



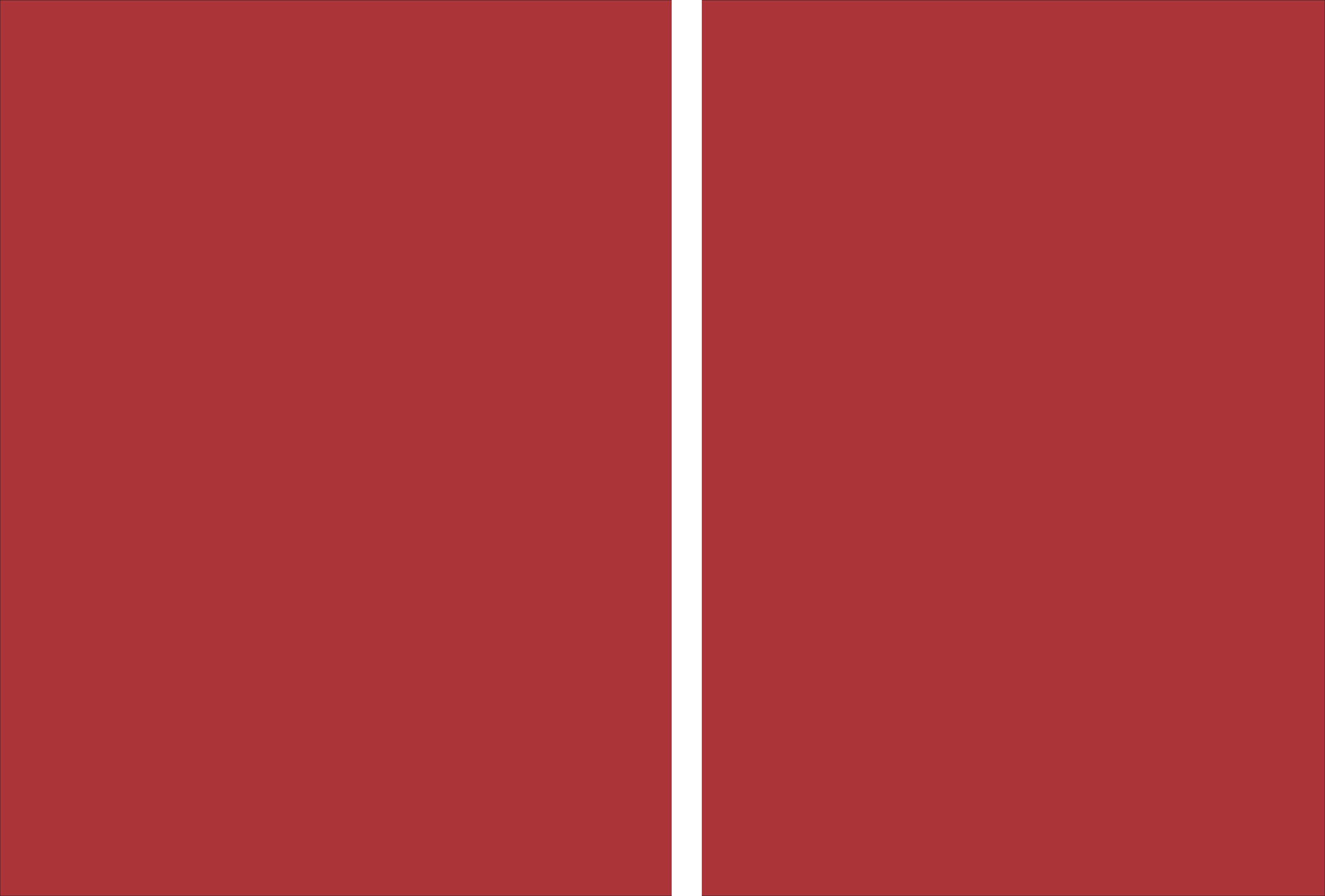
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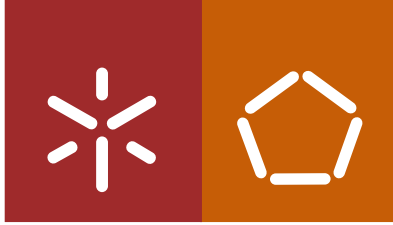
Jivago Serrado Gomes Aguiar Nunes

Polymer based sensors fabricated by printing technologies

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Escola de Engenharia

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Polymer based sensors fabricated by printing technologies

Tese de Doutoramento
Doutoramento em Engenharia de Materiais

Trabalho efetuado sob a orientação do
Professor Doutor Senentxu Lanceros-Méndez
e do
Professor Doutor José Gerardo Vieira Rocha

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Finally, I would like to dedicate this work to my parents, specially to my mother, since she had a dream of me becaming a doctor after seeing the movie *Doctor Zhivago*. By the way, I still haven't found Lara!

To my parents.

*Knowing is not enough,
We must apply.
Willing is not enough,
We must do.*

- Johann Wolfgang von Goethe -

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Sensores de base polimérica fabricados por tecnologias de impressão

Sensores podem ser encontrados em diversos objetos do cotidiano tais como como telemóveis, equipamentos de cozinha, ecrãs tácteis, teclados, brinquedos e outras inúmeras aplicações. Desde o aparecimento do primeiro sensor em 1860, a tecnologia de sensores cresceu exponencialmente devido aos avanços realizados na ciência e engenharia de materiais, sendo capazes de serem duráveis, leves, finos, flexíveis, baratos e rápidos de produzir. Nas últimas décadas inúmeros desenvolvimentos têm sido alcançados na formulação de tintas, tipos de substratos e técnicas de impressão, e atualmente os sensores flexíveis e impressos são aplicados em várias áreas tais como aeroespacial e automóvel, robótica, biomédica, eletrónica de consumo, embalagem e retalho, com uma fatia de mercado de US\$ 3,6 mil milhões em 2018. Esta tese centra-se no desenvolvimento de tintas eletroativas para produzir sensores impressos em substratos poliméricos, nomeadamente tintas piezoresistivas, magnetoelétricas e piezoelétricas. Estas tintas foram desenvolvidas para as tecnologias de impressão por serigrafia e por spray, que são as técnicas mais utilizadas pela a indústria. A tinta piezoresistiva foi baseada no elastómero termoplástico estireno-etileno/butileno-estireno (SEBS), como matriz polimérica, e em nanotubos de carbono de paredes múltiplas (MWCNT) como “fillers” condutores, utilizando a técnica de impressão por *doctor blade*. Foram utilizados três solventes amigos do ambiente e as suas propriedades foram avaliadas, revelando uma boa reprodutibilidade e uma boa resposta da sensibilidade, ideal para a produção de sensores de pressão. Compósitos magnetoelétricos (ME) à base de poli(fluoreto de vinilideno-co-trifluoretileno)/ferrite de cobalto (P(VDF-TrFE)/CoFe₂O₄) foram impressos por *spray* e uma elevada resposta ME foi obtida, demonstrando assim a adequação dos materiais desenvolvidos para a produção de sensores a baixo custo e de grande escala de produção. Uma tinta piezoelétrica, baseada em poli(fluoreto de vinilideno-co-trifluoretileno), (PVDF-TrFE), foi desenvolvida utilizando um solvente amigo do ambiente, e impressa através de três técnicas de impressão: *doctor blade*, spray e serigrafia, sendo posteriormente avaliadas as suas propriedades. Os filmes de PVDF-TrFE foram aplicados no desenvolvimento de uma tela táctil que permitiu a detecção da pressão e libertação dos toques exercidos. Finalmente, outro protótipo impresso foi desenvolvido, constituído por uma matriz capacitiva, e juntamente com uma eletrónica de leitura capacitiva foi obtido um touchpad capacitivo capaz de detectar vários toques em simultaneo e de identificar objetos previamente marcados. Em conclusão, foi demonstrada a possibilidade de fabricar sensores totalmente impressos utilizando diferentes tintas eletroativas e diversas técnicas de impressão. Dois protótipos totalmente funcionais foram desenvolvidos e testados, capazes de medir o toque/força e reconhecer objetos previamente marcados.

Palavras-chave: Sensores impressos, piezoresistivo, piezoelétrico, magnetoelétrico, polímero

Polymer based sensors fabricated by printing technologies

Sensors can be found in everyday objects such as mobile phones, kitchen appliances, touchscreens, keyboards, toys and other applications. Since the development of the first sensor in 1860, the sensor technology has grown almost exponentially due to advances in materials science and engineering, being able to be durable, light, thin, flexible, cheap and fast to produce. In the last decades developments have been achieved in terms of ink formulation, substrate materials and printing techniques, and nowadays, flexible and printed sensors are used in many areas including aerospace and automotive, robotics, biomedical, consumer electronics, packaging and retail, with a market share of \$3.6 billion in 2018.

This thesis focus on the development of electroactive inks to produce printed sensors on polymeric substrates, namely piezoresistive, magnetoelectric and piezoelectric inks. These inks were developed for screen printing and spray printing technologies, which are the most used techniques in the industry.

The piezoresistive ink was based on the thermoplastic elastomer styrene-ethylene/butylene-styrene (SEBS) as polymer matrix, and multi-walled carbon nanotubes (MWCNT) as conductive fillers, and printed by doctor blade. Three environmental friendly solvents were used and the proprieties evaluated, showing a good reproducibility and sensibility to produce pressure sensors. Magnetoelectric (ME) composites based on poly(vinylidene fluoride-co-trifluoroethylene)/cobalt ferrite (P(VDF-TrFE)/CoFe₂O₄) were printed by spray and a high ME response was obtained, demonstrating the suitability of the developed materials for large-scale and cost effective sensor production to be used in a wide range of applications. A piezoelectric ink, based on poly(vinylidene fluoride-co-trifluoroethylene), (PVDF-TrFE), was developed using an environmentally friendly solvent N,N-dimethylpropyleneurea (DMPU). Three printing techniques were used: doctor blade, spray printing and screen printing, and the proprieties of the inks were evaluated. The PVDF-TrFE films were applied in the development of a touch screen which allowed the detection of both touch and release events, revealing as a good candidate for a new generation of touch panels with a low environmental impact. Finally, another printing prototype was developed capable of detecting touch and marked objects. This flexible screen printed sensor consisted on a capacitive matrix based on silver ink with diamond shape, and a polyethylene terephthalate (PET) substrate. Coupled with conventional capacitive reading electronics, a high functional capacitive touchpad with a resolution of 36 points/mm was obtained, capable of detecting several touches simultaneously and to identify marked objects.

In conclusion, it was demonstrated the possibility of fabricating complete printed sensors with different electroactive inks, using several printing techniques. Two fully functional prototypes were developed and tested, capable of measuring the touch/force and recognizing marked objects.

Keywords: Printed sensors, piezoresistive, piezoelectric, magnetoelectric, polymer

Table of Contents

List of figures	ix
List of tables.....	xii
List of symbols	xiii
List of acronyms.....	xv
1. Introduction	1
1.1. Printed sensors	2
1.2. Materials	7
1.2.1. Inks.....	7
1.2.2. Substrates	9
1.3. Printing technologies	10
1.3.1. Spray coating.....	12
1.3.2. Screen printing	13
1.4. Objectives.....	15
1.5. Thesis structure.....	15
1.6. References	16
2. The influence of different solvents on the stability and performance of piezoresistive inks for flexible electronics.....	21
2.1. Introduction.....	22
2.2. Experimental	23
2.2.1. Materials.....	23
2.2.2. Sample preparation	23
2.2.3. Sample characterization	24
2.3. Results and discussion	25
2.4. Conclusions.....	31
2.5. References	32
3. Spray-printed magnetoelectric multifunctional composites	35
3.1. Introduction	36
3.2. Experimental	37
3.2.1. Materials.....	37
3.2.2. Ink preparation and printing conditions.....	38
3.2.3. Sample characterization	38
3.3. Results and discussion	39

3.4.	Conclusions.....	44
3.5.	References	44
4.	Environmental friendlier printable piezoelectric inks and their application for the development of highly sensitive all-printed touchscreens.....	47
4.1.	Introduction	48
4.2.	Experimental	49
4.2.1.	Materials.....	49
4.2.2.	Ink preparation and processing of the films	50
4.2.3.	Characterization techniques.....	51
4.2.4.	Piezoelectric touchscreen prototype fabrication	52
4.2.5.	Equivalent circuit of the sensors	53
4.3.	Results and discussion	55
4.3.1.	Rheological characterization	55
4.3.2.	Morphological, polymer phase and thermal properties.....	56
4.3.3.	Dielectric and piezoelectric properties.....	59
4.3.4.	Pressure sensing properties.....	61
4.3.5.	Touch detection	61
4.4.	Conclusions.....	63
4.5.	References	63
5.	Marked Object Recognition Multitouch Screen Printed Touchpad for Interactive Applications	67
5.1.	Introduction	68
5.2.	Experimental	69
5.2.1.	Printed Geometry.....	69
5.2.2.	Capacitive Detection Circuit	70
5.2.3.	Touchpad Fabrication	71
5.3.	Results and discussion	72
5.4.	Conclusions.....	76
5.5.	References	77
6.	Final remarks, conclusions and future work	80
6.1.	Final remarks	81
6.2.	Conclusions.....	84
6.3.	Future work.....	86

List of figures

Figure 1.1. (a) Foldable OLED display (reprinted from [9]). (b) Organic photovoltaic cells (reprinted from [10]).	3
Figure 1.2. Applications of batteries with new form and structural factors	3
Figure 1.3. (a) Plastic flexible OLED lighting panel (reprinted from [14]). (b) Printed sensor (reprinted from ([15]).	4
Figure 1.4. Market share of the printed, flexible and organic electronics in 2018.	4
Figure 1.5. Number of publications per year with titles including <i>wearable electronics</i>	5
Figure 1.6. Printed and flexible sensor market segments forecast 2017-2027 according to <i>IDTechEx</i> .	6
Figure 1.7. Example of different technologies used to produce printed sensors able to measure specific proprieties	7
Figure 1.8. Classification of the main printing technologies to produce printed sensors.	10
Figure 1.9. Functional and Industrial Printing Market evolution from 2012 to 2022 regarding to the main printing technologies	11
Figure 1.10. Usage percentage of different printing processes according to volume production.	12
Figure 1.11. Graphical representation of the spray coating technique].	13
Figure 1.12. Schematic drawing of the screen printing setup	14
Figure 2.1. Surface SEM images of SEBS composites prepared by doctor-blade with the different solvents: a) p-cymene for 5 wt.% and b) 7 wt.%, 2-MeTHF for c) 5 wt.% and d) 7 wt.%.	26
Figure 2.2. Electrical conductivity of the MWCNT/SEBS composites using different solvents.	28
Figure 2.3. Electromechanical resposner of SEBS composites prepared with different solvents: a) Toluene (3 wt.%), b) CPME (3 wt.%), c) 2-MeTHF (5 wt.%), d) p-cymene (5 wt.%), of the samples around the percolation limit.	29
Figure 2.4. Electrical resistivity variation as a function of the applied pressure for the different nanocomposites for applied pressures up to 1 MPa.	30
Figure 3.1. a) Transversal and b) surface. SEM images of the P(VDF-TrFE)/CoFe ₂ O ₄ printed composites with 20 wt.% of ferrite content.	40
Figure 3. 2. Characteristic stress-strain curve in the tensile mode of the P(VDF-TrFE)/ CoFe ₂ O ₄ composite (the inset shows the linear fit to obtain the Young 's modulus and a photograph of the printed ME composite). b) Room-temperature magnetization as a function of the applied DC magnetic field. The inset shows the room-temperature magnetization of the CoFe ₂ O ₄ nanoparticles.	40

Figure 3.3. a) Frequency dependence of the real part of the permittivity (ϵ') and b) room-temperature piezoelectric response of the ME P(VDF-TrFE)/CoFe ₂ O ₄ sample.	42
Figure 3. 4. Room-temperature ME response of P(VDF-TrFE)/CoFe ₂ O ₄ spray-printed composite as a function of the: a) frequency and; b) DC magnetic field.....	43
Figure 4.1. Schematic representation of the different techniques and procedures used for the preparation of the films. Notice that the mask was not used in the present work, as only non-patterned films were prepared.	50
Figure 4.2. a) Layout of the all printed touchscreen comprising a 30 μm thick PVDF-TrFE film and six silver paint printed electrodes (grey – top; light green – bottom; dark green – top and bottom). b) Photograph of the piezoelectric touchscreen.....	53
Figure 4.3. Equivalent model of a piezoelectric sensor: a) generic piezoelectric component; b) considering the capacitance and resistance of the electrodes; c) charge source represented by a controlled current source.	54
Figure 4.4. a) Flow curves of PVDF-TrFE solutions dissolved at different concentrations in DMPU (open symbols) and DMF (solid symbols). b) Concentration dependence of the specific viscosity of DMPU based solutions (open symbols) and DMF based solutions (solid symbols). Lines and numbers indicate slopes. Inset: mechanical spectrum (storage modulus G' : triangles; loss modulus G'' : squares) for a 23.9 wt.% PVDF-TrFE solution in DMPU. Lines in the inset highlight the terminal regime with slopes of 1 and 2 for G'' and G' respectively.	55
Figure 4.5. Surface SEM images of PVDF-TrFE obtained by a) spray printing and b) screen printing with 23 wt.%. c) FTIR spectra, d) TGA plots, e) DSC heating scans and f) degree of crystallinity for the PVDF-TrFE films produced by different techniques.	57
Figure 4.6. a) Dielectric constant and b) $\tan \delta$ as a function of frequency and c-d) piezoelectric coefficient immediately after polarization and as a function of time, respectively, for the different PVDF-TrFE printed films.	60
Figure 4.7. a) Touchpad response upon finger pressing and release, b) piezoelectric sensor under cycling a pressing and releasing events and c) sensor matrix on touch event in one of the sensors and corresponding signals for each sensor. See also the supplementary video.....	62
Figure 5.1. Illustration of the capacitive matrix silver electrodes geometry: (a) diamond electrodes pattern front view; (b) diamond electrodes pattern perspective view.	70
Figure 5. 2. Schematic representation of the hardware: Communication PCB as I2C-USB converter (a) and capacitive controller instrumentation circuit (b).	71

Figure 5. 3. Process fabrication flow diagram (a) and printed capacitive matrix connected to the PCB with the capacitive touch controller IC (b).	72
Figure 5. 4. Test were performed with the CT210 programmer for the maximum of possible touches using a 5 mm thick glass as an overlay (a), folded surface finger detection (b) and capacitive distribution with glass overlay of the matrix with and without touch (c).	73
Figure 5. 5. (a) Marked objects can be detected by software with the aid of a specific number of points and distances between them in a C# environment; (b) System process and software processing main algorithm.....	75

List of tables

Table 1.1. Main smart materials, proprieties and applications.....	8
Table 1.2. Comparison between the main polymeric substrates used in printed sensors.	9
Table 1.3. Main characteristics of the printing techniques used on this work, and the corresponding requirements needed for the inks and substrates.	14
Table 2.1. Nomenclature for the different samples.	24
Table 2.2. Pressure sensibility of MWCNT/SEBS composites with different solvents, for 3 and 5 wt.% of MWCNT.....	31
Table 3.1. Coercive field (HC), magnetic remanence, magnetic saturation and CoFe ₂ O ₄ wt.% for P(VDF-TrFE)/ CoFe ₂ O ₄ samples prepared by spray-printign and bar-coating, as well as for CoFe ₂ O ₄ nanoparticles.	41
Table 3.2. α as a function of k.	44

List of symbols

wt. %	Weight percentage
ρ	Electrical resistivity
R_0	Initial electrical resistance
ΔR	Electrical resistance variation
P	Applied pressure
λ	Magnetostrictive coefficient
C	Electrical capacity
d	Thickness
A	Electrode area
ε'	Real part of dielectric constant
d_{33}	Piezoelectric response
α_{33}	ME voltage coefficient
ΔV	Output voltage
H_{AC}	Amplitude of the AC magnetic field
T	Sample thickness
m_v	Ferrite volume fraction
ε_0	Vacuum permittivity
E	Relative permittivity of the material
E_Y	Young's modulus
L	Sample length
W	Sample width
T_g	Glass transition temperature
T_m	Melting temperature
T_c	Curie Temperature
ΔX_{cryst}	Degree of crystallinity
ΔH_f	Melting enthalpy
ΔH_{100}	Melting enthalpy for a 100% crystalline sample

Q_p	Electrical charge
F	Applied force
ω_p	Cut-off angular frequency
s	Complex Laplace's domain
η_0	Newtonian viscosity of the solution
η_s	Solvent Newtonian viscosity

List of acronyms

A

AC	Alternating current
AI	Artificial Intelligence

B

BPF	Band-pass filter
B2B	Business to business

C

CPME	Cyclopentyl Methyl Ether
COM	Communication port
CAGR	Compound annual growth rate
CoFe ₂ O ₄	Cobalt ferrite

D

DMPU	N,NO-dimethylpropyleneurea
DSC	Differential scanning calorimetry
DC	Direct current
DMPU	N, N-dimethylpropyleneurea
DMF	N,N-dimethylformamide

F

FTIR	Fourier transform infrared spectroscopy
FE-PE	Ferro-paraelectric

G

GF	Gauge Factor
----	--------------

I

ITO	Indium tin oxide
I ² C	Inter-Integrated Circuit
IC	Integrated circuit
IoT	Internet of Things

L

LPF	Low-pass filter
-----	-----------------

M

ME	Magnetoelectric
MEMS	Microelectromechanical systems
2-MeTHF	2-Methyltetrahydrofuran
MWCNT	Multi-walled carbon nanotubes

O

OFET	Organic field-effect transistor
OLED	Organic light-emitting diode
OPV	Organic photovoltaic

P

PC	Polycarbonate
PCB	Printed circuit board
PDMS	Polydimethylsiloxane
PE	Printed electronics
PEN	Polyethylene naphthalate
PET	Polyethylene terephthalate
PU	Polyurethane
PVDF	Polyvinylidene fluoride
PVDF-TrFE	Poly(vinylidene fluoride-co-trifluoroethylene)
PI	polyimide
PEDOT:PSS	poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid)
PCB	Printed Circuit Board
PS	pressure sensitivity

R

RFID	Radio frequency identification
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S

SEBS	Styrene-ethylene/butylene-styrene
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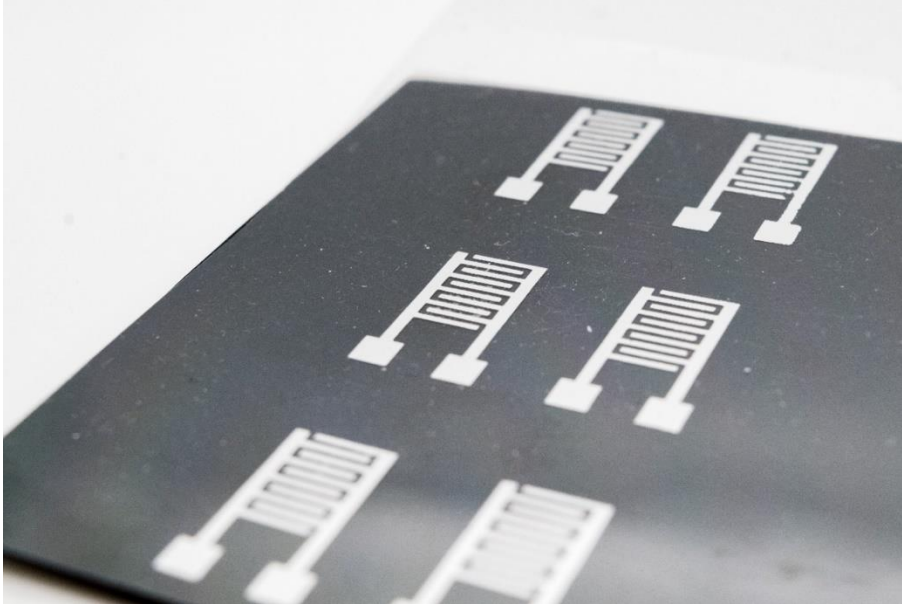
TGA	Thermogravimetric analysis
TPU	Thermoplastic polyurethane

U

UART	Universal Asynchronous Receiver/Transmitter
UV	Ultraviolet (radiation)

W

WHO	World Health Organization
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1. Introduction

Printed and flexible sensors represent a growing market, which is estimated to reach \$7.6 billion by 2027. The next generation of printed sensors will enable many applications, from human-machine interfaces to environmental sensing. These sensors benefit from the latest materials and technologies in the printed electronics industry. They have the capability to be manufactured on polymeric substrates, which offer advantages in terms of mechanical flexibility, thickness and weight reduction.

This chapter introduces the concepts related to printed sensors, materials and the technologies to fabricate them. Also presents the main objectives and the structure of this thesis.

1.1. Printed sensors

When a printing method is used to develop electrical devices on a substrate, it is named Printed Electronics (PE) [1].

The first concept of printed electronics is credited to Albert Hanson when in 1903 filled a patent for “Printed wires”, but the real first printed circuit was produced only in 1936 by the Austrian engineer Paul Eisler as a part of a radio set. In 1943 the USA began to use the technology on a large scale production of radios during World War II. Printed circuit technology was released for commercial use in the USA in 1948 [2].

In the over 50 years, since its origin, printed electronics has progressed from the production of printed circuit boards (PCBs), through the ordinary use of membrane switches, to today’s radio frequency identification (RFID), smart labels, electronic skin patches, active clothing and flexible displays [3].

Due to a rapid emergence of an extensive range of nanomaterials and solution processability, the production of thin and flexible electronics to be operated at room temperature and with a cost-effective manufacturing has become possible [4].

Flexible and printed electronics continues to grow and it is being applied by most of the industries around the world, including automotive, aerospace, healthcare, consumer electronics, retail and packaging [5], among others. The main markets are the organic light-emitting diode (OLED) displays, photovoltaics, logic/memories, batteries, several types of displays, including e-paper and electroluminescent technologies, and sensors.

Most of the OLED displays are not printed, however one of the main goals from the OLED industry is to have most of the technology fabricated on plastic substrates by 2020, overtaking those on glass substrates, obtaining thinner, lighter, curved and foldable displays [6] (figure 1.1 (a)). Organic photovoltaics (OPV) that can be printed is already a reality. They are very thin and light weight, which helps the installation of this device in a variety of locations, and the shape and color can also be customized [7] (figure 1.1 (b)). However the efficiency of OPV has not yet reached that of silicon solar cells. Until June of 2019, the best ratio of energy output to light input obtained was over 22 percent, by the addition of selenium on cadmium telluride solar cells [8].



Figure 1.1. (a) Foldable OLED display (reprinted from [9]). (b) Organic photovoltaic cells (reprinted from [10]).

Flexible, thin and printed batteries has become a very active field thanks to the rise of Internet of Things (IoT), wearables and environmental sensors. All of these applications require ultra-thin, flexible, rollable or stretchable battery designs that traditional battery technologies cannot provide. Many applications are still emerging, and the requirements are fast evolving (figure 1.2) [11].

IoT, MEMS, CMOS memories, Medical implantable	Smart cards, Skin patch, RFID	Wearables, E-textile, Medical device	Smartphone, Tablet, Power tool, Toy	Transport	Large-scale energy storage
Capacity range →					
1 mAh	10 mAh	100 mAh	1 Ah	100 Ah	> 1 kWh
Important features					
• Rechargeable • Small footprint, many micro-batteries • Long life time • Rapid discharge • Tend to incorporate with energy harvesting	• Can be both disposable and rechargeable • Laminar and thin, some with special form factor • Relatively low power • Cost sensitive	• High energy density for small volume • Long working hours • Flexible, stretchable or thin, some with special form factor	• Light-weight and small volume • Long working hours • Some with special form factors • High power	• Safe • Reliable • High power • High capacity	• Cost advantage • Long life time • Reliable • High capacity
Technology Status					
Small volume production	Available, mostly customized	Prototypes available	Research to prototype	Research	Very early stage

Figure 1.2. Applications of batteries with new form and structural factors [11].

Another area where printed electronics is applicable is OLED lighting, which is an emerging solid-state lighting technology. OLED lighting has the potential to emit warm light across large surfaces with good efficiency and to create new form factors into the lighting sector (figure 1.3 (a)) [12].

Printed and flexible sensors are a well-established subcategory of the PE market and is still growing. There are many types of printed sensors today, some with a very simple structure with a few electrodes, while others are much more complex implying multiple layer depositions. All these sensors have the capability to be manufactured on plastic substrates, which confers mechanical flexibility, thinness and weight reduction (figure 1.3 (b)) [13].

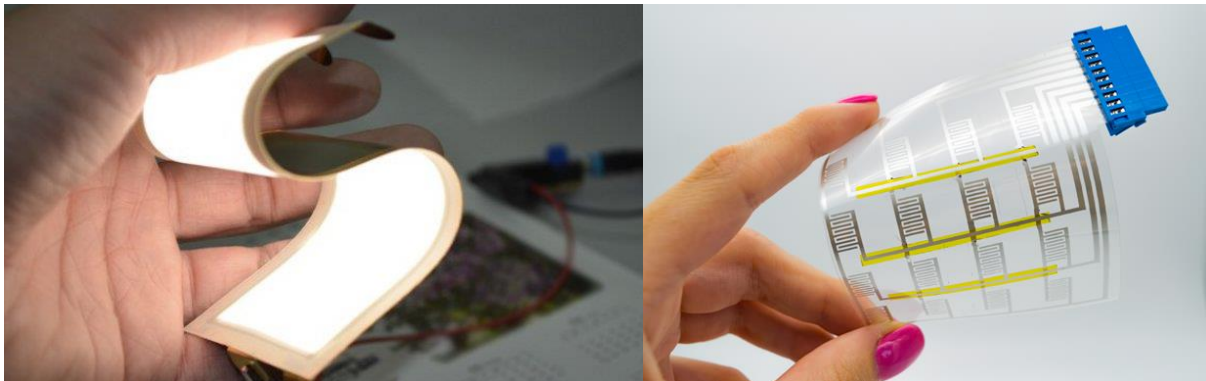


Figure 1.3. (a) Plastic flexible OLED lighting panel (reprinted from [14]). (b) Printed sensor (reprinted from ([15])).

In 2018 the total market for printed, flexible and organic electronics was \$31.6 billion, however the value of components fully produced by printing was \$5.8 billion and it is expected to rise to \$8.5 billion in 2029 (figure 1.4).

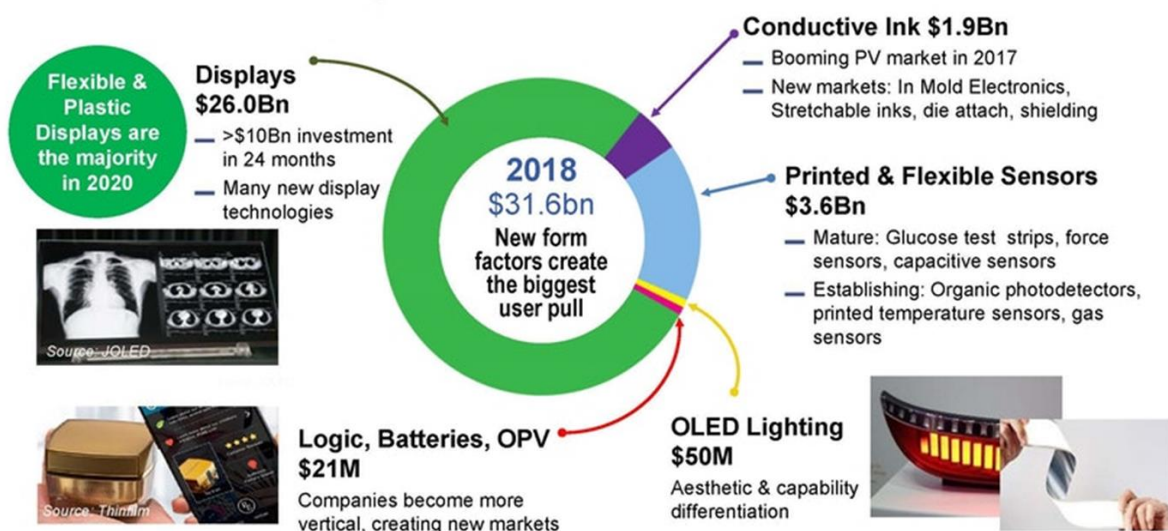


Figure 1.4. Market share of printed, flexible and organic electronics in 2018 [6].

The largest applications using printing technologies comes from the printed sensors market, which will be the main topic in this thesis.

The largest segment in the printed sensor industry, by market value, is the glucose test strips. This biosensor monitor the blood sugar levels in patients and transmit the captured data to doctors, enabling them to analyze the sensor-collected data and initiate personalized treatments and medications for patients [16]. The healthcare market is huge and a particular segment is growing in a fast pace, which is the one related to wearable electronics and sensors. According to research firm *Allied Market Research*, this market is projected to reach \$2.26 billion by 2022, growing at a compound annual growth rate (CAGR) of 52.9% from 2016 to 2022 [17]. This growth can also be perceived by the number of publications released since 2010 (figure 1.5) [18].

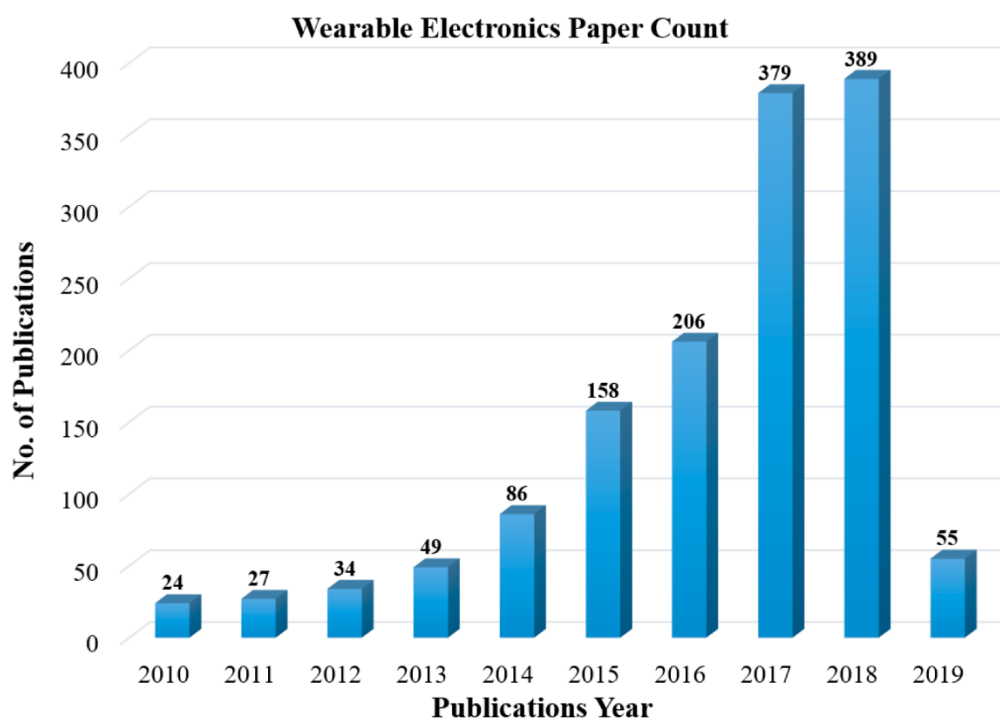


Figure 1.5. Number of publications per year with titles including *wearable electronics* [18].

Wearable technology has a variety of applications which grows as the field itself expands and it is being incorporated into navigation systems, health fitness monitoring, advanced textiles, entertainment, and fashion industry [18].

Other market segments of the printed sensors are now moving into mass production, such as gas sensors which are expected to become the second largest segment in the next few years, according to the market research firm *IDTechEx* (figure 1.6). One of the main reasons is due to the fact that 91% of the world's population lives in places where air quality exceeds *World Health Organization* (WHO) guideline limits, meaning that nearly 4.2 million deaths occurs every year as a result of exposure to ambient (outdoor) air pollution [19].

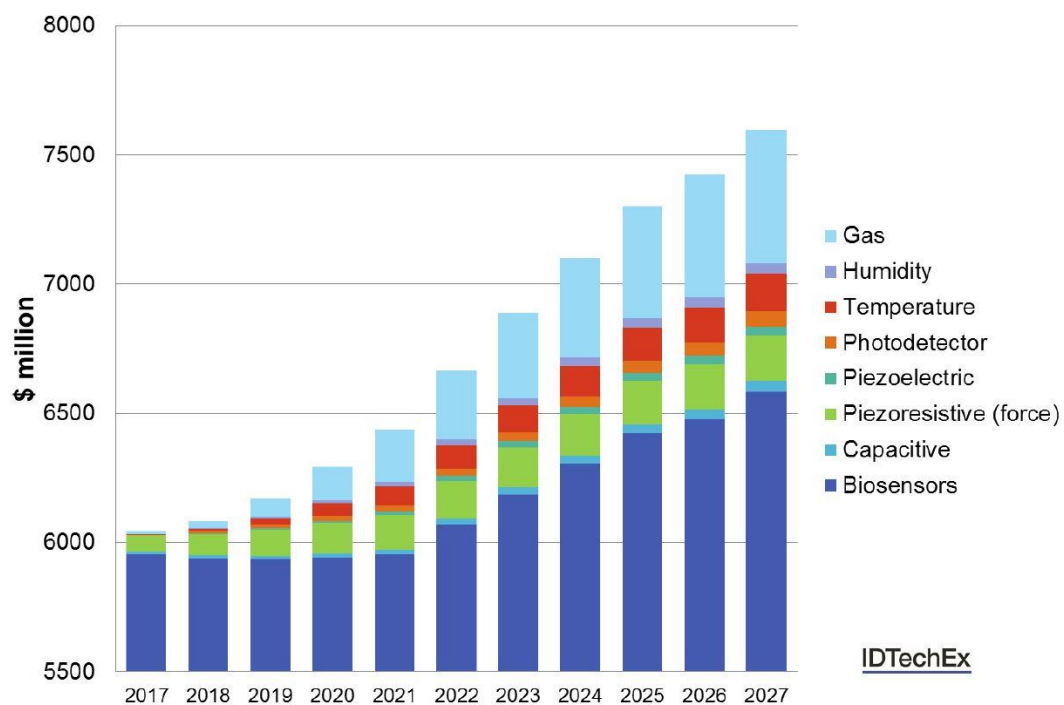


Figure 1.6. Printed and flexible sensor market segments forecast 2017-2027 according to *IDTechEx*.

Printed gas sensors will be compact and cheap, and they will be able to detect a wide variety of gases, outdoor and indoor, in real time. This is why environmental sensing and pollution monitoring will play a huge role in the next decade [20].

Other types of printed sensors (figure 1.7) are also very important since they contribute to the development of new products and applications for different industries such as automotive, aerospace, consumer electronics, retail and packaging, among others.

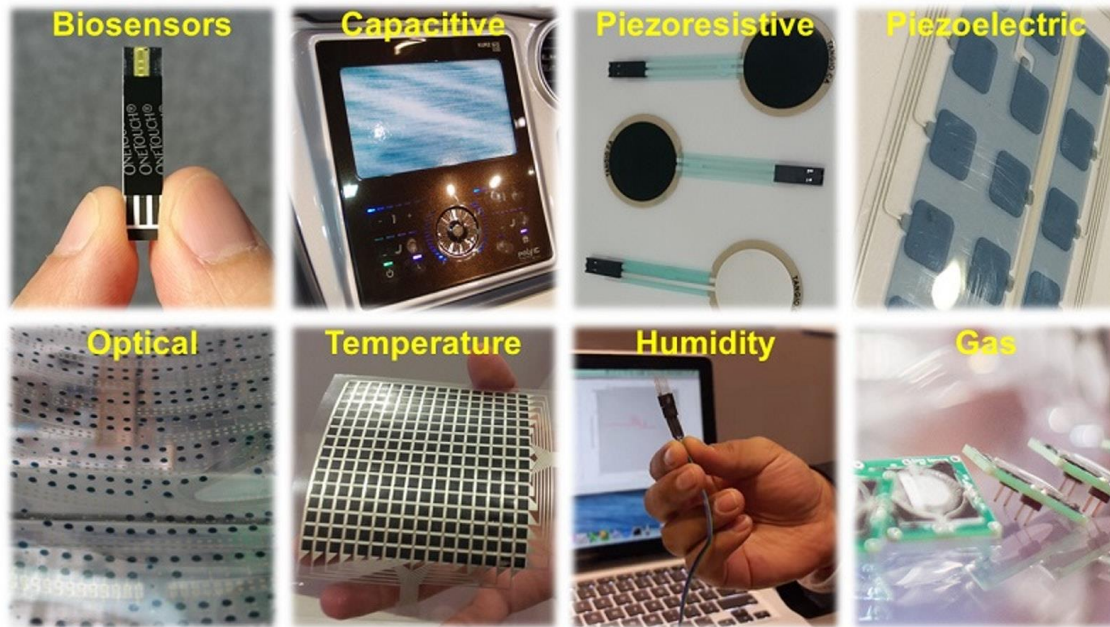


Figure 1.7. Example of different technologies used to produce printed sensors able to measure specific proprieties [13].

1.2. Materials

1.2.1. Inks

Advances in new material formulations are enabling many an increasing number of applications and with reduction of costs to produce it, leading to the growing of the flexible and printed electronics market [21].

Regarding to materials for printed electronics, both organic and inorganic are used and their selection will depend on several factors, such as cost, transparency, conductivity and other requirements needed for each type of application. Organic materials include conjugated polymers with specific characteristics such as conducting, semiconducting, photovoltaic and electroluminescent properties. Other polymers can be used but typically they are used as insulators and dielectrics. Inorganic materials, such as silver and gold nanoparticles, may be used and they achieve some goals that organics and polymers can't provide, such as highly ordered interfaces and layers.

Inks, in liquid form, must act as conductors, semiconductors, dielectrics or insulators [22]. Using one or several of these inks, it is possible to produce organic field-effect transistor (OFET), OLED, OPV, RFID, batteries, sensors, etc. [23].

When it comes to inks for printed sensors, there are several groups of active smart materials which exhibit specific proprieties useful for a wide range of applications. These materials includes piezoelectric, piezoresistive, magnetoelectric, magnetostrictive, shape memory, pH sensitive and chromic materials [24-30], which are used as sensors and actuators for many applications. Many materials are used to produce functional inks and the main ones are indicated in the Table 1.1 according to the type of application [31].

Table 1.1. Main smart materials, proprieties and applications [31].

Smart material	Representative Materials	Applications
Piezoelectric and electrostrictive	PZT, PVDF, BaTiO ₃ , Quartz, Parylene-C, ZnO P(VDF-TrFe); Pb(Mg _{1/3} Nb _{2/3})O ₃ -PbTiO ₃ (PMN-PT)	Touch screen; Led's; Piezofibers; Smart cloths, Actuators and transducers; Tactile sensors; Energy and power harvesting; Energy conversion
Piezoresistive	Carbon or silver fillers; Microcrystalline silicon; Graphene; PEDOT:PPS	Pressure sensor; Touch screen; MEMS; Biomedical sensors; Strain gauges Tactile sensor; Stress-strain sensors
Magnetostrictive	Terfenol -D; Metglas, CoFe ₂ O ₄	Transducers Magnetic sensors; Gas sensor, Magnetoelectric sensor; Energy harvesting; Magnetic field sensing;
pH sensitive and thermo-responsive	Stimuli response polymers (<i>N</i> -isopropylacrylamide (NIPAM), <i>N,N</i> -diethylacrylamide (DEAM), methylvinylether (MVE), <i>N</i> -vinylcaprolactam (NVCII)); Shape memory alloys; Poly(<i>N</i> -isopropylacrylamide) (PNIPAAm)	Biomedical sensors; Tissue engineering; Drug delivery Biosensing

After the printing process the inks need to be cured, i.e. dried, and there are two main curing processes: thermal and ultraviolet (UV) curing.

Thermal curing is based on evaporation of volatile components and a loss in the dried coating thickness occurs, whereas UV curing is based on polymerization and the thickness of the dry coating remains the same [32, 33]. The advantages of UV curing comparing to thermal curing include being a high speed curing (in the range of seconds or minutes) which translates to high throughput, requiring low energy (no heating is necessary), allowing high-resolution patterns and the reduction of ecological problems based on the lack of solvents [34, 35].

The next generation materials will be adapted to high speed printing and with integrated curing capabilities, being able to show a good printability and adhesion of the materials in the shortest period of time. It will be also possible to print entire smart device system using different types of inks which will allow to produce low cost devices, with large areas processing and flexibility [31]. According to IDTechEx and MarketsandMarkets, the global market for conductive inks, pastes and other materials for 2018 was around \$2 billion, and it is projected to reach \$3.91 billion by 2021, driven by photovoltaics and the automotive market [21, 36].

1.2.2. Substrates

Substrate is the technical term used to entitle any material to be printed. They can be based on a wide variety of materials and need to be clean and free from surface contamination to allow proper ink adhesion. The most important characteristics are smoothness and wettability, where sometimes a surface pre-treatment is needed, such as coating or corona discharge, in order to achieve these characteristics [1].

Today flexible sensors are printed in many kind of substrates such as paper [37, 38] plastic, foils and fabrics [39], according to the application requirements. They are flexible, transparent to opaque, light weight, durable, low cost and can be used in any size and shape. Regarding polymer substrates, in which this work is focused, there are many types of polymers that can be used as flexible substrates such as polyimide (PI), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyvinylidene fluoride (PVDF), polycarbonate (PC), polydimethylsiloxane (PDMS), polyurethane (PU) and thermoplastic polyurethane (TPU), among others. The main properties of flexible polymeric substrates are shown in table 1.2 [40].

Table 1.2. Comparison between the main polymeric substrates used in printed sensors (T_g: glass transition temperature, T_m: melting temperature, CTE: coefficient of thermal expansion) [40].

Substrate	PI	PET	PC	PEN	PDMS	TPU
T _g (°C)	155–270	70–110	145	120–155	–125	80
T _m (°C)	250–452	115–258	115–160	269	–	180
Density (g/cm ³)	1.36–1.43	1.39	1.20–1.22	1.36	1.03	1.18
Vol.Res.(Ω.cm)	1.5×10^{17}	1.0×10^{19}	10^{12} – 10^{14}	10^5	1.2×10^{14}	3.0×10^{14}
Modulus (MPa)	2.5×10^3	2 – 4.1×10^3	2.0 – 2.6×10^3	0.1 – 0.5×10^3	1	7
WorkTemp. (°C)	Up to 400	–50 to 150	–40 to 130	–	–45 to 200	130
CTE (ppm/°C)	8–20	15–33	75	20	310	153
Water absorption (%)	1.3–3.0	0.4–0.6	0.16–0.35	0.3–0.4	>0.1	0.2
Solvent resistance	Good	Good	Poor	Good	Poor	Good
Dimensional stability	Fair	Good	Fair	Good	Good	Good-

The choice for the most suitable substrate will depend on various factors, such as the substrate's surface energy, roughness and solubility, as well as the solutions' surface tension, solute chemistry and vapor pressure. All those issues play important roles in controlling the resulting printed feature's shape, position and structure. Besides these factors, the choice of the right ink and the right printing technology is also important [1].

1.3. Printing technologies

In order to print the materials described in the previous section, it is necessary to use appropriate printing technologies according to the ink and substrate to be used. There are two categories of printing techniques: non-contact and contact printing (figure 1.8).

In the non-contact technique only the deposition material gets in contact with the substrate, whereas in the contact technique the printing plate is in direct contact with the substrate [41].

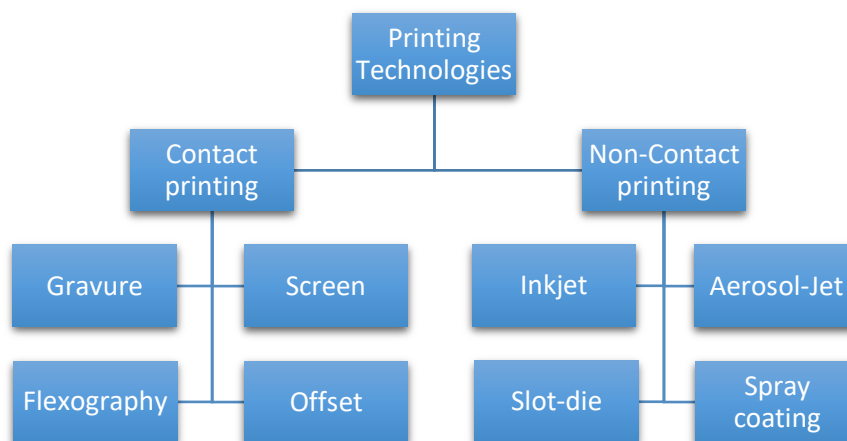


Figure 1.8. Classification of the main printing technologies to produce printed sensors.

According to *Smithers Pira*, a market research consulting firm, the industrial and functional printing market will grow to \$114.8 billion by 2022 (figure 1.9). This market is growing and includes the sectors of décor and laminates, ceramics, electronics including displays and photovoltaics, aerospace and

automotive, glass, biomedical, promotional and miscellaneous items, 3D printing and inkjet printed textiles [42].

Printing techniques such as screen, pad printing, gravure and foiling are perfectly adequate for many of the long-established applications in our days, however there is a strong growth in digital methods, like the inkjet printing, which is opening new opportunities for the printed market.

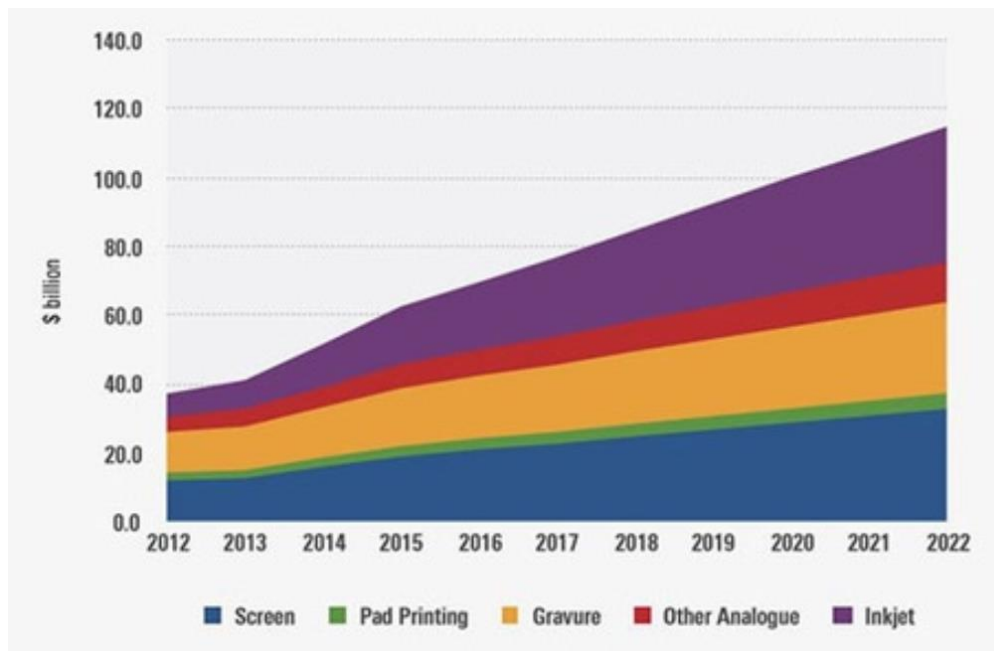


Figure 1.9. Functional and Industrial Printing Market evolution from 2012 to 2022 regarding to the main printing technologies [42].

All printing technologies require different and optimized characteristics such as viscosity, surface tension, particle diameter, conductivity, type of substrate and optimum temperature [31].

Regarding the printed electronics market, the screen printing technique dominates commercial printed electronics devices, being the main applications the printing of photovoltaic solar busbars, force sensors, touchscreens electrodes, glucose test strips, heating elements and membrane circuits (figure 1.10) [43].

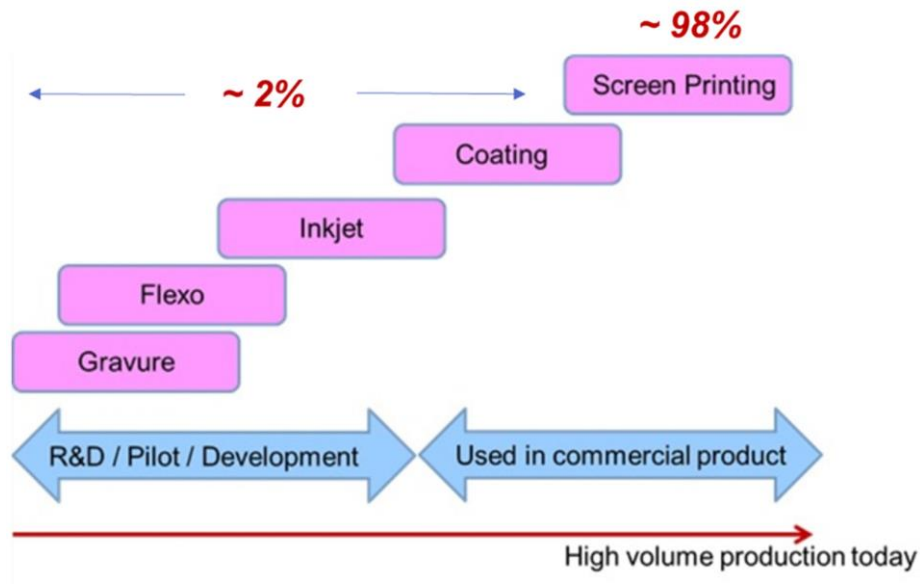


Figure 1.10. Usage percentage of different printing processes according to volume production.

Inkjet printing is increasingly used in new applications since, theoretical, it has a better resolution, less material waste and more precise material replacement. However the screen printing industry continues to improve in terms of printed line width size, which makes difficult for inkjet printing industry to dominate the printed electronic market. The biggest commercial application used by inkjet printers is for OLED displays and printing polymer layers in barrier films for encapsulation [43].

This work will focus mainly on the two most used printing techniques in the industry: spray coating and screen printing.

1.3.1. Spray coating

Being a non-contact technique, spray coating uses a gas to create a suspension of fine liquid droplets and to print it on the substrate. The liquid coming out from a nozzle is atomized by ultrasonic vibrations or pressure and the droplets, of micron size, are randomly deposited. An inert gas, for example nitrogen, is used as a carrier gas. The nozzle travel all over the substrate in order to cover all surface [34] (figure 1.11). The thickness of the printed layer can be controlled depending on the solution flow rate and the moving nozzle speed. This deposition method allows to print complex patterns with the help of a mask.

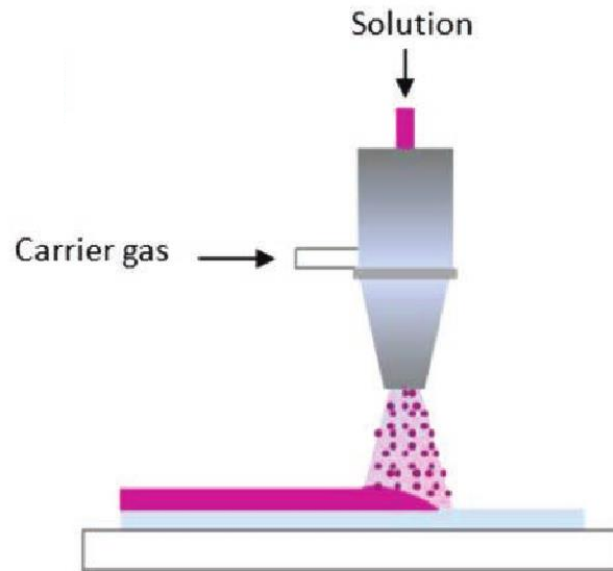


Figure 1.11. Graphical representation of the spray coating technique [34].

1.3.2. Screen printing

Screen printing technique uses a mesh/stencil to transfer the ink, located above the pattern, to the substrate. A squeegee press the mesh against the substrate along the entire mesh, transferring the ink to the substrate (figure 1.12). This technique allows to have complex printed patterns with a typical resolution of about 100 μm [41]. Today it is possible to obtain 35 μm width screen printed tracks in commercial products, and 20 to 30 μm screen printed line widths will come to market in the next few years [43].

Screen printing shows the advantage of being a low-cost mass production technique with repeatable accurate printing of large patterns for electronic components. Nevertheless, some parameters such as printing and ink conditions, as well screen conditions, must be controlled with precision [44]. Thermal treatment processing might be required, depending on the ink composition and the interaction between the ink and the substrate [41].

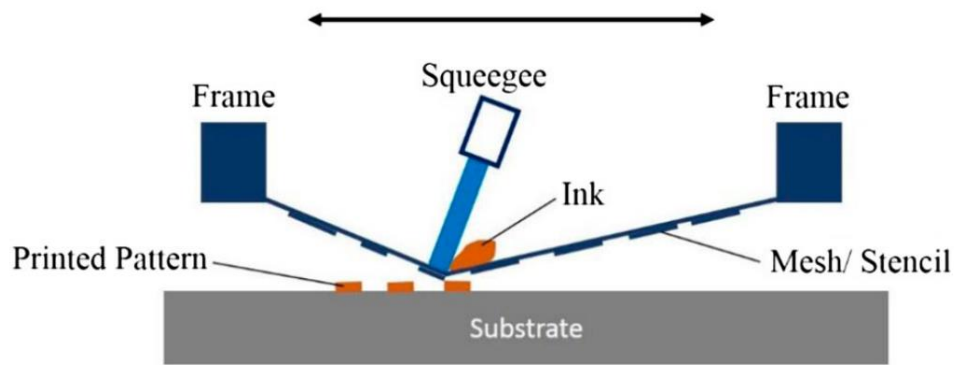


Figure 1.12. Schematic representation of the screen printing setup [41].

Both printing techniques are widely used in the industry and have many advantages, however each one of them have their own limitations, which are illustrated in table 1.3.

Table 1.3. Main characteristics of the printing techniques used on this work, and the corresponding requirements needed for the inks and substrates [31].

Printing technology	Characteristics	Ink's limitations	Substrate limitations
Spray	• Low resolution patterns • Simple process, • Low time to market; • Low-cost equipment. • Very low resolution up to 1 mm	• Viscosity: 1-1000cPs • Max particle diameter 10μm; • Flash point: >45 °C.	• From small to very large size areas; • Any substrate; • Any roughness.
Screen	• Needs a different frame for each different pattern; • Simple process, widely used in the industry; • Ideal for small, medium and high production volumes; • Low time to market; • Typical resolution of 0.2 mm • Low-cost equipment.	• Viscosity: 1k-40k cPs • Surface Tension: 25-36mN/m • Max particle diameter depends on the mesh	• From small to medium size areas; • Flat and curved substrates with small roughness.

1.4. Objectives

The main objective of this work is to produce inks with appropriate characteristics for specific printing technologies and, as consequence, to obtain different types of printed sensors. The development of piezoelectric, piezoresistive and magnetoelectric inks, for screen-printing and spray coating will be performed and different printed sensors will be obtained, as well as proofs of concept of touchpads for interactive applications.

In summary, the specific objectives are:

- Development of inks based on different electroactive polymers with different fillers in order to tailor printability. Select the type and content of the solvent taking into account ink performance and green chemistry approaches.
- Study the possibility of tailoring the desired properties with the inclusion of the selected nanofillers (conductive fillers for piezoresistive materials and magnetostrictive fillers for magnetoelectric materials).
- Obtain fundamental knowledge on the printing materials through the relationship between processing, structural properties and morphology, and the micro and macroscopic response of the materials.
- Study electrical and mechanical behavior, and the compatibility of the different printed layers.
- Selecting the best materials and microstructures from the point of view of the selected applications.
- Construction and test sensor prototypes on different substrates.

1.5. Thesis structure

The presented thesis is divided in six chapters, four of them based on published or submitted scientific papers, and arranged in a sequential order corresponding to the progress of this work.

Chapter 1 presents a general overview on printed sensors, materials used to develop the inks and the main printing technologies used in the industry. It is to notice that the specific state of the art related to the different works is provided in each chapters. The main objectives and the structure of the thesis are also reported in this chapter.

Chapter 2 reports the influence of different solvents in the production of piezoresistive inks and the performance of pressure sensors based on thermoplastic elastomer styrene-ethylene/butylene-styrene (SEBS) and multi-walled carbon nanotubes (MWCNT).

Chapter 3 is dedicated to the discussion of the performance of spray printed magnetoelectric composites, based on poly(vinylidene fluoride-co-trifluoroethylene)/cobalt ferrite P(VDF-TrFE)/(CoFe₂O₄), suitable for sensor and actuator applications.

Chapter 4 presents the development of piezoelectric inks, based on poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE), using green solvents to be used by doctor blade, spray coating and screen printing. The films obtained by these printing techniques were used to develop a touchscreen.

Chapter 5 shows a flexible screen printed sensor matrix, fabricated with silver ink in a polyethylene terephthalate (PET) substrate. This functional capacitive touchpad is obtained using a diamond shaped capacitive electrodes coupled with conventional capacitive reading electronics, and also allows the identification of marked objects.

Chapter 6 ends this thesis, presenting some final remarks, the main conclusions of this thesis and some suggestions for future work.

1.6. References

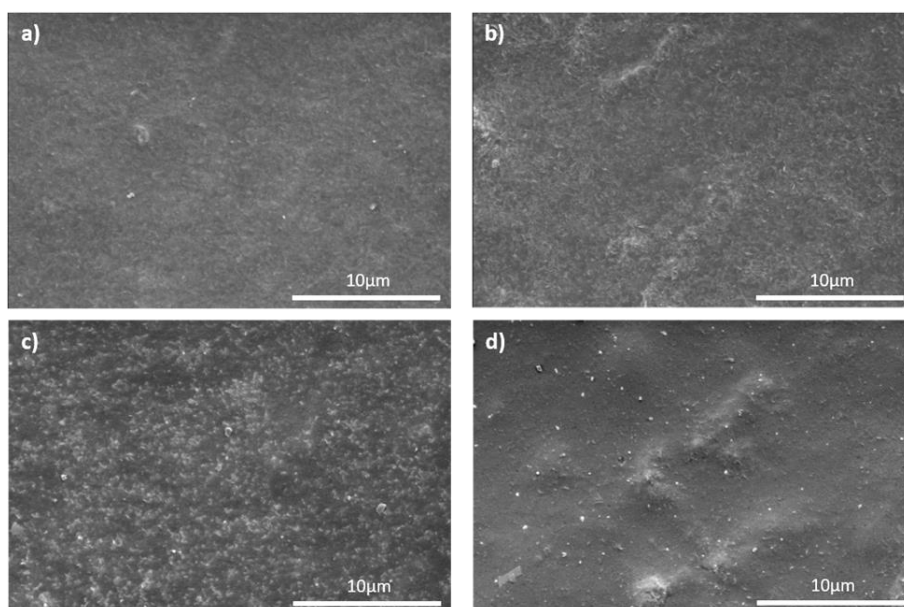
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2. The influence of different solvents on the stability and performance of piezoresistive inks for flexible electronics

This work reports on polymer-based piezoresistive sensors based on the biocompatible thermoplastic elastomer styrene-ethylene/butylene-styrene (SEBS) as polymer matrix and multi-walled carbon nanotubes (MWCNT) as conductive fillers. The effect of different solvent for the preparation of screen printable ink is evaluated. The MWCNT/SEBS composites have been prepared with different environmental friendly solvents, including cyclopentyl methyl ether (CPME), 2-MeTHF and p-cymene, in order to reduce the environmental impact of the sensor development. The piezoresistive response of the printed sensors developed, using this greener approach, shows good reproducibility and a pressure sensibility in the range of 0.4 to 0.8 MPa⁻¹. Overall, the results confirm that it is possible to obtain excellent piezoresistive performance in these composites, allowing the development of a new generation of environmentally friendlier pressure sensors.

2.1. Introduction

Flexible and stretchable sensing elements to monitoring systems based on smart and multifunctional materials are playing an increasing role in the development of electronic devices [1]. Important innovations in this field are based on the development of a novel generation of multifunctional materials processable by additive manufacturing technologies and, therefore, with simple integration into electronic devices [1].

In this context, research in the area of polymer composite with tailored active response is strongly growing [2], in particular with respect to functional composites reinforced with conductive fillers for sensor applications [3-5]. The piezoresistive response of these composites, variation of the electrical resistivity with an applied stimulus, allows the development of stretchable/flexible force and deformation sensing systems [6, 7].

Most of those composites are based on multi-walled carbon nanotubes (MWCNT) as active filler to provide the necessary electrical conductivity of the composite [8], based on their high aspect ratio, mechanical and electrical properties [9]. In particular, the high aspect ratio of MWCNT allows to obtain high electrical conductivity in the composites at low percolation thresholds, maintaining therefore the main mechanical characteristics of the pristine polymers, such as flexibility and stretchability [10-12].

Commercial piezoresistive sensors are based on semiconductor or metal strain gauges [13], showing several drawbacks and difficulties to be integrated into devices, mainly due to the low mechanical flexibility and sensitivity to environment conditions [14, 15]. Based on the wide range of polymers-based composites, low-cost and easy processability with additive manufacturing technologies, it is possible to design improved piezoresistive materials with high levels of flexibility, stretchability and simple integration in large area applications [16].

Polymer-based materials have been largely studied in view their intrinsic properties and applicability. Conventional strain gauges are typically attached to a polymeric substrate and their piezoresistive sensibility is near Gauge Factor (GF) ≈ 2 [17]. Piezoresistive materials based in polymer can reach to $GF \geq 100$ [13], show improved mechanical properties as well as tailorable properties and electromechanical response, due to the large range selection possibilities of polymers and fillers..

Tailoring polymer-based materials for sensor applications to be implemented by solvent based printing technologies, such as screen [3, 18, 19] or spray printing [1, 4, 13, 20], involves proper selection of solvent the polymer solvent, allowing polymer dissolution, good dispersion of the fillers, and being human and environmental friendly.

Within polymers, thermoplastic elastomers combine the best properties of thermoplastics with the stretchability of the elastomers, without vulcanization process [21, 22]. Thermoplastic elastomer styrene-ethylene/butylene-styrene (SEBS) triblock copolymers present excellent mechanical properties, including high maximum strain and low mechanical hysteresis, and chemical stability [13], being therefore a suitable selection for the development of force and deformation sensors, from low to large mechanical deformations.

In this context, the present work reports on the processing and characterization of nanocomposite films and inks suitable for screen printing based on MWCNTs as conductive filler and the thermoplastic elastomer, styrene-ethylene-butylene-styrene as polymer matrix. Different environment-friendly solvents, including cyclopentyl methyl ether (CPME), 2-MeTHF and p-cymene were used in order to produce piezoresistive strain sensors, that were compared with samples prepared with Toluene, the most used solvent in this context [5, 22].

2.2. Experimental

2.2.1. Materials

The thermoplastic elastomer Calprene CH-6120, a SEBS copolymer with a ratio of ethylene-butylene/styrene of 68/32 and a molecular weight of 245.33 g/mol, was supplied by Dynasol. MWCNTs were supplied by Nanocyl: reference NC7000, purity of 90%, length of 1.5 μm and diameter of 9.5 nm. Cyclopentyl methyl ether (CPME) and 2-methyltetrahydrofuran (2-MeTHF) were supplied from Carlo Erba. Toluene was supplied by Fisher and p-cymene by Acros Organics.

2.2.2. Sample preparation

MWCNT/SEBS composites with filler weight contents ranging from 0 to 12 wt.% were prepared by dispersing the corresponding MWCNT loading in the solvents: CPME, toluene, 2-MeTHF and p-cymene solvents within an ultrasound bath (ATU, Model ATM40-3LCD) for 4 h with temperature ranging from 25 to 35 $^{\circ}\text{C}$ for homogeneous dispersion and for avoiding agglomerates.

After achieving a good dispersion of the nanofillers, SEBS was added with an appropriate polymer/solvent ratio based on the density of the solvent in order to achieve similar viscosities for the inks: 1g: 9ml for p-cymene and 2-MeTHF, and 1g: 6ml for toluene and CPME. Then, the solution was

magnetically stirred at 25 °C until complete dissolution of the copolymer and the MWCNT/SEBS films were then prepared by doctor blade technique in the conditions reported on [13]. After printing, the samples were dried for 24 h at room temperature. Thin films with thickness varying from 30 to 100 µm and 13 to 16 µm were obtained for doctor-blade and screen printing, respectively.

The screen-printing technique was performed using a home-made manual screen-printer. A polyester mesh screen was used with a mesh with 65 threads/cm, a thread diameter of 52 µm and a square-edged mesh opening of 102 µm. The squeegee orientation angle was set around 45° relative to the print substrate and the tension of the mesh was 20 N. Table 2.1 shows the nomenclature for the different samples.

Table 2.1. Nomenclature for the different samples.

<i>Nomenclature</i>	<i>MWCNT (wt. %)</i>	<i>Solvent</i>
<i>3MWCNT/SEBS-CPME</i>	3	CPME
<i>3MWCNT/SEBS-T</i>	3	Toluene
<i>SEBS-p</i>	0	p-cymene
<i>3MWCNT/SEBS-p</i>	3	
<i>5MWCNT/SEBS-p</i>	5	
<i>7MWCNT/SEBS-p</i>	7	
<i>9MWCNT/SEBS-p</i>	9	
<i>12MWCNT/SEBS-p</i>	12	
<i>SEBS-2M</i>	0	2-MeTHF
<i>3MWCNT/SEBS-2M</i>	3	
<i>5MWCNT/SEBS-2M</i>	5	
<i>7MWCNT/SEBS-2M</i>	7	
<i>9MWCNT/SEBS-2M</i>	9	
<i>12MWCNT/SEBS-2M</i>	12	

2.2.3. Sample characterization

Scanning electron microscopy (SEM) of the film surface was used to evaluate the MWCNT dispersion within the polymer matrix with a SEM- FEI - NOVA NanoSEM 200. Before the measurements, the samples were coated with an Au layer with a Polaron SC502 sputter coater.

The d.c. electrical resistivity of the films was obtained from I-V measurements with an automated Keithley 487 picoammeter/voltage source with an applied voltage in the range -1 V and +1 V and measuring the current. The measurement geometry and the electrodes are the ones described for the dielectric measurements. The electrical resistance (R) of the composites was calculated from the slope of the obtained I-V curves, and the electrical resistivity (ρ), equation 2.1, was obtained taking into account the geometrical characteristics of the samples.

$$\rho = R \frac{d}{A} \quad (2.1)$$

Electromechanical measurements were performed by measuring the electrical resistance of the samples (Agilent 34401A multimeter) through silver pattern while the sample is subjected to a mechanical deformation under compression (Shimadzu AG-IS universal testing machine), with a load cell of 500 N. The piezoresistive tests were carried out for applied forces up to 400 N in 10 loading-unloading cycles, at a test velocity of 1 mm/min.

2.3. Results and discussion

The morphology of the MWCNT/SEBS films was studied in order to evaluate if the dispersion of the MWCNT within the SEBS is affected by the use of different solvents (Figure 2.1.)

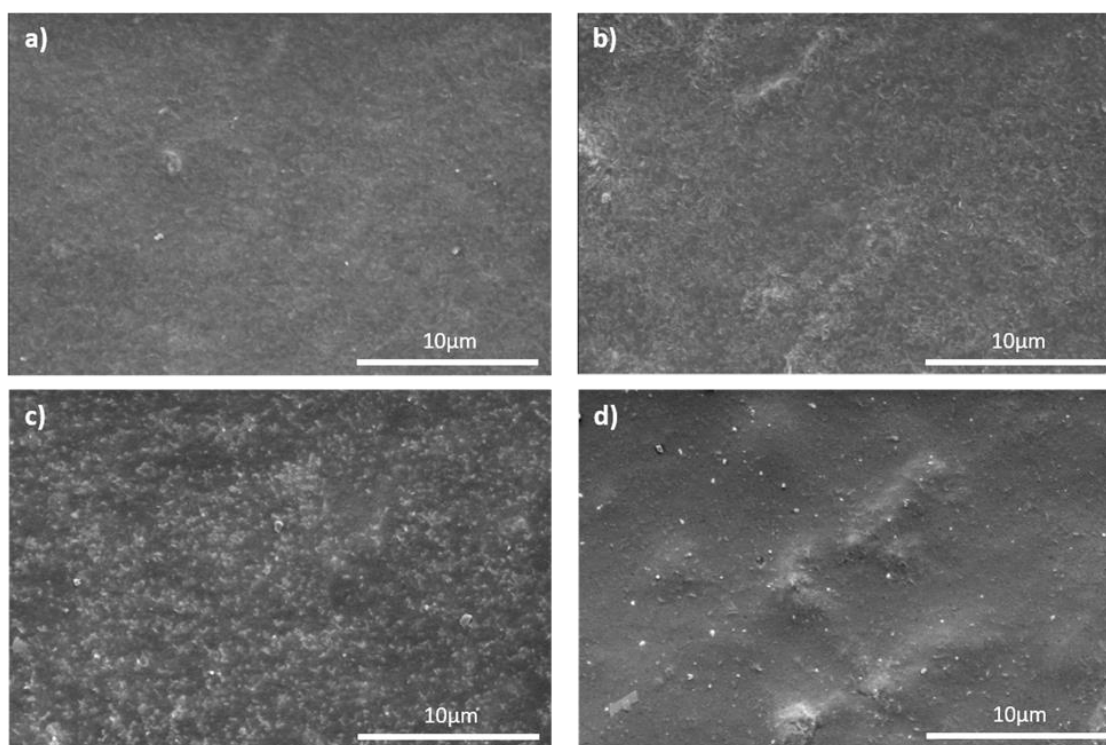


Figure 2.1. Surface SEM images of SEBS composites prepared by doctor-blade with the different solvents: a) p-cymene for 5 wt.% and b) 7 wt.%, 2-MeTHF for c) 5 wt.% and d) 7 wt.%.

Surface SEM images of the different nanocomposites (Figure 2.1.) show a homogeneous dispersion of MWCNT small agglomerates. The SEM images for composites prepared with toluene and CPME solvents have been reported in [13], showing clusters with an average diameter of $\approx 5 \mu\text{m}$. Amongst the different solvents, the one leading to a more homogenous dispersion of MWCNT in the composite is p-cymene, as can be observed in Figures 2.1 a) and 2.1 b). Further, 2-MeTHF composites show homogeneous cluster agglomerates with an average diameter of $\approx 3 \mu\text{m}$, as observed in Figure 2.1 c) and 2.1 d). It is to notice that a homogenous cluster distribution within the polymer, increases the electrical conductivity of the sample and also plays an essential role in the piezoresistive properties of the composites [18, 23], when compared to individual MWCNT dispersion.

The d.c. conductivity of the different composites is presented in Figure 2.2 a) in function of the filler content. It is shown that the electrical conductivity increases from $3 \times 10^{-13} (\Omega \cdot \text{m})^{-1}$ of neat SEBS up to 2×10^{-3} and $9 \times 10^{-3} (\Omega \cdot \text{m})^{-1}$ for composite with 12 wt.% MWCNT for 2-METHF and p-cymene, respectively. The solvent used in the composite preparation influences the electrical properties of the composites, as seen in the composites with 3 wt.% CNT for different four solvents: toluene, CPME, 2-MeTHF and p-cymene.

For the same MWCNT content (3 wt.%), composites prepared with toluene and CPME show higher values of conductivity when compared with the ones prepared with p-cymene and 2-MeTHF, two and four orders of magnitude, respectively. The electrical conductivity for the samples prepared with toluene and CPME are of 8.4×10^{-3} and $8.8 \times 10^{-3} (\Omega.m)^{-1}$, respectively, for the sample with 3 wt.% MWCNT content. It is necessary having composite with near 10 wt.% MWCNT using 2-MeTHF and p-cymene as solvent to obtain the electrical conductivity of toluene or CPME composite with 3 wt.% MWCNT. The electrical response of the composites is related with the interfacial effects of the MWCNT with the polymeric matrix [17, 24, 25]. Toluene and CPME (environment-friendly solvent) present improved conductivity compared to remain solvent due to better fillers dispersion of MWCNT in SEBS matrix. The strong increase of conductivity from neat SEBS to 5 wt.% MWCNT allows the identification of the percolation threshold [26], explained theoretically by the percolation theory [21]. In Figure 2.2 b) we can observe that the SEBS reinforced with CNT nanomaterials and different solvent shown percolation threshold, near 0.13% and 0.24% in volume for p-cymene and 2Me-THF composites (Figure 2.2 b), respectively. Respectively, these values represent near 1 and 2 wt.% MWCNT in composites. Through the electrical conductivity behavior in function of the filler content, it is possible determine the percolation threshold of the both composites, the following equation was used [27]:

$$\sigma = \sigma_0(f - f_c)^t \quad (1)$$

where σ_0 the filler conductivity, f the filler content, f_c the percolation threshold and t the universal critical exponent that depends on the system dimensionality ($1 < t < 1.3$ for a 2D network and $1.5 < t < 2$ for a 3D network [27]). For MWCNT/SEBS with p-cymene, the $t=4.3$ and for 2Me-THF is $t=2.7$. Critical exponent values larger than estimated can be found in literature for composites [27], where authors attributed this behavior to the inhomogeneity of the filler dispersion.

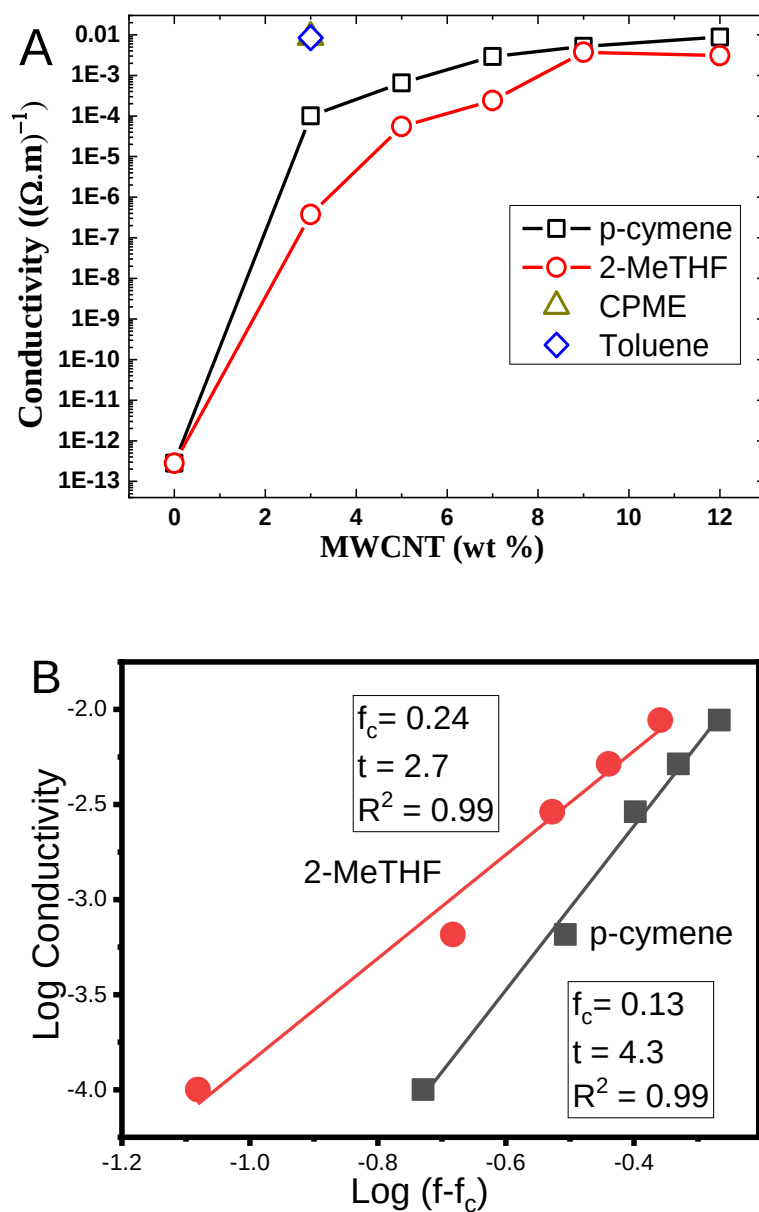


Figure 2.2. a) Electrical conductivity of the MWCNT/SEBS composites up to 12 wt.% using different solvents: toluene, CPME, 2-MeTHF and p-cymene. b) Percolation theory for p-cymene and 2-MeTHF solvents used in MWCNT/SEBS composites.

The piezoresistive responses of the composites was evaluated above the percolation threshold for the composites prepared with toluene (3 wt.%), CPME (3 wt.%), p-cymene (5 wt.%) and 2-MeTHF (5 wt.%), in view the materials response up to high applied pressures with linear electromechanical performance. The measurements were evaluated after 10 loading-unloading compressive mechanical stress using 400

N of pressure. The electromechanical behavior of the MWCNT/SEBS nanocomposites is shown in figure 2.3.

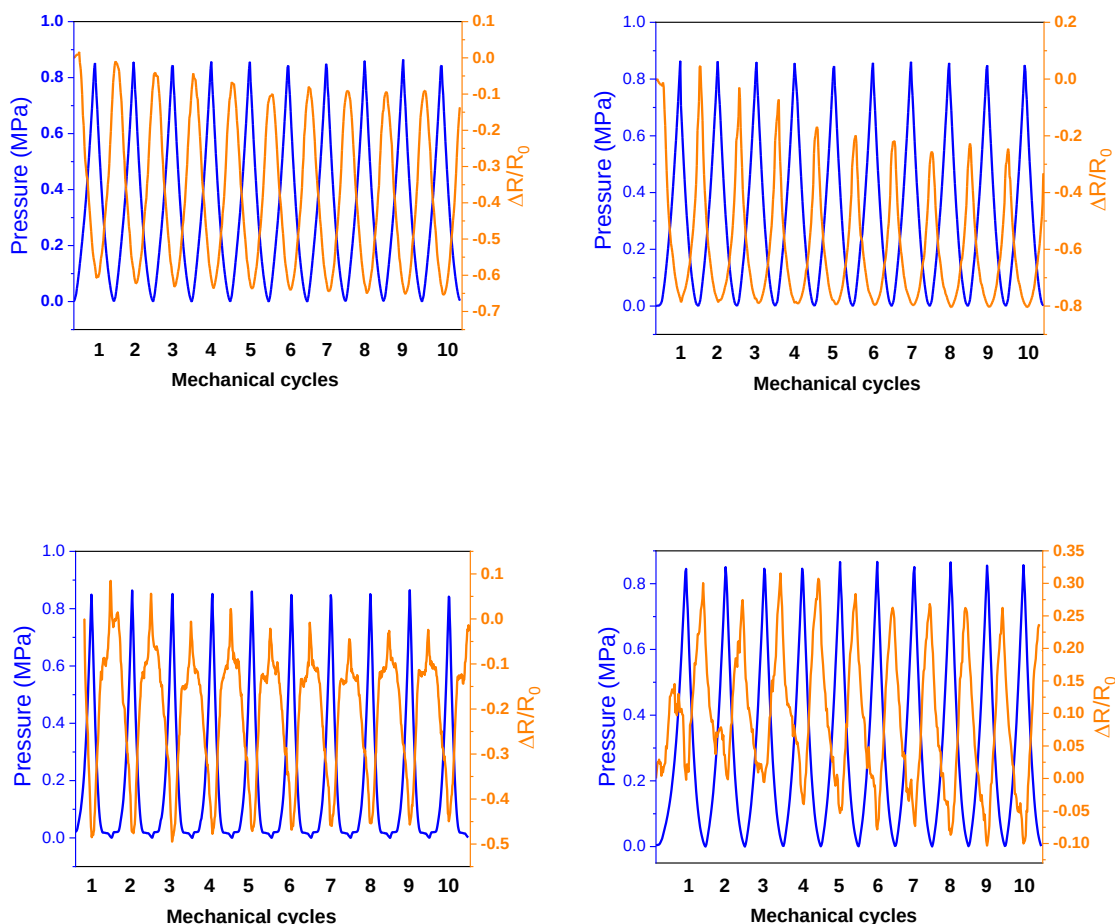


Figure 2.3. Electromechanical response of SEBS composites prepared with different solvents: a) Toluene (3 wt.%), b) CPME (3 wt.%), c) 2-MeTHF (5 wt.%), d) p-cymene (5 wt.%), of the samples around the percolation limit.

The electromechanical response shows that the electrical resistance variation is inversely proportional to the mechanical compressive deformation applied to the composites: the electrical resistance of the composites decreases with applied deformation and increases with decreasing deformation. In volume compression, the MWCNT are getting closer to each other due to the increasing pressure in composites. When the pressure is released in composite, the electrical resistance returns to the initial values.

Although the samples are composed of the same materials (with different solvent) the electromechanical performance is a little bit different. Toluene and CPME composites show a linear behavior under cycle's compression, with a slight decrease of the electrical resistance. Composites with 2-Me-THF present a lower electrical resistance variation (due to larger filler content) and is more sensible at lower pressures than p-cymene composite. This last composite is the material that shows lower electrical resistance variation, compared to all sensor materials.

The piezoresistive behavior was quantified by the pressure sensitivity (PS), calculated after equation 2.2:

$$PS = \frac{\Delta R/R_0}{P} \quad (2.2)$$

where R_0 is the initial electrical resistance in the unloaded state, ΔR is the electrical resistance variation and P is the applied pressure.

Figure 2.4. shows the variation of the electrical resistance as a function of the applied pressure for the four different nanocomposites.

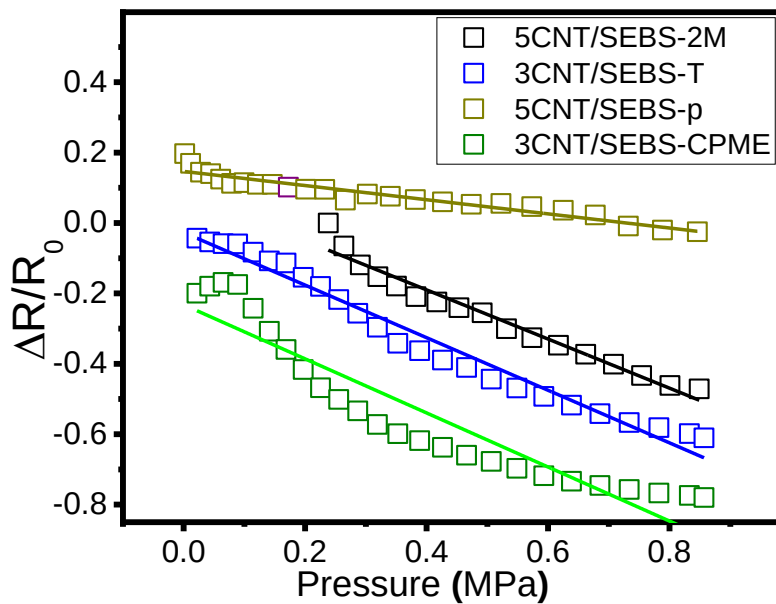


Figure 2.4. Electrical resistivity variation as a function of the applied pressure for the different nanocomposites for applied pressures up to 1 MPa.

Table 2.2. Pressure sensibility of MWCNT/SEBS composites with different solvents, for 3 and 5 wt.% of MWCNT.

Sample	Pressure sensibility (MPa ⁻¹)
Toluene (3 wt.%)	0.73 ± 0.03
CPME (3 wt.%)	0.62 ± 0.07
2-MeTHF (5wt.%)	0.53 ± 0.08
p-cymene (5 wt.%)	0.34 ± 0.09

It is shown that the $\Delta R/R$ shows a linear behavior and decreases as the pressure applied increases for all the nanocomposites. The pressure sensibility was calculated by a linear fitting of the result. Table 2 shows that the composite with toluene 3 wt.% is the one with the higher sensibility (0.73 MPa⁻¹), followed by CPME 3 wt.% (0.62 MPa⁻¹), 2-Me-THF 5 wt.% (0.53 MPa⁻¹) and p-cymene 5 wt.% (0.34 MPa⁻¹). Despite toluene 3 wt.% is the composite with higher sensibility, this is the one that uses the most hazardous solvent. The remaining three composites comprises environmentally “friendly” solvents and despite the lower value of sensibility, in case of CPME and 2-MeTHF the values are comparable with toluene and suitable for applications. The dispersion of the MWCNT in SEBS matrix affect the electrical and electromechanical behavior for several solvent used, with p-cymene present higher conductivity but smaller electrical resistance variation for pressure applications.

Depending of the filler content, all MWCNT/SEBS composites materials in function of the hazard or environment-friendly solvents can works as pressure sensor material.

2.4. Conclusions

Polymer-based printable piezoresistive sensors were developed using different solvents. In a step to develop environmental friendly materials for pressure sensor applications, three different “green” solvents were used, including CPME, 2-MeTHF and p-cymene.

The composites, show an excellent variation of the electrical resistance with mechanical deformation, where the resistance decreases with applied deformation and increases with decreasing deformation, showing a piezoresistive response suitable for pressure sensing applications. In particular, all composites prepared with environmental friendlier solvents show a pressure sensibility values comparable with the

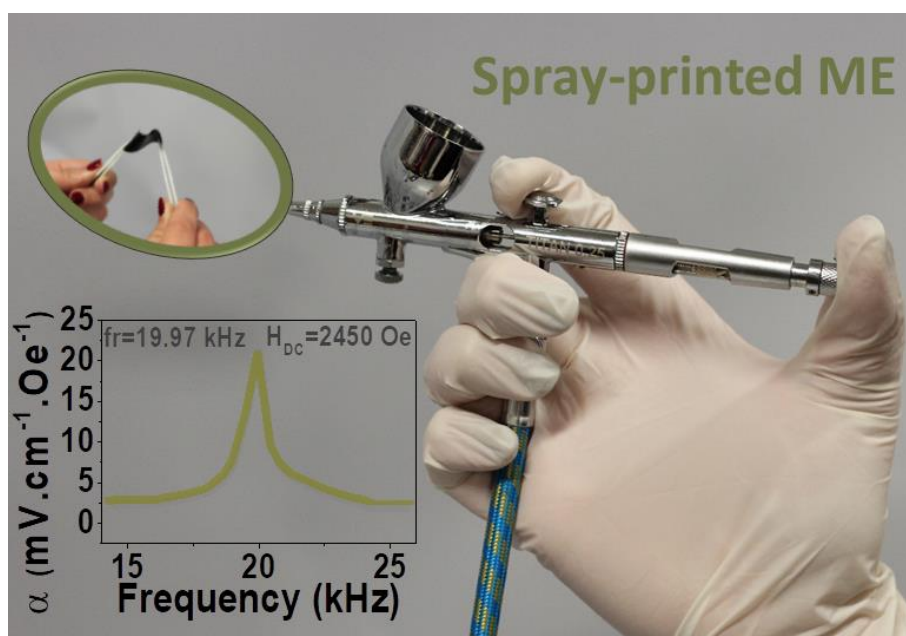
non-environmentally friendly toluene, being good candidates for a new generation of piezoresistive environmental friendly inks for pressure sensors applications.

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3. Spray-printed magnetoelectric multifunctional composites

This work reports the performance of spray printed magnetoelectric (ME) composites based on poly(vinylidene fluoride-co-trifluoroethylene)/cobalt ferrite, P(VDF-TrFE)/CoFe₂O₄. It is shown that for a 20 wt.% ferrite content the composite exhibits a fibrillar-porous structure, ≈ 1.8 GPa Young's Modulus, saturation magnetization of 11.2 emu.g⁻¹, 6.0 emu.g⁻¹ magnetic remanence and a magnetic coercivity of 2050 Oe. Further, it is demonstrated a 34 dielectric constant (at 10 kHz) and a 27 pC.N⁻¹ piezoelectric coefficient. Such high dielectric and piezoelectric responses explain the ME response of 21.2 mV·cm⁻¹·Oe⁻¹ at an optimum magnetic field of 2450 Oe, which is superior to the response of similar composites prepared by bar-coating. The high ME response and the simple and scalable printing method demonstrates the suitability of these materials for cost effective and large-scale sensor/actuator applications.

This chapter is based on the following publication: J. Serrado Nunes, et al., submitted on Additive Manufacturing 2019.

3.1. Introduction

Additive manufacturing is rapidly expanding and modifying the way in which products are designed, optimized, manufactured and integrated [1]. With the possibility to transform digital information into physical components, this technology is leading to new routes in the manufacturing industry by producing complex geometries with tailored material properties, freedom on the design and environmental benefits, by transforming pre-defined files into fully functional products [2].

In this scenario, printing technologies are becoming increasingly popular for the development of functional devices [3]. Particularly interesting is the development of smart materials compatible with printing technologies, such as shape-memory materials, electroactive and magnetoactive materials [4].

Smart materials obtained through printing technologies are particularly suitable for the development and implementation of printed electronics field, a highly increasing research and technological field [4]. Despite several reports regarding the development of conductors, dielectric, and semiconductor inks for different electronic components, there are still few reports of fully-printed devices [3, 4]. In particular, for an effective next generation of fully printed sensing devices and systems, it is required the development of functional inks based on smart materials, including magnetic, ferroelectric, piezoelectric and in some cases magnetoelectric [3, 4, 5]. ME materials are particularly interesting as they provide effective coupling between electric and magnetic orders, being actively used in multifunctional integrated devices [4, 6]. Since the ME response in single-phase ME materials is very small at very low temperatures, their ME coupling cannot be used in technological applications [7]. This is why most studies are related with the development of ME composites consisting of two phases, one piezoelectric and the other magnetostrictive, mechanically coupled, and which give rise to ME coefficients 3 orders of magnitude higher than the ones found in single-phase ME materials [5, 8]. Theoretical research as well as some recent experimental studies have shown that piezoelectric polymers, in addition to solve some problems found in ceramic-based ME materials such as fragility, low electrical resistance and high dielectric losses [8, 9], can allow colossal ME response in composites due to large piezoelectric stress coefficients and great displacement transfer capability of the piezoelectric polymer [6].

Polymers also offer several advantages for an effective printing of smart materials due to the higher versatility than inorganic materials, higher flexibility, suitability to be implemented in a variety of substrates, possibility of tailoring their side-chains and molecular structure, opportunity to introduce active (nano)fillers, as well as particles with specific properties into the material, enabling materials to be fabricated with specific chemical and physical properties [4]. Despite this favourable context, many

printing methods are very specific for a given application and only a few are applicable to a wide range of materials and surfaces [4]. An effective and simple solution-based method for the preparation of polymer-based ME composite films is spray printing due to its high production velocity, efficient use of materials, good reproducibility and compatibility with different substrates [10].

Despite this favourable context for the emergence of printed polymer-based ME materials, it is highly surprising that the only work found in the literature, as far as we know, is the report of Chlaihawi *et al.* [11]. Nevertheless, such ME material was produced by screen printing poly(vinylidene fluoride) (PVDF) piezoelectric polymer into a magnetostrictive Metglas® substrate, not being in this way a fully-printed ME material and therefore limiting the aforementioned advantages of printed devices. Additionally the flexibility, simple fabrication (solvent based), easy shaping, the possibility of miniaturization and/or to produce large uniform areas and the absence of degradation at the piezoelectric/magnetostrictive interface are obvious advantages of nanocomposites when compared to such laminated structures [7, 8].

In this context, this paper presents a poly(vinylidene fluoride-co-trifluoroethylene)/CoFe₂O₄-based ink, which is then printed in a glass substrate through spray-printing and fully characterized with respect to its functional response, including piezoelectric, magnetic and magnetoelectric responses.

Poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) was selected due to its high piezoelectric response ($|d_{33}| \approx 30 \text{ pC.N}^{-1}$) at room temperature and physicochemical stability; while CoFe₂O₄ was selected due to its high magnetostrictive coefficients ($\lambda = 200 \text{ ppm}$), high Curie temperatures, chemical stability, wear resistance and simple processability [7, 12].

3.2. Experimental

3.2.1. Materials

CoFe₂O₄ nanoparticles ($\approx 35\text{-}50\text{nm}$) were purchased from Nanostructured & Amorphous Materials, Inc. (Texas, USA). N,N-dimethylformamide (DMF), pure grade, was supplied by Fluka (New Jersey, USA) and P(VDF-TrFE) was supplied by Solvay (Brussels, Belgium). All the chemicals and particles were used as received from the suppliers.

3.2.2. Ink preparation and printing conditions

The composite solutions were prepared following the general guidelines presented in the protocol [13] for the development of piezoelectric PVDF composites. In short, in order to obtain a good dispersion of the CoFe_2O_4 particles within the P(VDF-TrFE) matrix, the desired amount of ferrite (20% in weight percentage – wt.%) was added to DMF (10 mL) and then placed in an ultrasound bath (ATU ATM 3LCD) during 8 h to avoid a magnetic agglomeration, then 2 g of P(VDF-TrFE) were subsequently added and a CoFe_2O_4 / P(VDF-TrFE)/DMF-based ink was obtained. The 20 wt.% of ferrite content was chosen once it ensures a high ME coupling and flexibility [7]. Flexible films were obtained by spray-printing the CoFe_2O_4 / P(VDF-TrFE)/DMF ink, using a commercial airbrush (Ventus Titan Dual Action 0.25mm), at 10 cm of the glass substrate using a pressure of 3 psi. Solvent evaporation was performed inside an oven at controlled temperature of 210 °C for 10 minutes [13]. It is to notice that the solvent evaporation temperature is above the melting temperature of the polymer, but that it crystallizes in the electroactive phase when cooled down to room temperature [13]. Then, the films (≈ 50 μm thick) were removed from the oven and allowed to cool at room temperature.

3.2.3. Sample characterization

The morphology of the P(VDF-TrFE)/ CoFe_2O_4 printed layers were evaluated via scanning electron microscopy (SEM) with a Hitachi S-4800 set-up at 10 kV. Previously, samples were coated with a thin gold layer using a sputter coating (Polaron, model SC502).

The mechanical characterization was carried out in the tensile mode with a Shimadzu AGS-J 500N universal testing set-up. The samples were cut into rectangular geometry of 20 mm x 6 mm with a sample thickness of ≈ 50 μm . The Young's modulus was calculated based on the evaluation of three replicas from the first linear slope of the stress-strain curves (in the range 0.5-1%). The standard deviation of the measurement was estimated to ± 0.08 GPa.

The measurements of the capacity and dielectric loss $\tan \delta$ were performed with an Agilent E4980A Precision LCR Meter in the measuring frequency range of 1 kHz to 1 MHz at an applied voltage of 0.5 V. In order to obtain a plane parallel condenser geometry, Au contacts with 5 mm diameter were deposited on both sides of the samples using a Polaron SC502 sputter coater (40 nm of gold thickness). The real part of the dielectric constant, ϵ' , was determined from the electrical capacity (C) taking into account the geometry of the sample (thickness (d) and electrode area (A)) (equation 3.1):

$$\epsilon' = \frac{C \times d}{A} \quad (3.1)$$

Magnetic hysteresis loops were measured at room temperature using a Microsenses ADE 3473-70 Technologies vibrating sample magnetometer (VSM).

The poling of the samples was achieved, after an optimization procedure, (60 min of corona poling at 120 °C in a home-made chamber). In order to optimize the piezoelectric response, the electric field was kept applied when the samples were cooled to room temperature. The piezoelectric response (d_{33}) of the poled samples was obtained with a wide range d_{33} -meter (model 8000, APC Int. Ltd).

The ME response was obtained by measuring the transversal ME voltage coefficient (α_{33}) using the dynamic lock-in amplifier method¹⁴. A pair of Helmholtz coils was used to generate an AC magnetic field with amplitude of 1 Oe and frequency of ≈ 20 kHz (electromechanical resonance of the composite) that is superimposed to a DC bias field driven by an electromagnet. Both fields are applied out of plane of the nanocomposite film and the generated voltage across the sample thickness is measured using a digital Lock-in amplifier (Stanford Research SR530). The ME voltage coefficient (α_{33}) was calculated from the measured voltage using equation 3.2:

$$\alpha_{33} = \frac{\Delta V}{H_{AC} \times t} \quad (3.2)$$

where ΔV is the measured output voltage, H_{AC} is the amplitude of the AC magnetic field, and t is the thickness of the nanocomposite film.

3.3. Results and discussion

The morphology of the samples are shown in the SEM images presented in Figure 3.1. Both transversal (a) (obtained by cutting the samples after 1 minute immersion in liquid N_2) and surface (b) images reveal a fibrillar microstructure induced by the printing procedure.

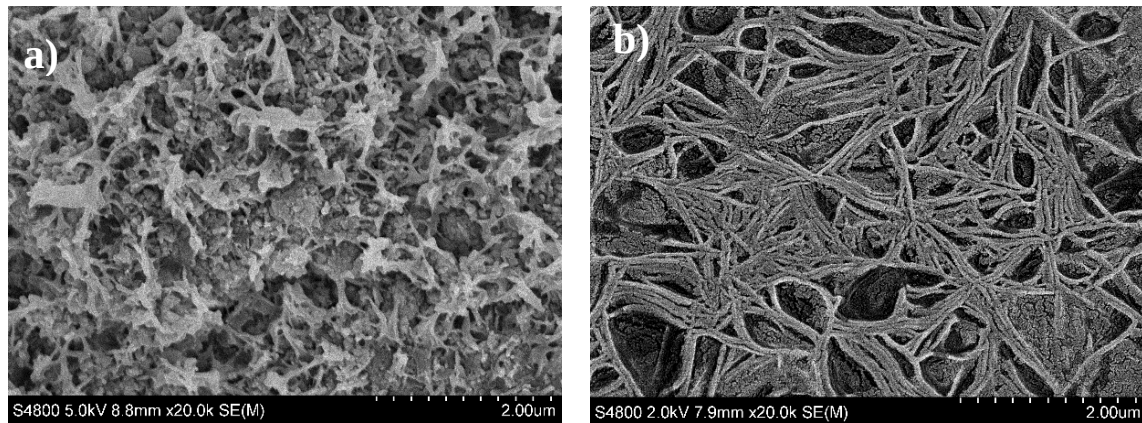


Figure 3.1. a) Transversal and b) surface. SEM images of the P(VDF-TrFE)/CoFe₂O₄ printed composites with 20 wt.% of ferrite content.

Such fibrillar microstructure is typical for P(VDF-TrFE) [15], but, in the present case is reinforced by the mechanical energy of the gas flow followed by the polymer solidification in the form of fibers [16]. It is to notice that no filler agglomeration is observed, indicating a good dispersion of the magnetic nanoparticles. To verify if the obtained reinforced fibrillar microstructure affects the mechanical properties of the spray-printed ME composites when compared with the ones obtained by bar coating [17], stress-strain measurements were performed (Figure 3.2).

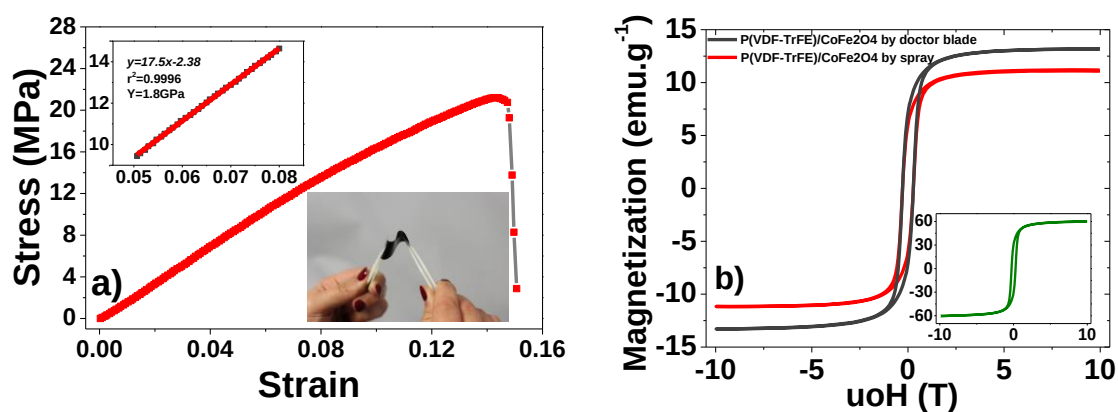


Figure 3.2. a) Characteristic stress-strain curve in the tensile mode of the P(VDF-TrFE)/ CoFe₂O₄ composite (the inset shows the linear fit to obtain the Young 's modulus and a photograph of the printed ME composite). b) Room-temperature magnetization as a function of the applied DC magnetic field. The inset shows the room-temperature magnetization of the CoFe₂O₄ nanoparticles.

The $\text{CoFe}_2\text{O}_4/\text{P(VDF-TrFE)}$ samples shows a good mechanical stability (inset in figure 3.2 a) with the typical thermoplastic behaviour of pristine P(VDF-TrFE) polymer. From the initial slope of the mechanical stress–strain curve, in-plane Young's modulus value, E_r , has been determined as ≈ 1.8 GPa. This value is the double of the pristine P(VDF-TrFE) polymer and other ME composites reported in the literature for the same ferrite content [18]. The increase in the Young's modulus and slight decrease in the value of elongation at the break point (from 3% to 2%) can be related with the enhancement in the crystalline zones, high levels of chain orientation and improved chain extension promoted by the elongation forces from the spray's gas flow [19].

The spray-printed $\text{P(VDF-TrFE)}/\text{CoFe}_2\text{O}_4$ exhibits room-temperature ferromagnetism (Figure 3.2 b) with a saturation magnetization of 11.2 emu.g^{-1} , 6.0 emu.g^{-1} remanence and coercivity of 2050 Oe, values which are similar to the ones obtained for bar-coated $\text{P(VDF-TrFE)}/\text{CoFe}_2\text{O}_4$ composites, showing the lack of influence of the processing conditions on the nanofiller magnetic response.

Table 3.1. Coercive field (H_c), magnetic remanence, magnetic saturation and CoFe_2O_4 wt.% for $\text{P(VDF-TrFE)}/\text{CoFe}_2\text{O}_4$ samples prepared by spray-printing and bar-coating, as well as for CoFe_2O_4 nanoparticles.

Material	H_c	M_r	M_s	CoFe_2O_4 wt.%
Spray-printed $\text{CoFe}_2\text{O}_4/\text{P(VDF-TrFE)}$	2050	6	11	20
Bar-coated $\text{CoFe}_2\text{O}_4/\text{P(VDF-TrFE)}$	2050	7	12	20
CoFe_2O_4 nanoparticles	2050	39	59	100

Magnetization measurements (Figure 3.2 b) were also used to calculate the CoFe_2O_4 content on the spray-printed $\text{P(VDF-TrFE)}/\text{CoFe}_2\text{O}_4$ composite by the method proposed in [20], and compared with the value obtained in a similar composite obtained by bar-coating (Table 3.1). It is observed that the printing procedure does not affect the ferrite content in the composite.

Once the dielectric and piezoelectric properties of ME composites have a high impact on their multifunctional performance [18a, 21], the room-temperature dielectric response as a function of frequency and the room-temperature piezoelectric response as a function of the number of days after poling are presented in Figure 3.3.

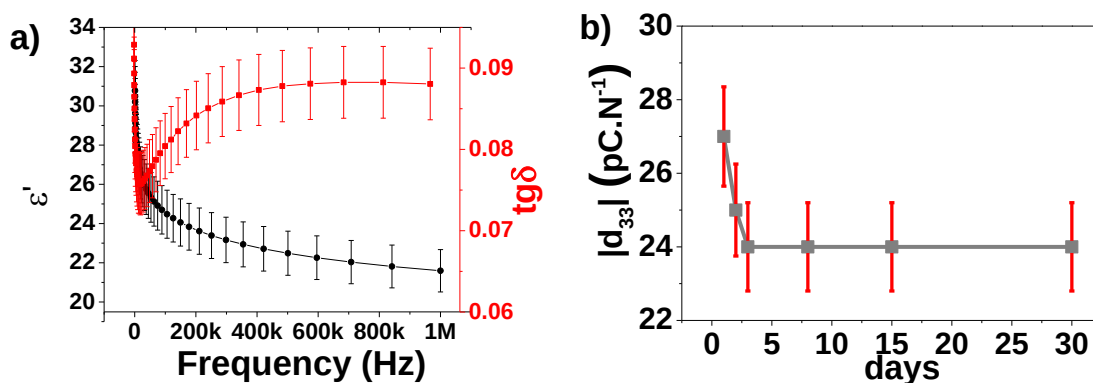


Figure 3.3. a) Frequency dependence of the real part of the permittivity (ϵ') and b) room-temperature piezoelectric response of the ME P(VDF-TrFE)/CoFe₂O₄ sample.

Figure 3.3 a) shows that the real part of the dielectric response decreases rapidly with increasing frequency and decreases more moderately for frequencies above 10 kHz. This behaviour at the lower frequencies is explained by the Maxwell–Wagner type interfacial polarization, in agreement with Koop's phenomenological models [22]. Additionally, the inclusion of CoFe₂O₄ particles into the P(VDF-TrFE) matrix leads to a significant increase of the dielectric constant when compared with the dielectric response of the pristine polymer (from ≈ 10 [23, 24] to 31 at 10 kHz) explained by the interfacial polarization at the particle/polymer interfaces [9, 25]. The dielectric losses ($\tan \delta$) show a similar behaviour as the pure P(VDF-TrFE) polymer [18a] or other PVDF/CoFe₂O₄ composites with the same ferrite content and produced by bar coating, being at 10 kHz lower than 0.1 [23], indicating a low electrical conductivity in these materials.

The result of the interfacial polarization at the particle/polymer interfaces is also noted in the difference between the piezoelectric responses reported on both pristine polymer (≈ 15 –20 pC.N⁻¹ [18a]) and other P(VDF-TrFE)/CoFe₂O₄ composites with the same ferrite content and produced by bar coating (15 pC.N⁻¹ [26]), and the one observed on the printed P(VDF-TrFE)/CoFe₂O₄ composite (24 pC.N⁻¹).

Such improved dielectric and piezoelectric responses anticipate a better ME coupling in the P(VDF-TrFE)/CoFe₂O₄ spray-printed composite (Figure 3.4).

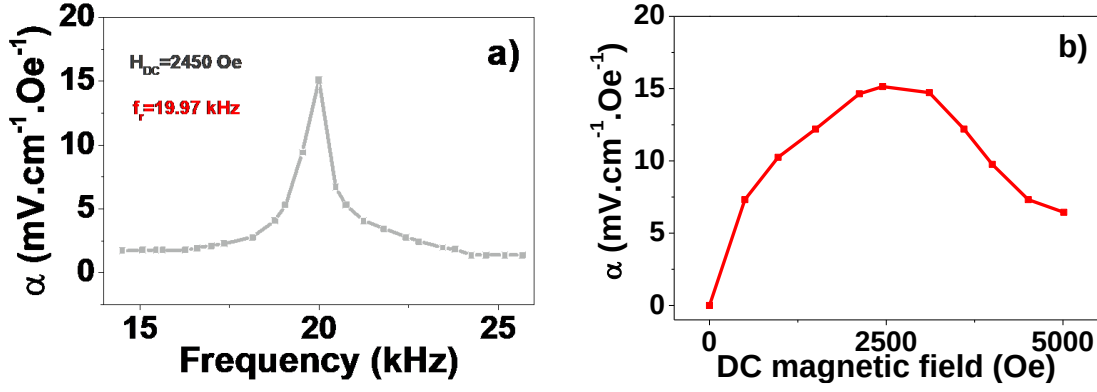


Figure 3.4. Room-temperature ME response of P(VDF-TrFE)/CoFe₂O₄ spray-printed composite as a function of the: a) frequency and; b) DC magnetic field.

The harmonic mode order, thickness, in-plane Young's modulus and density of the composites [27] placed the resonance of the P(VDF-TrFE)/CoFe₂O₄ spray-printed composite at 19.97 kHz. The DC ME characterization was performed at such frequency and it was verified a similar behaviour than for bar-coated composites [27], being observed that the ME coefficient increases with increasing DC magnetic field until a maximum of 15.2 mV.cm⁻¹.Oe⁻¹ in the case of the spray-printed composite and 12.1 mV.cm⁻¹.Oe⁻¹ in the case of the bar-coated-printed composite [17], both at an optimum magnetic field of 2450 Oe. Such behaviour is explained by the increase of the effective piezomagnetic coefficient until the optimum DC magnetic field is reached. With further increase in the DC magnetic field, a decrease in the induced voltage is observed for both composites resulting from the saturation of the magnetostriction coefficient [7].

Knowing that the ME coefficient (α) can be written as:

$$\alpha = \frac{dS}{dH} \times m_v \times (1 - m_v) \times \left(\frac{d_{33}}{\epsilon_0 \times \epsilon} \times \frac{E_Y \times l \times w}{t} \right) \quad (3.3)$$

where (dS/dH) is the strain derivative, m_v the ferrite volume fraction, ϵ_0 the vacuum permittivity, ϵ the relative permittivity of the material, d_{33} the piezoelectric voltage coefficient, E_Y the Young's modulus, l the sample length, w the sample width and t the sample thickness, is possible to theoretically quantify the influence of the optimized E_Y , d_{33} and ϵ in the ME voltage coefficient, by making the remaining elements of the equation equal to **k**. (Table 3.2).

Table 3.2. α as a function of k.

Material	E_y	$ d_{33} $	ϵ	α (as a function of k)
Spray-printed $\text{CoFe}_2\text{O}_4/\text{P(VDF-TrFE)}$	1.8	24	31	1.4k
Bar-coated $\text{CoFe}_2\text{O}_4/\text{P(VDF-TrFE)}$	1.0	15	13	1.2k

From Table 3.2 is theoretically predicted a 17% higher ME response on the spray-printed sample, being the (20%) $\approx 3 \text{ mV}\cdot\text{cm}^{-1}\cdot\text{Oe}^{-1}$ superior coefficient detected on the printed sample explained by the higher dielectric coupling, superior piezoelectric response and higher Young's modulus of the spray-printed composite when compared to the bar-coated composite [7].

3.4. Conclusions

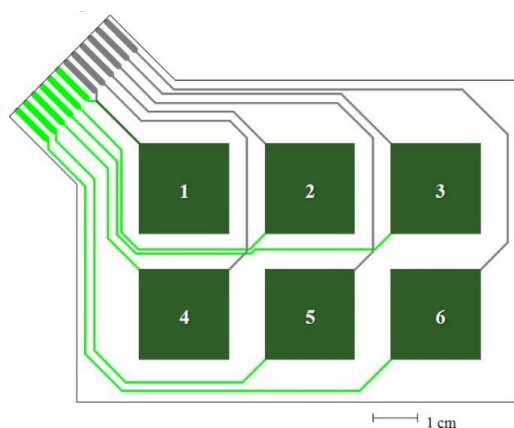
A simple upscalable method for the preparation of ME materials based on spray-printing is reported. The resulting $\text{P(VDF-TrFE)/CoFe}_2\text{O}_4$, with 20 wt.% of ferrite content and a reinforced fibrillar structure exhibits improved dielectric and piezoelectric responses when compared to a composite with a similar composition but obtained by bar-coating, leading to an $21.2 \text{ mV}\cdot\text{cm}^{-1}\cdot\text{Oe}^{-1}$ ME coupling coefficient at an optimum magnetic field of 2450 Oe suitable for sensor/actuator applications. The simple printing process, easy integration into devices and the possibility to be obtained over flexible and large areas validate the developed ME material for applications such as printed electronics, sensors, actuators, and energy harvesters.

3.5. References

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4. Environmental friendlier printable piezoelectric inks and their application for the development of highly sensitive all-printed touchscreens

This work reports the development of piezoelectric inks based on poly(vinylidene fluoride-co-trifluoroethylene), PVDF-TrFE, dissolved in the environmentally friendly solvent N, N-dimethylpropyleneurea (DMPU). The inks were prepared for different printing techniques, including doctor blade, spray-printing, and screen-printing, representing therefore a relevant step for the additive manufacturing of sensors, actuators and touch screens, among others. The rheological properties of the inks demonstrate that DMPU is a good solvent for this polymer and allows to obtain dense piezoelectric films with the different printing techniques, showing also similar physico-chemical and electrical properties. The highest piezoelectric coefficient $|d_{33}| = 19 \text{ pC/N}$ is obtained for films processed by screen-printing, the piezoelectric coefficient being stable over more than six weeks. The corresponding PVDF-TrFE films were applied in the development of a touch screen by additive manufacturing, with two screen-printed silver electrodes in the form of an array of touch buttons. The all-printed piezoelectric touch-screen allows easy fabrication, therefore, improved integration into a variety of substrates, including flexible ones.

This chapter is based on the following publication: J. Serrado Nunes, et al., submitted in 2019.

4.1. Introduction

Considering the rapid technological advances and the need for low cost, simple processing and large area applications, additive manufacturing technologies are becoming increasingly interesting for applications including sensors, light-emitting devices, flat panel displays, solar cells, and batteries, among others [1-3]. These applications require materials with specific properties, being piezoelectric materials particularly relevant for sensor and actuator applications [4, 5].

The most suitable piezoelectric polymer for sensor and actuator applications is poly (vinylidene fluoride) (PVDF) and its co-polymers due to their high piezoelectric d_{33} coefficient, ranging from -18 to -32 pC/N and high dielectric constant ($\epsilon=7-12$) [6-8].

PVDF is a semi-crystalline polymer, exhibiting different crystalline phases, α , β , γ , δ and a morphology strongly dependent on the processing conditions (temperature and crystallization time), the β -phase exhibiting the largest piezoelectric properties [7-9].

PVDF shows a glass transition temperature, T_g , around -34 °C and a melting temperature, T_m , ranging between 165 °C and 189 °C, depending on the crystalline phase present in the polymer. The degree of crystallinity of the polymer depends on the processing method and can vary from 45% to 60% [7, 10, 11]. Within the PVDF co-polymers, poly(vinylidene fluoride-trifluoroethylene), PVDF-TrFE, is of particular interest in the context of printed electronics and additive manufacturing of sensors and actuators due to its high piezoelectric coefficient and, in particular, because at VDF/TrFE specific molar ratios, the polymer crystallizes in the polar phase, independently of the processing conditions [12].

P(VDF-TrFE) shows the ferro-paraelectric (FE-PE) transition (Curie Temperature, T_c) below the melting temperature, T_m , and for the molar ratio (VDF/TrFE) (75/25), the FE-PE transition is at a temperature of 140 °C on heating, and the PE-FE transition is at 75 °C on cooling. Further, the glass transition temperature, T_g , is around -26 °C and the melting temperature, T_m , at 147 °C [13-15].

Several processing techniques have been used for the preparation of PVDF-TrFE films including solvent casting [16], electrospinning [17], Langmuir–Blodgett [18], spin-coating [19] or screen-printing [20], among others. Piezoelectric PVDF-TrFE has been used for several applications, such as, medical ultrasound transducers [21], energy harvesting [22], MEMS resonators [23], battery separator [24], sensors and actuators [25] and tissue engineering applications [26].

Among the different possible applications, piezoelectric materials and, in particular, piezoelectric polymers presents excellent characteristics for the development of touch sensors due to their accuracy, sensitivity and ability to measure dynamic events, when compared to the capacitive sensors. Thus,

piezoelectric polymers PVDF and PVDF-TrFE are often used in this type of applications [27, 28], sometimes being processed by additive manufacturing technologies.

Flexible pressure sensors have been thus developed by screen-printing with PVDF-TrFE and their nanocomposite with multi-walled carbon nanotubes (MWCNTs), the active materials being sandwiched between printed metal electrodes in a parallel plate structure placed on polyimide (PI) and polyethylene terephthalate (PET) substrates [29]. The nanocomposite presents a uniform dispersion of conductive nanofillers within the matrix and excellent response as foldable pressure sensor [29].

Further, an active matrix sensor array was also developed based on PVDF-TrFE films with top and bottom conductive PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid)) polymer layer ink deposited on PET substrates. The piezoelectric d_{33} response of the polymer was 32 pC.N⁻¹ [30].

Only recently printable piezoelectric sensors based on a PVDF-TrFE polymer ink have been fabricated on flexible PET substrates, where silver was evaporated on the PET substrates to act as bottom electrodes and painted silver glue was used as the top electrode. These sensors show bending-mode sensitivity values up to 200 nCN⁻¹, which is 4 orders of magnitude larger than the force sensitivity in the normal direction [20].

Considering the state-of-art for printable piezoelectric pressure sensors, the goal of this work is the development of piezoelectric inks for different additive manufacturing technologies, including spray printing and screen-printing, as well as to fabricate an all-printed touchscreen to demonstrate the suitability of the approach. In the area of solvent-based additive manufacturing techniques, environmental issues are particularly relevant and, therefore, inks are prepared based on the green solvent N,NO-dimethylpropyleneurea (DMPU).

The most common solvent used in PVDF-TrFE solutions is N,N-dimethylformamide (DMF) which it is classified as hazardous, being its replacement by environmental friendlier and less hazardous solvents a priority [31].

4.2. Experimental

4.2.1. Materials

PVDF-TrFE (Solvane 250, VDF/TrFE = 70/30) was acquired from Solvay and N,N-dimethylformamide (DMF) and N,NO-dimethylpropyleneurea (DMPU) were obtained from Merck and LaborSpirit, respectively.

4.2.2. Ink preparation and processing of the films

The inks were prepared following the general guidelines presented in [32]. PVDF-TrFE copolymer concentration in solution ranging from 6 to 23 wt.% was dissolved in DMPU or DMF solvents at 30 °C (three hours under magnetic stirring) until a transparent and homogeneous solution was obtained. After the complete dissolution of PVDF-TrFE, different manufacturing techniques were used for film preparation, as schematically represented in Figure 4.1.

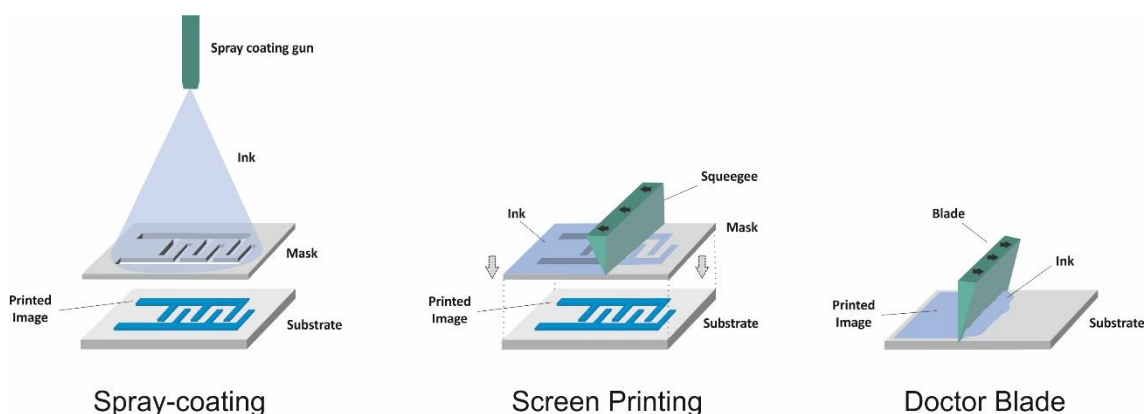


Figure 4.1. Schematic representation of the different techniques and procedures used for the preparation of the films. Notice that the mask was not used in the present work, as only non-patterned films were prepared.

As the result of a preliminary optimization study, the solution of PVDF-TrFE with weight fraction of 6 % was selected for spray-printing of the films on a clean glass substrate with a commercial airbrush (Airbrush Kit - Ventus), at a distance of 10 cm using an airbrush pressure of 3 psi.

Solutions of PVDF-TrFE with weight fractions of 17 % and 23 % were used for the preparation of the films by screen-printing by pressing the ink with a squeegee over the screen (polyester mesh with 62 monofilaments per cm) placed at a 10 mm distance of a clean glass substrate.

Finally, a solution with a weight fraction of 15 % of PVDF-TrFE was used for the preparation of the films by the doctor blade coating method. Note here that all films were prepared using solutions formulated with the green solvent DMPU. DMF based solutions were only prepared for comparison purposes with respect to the properties of the polymer solutions.

Independently of the processing technique used to prepare films, the DMPU solvent was evaporated at 230 °C in an air convection oven (Binder, ED23). Then, the PVDF-TrFE films were removed from the

oven and cooled down to 25 °C. The final thickness of the films was $\sim 30 \pm 5 \mu\text{m}$ for all printing techniques.

In order to optimize the piezoelectric response, the films were poled using the electrode poling method in a hot plate home-made chamber, after an optimization procedure, with an applied voltage of 1 MV/cm, poling time of 15 minutes and poling temperature of 120 °C [33].

In the following, the different prepared PVDF-TrFE films will be identified by the experimental technique by which they were produced.

4.2.3. Characterization techniques

The rheological behavior of the PVDF-TrFE polymer solutions was characterized at 25 °C using a stress-controlled rotational rheometer MCR-300 (Anton Paar, Austria) coupled to a Couette geometry. After loading the solutions, steady shear rates were ramped from 1500 s⁻¹ down to 10 s⁻¹ within 5 min, immediately followed by another ramp with steady shear rates from 10 s⁻¹ up to 1500 s⁻¹ also within 5 min. The viscosity data obtained from the two ramps nicely overlapped indicating that flow curves were obtained under steady-state conditions and that the polymer solutions showed no thixotropy under such experimental conditions.

The morphology of the PVDF-TrFE films was examined with a scanning electron microscope, Jeol JSM-5410, after the deposition of a 20 nm gold conductive layer by magnetron sputtering (Polaron SC502 apparatus).

The polymer phase of the films was determined by Fourier transformed infrared spectroscopy (FTIR), using a Spectrum 100 set up from Perkin-Elmer in ATR mode over a range of 650–1750 cm⁻¹ with a resolution of 4 cm⁻¹. 64 scans were performed in each sample.

Differential scanning calorimetry (DSC) analysis was carried out with a Mettler-Toledo DSC821e apparatus. Samples were placed in 40 μL aluminum pans with perforated lids to allow the release and removal of decomposition products and measurements were performed between 25 and 200 °C at a heating rate of 10 °C.min⁻¹ for cooling and heating under a flowing nitrogen atmosphere. Degree of crystallinity (ΔX_{cryst}) of the samples was calculated after equation 4.1:

$$\Delta X_C = \frac{\Delta H_f}{\Delta H_{100}} \quad (4.1)$$

where ΔH_f is the measured melting enthalpy and ΔH_{100} is the melting enthalpy for a 100% crystalline sample (103.4 J.g⁻¹) [8].

The degradation temperature of the films was determined by thermogravimetric analysis (TGA) with PerkinElmer instrument, Pyris1TGA. The samples were transferred to open ceramic crucibles and analysed using a thermobalance operating between 40 and 800 °C at a heating rate of 10 °C.min⁻¹ under a nitrogen flow of 50 mL/min.

Dielectric measurements were performed using a Quadtech 1920 LCR precision meter. The capacity of the samples and the dielectric losses were measured at room temperature in the frequency range of 20 Hz to 1 MHz with an applied voltage of 0.5 V in samples in the geometry of a parallel plate capacitor. Circular gold electrodes of 5 mm diameter were deposited by magnetron sputtering with as Polaron SC502 apparatus. The dielectric constant was then obtained taking into consideration the geometrical characteristics of the samples.

The piezoelectric d_{33} coefficient was measured in the poled samples with an APC YE2730A d_{33} meter.

4.2.4. Piezoelectric touchscreen prototype fabrication

A multi-touch detection 2 × 3 sensors matrix was designed in which each sensor was individually connected to the readout electronic system to reduce cross-talking between sensors. Figure 4.2 a) shows a schematic representation of the implemented layout, comprising the screen-printed piezoelectric film and electrodes on both surfaces of the film. The electrodes were screen-printed using a silver nanoparticle ink (Novacentrix HPS-021LV). The PVDF-TrFE film with 23 wt.% was used for this prototype, which was 30 µm thick and the printing method resulted in conductive layers with an average thickness of 12 µm in each side.

After printing the electrodes, the film was heated up to 80 °C for an hour to cure the ink. Then, an insulating adhesive coating was applied as protection, and the connector incorporated into the printed connection lines (Amphenol FCI 65801-012LF). The final result is a thin and elastic enough touchscreen that keeps the functional properties even when the film is bent (Figure 4.2 b).

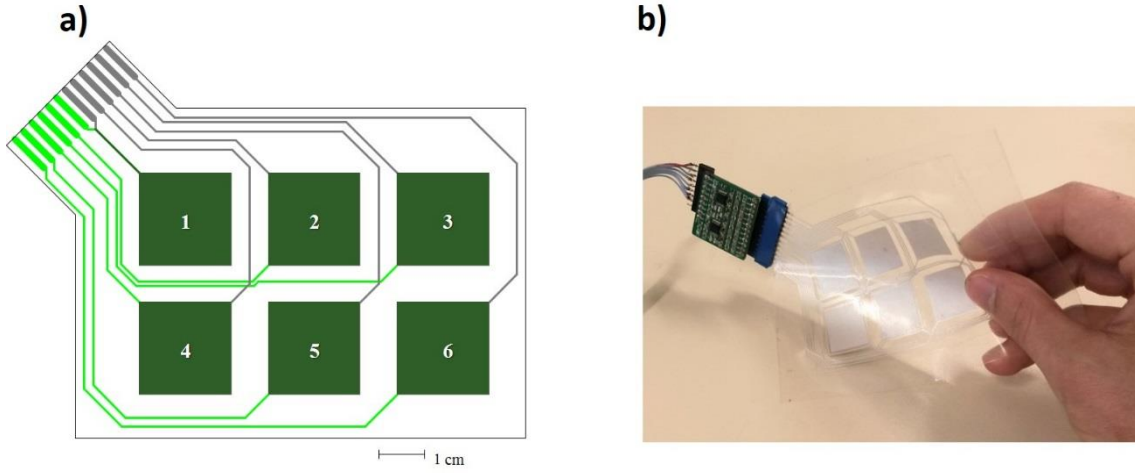


Figure 4.2. a) Layout of the all printed touchscreen comprising a 30 μm thick PVDF-TrFE film and six silver paint printed electrodes (grey – top; light green – bottom; dark green – top and bottom). b) Photograph of the piezoelectric touchscreen.

The resistance of the electrodes plus connecting wires was $< 24 \Omega$ for each sensor, while the capacitance is between 600 to 640 pF, corresponding to a saturation frequency of 10.4 MHz in the worst-case scenario. Electrical measurements were performed with a Fluke 117 multimeter. For the readout electronics, a charge amplifier was used to convert the electrical signal generated by the piezoelectric sensors and a digital acquisition system was implemented based on the ADC (analog-to-digital converter) of the microcontroller Microchip ATmega328P @ 8 MHz. The data was sent to a computer via UART (universal asynchronous receiver-transmitter) serial port, where a Java graphical application displayed the data. The ADC used 8 bits at a rate of 7.3 kS/s. The baud rate of the serial communication was 115,200 bit/s.

4.2.5. Equivalent circuit of the sensors

The displaced charge in the piezoelectric sensors does not depend on the area of the electrodes nor the thickness of the film for a certain amount of force. However, larger electrodes represent the difficulty in uniform deformations along the electrodes. In fact, in the printed piezoelectric PVDF-TrFE films, the coefficient d_{33} correlates the displaced electrical charge Q_p (in C) with the applied force F (in N) by:

$$Q_p = d_{33} \cdot F \quad (4.2)$$

Therefore, the displaced charge Q_p can be represented by a charge source, instead of a voltage source or a current source. As shown in Figure 4.3 – where the subscript p indicates the piezoelectric element –, the electrodes contribute with a capacitance C_p (in F) and a resistance R_p (in Ω) which influences the maximum voltage and current.

The current I_p (in A) that flows through the circuit, given by the derivative of Q_p over time t (in s):

$$I_p = \frac{dQ_p}{dt} \quad (4.3)$$

allows representing the charge source as a current source.

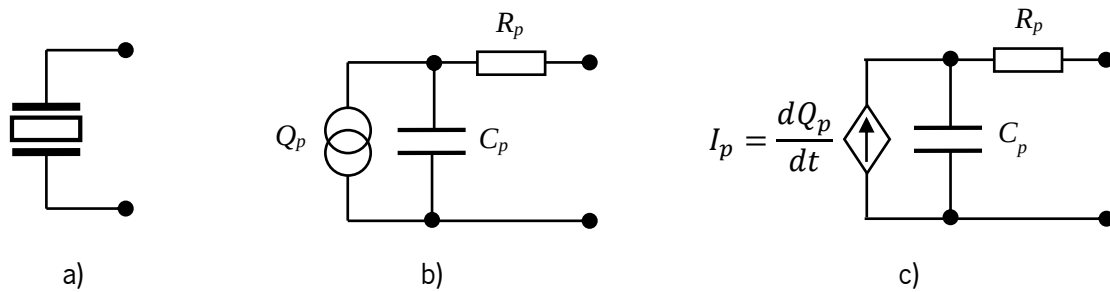


Figure 4.3. Equivalent model of a piezoelectric sensor: a) generic piezoelectric component; b) considering the capacitance and resistance of the electrodes; c) charge source represented by a controlled current source.

Together, R_p and C_p create a low-pass filter (LPF) and the resulting transfer function of the sensor in Laplace's domain (for Fourier transform use $s = j\omega$) $H_p(s)$ is:

$$H_p(s) = \frac{Q_{out}(s)}{Q_p(s)} = \frac{1}{\frac{s}{\omega_p} + 1}, \quad \omega_p = \frac{1}{C_p R_p} \quad (4.4)$$

where $Q_p(s)$ and $Q_{out}(s)$ are the total charge displacement in the piezoelectric element and its actual output, respectively; s is the complex Laplace's domain, and ω_p the cut-off angular frequency (in rad/s) of the LPF.

4.3. Results and discussion

4.3.1. Rheological characterization

Figure 4.4 a) shows the flow curves of two sets of PVDF-TrFE solutions produced with different concentrations of polymer dissolved in DMPU or DMF. As concentration increases, solution viscosity increases and evolves from a Newtonian solution to a shear thinning solution.

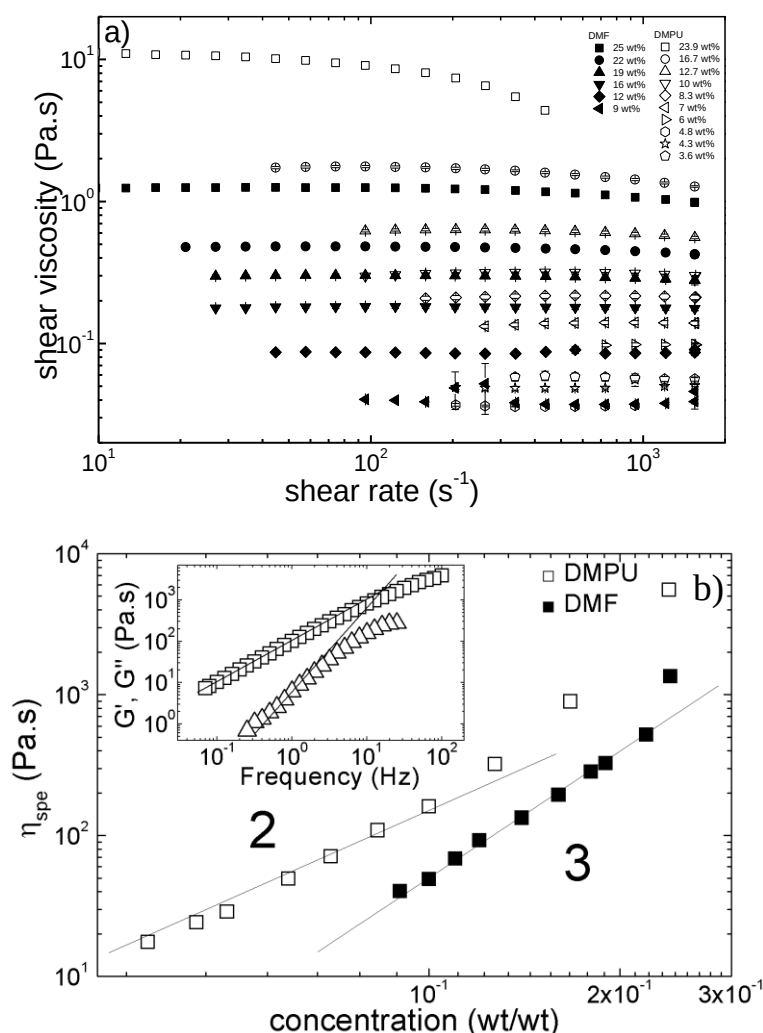


Figure 4.4. a) Flow curves of PVDF-TrFE solutions dissolved at different concentrations in DMPU (open symbols) and DMF (solid symbols). b) Concentration dependence of the specific viscosity of DMPU based solutions (open symbols) and DMF based solutions (solid symbols). Lines and numbers indicate slopes. Inset: mechanical spectrum (storage modulus G' : triangles; loss modulus G'' : squares) for a 23.9 wt.% PVDF-TrFE solution in DMPU. Lines in the inset highlight the terminal regime with slopes of 1 and 2 for G'' and G' respectively.

Overall, solutions based on DMPU are more viscous than those based on DMF. This is expected since DMPU viscosity is roughly twice that of DMF. Figure 4b reports the concentration dependence of the specific viscosities of the solutions $\eta_{spe} = \frac{\eta_0 - \eta_s}{\eta_s}$, where η_s is the solvent Newtonian viscosity and η_0 the Newtonian viscosity of the solution (extracted from the plateau in the viscosity data recorded at lower shear rates). This plot allows the evaluation of the effect of the polymer in the viscosity of the solutions as the solvent contribution is subtracted. A power law behavior with an exponent of 2 is obtained for DMPU based solutions at lower polymer concentrations. This scaling behavior is reminiscent of semi-dilute and non-entangled solutions of polymers in theta solvent [34, 35] (a solution with no polymer-solvent interactions). At the largest concentration tested, a departure from this scaling behavior is evident, suggesting the onset of additional polymer-polymer interactions. These interactions are at the origin of the pronounced shear thinning taking place at larger shear rates. Considering that the typical shear rate associated with doctor blade and screen printing processes is of the order of 100 s^{-1} , the rheological data in Figure 4.4 a) indicate that flow-induced orientation of polymer chains occurs during the screen printing of the 23 wt.% PVDF-TrFE solution, whereas it is not the case for the remaining solutions with smaller polymer concentrations. The mechanical spectrum measured at the largest evaluated concentration does not reveal any crossover between G' and G'' (see inset to Figure 4.4 b). This confirms that all polymer solutions used to prepare the films belong to the semi-dilute and non-entangled regime. Furthermore, the mechanical spectrum shows that the longest relaxation process is of the order of 0.05 s. As such, flow-induced orientation occurring during the screen printing of the 23 wt.% solution is surely lost before solvent evaporation in the oven. Rheological data measured with DMF based solutions are essentially qualitatively different from those assessed with DMPU based solutions, as smaller specific viscosities and a power law behavior with exponent 3 for the concentration dependence are measured. The latter is the hallmark of non-dilute isotropic solutions of rod-like Brownian particles and polymers [36]. Overall, the different concentration scaling in DMPU and DMF shows that PVDF-TrFE adopts a different chain conformation from coil-like (in DMPU) to rod-like (in DMF) due to significant differences in polymer-solvent interactions.

4.3.2. Morphological, polymer phase and thermal properties

Different manufacturing techniques were successfully applied to obtain PVDF-TrFE films for printable piezoelectric sensor applications (Figure 4.5). Typically, the microstructure of the PVDF-TrFE films is determined by the crystallization temperature during film formation [37] and the SEM images for PVDF-

TrFE obtained for the films obtained by spray printing and screen printing with 23 wt.% are shown in Figure 5 a-b), respectively. For other doctor blade technique, the microstructure is similar to that observed in Figure 4.5 b).

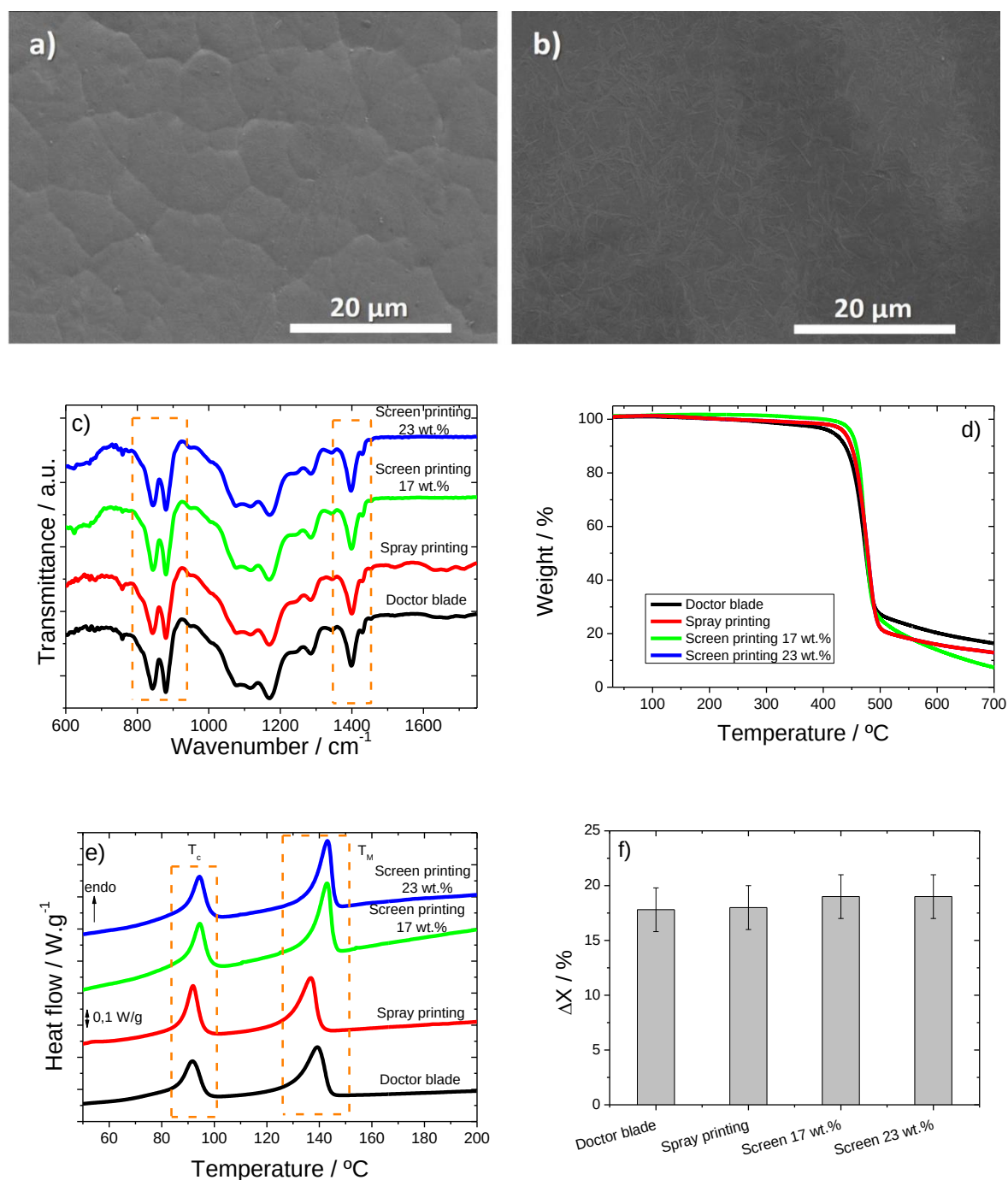


Figure 4.5. Surface SEM images of PVDF-TrFE obtained by a) spray printing and b) screen printing with 23 wt.%. c) FTIR spectra, d) TGA plots, e) DSC heating scans and f) degree of crystallinity for the PVDF-TrFE films produced by different techniques.

For all fabrication techniques, the films were processed by heating to and cooling from 230 °C, above the melting temperature, which improves solvent evaporation and polymer diffusion due to high polymer chain mobility, which results in polymer crystallization into a compact film morphology (Figure 4.5 a).

The morphology of the PVDF-TrFE films is either spherulitic (Figure 4.5 a), for spray printing) or rod/fiber like (Figures 5 b), for doctor blade and screen printing), which are typical microstructures observed from PVDF-TrFE polymer [37].

For the films processed by screen printing (Figure 4.5 b), the presence of ellipsoidal fibers (edge-on lamellae grains) is observed, their size increasing with increasing polymer concentration [38].

The dense films observed in Figure 4.5 a-b), with compact morphology and the absence of voids or defects show that all production techniques can be used to obtain the PVDF-TrFE films suitable for piezoelectric sensor applications, allowing the suitable poling of the films.

Fourier transform infrared spectroscopy (FTIR) was used to identify the polymer phase of the PVDF-TrFE polymer and Figure 4.5 c) shows the FTIR spectra between 1750 at 600 cm^{-1} for the different films obtained through the different processing techniques.

All films show (Figure 4.5 c) the main absorption bands at 840, 880 and 1402 cm^{-1} of the PVDF-TrFE polymer corresponding to the CF_2 rocking or CF_2 symmetric stretching and CH_2 wagging, respectively [39] that are characteristic of the electroactive β -phase [8]. Thus, the processing technique does not affect the vibration bands and therefore the crystallization polymer phase of PVDF-TrFE, which is mainly determined by the copolymer composition and crystallization conditions, which are the same for all films.

The thermal properties of the PVDF-TrFE films were evaluated in heating scans by TGA (Figure 4.5 d) and DSC, from which the degree of crystallinity (Figures 4.5 e-f) was obtained. The TGA characteristic curves for the different PVDF-TrFE films are presented in Figure 4.5 d, showing that, independently of the processing technique, the degradation behavior of PVDF-TrFE occurs in a single step with degradation temperature around 466 °C due to the scission of carbon-hydrogen (C-H) bond [40]. A residual weight at 700 °C for PVDF-TrFE polymer is also observed.

Figure 4.5 e) shows the heating DSC thermograms for the PVDF-TrFE films where two endothermic peaks are observed independently of the processing techniques. The lower temperature peak, around 93 °C, corresponds to the FE-PE transition (Curie transition) and the higher temperature peak, at 137-143 °C, corresponds to the melting temperature of the PE phase [39]. It is observed that the different processing techniques do not affect the thermal behavior of PVDF-TrFE films as well as the degree of crystallinity value ($\sim 18\%$) as shown in figure 4.5 f) [39].

4.3.3. Dielectric and piezoelectric properties

The evaluation of the dielectric behavior, including dielectric constant, ϵ' , (Figure 4.6 a) and $\tan \delta$ (Figure 4.6 b) and piezoelectric coefficient (Figure 4.6 c-d) is essential for sensor applications.

Figure 4.6 a) shows the variation of ϵ' for the PVDF-TrFE films produced with different processing techniques as a function of frequency at room temperature. For the doctor blade technique, the dielectric behavior is similar to the one observed for screen printing.

For all PVDF-TrFE films, it is observed that ϵ' decreases with increasing frequency in a similar way. This behavior is related mainly to the cooperative relaxation of the orientational movement of the dipoles with strong contributions from the crystalline-amorphous interphases [41, 42].

Further, it is also observed that the dielectric constant ϵ' (Figure 4.6 a) is similar for all samples, independently of the processing technique.

Also, the $\tan \delta$ decreases as the frequency increases for all samples due to d.c. conductivity contribution [43], being this behavior also independent of the processing technique. The $\tan \delta$ is higher at low frequencies due to the semicrystalline nature of the polymer, leading to interfacial polarization contributions [44].

The piezoelectric d_{33} response was evaluated for the different printed samples immediately after sample poling and as a function of time, as represented in Figure 4.6 c-d.

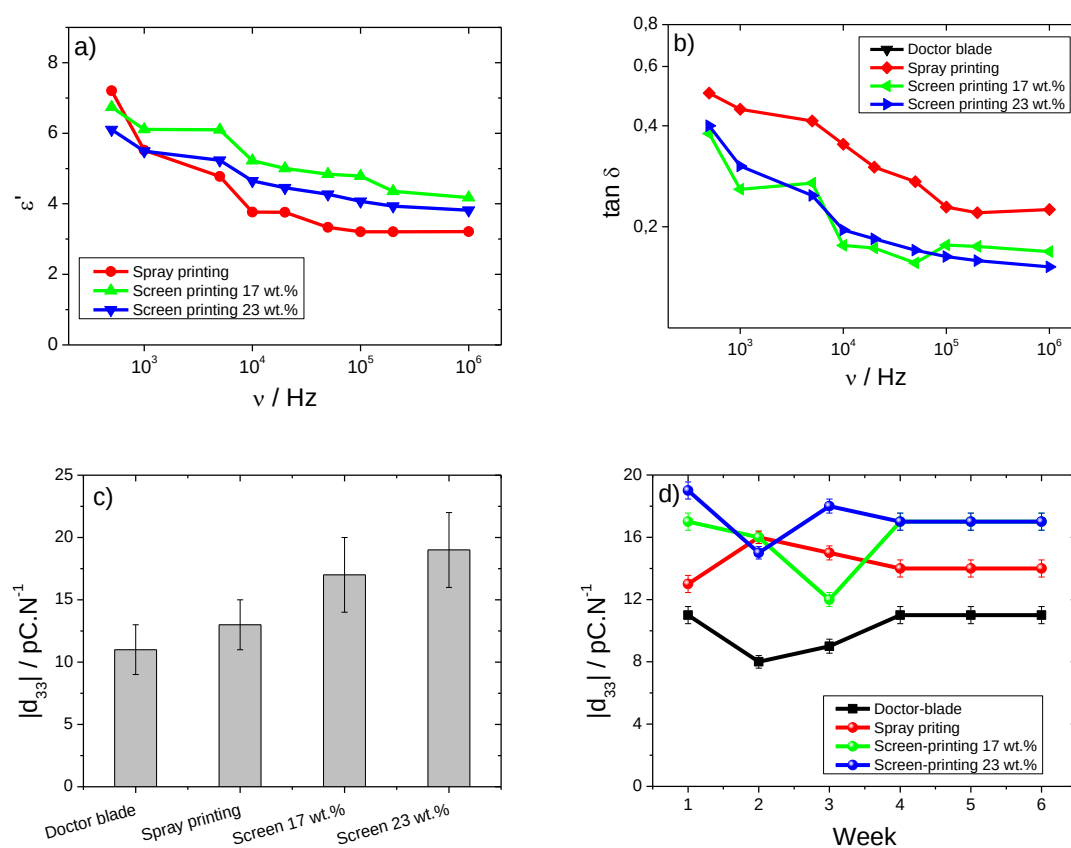


Figure 4.6. a) Dielectric constant and b) $\tan \delta$ as a function of frequency and c-d) piezoelectric coefficient immediately after polarization and as a function of time, respectively, for the different PVDF-TrFE printed films.

It is observed that the piezoelectric d_{33} coefficient is slightly different for all processing techniques but its value is similar to those reported in the literature [45], the higher d_{33} coefficient being obtained for the screen-printed samples, basically attributed to the slight variations in electrical properties and morphological features among the different samples. Figure 4.6 d) shows that the piezoelectric d_{33} coefficient is stable over time independently of the printing technique, showing the suitability of this material for applications. Thus, it is demonstrated that suitable inks for screen and spray printing can be prepared based on a green solvent (DMPU) and that the electroactive response is suitable for sensor and actuator applications.

4.3.4. Pressure sensing properties

The PVDF-TrFE film with 23 wt.% produced by screen printing was used for the development of the all-printed piezoelectric touchscreen prototype, with screen-printed silver ink electrodes, printed as indicated in the experimental section.

The sensors were tested for fingertip touch together with the readout electronic circuit based on a charge amplifier with a band-pass filter (BPF), with a passing band from 5 to 10 Hz, capable of detecting finger touch signals and, at the same time, rejecting the 50/60 Hz grid and the low-frequency electrostatic noises. The output of the circuit was evaluated in terms of noise and in press/release signal events.

4.3.5. Touch detection

The developed piezoelectric touchpad was evaluated for fingertip touch. The human body is a source of electromagnetic noise due to its conductive properties, and since the developed circuit uses single-ended topology, it is important, when possible, to arrange the film in a way that the user touches the sensors on the side of the electrodes connected to $V_{cc}/2$, so that the electrode itself acts as shielding for the finger. In case of not being possible, a differential-signaling input should be used.

Figure 4.7a) shows the output voltage V_{out} of the amplifying circuit when sensor 3 is pressed and then released. The signal averages on 2.5 V as expected and develops a negative peak when being pressed, and then a positive peak when released.

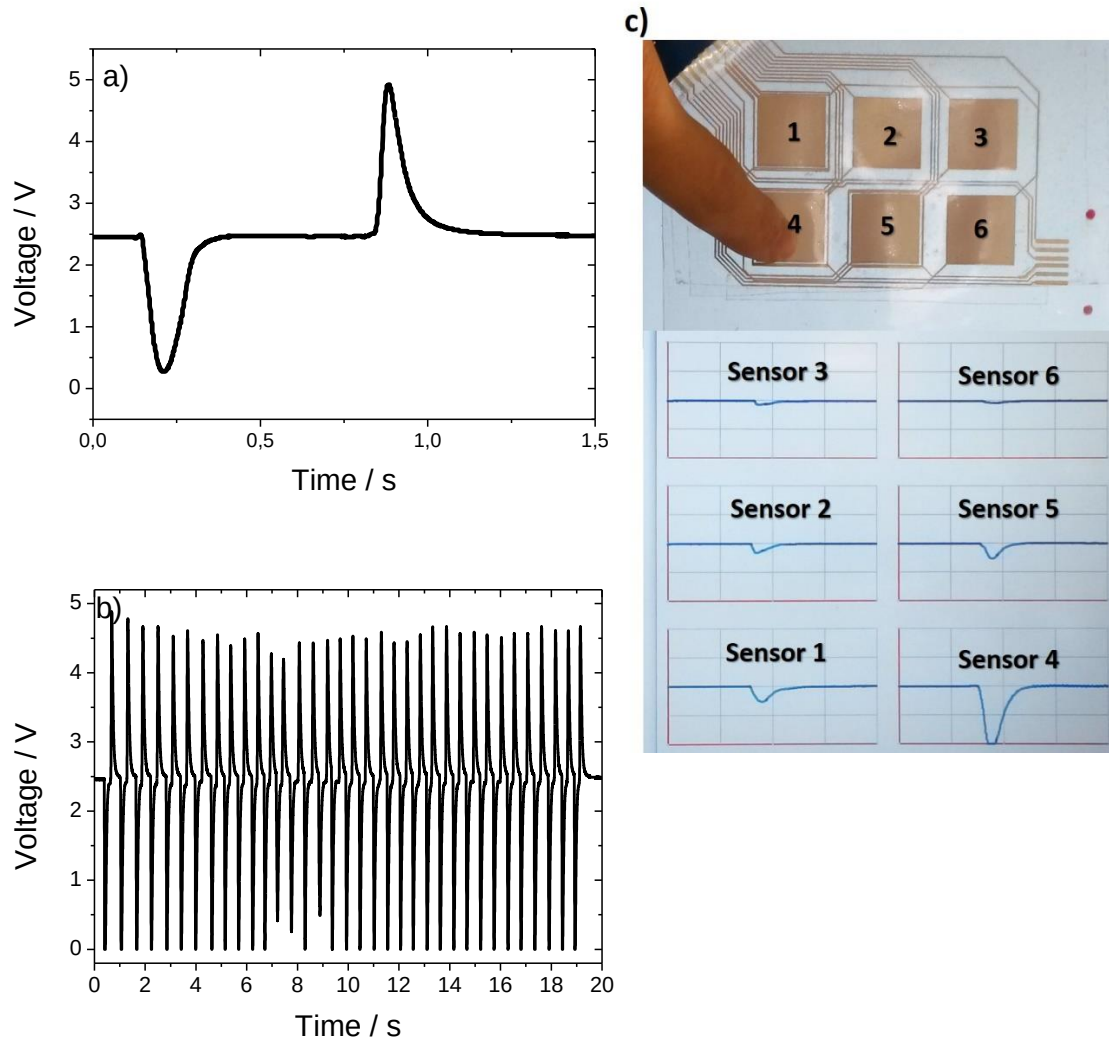


Figure 4.7. a) Touchpad response upon finger pressing and release, b) piezoelectric sensor under cycling a pressing and releasing events and c) sensor matrix on touch event in one of the sensors and corresponding signals for each sensor. See also the supplementary video.

The output signal is almost noise-free due to the BPF implemented with a narrow passing frequency.

To verify the stability of the signal, Figure 4.7 b) shows one of the sensors being continuously pressed and released. The same behavior is observed for other sensors.

It is observed in Figures 4.7 c) the existence of cross-talking, which is explained due to film vibration when sensor 4 is touched. Nonetheless, it is possible to reduce this error by comparison of the various sensors with their peak value (see supplementary video).

Thus, figure 4.8 shows that the piezoelectric sensors present an excellent response without hysteresis and that, therefore, the developed inks can be applied for the development of touch panels produced by additive manufacturing techniques.

4.4. Conclusions

Piezoelectric films of poly(vinylidene fluoride-co-trifluoroethylene), PVDF-TrFE, were prepared by different additive manufacturing techniques, including, doctor blade, spray-printing and screen-printing for touch-screen application.

A green solvent N,N0-dimethylpropyleneurea (DMPU) was used and the rheological properties demonstrate that this is a good solvent for PVDF-TrFE. Regardless of the printing technique, dense films were obtained with suitable morphology, polymer phase, thermal and electrical properties for piezoelectric sensing applications.

Screen-printing was used to prepare piezoelectric films that, after poling, showed a piezoelectric coefficient of $|d_{33}| = 19 \text{ pC/N}$, showing suitable performance as touchpad with screen-printed silver electrodes, allowing to detect both touch and release events in the piezoelectric film with low cross talk due to the implemented sensor geometry and electronic readout systems based on charge amplifier with a band-pass filter (BPF).

It was observed cross-talking in the sensors due to film vibration on finger touch, however, it is possible to determine which sensor was stimulated by peak signal comparison.

Thus, it is concluded that the all-printed piezoelectric touch-screen developed in this work is promising for applications in printed electronics for a new generation of touch panels produced by additive manufacturing techniques, taking also into account the environmental issues with respect to ink formulation.

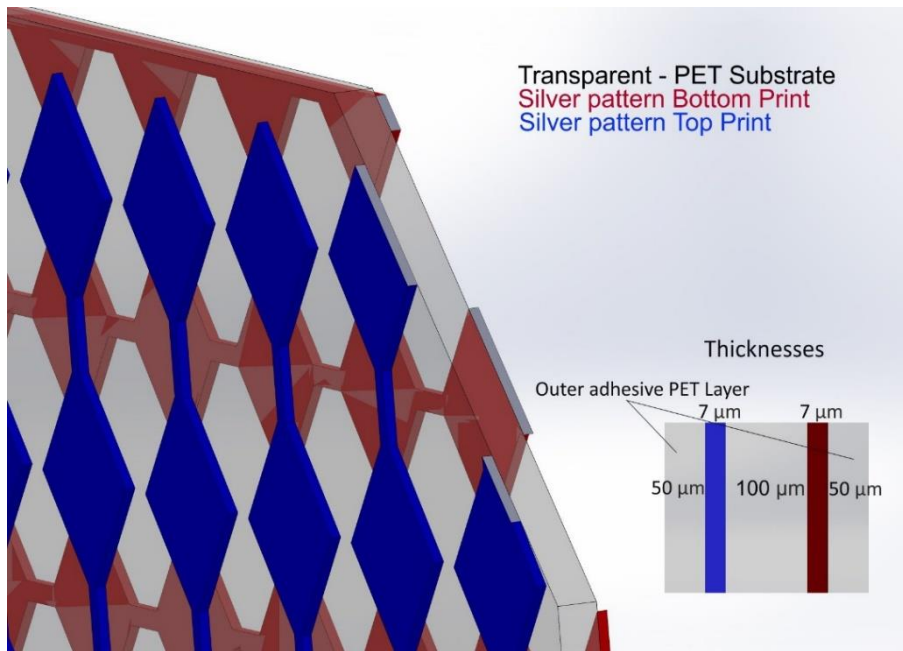
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5. Marked Object Recognition Multitouch Screen Printed Touchpad for Interactive Applications

In this work, a flexible screen printed sensor matrix is fabricated based on silver ink in a polyethylene terephthalate (PET) substrate. Diamond shaped capacitive electrodes coupled with conventional capacitive reading electronics enables fabrication of a highly functional capacitive touchpad, and also allows for the identification of marked objects.

This chapter is based on the following publication: J. Serrado Nunes, et al., Marked Object Recognition Multitouch Screen Printed Touchpad for Interactive Applications; Sensors 2017, 17(12), 2786.

5.1. Introduction

Innovations in the areas of materials development and production are strongly affecting information and communication technologies, with a strong impact in a large variety of human activities, ranging from industrial processes to entertainment. Ubiquitous computation paradigms, tangible user interfaces, and physical computation have been playing an increasing role in the human–computer interaction field, giving rise to a new perspective of the fusion between computer and materials [1].

Circuit printing methods and sensitive electronics are enabling materials and digital technology to work together as complementing parts of novel devices, allowing to present information in a large variety of forms, colours, and textures [2–4] and at the same time allowing for the development of a new generation of sensors and actuators.

In this context, the touch sensors market and applications have experienced a strong growth mostly based on capacitive technologies, since the iPhone® had its debut back in 2007 [5, 6].

The projected capacitive technology can be implemented through two reading methods: the self-capacitance method and the mutual-capacitance. The self-capacitance consists in analysing the capacitance of the electrodes to ground, when a finger is placed close together to the electrode. This allows the detection of just two fingers, though the hardware is of lower cost. On the other hand, the mutual-capacitance is a more robust method based on the mutual capacitance between two electrodes, where one electrode acts as a driver and the other one acts as a sensor. This method allows the detection of several touches, though it implies higher hardware costs. In both methods, the matrix of electrodes is scanned at high frequency [6, 7]. Capacitive touch technology and market share is covered quite well in the literature [6, 7].

Capacitive surfaces are composed by a dielectric substrate such as glass, acrylic, or polyester, and a coating based on a conductive transparent material. Indium tin oxide (ITO) conductive coating is the most used material in order to achieve the required conductivity and transparency, but the ITO deposition technology is not cost efficient [8, 9], paving the way for replacement by printed technology solutions.

Together with transparent capacitive touch surfaces for big monitors, smartphones, and tablets, there is an increasing demand of opaque capacitive applications as well, such as keyboards [10], touchpads [11], position tracking surfaces [12, 13], proximity buttons [14], and pen-shaped haptic devices [15].

Other applications that do not require transparency, such as humidity sensors, can also use capacitance variations to measure physical variables. These sensors can be produced by printing conductive ink over a polymer substrate [16, 17].

The scientific and technological communities are addressing polymer-based sensors and sensor matrices for an increasing number of applications, as they are characterized by a cost-effective production based on additive manufacturing, being able to be produced on large scale [18, 19]. Presenting further advantages, printing electronic components on plastic substrates offers devices the potential of being thin, foldable/rollable, lightweight, and wearable [20]. Thus, there is a growing trend on the development of polymers and polymer composites for the development of new devices [21–23].

In this work, we present a method for producing an opaque projected capacitive touch surface, based on the mutual-capacitance method, with the corresponding readout electronics and software data treatment. Using a screen printing method and silver ink, a Melinex® substrate, and an adhesive PET encapsulation, a functional capacitive surface was fabricated. This surface also incorporates an object recognition module and multi-functional touch input for smart books or smart surface applications, among others. These functionalities enhance multimedia interaction content for development purposes and demonstrate the important possibilities offered by polymer-based materials for a new generation of low-cost capacitive touchscreens.

5.2. Experimental

5.2.1. Printed Geometry

Capacitive sensors may have many different geometries, each with advantages and disadvantages as it is explored in [24]. In the present work, the selected geometry is based on a diamond pattern, which is one of the most commonly used. In such a pattern, the capacitors are spread over two layers and arranged in a diamond-like structure [9, 25, 26]. The dielectric material is between rows and columns, thus providing a capacitance between each intersection, providing the possibility to determine the touch location when the capacitance changes with the approximation of any surface with enough conductivity, such as skin. Figure 5.1 shows the geometries used for the development of the touchpad with an area of 102 x 67 mm², and the corresponding layers.

Every capacitive square in the electrodes has an area of 16 mm^2 except on the borders, which are 8 mm^2 triangles, and the corners with an area of 4 mm^2 . With this resolution, it is possible to detect human fingertip size conductive objects. A similar size matrix with higher resolution would require a capacitive controller with a higher number of channels than the one used in the present work. Lowering the resolution could still be suitable to detect larger conductive areas like hands or feet. For non-transparent printed touchpads, conductive silver ink is a suitable choice, as it can be simply cured in a normal oven at a constant temperature, without temperature curve requirements or special treatments. In this work, the selected silver ink was HPS-21LV from Novacentrix® (Austin, TX, USA), which was cured at 120°C in a P Selecta oven model 2005165 for 30 min. The used substrate was Melinex® (Lohmann Technologies UK Ltd., Milton Keynes, UK), which is a PET sheet with an ink adhesion treatment for improved printing process.

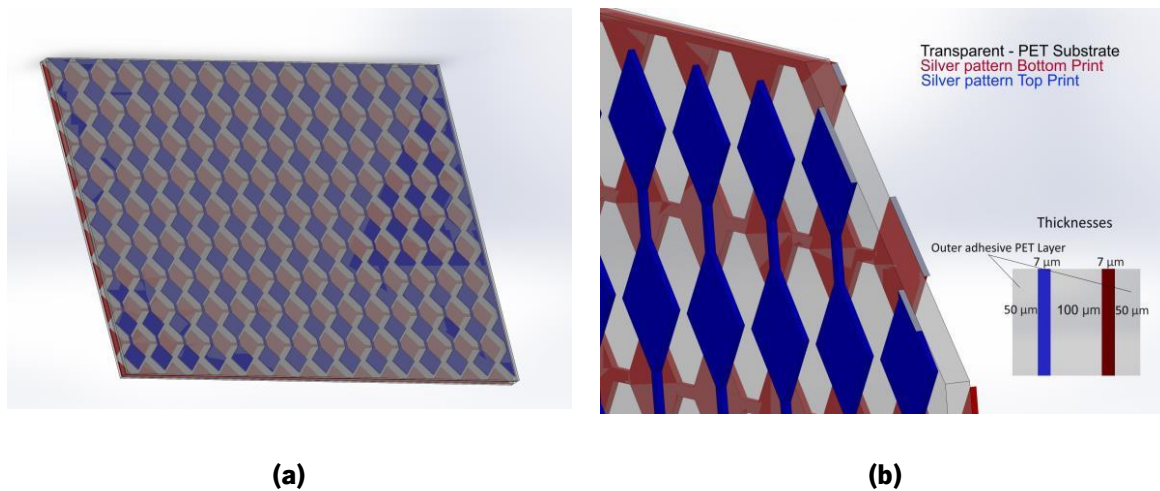


Figure 5.1. Illustration of the capacitive matrix silver electrodes geometry: (a) diamond electrodes pattern front view; (b) diamond electrodes pattern perspective view.

5.2.2. Capacitive Detection Circuit

The capacitive variation between the intersections on the matrix can be detected by amplitude [27, 28] or frequency [29, 30] analysis, methods that can be used to detect single point-to-point variations. However, for a matrix of capacitive sensors, a multiplexing method for rows and columns would be needed in order to sample each intersection. Using a commercial controller, this requirement is bypassed with the high number of reading channels. The capacitive controller used was the IQS550 from Azoteq Ltd.

(Paarl, South Africa). According to manufacturer instructions, the complete interface circuit was designed as presented in Figure 5.2 b), to obtain the touch locations of the trackpad. The digital data provided by the controller is sent through a firmware communication via I2C (Inter-Integrated Circuit) to the microcontroller dsPIC33FJ128GP804, from Microchip Technology Inc. (Chandler, ZA, USA).

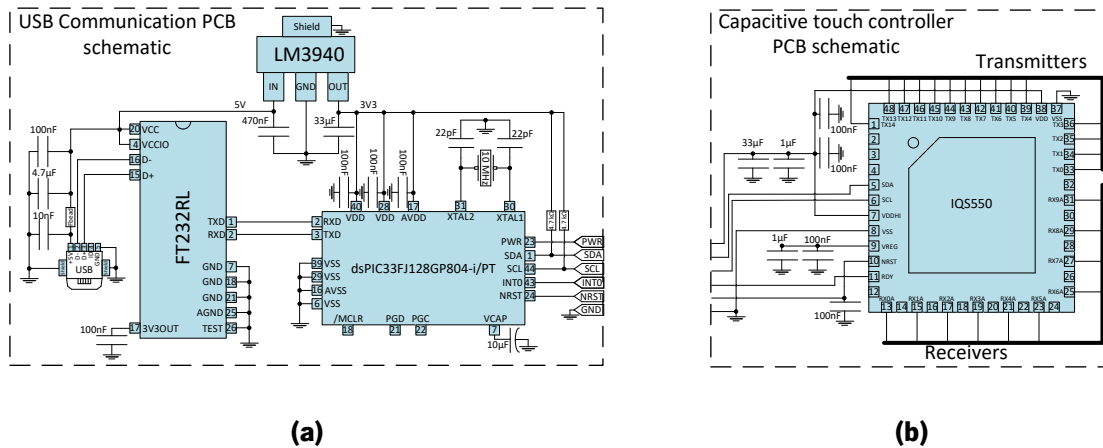


Figure 5.2. Schematic representation of the hardware: Communication PCB as I2C-USB converter (a) and capacitive controller instrumentation circuit (b).

In order to transmit the data from the IQS550, another Printed Circuit Board (PCB) was built to serve as interface to a USB terminal (Figure 5.2 a)). For a direct USB communication, a FT232RL from Future Technology Devices International Ltd. (Glasgow, UK) was used, trading data with the microcontroller through a UART (Universal Asynchronous Receiver/Transmitter) connection.

5.2.3. Touchpad Fabrication

The printing method was performed by screen printing with a polyester mesh with 62/64 wires.

First, the matrix was printed in one side of the polymer (top print) and dried out at room temperature for 6 h. Then, the bottom side of the polymer was printed with the aid of aligning points. The completed matrix was cured then for 30 min at 120 °C in order to evaporate the solvent. The top layer print was not immediately cured in order to avoid mechanical shrinkage or deformation of the substrate, which would highly affect the alignment when printing the bottom layer pattern. Further, an Amphenol FCI connector was used for the electrical connection, and an adhesive PET layer was applied on each side of the film

to protect the circuits from corrosion and oxidation, as well as to serve as an isolating layer between the printed circuit and the fingers. The FCI connector to the printed matrix contacts were fabricated by pressure sealing. The connectors perforate the PET substrate and keep a tight connection between the flexible silver traces and rigid tin. The complete system process is summarized in the diagram of the Figure 5.3 a). The matrix was then connected to the capacitive controller board (schematic representation in Figure 5.2 b). The final printed touchpad connected to the PCB is shown in Figure 5.3 b). It is worth noting that the final surface is a $\sim 220\ \mu\text{m}$ thick plastic sheet, so it is a flexible structure to fit in any rigid plane or rounded surface.

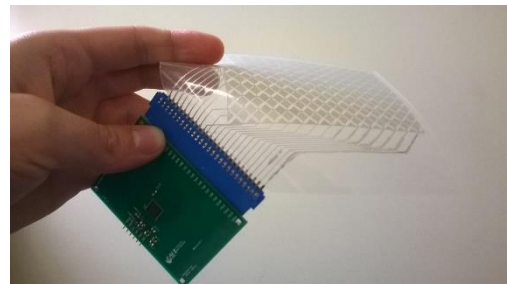
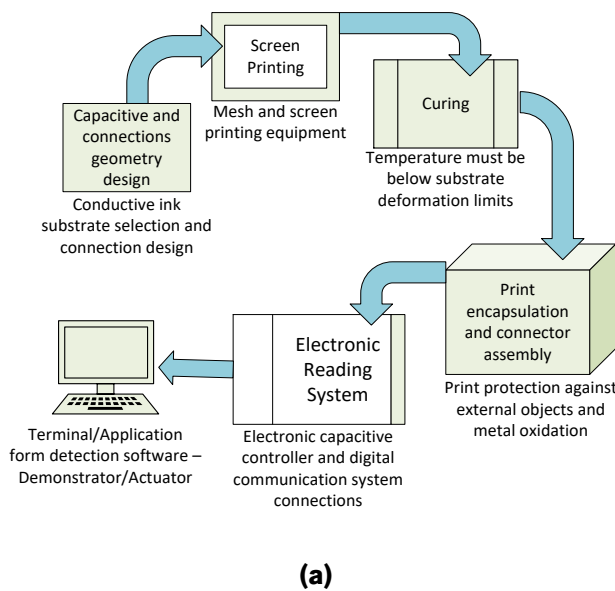


Figure 5.3. Process fabrication flow diagram (a) and printed capacitive matrix connected to the PCB with the capacitive touch controller IC (b).

5.3. Results and discussion

The system performance was first evaluated in the application provided by Azoteq with a CT210 programmer. Thus, it was possible to obtain all the applied signal delays in each intersection and calibrate the sensitivity, approximation threshold, and balance of the capacitive intersections. A header file is generated in order to apply at the IQS550 at system start. The matrix calibration was achieved through a process of trial and error in order to get touch stability and precision.

The surface displayed a suitable response to finger touch, though it was greatly improved with a glass overlay when fixed to a table in a flat disposition (Figure 5.4 a). Removing the glass and folding the

surface while fixing to the edge of a table still allowed the detection of the finger touch, demonstrating the flexibility of the touchpad (Figure 5.4 b). Applying a covering glass as an extra overlay gives the system improved mechanical and electrical stability, as fingers cannot reach too close to the capacitors' dielectric film and will not saturate the sensors as easily. It will also provide more steadiness to the contacts, as the terminals are the most sensitive part of the system in terms of mechanical stability.

It worth noting that the use of a glass overlay requires a new software calibration, as the overall physical properties of the sensors are also changed. Any vibration, stretch, or deviation in the contact position can lead to variations of the electrical resistance of the rows and columns, affecting the signal response and unbalancing the capacitances along the matrix. Therefore, special attention must be paid to these connections. Figure 5.4 c) shows the capacitance distribution of the matrix with glass overlay with and without touch, based on the injected signal and circuit electrical resistance, revealing a fair distribution among the most part of the 150 channels with small deviations that are handled by the calibration software. The response time is 100 Hz for the 150 channels, though it decreases with every extra touch (a maximum of 5 going as low as 88 Hz). A fair capacitance drift of 40 pF between the extremes of the spectrum is observed, easily calibrated by software. A 30~50 pF variation can be found in the strongest points of the touch, providing good sensitivity for the controller to detect.

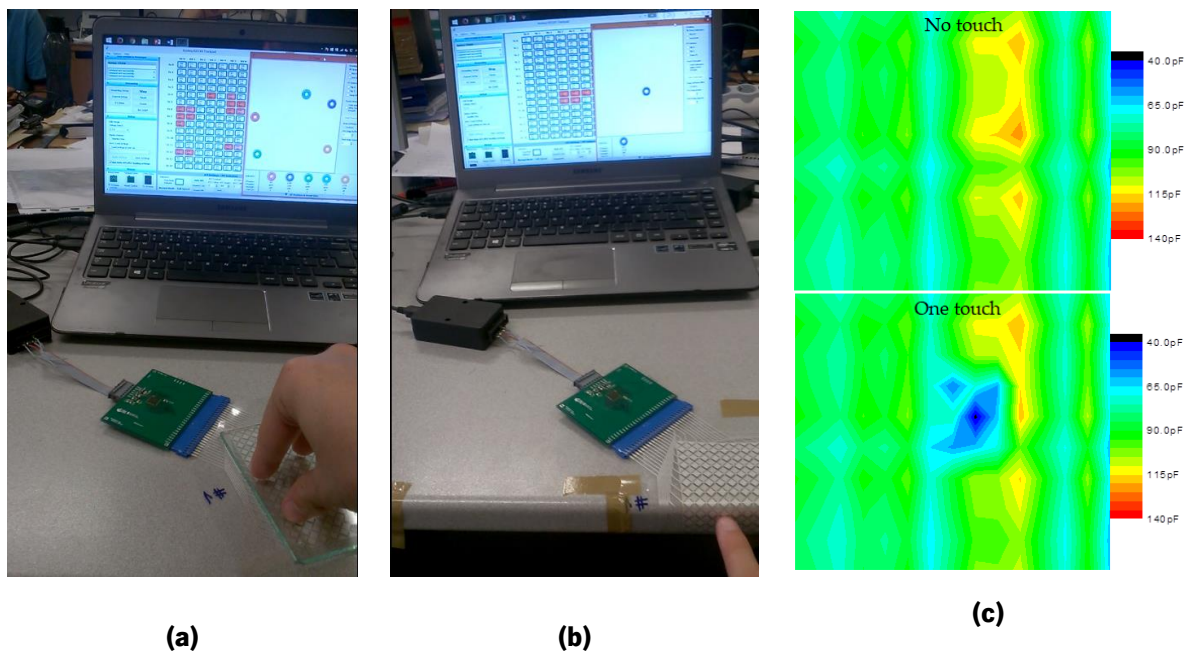
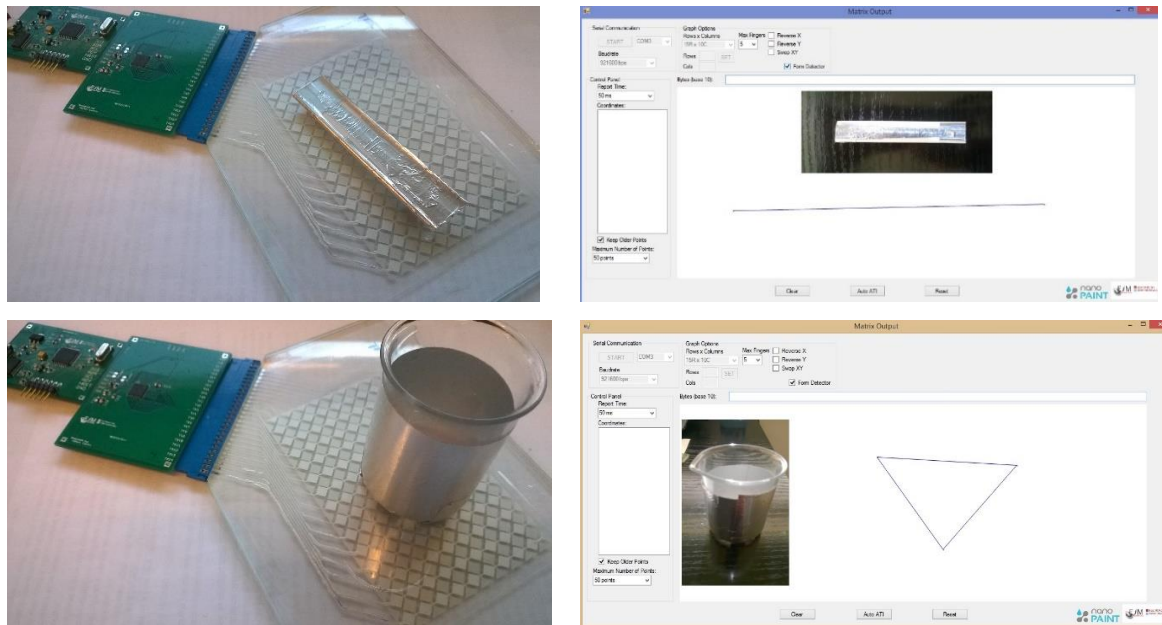


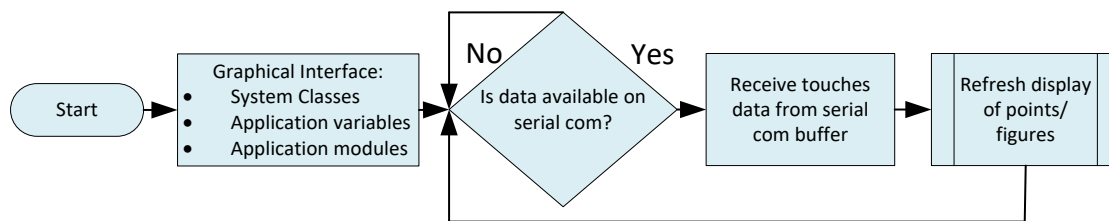
Figure 5.4. Test were performed with the CT210 programmer for the maximum of possible touches using a 5 mm thick glass as an overlay (a), folded surface finger detection (b) and capacitive distribution with glass overlay of the matrix with and without touch (c).

A C# application was developed in order to acquire the touch coordinates, using more than one touch position, such as touch identification and touch intensity. The IQS550 provided with 10 rows x 15 columns, a resolution of 2304 x 3584 points, converting into ~ 36 points/mm, allowing high precision and even the interpretation of the touch intensity, which is measured by the capacitive area triggered by finger expansion, as strength pressure. As for the reading process, the IC controller applies a high frequency signal in each column while grounding all the other columns (isolating a particular group of points between that column and all the rows simultaneously), then it grounds all other rows except one and measures the signal frequency and checks for delay. The method continues with the next row until the last, and then restarts with another column. The scanning frequency is 100 Hz.

Together with the readout and display software, a module was developed to identify marked objects with the aid of a specific number of points and distance between them that acted as a conductive signature for each object. Thus, a different pattern identified each object, allowing its recognition when in contact with the touchpad. The objects were marked using silver tape as a conductive material with small elevations (fingertip size) in order for the capacitive controller to identify each touching place (Figure 5.5 a)).



(a)



(b)

Figure 5.5. (a) Marked objects can be detected by software with the aid of a specific number of points and distances between them in a C# environment; (b) System process and software processing main algorithm.

The application is comprised of a graphical interface in order to select, configure, and connect to the serial COM (communication port) port in order to stream the data of the touches. The system control process is represented in Figure 5.5 b). It is shown that the system can configure the display format, touch drawing refresh rate, number of displayed points, and enable object detection in relation to the different patterns to be recognized, among others.

Two different objects were used as demonstrator: a cup silver-coated with tape, a base of three points linked as a triangle, and a flat object with two identification points. Touching in the conductive tape of the object closes the circuit to the ground through the human body, allowing the objects to be

identifiable through the touching points, as the distances between points fall within a certain range of tolerance, with an error of $\sim 7\%$. This method is implemented with real-time calculations, as in [13] and it is valid for 2D objects. It is worth noting that the main issue is not the identification of the objects by the touchpad, but to identify the different shapes (patch patterns) by the software.

These results demonstrate the versatility of the printed technologies in the replacement of the traditional rigid and flat interfaces with the user. Furthermore, as long as it is possible to keep contacts well fixed to the rigid parts, there is no commitment with a regular plane surface in a device. This means that we can place the touch panel on a curved surface, but after that it cannot be moved without recalibration to another type of surface.

5.4. Conclusions

The present work reports on the fabrication and performance of a touch and object detection printed capacitive matrix. The printed matrix was fabricated with a PET substrate and two printed silver layer patterns, one on each side. Adhesive PET was applied on both sides over the printed layers for protection against touches and oxidation. A commercial capacitive controller IC was used in order to convert the capacitance in each intersection to digital values, followed by communication to a microcontroller, which treats the data to be sent to a computer software application. The resolution of 36 points/mm obtained from the digital controller connected to the printed matrix enables handwriting applications, touch buttons, gesture detection, and hovering direction sensors. The inexpensive nature of the materials/quantities required allows the fabrication of larger surfaces (as large as the printed pattern electrical resistance allows). However, it is important to pay attention to the electrical noise introduced by mechanical deformations in the PCB connector through proximity, which can be greatly improved by using flexible ribbon cable connectors.

Printing enables the application in any object and any plain or curved surface, such as in flexible paper sheets of a smart book, curved control touch panels in machines, robots or tubes to control flow/pressure, among others. Finally, its use for object interaction by capacitive pattern recognition has been demonstrated, relying on the number of points and distance between them with an error of $\sim 7\%$. A good alignment between top and bottom patterns is required to obtain suitable response times and precision. The number of potential object signatures will strongly increase with surface size and number of points, allowing rich multimedia environments. Thus, this work demonstrates the suitability of printed

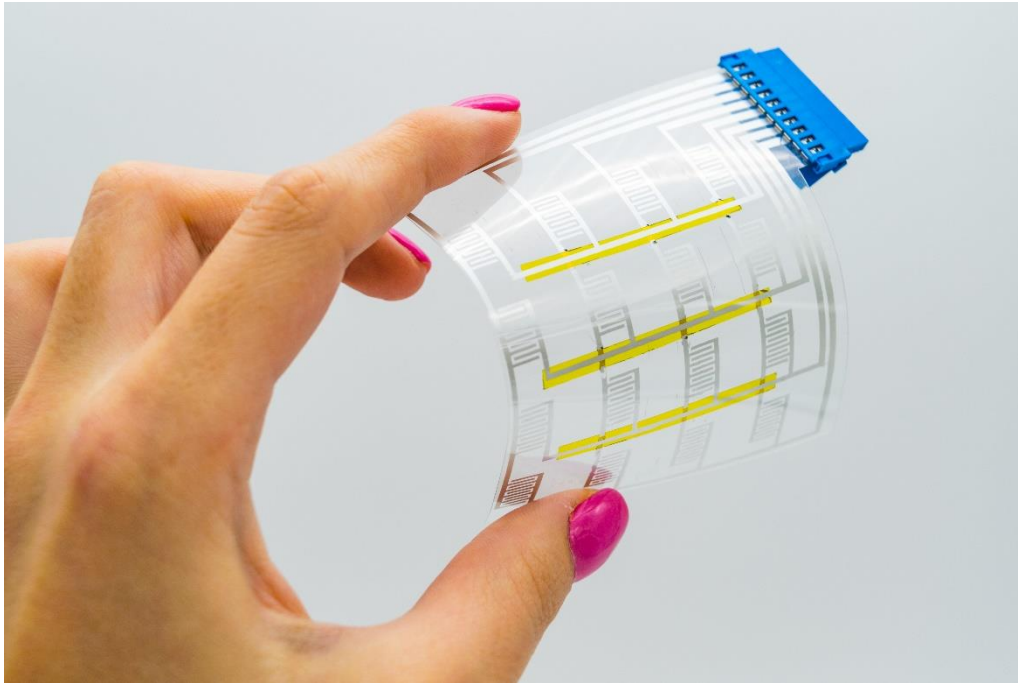
technologies and polymer-based material for developing low-cost smart objects/surfaces for flexible multimedia applications

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6. Final remarks, conclusions and future work

This chapter presents some final remarks related to the printed sensors global market, as well the main conclusions of the present work, which was devoted to the development of polymer-based sensors using different types of inks and printing technologies. A few suggestions for future works are also provided.

6.1. Final remarks

In order to understand the big picture of this work in a global economic perspective, it is important to point out some facts that are linked with the printed and flexible sensor technology.

As mentioned in chapter 1, the market of printed electronics is still growing, and mainly because of the Internet of Things (IoT). IoT is already being used in multiple application areas like autonomous driving, smart cities, industrial applications, home and building automation, among others [1]. As IoT grows, more and different types of sensors are needed, and some features are required such as low-cost, lightweight, ease of production and integration technology that can sense, store information securely, and transmit data [2]. For these reasons, printed memories, printed sensors, and communications devices will play a very important role as a part of the IoT market.

With the increasing number of device connections it is expected to have a significant intensification of data transmission and required bandwidth, and to diminish this issue, the use of artificial intelligence (AI) in smart sensors will contribute to reduce the communication infrastructure [1]. This will allow to have sensor networks able to communicate with each other, collecting large amounts of data and actuating accordingly. These sensor networks could be applied in agriculture, environment, security, industrial technology and entertainment, among other areas [3]. The IoT allows for virtually endless opportunities and connections to take place, many of which we cannot even think of or fully understand the impact of today [4].

In 2018 the number of IoT devices reaches 7 billion, not including smartphones, tablets, laptops or fixed line phones. The worldwide connection growth is mainly driven by IoT devices, both by the consumer (e.g., Smart Home) as well as by enterprises/B2B (e.g., connected machinery). The number of IoT devices that are active is expected to reach 10 billion by 2020 and will double by 2025 (figure 6.1.) [4].

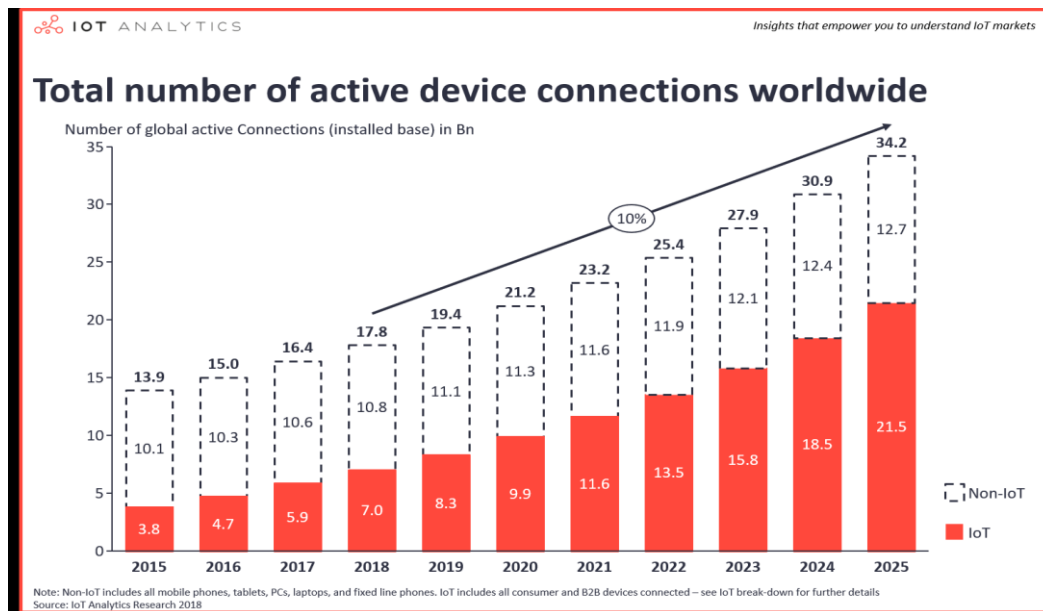


Figure 6.1. Number of active IoT and Non-IoT device connections from 2015 to 2025.

The global market for IoT (end-user spending on IoT solutions) was \$150 billion on 2017 and, due to the market acceleration for IoT, it is expected to reach \$1.6 trillion by 2025, at a compound annual growth rate (CAGR) of 39% (figure 6.2.) [4].

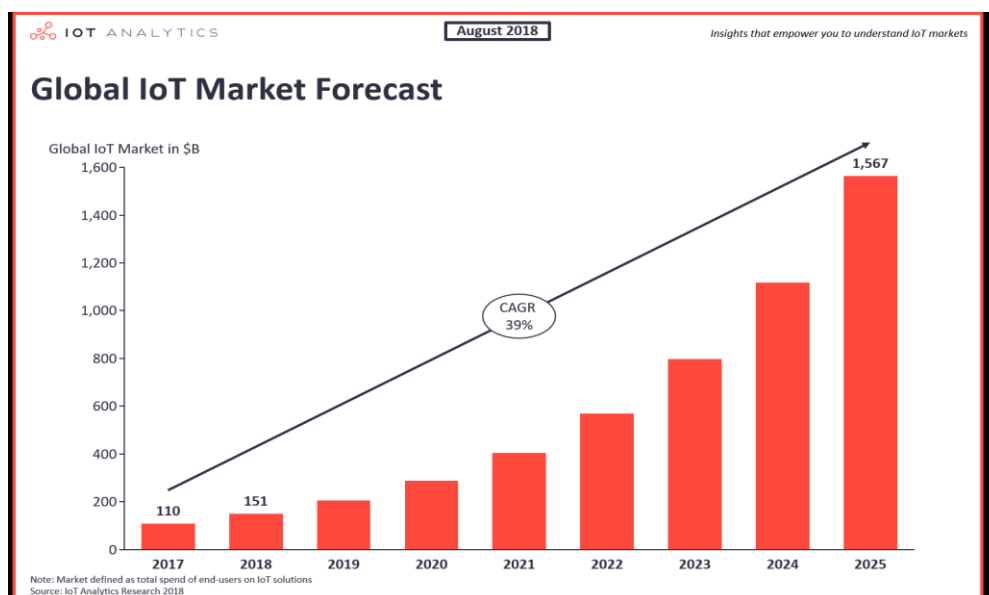


Figure. 6.2. Global IoT market forecast up to 2025.

The IoT will impact our lives, and many opportunities and challenges are yet to come as more and more devices start to join the IoT, and the role of smart materials is key [5].

This work was co-financed by *Fundação para a Ciência e a Tecnologia* (FCT) and by the company *Somatica, Materials & Solutions, Lda*, which is the market leader in Portugal of input devices for the industry (keypads, keyboards, control panels, trackballs, touchpads, etc.). With this work, *Somatica* had the goal to achieve new materials that could be used to manufacture its own input devices, and thus be more internationally competitive and increase its exports. Due to the successful results obtained, the company is already analyzing the possibility to implement some of the developed inks to produce customized keyboards for different industries.

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6.2. Conclusions

The development of polymer based sensors has been demonstrated as a suitable approach for the fabrication of new flexible and printed sensors to be applied in many applications on printed electronics industry. These sensors can be made by using different types of inks, where specific materials and solvents are selected achieve specific requirements characteristics and proprieties. The selection of the polymer substrate is also an important parameter to take into account in order to guarantee a good adhesion of the ink and to control the resulting printed feature's shape, position and structure.

In this scope, the presented work was focused on the development of novel functional inks using different printing technologies, such as doctor blade, spray coating and screen printing, which are one of the most used techniques in commercial printed electronics devices in our days.

Thus, polymer-based piezoresistive sensors were developed and printed using three different types of “green” solvents: CPME, 2-MeTHF and p-cymene. The composites revealed an excellent variation of the electrical resistance with mechanical deformation, increasing and decreasing inversely with the applied deformation, showing a piezoresistive response suitable for pressure sensing applications. All composites, prepared with environmental friendlier solvents, shown close results when comparing with the non-environmentally friendly toluene solvent, being noble candidates for a new generation of piezoresistive environmental friendly inks for pressure sensors. This successfully used method, for piezoresistive ink development, allows the creation of a novel solution in this area using a non-toxic solvent approach.

Further, a functional all-printed ME materials were developed using a simple upscalable method based on spray-printing, in order to fully demonstrate the potential of the technological approach. The reinforced fibrillar structure of P(VDF-TrFE)/CoFe₂O₄, with 20 wt.% of ferrite content, exhibits improved dielectric and piezoelectric responses when compared to a composite with a similar composition obtained by bar-coating. The ME coupling coefficient was about 21.2 mV·cm⁻¹·Oe⁻¹ at an optimum magnetic field of 2450 Oe, which is suitable for sensor/actuator applications, demonstrating the good performance of the printed ME material. The simple printing method, easy integration into devices and the possibility to be obtained over flexible and large areas, validate the developed of ME materials for applications in areas of the printed electronics and energy harvester devices.

Piezoelectric films of PVDF-TrFE, using also an environmental-friendly approach with DMPU as a green solvent, were prepared by different additive manufacturing techniques, including doctor blade, spray printing and screen printing for touch-screen application. Regardless of the printing technique used,

dense films were obtained with suitable morphology, polymer phase, thermal and electrical properties for piezoelectric sensing applications. Piezoelectric films were obtained by screen printing and showed a piezoelectric coefficient of $|d_{33}| = 19 \text{ pC/N}$ after poling, showing suitable performance as touchpad to detect both touch and release events in the piezoelectric film with low cross talk due to the implemented sensor geometry and electronic readout systems based on charge amplifier with a band-pass filter (BPF). A BPF frequencies between 5 to 10 Hz successfully eliminated the electrostatic noise and 50/60 Hz grid noise. The observed cross-talking in the sensors, due to film vibration caused by finger touch, was determined by peak signal comparison. At the end, an all-printed piezoelectric touch-screen, using an environmental friendly solvent, was developed showing a good promising for a new generation of touch panels produced by additive manufacturing techniques.

Finally, a touch and object detection printed capacitive matrix was fabricated with a PET substrate and two printed silver layer patterns, one on each side. A commercial capacitive controller IC was used in order to convert the capacitance in each intersection to digital values, followed by communication to a microcontroller, which treats the data to be sent to a computer software application. The resolution of 36 points/mm obtained from the digital controller, connected to the printed matrix, enables handwriting applications, touch buttons, gesture detection, and hovering direction sensors. The inexpensive nature of the materials/quantities required allows the fabrication of larger surfaces for object interaction by capacitive pattern recognition. This application demonstrated the suitability of printed technologies and polymer-based material for developing low-cost smart objects/surfaces for flexible multimedia applications.

Thus, this work demonstrates that polymer-based sensors fabricated by different printing technologies can be produced to be applied in large areas and be used in many applications. These printed sensors can be fully printed using the most common printing technologies in the industries, with different functional inks and environmental friendly solvents. With the growth of the IoT and AI, flexible and printed sensors will be in greater demand for the coming years.

6.3. Future work

In the present work it has been proven that polymer sensors can be achieved using the most common printing technologies in the industry. In this perspective, several studies can be carried out in order to upscale the ink preparation for industrial production. An interesting future work to explore would be:

- Improve the stabilization of the inks, by adding appropriate additives, such as dispersants. This will maintain particles well dispersed during time and avoid their agglomerations.
- Develop UV curable formulations of the developed inks, since ultraviolet curing process is increasingly used in the industry. This will allow to increase the speed production of printed sensors.
- Optimize and characterize all inks to other types of printing technologies such as inkjet, gravure and offset printing. These three printing technologies are also very used in the industry.