited and irradiated area, and both are directly related to the DC.

In most of the cases the frequency does not produce a significant change in the sheet resistance. However, at low and moderate laser speed (300 mm min\(^{-1}\) and 600 mm min\(^{-1}\)), the sheet resistance shows a slightly increasing trend directly related to the increase of the frequency. This tendency can be attributed to a higher number of on and off cycles per unit of time. The number of laser-scribed spots increases and the overlapping effect is more pronounced. However, the favourable effect in the reduction of the sheet resistance is tempered by the reduction of the size of the laser-scribed spots. Also, the influence of the frequency is hindered by the fact that a determined laser power has the same duty cycle at any laser frequency. This latter fact could provide an explanation why the sheet resistance is marginally affected by the frequency changes. At higher speeds (900 mm min\(^{-1}\) and 1200 mm min\(^{-1}\)) the influence of the frequency on the sheet resistance is not noticeable. Further characterisation of the laser scribed areas using Raman Spectroscopy reveal the reduction of the GO-based surface upon laser irradiation. Figure 3.43 shows the characteristic Raman peaks of GO where the I(D) and I(G) peak ratio is 0.82. After the laser irradiation process is performed, the Raman peaks of the irradiated surface correspond to new D and G peaks with a I(D)/I(G) ratio of 1.01 that is attributed to the presence of reduced GO.\(^{78–81}\) The intensity of the D and G peaks can be used as an indicator of the quantity of defects on the structures resulting from the oxidation process to obtain GO. The increase of the I(D)/I(G) ratio can be related to the presence of higher amounts of graphene domains resulting from the GO reduction. This change in the ratio can be also attributed to a smaller size of the sp\(^2\) domains upon reduction of the GO-based material by laser irradiation. So far, the production of the rGO-based CCCs in this research effort is the result of the reduction of GO upon laser irradiation. However, GO reduction can be also obtained by chemical methods. A green and mild GO reduction process can be performed using ascorbic acid (AA) or more commonly known as Vitamin C. This reducing process removes the oxygen functionalities from the GO dispersed in water. One of the greatest advantages of this method is that it can be carried out in aqueous colloid blends. The resulting rGO stays suspended in the colloid blend with a higher chemical
stability compared with other chemical methods. Additional to this, the reduction as a colloid
does not result in an immediate aggregation of rGO sheets as produced by many other harmful
chemicals such as hydrazine, sodium hydride, sodium borohydride, lithium aluminium hydride
and strong acids. In this investigation AA has been used as a pretreatment on the GO-based blend
before the 3D printing and laser irradiation process. AA was added to the GO-based aqueous
blend just before the 3D printing of the GO-based blend. The addition of AA in the PEO/GO-based
blend was performed with a ratio of 1:5 (AA:GO) by weight. If the ratio of AA:GO is increased
the rGO stays suspended within the polymer blend but small agglomerations can be produced.
This effect is not highly noticeable until the 3D-printing process is performed. In this latter stage,
the small bits of agglomerated rGO can clog the nozzle of the 3D-printing system. To avoid this
agglomeration and obtain a good trade-off between the electrical conductivity and the capacity to
be 3D-printed, the ratio of AA:GO of 1:5 was kept in the PEO/GO-based blend.

The reduction process continues as long as water is present in the GO-based models. After
the solvent (water) completely evaporated, no further reduction takes place. The GO-based
models with AA does not show a noticeable difference compared with those without AA upon 3D
printing. The obtained new models are subjected to the same previously reported laser irradiation
process to obtain conductive laser-induced graphene-based surfaces. A complete new batch of
laser irradiated CCC samples were produced and evaluated by sheet resistance measurements.
Additional to that, the influence of the variation of the laser parameters on the resulting sheet
resistance was tested after the laser-scribing processes. Figure 3.51 shows the sheet resistance
obtained from the laser irradiated surfaces of AA-pretreated 3D-printed GO-based models. Figure
3.44(a) reveals the sheet resistance obtained from a chemically-reduced-GO-based model upon

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![Figure 3.43. Raman spectra of a GO-based surface and a laser induced rGO surface.](image)
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Figure 3.44. Variation in sheet resistance of laser-scribed of chemically-reduced GO-based surfaces with different laser parameters: a) at 300 mm min\(^{-1}\) b) at 600 mm min\(^{-1}\) c) at 900 mm min\(^{-1}\) d) 1200 mm min\(^{-1}\)

laser irradiation at 300 mm min\(^{-1}\). This shows a decreasing trend related to the increments of the laser power. This tendency is similar to the data reported on the PEO/GO-based models. However, a difference can be found in the sheet resistance values obtained at lower laser powers. The initial sheet resistance attained at 10% laser power is in the order of tens of millions of \(\Omega/\text{sq}\). This value is 4 orders of magnitude higher than the initial values obtained at the same laser power used on the untreated PEO/GO-based samples. The results of the initial sheet resistance values reported here can be related to a possible agglomeration of the reduced GO material upon pretreatment with AA. This process could produce separated centres of agglomerated rGO. The laser-scribing process further reduces the GO contributing to the decrease of the sheet resistance. However, there would be zones with lower amounts of rGO because of the agglomeration. These zones will not present a lower sheet resistance compared with the zones rich in rGO as was reported in Section 3.3.4.2. The resulting sheet resistance keeps decreasing when the laser power is increased to reach values as low as 16 \(\Omega/\text{sq}\). These results are similar for the laser-scribed models at frequencies of 25 Hz, 50 Hz, 75 Hz and 100 Hz. The frequency variation does not produce
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A significant change in the resulting sheet resistance. This outcome can be attributed to the overlapping effect of the irradiated spots, mostly driven by the laser speed and the duty cycle of the laser (laser power). The attained sheet resistance of these models makes them good candidates to be used as CCCs. The sheet resistance obtained for the models scribed at 600 mm min\(^{-1}\) shows a similar trend compared to those scribed at 300 mm min\(^{-1}\). However, the initial values obtained for the surfaces irradiated at the lowest frequencies (25 Hz and 50 Hz) are extremely high and cannot be evaluated with the current available equipment. Conversely, the sheet resistance becomes measurable with a decreasing tendency related to the increment of laser power. The lowering of the sheet resistance is not as pronounced as obtained at 300 mm min\(^{-1}\) in the range of 5% to 50% laser power. In spite of this less pronounced trend, the sheet resistance reaches values as low as 25 Ω/sq at maximum laser power irradiated at the higher frequencies of 75 Hz and 100 Hz. These results could be attributed to the overlapping effect driven by an increase in the duty cycle of the laser. The latter will produce a greater overlapping effect. The profiles of sheet resistance obtained at laser speeds of 900 mm min\(^{-1}\) and 1200 mm min\(^{-1}\) show high measured values. These results reveal resistive laser irradiated surfaces that cannot be used as potential CCCs. These results are related to the possible agglomeration of rGO particles formed upon AA-based chemical reduction of the GO-based material. The agglomerated particles contribute to the overall conductivity of the laser-scribed surfaces. However, the agglomeration produces non-conductive spaces between the agglomerated particles. The spaces become conductive upon laser irradiation, however, their contribution to the overall conductivity is not as high as that produced by GO-based laser-irradiated surfaces. The laser-scriber speed of 300 mm min\(^{-1}\) is preferred over other higher laser speeds because it can produce models with accuracy on the order of hundreds of micrometres. The laser-scribing process executed at higher speeds still produce accurate and precise patterns. However, at the edges of the models some over-scribed areas can be found.

![intended pattern](image)

**Figure 3.45.** Loss of accuracy of the laser-scribed patterns caused by high laser-speed
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This effect could be produced from lost movement steps in the stepper motors operating at such high speeds. Figure 3.45 shows a laser scribed pattern with loss of accuracy caused by high speed operation. The model also revealed undesired short circuits between scribed regions. This phenomena can be corrected by increasing the current to feed the stepper motors. This last procedure can produce excess heating during the laser-scribing process and can reduce the lifetime of the electronics and components of the system.

With the previous detailed settings of the laser-scriber system, porous CCCs have successfully been obtained. These CCCs have been evaluated according their porosity and sheet resistance as the more important factors to be considered as potential candidates to be used in the construction of energy storage devices.

3.3.5 Silicon rubber attachment

The development of GO-based laser-irradiated CCCs has been reported in Section 3.3.4.6. However, the developed CCCs were attached to rigid surfaces such as glass or polyethylene terephthalate (PET). The glass substrate is neither flexible or stretchable. Likewise, the PET substrate can be bent as a flexible substrate but it cannot be stretched, limiting its use as stretchable surface to prepare CCCs. One of the most promising flexible and stretchable substrates used in soft electronics are silicone-based materials such as silicone rubber or polydimethylsiloxane (PDMS). In spite of their versatility as flexible and stretchable materials, their combination with conductive GO-based materials has been a challenging process because of the hydrophilicity of the silicone-based materials. One of the most accepted methods consists of combining the conductive materials directly on the surface of the silicone-based flexible substrate. This method is limited to the interactions between the surfaces in contact and requires additional elaborate pretreatment of the substrate surface such as ion implantation or UV-ozone treatment.\textsuperscript{82,83} The previous process required to bind the CCC and the flexible substrate can be long and complex and increase the fabrication process and the manufacturing time significantly. In the present research work, the adhesion between the GO-based material and a flexible substrate such as silicone rubber is replaced by a process performed after the laser-scribing process. The binding procedure takes place between the laser-induced graphene and the flexible silicone rubber. The process is attained by 3D printing layers of viscous silicone rubber on the laser-scribed surface. The extruded silicone rubber is cured to obtain a hardened self-standing, flexible, and stretchable material. The most interesting outcome of this procedure is that the laser-scribed surface is strongly attached to the hardened silicone rubber. Once the hardening or curing process is finished, the flexible silicone rubber can be easily peeled from the surface with the conductive laser-induced graphene attached to the flexible cured silicone rubber. This result could be attributed to the infiltration of the 3D-printed silicone rubber within the porous laser induced graphene. This statement is supported by morphology studies performed using SEM. Figure 3.48 shows the SEM micrograph of the porous laser-induced graphene (LIG) surface infiltrated by silicone rubber.
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**Figure 3.46.** 3D printed and laser-scribed models covered with silicone rubber

**Figure 3.47.** 3D-printed and laser-scribed models peeled off with cured silicone rubber from glass substrate

**Figure 3.48.** Transverse view of silicone-infiltrated laser-induced graphene
The infiltration takes place within the porous laser-induced graphene. The infiltration is produced with uncured silicone rubber, which can reach the voids and pores of the irradiated material. The hardening of the infiltrated silicone rubber can be produced by heat, a platinum-catalyzed curing process or other external curing agents such as UV radiation. There are several examples of commercial available silicone rubbers used for actuators and components for soft robotics. These latter are commonly delivered in a 2-part formulation, where one part has a catalyst and a second part contains the crosslinker. Once the two parts are mixed, the curing process starts and it is completed at room conditions in specific times provided by the manufacturer. In this research effort, Ecoflex and Dragon Skin (Smooth-On, USA) were used as elastomers (see Section A.1.2 for technical details). A UV-curable silicone rubber UV Electro 225-1 (Momentive Performance Materials, USA) was tested as well. All of the materials can be easily extruded by the customised 3D printers to construct bespoke models and components. The processing time of the silicone rubbers is one of the most important characteristics to consider for a rapid prototyping and manufacturing process. In this regard, the UV-curable silicone rubber becomes a better option considering its long pot life and fast curing compared to that of the 2-parts-based vulcanising process. This UV-curable silicone rubber does not cure until the blend is exposed to UV radiation. The curing process takes just seconds after the exposure to UV light making it ideal for a manufacturing and rapid prototyping line. The curing process was attained with a 3700 mW UV led (365 nm wavelength) mounted on the customised 3D printer. The UV light irradiation after the 3D printing of UV-curable silicone rubber allowed a smooth curing process that ensured the hardening of the infiltrated silicone rubber in a rapid prototyping construction process. This latter procedure promotes the interaction of the laser scribed material and the hardened silicone rubber.

3.3.5.1 Morphology determination of the flexible conductive current collectors

Flexible CCCs were achieved using the attachment process of laser-induced graphene to a flexible silicone rubber-based substrate. The sheet resistance keep its value after the laser-reduced-GO is transferred to the silicone rubber. However, the flexible CCCs show different mechanical properties at bending or stretching. These mechanical properties could be related to the laser parameters used during the laser irradiation process.

The irradiated PEO/GO-based material shows a plethora of sheet resistance values related to the laser parameters set during the laser-scribing process. The variations of the evaluated sheet resistance was reported in Section 3.3.4.6. However, further mechanical tests revealed that the laser-irradiated material at high laser power is not suitable for flexible CCCs.

Simple bending and stretching tests revealed different results for the flexible CCCs. Most of the silicone-attached laser-induced graphene-based CCCs irradiated at low and medium laser power showed mechanical stability. Conversely, the CCCs irradiated at high laser power were delaminated upon bending or stretching.
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The stretching tests allowed to find a good trade-off between sheet resistance and mechanical stability. In general, the models scribed at laser powers greater than 50% reveal delamination over bending or strain tests. This effect becomes more noticeable for the samples based on PEO/GO pretreated with ascorbic acid. This result could be attributed to zones of agglomerated pre-reduced GO subjected to laser irradiation. Over all, the mechanical stability is a critical variable to consider for a flexible CCC. This tempers the practical use of the CCC models laser-scribed at laser powers greater than 50%.

Additional investigation was carried out by SEM and EDX techniques. These latter helped to understand the morphology of the CCC attached to the silicone-rubber-based substrate. Figure 3.49 shows the SEM micrograph of the top view of silicone rubber-attached CCC laser-scribed at 15% laser power with a sheet resistance of 30 Ω/sq. This CCC is stable during bending and stretching tests performed in Section 6.3.6. Conversely, a silicone rubber-attached CCC irradiated at a laser power of 100% (Figure 3.50) shows a sheet resistance of 26 Ω/sq. However, this new sample is easily delaminated during bending or stretching processes.

Further qualitative analysis was obtained with Energy-dispersive X-ray spectroscopy (EDX). Figure 3.51(a) shows a depleted amount of oxygen on the surface of the attached laser-induced graphene to the silicone rubber-based substrate. Likewise, Figure 3.51(b) shows the presence of higher content of carbon on the same analysed area. These results could be attributed to the presence of laser-reduced GO-based material successfully attached to the silicone-based substrate. The analysis presented in this Section suggests that a flexible CCC with a low sheet resistance must show good mechanical stability upon bending or stretching processes. Amongst the laser-induced graphene-based samples, the lowest values of sheet resistance are attained with laser powers greater that 50%. However, the samples irradiated at those high laser power are not mechanically stable and delaminate during stretching and bending. A few samples were obtained with low sheet resistance at laser powers lower than 50% and were the best candidates

![SEM micrograph of the top view of silicone rubber-attached CCC laser-scribed at 15%](image-url)
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Figure 3.50. Silicone-attached laser-scribed model scribed at 100% indicating large flake-like structures on the surface

Figure 3.51. EDX micrographs of the laser-induced graphene attached to a Silicone rubber-based substrate: a) Oxygen content b) Carbon content.

as flexible and stretchable CCCs.

3.3.5.2 Silicon rubber curing time

The curing time of the silicone rubber is an important variable in the overall time in a rapid prototyping process. Hence, in this research work the decrease in the manufacturing process with the silicone rubber has been explored. As detailed before in Section 3.3.5, commercial silicone rubbers have different curing processes and hardening times. The silicone rubbers provided with two precursors require additional hardware to be processed. The 3D printer was adapted with a double head system (Figure 3.52) to attain a dual extrusion process. This setting permits the 2 precursors to be smoothly and alternately deposited. This controlled and alternate extrusion process allows a good combination of the 2 precursors, with the hardening process taking place in the times provided by the manufacturer of the silicone rubber precursors. Figure 3.53 shows a
3.3. RESULTS AND DISCUSSION

**Figure 3.52.** 3D printer customised with a dual-head system

resulting model after the 3D-printing and curing processes. The models obtained are flexible and stretchable as expected. When this process is used to bind the silicone rubber to the laser-induced graphene, the resulting flexible CCCs have good mechanical characteristics and sheet resistance comparable to those obtained with UV-curable silicone rubber. The fastest curing times for a

**Figure 3.53.** 3D-printed model using 2-precursors-based silicone rubber

2 precursors-based silicone rubber can vary from 10 to 15 min. The pot life is not a problem because the mixture takes place when a layer of the precursor B is extruded on top of a previously extruded layer of the precursor A. Despite the required curing times after 3D-printing the 2-precursors-based UV-curable silicone rubber was found to be the fastest manufacturing procedure in the fabrication process. The UV-curable rubber deposited with a 1-head system notably reduces the hardware requirements. Additional to that the curing process is faster compared to the 2-precursors-based silicone rubber. The curing process is possible with the use of a 365 nm
wavelength LED mounted in the 3D printer. This LED-based system irradiates a UV beam on top of the extruded UV-curable silicone rubber triggering a straight forward curing process. The process has been optimised so the UV LED travels the same paths previously described by extruders of the UV-curable silicone rubber during the 3D-printing process. This last procedure is carried out by setting the UV-Led system as one of the head extruders.

With this approach, the overall curing time is directly related to the 3D-printing time of the silicone rubber and does not depend on any additional curing or hardening time.

The techniques of 3D-printing, laser-scribing and UV-curing can be combined in one customised 3D-printer system. With this strategy, the hardware required, the cost and the overall manufacturing process time are all reduced.

3.3.6 Stretchability of the CCCs
The developed CCCs showed conductive properties evaluated by sheet resistance measurements presented in Section 3.3.4.6. Additional to the low sheet resistance, the prepared CCCs also present mechanical flexibility. This feature was evaluated by sheet resistance measurements performed after bending the CCCs in different angles as detailed in Section 2.2.4.2 of methods. Figure 3.54 shows the sheet resistance changes regarding the bending angle of the CCCs. It can be observed that the sheet resistance is not affected when the CCCs are subjected to different bending angles making the CCC ideal for applications for flexible electronics. Also, the mechanical stretchability of the CCCs have been evaluated by measuring the resistance of the developed devices at different strain percentages. Figure 3.55 shows the resistance obtained when the CCCs are stretched to 120% of its original length. The increase in the measured resistance does not change one magnitude with a strain of 60%. This result shows the potential application of the
3.4 Conclusions

In this research work we have demonstrated the feasibility of a rapid prototyping process to produce CCCs. The engineered hybrid method is a versatile and facile combination of 3D printing and laser-scribing to successfully attain a porous conductive material. The 3D-printing process allows a smooth deposition of the PEO/GO-based material with accurate fashion and precision. This deposition process was enabled by testing and optimising procedures of soft-materials printing and multi-material printing. The attained surfaces are flat and even enough to be laser-scribed to reduce the GO into laser-induced graphene. The latter is attained with an efficient and versatile one-step laser-engraving technique with optimised engineered and precisely controlled parameters of power, speed and frequency. This analysis successfully showed a qualitative interaction of the multiple laser-related variables involved in this strategy. This technique also endows the CCCs with accurate arbitrary shapes and patterns that can be performed in short periods of time on large surfaces. In addition, the process of tuning laser parameters promotes porous laser-induced surfaces upon laser irradiation.

After the 3D-printing and laser-scribing techniques were carefully and successfully developed and optimised, they have been used as a strategy for the production of porous and conductive materials.

The resulting material shows a porous structure upon SEM characterisation. This porosity successfully fosters an easy infiltration of commercially available UV-curable silicone rubber in CCCs as stretchable material for applications in energy storage, soft electronics and wearables. The potential use of the CCCs in the abovementioned fields is possible because the charge and discharge times of supercapacitors are in the orders of tens of seconds or minutes. These charge and discharge times can be attained with the developed CCCs.
the voids of the porous material. The processes were further optimised with a UV-curing unit with a UV-LED that efficiently cures the extruded and infiltrated UV-curable silicone rubber. This strategy completely secured a strong binding process between the laser-induced conductive material and flexible and stretchable silicone rubber. This aim was achieved by the UV-curing system mounted and adapted to the commercial 3D-printer.

The synergistic effect of the different stages of the developed process have produced a flexible and stretchable CCCs on a production line. This manner of fabricating the CCCs paves the way for a scalable manufacturing process to obtain specific designs. This production line promotes manufacturing to fulfill specific requirements such as bespoke devices with accurate shapes and patterns for applications in soft and flexible electronics, wearables and implantables.

Also the developed CCCs are established as a prototype for the next stages of this research. This prototyping is only possible as the models and their characteristics are highly reproducible, with lateral feature sizes on the order of 100 um. The attained accuracy is of notable importance as the models are used to evaluate new materials developed to interact with the obtained CCCs. Also, the developed method presents a simple manner to change variables to obtain required characteristics and features. In this regard, the CCCs will be evaluated as current collectors in the construction of 3D-printable flexible and stretchable energy storage devices.

The simplicity and low cost required in the manufacturing process paves the way for commercial scalability and a next generation of bespoke electronics and microelectronics for applications in wearables, flexible sensors and implantables.

3.5 References


CHAPTER 3. SYNTHESIS AND PREPARATION OF CONDUCTIVE CURRENT COLLECTORS


3.5. REFERENCES


(67) S. Tagliaferri; A. Panagiotopoulos; C. Mattevi Materials Advances 2021, 2, 540–563.

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4.1 Abstract

Flexible Electrical Energy Storage Devices (EESD) have attracted high attention because of their remarkable advantages such as flexibility, light weight, geometric variety and mechanical robustness. These properties promote their application in portable and wearable electronics, soft electronics, medical devices, and internet of things tags. The construction of these devices demands not only a flexible electroactive material, but also a rapid prototyping process for the manufacturing process. This chapter details the fruitful scientific efforts to fulfill these requirements by using an environmentally friendly and easy to synthesise electroactive polymer called Polyaniline (PAni). This polymer is successfully synthesised and processed to obtain a 3D-printable electroactive blend. The latter is effectively optimised to obtain competitive values of specific capacitance in a 3D-printed and laser-scribed flexible energy storage device.

4.2 Introduction

Smart and multifunctional flexible devices are demanded in different shapes and designs. They are constructed for applications in wearable electronics, soft and flexible robotics and implantable electronics. Among these flexible devices, energy storage devices have attracted great interest from both industrial and academic sectors because of their fundamental application in portable electronics. The current requirements is this areas demand devices with the capability to accommodate to the arbitrary shapes and deformations of the human body. Also there is a growing amount of techniques to produce flexible energy storage devices incorporating environmentally friendly inorganic and organic materials. These techniques also promote strategies to develop
safe materials for their use in wearable electronics or devices that are in contact with the human body in a safe fashion.\textsuperscript{8–12}

Another important aspect to consider in the fabrication of flexible energy storage devices is the specific capacitance per unit of area or volume of a prototype. This is a key variable in supercapacitor design and prototyping. Likewise, the rate to deliver the stored energy into a load to perform work is also a critical factor in the design of energy storage devices. For this reason the variable of amount of energy that a device can supply is quantified by measuring the specific capacitance and energy density of this device or material. In a similar fashion, the rate that a supercapacitor can deliver the stored energy determines its power density as explained in Section 1.1.1. A good trade-off between these values should be found to obtain an effective energy storage device. However, many different applications can require either higher energy density or higher power density. In this regard, carbon-based materials such as the laser-induced graphene previously developed in this research effort, are suitable to store and deliver small amounts of energy in short periods of time. This stored energy can be increased combining the porous laser-induced material with an electroactive material. The latter stores larger amounts of energy through redox reactions that take place at a molecular level on its surface. This higher capacity to store energy and the speed of delivering the stored energy in the electroactive material can be attained by the synergistic contributions of a porous conductive current collectors (CCCs) and a electroactive polymer such as PAni.\textsuperscript{13,14}

The requirements of energy density, power density and flexibility have been considered in this scientific effort to obtain a suitable electroactive material. This chapter details the development of a PAni-based electroactive material suitable for the fabrication flexible and stretchable supercapacitor prototypes. This material has been optimised to obtain competitive values of specific capacitance. The attained enhanced material is combined with a polymer matrix to explore its use as an extrudable material that can be 3D-printed in a manufacturing line. The obtained blends are further enhanced to obtain better 3D-printable electroactive materials with higher performance for energy storage devices. These efforts successfully resulted in an enhanced 3D-printable material free of polymer matrices. This material can be directly used in the manufacture of flexible energy storage prototype devices. The research carried out in this chapter also demonstrated the feasibility of the combination of the developed electroactive material with the developed CCCs and a suitable electrolyte to produce the required prototypes.

4.3 Results and discussion

4.3.1 Synthesis of PAni

Nowadays there are several synthetic routes towards electroactive PAni-based materials.\textsuperscript{15–18} In particular, the synthesis of PAni has been performed by simple polymerisation in aqueous solutions. One conventional chemical route is oxidative polymerisation of the aniline monomer in
the presence of a strong acidic environment and initiated by the addition of an oxidant such as ammonium persulfate (APS). In this research work, this mentioned synthetic route was initially explored to obtain the electroactive polymer that can be utilised as an electrode material for energy storage devices. Many authors such as Pan et al.\textsuperscript{19} and Dou et al.\textsuperscript{20} demonstrated the easy synthesis of PAni gels. Briefly, in these synthesis routes, the acidic environment is provided by the presence of acids such as phytic acid or amino trimethylene phosphonic acid in aqueous solution. The obtained solution is mixed with aniline monomer to form a clear solution A. The initiator (APS) is dissolved in water to form solution B. Solutions A and B are cooled down to 4°C, and the polymerisation process takes place after mixing the A and B at 4°C (Figure (4.1)). In total, the polymerisation process is completed approximately 5 minutes after mixing A and B. Details of this synthesis method can be found in Section 2.1.3.1. In this synthesis route, the acid

\[
\begin{align*}
\text{Phytic acid} & \quad + \quad \text{aniline} \\
\text{Deionised Water} & \quad + \quad \text{Ammonium persulfate} \\
\text{Solution A} & \quad \rightarrow \\
\text{Solution B} & \quad \rightarrow \\
\end{align*}
\]

acts not only as a gelator but also as a dopant of the resulting PAni material. Previous studies reveal the possibility that the acid star-like molecules interact with several PAni chains by protonating their amine and imine groups.\textsuperscript{19,20} The resulting material is a PAni porous network. The morphology studies of the resulting materials were performed by SEM experiments. The obtained SEM images (Figure 4.2(a) and Figure 4.2(b)) show the morphology of a rough surface of the synthesised PAni. The micrographs also reveal a porous 3dimensional network-like surface characteristic of PAni synthesised using the previously detailed method.\textsuperscript{21,22} To further support these preliminary results, the specific surface area of the synthesised PAni is measured and calculated using the Brunauer–Emmett–Teller method (BET). The results of the surface-area investigation experiments show a porous material with a surface area of 40 m\textsuperscript{2} g\textsuperscript{-1} and a 3.4 nm peak pore size distribution. This latter characteristic makes the polymer a good candidate to be infiltrated with a liquid or gel electrolyte for energy storage purposes.\textsuperscript{19,20,23,24}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.1.png}
\caption{PAni synthesis route using phytic acid (PA).}
\end{figure}
CHAPTER 4. SYNTHESIS OF ELECTROACTIVE MATERIAL

The obtained polymer produced with this method was then further processed to obtain additional porosity. The post-processing procedure was carried out using liquid nitrogen-induced ice-templating and freeze-drying strategies. The detailed method used for ice-templating the PAni-based material can be found in Section 2.1.3. The morphology studies of this new material were performed by SEM. Figure 4.3 shows the voids created by the ice-templating process. The voids have a parallel vertical channel-like shape in the ice-templating direction with a size of approximately 10 µm. The pore size of this new sample characterised by BET showed the same pore distribution compared to the original samples without an ice-templating treatment. These latter results revealed that the ice-templating step was not enhancing the porosity of the PAni-based material.

The described method can be also modified with the introduction of nanofillers to enhance the
strength of the polymer backbone. This addition of nanofillers, such as graphene oxide (GO) and reduced graphene oxide (rGO), is a well known procedure to provide mechanical stability to the PANi chains\textsuperscript{27–29} In this regard, a GO aqueous solution (5 mg ml\textsuperscript{-1}) was used instead of deionised water in the preparation of the solution A. The polymerisation process was carried out following the same procedure previously described i.e. by mixing A and B to achieve a PANi/GO-based material. To obtain a PANi/rGO-based material further post-processing steps were performed using ascorbic acid as a reducing agent of the GO component in the PANi/GO-based material as described in Section 2.1.3.1.

Additional to the synthesis method of mixing A and B solutions, a second strategy was carried out to obtain a PANi-based material. This procedure included the use of different acids rather than phytic acid or amino trimethylene phosphonic acid. The latter acids were replaced by camphorsulfonic acid (CSA) and dodecylbenzenesulfonic acid (DBSA), well known dopants for PANi\textsuperscript{30–33} The synthesis method (Figure 4.4) consists of the polymerisation of the aniline monomer in presence of an acidic aqueous blend of CSA and DBSA. Briefly, the aniline monomer is combined with CSA powder and liquid DBSA at 4°C. An APS aqueous solution is slowly added drop-wise onto the previously obtained slurry and under constant stirring. Finally the reaction is completed after 4 hours of constant stirring at 60°C and left to cool down to room temperature. Compared to the previous synthesis approach, this method also includes the use of APS as an initiator of the polymerisation process. The resulting product is a 3D-printable blend with viscosity properties that allows a controlled extrusion process using the customised 3D-printers. This processability for extrusion purposes is achieved because of the presence of remaining DBSA upon completion of the polymerisation process. This result can be attributed to the excess of DBSA and CSA used in the synthesis procedure. This excess of acid ensures the acidic environment and doping effect required during the polymerisation of the aniline monomer for the formation of

\begin{center}
\includegraphics[width=\textwidth]{figure4.4.png}
\end{center}

**Figure 4.4.** PANi synthesis route using CSA and DBSA.
CHAPTER 4. SYNTHESIS OF ELECTROACTIVE MATERIAL

PAni in its conductive state. The extra amount of DBSA forms a viscous material or matrix to hold the obtained PAni polymer chains. This latter characteristic is particularly important to obtain a 3D-printable conductive polymer suitable for energy storage purposes.

The described strategies to synthesise an electroactive material can be applied for the construction of energy storage devices. The selected approach depends on the technical challenges and requirements encountered during the building process. In this scientific effort, many factors referring to the polymer processability have been identified during the prototyping process of flexible energy storage devices using a PAni-based electroactive material. These aspects are related to the suitability of the PAni-based blend to be 3D-printed. Also, the resulting adhesion between the synthesised electroactive material and the CCCs is a critical challenge during the manufacture process. At the same time the electroactive material must be smoothly combined with a suitable gel electrolyte for energy storage purposes. Taking all of this variables into account, the next section (Section 4.3.1.1) details the ways to address the prototyping requirements. Also, the procedures and strategies to obtain competitive values of capacitance of the prototypes are discussed.

In summary, the two described methods are potential routes to obtain an electroactive material suitable for energy storage purposes. These two different synthesis routes are particularly chosen because they ease the procedures to obtain a PAni-based electroactive material. The synthesised materials are further characterised and evaluated along the next stages of this research work to obtain a suitable electroactive material for rapid prototyping of flexible energy storage devices.

4.3.1.1 In situ polymerisation

The synthesis routes to obtain PAni-based electroactive materials can be chosen depending on the application of the material. The initial efforts to obtain an electroactive material suitable for supercapacitors included the combination of a PAni-based material with flexible conductive carbon cloths. In this regard the phytic acid-based synthesis with an easy combination of two liquid precursors can be performed on the surface of treated carbon cloths. Using this synthesis route, the carbon cloths were prepared by a UV-ozone treatment to functionalise their surface into a hydrophilic material. After this functionalisation step, the treated carbon cloths can be smoothly coated by the PAni-based material. This strategy can be performed by preparing the solutions A and B and have them ready for combination. These precursor solutions are mixed following the method briefly described in the previous section (Section 4.3.1) and the carbon cloths are immediately immersed into the resulting blend to quickly soak them before the mixture turns into a polymerised product. The carbon cloths are pulled out after a very short soaking step of 10 seconds and the polymerisation process takes place on the surface of the conductive threads of the carbon cloths coated with the reacting mixed precursors. The morphology characterisation of the PAni-treated carbon cloths is performed by SEM and further supports that PAni-based material is obtained by the in-situ polymerisation of the aniline monomer on the surface of the conductive carbon cloth threads. The SEM image in Figure 4.5(b) shows the PAni-based coral-
like nanofibers growing from the conductive carbon thread. This result reveals the conductive fabric successfully coated with the electroactive material. Also, the close contact of the PANi-based material and the carbon thread promotes a conductive connection between these two materials. In contrast, the Figure 4.5(a) shows the surface of a plain carbon cloth thread before being immersed into the PANi precursors blend. A second approach was explored by immersing UV-ozone pretreated carbon cloths in solutions A and B sequentially. The carbon cloth is first immersed into the aniline/phytic acid aqueous precursor A. Then, the soaked carbon cloth is immersed into the precursor APS-based aqueous solution and then taken out. Once again, the polymerisation process takes place on the surface of the carbon cloths threads soaked sequentially in the precursors A and B. The resulting coating is similar to the one obtained by immersing the carbon cloth in the blended mixture of solutions A and B. The morphology of the resulting PANi-coated carbon cloth thread can be observed in the SEM image of Figure 4.6. Compared with

![Figure 4.5](image1.png)

**Figure 4.5. SEM images of carbon cloth thread:** a) plain carbon cloth thread b) PANi-coated carbon cloth thread.

![Figure 4.6](image2.png)

**Figure 4.6. SEM image of a carbon cloth coated sequentially with A and then B liquid precursors**

the previous coating method with a mixed blend of A and B precursors, the carbon cloth threads
coated sequentially in A and then in B solutions has some uncoated areas. This result could be attributed to the precursor A being washed during the immersion procedure into the precursor B. The in-situ polymerisation procedures cannot be performed by 3D-printing the phytic acid-doped PAni precursors. These liquid solutions can not be used by the 3D-printers due to their low viscosity. This latter characteristic hampered the potential use of the A and B solutions for a controlled extrusion process.

In addition, the previous in-situ polymerisation methods cannot be used to synthesise CSA/DBSA-doped PAni on the surface of the threads of the carbon cloths. The synthesis procedure used to prepare the CSA/DBSA-doped PAni does not include liquid precursors that can be potentially used to soak the carbon cloths. The CSA/DBSA-doped PAni precursors are slurrys, or viscous blends that require different treatment to obtain the polymerised electroactive material. Despite the CSA/DBSA-doped PAni materials not being suitable for in-situ polymerisation, this electroactive PAni-based product is appropriate for 3D-printing procedures on the surface of conductive current collectors. The use of the CSA/DBSA-doped PAni as a feasible extrudable material is analysed in Section 4.3.4

4.3.2 Oxidation State of the PAni-based electroactive material

A conductive redox electroactive material is a critical component in the fabrication of energy storage devices. A redox-active polymer such as PAni is used as an electrode material to increase the energy density of a supercapacitor. This energy density can be attained by the energy storage process facilitated by the contributions of conductivity and redox-activity of the electroactive polymer. The overall capacitance of an energy storage device is the result of two contributions: the electric double-layer capacitance (EDLC) and the pseudocapacitance. The first takes place in the porous surface of the electrodes and is the 1-10% of the overall capacitance. The second is the result of redox-reactions in the electroactive polymer with a 90-100% capacitance contribution.

In both cases the electronic conductivity during the energy storage process is provided by the CCCs. The latter transport the charges from the power source to the electrodes and from the electrodes to the load. However, during the energy storage process, the pseudocapacitive redox reactions take place with the molecules of the electroactive material. This energy storage process involves charge transfer phenomena happening not only at the surface of the electroactive material electrodes but also within the bulk material. In this regard, the charges move to reach the electroactive sites in the bulk polymer. This charge movement is attained by the intrinsic conductivity of the electroactive polymer. For this reason the use of a conductive electroactive polymer is critical to obtain the expected capacitance. PAni is a good candidate to fulfill these requirements. To obtain a PAni-based material with these conductive properties, the synthesis process must endow the electroactive polymer with desired characteristics. The conductive state of PAni is achieved by protonation of the imine groups of the polymer chains. This latter process can be achieved through the synthesis path towards the phytic acid-doped PAni, where the
molecules of the acid can interact and protonate several polymer chains upon polymerisation of the aniline monomer. The oxidation state of the obtained phytic acid-doped PANi material was characterised by Ultraviolet-Visible-near-IR Spectroscopy (UV-Vis-NIR) and Fourier transform infrared spectrometry (FT-IR). The samples for the UV-Vis-NIR and FT-IR characterisations were prepared as detailed in Section 2.2.2.1 and Section 2.2.2.1 respectively. The resulting UV-Vis-NIR spectra (Figure 4.7) shows the characteristic peaks of the emeraldine salt oxidation state of PANi at 340 nm, 400nm and 800nm, attributed to the $\pi-\pi^*$, polaron-$\pi^*$ and $\pi$-polaron transitions respectively. Compared to the UV-Vis spectra of PANi, PANi/GO and PANi/rGO materials, the PANi-based material spectra does not present a noticeable difference, which could be attributed to the higher content of PANi compared with the GO or rGO supporting material.

The FT-IR characterisation (Figure 4.8) reveal the spectra for the PANi/GO, PANi/rGO and PANi-based materials. The obtained data support that the obtained polymer is in the emeraldine salt form with two characteristic peaks located close to 1570 cm$^{-1}$ and 1490 cm$^{-1}$ corresponding to
CHAPTER 4. SYNTHESIS OF ELECTROACTIVE MATERIAL

the aromatic rings stretching vibrations of the quinoid (Q) and benzenoid (B) units respectively with comparable intensity.\textsuperscript{16,38,39}

The UV-Vis-NIR and FT-IR characterisation experiments also were performed for the CSA/DBSA-doped PAni material. The resulting UV-Vis-NIR spectra of this PAni-based blend (Figure 4.9) show similar absorbance results compared to the UV-Vis-NIR spectra of the phytic acid-doped PAni. The peaks found for the CSA/DBSA-doped PAni samples could be attributed to the emeraldine salt oxidation state of PAni. These peaks are located from 340 nm to 400 nm and around 800 nm, and can be assigned to the transitions from $\pi$ band to $\pi$ band, polaron band to $\pi$ band, and $\pi$ band to polaron band, respectively.\textsuperscript{40,41} These results are independent of the change in the ratio of the DBSA with respect to the CSA used in the synthesis process.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig4_9.png}
\caption{CSA/DBSA-doped PAni UV-Vis-NIR spectra}
\end{figure}

Similarly, the FT-IR spectra of the Figure 4.10 show the presence of peaks close to the 1550 cm\textsuperscript{-1} band and 1490 cm\textsuperscript{-1} band corresponding to the quinoid (Q) and benzenoid (B) units respectively. However, the latter are not the only contributions close to these bands: there is a peak close to the band of 1450 cm\textsuperscript{-1} that could be related to the C=C stretching in the benzene rings. This peak is present in all the samples where the DBSA was used in excess in the PAni synthesis.

The peaks observed at 2958 and 2855 cm\textsuperscript{-1} can be attributed to the (C-H) stretching vibration in benzene ring and aliphatic chain respectively. These peaks are noticeable in the PAni samples containing excess of DBSA.

The characterisation techniques carried out on the PAni samples showed a resulting acid-doped polymer. These results are independent of the synthesis method utilised and the acid precursors used to prepare the polymer. In addition, the attained material is an electroactive product with optoelectronic properties that promote its use for energy storage purposes.
4.3. RESULTS AND DISCUSSION

4.3.3 Electroactive material attachment to the current collectors

The energy storage mechanism in the supercapacitor prototypes is achieved by EDLC and pseudocapacitance. Both phenomena rely on proper contact between the synthesised electroactive material and the CCCs during the manufacturing process and the mechanical tests. At the same time the electroactive material must be smoothly combined with a suitable gel electrolyte for energy storage purposes. Taking these variables into account, the synthesised PAni-based electroactive material was evaluated by combining the polymer with the conductive carbon cloths. As discussed in Section 4.3.1.1, the precursors A and B can be deposited on the surface of the carbon cloths by two methods. The first is by a fast soaking of the carbon-based fabric in the blend resulting of mixing these A and B solutions immediately after mixing the precursors. The second method is a sequential soaking process where the carbon cloths are first immersed in the A and then in the B solution. In both cases polymerised material can be observed on the surface of the threads of the carbon cloths.

The carbon cloths coated with the polymerised material were left at room temperature to allow the solvent to evaporate. When the carbon cloths were bent by hand some of the material dislodged from the surface. SEM characterisation revealed that the bending process caused the PAni-based material to crack and break (Figure 4.11).

This cracking and breaking process took place in both the sample prepared by immersing the carbon cloth in the blend of A and B precursors, as well as the sample prepared by immersing the carbon cloth sequentially in A and then in B precursors.

The mechanical issue of the phytic acid-doped PAni material cracking and breaking after simple bending tests hampered the use of this electroactive polymer in the construction of flexible
supercapacitor prototypes. However, additional scientific efforts were conducted to construct standard rigid models for capacitance evaluation of the synthesised electroactive material. During the manufacture of the supercapacitors the electroactive material deposited on the surface of the carbon cloths became flexible. This result could be attributed to the electroactive polymer sample being in contact with an aqueous electrolyte. This latter provides moisture to the PANi material keeping it flexible. These procedures allowed the evaluation of the capacitance of the PANi, PANi/GO and PANi/rGO-based materials evaluated by cyclic voltammetry. The results of this latter characterisation technique are detailed in the Chapter 5 of this thesis.

In the case of the CSA/DBSA-doped PANi, the attachment of the electroactive material was tested by 3D-printing the electroactive polymer on the surface of the CCCs. This extrusion procedure allows a smooth deposition of the CSA/DBSA-doped PANi material directly on the surface of the CCCs. The 3D-printing process of the CSA/DBSA-doped PANi-based inks is presented in Section 4.3.4.

Once the CSA/DBSA-doped PANi-based is deposited on the surface of the CCCs an adhesion process takes place. The latter was evaluated by sessile and pendant drop methods with a drop shape analyser as described in Section 2.2.2.2.

The sessile drop method (SDM) and pendant drop method (PDM) experiments were conducted to find the surface free energy (SFE) of the CCCs, as these will be the substrate for the CSA/DBSA-doped PANi material upon 3D-printing of the electroactive blend. In addition, the SFE of a suitable gel electrolyte is investigated as the CSA/DBSA-doped PANi-based material will be directly in contact with this electrolyte-based material following a layer-by-layer architecture in the prototyping of the supercapacitor device as detailed in Section 3.3.2.1 of this thesis.

The SFE can be used as the first part in the calculation of the work of adhesion (WA) to
evaluate the binding process between the surfaces in contact. The second part required to complete the WA calculation is the surface tension (ST) of the materials in contact. The ST is also obtained by SDM and PDM experiments. The WA provides the quantification of the physisorption related to the hydrophobicity and hydrophilicity of the materials. These latter characteristics of the materials in contact can influence the capacitance of a supercapacitor prototype.

The WA also provides good insight into the adhesion behaviour of the CSA/DBSA-doped PAni-based material when the DBSA:CSA ratios are modified in the polymer synthesis.

![Figure 4.12](image)

**Figure 4.12.** Work of adhesion characterisation: a) surface free energy of the CCCs and gel electrolyte and b) surface tension of the CSA/DBSA-doped PAni material.

Figure 4.12(a) shows the polar contribution ($\sigma^P$) and disperse contribution ($\sigma^D$) of the SFE’s of the CCCs and the gel electrolyte. The polar and disperse parts are represented by orange and blue bars, respectively, in the graph. In the case of the CCCs, the low value of $\sigma^P$ could be attributed to the predominant presence of laser-induced graphene in the CCCs. This result is consistent with previous reports of a dramatic decrease of the polar component of a GO-base material upon the deoxygenating process to obtain rGO. Furthermore, the disperse $\sigma^D$ contribution of the SFE of the CCCs is significantly greater compared with the $\sigma^P$ contribution. This latter result could be related to the wetting properties of the GO upon reduction. This latter process produced an increase in the $sp^2$ carbon atom content and a decrease in the oxygen content. So, the difference between the $\sigma^P$ component and the $\sigma^D$ component could be attributed to the disperse $\sigma^D$ contribution being an increasing function of the percentage of $sp^2$ carbon atoms of the rGO. The $\sigma^P$ component, despite its small value (0.12 mN m$^{-1}$), can be attributed to the hydrophilicity of the minor presence of ether groups of the PEO and remaining oxygen functionalities of GO in the PEO/GO-based precursor of the CCCs. The slightly greater $\sigma^D$ component (3.10 mN m$^{-1}$) can be explained as the result of different forces rather than the polar forces that arise from straightforward electrostatic interactions of charged or dipolar molecules. These different forces
are charge-fluctuation forces, electrodynamic forces, and induced dipole-induced-dipole forces. They are produced by non-polar atoms or non-polar molecules which are in average neutral but with finite instantaneous dipole moments. These latter generate an electric field that polarise any proximate neutral atom or molecule inducing a dipole moment on it. The original dipole and the induced dipole interact with each other by an attractive force with a finite time of duration.\textsuperscript{45}

In the case of the gel electrolyte, a SFE with considerable greater magnitude can be observed. This larger SFE can be related to an increased contributions of the $\sigma^D$ and $\sigma^P$ parts. The $\sigma^D$ (25.93 mN m$^{-1}$) contribution can be related to the long alkyl present in the PVA chains. The $\sigma^P$ (25.64 mN m$^{-1}$) can be attributed the result of larger hydrogen bonding produced for the high water and acid content in the hydrogel electrolyte. The values of the $\sigma^D$ part and the $\sigma^P$ are nearly balanced to result in a greater magnitude SFE for the gel electrolyte compared with the one of the CCCs.

The PAni-based blends were subjected to a similar analysis using PDM and SDM characterisation to obtain the ST of the polymer-based mixes. Figure 4.12(b) shows the ST trend of the PAni-based material when the ratio of the DBSA:CSA is varied from 0.5:1 to 2:1. The ST of the PAni-based material is greater compared with that of the CCCs and this applies for all DBSA:CSA ratios. The $\sigma^D$ part and the $\sigma^P$ part have a quite balanced contributions to the total ST of the PAni-based samples. The presence of water in the blends favour water-water hydrogen bonding promoting a greater $\sigma^P$ contribution. Likewise, the greater disperse contribution $\sigma^D$ attributed to instantaneous dipole interactions and van der Waals forces is produced by the presence of the DBSA. This latter result can be related to the DBSA acting as a surfactant in the PAni-based blend.\textsuperscript{46}

Despite the $\sigma^D$ part changing with the DBSA:CSA ratio, the $\sigma^P$ part remains predominantly constant. This could be the result of the presence of the surfactant molecules and their interfacial adsorption causing disruption of the hydrogen bonding in water producing a decrease in the polar contribution. However, the described $\sigma^P$ reduction can be compensated by the increased acid-base interaction of the Brønsted acid-surfactant leading to a total $\sigma^P$ mostly remaining constant.\textsuperscript{46,47} Also, the increasing ratio of BDSA:CSA rises the availability of DBSA during the synthesis of PAni. The greater amount of DBSA could replace the CSA as dopant of the PAni chains. In this case there would be more free CSA in the resulting polymer blend. The contribution of the free CSA to the polar part of the SFE could provide a possible explanation to the $\sigma^P$ remaining predominantly constant. This findings are consistent with the results reported by Farrokhzada et al.\textsuperscript{48} where DBSA is found to contribute to the disperse part and CSA to the polar part. Once the $\sigma^P$ and $\sigma^D$ contributions of the SFE and the ST are available, the WA can be calculated. The calculations were performed following the procedure detailed in Section 2.2.2.2. The resulting WA of the interfacial energy shows the physisorption between the surfaces in contact. This applies for the combinations [PAni-based blends - CCCs] and [PAni-based blends - PVA-based gel electrolyte]. Figure 4.13 shows a decreasing trend of the WA related to the increase of the DBSA:CSA ratio.
4.3. RESULTS AND DISCUSSION

This result could be attributed to the previously described trend of the $\sigma^P$ and $\sigma^D$ contributions. The $\sigma^P$ part of the PAni-based inks kept mostly constant with the increase of DBSA:CSA the ratio. At the same time the $\sigma^D$ decreased causing that the $\sigma^P/\sigma^D$ ratio of the PAni-inks increases. This ratio is particularly important to understand the trend found for the WA of the PAni-inks and the materials in contact with them. The polar part of the ST or SFE of a particular material are likely to interact with the polar part of the material in contact. In the same manner, the disperse contribution of the material will interact with the disperse part of the material in contact. Since the polar contribution stays mostly constant with the change in the DBSA:CSA ratio, the interactions and adhesion forces between the $\sigma^P$ part of the CCCs and the $\sigma^P$ part of the inks keep likewise constant. In the same manner, because the $\sigma^D$ of the PAni-based inks decreases, then the interactions between this disperse part and that of the CCCs drops as well. The overall result is a decreasing trend in the WA.

A similar WA trend can be observed for the contact interactions between the PAni-based inks and the gel electrolyte. The behaviour of the WA is a decreasing function of the DBSA:CSA ratio of the polymer blends. This result is expected as the variations in the WA will rely on the interactions between the disperse contributions of the materials in contact. The outcome is also consistent with the fact that the polar part contributions in the PAni-based blends keeps mostly constant.

These results of WA are consistent with the outcomes in the capacitance obtained from the supercapacitor prototype devices constructed with the electroactive polymer inks. These outcomes are detailed and further analysed in the Chapter 7 of this research work.

**Figure 4.13.** WA of the interfacial energy between the surfaces of the PAni-based blends and the surfaces of the CCCs and the PVA-based gel electrolyte
CHAPTER 4. SYNTHESIS OF ELECTROACTIVE MATERIAL

4.3.4 3D printing of PAni-based inks

The deposition of the PAni-based inks has been performed with the customised 3D-printers to extrude viscous materials. To attain a smooth extrusion process, the 3D-printable inks should have a viscosity in the range supported by the customised 3D printers. As mentioned in Section 3.3.2.2, the 3D-printers can extrude materials depending on their viscosity. The extrusion capability of the 3D-printers was studied in a previous investigation performed in the research group. The results obtained showed that any liquid or paste-like material with a viscosity between 10 Pa·s and 500 Pa·s can be dispensed by the customised 3D-printers.50 In this regard, research efforts have been devoted to tune the extrudability of PAni-based blends.

The first approach included the use of the phytic acid-doped PAni. This material was used after purification drying and grinding to obtain phytic acid-doped PAni powder as detailed in Section 2.1.3.2. The resulting dark green powder was mixed (starting from 6 wt% and increasing to 8 wt%) with an aqueous polymer solution of high molecular weight PEO (1 000 000 Da) with a 6 wt% content in the overall blend. The amount of PEO as a polymer matrix was chosen following the previous experience with PEO/GO-based blends analysed in Section 3.3.1.1. This PEO/GO-based blend demonstrated its feasibility as an extrudable ink. However, when using PAni-based powder as a nanofiller, the PEO-based polymer matrix hindered the capacity of the PAni-based particles to get in contact with each other and with the gel electrolyte or the CCCs. One way to avoid this phenomenon could be the reduction of the PEO in the overall blend to decrease the presence of the polymer matrix between the adjacent PAni-based particles. However, the decrease in the PEO content affects the viscous properties of the blend impeding its extrudability by the customised commercial 3D-printers. Likewise, an alternative using a PVA-based ink was explored by using the PVA as a polymer matrix to hold the particles of the electroactive PAni-based material. A similar result was obtained in terms of having the PAni-based particles separated by the PVA-based polymer matrix. Despite the high molecular weight of the PVA, the amount of the polymer matrix required to attain an extrudable blend hampered the contact between the particles of the electroactive PAni-based material. As an option to obtain contact between the PAni-based material, the content of the electroactive material was increased. Unfortunately the latter approach caused the PAni-based particles to agglomerate causing clogging in the 3D-printer nozzles during the extrusion process.

To avoid the introduction of a polymer matrix to hold the particles of the phytic acid-doped PAni material, an alternative approach was explored. This new strategy was attained by synthesising CSA/DBSA-doped PAni as an electroactive polymer for energy storage purposes. The resulting PAni-based material was not only characterised and showed to be in the conductive oxidation state, but also demonstrated the appropriate viscosity properties. The latter characteristic promoted the potential use of the electroactive PAni-based blend as a potential ink to be smoothly extruded by the customised commercial 3D-printers. The synthesis path discussed in Section 4.3.1 included the variation of the ratio of the dopant acids to enhance the properties of
4.3. RESULTS AND DISCUSSION

The variation of the DBSA:CSA ratio not only influenced the WA which results were detailed in the previous Section 4.3.3 but also modified the viscosity of the resulting blends. This characteristic is the utmost property that determines the required parameters to obtain a controlled extrusion process of the blends. Additional to that, the viscous characteristic of these 3D-printable materials remained after the extrusion process. This effect allowed the CCCs to be bent and stretched with no any noticeable detachment effect. The characterisation of the flexibility and stretchability of the CSA/DBSA PAni-based supercapacitors is detailed in the Chapter 6 of this thesis.

The initial viscosity of the blends was evaluated by rheology experiments. This evaluation allowed to have an insight of the initial conditions required to obtain a smooth 3D-printing of the PAni-based blends. Additional to that, two aspects of the blends can be evaluated by the rheology characterisation, first, the variation of the viscosity of the blends upon DBSA:CSA ratio changes and second, the response of the viscosity of the PAni-based inks related to the forces applied during the extrusion processes. A detailed analysis of these aspects is presented in Section 4.3.4.1.

4.3.4.1 Rheology of the inks

The rheology experiments of the inks can reveal the classification of the blends as Newtonian or non-Newtonian. The rheological characteristics of the inks can be evaluated by their shear viscosity as a distinctive feature for each case. Briefly, a constant shear viscosity independent of the stress state and velocity of the flow, denotes a Newtonian fluid. Conversely, a changing shear viscosity related to the variations of the force of speed of the fluid can represent a non-Newtonian fluid. In both cases the functions of the shear rate can be used to determine the behaviour of the blend under different circumstances of flow or velocity.\textsuperscript{51,52}

The prevailing amount of DBSA is the result of the excess of the protic acid during the synthesis process. The availability of the excess DBSA during and after the synthesis procedures could be the reason that a homogeneous CSA/DBSA-doped PAni blend is attained. The homogeneity of the PAni-based blends is a characteristic that does not seem to depend on the DBSA:CSA ratio.

Figure 4.14 shows the viscosity data as a decreasing function of the increment of the shear rate. This non-Newtonian shear-thinning behaviour is common for all the CSA/DBSA-doped-PAni blends. These result could be attributed to the excess of DBSA acting as a predominant matrix of the blends.

For a rapid prototyping process the speed of the extrusion of the materials is one of the most important factors. To keep consistency with the previous results obtained for the PEO/GO-based inks and reported in Section 3.3.2.3, the extrusion speed is calculated to 3D print a small section of 5 cm\textsuperscript{2} with a thickness of 0.1 mm. The model is considered to be extruded in 5 minutes (600 s). With these parameters the velocity can be obtained by using Equation 3.4 and Equation 3.5.
Briefly, the volume to be extruded with the model dimensions is:

\[ v = \text{length} \times \text{width} \times \text{height} \]

\[ v = 50 \text{ mm} \times 50 \text{ mm} \times 0.1 \text{ mm} \]

\[ v = 250 \text{ mm}^3 \]

the volumetric flow calculated to dispense this volume in 600 s is:

\[ Q = \frac{250 \text{ mm}^3}{600 \text{ s}} = 0.42 \text{ mm}^3 \text{ s}^{-1} \]

considering a standard 400 µm diameter nozzle, the speed of the ink flow can be determined:

\[ V = \frac{Q}{\pi r^2} = \frac{0.42 \text{ mm}^3 \text{ s}^{-1}}{\pi (0.2 \text{ mm})^2} = 3.32 \text{ mm s}^{-1} \]

These previous results can be used to calculate the variation of pressure \( \Delta P \):

\[ \Delta P = \frac{8\eta LV}{r^2} = \frac{8\eta \times 11 \text{ mm} \times 3.32 \text{ mm s}^{-1}}{0.2^2 \text{ mm}^2} \]

Then \( \Delta P \) can be expressed as a function of the viscosity:

\[ \Delta P = 7294.6\eta \]

\[ \text{Figure 4.14. Viscosity as a function of shear rate of CSA/DBSA-doped PANi extrudable inks.} \]
Additional to that, the shear rate of the PANi-based inks can be calculated accounting the non-Newtonian characteristic of the blends:

\[
\dot{\gamma} = \frac{4Q}{\pi r^3} = \frac{4 \times 0.42 \text{ mm}^3}{\pi \times 0.2^3 \text{ mm}^3} = 66.84 \text{ s}^{-1}
\]

Here the experimental results of the rheology characterisation of the PANi-based inks represented in the Figure 4.14 can be used to obtain the corresponding viscosity (\(\eta\)) for the calculated shear rate. In this example the curve of the CSA/DBSA-doped PANi ink with a DBSA:CSA ratio of 0.5:1 was used. A value of \(\eta = 4.45 \text{ Pa s}^{-1}\) was obtained. With the latter, the \(\Delta P\) value is worked out:

\[
\Delta P = 7294.6 \times 4.45 \text{ Pa} = 32460 \text{ Pa}
\]

\(\Delta P\) represents the pressure difference required between the entrance of the nozzle and its depositing end so the extrusion process is performed with a constant flow speed. The mechanism to keep the pressure at the nozzle entrance is provided by the contributions of the cylinder with an auger-like screw mechanical extruder and a compressed nitrogen line. This latter is precisely controlled by a pressure regulator. The complete system was previously described in Section 3.3.2.3. A good trade-off between the pressured nitrogen line and the extruder can ensure a smooth 3D-printing process of the PANi-based inks. Also, it is important to consider that the non-Newtonian nature of the CSA/DBSA-doped PANi-based inks allows to extend the range of extrusion of the 3D-printer. This result can be attributed to the different architectures that the inks must flow through. These architectures are constructed with greater diameter plastic cylinders where the inks flow before reaching the entrance of the nozzle. In those previous cylindrical paths the larger diameters could be related to slower flow velocities resulting in a higher viscosity according the rheology curves of the inks. The higher viscosity could contribute to a better control of the 3D-printing process. However, the effect of the different volumes and paths create a plethora of velocities in the flow of the ink before it reaches the screw-based mechanism. Additionally, the initial viscosity of the inks are the highest according to the rheology data at zero shear rate creating high resistance to flow. These two effects could eventually create pressure gradients or depletion zones producing undesired bubbles within the ink. These undesired results are nicely mitigated by the support of the external nitrogen gas-based source of controlled pressure connected to the PANi-based ink reservoir. The additional controlled pressure system keeps pushing the ink from the chamber as a common and effective strategy used on rapid prototyping processes.\(^{53}\)

The calculations of the viscosity and related difference of pressure required for the extrusion process are presented in the Table 4.1.
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Table 4.1. Calculated viscosity and difference of pressure of the CSA/DBSA-doped PANi inks

<table>
<thead>
<tr>
<th>DBSA:CSA ratio</th>
<th>0.5:1</th>
<th>1:1</th>
<th>1.5:1</th>
<th>2:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated shear rate ( \dot{\gamma} ) (s(^{-1}))</td>
<td>66.84</td>
<td>66.84</td>
<td>66.84</td>
<td>66.84</td>
</tr>
<tr>
<td>Corresponding viscosity ( \eta ) (Pa s(^{-1}))</td>
<td>4.45</td>
<td>3.84</td>
<td>4.08</td>
<td>3.48</td>
</tr>
<tr>
<td>Calculated difference of pressure ( \Delta P ) (kPa)</td>
<td>32.46</td>
<td>28.01</td>
<td>29.76</td>
<td>25.39</td>
</tr>
</tbody>
</table>

Until now there are two important scenarios to be analysed as a result of the rheology characterisation of the PANi-based inks. First, the initial viscosity at the lowest shear rate and, second the viscosity values obtained at the velocity of the flow expected in the 3D-printers for a rapid prototyping process.

![XRD spectra of the CSA/DBSA-doped PANi extrudable inks.](image)

The rheology curves reveal that the blend with the highest DBSA:CSA ratio shows the highest initial viscosity. Likewise, the initial viscosities of the blends with ratios of 1.5:1, 1:1 and 0.5:1 decrease as a function of the DBSA:CSA proportion. This result could be attributed to the PANi backbones being mostly doped by DBSA molecules making them more processable. This result is also supported by the XRD data of Figure 4.15. This spectra show a decreasing peak at \( 2\theta = 15.4^\circ \) as a function of the increasing DBSA:CSA ratio. This peak is related to a d-spacing of 5.7 Å corresponding to the layer stacking between CSA-doped PANi chains. The peak intensity is not noticeable any more at the highest ratio DBSA:CSA of 2:1. The alkyl chains of the doping DBSA molecules would be presented at the surface of the PANi bulky regions. The alkyl tails can interact by interdigitating with the alkyl groups of the DBSA molecules of the surrounding...
matrix of the overall blend.

In the same manner, the lower ratio of DBSA:CSA can produce greater possibilities of having PAni molecules doped by CSA rather than by DBSA, therefore reducing the possible interdigitating interactions and thinning the overall blend. This result is also supported by the XRD data of Figure 4.15. The sample of DBSA:CSA ratio of 0.5:1 shows a noticeable characteristic peak of CSA-doped PAni at $2\theta = 15.4^\circ$. Also, a peak at $2\theta = 27.1^\circ$ to $27.7^\circ$ related to the d-spacing of DBSA-doped PAni of 3.3 Å to 3.2 Å is not observable.55

The second scenario can be observed in the rheology curves at higher shear rates. In general, the non-Newtonian behaviour of the blends can be observed with a decreasing trend of the viscosity as a function of the shear rate. For the practicalities of the 3D-printing strategies, the results are discussed over the value of shear rate corresponding to the previously calculated volumetric flow. In this case, the determined shear rate for the expected flow velocity is 66.84 s$^{-1}$. At this shear rate, the viscosity values of the PAni-based inks with DBSA:CSA ratios of 1:1 and 1.5:1 do not follow a very clear tendency. However, an overall trend can be found showing a slight decrease of the viscosity as a function of the increase in the DBSA:CSA ratio.

This result could be attributed to the agglomerates of the PAni-based material being fragmented and split into smaller pieces by the increased shear rate. These smaller sections can produce less resistance to the flow thus reducing the viscosity of the blend. The described decreasing trend in viscosity related to the shear rate is more noticeable for the blends with higher DBSA:CSA ratios. Thus, the viscosity of the blend with 2:1 DBSA:CSA ratio decreases with a greater slope compared to the sample with 0.5:1 DBSA:CSA ratio. At the shear rate of 66.84 s$^{-1}$ the viscosity of the sample with 2:1 DBSA:CSA ratio has reached a lower value of viscosity compared to that of 0.5:1 DBSA:CSA ratio as shown in Figure 4.16.

![Figure 4.16. Viscosity as a function of shear rate of CSA/DBSA-doped PAni extrudable inks at 66.84 s$^{-1}$.](image)
CHAPTER 4. SYNTHESIS OF ELECTROACTIVE MATERIAL

The higher content of DBSA increases the possibility to obtain PAni doped with DBSA rather than with CSA. Therefore, a higher content of DBSA-doped polyaniline is expected in the blend. The decreasing effect of the viscosity in the rheology curves is related to a higher content of DBSA-doped PAni compared to the CSA-doped PAni in the blends. The DBSA-doped PAni content shows an inverse relationship with the viscosity at the calculated shear rate of 66.84 s\(^{-1}\). The obtained outcomes are consistent with the results reported by Pan et al.\(^{56}\) They found that the presence of higher content of DBSA-doped PAni at high shear rates produces a high amount of broken particulates of this electroactive material. These small particulates show a lubricant effect within the blend, promoting a thinning effect.

4.3.4.2 Extrusion speed

The investigation carried out by the rheology characterisation of the PAni inks is a necessary step to set the 3D-printing processing. Slower extrusion speeds could be set to obtain an easily controlled process. However, a rapid prototyping process requires fast 3D-printing speeds. Such high extrusion velocities can be attained by generating the required gradient between the pressure at the entrance of the 3D-printing nozzle and at the extruding end. The pressure difference is successfully created by the auger-like screw and cylinder mechanism. However, the path from the ink reservoir towards the extruder mechanism has several different cylindrical shapes. These different volumes create pressure-depleted zones because of the action of the extruder pulling the inks to extrude them towards the nozzle. The plethora of pressure gradients are well compensated and corrected by the support of the external nitrogen gas pressurised line connected to the 3D printers.

Despite all the infrastructure put in place for an accurate 3D-printing process, there are some additional results that account for the rapid prototyping process of the synthesised electroactive blends. The inks with DBSA:CSA ratios of 1:1 and 1.5:1 present a stable initial extrusion. However, during the 3D-printing process the 1:1 ink needed minimum adjustments of the external pressure source to keep a constant flow compared to the one with higher DBSA:CSA ratio.

The result could be related to the ink with higher initial viscosity being slower to flow at the beginning of the extrusion procedure. The 0.5:1 ink revealed the lowest viscosity producing an even and good coverage on the applied areas of the CCCs. This remarkable characteristic of the 0.5:1 ink makes it appropriate for the extrusion process and favourable for application. However, after its application, the ink lose definition of the printed patterns. This effect can be considered negligible for patterns with a definition greater than 400 \(\mu\)m but should be considered for smaller definition patterns.

The definition needs to be assessed as a part of an objective quality evaluation of the attained printed architectures. There are several approaches to perform this evaluation such as ultrasonic imaging, X-rays and electromagnetic methods.\(^{57,58}\) However, valid and objective quality metrics can be obtained from the analysis of the “road paths”. This method allows the identification of
under- and over-extrusion comparing the extruded path to predefined architectures. In this research work we have evaluated different printed samples to quantify the extent of the loss of definition in the 3D-printed patterns. The measurements taken from the extruded patterns reveal the deviation of the obtained PANi-based printing structures compared to the designed architectures. These measurements were taken with a periodicity of 300 µm and each one quantifies the difference between the designed models and the extruded patterns. Figure 4.17 presents the periodic measurements for a 400 µm width model, quantifying the differences between the extruded model and the designed pattern. The same procedure of measurement was performed on smaller width models (200 µm (Figure 4.18) and 300 µm width (Figure 4.19). Additional patterns extruded with nozzles of 500 µm and 600 µm were evaluated as shown in Figure 4.20, and Figure 4.21 respectively. After the ink is extruded by the 3D-printer head a flooding process of the extruded ink takes place, thus compromising the precision of the 3D-printed patterns. The results shown in Table 4.2 reveal that the patterns printed with 200 µm
Table 4.2. Deviation between the designed architecture and the models printed with nozzles of different diameters

<table>
<thead>
<tr>
<th>Nozzle diameter</th>
<th>200 μm</th>
<th>300 μm</th>
<th>400 μm</th>
<th>500 μm</th>
<th>600 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample 1</td>
<td>12.0 μm</td>
<td>14.3 μm</td>
<td>17.5 μm</td>
<td>53.0 μm</td>
<td>88.8 μm</td>
</tr>
<tr>
<td>sample 2</td>
<td>2.0 μm</td>
<td>1.4 μm</td>
<td>19.8 μm</td>
<td>54.2 μm</td>
<td>80.8 μm</td>
</tr>
<tr>
<td>sample 3</td>
<td>1.4 μm</td>
<td>2.8 μm</td>
<td>20.9 μm</td>
<td>75 μm</td>
<td>66.8 μm</td>
</tr>
<tr>
<td>sample 4</td>
<td>7.3 μm</td>
<td>6.0 μm</td>
<td>21.2 μm</td>
<td>81.8 μm</td>
<td>59.4 μm</td>
</tr>
<tr>
<td>sample 5</td>
<td>1.6 μm</td>
<td>8.6 μm</td>
<td>21.8 μm</td>
<td>51.8 μm</td>
<td>85.6 μm</td>
</tr>
<tr>
<td>sample 6</td>
<td>1.0 μm</td>
<td>21.4 μm</td>
<td>29.9 μm</td>
<td>57.1 μm</td>
<td>94.8 μm</td>
</tr>
<tr>
<td>sample 7</td>
<td>8.6 μm</td>
<td>14.3 μm</td>
<td>30.9 μm</td>
<td>68.1 μm</td>
<td>99.0 μm</td>
</tr>
<tr>
<td>sample 8</td>
<td>5.0 μm</td>
<td>28.6 μm</td>
<td>34.0 μm</td>
<td>74.0 μm</td>
<td>119.3 μm</td>
</tr>
<tr>
<td>sample 9</td>
<td>7.0 μm</td>
<td>5.1 μm</td>
<td>15.6 μm</td>
<td>45.1 μm</td>
<td>92.5 μm</td>
</tr>
<tr>
<td>sample 10</td>
<td>0 μm</td>
<td>7.2 μm</td>
<td>13.8 μm</td>
<td>60.3 μm</td>
<td>52.3 μm</td>
</tr>
<tr>
<td>Average deviation</td>
<td>4.6 μm</td>
<td>10.97 μm</td>
<td>21.84 μm</td>
<td>62.04 μm</td>
<td>83.93 μm</td>
</tr>
</tbody>
</table>

nozzle present the smallest deviation between the printed model and the designed architecture (the mean deviation is 4.6 μm equivalent to a deviation of 2.3%). It is important to mention that the measurements taken are based on the metrics provided by the software Image J per pixel. Use of the software is the reason that some measurements reached values in the order of 0.1 μm which is smaller than the optical microscope resolution (200 nm).

Figure 4.19. Difference in dimensions between a 300 μm PAni-based 3d-printed path and the designed path (horizontal yellow lines).

The feasibility of the 3D-printing process is further evaluated by analysing the deviation from the targeted paths of the models compared to the obtained 3D-prints. The deviation increases when the diameter of the nozzle is increased. The obtained mean deviation for the 500 μm model is 62 μm. The mean deviation for the 600 μm is 84 μm, which are 12.4% and 13.9% respectively. The obtained results can be attributed to an overflowing process produced by a greater amount of
ink being deposited by bigger diameter nozzles.

![Figure 4.20](image1.png)

**Figure 4.20.** Difference in dimensions between a 500 µm PAni-based 3d-printed path and the designed path (horizontal yellow lines).

One strategy to avoid any undesired flooding of the ink is the use of smaller diameter nozzles for the extrusion process such as the 200 µm-diameter or the 300 µm-diameter nozzles. This approach can describe high definition patterns, however, it could require several narrow width printed patterns to attain the width obtained with bigger diameter nozzles, thus increasing the manufacturing time. In order to keep the manufacturing time with nozzles of smaller diameter, the speed of the printing head and the extrusion can be increased. The last approach can result in under-extrusion problems as shown in the Figure 4.22 where the printed path cannot fulfill the required design of the model. This drawback of the process is produced by an increase in the speed of the 3D-printing operation. On the other hand, to fulfill the required design a decrease in the speed of the process is required, which negatively compromises the manufacturing time leading to dramatic increases it. Also, a very low printing speed can produce over-flowing that

![Figure 4.21](image2.png)

**Figure 4.21.** Difference in dimensions between a 600 µm PAni-based 3d-printed path and the designed path (horizontal yellow lines).
can generate a negative effect in the quality of the models as shown in the Figure 4.23. The above-mentioned variables to attain features and the time required to achieve these features can be used to define the design space of the system. Features with an accuracy of 2.3% can be attained in 10 min, whilst features with an accuracy greater than 10% can be achieved in 3 min. In between those, features with an accuracy of 5% can be extruded in 5 minutes. This approach provides a good trade-off between time and accuracy. The ink with a 2:1 ratio presents the highest starting viscosity and also the most pronounced slope as a function of the shear rate. The latter characteristics implied that further pressure adjustments are required after the material begins to shear and the viscosity sustainably drops. In this case a greater diameter nozzle could help to reduce the impact of the change in viscosity but sacrificing the definition of the printed patterns. Once the shear rate reached the value corresponding to the required velocity of flow, the viscosity stays mostly stable and no further pressure adjustments are required. This result suggested that the quicker steady flow is attained, the sooner the 3D-printing process reaches a stable operating regime. A strategy to reach the desired steady flow is extruding a sacrificial amount of the PAni-based blend before starting the required patterning.

The feasibility of the 3D-printing process is further evaluated by assessing the consistency of the thickness obtained for the 3D-printed models. The 3D prints created with the 400 µm nozzle demonstrated a dimensional accuracy in the X-Y plane with an average deviation of 21.8 µm.
4.4 Conclusions

In this chapter, various PAni-based materials that have been synthesised for the construction of supercapacitor prototypes. A phytic acid-doped PAni was prepared and combined with GO and rGO. The resulting materials were applied on conductive carbon cloths. The chains of the synthesised PAni were in the doped electroactive oxidation state of the polymer and could be used equivalent to 5.45%. The selection of a nozzle width of 400 µm is based on a trade-off between the manufacturing speed and the accuracy of the printed paths. To evaluate the thickness of the 3D-prints in the Z axis, the samples obtained with a 400 µm nozzle were characterized by optical microscopy. The thickness of the 3D-prints was registered for a 1, 2, 3, and 4-layer models. The obtained thickness for each layer is approximately 30 µm. The targeted thicknesses for 2, 3, and 4-layer models are expected to be 60 µm, 90 µm and 120 µm, respectively. Figure 4.24 shows

![Optical microscope images of the cross section of 3D-printed models with different thicknesses: (a) 1-layer pattern, (b) 2-layer pattern, (c) 3-layer pattern, and (d) 4-layer pattern.](image)

Figure 4.24. Optical microscope images of the cross section of 3D-printed models with different thicknesses: a) 1-layer pattern b) 2-layer pattern c) 3-layer pattern and 4-layer pattern.

the cross-section of 1-layer, 2-layer, 3-layer and 4-layer models. The increase of thickness after each printed layer is a consistent value of approximately 30 µm per extruded layer. Table 4.3 shows the average thickness of various samples of 1, 2, 3, and 4-layer 3D-printed models. The evaluation of the thicknesses provided the height change per layer that is accounted for in the code for the manufacturing process.

4.4 Conclusions
Table 4.3. Thickness of 1-layer, 2-layer, 3-layer and 4-layer 3D-printed models

<table>
<thead>
<tr>
<th>No. of layers</th>
<th>1-layer</th>
<th>2-layer</th>
<th>3-layer</th>
<th>4-layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample 1</td>
<td>31.8 µm</td>
<td>79.9 µm</td>
<td>94.5 µm</td>
<td>119.5 µm</td>
</tr>
<tr>
<td>sample 2</td>
<td>30.1 µm</td>
<td>70.2 µm</td>
<td>87.4 µm</td>
<td>116.0 µm</td>
</tr>
<tr>
<td>sample 3</td>
<td>31.5 µm</td>
<td>72.3 µm</td>
<td>92.5 µm</td>
<td>116.5 µm</td>
</tr>
<tr>
<td>sample 4</td>
<td>34.0 µm</td>
<td>63.6 µm</td>
<td>100.0 µm</td>
<td>117.2 µm</td>
</tr>
<tr>
<td>sample 5</td>
<td>33.3 µm</td>
<td>69.3 µm</td>
<td>99.5 µm</td>
<td>120.0 µm</td>
</tr>
<tr>
<td>sample 6</td>
<td>30.3 µm</td>
<td>62.7 µm</td>
<td>93.1 µm</td>
<td>117.1 µm</td>
</tr>
<tr>
<td>sample 7</td>
<td>28.5 µm</td>
<td>60.0 µm</td>
<td>88.4 µm</td>
<td>118.7 µm</td>
</tr>
<tr>
<td>sample 8</td>
<td>29.8 µm</td>
<td>57.2 µm</td>
<td>91.1 µm</td>
<td>122.3 µm</td>
</tr>
<tr>
<td>sample 9</td>
<td>30.1 µm</td>
<td>54.4 µm</td>
<td>90.5 µm</td>
<td>120.9 µm</td>
</tr>
<tr>
<td>sample 10</td>
<td>28.3 µm</td>
<td>51.7 µm</td>
<td>88.0 µm</td>
<td>117.5 µm</td>
</tr>
</tbody>
</table>

Average thickness: 30.8 µm, 64.13 µm, 92.5 µm, 118.57 µm
Error: 0.53 µm, 2.51 µm, 1.27 µm, 0.59 µm

for conductivity and energy storage purposes. The binding process between the phytic acid-doped PANi and the carbon cloths allowed a good contact between the polymer-based materials and the conductive fabrics. The phytic acid-doped PANi materials showed poor mechanical stability upon bending of the conductive carbon cloth, hampering the use of the polymer for flexible energy storage devices. Also the phytic acid-doped PANi required the support of a polymer matrix to obtain a 3D-printable version of the electroactive material. The attained extrudable blend required excessive amounts of the supporting polymer-based matrix that impeded the exploitation of the electroactive and conductive characteristics of the phytic acid-doped PANi material. A second synthetic route using a combination of CSA and DBSA was explored to obtain various doped-PAni-based 3D-printable blends. The modification of the DBSA:CSA ratios promoted important changes in the WA of the PAni-based blends and the CCCs and also between the blends and the layer of gel electrolyte. The characterisation and analysis carried out demonstrated that the PAni-blends with a lower ratio of DBSA:CSA have better adhesion to the CCCs and the gel electrolyte. Also, the variations of the ratios of DBSA:CSA changed the rheological characteristics of the blends and allowed to tune the parameters of the customised 3D-printers to extrude the PAni-based inks successfully. The 3D-printing specifications for the electroactive inks were obtained based on extrusion speeds calculated to keep consistent manufacturing times. These tuned parameters allow the integration of the 3D-printing procedures into a production line in the construction of supercapacitor prototypes.

The feasibility of a 3D-printable PAni-based ink has been demonstrated. The synthesis and optimisation of various CSA/DBSA-doped PAni-based blends has been successfully performed. The obtained blends are suitable candidates for a 3D-printing production line to construct flexible supercapacitor devices by a rapid prototyping process.
4.5 References


CHAPTER 4. SYNTHESIS OF ELECTROACTIVE MATERIAL


(51) Malkin, A., Rheology fundamentals, 1st; ChemTec publishing: Toronto, 1994; Vol. 1.


5.1 Abstract

The development of flexible Electrical Energy Storage Devices (EESD) has raised great scientific attention because of their remarkable characteristics such as the capability to sustain large deformations and adapt to complex geometries while maintaining their energy storage functions and reliability. As novel developments are attained in the field of EESDs, new challenging requirements are introduced by industry and everyday life. Bespoke devices for different applications involve new accurate techniques of manufacture such as 3D printing. This rapid prototyping approach can be used to construct the different individual components of a EESD. The latter procedure accounts for the close relationship between the components and their synergistic contributions combined in a complete 3D-printed device. In this regard, the encasement, the CCCs, the electroactive material and the electrolyte can be individually produced and optimised to obtain an EESD. To perform these procedures, the components should be prepared and enhanced so they can be extruded by a commercial 3D-printer in a software-controlled and accurate fashion. This chapter details the successful synthesis of a PVA-based electrolyte for the supercapacitor prototypes. The PVA-based electrolyte has been optimised and enhanced to obtain a 3D-printable electrolyte blend that can be used by the software-controlled extrusion system of the 3D-printers. The extrudable PVA-based electrolyte ink is further treated with glutaraldehyde (GA) to obtain a cross-linked gel electrolyte to avoid undesired leaking and enhance the safety and mechanical strength of the energy storage device. The PVA/GA-based electrolyte is successfully combined with the supercapacitor components to obtain a flexible EESD.
CHAPTER 5. SYNTHESIS OF A GEL ELECTROLYTE

5.2 Introduction

The electrolyte material is a fundamental part of the energy storage devices and their manufacturing process. It is a crucial component of the EESDs providing ionic conductivity and playing an essential role in the formation of the electronic double layer (EDL). Furthermore, the electrolyte is important for the reversible redox reactions related to the pseudocapacitive energy storage process. The characteristics of the electrolyte determine the properties of the EESD such as the operating voltage, the speeds of charge/discharge, the cycling functionalities and the overall capacitance.

The energy storage ability of an EESD is the result of two synergistic contributions: the EDL capacitance and the pseudocapacitance. These two contributions are influenced by the characteristics of the electrolyte used in an EESD. These features are determined by many factors such as the interrelationship between the electrolyte and the electrode materials, the interactions between the ions and the solvent, the ion concentration, the ion size, and the potential window. These electrolyte-related factors also influence the power/energy densities, the working potential window, and the cyclability/durability of a supercapacitor device.

All of the mentioned factors influence the overall performance of an EESD and must be accounted for the design and construction of the supercapacitor prototype devices.

In this research effort and as detailed in the previous chapters, the components of a supercapacitor prototype such as the CCCs and the electroactive material have been produced and enhanced to obtain flexible materials. In this regard, traditional rigid or brittle CCC have been replaced with flexible, large surface area, conductive and light weight 3D-printed and laser-scribed CCC. Similarly, stiff electrodes have been replaced by 3D-printed flexible electrodes obtained by synthesising, developing, and optimising PAni-based blends to attain extrudable inks successfully deposited and combined with the developed CCCs. Following these manufacturing strategies, the required electrolyte should be endowed with the same versatile property of flexibility and most important with the feature of extrudability.

As reported in the literature, the electrolytes are mostly classified as liquid electrolytes and solid-state or quasi-solid-state electrolytes. These types of electrolyte have their own properties, however, none of them can fulfill all the desired characteristics of an ideal electrolyte.

The liquid electrolytes can be further classified as aqueous electrolytes, organic electrolytes and ionic liquids. The aqueous electrolytes are well known for their wide application in the construction of EESDs. The EESDs built with water-based electrolytes can present superior conductivity and meritorious capacitance because of their higher ionic concentration and lower resistance. At the same time, these type of EESDs are limited in their working voltage (1.23 V) by the thermodynamic stability window or electrochemical window of the water present in the aqueous electrolyte. In terms of the overall performance, the low voltages of the EESDs with water-based electrolytes limit the capability of delivering high energy densities. However, these devices perform very well at delivering high power with low cost, in a safe manner with potential
5.2. INTRODUCTION

The organic electrolytes present a higher operation voltage window (up to 3.5 V$^{15,16}$) compared with the aqueous electrolytes. The increased potential allows enhanced energy and power densities of the EESDs. Also, occasionally, the organic electrolytes enable the use of cheaper materials for the CCCs and the supercapacitor encapsement. The organic electrolytes are normally prepared by dissolving conductive salts in acetonitrile (ACN) and propylene carbonate (PC). Despite ACN’s ability to dissolve larger amounts of salts, its use is hindered because of the toxicity and safety concerns. PC is more environmentally friendly but it presents resistivity issues compared to ACN.$^{13,14}$ Moreover, there are several other issues that should be considered before using the organic electrolytes for the fabrication of EESDs. For example, higher cost, smaller specific capacitance, lower conductivity, and all the safety concerns of high flammability, toxicity and volatility. Additional to that, the preparation of the organic electrolyte requires complex processes of assembling and purification in a highly controlled environment to avoid any impurities that can compromise the organic electrolyte performance.$^4$ The impurities such as traces of water in organic electrolytes reduce the window of the stable electrochemical potential and cause self discharge issues.$^8,17–19$

The ionic liquids (ILs) are the third category of the liquid electrolytes. ILs are pure molten organic salts at ambient temperature. The ILs allow high concentrations in solvent, or even the removal of the solvent. Normally, they are chemically stable with low toxicity or flammability. However, the drawbacks of the ILs are both, a significantly lower ionic conductivity, and a higher viscosity compared to aqueous electrolytes. Additional to these characteristics, the ILs present a higher internal resistance compromising the capacitance performance of the supercapacitor devices. In the practical aspects, their high cost and safety concerns should be carefully considered for their use in the construction of inexpensive and 3D-printed supercapacitors.$^6,13,14$

Quasi-solid electrolytes are currently being investigated in industry and academia. The quasi-solid electrolytes have become highly demanded to fulfill new requirements in these sectors. These requirements are related to the great interest in portable/wearable electronics, micro-electronics, printable electronics and particularly flexible/stretchable electronics. The quasi-solid electrolytes can be classified in three groups: solid polymer electrolytes, polyelectrolytes, and gel polymer electrolytes. Among these three groups, the solid polymer electrolytes are dry polymer-based materials with high mechanical strength, high resistivity and low ionic conductivity. In the other hand, the polyelectrolytes are made of charged polymer chains. This latter approach lead to higher potential windows, but sacrificing the ion conductivity.

The gel polymer electrolytes present the highest ionic conductivity. Despite their poor mechanical strength and narrow working potential window, they are preferred as a quasi-solid electrolyte material. This preference could be attributed to their ability to provide better accessibility of the ions to the active sites of the electrode materials compared to their solid polymer-based and ILs-based counterparts.$^{15,20–22}$
CHAPTER 5. SYNTHESIS OF A GEL ELECTROLYTE

In this research chapter, a series of polyvinyl alcohol (PVA)/acid-based polymer gel electrolytes are prepared and characterised to obtain an appropriate electrolyte for flexible supercapacitors. The developed electrolyte is optimised to attain a suitable blend for 3D printing and extrusion printing processes. Also, the developed blends are endowed with mechanical strength by crosslinking the PVA chains with glutaraldehyde.

Furthermore, a PVA/H_2SO_4-based gel electrolyte blend is further optimised to obtain a 3D-printable electrolyte blend with high capacitance response and remarkable cyclability. The enhanced blend is successfully extruded by the customised 3D-printers and smoothly integrated to the other materials of a supercapacitor prototype. With the latter step, the developed material and the 3D-printing process can be considered in the production line for the rapid prototyping of flexible energy storage devices.

5.3 Results and discussion

5.3.1 Synthesis of the electrolyte

In previous chapters of these research effort, CCCs and an electroactive material were developed and tested as parts of a supercapacitor prototype. The attained materials were further optimised into 3D-printable blends towards a fully 3D-printed supercapacitor prototype device. In this regard, parallel research activities were devoted to obtain a suitable electrolyte to test the performance of the developed CCCs and electroactive blends.

Initially, carbon cloth, a conductive carbon-based woven fabric were used as CCCs to test the progress of the development and enhancement of a PAni-based electroactive material. To fulfill the requirements of a standard electrolyte for tests, an aqueous 1 M H_2SO_4 was prepared as detailed in Section 2.1.4.1 of the Chapter 2 of this thesis. The H_2SO_4-based solution was selected because of its remarkable properties such as ionic conductivity and ion size. Additional to that, the H_2SO_4-based electrolyte has been reported in the literature as a suitable material for the manufacture of PAni-based supercapacitors and carbon-based supercapacitors.

The initial non-extrudable phytic acid-doped PAni materials were evaluated by performing electrochemical tests using a 3-electrode cell with a 1M H_2SO_4 aqueous electrolyte. The results of the electrochemical evaluation of the electrodes revealed the capacitance performance of the non-extrudable electroactive material. However, at the same time, parallel research efforts were carried out to obtain laser-scribed CCCs to replace the carbon cloth and also attain a 3D-printable PAni-based blend for the construction of the electrodes of a supercapacitor prototype. In this regard, the aqueous electrolyte needed further enhancement to obtain a 3D-printable electrolyte blend to be smoothly extruded and combined with the 3D-printed electroactive material. In addition, the software and hardware parameters required to tune the 3D-printing process of the new electrolyte blend must be integrated in the production line of the 3D-printed energy storage device prototypes.
The low viscosity of the liquid H$_2$SO$_4$-based electrolyte hampered its use in a 3D-printing process. To endow the aqueous electrolyte with 3D-printable feature some strategies were required. The latter approaches can also change the liquid material into a quasi-solid or a gel-like safer material to avoid undesired leakages in flexible energy storage devices.

Also, a quasi-solid gel electrolyte has essential features to improve the versatility, mechanical strength and safety requirements of bespoke energy storage devices.

The methods to obtain a quasi-solid gel electrolytes include the use of a polymer matrix introduced in the synthesis as a gelling agent. Also, the length of the polymer chains is an important factor to manipulate and attain a higher viscosity. In this regard polyvinyl alcohol (PVA) has been chosen to increase the viscosity of the H$_2$SO$_4$-based aqueous electrolyte. PVA is a cheap, non-toxic, water-soluble polymer with characteristics of chemical stability. Additional to that it presents film-forming and adhesive capabilities required for the construction of flexible and safe supercapacitor prototypes. In addition, PVA is a hygroscopic powder that can be dissolved into an aqueous blend. The polymer chains in the obtained blend can be crosslinked to obtain a mechanically strong, flexible and stretchable elastomer. The crosslinking process reduces the hydroxyl groups thus reducing the hygroscopicity of PVA preventing the polymer-based elastomer from absorbing further water. In the next section, the synthesis of a PVA-based gel electrolyte is detailed. Also the scientific efforts to optimise the mechanical and physical properties of the obtained quasi-solid electrolyte are described.

### 5.3.1.1 Polyvinyl alcohol gel-based electrolyte

The strategy of introducing a polymer matrix in the synthesis procedure was used to increase the viscosity of the electrolyte and attain a quasi-solid gel electrolyte. The detailed method of synthesis can be found in Section 2.1.4.1 of this thesis. Briefly, a 10 wt% aqueous mix of PVA (89-98 kDa Mw) was prepared and heated to 85°C. The blend was continuously stirred for 2 hours. The resulting clear viscous solution was mixed with 1g of H$_2$SO$_4$ and cooled to room temperature.

The viscosity of the obtained PVA-based electrolyte was still not suitable for 3D-printing. When the latter blend was set in the extrusion system of the 3D-printers it flowed with no control. However, the attained blend can be deposited by drop-casting on a mold and leaving at room temperature to evaporate the solvent to obtain PVA-based electrolyte films. At this point the PVA-based material was a quasi-solid film that can be directly applied on the surface of the electroactive material. This approach allows to obtain a self-standing electrolyte material that can be used in a supercapacitor prototype to enhance the mechanical strength of the device. However the latter approach was not suitable to obtain a 3D-printable electrolyte.

To obtain a 3D-printable PVA-based gel electrolyte an additional strategy is required. In this regard, the liquid PVA-based electrolyte can be optimised by increasing the molecular weight of the polymer to obtain a higher viscosity blend. The higher the molecular weight, the better controlled extrusion is attained by the software-controlled commercial customised 3D-printers.
this research effort three PVA with different molecular weight were used for the synthesis of the PVA-based gel electrolyte. The average molecular weight (AMW) of the PVA are: PVA1 with an AMW of 89-98 kDa, PVA2 with an AMW of 85-125 kDa and PVA3 with an AMW of 146-186 kDa. Additional PVA precursors with lower AMW were available in the Faul Research Group lab. These PVA precursors were not used as lower AMW would result in poorer viscosity of the obtained PVA-based electrolyte impeding its applicability to 3D-printing. The blend synthesised with PVA2 presented a viscosity that was successfully tested with the customised commercial 3D-printers. The latter blend was characterised by rheology experiments and the results are further analysed in Section 5.3.4.2. The PVA-based solution prepared with PVA3 showed a blend with a higher viscosity and was explored as a potential 3D-printable electrolyte-based ink. The latter blend was not homogeneous and presented small aggregates, which clogged the printer nozzle. The latter negative result was partially overcome by increasing the temperature of the synthesis to 95 °C and the stirring time to 4 hours maintaining the increased temperature. Despite the changes in the time and temperature of the preparation of the blend, the resulting PVA-based ink still presented a lack of smoothness during the 3D-printing process. The lack of uniformity during the extrusion of this blend required constant adjustments in the pressure-controlled nitrogen line connected to the ink reservoir. The mechanism of the supporting pressure controlled line was previously detailed in Section 3.3.2.3.

Table 5.1 summarises the preliminary results obtained from the synthesis of the PVA-based blends.

<table>
<thead>
<tr>
<th>PVA gel electrolyte</th>
<th>PV1</th>
<th>PV2</th>
<th>PV3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average molecular weight (kDa)</td>
<td>89 - 98</td>
<td>85 - 125</td>
<td>146 - 186</td>
</tr>
<tr>
<td>3D-printable blend</td>
<td>no</td>
<td>yes</td>
<td>partially</td>
</tr>
<tr>
<td>Additional remarks</td>
<td>liquid</td>
<td>homogeneous</td>
<td>heterogeneous</td>
</tr>
</tbody>
</table>

The preliminary results obtained from the developed PVA-based electrolyte blends allowed to start the 3D-printing with the most suitable ink. A smooth controlled extrusion process of the PV2 ink was performed on the surface of the laser-induced graphene CCCs as shown in Figure 5.1(a) and Figure 5.1(b). The 3D-printed PVA/H₂SO₄-based gel electrolyte gives a smooth surface after the extrusion process. In addition, if a surface irregularity is produced by the 3D-printing process, it settles in a short time period (less than 5 min) because of the viscosity of the blend. The thickness of a 3D-printed layer of the PVA/H₂SO₄-based gel electrolyte was evaluated by optical microscopy. Figure 5.3 shows the cross section of a single layer 3D-printed sample of the
5.3. RESULTS AND DISCUSSION

gel electrolyte. The measured thickness of a single is 100 µm. This thickness is kept constant during the characterisation process of the capacitance characterisation of the supercapacitor prototypes.

![Image](image_url)

**Figure 5.1.** 3D-printed PVA2-based gel electrolyte on the surface of the graphene based CCCs: a) 1 layer  b) 2 layers

The initial tests of the PVA-based ink allowed to characterise not only the extrudability of the blend, but also, the capacitive properties of this PVA/H$_2$SO$_4$-based gel electrolyte. In this regard a simple flexible supercapacitor prototype was constructed using the previously developed laser-induced graphene CCCs and UV-curable silicone rubber as substrate as detailed in Section 3.3.5 of this thesis. The graphene-based material was used as CCCs and as a carbon-based electrode for the capacitance characterisation purposes. The measurements were performed using cyclic voltammetry (CV) following the methods described in Section 2.2.4.1. The results of the capacitance measurements shown in the Figure 5.5(a) reveal a quasi-squared shape.

![Image](image_url)

**Figure 5.2.** Supercapacitor prototype model to test the capacitance of the PVA2-based 3D-printable gel electrolyte.
voltagmogram demonstrating the capabilities of the PVA-based blend to work as an electrolyte for flexible supercapacitors.

**Figure 5.3.** Optical microscope image of a cross section of a 3D-printed 1-layer gel electrolyte film.

**Figure 5.4.** Optical microscope image processed by Image J to obtain the 3D-printed gel electrolyte thickness.

**Figure 5.5.** Capacitance characterisation of the PVA/H$_2$SO$_4$-based gel electrolyte: a) Cyclic voltammetry  b) Capacitance retention over 4000 cycles or charge-discharge
5.3. RESULTS AND DISCUSSION

Also, Figure 5.5(b) shows the results of the supercapacitor prototype being tested over 4000 CV cycles with a capacitance retention of the 98%. These results could be attributed to the chemical stability of the gel electrolyte during intense charge and discharge cycling. The latter preliminary results are consistent with previous findings reported by Gao et al. and Karthika et al.\textsuperscript{30,31} about the capacitive performance and stability of a PVA/H\textsubscript{2}SO\textsubscript{4}-based gel electrolyte.

The developed PVA/H\textsubscript{2}SO\textsubscript{4} shows its potential as a suitable electrolyte material for 3D-printing in a production line of supercapacitor prototypes. Additional strategies such as testing different acids for the synthesis of the gel has been explored. This strategies will be further discussed in Section 5.3.2.

5.3.2 Gel electrolyte influence in the capacitance

The PVA/H\textsubscript{2}SO\textsubscript{4}-based gel electrolyte demonstrated its potential suitability for the fabrication of simple 3D-printed supercapacitor prototypes. Further research was devoted by exploring the results in capacitance and capacitance retention after replacing the H\textsubscript{2}SO\textsubscript{4}. Different acids such as phosphoric acid (H\textsubscript{3}PO\textsubscript{4}), hydrochloric acid (HCl) and phytic acid (C\textsubscript{6}H\textsubscript{18}O\textsubscript{24}P\textsubscript{6}) were used in the synthesis of the PVA-based gel electrolyte. For these tests, the supercapacitor prototypes were constructed not only with laser-induced graphene CCCs, but also with the extrudable phytic acid-doped PANi-based electroactive material developed in the previous part of this research work.

Figure 5.6 shows the initial capacitance of supercapacitors using PVA-based gel electrolytes synthesised with the different acids. In addition the capacitance retention of the constructed supercapacitor prototypes were evaluated over 3000 CV cycles. The resulting initial capacitance is

![Figure 5.6. Capacitance of PANi-based supercapacitor prototypes with different PVA-based gel electrolytes.](image)
similar for all the supercapacitor prototypes. The values of specific capacitance obtained are close to 600 F g\(^{-1}\). These values were expected for the phytic acid-doped polyaniline in this case used as a standard material for the gel electrolyte evaluation purposes. Interestingly, the capacitance retention behaviour of the supercapacitor prototypes showed different trends regarding the acid used for the synthesis of the gel electrolyte.

The initial value of capacitance obtained with a phytic acid-based gel electrolyte is the highest. However, the capacitance retention decreases upon the cyclability tests. In the first 1000 cycles the capacitance retention is close to the 80% of the initial capacitance. This result is consistent with previous research reported by Zhao et al. and Hu et al.\(^{32,33}\) Conversely, the supercapacitor prototype devices constructed with a PVA-based gel electrolyte made with HCl, H\(_2\)SO\(_4\) and H\(_3\)PO\(_4\) reveal better capacitance retention capabilities. In all cases there was a slight decrease in the capacitance retention. One small contribution to the decrease of the retention percentage could be attributed to the damage produced in the polymer backbone during intense cycling. The latter effect is reported as the result of swelling and shrinking effects of the PAni chains during the charge and discharge cycles.\(^{34-36}\) The repetitive process can damage the polymer network compromising the cyclability of the electroactive material.

The remaining contribution in the decrease of the capacitance retention could be related to the quasi-solid PVA-based gel electrolytes. In this regard the electrolytes synthesised with HCl, H\(_2\)SO\(_4\) and H\(_3\)PO\(_4\) have been chosen as potential candidates to be used towards 3D-printable gel electrolyte materials. The improved performance obtained from the PVA/H\(_2\)SO\(_4\)-based gel electrolyte can be attributed to its remarkable ionic conductivity (close to 82 ms cm\(^{-1}\)) and ion size. On the other hand, the gel electrolyte prepared with HCl shows stable performance as well. The latter can be caused by a decrease in the charge transfer resistance of the gel electrolyte as reported previously by other authors.\(^{37}\) The solvated anions SO\(_4^{2-}\) have a size smaller than 1 nm (3.79 Å radii) whilst PAni has porous with diameters in the order of tens of nm. The smaller size of the solvated anions compared to the pore size of the electrode material allows the allocation of the ions into the porosities during the charge cycle and the deallocation during the discharge cycles.\(^{38}\)

### 5.3.3 Dehydration influence in the capacitance

The PVA-based quasi-solid gel electrolyte was synthesised with an aqueous solution of the polymer matrix. In most of the cases, the gel electrolyte was left at room temperature to allow the evaporation of the excess of solvent. However, a extensive evaporation of the solvent can produce a dehydrated gel electrolyte. The current literature suggests an evaporation time of 4h to 6h and sandwiched prototypes that could help to protect the gel electrolyte material from additional solvent evaporation.\(^{22,39-41}\) However, any additional dehydration can potentially affect the capacitance performance of the supercapacitor prototype by diminishing the wettability and the ionic conductivity of the gel.\(^{42}\) Figure 5.7 shows the effect of a supercapacitor left to excessive
ventilation during the cyclability tests. The capacitance drastically drops during the first 1000 cycles. This result can be attributed to the dehydration hindering the ions from accessing the surface of the electrodes.

To prevent the previous dehydration effects some strategies can be explored. A suitable physical approach should be developed accounting for the architecture of the supercapacitor prototype. The first consideration to account is the shape of the developed capacitor prototypes having an in-plane interdigitated electrodes structure. This structure requires the deposition of the gel electrolyte on the surface of the interdigitated electrodes.

The latter physical description of the supercapacitor prototypes implies that there is not a sandwiched-electrodes architecture to prevent the dehydration of the gel electrolyte. Second, the gel electrolyte layer is the final part on the top of the layer-by-layer extruded structure, thus exposing the gel electrolyte to the ambient conditions.

To solve the described physical setbacks, an encasement using the UV-curable silicone rubber UV Electro 225-1 (Momentive Performance Materials, USA) was created by extruding it on top of the final 3D-printed gel electrolyte-based layer.

The Figure 5.8 shows the capacitance performance of an encased supercapacitor prototype constructed with a PVA-based gel electrolyte. Despite the enhanced cyclability of the encased supercapacitor prototype, there was still a drop in the capacitance retention upon intense charge-discharge cycling. The slight drop (up to 5%) in the capacitance retention could be attributed to the water-vapor permeability of the silicone rubber allowing a marginal dehydration effect of the PVA-based gel electrolyte. For this reason an additional strategy was explored by chemically crosslinking the PVA-based gel electrolyte. The latter approach is further detailed in Section

![Figure 5.7. Capacitance retention of a PANi-based supercapacitor prototype with air flow-exposed PVA-based gel electrolyte.](image-url)
5.3.4 Synthesis of a crosslinked gel electrolyte

The previously synthesised PVA-based gel electrolyte has a viscosity that was characterised and evaluated by rheology measurements that will be further detailed in Section 5.3.4.2. This objective evaluation supports the preliminary results of the PVA-based electrolyte blend being successfully extruded by the customised 3D-printers. Also, additional characterisation provided by optical microscope images and image analysis performed with Image J show the consistency in thickness of a single layer PVA/H$_2$SO$_4$-based gel electrolyte as shown in Figure 5.3 and Figure 5.4. The same approach was used to evaluate the 3D-printable inks used in the manufacturing process of the conductive current collectors and the electroactive material described in Chapter 3 and Chapter 4 respectively.

The structural strength of the 3D-printed gel electrolyte can be optimised without affecting the extrudability of the blend. The latter strategy can be attained by using a cross-linking agent added to the PVA-based gel electrolyte. The crosslinking agent produces a gelation process by a chemical reaction in presence of protons. One of the most important advantages of the described approach is the absence of any thermal treatment to attain the crosslinking. The process takes place in mild conditions and at room temperature and atmospheric pressure. The latter characteristic of the reaction is highly important for the production line of the supercapacitor prototypes where the extrusion procedures are performed without heating systems.

Figure 5.9 shows the reaction scheme where the hydroxyl groups of the PVA react with the aldehyde groups of the GA to form acetal links with the presence of protons as a catalyst.
5.3. RESULTS AND DISCUSSION

Regarding the chosen crosslinking route, PVA can be crosslinked in different ways.\(^ {46-50}\) In this research effort the PVA-GA chemical crosslinking approach has been utilised. The crosslinking procedure takes place in the presence of the acid in the polymer-based blend. The crosslinking process is triggered (catalysed) by the presence of H\(^+\) provided by the protic acid within the PVA-based blend.\(^ {51,52}\) The resulting reaction can be attributed to the PVA hydroxyl groups reacting with the aldehyde groups by forming acetal bonds. In this case, GA has an aldehyde group in each end of the molecule. These groups react forming the acetal bonds to the PVA chains upon the crosslinking reaction.\(^ {51}\) The detailed reaction can produce different types of crosslinking processes: intermolecular, intramolecular and an incomplete intramolecular. The type of crosslinking process depends on some factors such as the concentration of the PVA on the blend, the molecular weight of the polymer, and the pH of the blend.\(^ {53,54}\) In this research effort a group of acids, various PVA samples with diverse molecular weight, and different concentrations of GA have been tested for the preparation of the PVA-based blends to evaluate the impact of these factors during the crosslinking process.

The starting reaction was prepared following the current literature.\(^ {55,56}\) Briefly, the blend was synthesised by adding 10 g of the acid into 100 ml of deionised water and 10 g of PVA powder. The resulting slurry was heated to 90°C and kept for 2 h under continuous stirring until a clear solution was obtained. The attained viscous solution was let to cool down at room temperature before adding the crosslinker. Separately, the crosslinker was obtained by preparing a 1 wt% GA aqueous solution. Then, 1 ml of the crosslinker-based solution was added to 10 ml of the PVA-based blend. The method of adding the crosslinker to the PVA-based solution can be performed by following the procedure reported by Su et al. and Nohara et al.\(^ {57,58}\) where the GA-based solution was directly added to the PVA-based solution under rigorous stirring. The crosslinking process takes place in a time scale from seconds to minutes.

The qualitative properties of the PVA-based synthesised quasi-solid electrolytes are shown in the Table 5.2. The results shown correspond to the samples prepared with PVA of a Mw of 85000-125000 Da. These gels were chosen because they are 3D-printable as demonstrated in
The curing time is an important factor in the time scale of the production line and the 3D-printing process. Curing times around 5 minutes were obtained for the gel electrolytes prepared with phosphoric, sulfuric, nitric and phytic acids making them good candidates for the extrusion system of the customised 3D-printers. Conversely, the gel prepared with hydrochloric acid cures in less than a minute hampering its use in a production line with 3D-printing process with larger time scales. The mechanical and structural characteristics of the gels reveal noticeable differences between the gels. The gel electrolyte synthesised with sulfuric acid showed flexibility and stretchability. Despite the PVA-phosphoric acid-electrolyte possessing similar structural strength compared with the PVA-sulfuric acid-electrolyte, the resulting quasi-solid electrolyte shows syneresis, releasing liquid from the gel. In the case of the gel prepared with hydrochloric acid, the mechanical strength is enhanced compared with the electrolytes prepared with other acids. Additional to that the crosslinking process attained with the hydrochloric acid is extremely fast resulting in inhomogeneous quasi-solid electrolytes. In this regard, the gel electrolyte prepared with nitric acid also presents different densities and inhomogeneous characteristics. In addition the final cured gel tears easily showing a poor mechanical strength.

To evaluate the influence of a higher concentration of the crosslinker solution, a new batch of quasi-solid gels was prepared. The concentration of the GA-based solution was increased from 1 wt% to 2 wt%. Table 5.3 shows the resulting properties and curing times of the crosslinked gels using the new GA concentration.

The higher concentration of the crosslinker solution reduces the curing times in most of the cases. The curing time is still the lowest for the hydrochloric acid-based gel. The mechanical properties of the prepared quasi-solid gel electrolytes slightly change compared with the ones prepared with lower concentration of GA. The gel electrolyte prepared with phosphoric acid still presents some release of the liquid after the crosslinking process. These results obtained

### Table 5.2. PVA-based electrolytes with 1 ml of 1 wt% GA-based solution

<table>
<thead>
<tr>
<th>Acid used</th>
<th>PVA Mw (Da)</th>
<th>GA wt%</th>
<th>Time to cure</th>
<th>Observations</th>
<th>Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric</td>
<td>85000-125000</td>
<td>1</td>
<td>5 min</td>
<td>syneresis</td>
<td>≤25 µm</td>
</tr>
<tr>
<td>Sulfuric</td>
<td>85000-125000</td>
<td>1</td>
<td>4-5 min</td>
<td>flexible and stretchable</td>
<td>≤20 µm</td>
</tr>
<tr>
<td>Phytic</td>
<td>85000-125000</td>
<td>1</td>
<td>&gt; 5 min</td>
<td>poor mechanical strength</td>
<td>≤45 µm</td>
</tr>
<tr>
<td>Hydrochloric</td>
<td>85000-125000</td>
<td>1</td>
<td>10 s</td>
<td>very fast gelation</td>
<td>≤75 µm</td>
</tr>
<tr>
<td>Nitric</td>
<td>85000-125000</td>
<td>1</td>
<td>2-3 min</td>
<td>tears easily</td>
<td>≤55 µm</td>
</tr>
</tbody>
</table>
5.3. RESULTS AND DISCUSSION

Table 5.3. PVA-based electrolytes with 1 ml of 2 wt% GA-based solution

<table>
<thead>
<tr>
<th>Acid used</th>
<th>PVA Mw (Da)</th>
<th>GA Sol. conc. wt%</th>
<th>Time to cure</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric</td>
<td>85000-125000</td>
<td>2</td>
<td>4 min</td>
<td>syneresis</td>
</tr>
<tr>
<td>Sulfuric</td>
<td>85000-125000</td>
<td>2</td>
<td>3-4 min</td>
<td>flexible and stretchable</td>
</tr>
<tr>
<td>Phytic</td>
<td>85000-125000</td>
<td>2</td>
<td>5 min</td>
<td>poor mechanical strength</td>
</tr>
<tr>
<td>Hydrochloric</td>
<td>85000-125000</td>
<td>2</td>
<td>10 s</td>
<td>very fast gelation</td>
</tr>
<tr>
<td>Nitric</td>
<td>85000-125000</td>
<td>2</td>
<td>2 min</td>
<td>tears easily</td>
</tr>
</tbody>
</table>

regarding the curing times and the mechanical properties of the quasi-solid gel electrolytes could be related to the acid used in the preparation. Further analysis regarding the effects of the acid used in the gels is carried out in Section 5.3.4.1

5.3.4.1 Influence of the acid in the gelation process

The gelation process of the PVA-based electrolytes can be influenced by several factors. The results obtained and shown in the Table 5.2 and Table 5.3 reveal some trends in mechanical properties and gelation times that could be attributed to the influence of these abovementioned factors. The concentration and molecular weight of the PVA is the result of the qualitative evaluation of the 3D-printing of the synthesised polymer-based inks. A polymer concentration of 10% on the overall blend and a molecular weight between 85000 and 125000 Da were found to be an appropriate combination to obtain an extrudable polymer blend. At the same time, these values of concentration and molecular weight of PVA triggers a gelation process upon crosslinking with GA and acid as a catalyst as revealed in the previous section. The attained crosslinking is successfully produced with a combination of a concentration of 10% and a molecular weight close to 100000 Da. The obtained result keeps consistency with a previous work reported by Aharoni et al. as a combination to produce an intermolecular crosslinking of the PVA chains under the presence of a catalyst. A lower concentration of the polymer in the overall PVA-based blend could produce an intramolecular crosslinking. The latter can potentially decrease the viscosity of the blend upon the addition of the crosslinking agent. This effect could be attributed to the crosslinking agent exclusively producing a self-linking of single PVA chains (the crosslinking agent links different parts of the polymer long molecule) and changing the linear polymer into a 3D-network and not changing its original molecular weight. In this research effort all the obtained quasi-solid gel electrolytes present a similar crosslinked structure. The latter is insoluble in water and shows higher mechanical strength. These properties could be attributed to
a crosslinking process successfully performed. The mechanical features support an intermolecular process rather than an intramolecular process.\(^{59}\)

The previous qualitative evaluation of the mechanical strength revealed that the PVA-based electrolytes were successfully crosslinked into a quasi-solid gels. There was not any noticeable decrease in viscosity upon crosslinking. In all cases the result was a quasi-solid gel insoluble in water. Despite the fact that all the PVA-based blends were successfully crosslinked, the crosslinking times varied depending on the acid used for their synthesis as shown in Table 5.2 and Table 5.3. The PVA-based blends prepared with phytic acid showed the highest gelation times followed by the samples containing phosphoric acid. Lower gelation times are attained with the samples synthesised with sulfuric, nitric and hydrochloric acids. These results are similar for both concentrations 1 wt% and 2 wt% of the GA in the crosslinking solution. Further analysis of the results reveal a noticeable trend in the gelation times related to each acid. The gelation times have a decreasing tendency starting with the highest gelation time of the samples prepared with phytic acid, followed by the phosphoric, sulfuric, nitric and hydrochloric, respectively. The decreasing trend can be attributed to the availability of H\(^+\) favouring the crosslinking process of the polymer chains according the reaction described in the Figure 5.9. The amount of the available protons is related to the pKa of the utilised acids.\(^{62}\) The pKa is a measure of the tendency of a molecule or ion to keep a proton H\(^+\) at its ionization centre(s). The pKa is defined as the negative logarithm of the acid dissociation constant Ka as shown in Equation 5.1. A negative value of pKa represents a large value of Ka and it is a property of strong acids.\(^{62}\) The trend found in the gelation times, is consistent with the values of pKa of the acids used.

\[
pKa = -\log(Ka) \tag{5.1}
\]

The longest gelation time is obtained with phytic acid which pKa is 6.8-7.6.\(^{63}\) Then the gelation time decreases when the acid used is phosphoric with a pKa of 2.16. The time-decreasing trend continues with the sulphuric acid with a pKa of -2, nitric with a pKa of -1.4 and finally with the hydrochloric with a pKa of -7.\(^{64}\) These results are consistent with a previous report of Marin \textit{et. al}\(^{54}\) where the strength of the acid has direct influence in the gelation times.

To this point, the characterisation of the PVA/acid-based quasi solid gel electrolytes has revealed the properties of the obtained materials. Table 5.2 and Table 5.3 show that the poorest mechanical strength of the nitric acid-based quasi solid electrolyte. The attained crosslinked gel tears easily under minimal qualitative strain. The latter characteristic hampers the potential use of the gel in the construction of flexible and stretchable energy storage devices. The remaining samples synthesised with the other acids such as phosphoric, sulfuric, phytic and hydrochloric were further characterised with Fourier transform infrared spectrometry (FT-IR). The Figure 5.10 shows the FT-IR spectra of the PVA-based crosslinked gel electrolytes prepared with those acids.
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The broad peaks found close to the 3400 cm\(^{-1}\) band can be related to the stretching vibration of the O-H groups of the PVA. The peaks at the 2900 cm\(^{-1}\) band are identified to be related to the C-H stretching of the CH\(_2\) groups of the PVA. The sharp peaks at the 1100 cm\(^{-1}\) band can be attributed to the stretching frequencies of the acetal (C-O-C) bonds present indicating the crosslinking between the PVA and GA was successful.\(^{44,65,66}\)

An additional evaluation of the stretchability of the gel electrolytes was performed before starting the use of the synthesised gel electrolytes for the rapid prototyping stage. The samples of PVA-based gel electrolytes prepared with hydrochloric acid produced inhomogeneous quasi-solid electrolytes upon crosslinking. The obtained samples tore easily upon mechanical strain tests and could not be evaluated. Conversely, the samples prepared with sulfuric, phytic and phosphoric acids were successfully evaluated by tensile strain tests. The Figure 5.11 reveals the resulting tensile stress obtained upon tensile strain tests of the crosslinked quasi-solid gel electrolytes. The tests allow to obtain the tensile strength of the crosslinked PVA-based electrolytes.\(^{67}\) The sample of gel electrolyte synthesised with phytic acid shows the lowest tensile strength at a tensile strain of approximately 170\% of the original length of the sample.

Conversely, the samples prepared with phosphoric and sulfuric acid show higher tensile strengths. However, the sample prepared with phosphoric acid reaches its highest tensile strength at 180\% of its original length. The sample prepared with sulfuric acid demonstrates the highest tensile strength at 225\% of its original length. Also, the tensile stress of the sulfuric acid-based sample is lower compared with the samples synthesised with phytic and phosphoric acids. The latter feature of the sulfuric acid-based sample reveals a more compliant quasi-solid electrolyte compared with its counterparts prepared with phosphoric and phytic acid. Thus, the sample prepared with sulfuric acid shows characteristics of mechanical strength to be a potential candidate to be used for the process of rapid prototyping of flexible and stretchable energy storage.
CHAPTER 5. SYNTHESIS OF A GEL ELECTROLYTE

FIGURE 5.11. Tensile strain-stress curves of the PVA/GA/acid quasi-solid gel electrolytes.

5.3.4.2 Electrolyte deposition and 3D printing of electrolytes on electroactive material

Once the PVA-based gel electrolyte with the most remarkable characteristics has been determined, the next stage is the rapid prototyping process using this blend.

The PVA-based blend was qualitatively evaluated in Section 5.3.1.1. The preliminary results of the evaluation revealed that the polymer-based blend synthesised with a PVA with an AVM of 85-125 kDa is suitable for a smooth and controlled 3D-printing process. Additional to the latter evaluation, an additional quantitative evaluation by rheology experiments has been performed. The quantitative evaluation of the polymer-based blend provides a clearer insight of the mechanical properties of the blend once the sulfuric acid has been added to the aqueous polymer matrix. Figure 5.12 shows the rheology results of the PVA/sulfuric acid-based blend. The variation of the viscosity of the blend shows a slight decreasing trend related to increase of the shear rate. The latter shear-thinning or pseudoplastic behaviour is characteristic of a PVA aqueous solution with a 10 wt% content of the polymer.\textsuperscript{68,69}

The resulting range of viscosity related to the applied shear rates (0.1 to 100 s\textsuperscript{-1}) could be attributed to the high AMW of the polymer allowing an entanglement process between the polymer chains. The viscosity values of the PVA-based blend are important to find the parameters of the pressure required for a controlled extrusion process of the prepared ink. For calculation
purposes, the nozzle diameter of the extrusion system is kept to 400 µm. The latter nozzle diameter was successfully used in the previous scenarios for the 3D-printing of the CCCs precursors and electroactive inks of the Section 3.3.2.3 and Section 4.3.4.1 respectively. In addition, the tests performed with different PVA/acid-based gel electrolytes and results detailed in Table 5.2 showed that the use of the PVA/H$_2$SO$_4$-based gel electrolyte promotes a smooth and controlled 3D-printing process with a resolution of 25 µm. For the rapid prototyping of a 3D-printed energy storage device, an in-plane architecture has been considered. To keep consistency with the architecture of the models defined in Section 3.3.2.3 and Section 4.3.4.1, the extrusion speed is calculated to 3D-print a section of 5 cm$^2$ with a height of 0.1 mm in the Z axis. Additional to that, the rapid prototyping extrusion process is estimated to 5 minutes (600 s). Using Equation 3.4 and Equation 3.5, the velocity of the ink flow can be calculated. To use the equations, the required volume to be extruded is determined:

\[ v = \text{length} \times \text{width} \times \text{height} \]

\[ v = 50 \text{ mm} \times 50 \text{ mm} \times 0.1 \text{ mm} \]

\[ v = 250 \text{ mm}^3 \]

the volumetric speed flow can be calculated considering the 250 mm$^3$ volume being 3D-printed
in 600 s as the result of the volume dispensed over the time:

\[ Q = \frac{250 \text{ mm}^3}{600 \text{ s}} = 0.42 \text{ mm}^3 \text{ s}^{-1} \]

considering the standard 400 \( \mu \text{m} \) diameter of the dispensing nozzle, the speed of the ink flow can be calculated:

\[ V = \frac{Q}{\pi r^2} = \frac{0.42 \text{ mm}^3 \text{ s}^{-1}}{\pi \times (0.2 \text{ mm})^2} = 3.32 \text{ mm s}^{-1} \]

Also, the variation of pressure \( \Delta P \) can be obtained using the length of the nozzle and the speed of the ink flow:

\[ \Delta P = \frac{8\eta L V}{r^2} = \frac{8\eta \times 11 \text{ mm} \times 3.32 \text{ mm s}^{-1}}{0.2^2 \text{ mm}^2} \]

The obtained \( \Delta P \) is still a function of the viscosity:

\[ \Delta P = 7294.6\eta \]

The required viscosity \( \eta \) can be worked out from the shear rate \( \dot{\gamma} \), to calculate this latter we can use the volumetric flow and the nozzle diameter:

\[ \dot{\gamma} = \frac{4Q}{\pi r^3} = \frac{4 \times 0.42 \text{ mm}^3 \text{ s}^{-1}}{\pi \times 0.2^3 \text{ mm}^3} = 66.84 \text{ s}^{-1} \]

At this stage, the experimental curves obtained from the rheology characterisation of the PVA-sulfuric acid-based blend (Figure 5.12) are used to obtain the viscosity of the blend at the calculated shear rate. A value of \( \eta = 204.63 \text{ Pa s}^{-1} \) was obtained. Using this latter, the \( \Delta P \) value is calculated:

\[ \Delta P = 7294.6 \times 204.63 \text{ Pa} \]

\[ \Delta P = 1492.63 \text{ kPa} \]

\( \Delta P \) is the difference of pressure between the entrance of the nozzle and the extruding end to keep the velocity of the flow during the 3D-printing process. To support the required pressure difference and avoid any formation of bubbles or inhomogeneous pressure depletion zones between the reservoir and the nozzle, the pressure controlled nitrogen line described in the section 3.3.2.3 is used.

To obtain the crosslinked version of the PVA/sulfuric acid-based gel electrolyte, two strategies were implemented. First, an in-situ crosslinking process was used. The latter strategy required that the PVA/sulfuric acid-based electrolyte and the GA aqueous solution were mixed and immediately extruded using the customised 3D-printer. The disadvantage of this strategy is the
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limited time to 3D-print the gel electrolyte before it becomes completely crosslinked compromising its fluidity to be 3D-printed.

To overcome the latter setback a second strategy was performed by a double printing head system. The heads were set to extrude 2 PVA-based blends. The first ink is made of a PVA/GA-based blend and the second is a PVA/sulfuric acid-based blend. During the 3D-printing process the 3D-printing heads print sequential layers of the PVA-based blends and the crosslinking process takes place in the interface between the 3D-printer parts. To obtain a homogeneous crosslinked quasi-solid gel electrolytes, smaller amounts of material can be extruded. The latter approach allows to obtain thinner layers of the PVA-based inks. Figure 5.13(a) shows an optical microscope image of a 3D-printed single layer PVA/sulfuric acid-based blend with a thickness of 60 µm. Similarly, Figure 5.13(b) shows an optical microscope image of a 3D-printed 3-layer model with an alternate combination of a layer of the PVA/sulfuric acid-based, a second layer of the PVA/GA-based blend and a final layer of a PVA/sulfuric acid-based blend. This combined model exhibits a 180 µm thickness consistent with the measured thickness of 60 µm per layer. This process of combining the PVA-based blends layer-by-layer ensures the mixture between the PVA-based precursors prior to the crosslinking reaction.

Additional characterisation was performed to analyse the morphology of the 3D-printed samples of the PVA/sulfuric acid-based quasi-solid gel electrolytes. After the extrusion process, the electrolyte samples were lyophilised according the methods described in Section 2.2.3.1. The morphology of the electrolyte was investigated by SEM experiments performed over the lyophilised samples. Figure 5.14 shows the SEM images of a PVA/sulfuric acid-based crosslinked sample. The micrographs reveal a rough surface and inner aqueous channels. The aqueous channels are interconnected which can favour the ionic conductivity via the Grötthuss mechanism, in which protons transfer from one water molecule to another, otherwise known as “proton hoping”.

To further quantify the performance of the obtained PVA/sulfuric acid-based quasi-solid gel
electrolyte regarding the sample geometry, a group of supercapacitors with different architectures were tested by capacitance measurements. The distance between the electrodes of the supercapacitor prototypes was varied from 300 µm to 2 mm. In order to keep consistency in the electrodes architecture the size and width of the arms of the supercapacitor were not changed. The preliminary results show that the capacitance of the supercapacitors with smaller distance between electrodes is higher compared to those of wider distance.

**Figure 5.14.** SEM images of PVA/sulfuric acid-based quasi-solid gel electrolytes: a) SEM image of a cross section of the 3D-printed crosslinked PVA/sulfuric acid-based quasi-solid gel electrolyte and b) SEM image of a sample cut in a perpendicular direction of the extrusion.

**Figure 5.15.** Evaluation of the PVA/sulfuric acid-based quasi-solid gel electrolyte in supercapacitor prototypes.
The supercapacitor with electrode arms separated 300 µm exhibit the highest capacitance value (0.64 mF cm$^{-2}$), when the distance between the electrodes is increased to 500 µm, the capacitance decreases to 0.51 mF cm$^{-2}$. This trend is consistent for wider distances of 1 mm and 2 mm where the attained capacitance is 0.39 mF cm$^{-2}$ and 0.30 mF cm$^{-2}$ respectively as shown in Figure 5.15. The attained results can be attributed to the capacitance inverse relationship to the distance between electrodes that has been reported in previous works. Larger distances increase the ion diffusion path, resulting in a decrease in the capacitance of the supercapacitor prototypes. An additional detailed analysis of the influence of the the architectures in interdigitated electrodes will be addressed in Section 6.3.4 of this research work. This evaluation further supports the feasibility of the 3D-printing method to obtain a functional quasi-solid gel electrolyte for supercapacitor prototypes.

5.4 Conclusions

Options to find a suitable electrolyte for energy storage devices has been explored. To avoid leakages and obtain a gel electrolyte, an aqueous liquid acid-based electrolyte was endowed with viscosity upon the introduction of a water-soluble polymer matrix of PVA. The molecular weight of the PVA was varied to obtain different viscous blends which were used in the customised 3D-printers to evaluate their extrudability.

Additional to that, a series of PVA/acid-based gel electrolytes were successfully prepared with different acids. These electrolytes were tested to determine their influence in the capacitance of supercapacitor prototypes. Also the capacitance retention were tested upon CV cycling tests. The blends prepared with sulfuric, phosphoric and hydrochloric acids demonstrated the higher capacitance retention. Also the tests revealed that the phytic acid-based blend did not show a stable capacitance retention that hampered its use as a potential gel electrolyte for the supercapacitor prototypes.

Further capacitance experiments revealed that the electrolyte blends could be dehydrated and produce a decreasing capacitance retention upon intense charge-discharge cycling. As a strategy to overcome the dehydration of the gel electrolyte, a layer of UV-curable silicone rubber was extruded on the supercapacitor prototype as encasement. In addition a crosslinking process of the PVA polymer chains using GA was performed.

The electrolyte blends were crosslinked upon the addition of GA. However, they showed different crosslinking times. Further analysis revealed that the samples prepared with stronger acids are crosslinked faster compared with those prepared with weaker acids. This result was related to the protons availability in the aqueous acidic PVA-based blends. The crosslinking times were also found to be related with the molecular weight of the PVA. Longer chains of the polymer can reduce the gelation time and produce intermolecular crosslinking rather than intramolecular crosslinking.
The crosslinked gel electrolytes were studied to obtain the tensile stress as a function of the tensile strain. The quasi-solid gel electrolyte prepared with sulfuric acid showed to be the most compliant material compared with its phosphoric and phytic acid-based quasi-solid counterparts. Also the sulfuric acid-based sample revealed the highest tensile strain before rupture.

The sulfuric acid-based gel electrolyte demonstrated the best characteristics to be used in the rapid prototyping of a flexible supercapacitor prototype. This gel was evaluated by rheology experiments and demonstrated to be extrudable using the customised 3D-printers and external pressure system. The parameters of pressure and velocity of the ink flow were successfully calculated and the obtained values were found to be in the range of the customised 3D-printing systems developed for this research work.

The SEM experiments showed that the obtained 3D-printed gels have interpenetrating aqueous networks allowing the ionic conductivity through the micro channels. Figure 5.14(a) shows a SEM image of a cross section of the 3D-printed crosslinked PVA/sulfuric acid-based quasi-solid gel electrolyte. The observed sample was obtained by cutting a 3D-printed film in the direction of the extrusion. This image reveals how the channels are distributed along the section of the sample. On the other hand Figure 5.14(b) shows a SEM image of a sample cut in a perpendicular direction of the extrusion. This image exhibits how the micro channels are interconnected each other, thus allowing the mentioned ionic conductivity.

The sulfuric acid-based quasi-solid gel electrolytes are the best candidates to be used in the construction of flexible and stretchable energy storage devices. The use of the developed quasi-solid electrolytes are evaluated in the next chapter of this research work. The feasibility of a 3D-printable gel electrolyte was demonstrated and its performance will be evaluated in a complete flexible 3D-printed supercapacitor prototype.

5.5 References


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6.1 Abstract

Nowadays there are increasing requirements to use supercapacitors for energy storage applications. The increasing demand of these devices can be attributed to their exceptional fast charge/discharge capabilities, impressive power density, and long cyclability. The remarkable properties of the supercapacitors are only possible by enhancing the overall capacitance of the device. This enhancement can be attained by improving the performance of each one of the supercapacitor’s individual components. Also, flexible and stretchable supercapacitors have garnered extensive attention because of their practical application in wearable electronics. The astonishing flexibility and stretchability in a supercapacitor device can be achieved with the synergistic combination of flexible and stretchable components. The strategies to obtain stretchable supercapacitor devices are aimed to construct stretchable conductive current collectors (CCCs) and electrodes in flexible and stretchable substrates or encasing structures. Also, the constituent parts of the energy storage devices such as the electroactive material and the gel electrolytes should be constructed with flexible and stretchable materials. In addition, the interfaces between the building layers of the flexible energy storage devices needs to be carefully explored to avoid faulty contacts or poor diffusion of the materials into the porous components. All the aforementioned challenges are carefully addressed in this chapter to obtain a flexible and stretchable supercapacitor. The scientific efforts devoted to obtain the flexible energy storage device are supported by the successful synthesis and preparation of the CCCs, electroactive material, electrolytes and the protective substrate or encasement, all attained in the previous chapters of this thesis. Each component was prepared, characterised and enhanced to obtain the best performance. The attained materials were further processed and optimised to obtain 3D-printable blends that
can be extruded and combined with precise and software-controlled procedures. The energy storage devices constructed with the obtained materials are evaluated to explore the resulting capacitance performance and flexibility during the different stages of optimisation. The optimised energy storage devices are tested to evaluate the results of the synergistic contribution of the enhanced 3D-printed and laser-scribed materials in a fully 3D-printed flexible energy storage device.

6.2 Introduction

The growing sector of electronics, in particular flexible electronics, demands circuits and electronic devices that can retain their function when are bent or stretched. The increasing commercial impact of these flexible devices has caught wide attention from industry and academia.\textsuperscript{3-5} The outcome of the scientific and industrial efforts in the flexible electronics field is the availability of wearable electronics. Also, the presence of the 4G and 5G technologies has facilitated the connection of sensors, treatment systems, navigation and communication devices to the internet, thus, promoting the interconnection of the wearable systems or sensors to the Internet and exchange data world wide. All the electronics including flexible and stretchable devices need energy to be driven. The energy storage devices that provide the required driving energy should have the same flexible and stretchable characteristics. Traditional batteries and stiff supercapacitor devices cannot meet the requirements of wearable electronic systems. Then, one of the best alternatives to provide energy is the use of flexible and stretchable all-solid supercapacitors.\textsuperscript{3,6,7}

A supercapacitor device with the abovementioned characteristics should have the required flexibility and stretchability without sacrificing the main features of a supercapacitor device such as high energy and power densities, very long cyclability and optimised safety. To obtain a flexible energy storage device that shows the required features, each constituent part of the device should have the individual characteristics of flexibility and stretchability.

In this study, the research effort devoted to obtain the flexible and stretchable supercapacitor has been focused separately in each one of the constituent elements of the device by preparing, characterising, and optimising the materials for each part. This parts were developed in different stages. The first stage included the preparation and optimisation of flexible and stretchable electrodes. The second part was devoted to the synthesis and preparation of a suitable flexible and stretchable electroactive material. The third stage included the synthesis and enhancement of a flexible quasi-solid gel electrolyte. During the development of the above-mentioned stages, the obtained supercapacitor devices were constantly evaluated to register the evolution of the research and optimisation of the materials. Extensive attention has been devoted to the results of the combination of the different parts of the energy storage device to attain highly optimised materials for a complete device. Additionally, the construction of the device must be reliable and reproducible. The current demands of industry and academia to develop complex shapes
or bespoke models has promoted the use of precise techniques to obtain the desired accuracy and precision. To attain the latter characteristics, computer-assisted methods are available for the design and construction of 3D models. In addition, the designed models can be precisely constructed using 3D printing techniques performed by current available cheap commercial customisable 3D printers. Using these 3D printing techniques the manufacturing of flexible devices is attained by keeping the characteristics of viscosity of the materials. The materials required for the construction of CCCs, electrodes of electroactive material, gel electrolytes, and the flexible encasement have been developed, characterised and optimised to obtain extrudable blends that can be 3D-printed and combined in a precise and software-controlled fashion. The attained precision and building times allow the combination of the extrusion procedures with highly accurate laser-scribing processes in a manufacturing line-like system. The latter has been developed with cheap commercial 3D printers and laser-scribers customised in the present research. The reliability of the hardware and software of the 3D-printers and laser-scribers allowed repeatable results and the controlled change of different variables to optimise the materials to attain enhanced results in this research effort. Finally, the results of capacitance and stability of the constructed supercapacitors are monitored during the optimization processes, and the final optimised devices are presented with the best values attained.

6.3 Results and discussion

6.3.1 General structure of a 3D-printable supercapacitor

An energy storage device can be designed with different configurations. The most considered architectures in 3D-printed devices are in-plane architectures or sandwiched structures as shown in the Figure 6.1. The advantages of each architecture depends on the requirements of the application of the energy storage device. In the first stage of this research work, a sandwiched-
like structure was used. This architecture allowed to test and evaluate the performance of the potential electroactive materials and electrolytes to be used in the construction of the flexible supercapacitor prototypes.

However, in later stages of this research effort a sandwiched architecture always required a separator when an electrolyte with low viscosity was used. The latter procedure was utilised to avoid any probable short circuit between electrodes upon bending tests. In the in-plane configuration, there is no risk of short circuit produced under bending tests.

Also, in the sandwiched configuration, a constant electrolyte thickness can not be maintained upon mechanical tests of bending. Whilst in the in-plane configuration the electrolyte thickness is not affected upon bending tests. From the manufacturing prospective, the in-plane configuration allows the precisely controlled deposition of the electrolyte without of the formation of bubbles or undesired voids that can be formed upon the assembly of the sandwiched version of the supercapacitors. The latter setbacks are overcome by a 3D-printed layer-by-layer architecture where interdigitated CCCs are coated with a PANi-based electroactive material and a layer of a PVA-based gel electrolyte. A final 3D-printed layer of the encasing or protective material covers the surface of the supercapacitor prototype prior the capacitance and mechanical tests. Also, the in-plane interdigitated architecture has been attributed a higher capacitance performance by previous studies.11,12

The precision of the models relays on the precision of the laser scriber. In this research work the precision of the laser scriber was evaluated by measuring the width of the laser-engraved

![Figure 6.2. In-plane design of interdigitated electrodes of a supercapacitor.](image)
6.3. RESULTS AND DISCUSSION

patterns. The laser spot size was calibrated to 100 μm by carefully setting the focus of the laser. The scribed surface was set to a 4-line width. These set of dimensions are expected to generate a 400 μm width pattern. The attained pattern was characterised by optical microscopy measurements. Figure 6.3 shows an optical microscope image of a laser-scribed pattern with measurements of width performed by using the image analysis program Image J. The results obtained are shown in Table 6.1 where the deviation of the scribed patterns width from the targeted width is less than 5 μm.

![Figure 6.3](image_url)

**Figure 6.3.** Optical microscope image of a laser-scribed pattern evaluated by the image analysis program Image J.

**Table 6.1.** Measurements of width performed over an optical microscope image of a 4-line width laser-scribed model by using the image analysis program Image J.

<table>
<thead>
<tr>
<th>No. of lines</th>
<th>4-lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample 1</td>
<td>401.3 μm</td>
</tr>
<tr>
<td>sample 2</td>
<td>401.4 μm</td>
</tr>
<tr>
<td>sample 3</td>
<td>393.3 μm</td>
</tr>
<tr>
<td>sample 4</td>
<td>397.3 μm</td>
</tr>
<tr>
<td>sample 5</td>
<td>402.7 μm</td>
</tr>
<tr>
<td>sample 6</td>
<td>405.3 μm</td>
</tr>
<tr>
<td>sample 7</td>
<td>404.0 μm</td>
</tr>
<tr>
<td>sample 8</td>
<td>396.0 μm</td>
</tr>
<tr>
<td>sample 9</td>
<td>400.0 μm</td>
</tr>
<tr>
<td>sample 10</td>
<td>397.4 μm</td>
</tr>
</tbody>
</table>

Average width 399.8 μm

The laser-scribing process creates a porous architecture with a thickness of 100 μm as shown
in the SEM image of a cross-section of the model shown in Figure 6.4. This thickness is constant over the whole model supporting the consistency of the method to create the laser-scribed architecture.

**Figure 6.4.** Optical microscope image of a cross-section of a laser-scribed pattern obtained by microtome sectioning process.

In addition, the surface of the laser-scribed electrodes shows a porous morphology. Figure 6.5 shows the irradiated area revealing an irregular surface with porosities that will be infiltrated by the PAni-based blends or a PVA-based gel electrolyte during the manufacturing process of the supercapacitor prototypes.

**Figure 6.5.** SEM image of the surface of a laser-scribed pattern.

As precise patterns can be obtained by the laser-scribing system, the interdigitated configuration can be attained with high accuracy. The distances between the electrodes can be successfully obtained in the order of hundreds of micrometres.
The precise control of the distance between electrodes of the supercapacitor allows the exploration of the effects of this variable in the capacitance. A simulation of the capacitance performance of a supercapacitor device related to the distance between electrodes was performed using a finite element analysis software package and the results are presented and further analysed in Section 6.3.4 of this thesis.

6.3.2 Combination and attachment between the components layer-by-layer

The developed CCCs, electroactive materials and gel electrolytes were constantly evaluated to optimise their performance in a supercapacitor prototype device.

The initial synthesis and optimisation of a suitable electroactive material required a recurrent electrochemical evaluation to obtain an enhanced product. During the initial part of the studies, the developed PANi-based, PANi/GO-based, and PANi-rGO blends were tested to obtain the specific capacitance related to the weight of the material. The electroactive polymer and the combinations of it with GO and rGO were tested as an electrode material synthesised in the surface of conductive carbon cloths. Further characterisation was performed by exploring some electrolytes based on sulfuric acid, phytic acid and phosphoric acid respectively to evaluate the potential improvement of capacitance with the use of a suitable electrolyte.

![Figure 6.6. Specific capacitance of PANi-based materials on conductive carbon cloths.](image)

The results of this electrochemical characterisation can be found in Figure 6.6. The highest capacitance were obtained with the samples with predominant electroactive material. The result is consistent with the fact that the GO and rGO were added to provide structural strength to the polymer backbone rather that for increasing the capacitance of the polymer-based material. This latter could be compromised by the charge and discharge cycles that swell and shrink the polymer.
The values of capacitance obtained are consistent with results reported in previous studies. The developed electroactive materials are not suitable for 3D-printing as explained in Section 4.3.1.1. However, they allowed insight into the capacitance that can be obtained with a PANi-based material.

In addition, the obtained results could be attributed to good contact between the electroactive material and the carbon-based fabrics. The carbon cloths were coated with the PANi-based materials by an in-situ polymerisation process. The latter included procedures of soaking of the carbon cloths into the aqueous precursors of the polymer as the morphology studies revealed in Section 4.3.1.1.

The constructed prototypes using carbon cloths as conductive current collectors can not be stretched. This result is related to the structural limitations of the carbon fabric to be strained. The next stage in the development of the materials was a successful preparation and construction of flexible and stretchable CCCs reported in the Chapter 3. These new 3D-printed and laser engraved structures were used in the next generation of supercapacitor prototypes. They were constructed with 3D-printing procedures where the electroactive material was smoothly extruded on the surface of the CCCs and the gel electrolyte was deposited on top of the electroactive material. In both extrusion procedures, the accurate and precise patterns are attained by software-controlled systems. The latter were developed and optimised by customising the hardware and software of the commercial 3D-printers available in the Faul Research Group laboratories.

The characterisation of the capacitance was realised by evaluating the supercapacitor prototypes. The new evaluation permits to quantify the capacitance performance of the fully constructed prototype rather than the individual parts. The individual evaluation of the elements was successfully performed in the Chapter 3, Chapter 4 and Chapter 5. To have an overall value of capacitance of the developed prototypes, the superficial specific capacitance was used. This method of measurement is consistent with previous characterisations of capacitance for in-plane supercapacitors.

Figure 6.7 shows the specific capacitance of 3D-printed supercapacitor prototypes constructed with the optimised 3D-printed and laser-scribed PEO/GO conductive current collectors, 3D-printed PANi-based electroactive material electrodes and PVA/H$_2$SO$_4$-based gel electrolyte. The highest capacitance corresponding to 2.3 F cm$^{-1}$ was obtained with the fully optimised electroactive CSA/DBSA/PANi-based blend developed in the Section 4.3.1 of this thesis.

The interfaces between the developed materials and 3D-printable blends are crucial for the capacitance behaviour of the supercapacitor prototypes. The porous laser-induced graphene is coated with the 3D-printed electroactive material. The software-controlled extrusion process allows to 3D-print precise surfaces, shapes, and patterns of the electroactive material. The accuracy reached with the 3D-printing process of the electroactive material is 5% evaluated by analysis of the "road paths" performed in Section 4.3.4.2 of this research effort. Likewise, the accuracy attained for the extrusion process of the PVA-based gel electrolyte is 5% as detailed.
in Section 5.3.4. In both cases the attained accuracy was obtained using a 400 µm nozzle. The accuracy can be increased by reducing the diameters of the nozzles used for the 3D-printing process. However, this approach can compromise the manufacturing time of the supercapacitor prototypes becoming one of the possible limitations of the process as explained in Section 4.3.4.2. The extrusion of each material should be performed after a careful process of alignment. The alignment can be automatically set in the code for the manufacturing line. However, the alignment step can become a setback in case different 3D printers are used for each material instead of a multiple head 3D printer.

The extrusion system of the 3D-printers pushes the PAni-based blends to the surface of the CCCs. The latter pushing effect could promote a better surface contact between the CCCs and the PAni-based material, and an infiltration effect inside of the porosities previously created during the manufacture of the laser-scribed CCCs. In addition, despite the possible positive contribution of the pushing effect, the work of adhesion analysis of the surfaces in contact performed in Section 4.3.3 and Section 6.3.3 suggests a good interaction between the two materials.

In the case of the interface formed between the PAni-based material and the gel electrolyte, both materials are the result of the extrusion of aqueous viscous blends. The work of adhesion of the electroactive material and the gel electrolyte reveals that the disperse and polar contributions...
for each material are very similar. Thus, the adhesion of the gel electrolyte and the PANi-based electrodes allows the obtained performance in capacitance. The SEM image in Figure 6.8 shows the morphology of a dried PANi-based blend previously extruded on the surface of the CCCs. The micrograph reveals a rough, porous surface with a random orientation of the PANi structures. However, in a non-dried sample, the PANi structures are flooded with excess DBSA. The latter allows the extrudability of the blend and also mostly contributes with the disperse and polar fractions to the work of adhesion between the surfaces.

6.3.3 Surface free energy of the conductive current collectors, PVA based gel electrolyte and PANi based inks

The surface free energy (SFE) of the materials were analysed as part of the calculation of the work of adhesion (WA) in Section 4.3.3 of this thesis. However, the WA previously obtained can potentially influence to the capacitance attained for the 3D-printed supercapacitor prototype device. A greater WA also shows a better capacitance performance.

Figure 6.9 contrasts the capacitance of the supercapacitor prototypes with the WA between the CCCs and the electroactive material and the WA of the electroactive material with the gel electrolyte. The highest capacitance of 2.38 F cm$^{-2}$ is attained with the electroactive material with the best WA. The latter was evaluated in the interface with the CCCs underneath and between the 3D-printed gel electrolyte extruded on top of the PANi-based surface. The Owens, Wendt, Rabel and Kaelble (OWRK) method uses the surface tension (ST) and the surface free energy (SFE) to calculate the WA of the interface energy. The trend observed as a result of the increasing DBSA content of the PANi-based blends is a decreasing tendency in the adhesion between the inks and the CCCs or the gel electrolyte. Figure 6.9(c) shows that the decreasing
6.3. RESULTS AND DISCUSSION

**FIGURE 6.9.** Work of adhesion and capacitance of a supercapacitor prototype: a) Surface free energy of the CCCs and the gel electrolyte  b) Surface tension of the PANi-based blends  c) Work of adhesion of the PANi-based with the CCCs and the gel electrolyte d) Capacitance of the supercapacitor prototypes. Note: a) and b) copied from Figure 4.12 in Section 4.3.3. c) copied from Figure 4.13 in Section 4.3.3. d) copied from Figure 6.7 in Section 6.3.2.

A similar trend applies for the interface between the PANi-based blends and the CCCs. The latter result could be attributed to the low polar contribution in the SFE of CCCs and the dominating disperse contribution in both, the CCCs and the PANi-based blends. Consequently, as the polar contribution increases and the disperse contribution decreases with the increase of DBSA in the PANi-ink, a drop in the WA is observed. However, the decreasing trend in capacitance is larger compared with the trend in the WA. This result could be attributed to the disperse contribution being the largest to the physisorption between the CCCs and the PANi-based inks. The disperse contribution is provided by the weak dispersion or London forces. Hence, small reductions in the disperse forces can affect the contact between the surfaces, diminish any possible infiltration and compromise the formation of the electronic double layer between the two materials. A similar trend applies for the interface between the PANi-based blends and the CCCs.
and the gel electrolyte. In this regard, Figure 6.9(c) shows a decreasing WA with the increasing DBSA concentration and supports the influence of the WA in the capacitance results. Despite the WA decrease, the adhesion still remains greater compared with the one of the CCCs, with the disperse and polar contributions noticeably balanced compared to the ones of the CCCs. Also, the shift in the dominant contributors of the ST of the PANi-based inks is outweighed by the overall decrease in the total ST. The overall decrease in adhesion of the interfaces could massively contribute to the reduction of capacitance. However, many structural and chemical factors can compromise electrochemical processes and negatively impact the capacitance of the supercapacitor devices. 19–21

6.3.4 Design of the structure of the 3D printable supercapacitor

The supercapacitor prototype devices were constructed using several designs. Figure 6.10 shows different supercapacitors designs. The first stages of this research effort included the tests of rigid models to evaluate the performance of the early stages electroactive materials. Figure 6.10(a) and Figure 6.10(b) show the rigid supercapacitors constructed and assembled by hand. This latter configurations allowed the optimisation of the electroactive material and the enhancement of the gel electrolytes.

Figure 6.10(c) shows a flexible supercapacitor prototype build using a combination of manual assembly and 3D-printing. The devices built using the latter hybrid techniques of construction allowed the evaluation of the flexibility of the PANi-based electroactive material, as well as the gel electrolyte. During the stage of the latter tests, conductive carbon cloths were used as current collectors in the supercapacitor prototype devices.

Figure 6.10(d) shows a fully 3D-printed supercapacitor prototype. The model was constructed with the thoroughly optimised 3D-printing and laser-scribing techniques and the enhanced materials detailed in the Chapter 3, Chapter 4 and Chapter 5 of this thesis.

During the characterisation and optimisation of the phytic acid-doped PANi electroactive material, the specific gravimetric capacitance of the polymer was evaluated. The EESDs tested were manufactured with carbon cloth-based conductive current collectors, PVA/H₂SO₄-based gel electrolyte and the electroactive polymer. The latter electroactive material synthesised by the in-situ polymerisation attained up to 400 F g⁻¹, which is a competitive value of specific capacitance compared to the current literature as shown in Table 6.2.

However, the obtained polymer-based electroactive material could not be directly 3D printed. As an alternative, polymer blends of PEO or PVA were tested as a potential polymer matrix to hold the electroactive material to obtain an extrudable PANi-based 3D-printable ink. The resulting materials were suitable for 3D-printing but the presence of the holding matrices compromised the performance of the electroactive polymer as detailed in Section 4.3.4. A second approach using a DBSA/CSA-doped PANi was successfully developed towards a 3D-printable PANi-based blend. The developed blend were smoothly extruded in the construction process of the supercapacitor.
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Figure 6.10. Evolution of the constructed supercapacitor prototypes: a) Rigid prototype for electroactive material optimisation  b) Rigid prototype for gel electrolyte optimisation  c) Flexible prototype to test the flexibility of the materials  d) Fully 3D-printed flexible supercapacitor

Prototype devices as shown in Section 4.3.4.1. In the latter stage, a 3D-printable blend was successfully obtained and the evaluation of the specific capacitance was realised regarding the surface of the new developed supercapacitors. The new way of obtaining the capacitance performance provides a better overall vision of the evaluated complete device rather than only a part of it. In addition, in Section 6.3.1 the architecture of the supercapacitors was evaluated. The results of the evaluation promoted the use of a planar or an in-plane architecture of the supercapacitors.

The in-plane interdigitated supercapacitor devices are widely evaluated by the areal specific
Table 6.2. Comparison of the capacitance obtained in the present work with other works with PANi-based supercapacitors.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Capacitance $F \text{ g}^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D-printed polymer-based gel electrolyte</td>
<td>400</td>
<td>This work</td>
</tr>
<tr>
<td>Polymer-based electrolyte</td>
<td>480</td>
<td>Sivaraman et al. $^{22}$</td>
</tr>
<tr>
<td>Polymer-based electrolyte</td>
<td>250</td>
<td>Prasad et al. $^{23}$</td>
</tr>
<tr>
<td>1M $\text{H}_2\text{SO}_4$</td>
<td>480</td>
<td>Pan et al. $^{14}$</td>
</tr>
<tr>
<td>1M $\text{H}_2\text{SO}_4$</td>
<td>420</td>
<td>Duo et al. $^{15}$</td>
</tr>
<tr>
<td>1M $\text{H}_2\text{SO}_4$</td>
<td>503</td>
<td>Dhawale et al. $^{24}$</td>
</tr>
</tbody>
</table>

capacitance rather than using the gravimetric one related to the electroactive material. This way of obtaining the specific capacitance is more suitable than the gravimetric way because it allows to assess the real application of the in-plane electrodes of a flexible energy-storage device.\cite{25} The accuracy of the 3D-printers and laser-scribers allow precise patterning processes. The precision attained is of 5% for the 3D-printing work and less than 3% for the laser scribe as detailed in Section 4.3.4.2 and Section 6.3.1 respectively in this scientific effort. This precision constitutes the difference between the designed paths and the obtained 3D-printed and laser-scribed paths. One strategy to increase the capacitance is the reduction of the distance between the electrodes. The latter approach also reduces the migration distances for the ions in the gel electrolyte. The small spaces between interdigitated electrodes promote the elimination of separators and increase the accessibility of the electrolyte ions to the edges of the laser-scribed and 3D-printed electrodes. Also, the planar architecture of the electrodes is more flexible and bendable compared to the sandwiched counterparts.\cite{26,27}

The patterns and shapes required to attain highly precise electrodes were designed in CAD packages such as Autodesk® Inventor® Professional Software and Blender Software as detailed in Section 3.3.2.1 of this thesis. The 3D-printers can precisely extrude the 3D printable blends following the CAD designs. The gaps between extruded patterns are in micrometres. These distances between patterns also depend on how viscous the extruded material is, and how it flood after the extrusion process. In this regard, the PANi-based blends and the gel electrolyte have a neglectable flooding behaviour after the extrusion process. However, in the case of the laser-scribed electrodes, the size of the gaps could be affected by the power of the laser. The accuracy of the patterns accounts for the size of the laser-scribed spots. The latter can be tuned by changing the engineering parameters of power, speed and frequency of the laser-scribing system as demonstrated in Section 3.3.4. The current literature reports of the increase in the specific capacitance related to the reduction of the gap between electrodes.\cite{28-30} This effect is further supported in this thesis work by the results of experimental test and software simulations. The simulations were carried out using FEMM 4.0, a finite element method for solving 2D and 3D low frequency magnetic, magnetostatic, and linear electrostatic problems.\cite{31} The accuracy of the
laser-scribing system allows to produce patterns for interdigitated electrodes with gaps sizes as small as 300 µm. This gap size can be obtained after the engineering parameters of the laser system have been properly tuned to reach the optimised laser-induced graphene-CCCs according the results reported in Section 3.3.4.

![Figure 6.11](image)

**Figure 6.11.** Interdigitated supercapacitor prototypes: a), b) Pattern designs c) Laser-scribed and 3D-printed supercapacitor devices

Additional supercapacitor prototypes with larger gap sizes (0.5 mm, 1 mm, and 2 mm) between electrodes were laser-scribed and 3D-printed to evaluate the impact of the variation of the gap in the specific capacitance.

Figure 6.11 shows the pattern designs of the interdigitated supercapacitor prototypes and the manufactured laser-scribed and 3D-printed models.

Figure 6.12 shows the experimental specific capacitance obtained from the laser-scribed and 3D-printed supercapacitor prototypes with a PVA-sulfuric acid-based gel electrolyte. The latter results reveal an increasing trend of the areal specific capacitance related to the reduction of the gap size. Values decrease from 0.63 mF cm⁻² (0.3 mm gap) to 0.29 mF cm⁻² (2 mm gap). The latter outcome could be attributed to a reduction of the length of ion diffusion. The results are consistent with previous reports in the literature.²⁸–³⁰
The previous experimental results are further supported by the simulations performed using the finite element method magnetics software FEMM 4.0. The results of the simulations are shown in Figure 6.13. The obtained specific capacitance of the models reveal a similar trend compared to the experimental results. The increasing tendency in the band gap produces a decrease trend in the specific capacitance as expected. The obtained values of the specific capacitance in the simulations are in the order of nF cm$^{-2}$. The latter capacitance values can be attributed to the nature of the surfaces of the electrode selected for the simulation process. The electrodes are represented in FEMM 4.0 as flat surfaces rather than porous carbon. This limitation lead to the very small values of specific capacitance. However, the dependence of the specific capacitance related to the gap between the interdigitated electrodes is noticeable in the simulations thus supporting the experimental results. These results can be related to the dependence of the increase in capacitance related to the distance between electrodes. The reduction of the ionic path between the electrodes decreases the electrolyte resistance between the arms with the electroactive material, thus reducing the transport limitations of the ions through the separation distances. The results are consistent with previous results reported by Igreja et al.$^{32}$

The experimental results supported by the simulations showed that the highest capacitance is obtained with the smallest gap between the interdigitated electrodes. The latter outcome promoted the use of the gap of 300 μm in the architecture of the interdigitated electrodes of the laser-scribed and 3D-printed supercapacitor prototypes.
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6.3.5 Electrochemical tests

The constituent parts of the supercapacitor prototypes were successfully optimised in the previous stages of this research effort. The components such as the CCCs, electroactive material and gel electrolyte were evaluated and enhanced independently. However, the synergistic combination of the components must be characterised to evaluate the overall performance of the supercapacitor prototype. In this regard, capacitance measures were carried out using electrochemical characterisation techniques such as cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD). The Figure 6.14 shows the CV of a fully 3D-printed supercapacitor. The measurement was carried out at different scan rates from 1 mV s$^{-1}$ to 100 mV s$^{-1}$. The broader peak of the curves could be related to the change in oxidation state of the electroactive polymer. The PANi-based material can change from the leucoemeraldine oxidation state (or full reduced) to the emeraldine form, and from the emeraldine oxidation state to the pernigraniline oxidation state,$^{33}$ as detailed in Section 1.7. The changes in the polymer oxidation state are reversible as long as the working potential window is kept under or equal to 0.8 V. If the potential window is increased, the electroactive polymer-based network could be compromised by the effect of the electrochemical
CHAPTER 6. DEVICE FABRICATION AND TESTING

Figure 6.14. CV of the 3D-printed and laser-scribed supercapacitor prototypes.

degradation of the polymer.\textsuperscript{34,35} A potential close to 0.8 V could maintain the polymer between the leucoemeraldine oxidation state and the emeraldine oxidation state. A neglectable amount of the species fully oxidised into pernigraniline form of the polymer can undergo degradation of the electroactive material. In addition, the potential window of 0-0.8 V keep the supercapacitor device prototype within a working voltage that maintains the electrochemical stability of the aqueous PVA/sulfuric acid-based gel electrolyte.\textsuperscript{36–39}

The specific capacitance $C_s$ of the supercapacitor prototype devices is calculated using the Equation 6.1:

$$ C_s = \frac{C}{m} = \frac{\int_{E_1}^{E_2} i(E) \, dE}{m V (E_2 - E_1)} $$  \hspace{1cm} (6.1)

where $i(E)$ is the voltammetric discharge current in amperes, $V$ is the scan rate in V s\textsuperscript{-1}, $E_1$ and $E_2$ are the integration potential limits of the CV curve.

The specific capacitance can also be calculated considering not only the mass $m$, but also, the surface $s$, or the volume $v$ of the electroactive material or the electrode evaluated.

The highest value of specific capacitance obtained from the CV curves is 2.3 F cm\textsuperscript{-2} at a scan rate of 1 mV s\textsuperscript{-1}. The attained capacitance is comparable to other works previously reported. Wang et.al\textsuperscript{40} reported a capacitance of 1.3 F cm\textsuperscript{-2} in a PANi-based micro-supercapacitor with polystyrene/silver paste-based conductive current collectors and PVA/H\textsubscript{2}SO\textsubscript{4}-based electrolyte. Likewise, Khosrozadeh et.al\textsuperscript{41} reported a capacitance of 3.84 F cm\textsuperscript{-2} for a PANi-based micro-supercapacitor with stainless-steel-based conductive current collectors and aqueous H\textsubscript{2}SO\textsubscript{4}-based electrolyte. In addition to the above mentioned values of capacitance, Bellani et.al\textsuperscript{42}, Jiang et.al,\textsuperscript{43} and Zhang et.al\textsuperscript{44} reported micro-supercapacitor capacitances of 1.32 F cm\textsuperscript{-2}, 2 F cm\textsuperscript{-2},
and 1.29 F cm$^{-2}$, respectively. The capacitance characterisation results of our work show a good agreement with previously reported works in supercapacitor prototypes. This could be attributed to the contribution of the electroactive polymer pseudocapacitance to the overall capacitance. The reported capacitance values are obtained under similar small voltage scan rates or current densities such as 1 mV s$^{-1}$ and 4.2 mA cm$^{-2}$, respectively.

The value of capacitance decreases at higher scan rates. This result could be attributed to the fact that the energy storage process involves charge transfer phenomena happening not only at the surface of the electroactive material electrodes but also within the bulk material as explained in Section 4.3.2.$^{45}$ Similar results from the galvanostatic charge discharge (GCD) curves are obtained and contrasted with the ones obtained from the CV curves.

![Figure 6.15. Capacitance retention of the 3D-printed and laser-scribed supercapacitor prototype device over 10,000 cycles.](image)

In addition, the electrochemical stability of the supercapacitor prototype device was further supported by cycling tests performed by charging and discharging the 3D-printed and laser-scribed energy storage device.

Figure 6.15 shows the results of the capacitance retention of the supercapacitor prototype device over 10,000 CV cycles. The latter performance can be related to the electrochemical stability of the components of the supercapacitor prototype device. This result supports that the stability of the components of the prototype is not affected by the processes of combination and construction of the supercapacitor. The capacitance drop is less than 3% after 10,000 cycles of charge discharge. This outcome, compared with the current literature, is a competitive result for the developed supercapacitor prototype.$^{46}$ In this regard, previous authors such as Wang et.al$^{47}$
have reported 4% drop in capacitance over 10,000 cycles. Likewise, Yufei et al.\textsuperscript{48} reported a 7% drop over 10,000 cycles and Ruiying et al.\textsuperscript{49} reported a loss of 3.2% of the original capacitance over 5,000 cycles.

The electrochemical performance of the supercapacitor prototypes was further tested by GCD experiments. The Figure 6.16 shows the results of the GCD characterisation of the supercapacitors at different current densities. The values of capacitance obtained from the GCD curves are consistent with the values obtained from the CV experiments with a maximum value of specific areal capacitance of 2.14 F cm\textsuperscript{-2}. Compared to the results of the CV characterisation, the GCD experiments show a similar decreasing electrochemical behaviour at higher current densities.

![Figure 6.16. Galvanostatic charge/discharge curves of the 3D-printed and laser-scribed supercapacitor prototypes at different current densities (2, 4, 6, 8, 10, 20 mA cm\textsuperscript{-2}).](image)

This result could be attributed to the loading by 3D-printing of the electroactive material on the CCCs. The charges need to move from the CCCs through the extruded PAni-based material to reach the electroactive sites of the bulk parts of the polymer-based blend.\textsuperscript{50} A lower loading of the electroactive material can reduce the drops in capacitance at higher scan rates or higher current densities. However, this reduction in the amount of the electroactive material compromises the overall areal capacitance. A good trade-off between the specific areal capacitance and the electrochemical performance at higher scan rates could be attained by changing the volume of the PAni-based material extruded for the rapid prototyping of the supercapacitor prototype devices.

The results of the CV and GCD characterisation of the supercapacitors were used for the calculation of the energy density and power density of the energy storage devices. The results obtained are shown on Figure 6.17. The power density VS energy density diagram or Ragone plot of the supercapacitors show the position of the maximum energy and power per unit of
surface obtained from the 3D-printed and laser-scribed devices. The values obtained in this work from the 3D-printed and laser-scribed supercapacitor prototype devices are contrasted with previous results reported in the current literature for a similar kind of supercapacitor prototypes. The latter comparison shows that the energy storage devices developed in this research effort have competitive values of energy and power densities compared with many state-of-the-art PANi-based supercapacitor devices. Eustache2017HighElectrolytes, 25,50–52

![Ragone plot of the 3D-printed supercapacitors compared with previously reported works: PAni-GO-fMSC from reference 50, PAni-CNTs from reference 52, PAni-FSSCs from reference 51, N3-CNFs/RGO/BC from reference 25, PG/WJM-graphene:SWCNTs from reference 42, MnO2-based MSC from reference 53.](image)

**Figure 6.17.** Ragone plot of the 3D-printed supercapacitors compared with previously reported works: PAni-GO-fMSC from reference 50, PAni-CNTs from reference 52, PAni-FSSCs from reference 51, N3-CNFs/RGO/BC from reference 25, PG/WJM-graphene:SWCNTs from reference 42, MnO2-based MSC from reference 53.

The attained competitive values of power density and energy density can be attributed to the synergistic combination of the laser-induced graphene-based CCCs, a CSA/DBSA-doped PANi electroactive material and an optimised gel electrolyte. Also, the architecture of the electrodes of the supercapacitor play a fundamental role in the electrochemical properties of the 3D-printed prototypes. The energy density are mostly related to the energy storage capacity of the electrodes. This latter is achieved by the pseudocapacitive contribution of the electroactive material to the overall capacitance. Likewise, the power density relays on the EDLC, the conductivity of the electrodes to transport the charges, and the kinetics of the electrolyte ion transport. In addition, the obtained power density results can be related to the CCCs being made with laser-induced
CHAPTER 6. DEVICE FABRICATION AND TESTING

Graphene rather than active carbon-based electrodes. The two-dimensional sheet-like structure of the graphene allows the electrolyte to reach large open surface areas with a smaller diffusion barrier compared with that of activated carbon.\textsuperscript{54}

The architecture of the device also can contribute to obtain optimised results in the electrochemical properties. The reduction in the gap between electrodes of the interdigitated design not only improves the capacitance abilities of the supercapacitor prototype as previously demonstrated in Section 6.3.4, but also, plays an essential role in the power that can be obtained from the supercapacitor prototype devices. Smaller gaps are directly translated into shorter ionic diffusion paths, thus, decreasing the electrolyte resistance between the electrode arms.\textsuperscript{28–30,54} The dimensions of the gaps can be easily adjusted using the software CAD-packages such as Autodesk® Inventor® Professional Software and Blender Software.

6.3.6 Flexibility and stretching tests

The 3D-printed and laser-scribed supercapacitors performance was evaluated by bending and strain tests. The result of the bending tests are shown in Figure 6.18. The supercapacitor prototype device exhibits a remarkable mechanical strength upon bending tests. The electrochemical evaluation of the supercapacitor at various bending angles show CV curves revealing the same capacitive behaviour. The latter results demonstrate that the variations of the device electrochemical characteristic is neglectable under distinct bending angles. The supercapacitors tested at the different bent states exhibits almost the same CV area as the ones tested at normal state.

![Figure 6.18. CVs of the flexible supercapacitor prototype device with bending angles of 0, 45°, 90°, 135°, and 180° at a fixed scan rate of 20 mV s\textsuperscript{-1}.](image)

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in Figure 6.14. The stability in the electrochemical performance of the supercapacitor prototype upon bending tests can only be attained by the combination of flexible and compliant components. The CCCs, electroactive material, gel electrolyte and silicone rubber-based encasement must be flexible and stretchable so these properties are reflected in the constructed prototype.

The CCCs are attached to a flexible and stretchable substrate of UV-curable silicone rubber UV Electro 225-1 (Momentive Performance Materials, USA). This silicone rubber can be elongated up to 500% of its original length (see data sheet in Appendix Section A.1.1). The 3D-printed PANi-based material extruded on the CCCs is a paste-like compliant blend. The electroactive material does not break or separate upon strain tests of its supporting substrate. The PVA/sulfuric acid-based quasi-solid gel electrolyte can be elongated up to 120% of its original size (Section 5.3.4.1). Taking into account the previous data, strain tests were performed on the supercapacitor prototype devices.

![Figure 6.19. Capacitance performance of the 3D-printed and laser-scribed supercapacitor prototype: a) Cyclic voltammetries of the supercapacitor under tensile strain of 0%, 10%, 20%, and 30% b) Capacitance retention at 0%, 10%, 20%, and 30% tensile strain](image)

The capacitance performance upon stretching of the supercapacitor was evaluated by CV tests. Figure shows the result of the stretching tests. The CV voltammograms show similar shapes supporting the ability of the supercapacitor to keep the capacitance properties under tensile strain. The 3D-printed supercapacitor retains 87% of its original capacitance at a tensile strain of 30% of its original size. These results could be attributed to the change in the internal conformation of the 3D-printed materials rather than in the characteristics of the geometry of the architecture of the supercapacitor prototypes such as the gap between electrodes. In order to keep a consistent inter-electrode gap, the stretching tests were performed in the direction of the arms of the supercapacitor. These results demonstrate that the supercapacitor prototype devices not only present properties of flexibility but also abilities of stretchability which increases its
CHAPTER 6. DEVICE FABRICATION AND TESTING

potential application in wearable electronics, soft robotics and implantable technologies.

6.4 Conclusions

The constituent parts of a supercapacitor prototype have been successfully prepared, characterised, tested and optimised to obtain 3D-printable components. These parts such as the CCCs, electroactive material and gel electrolyte have demonstrated remarkable performances individually. Now the synergistic contributions of the parts have been successfully combined in a fully 3D-printed supercapacitor prototype device. The constructed device shows competitive features of capacitance, energy and power densities, very long cyclability and optimised safety. The 3D-printed supercapacitor prototypes exhibit an areal capacitance of 2.3 F cm\(^{-2}\) which is comparable with previous works. Values of 1.3 F cm\(^{-2}\), 3.84 F cm\(^{-2}\), 1.32 F cm\(^{-2}\), 2 F cm\(^{-2}\) and 1.29 F cm\(^{-2}\) have been reported by Wang et.al,\(^{40}\) Khosrozadeh et.al,\(^{41}\) Bellani et.al,\(^{42}\) Jiang et.al,\(^{43}\) and Zhang et.al,\(^{44}\) respectively.

The values of energy and power density of the 3D-printed supercapacitor prototypes are 0.21 mWh cm\(^{-2}\) and 39.4 mW cm\(^{-2}\) respectively. Table 6.3 shows the values of energy and power density attained with the 3D-printed supercapacitor prototypes compared to other research works in similar supercapacitors reported in the current literature. The values of power density in previously reported works are in a range that goes from 4 mW cm\(^{-2}\) to 37.5 mW cm\(^{-2}\). Our 3D-printed supercapacitor prototype exhibits a power density of 39.4 mW cm\(^{-2}\) being competitive with the formerly reported PANi-based and carbon-based supercapacitor prototypes. Likewise, the attained value of energy density in this work (0.21 mWh cm\(^{-2}\)) is in the same magnitude range of the previous reported works.

The obtained 3D-printed supercapacitors also show high electrochemical stability over 10,000 cycles of charge/discharge with a capacitance retention of 97\% after the cycling test. Similar PANi-based supercapacitor prototypes have been reported as electrochemically stable in previous investigations such as the works reported by Wang et.al,\(^{47}\) Yufei et.al\(^{48}\) and Ruiying et.al\(^{49}\) with capacitance retentions of 96\%, 93\% and 96.8\% over 10,000, 10,000 and 5,000 cycles, respectively. Thus supporting that the attained stability is competitive with the existing PANi-based supercapacitors.

The durability of the supercapacitor prototypes is addressed not only by attaining a competitive electrochemical stability but also by keeping an appropriate encasement. The encasement prevents the dehydration of the 3D-printed gel electrolyte and provides a safe interface between the prototype and the external world. The encasement was 3D-printed using the developed 3D-printers in this research work as demonstrated in Section 5.4. The material used for the encasement is the extrudable UV-curable silicone rubber UV Electro 225-1 (Momentive Performance Materials, USA) as shown in Section 6.3.4 and Figure 6.10.

The supercapacitor device prototype has been successfully proven to be flexible and stretchable.
without compromising any of the main features of a supercapacitor prototype.

The building techniques to prepare the 3D-printed supercapacitor have been tested and demonstrated to be reliable and reproducible. Also, the 3D-printing and laser- engraving techniques allow to obtain bespoke designs to enhance the performance of the supercapacitor prototype devices. The successful design-driven optimisation in the capacitive behaviour of the prototypes was further supported by software simulations, thus confirming the feasibility and validity of the developed techniques.

The micro-scale design has been determined as a key component in the supercapacitor optimisation. The achieved precise micro patterns of the laser-scribed CCCs allowed the test of different designs and configurations to reduce the gap between electrodes. The gap reduction was demonstrated to be a key factor in the electrochemical performance of the supercapacitor prototype devices. The precise patterns attained by the 3D-printing systems allowed a smooth and highly controlled deposition of the developed extrudable inks. The software controlled extrusion processes attained the same precision of the laser-engraving system, thus allowing an accurate deposition of the electroactive material on the surface of the micro-patterns of the CCCs. Likewise, the gel electrolyte-based blend and the silicone rubber-based encasing blend can be extruded in a precise software-controlled fashion promoting a smooth integration of the blend to the constructed device. One of the most important results of this thesis chapter is the successful integration of the

<table>
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<th>Electrode material</th>
<th>Specific capacitance (F cm⁻²)</th>
<th>Energy density (mWh cm⁻²)</th>
<th>Power density (mW cm⁻²)</th>
<th>Stability</th>
<th>Ref.</th>
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<tr>
<td>PG/WJM-graphene:SWCNTs</td>
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<td>0.361</td>
<td>20.13</td>
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<td>80% @ 6k cycles</td>
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<td>5.07</td>
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<td>0.05</td>
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<td>76% @ 10k cycles</td>
<td>40</td>
</tr>
<tr>
<td>PANi-CSA/DBSA</td>
<td>2.3</td>
<td>0.21</td>
<td>39.4</td>
<td>97% @ 10k cycles</td>
<td>this work</td>
</tr>
</tbody>
</table>

previously developed supercapacitor parts in a complete assembled device. The fully 3D-printed supercapacitor device reveals a remarkable electrochemical performance. This result is attained

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with the supercapacitor prototype having the electroactive PANi-based blend with the best WA to its adjacent CCCs and gel electrolyte. The outcome of the WA experiments demonstrates the validity of the technique to evaluate the adhesive forces between the constituent parts of the supercapacitor device.

The optimisation algorithm used in the development of the 3D-printed supercapacitor prototypes was based on a design-driven process. This procedure allowed to combine the software simulations with the production challenges to attain the simulated architectures. The values of precision obtained for each 3D-printed and laser-scribing process were the limiting factors during the optimisation processes. The optimisation procedures and the attained performances are not compromised by the introduction of a safe encasement. Conversely, the use of an encasement architecture enhanced the safety and durability of the supercapacitor prototypes as shown in Chapter 5.

The customised 3D-printing techniques and the laser engraving processes have been successfully used to produce and integrate the components of a supercapacitor device. The latter presents an areal capacitance of 2.3 F cm⁻², excellent cycling stability (97% retention after 10,000 cycles). Also the developed supercapacitor prototype can deliver a high energy density of 0.21 mWh cm⁻² and a maximum power density of 39 mW cm⁻² making it competitive compared with similar micro-supercapacitors reported to date as shown in Table 6.3. Our work shows that the developed 3D-printing and laser-scribing procedures are powerful and competitive ways to produce a flexible and stretchable supercapacitor device.

The precise software-controlled processes could be easily integrated in a production line with determined manufacturing times and keeping the resulting devices with their remarkable electrochemical performance. The feasibility of a production line-like processes are only possible once the components have been demonstrated to be integrated without compromising their individual performance. The attained integration results pave the way towards automated fabrication processes of energy storage devices with industrial and academic applications.

### 6.5 References


7.1 Conclusions

In this research effort we have proposed and demonstrated a combination of techniques to produce 3D-printed flexible and stretchable energy storage devices. Each individual component of these devices went through a process of synthesis, preparation and production. These procedures were developed and optimised to obtain the highest performance of the produced components. The integration of the parts was achieved and combined towards a fully 3D-printed supercapacitor prototype device. Although 3D printers and laser engraver were developed to attain bespoke complex shapes and patterns, the manufacturing process was performed with low cost commercially available parts. The obtained were fully tested, and their performance was supported by characterisation techniques, not only at the nano-scale and micro-scale, but also at the macro-scale. The investigations carried out in this work show the potential practical application of the performed studies and attained processes and devices. The simple and efficient methods and techniques developed in this research can be potentially employed on an industrial and high throughput application level.

From this research work we have learnt valuable lessons. First, the strategies of synthesis and production can be optimised and successfully combined with a laser-engraving and 3D-printing-based manufacturing processes towards low-cost and high-performance flexible and stretchable supercapacitor prototypes. Second, complex designs and precise patterns of the supercapacitor prototypes can be successfully achieved with customised affordable 3D printers and laser scribers. Third, the requirements for bespoke energy storage devices can be initially fulfilled for applications of the supercapacitor prototypes in wearable electronics, soft robotics and human-machine interfacing.
The developed technology has potential applications for shape-adaptive/wearable/portable electronics, soft sensors, stretchable circuits, pressure and strain sensors, epidermal-compatible electronics, and implantable medical circuits/devices. In this regard, our work provides the initial answers for the challenges in each broad field.

7.1.1 Conductive current collectors and laser-scribing

This work has demonstrated the feasibility to manufacture of flexible and stretchable CCCs using these 3D-printing and laser-scribing strategies. The extrusion process can be precisely set to obtain accurate bespoke thickness for the models. The laser-scribing process can be set to obtain competitive results of sheet resistance compared to the current state-of-the-art results obtained with highly expensive femto-seconds lasers. This achievement was attained by investigating, tuning and optimising the engineering parameters of power, speed and frequency of an affordable laser system mounted in the commercial 3D-printer. The most remarkable consequence of obtaining an interconnected laser-induced conductive material is that the developed CCCs do not need an additional metal-based conductive coating. This fact allows the CCCs to be directly applied in the construction of flexible and stretchable energy storage devices, which represents a significant step forward in terms of high throughout and low cost manufacturing of specialised devices. At the same time for high power density-demanding applications, the developed laser-scribed conductive porous material can be combined with flexible conductive blends or additional metal-based substrates or coatings.

7.1.2 Electroactive material

The research carried out in this thesis demonstrated that a 3D-printable electroactive material can be successfully obtained. The research efforts allowed to understand the limitations in performance when a polymer matrix is used to support the electroactive material and turn it into a extrudable blend. The initial obtained ink did not demonstrate the properties required as a potential material to be used in the supercapacitor prototypes. To enhance the low-performance polymer matrix/electroactive material blend, a new synthesis strategy was implemented to replace the polymer matrix. This new procedure included the use of new doping acids as precursors added in excess during the synthesis of the electroactive material. This new synthesis procedure resulted in a high electrochemical performance 3D-printable electroactive material. This experience paved the way to understand and create synthesis strategies to obtain enhanced extrudable materials without supporting polymer matrices.

7.1.3 Electrolyte

The research carried out in this scientific effort has demonstrated that a 3D-printable gel electrolyte can be synthesised and optimised to obtain competitive values of capacitance. Also, the
produced extrudable gel electrolyte was successfully integrated as a constituent part of a flexible and stretchable supercapacitor prototype. The research performed to attain the above-mentioned results allowed us to understand that there are a plethora of acids that can be used to synthesise an extrudable gel electrolyte. Also, the performed studies demonstrated the potential mechanisms and precursors to obtain a mechanically enhanced bendable and stretchable gel electrolyte to integrate it as a part of the desired supercapacitor prototype devices.

7.1.4 Supercapacitor prototype device

We have proposed and demonstrated successful methods and strategies to produce a flexible and stretchable supercapacitor prototype device by 3D-printing and laser-scribing processes. During this research work, the processes of production and optimisation revealed that the constituent parts needed to be optimised and tested not only individually, but also integrated with the other constituent parts of the supercapacitor. These parallel activities of constant integration trials during the optimisation of each part allowed us to arrive at an overall complete supercapacitor device with high-capacitance, flexible and stretchable capabilities. We have demonstrated as well that the developed supercapacitors can be applied in the fields of soft robotics, wearable and portable electronics. The latter potential application is related to the capabilities of the supercapacitor device to keep its remarkable capacitance performance upon bending and stretching tests. We learnt that the individual optimisation of the parts carried out in parallel with constant integration tests lead to a successful combination of the synergistic contributions of the parts, resulting in a high-performance supercapacitor prototype device. In addition, the combination process not only promoted the controlled assembly of the parts, but also allowed the integration of the manufacturing processes. These results pave the way towards a fully automated production line, scalable to an industrial level.

7.2 Outlook

There are a plethora of aspects of this research work that could be addressed and continued to further develop this scientific effort. Similarly, new research projects can be developed from the outcomes obtained in this investigation.

Challenging the design rules for device design is one of the main tasks that should be considered as a future work with potentially significant impact. The integration of the developed flexible and stretchable supercapacitor device to wearables requires new properties. These new capabilities will require focused efforts in aspects such as increased power density or energy density. These challenges open the possibilities for different energy storage materials such as MXenes (2D transition metal carbides, nitrides, and carbonitrides, where M represents early transition metals -M = Ti, Sr, V, Cr, Ta, Nb, Zr, Mo, or Hf-, and X represents either C or N as well as both)\textsuperscript{1–3} or diverse electrolytes such as ionic liquids or organic electrolytes, all of which can be
used in these applications while maintaining the flexible and stretchable capabilities. Likewise, mechanical enhancements would be required, including washable capabilities and impact tests.

Further complex applications can be envisaged for the supercapacitor prototypes such as use in extreme environments. The latter scenarios require major attention to variables that were considered as constants during this research effort. High temperatures or freezing environments will need special attention to the temperature tolerances of the materials and processes during the fabrication process. Also the potential risks in the overall performance of the supercapacitor device under the extreme circumstances must be addressed to endure the abovementioned environments and keeping the highest performance possible. More interesting applications in other sectors could include the aerospace industry, for example, the extreme conditions of pressure, impact and temperature need to be addressed in the manufacturing process and the chosen materials. The reported processes used in this research effort have been executed at ambient conditions. The inclusion and integration of the manufacturing processes of 3D-printing, laser-scribing and Uv-curing in vacuum can be good solutions to address the extreme requirements and new design rules for the aerospace industry.

All the experimental research can be well complemented and further advanced with the support of the corresponding simulations. The different aspects of the overall behaviour of the supercapacitor prototype device could be addressed. The capacitance mechanism conditions can be modelled as well as the response of the materials to different mechanical and electrical conditions. The bending and stretching response could be predicted by finite element analysis (FEA) simulations performed with a plethora of potential flexible material profiles. Beyond these proposed simulation scenarios, one of the most interesting fields of investigation is the phenomena produced in the interfaces between materials such as gel electrolyte-electroactive material and electroactive material-conductive current collectors.

Also, broader future applications for the supercapacitor-related research should account for multifunctional devices. Such challenges for the supercapacitor prototypes in science and industry can be addressed by endowing these devices with novel functionalities. Supercapacitors with specific functions such as mechanical, interfacial, thermal, electronic, energy harvesting, energy conversion can be developed to fulfill the requirements of an industry in constant evolution.

Finally, it is the hope that the output from this thesis will inform future developments in a wide range of areas as mentioned above, ensuring uptake and application of these exciting processes and materials.

### 7.3 References


A.1 Material data sheets

All data sheets are shown as received from the supplier. Only pages with relevant information on material characteristics and composition are included.
A.1.1 UV-curable silicone rubber UV Electro 225-1

Silopren™ UV Electro 225-1 by Momentive Performance Materials is a UV-curable, silicone rubber. Exhibits high voltage of 3.5 kV, efficient processing, high-speed curing at low temperatures and reduced cycle times to increase productivity.

Offers low shrinkage, better scorch performance and enables two-component combinations. Silopren™ UV Electro 225-1 is suitable for use in high-quality parts, healthcare products, kitchenware, automotive parts, electronic components and LEDs.

**Product Type**
Silicone Rubber

**Physical Form**
Liquid

**Product Status**
COMMERCIAL

**Applications/ Recommended for**
Households products/ Consumer Goods > Kitchen utensils
Optics > LED (Light-Emitting Diode)
Healthcare / Medical
Automotive
Electronics / Computers > Electronic components (capacitors...)

**Key Features**
Cycle Time, Short
Processability, Good
Shrinkage, Low

### Silopren™ UV Electro 225-1 Properties

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<th>Physical</th>
<th>Value &amp; Unit</th>
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<th>Test Method</th>
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**Mechanical**

| Value & Unit | Test Condition | Test Method |
|--------------|----------------|-------------|-------------|

Lasted edited August 19, 2018
http://omnexus.specialchem.com
## Universal Selector™

### A.1. MATERIAL DATA SHEETS

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<th>Property</th>
<th>Value</th>
<th>Methodology</th>
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<td>DIN 53505</td>
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**Help us improve the Universal Selector**

You can’t find what you are looking for? Please report missing products / suppliers, point out errors, or simply tell us how we could make the Universal Selector better.

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Last updated: August 19, 2018

http://omnexus.specialchem.com
A.1.2 Smooth-On DragonSkin technical data sheet

**PRODUCT OVERVIEW**

Dragon Skin™ silicones are high performance platinum cure liquid silicone compounds that are used for a variety of applications ranging from creating skin effects and other movie special effects to making production molds for casting a variety of materials. Because of the superior physical properties and flexibility of Dragon Skin™ rubbers, they are also used for medical prosthetics and cushioning applications. Dragon Skin™ rubbers are also used for a variety of industrial applications and have a service temperature range of a constant -65°F to +450°F (-52°C to +232°C).

**Great for Making Molds for a Variety of Applications** - Available in Shore 10A, 20A and 30A. Dragon Skin™ silicones can be used to make exceptionally strong and tear resistant molds for casting plaster, wax, concrete (limited production run), resins and other materials. Dragon Skin™ 10 AF is an anti-fungal silicone suitable for making a variety of skin-safe cushioning device configurations.}

**Time Tested, Versatile Special Effects Material** - Soft, super-strong and stretchy, Dragon Skin™ 10 (Very Fast, Fast, Medium and Slow speeds) is used around the world to make spectacular skin and creature effects. An infinite number of color effects can be achieved by adding Silc Pig™ silicone pigments or Cast Magic™ effects powders. Cured rubber can also be painted with the Psycho Paint™ system. Cured rubber can also be painted with the Psycho Paint™ system.

**Easy To Use** – Dragon Skin™ silicones are mixed 1A:1B by weight or volume. Liquid rubber can be thinned with Silicone Thinner™ or vacuum degassing is recommended to minimize air bubbles in cured rubber.

**TECHNICAL OVERVIEW**

<table>
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<th>Specific Gravity (g/cm³)</th>
<th>Specific Volume (cu. in./lb)</th>
<th>Shore A Hardness</th>
<th>Shore B Hardness</th>
<th>Cure Time</th>
<th>Density</th>
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<th>Dielectric Strength (ASTM D-149)</th>
<th>Dielectric Strength (ASTM D-149)</th>
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<td>Dragon Skin™ 10 Medium</td>
<td>23,000 cps</td>
<td>1.07</td>
<td>25.8</td>
<td>20 min.</td>
<td>5 hours</td>
<td>10A</td>
<td>475 psi</td>
<td>22 psi</td>
<td>100%</td>
<td>102 psi</td>
</tr>
<tr>
<td>Dragon Skin™ 10 Slow</td>
<td>23,000 cps</td>
<td>1.07</td>
<td>25.8</td>
<td>45 min.</td>
<td>7 hours</td>
<td>10A</td>
<td>475 psi</td>
<td>22 psi</td>
<td>100%</td>
<td>102 psi</td>
</tr>
<tr>
<td>Dragon Skin™ 10 AF</td>
<td>23,000 cps</td>
<td>1.07</td>
<td>25.8</td>
<td>20 min.</td>
<td>5 hours</td>
<td>10A</td>
<td>475 psi</td>
<td>22 psi</td>
<td>100%</td>
<td>102 psi</td>
</tr>
<tr>
<td>Dragon Skin™ 10 Very Fast</td>
<td>23,000 cps</td>
<td>1.07</td>
<td>25.8</td>
<td>16 hours</td>
<td>30A</td>
<td>500 psi</td>
<td>86 psi</td>
<td>36%</td>
<td>108 psi</td>
<td>&lt; .001 in./in.</td>
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*All values measured after 7 days at 73°F/23°C.*

**PROCESSING RECOMMENDATIONS**

**PREPARATION... Safety** – Use in a properly ventilated area ("room size" ventilation). Wear safety glasses, long sleeves and rubber gloves to minimize contamination risk. Wear vinyl gloves only. Latex gloves will inhibit the cure of the rubber.

**Store and use material at room temperature (73°F/23°C).** Warmer temperatures will drastically reduce working time and cure time. Storing material at warmer temperatures will also reduce the usable shelf life of unused material. These products have a limited shelf life and should be used as soon as possible. Mixing containers should have straight sides and a flat bottom. Mixing sticks should be flat and stiff with defined edges for scraping the sides and bottom of your mixing container.

**Cure Inhibition** – Addition-cure silicone rubber may be inhibited by certain contaminants in or on the pattern to be molded resulting in tackiness at the pattern interface or a total lack of cure throughout the mold. Latex, tin-cure silicone, sulfur clays, certain wood surfaces, newly cast polyester, epoxy, tin cure silicone rubber or urethane rubber may cause inhibition. If compatibility between the rubber and the surface is a concern, a small-scale test is recommended. Apply a small amount of rubber onto a non-critical area of the pattern. Inhibition has occurred if the rubber is gummy or uncured after the recommended cure time has passed.

Because no two applications are quite the same, a small test application to determine suitability for your project is recommended if performance of this material is in question.
To prevent inhibition, one or more coatings of a clear acrylic lacquer applied to the model surface is usually effective. Allow any sealer to thoroughly dry before applying rubber. Note: Even with a sealer, platinum silicones will not work with modeling clays containing heavy amounts of sulfur. Do a small scale test for compatibility before using on your project.

Applying A Release Agent - Although not usually necessary, a release agent will make demolding easier when pouring into or over most surfaces. Ease Release™ 200 is a proven release agent for making molds with silicone rubber. Mann Ease Release™ products are available from Smooth-On or your Smooth-On distributor.

IMPORTANT: To ensure thorough coverage, lightly brush the release agent with a soft brush over all surfaces of the mold. Follow with a light mist coating and let the release agent dry for 30 minutes.

If there is any question about the effectiveness of a sealer/release agent combination, a small-scale test should be made on an identical surface for trial.

MEASURING & MIXING...

Stir Part A and Part B thoroughly before dispensing. After dispensing required amounts of Parts A and B into mixing container (1A:1B by volume or weight), mix thoroughly for 3 minutes making sure that you scrape the sides and bottom of the mixing container several times. After mixing parts A and B, vacuum degassing is recommended to eliminate any entrapped air. Vacuum material for 2-3 minutes (29 inches of mercury), making sure that you leave enough room in container for product volume expansion.

POURING, CURING & MOLD PERFORMANCE...

For best results, pour your mixture in a single spot at the lowest point of the containment field. Let the rubber seek its level up and over the model. A uniform flow will help minimize entrapped air. The liquid rubber should level off at least 1/2" (1.3 cm) over the highest point of the model surface.

Curing / Post Curing - Allow rubber to cure as prescribed at room temperature (73°F/23°C) before demolding. Do not cure rubber where temperature is less than 65°F/18°C. Optional: Post curing the mold will aid in quickly attaining maximum physical and performance properties. After curing at room temperature, expose the rubber to 176°F/80°C for 2 hours and 212°F/100°C for one hour. Allow mold to cool to room temperature before using.

If Using As A Mold - When first cast, silicone rubber molds exhibit natural release characteristics. Depending on what is being cast into the mold, mold lubricity may be depleted over time and parts will begin to stick. No release agent is necessary when casting wax or gypsum. Applying a release agent such as Ease Release™ 200 (available from Smooth-On) prior to casting polyurethane, polyester and epoxy resins is recommended to prevent mold degradation.

Thickening Dragon Skin™ Silicones - THI-VEX™ is made especially for thickening Smooth-On’s silicones for vertical surface application (making brush-on molds). Different viscosities can be attained by varying the amount of THI-VEX™. See the THI-VEX™ technical bulletin (available from Smooth-On or your Smooth-On distributor) for full details.

Thinning Dragon Skin™ Silicones - Smooth-On’s Silicone Thinner™ will lower the viscosity of Dragon Skin™ for easier pouring and vacuum degassing. A disadvantage is that ultimate tear and tensile are reduced in proportion to the amount of Silicone Thinner™ added. It is not recommended to exceed 10% by weight of total system (A+B). See the Silicone Thinner™ technical bulletin (available from Smooth-On or your Smooth-On distributor) for full details.

Mold Performance & Storage - The physical life of the mold depends on how you use it (materials cast, frequency, etc.). Casting abrasive materials such as concrete can quickly erode mold detail, while casting non-abrasive materials (wax) will not affect mold detail. Before storing, the mold should be cleaned with a soap solution and wiped fully dry. Two part (or more) molds should be assembled. Molds should be stored on a level surface in a cool, dry environment.

Call Us Anytime With Questions About Your Application.

Toll-free: (800) 381-1733 Fax: (610) 252-6200

The new www.smooth-on.com is loaded with information about mold making, casting and more.

031621-JR
A.1.3 Elemental analysis of graphene oxide

Table A.1: Elemental analysis of graphene oxide. The relative amounts (in percent) of nitrogen, carbon, and hydrogen are given for each batch of GO.

<table>
<thead>
<tr>
<th></th>
<th>Graphenea 2016 (%)</th>
<th>Graphenea 2018 (%)</th>
<th>Graphtene (%)</th>
<th>Own production (%)</th>
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<tbody>
<tr>
<td>N</td>
<td>0.35</td>
<td>49.0</td>
<td>0.76</td>
<td>0.64</td>
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<td>C</td>
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<td>42.73</td>
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<tr>
<td>H</td>
<td>2.88</td>
<td>&lt;1.00</td>
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