

University of Minho
School of Engineering

Sara Coelho Ribeiro

Fabrication of PEDOT:PSS/silver nanowire based films for the development of transparent heating systems



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Statement of Integrity

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University of Minho, Braga, december 2023

Sara Coelho Ribeiro

Abstract

Transparent and flexible heating systems have become increasingly important for applications such as in defrosting windows, sensors, or heating displays. PEDOT:PSS and silver nanowire (AgNW) films offer the possibility of high transparency, flexibility, and conductivity, making them promising substitutes for ITO, the most used material in these systems. In this work, these films were studied with the aim of utilizing screen-printing as a reproducible method to produce effective transparent and flexible heating systems with low input voltages. With that purpose, AgNWs were synthesized and the effect of different factors on the films' resistances was studied: the films' thickness; PEDOT:PSS modifications with water, PEG, glycerol, methanol, or DMSO; post-treatments with methanol, DMSO, CTAB or sodium borohydride, and the utilization of sintered AgNWs, an ionic liquid, and PVA.

The results showed that depositing a layer of AgNWs on PEDOT:PSS decreased its resistance slightly, while another layer of PEDOT:PSS decreased it considerably. Modifying PEDOT:PSS and post-treating it with methanol had an insignificant effect on the resistances, while post-treatment with DMSO generally lowered them. Utilizing sintered AgNWs, an ionic liquid, PVA, or post-treating the films in CTAB or sodium borohydride was ineffective. As such, it was concluded that the resistance depended mainly on the thickness of the films. When characterized thermally with an input voltage of 12 V, most films showed an insignificant increase in their temperature. Nevertheless, films with two manually deposited layers of PEDOT:PSS post-treated with methanol with a layer of AgNWs, and films with screen-printed PEDOT:PSS with a big mesh size and a layer of AgNWs were able to increase their temperature values by almost 5 °C.

In conclusion, different methods were studied to improve the conductivity of films for transparent and flexible heating systems, which showed that the films' thickness is a key factor in their resistance and, consequently, in their heating abilities.

Keywords Transparent flexible heating systems, PEDOT:PSS, silver nanowires, solvents, post-treatments, films deposition, screen-printing, resistance

Resumo

Sistemas de aquecimento transparentes e flexíveis têm ganhado importância em aplicações como o desembaciamento de janelas, em sensores ou no aquecimento de *displays*. Os filmes de PEDOT:PSS e nanofios de prata (AgNWs) podem atingir alta transparência, flexibilidade e condutividade, tornando-os substitutos promissores do ITO, o material mais usado nestes sistemas. Neste trabalho, estes filmes foram estudados com o objetivo de utilizar a serigrafia como um método reprodutível para produzir sistemas de aquecimento transparentes e flexíveis eficazes com baixas voltagens de entrada. Assim, AgNWs foram sintetizados e foi estudado o efeito de vários fatores nas resistências dos filmes: espessura dos filmes; modificações do PEDOT:PSS com água, PEG, glicerol, metanol ou DMSO; pós-tratamentos com metanol, DMSO, CTAB ou borohidreto de sódio, e utilização de AgNWs sinterizados, de um líquido iônico, e de PVA.

Os resultados mostraram que a deposição de uma camada de AgNWs sobre PEDOT:PSS diminuiu ligeiramente a resistência, enquanto outra camada de PEDOT:PSS a diminuiu consideravelmente. As modificações do PEDOT:PSS e o pós-tratamento com metanol tiveram um efeito insignificante nas resistências, enquanto o pós-tratamento com DMSO geralmente teve um efeito redutor. A utilização de AgNWs sinterizados, líquido iônico, PVA, ou o pós-tratamento dos filmes com CTAB ou borohidreto de sódio foram ineficazes. Como tal, concluiu-se que a resistência dependia principalmente da espessura dos filmes. Quando caracterizados termicamente com uma voltagem de entrada de 12 V, a maioria dos filmes teve um aumento insignificante na sua temperatura. No entanto, filmes com duas camadas de PEDOT:PSS depositadas manualmente e pós-tratadas com metanol e com uma camada de AgNWs, e filmes com PEDOT:PSS serigrafado com um grande tamanho de malha e uma camada de AgNWs, aumentaram a sua temperatura cerca de 5 °C.

Em conclusão, foram estudados diferentes métodos para melhorar a condutividade de filmes para sistemas de aquecimento transparentes e flexíveis, tendo-se observado que a espessura dos filmes é um fator chave na sua resistência e, conseqüentemente, no seu aquecimento.

Palavras-chave Sistemas de aquecimento transparentes e flexíveis, PEDOT:PSS, nanofios de prata, solventes, pós-tratamentos, deposição de filmes, serigrafia, resistência

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Acronyms

[EMIM][BF₄] 1-ethyl-3-methylimidazolium tetrafluoroborate

EDOT 3,4-ethylenedioxythiophene

GBL γ -butyrolactone

CTAB Cetyltrimethylammonium bromide

CTAC Cetyltrimethylammonium chloride

DMF Dimethylformamide

DMSO Dimethyl sulfoxide

EDA Ethylenediamine

EDTA Ethylenediamine tetraacetic acid

EG Ethylene glycol

GLY Glycerol

ITO Indium tin oxide

IPA Isopropyl alcohol

LPDP Liquid phase depositional polymerization

MeOH Methanol

MaBr Methylammonium bromide

MAI Methylammonium iodide

NMP N-methyl-2-pyrrolidone

OTAC Octadecyltrimethylammonium chloride

Ω Ohm

o-CVD Oxidative chemical vapor deposition

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

PC Polycarbonate

PEG Polyethylene glycol

PEN Polyethylene naphthalate

PET Polyethylene terephthalate

PMMA Poly(methacrylic acid)

PVA Polyvinyl alcohol

PVP Polyvinylpyrrolidone

RPM Rotations per minute

SCE Saturated calomel electrode

AgCl Silver chloride

AgNPs Silver nanoparticles

AgNWs Silver nanowires

AgNO₃ Silver nitrate

NaBH₄ Sodium borohydride

NaCl Sodium chloride

NaOH Sodium hydroxide

NaClO₄ Sodium perchlorate

TBAC Tetrabutylammonium chloride

VPP Vapor phase polymerization

Chapter 1

Introduction and state of the art

Transparent heating systems are devices that appear transparent to the human eye due to their high transmittance of visible light. Despite being transparent and often flexible, these devices are able to generate heat utilizing an electric input. The maximum temperature they can reach can be controlled through the variation of the input voltage [1].

Transparent flexible heating systems have been gaining importance due to their possible applications in numerous areas, such as in the defrosting of windows, in thermochromic displays (that change their color according to their temperature), in sensors, or in heating outdoor displays [1, 2].

The most used material for transparent heaters is indium tin oxide (ITO) due to its high transmittance of visible light (90%) while maintaining a low sheet resistance of around $10 \Omega/\text{sq}$, which corresponds to a high electrical conductivity. Nevertheless, ITO's high cost of manufacturing, high brittleness, low flexibility, and slow thermal response are detrimental to its use at a large scale [2, 3].

As a consequence of the disadvantages associated with ITO, there have been many attempts at creating transparent flexible heating systems with other materials. Carbon nanotubes, graphene, nanowires, and various conductive polymers have been used for this purpose [1].

One promising approach to this problem is the use of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), a polymer that can achieve great thermal stability and transparency, which are important characteristics for this application, although its electrical conductivity often needs to be improved [1, 3, 4].

Silver nanowires (AgNWs) have also been used to substitute ITO on transparent flexible heating systems due to their high electrical and thermal conductivity and high transmittance of visible light. Films obtained through the deposition of AgNWs have been reported to have similar sheet resistance and transmittance of visible light to ITO films ($10 \Omega/\text{sq}$ and 90%, respectively) [2].

Furthermore, both approaches have been adopted simultaneously in films containing PEDOT:PSS and silver nanowires. The PEDOT:PSS solution aids in the even dispersion of the AgNWs on the films, which

can decrease temperature variations throughout the film [5]. These films can be deposited, for instance, by micro gravure or slot-die [3], spray-coating [5, 6, 7], doctor blading [5], or screen-printing [1]. There have been reports of films with sheet resistances higher ($15 \Omega/\text{sq}$ [3], $19.4 \Omega/\text{sq}$ [6]), similar ($8 \Omega/\text{sq}$ [6], $10.76 \Omega/\text{sq}$ [7]), or lower ($3 \Omega/\text{sq}$ [5]) than ITO films, while maintaining high transmittance in the visible range. The films' sheet resistance (and, consequently, the electrical conductivity) and the transmittance of visible light depend on several factors, namely the concentration of the reagents used, the thickness of the films, the added solvents or even the post-treatments of the films. These factors, which will be discussed in the sections below, are the justification for the differences in sheet resistance reported.

Here, films of PEDOT:PSS and AgNWs have been studied with the objective of obtaining and optimizing flexible transparent conducting films for application in heating systems.

1.1 PEDOT:PSS

Poly(3,4-ethylenedioxythiophene), or PEDOT, is a conducting polymer that was first reported in 1988 by the German company Bayer AG, and it is composed of the monomer EDOT (3,4-ethylenedioxythiophene) [8].

PEDOT can be obtained mainly through electrochemical polymerization and oxidative polymerization, although in 1999 Yamamoto & Abla reported the production of PEDOT through a transition metal-mediated polymerization [8, 9].

The electropolymerization of EDOT is carried out with three electrodes (working, counter, and reference) in an electrolyte, for example, lithium perchlorate (LiClO_4). A PEDOT film is formed on the working electrode and its characteristics, such as the thickness and the electrical conductivity, are dependent on the voltages and/or currents applied and on the time of the reaction. In 2007, for instance, Yang et al. reported producing a fibrillar PEDOT:PSS coating of $7 \mu\text{m}$ in an electropolymerization carried out at a current density of 5 A/m^2 for 30 minutes [10]. In 2010, Poverenov et al. deposited PEDOT films of around $1 \mu\text{m}$ at a constant potential of $1.15 - 1.20 \text{ V}$ and a charge of 50 mC , or in cyclic voltammetry with voltages between -1.0 and 1.4 V , or -1.0 and 1.6 V , at a scan rate of 100 mV/s for 10 to 15 cycles [11]. In the same year, Lee et al. reported the electropolymerization of EDOT at 1.20 V for 15 seconds, which resulted in a PEDOT film of thickness 300 nm [12]. Furthermore, in 2019, Seki et al. showed that increasing the electropolymerization time resulted in films with higher thickness and lower conductivity [13].

The oxidative polymerization of PEDOT resorts to the use of an oxidizing agent and can be divided into various methods. This process was utilized in 1988 by Bayer AG and consisted of mixing an oxidizing agent,

EDOT, and a solvent, which resulted in insoluble PEDOT [8]. Additionally, PEDOT can be produced through vapor phase polymerization (VPP), in which a substrate with a deposited oxidant is subjected to EDOT vapors. In this case, the velocity of the reaction influences the resulting PEDOT chains. Consequently, it has been reported the use of a solvent that can slow the reaction, forming longer polymer chains, and increasing the conductivity of the PEDOT film [14]. In 2004, Winther-Jensen & West utilized pyridine with this objective, while simultaneously reducing additional acidic reactions, which happened as a result of the low pH value due to the presence of iron(III) (Fe^{3+}) in the oxidant, originating unwanted short PEDOT chains [15]. Furthermore, the oxidative polymerization of PEDOT can be achieved through oxidative chemical vapor deposition (o-CVD), in which vapors of the oxidant and the monomer intersect at the substrate. In this method, the oxidant must have high enough volatility for the reaction to occur, but not too high as to not cause damage to the system. The characteristics of the resulting PEDOT depend on the conditions of the reaction such as the pressure or the temperature of the substrate [14]. In 2018, for instance, Wang et al. reported utilizing a pressure of around 1 mTorr, temperature values between 190 and 300°C, and reaction times of 20 minutes to 2 hours to obtain films with thicknesses between tens and hundreds of nanometers [16]. In 2020, Gharahcheshmeh et al. used a pressure of 1 Torr and temperature values between 80 and 140°C to deposit PEDOT films of thicknesses varying between similar values [17].

PEDOT has also been fabricated by liquid phase depositional polymerization (LPDP), a process in which a substrate with an oxidant is immersed in an EDOT solution. The reaction occurs at the substrate, where a film is produced. This method allows better control of the reaction's conditions in comparison to other methods, especially VPP and o-CVD, making it easily reproducible and, consequently, more attractive for mass production [18, 19, 20].

Furthermore, Bayer AG introduced, in 1990, the oxidative polymerization of EDOT in the presence of PSS, a water-soluble substance. PSS's negative charge balances PEDOT's positive charge, forming a stable and highly conductive polymer, PEDOT:PSS [8, 21]. PEDOT:PSS is an aqueous dispersion which structure is theorized to consist of PEDOT chains linked to sections of the longer PSS chains by Coulombic forces, in a random coil format, due to the repulsion between unbound PSS molecules (Figure 1) [4, 6].

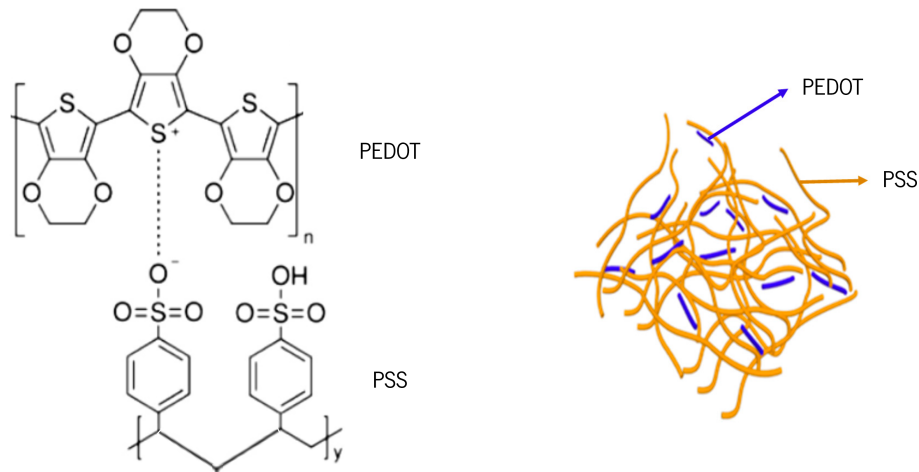


Figure 1: PEDOT:PSS's structure. Adapted from [22, 23].

PEDOT:PSS's conductivity can be increased using UV light or thermal and chemical treatments [4].

In 2007, for example, Lin et al. reported an increment of the conductivity in PEDOT:PSS films subjected to UV light for 30 minutes, which was attributed to an alteration of the PEDOT:PSS structure from coil to extended coil or linear structure [24].

Furthermore, PEDOT:PSS films can become more conductive through thermal treatments, as reported in 2003 by Huang et al. In that work, films of this polymer were treated with temperature values ranging from 100 to 250°C, always resulting in an increase in the conductivity, although higher temperature values or excessive times of treatment could lead to the damage of the films and consequently the increase of their resistivity [25]. In 2004, for example, Nguyen et al. reported small decreases in the conductivity of PEDOT:PSS films subjected to temperature values from 120 to 250°C for two hours, with higher temperature values resulting in even lower conductivities [26].

Additionally, PEDOT:PSS's conductivity can be increased by solvents such as dimethyl sulfoxide (DMSO), methanol, glycerol, or ethylene glycol (EG) [4]. In 2005, for instance, Snaith et al. reported an increase of three orders of magnitude in the conductivity of PEDOT:PSS films through the addition of 8% (V/V) of glycerol [27]. Alemu et al. studied, in 2012, the effects of methanol on the conductivity of PEDOT:PSS films and determined that using a drop of methanol on the films, immersing them in it, or a combination of both methods, resulted in an increase in the conductivity. According to the authors, this increase was due to the removal of PSS mainly from the films' surface, which also increased their stability [28]. Furthermore, Jikei et al. reported, in 2014, the enhancement of PEDOT:PSS films' conductivity using vapor treatments of various solvents, from which the highest conductivities were obtained with methanol, DMSO, dimethylformamide (DMF), EG, and N-methyl-2-pyrrolidone (NMP) [29]. In 2019, Lingstedt et al.

studied three different methods that utilized DMSO to decrease the resistivity of PEDOT:PSS films through the separation of PEDOT:PSS and PSS abundant zones – mixing DMSO with PEDOT:PSS, subjecting PEDOT:PSS films to DMSO vapor and immersing PEDOT:PSS films in DMSO – and found that the most effective method was the immersion of the films [30].

Other solvents such as polyethylene glycol (PEG) have also been used. In 2005, Wang et al. reported the effect of different molecular weights and concentrations of PEG added to PEDOT:PSS in the conductivity of the resulting films. In the studied solutions of PEDOT:PSS with PEG (with molecular weights (g/mol) of 400, 800, 1500, or 2000) the increase of PEG's concentration caused an increase in the conductivity until a certain concentration, from which the conductivity decreased. The highest conductivity of 17.7 S/cm was obtained for PEDOT:PSS with 40.6 mM of PEG-400, which was 177 higher than that of the PEDOT:PSS film without any PEG addition, which was only 0.1 S/cm. The maximum conductivities for films with PEG-800, PEG-1500 and PEG-2000 were 14.2, 9.4, and 6.5 S/cm, respectively, indicating that the highest conductivities achieved decreased with the increase of PEG's molecular weight [31]. In 2013, Mengistie et al. observed the same trend for PEG with various molecular weights, although they were able to enhance the conductivity of their films by a factor of more than two thousand times by adding 2% (V/V) of PEG with molecular weights (g/mol) of 200, 300 or 400 to PEDOT:PSS, while keeping the transmittance of visible light of the film above 90%. Further treatments, either by dropping methanol or dipping the films in it, resulted in an increment of the conductivity for films with PEG-200 and up to 2% (V/V) of PEG-300 [32]. In 2020, Li et al. reported reaching an even higher conductivity of 1399 S/cm in a film of PEDOT:PSS with 4% (V/V) of PEG-400 that was soaked in methanol for 20 minutes [33]. The addition of PEG to PEDOT:PSS increases the conductivity of films by distancing PEDOT:PSS and PSS-rich zones, but from a certain concentration its accumulation on the surface of the films begins to cause an isolating effect, which decreases the conductivity [31, 34].

Moreover, ionic liquids have also been used to reduce the resistivity of PEDOT:PSS films. In 2020, Yemata et al. reported using ionic liquids, as well as nitric acid, as post-treatments to reduce the resistivity of PEDOT:PSS films, concluding that the acid treatment was more effective, although the ionic liquids 1-butyl-3-methylimidazolium with trifluoromethanesulfonate ([BMIM][OTf]-OTf) or with tetrafluoroborate ([BMIM][BF₄]) also increased the conductivity of the films [35]. In 2022, Imae et al. utilized the ionic liquid 1-ethyl-3-methylimidazolium tetracyanoborate ([EMIM][TCB]) to increase the conductivity of PEDOT:PSS films through the removal of PSS, which is replaced by the TCB anion [36].

Furthermore, other acids and bases have also been utilized to optimize PEDOT:PSS's films conductivity. In 2017, Fan et al. studied the effects of a post-treatment with a sulfuric acid (H₂SO₄) solution followed

by a sodium hydroxide (NaOH) solution on the conductivity of PEDOT:PSS films and observed that the first solution caused an increase in the conductivity, while the second caused the opposite [37]. Wu et al. reported, in the same year, mixing chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) to PEDOT:PSS, obtaining films with an enhancement in conductivity by a factor of a thousand. According to the authors, this was due to the oxidation of PEDOT and the reshaping of PEDOT:PSS's structure from coil to linear or extended coil structure [38].

PEDOT:PSS films can have their conductivity increased by salts as well. In 2016, Yu et al. studied the conductivity of PEDOT:PSS films with methylammonium iodide (MAI) and methylammonium bromide (MABr) solutions in different organic solvents such as water, ethanol, methanol, acetone, DMSO, EG, dimethylformamide (DMF) or γ -butyrolactone (GBL). For a concentration of 0.1 M, for instance, the conductivity always increased, in most cases by four orders of magnitude. The highest conductivity, more than nine thousand times that of a PEDOT:PSS film, was registered for a film of PEDOT:PSS with 0.1 M of MAI in GBL. Furthermore, it was concluded that MAI is a better conductivity enhancer than MABr in DMF and GBL solutions, due to its stronger interaction with PEDOT allied with the effect of the solvent [39]. Li et al. studied, in 2020, the effect of different-sized cations on PEDOT:PSS films doped with salts, concluding that smaller cations enhance more the conductivity likely due to their faster mobility, which allows them to easily bond to PSS, leaving anions to bond to PEDOT, thus breaking many PEDOT's bonds to PSS and increasing the conductivity [40, 41]. In that work, the conductivity of a PEDOT:PSS film was increased more than five hundred times through the addition of 0.05 mmol/g of bis(trifluoromethanesulfonyl)imide lithium salt to the solution [40].

1.2 Silver nanoparticles and nanowires

Nanoparticles, such as silver nanoparticles (AgNPs), have particular properties that are different than the bulk materials they are composed of due to their high surface-to-volume ratio. These properties vary with the nanoparticles' dimensions and shapes, which has prompted their application and investigation in many areas [42]. In 2012, for instance, Melendez et al. reported that silver nanoparticles (AgNPs) with bigger diameters caused an increase in the conductivity of films of PEDOT:PSS [43].

Silver nanoparticles can be produced through many methods. One of them is the physical deposition, which utilizes evaporation and condensation of source materials. In 2006, for instance, Jung et al. reported the synthesis of spherical silver nanoparticles using this method, by heating silver with a ceramic heater. The diameter of the nanoparticles ranged between 6.2 and 21.5 nm, with the size increasing with the

increase of the temperature of the heater [44]. Nanoparticles can also be produced by using laser ablation, as was reported, for example, in 2019, by Alhamid et al., to produce spherical AgNPs with diameters of tens of nanometers [45]. Silver nanoparticles can be synthesized through chemical methods as well, which consist of the reduction of the silver cation (Ag^+) and the further aggregation of the silver atoms with the use of a stabilizer such as polyvinylpyrrolidone (PVP) or poly(methacrylic acid) (PMMA) [42]. Electrochemical synthesis and the polyol method are some of the most widely used methods to chemically fabricate AgNPs. The electrochemical synthesis utilizes two or three electrodes. The flowing current oxidizes the anode, freeing electrodes that are then used in the reduction of silver ions from the electrolyte solution at the cathode/working electrode, forming the nanoparticles at its surface. This is a process with high yield [46]. The polyol method consists of using a polyol such as ethylene glycol (EG), glycerol, or polyethylene glycol (PEG) as the solvent and the reducer simultaneously [47], alongside a stabilizer such as PVP. Furthermore, silver nanowires have been produced with the aid of templates, such as membranes [48, 49]. In contrast to AgNPs, AgNWs are a promising approach to obtaining flexible and transparent electrodes to use in heating systems due to their high thermal and electrical conductivity, high transmittance of visible light, and straightforward methods of fabrication [50]. In 2022, for example, Barbic et al. reported the use of a polycarbonate membrane with pores to synthesize AgNWs. A gold layer was deposited on one side of the membrane and a commercial silver enhancement solution was made to reach this layer only through the pores. The reduction of the silver ions started automatically at the gold layer, which also functioned as a catalyst. The AgNWs were obtained after subjecting the structure to ultrasounds, which removed the gold layer, and using chloroform for 1 hour with agitation to dissolve the membrane. The resulting silver nanowires had diameters of (30 ± 5) or (70 ± 15) nm for membranes with pores of diameter of 15 or 30 nm, respectively [49].

1.2.1 Synthesis of silver nanowires - electrochemical synthesis

Zhu et al. utilized this technique, in 2002, to produce silver nanowires by two different approaches. Both syntheses took place in an ultrasonic bath of 50 Hz and 100 W, under a nitrogen atmosphere, at a temperature of 30°C , and with an aqueous solution of 50 mL of distilled water with 0.10 g of silver nitrate (AgNO_3) and 1.00 g of ethylenediamine tetraacetic acid (EDTA) as the electrolyte. Following the reactions, the deposits were centrifugated, cleaned with distilled water and ethanol multiple times, and dried in a vacuum. The authors reported that the ultrasounds might help in the formation of AgNWs due to the partial removal of silver nanoparticles from the working electrode, promoting the growth in a wire shape through the aggregation of more silver nanoparticles. Furthermore, it was determined that EDTA in concentrations

over 20 g/L facilitated the growth of AgNWs by slowing the reaction through a decrease in the number of silver ions, due to the creation of silver-EDTA complexes. In the first approach, AgNWs were generated with a two-electrode configuration with a 5 x 5 mm platinum sheet as the working electrode and a platinum wire as the counter electrode. The reaction occurred at a constant current of 10 mA for 30 minutes and resulted in nanowires of diameter 40 nm and length 6 μm . The second approach used a three-electrode configuration with the same electrodes but with the addition of a saturated calomel reference electrode (SCE). The synthesis was carried out at a constant potential of -0.3 V for 45 minutes and produced bent silver nanowires with diameters of 80 nm and lengths over 15 μm [51].

In the following year, Tian et al. used a polycarbonate membrane with pores (10 nm in diameter, 6 μm in thickness, 6×10^8 pores per cm^2), as a template for the growth of AgNWs. The electrochemical reaction utilized a 200 nm gold film evaporated on one side of the membrane as the working electrode, a platinum wire as the counter electrode, and a SCE as the reference. The electrolyte consisted of a solution of 20 mL of a commercial silver bath with the addition of around 2% (w/w) of gelatin and further dilution in water until it reached a volume of 40 mL. The reaction occurred at a temperature of 40°C and a high negative voltage for 1 to 2 minutes, followed by a constant deposition potential lower than -0.9 V. Subsequently, the membrane was dissolved in dichloromethane and the silver nanowires were precipitated through centrifugation. The resultant AgNWs had 40 nm of diameter and 3 to 5 μm of length [48].

Lin & Wang reported, in 2005, the electrochemical synthesis of AgNWs in a solution of 20 mM of AgNO_3 , 0.1 M of potassium nitrate (KNO_3), and 1.0 g/L of PMMA in distilled water. A bare glassy carbon disk with 4 mm of diameter, a platinum wire, and a SCE were used as the working, counter, and reference electrodes, respectively. The working electrode was treated electrochemically at a constant potential of 1.8 V for 2 minutes in a distilled water solution of 1 M of sodium hydroxide (NaOH) prior to the production of the silver nanowires, which took place at a voltage of -0.2 V for 5 minutes and at around 22°C. This process resulted in AgNWs of a diameter of 30 to 40 nm and length of 3 μm with some silver nanoparticles connected. Furthermore, the lack of PMMA in the electrolyte or the increase of its concentration to 3.0 g/L yielded spherical nanoparticles or dendritic structures, respectively [52].

In 2007, Zheng et al. utilized two electrolytes for the electrochemical growth of AgNWs. Highly oriented pyrolytic graphite or an iron plate previously mechanically polished and washed with distilled water, and a platinum electrode were employed as working and counter electrodes, respectively, in the production of silver nanowires, which was carried out in a constant potential mode with a current density of 1 mA/cm^2 for 2 hours. For one of the electrolytes, composed of 500 mL of an aqueous solution of 1.0 mM of AgNO_3 , the resulting nanowires had diameters of 10 to 50 nm and lengths of several μm . For the other electrolyte,

which had a similar composition except for the addition of 0.02 mM of citric acid ($C_6H_8O_7$), the obtained AgNWs were smoother and with diameters of 30 to 50 nm and lengths up to 5 μm [53].

Fang et al. reported, in 2009, the production of AgNWs through the fragmentation of silver dendrites. Two 5 x 5 x 0.5 mm silver plates placed 10 mm apart were used as the working and counter electrodes, in an electrolyte solution of 10 mM of $AgNO_3$ in ultrapure water. The dendrites were electrochemically grown at 30 V for 10 seconds and left in the solution for 120 minutes without the application of a potential, which resulted in the separation of nearly all branches from the dendritic structures. The authors hypothesized that the formation of nanowires could occur due to the disintegration of the dendrites followed by Ostwald ripening, which consists of the consolidation of nanorods into the existing nanostructures. This process resulted in silver nanowires of diameters between 50 and 100 nm and lengths around 5 μm and several nanorods of lengths from 0.5 to 1 μm [54].

1.2.2 Synthesis of silver nanowires - polyol method

In 2014, Kim et al. employed this method to grow silver nanowires. For that, 35.5 mL of an EG solution of 0.35 M of PVP and 71.5 mL of another EG solution of 0.1 M of $AgNO_3$ were simultaneously dissolved in 170 mL of EG under vigorous agitation. Subsequently, 14.5 mL of another EG solution of 0.006 M of tetrapropylammonium chloride was added. A syringe was used to move the solution to an autoclave and its temperature was raised to 170°C. After the reaction, the remaining PVP and EG and other impurities were washed with acetone and the deposited material was redistributed in water. This process yielded silver nanowires of average diameter and length of 30 nm and 20 μm , respectively [3].

The synthesis of AgNWs through this technique was reported by Ji et al. in the same year, as well. The experimental procedure began with the agitation of 30 mL of an EG solution of 0.052 M of $AgNO_3$ and 0.067 M of PVP followed by the addition of 2.5 mL of an EG solution of 0.6 mM of iron trichloride ($FeCl_3$) to 30 mL of EG that was previously heated at 130°C for 1 hour. This solution was heated and agitated for 5 to 10 minutes. Thereafter, the silver solution was added at a rate of 0.5 mL/min for 20 minutes, heated and agitated for 1 hour, and this step was replicated 2 to 3 times. The resultant solution was left to cool to room temperature, ultrasonicated with ethanol for 10 minutes, filtered, and the product redispersed in ethanol. The AgNWs precipitate was formed by centrifugation at 2000 rotations per minute (RPM) and recurrently washed by these ultrasonication and centrifugation steps. The resulting nanowires had an average diameter of 100 nm and lengths between 50 and 100 μm [5].

In 2017, He et al. achieved the production of long silver nanowires. Deionized water solutions of 2 mmol of glucose, 1.5 mmol of $AgNO_3$, and 0.3 mmol of ferric sulfate ($Fe_2(SO_4)_3$) were mixed at a

volume ratio of 2:2:1 and magnetically stirred for several minutes, at room temperature, originating a yellow solution. Subsequently, 4.5 g of PVP were added and the solution was magnetically stirred until complete dissolution. The solution was moved to a 100 mL autoclave, sealed, and heated at 180°C for 6 hours. The gray-green deposit that formed was repeatedly cleaned with a dilute nitric acid solution to remove any oxidation on the AgNWs. Centrifugations in ethanol were performed to remove the excess nitric acid and the AgNWs were further obtained by successive suction filtrations. Lastly, the silver nanowires, of diameters around 100 nm and lengths up to hundreds of μm , were dispersed in ethanol [1].

Sharma et al. reported, in 2019, the growth of AgNWs in glycerol. In this process, 0.4 M of PVP was added to 80 mL of glycerol and 0.03 M of AgNO_3 to 20 mL of the same polyol. These solutions were agitated together for several minutes and the resulting solution was subjected to a temperature of 160°C for 8 hours in an autoclave. The solution was cooled after becoming yellow, diluted in acetone, and centrifugated at 1800 rotations per minute for 10 minutes. The supernatant was removed and the precipitate was washed and redistributed in isopropyl alcohol (IPA), yielding silver nanowires with diameters and lengths between 20 and 30 nm and between 10 and 20 μm , respectively [55].

In 2021, Zheng et al. published the fabrication of AgNWs without the use of PVP. In this approach, 0.008 g of tetrabutylammonium chloride (TBAC), 0.024 g of iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$), and 0.477 g of AgNO_3 were added to 50 g of EG that had been previously heated at 125°C for 90 minutes. This solution was left to react at 140°C for 18 hours and further centrifugated three times with ethanol at 10 000 RPM, resulting in a deposit of nanowires of diameter around 46 nm and length from 20 to 40 μm . In that work, Zheng et al. concluded that TBAC could replace PVP in the management of the AgNWs structure during the reaction [6].

Lahane et al. reported, in 2022, an optimization of the polyol method for the production of silver nanowires through the use of two salts. The process began by dissolving 75 mg of PVP in 10 mL of EG and heating it to 170°C for 1 hour with agitation. Subsequently, 40 μL of an EG solution of 3.5 mM of sodium chloride (NaCl) and 20 μL of another EG solution of 1.8 mM of potassium bromide (KBr) were added, while maintaining heat and agitation. The reaction occurred for 20 to 30 minutes and, subsequently, 5 mL of an EG solution of 30.5 mM of AgNO_3 was added using a syringe infusion pump at a rate of 0.2 mL/min, originating a yellow solution. The resulting solution was kept at 170°C and in agitation for 3 hours and then cooled to room temperature, yielding a black solution. To obtain the AgNWs, the solution was subjected to centrifugation in acetone at 5000 RPM for 15 minutes for three different times, with further removal of the supernatant and washing of the nanowires in ethanol. Finally, the produced AgNWs, of diameter 40 to 50 nm and an average length of 37 μm , were dispersed in 5 mL of ethanol [56].

In the same year, Shi et al. used PEG to grow silver nanowires. 5 mL of EG, 1 mL of PEG, 0.5 mL of an EG solution of 100 mM of NaCl, and two 5 mL EG solutions of 25 mg/mL of AgNO₃ and 20 mg/mL of PVP were all added to a 50 mL conical flask in order and agitated at 1200 rotations per minute for 30 minutes at room temperature. The solution was further heated at 120°C for 12 hours and subsequently cooled through the addition of 40 mL of cold deionized water. This process produced AgNWs of average diameter and length of 24.3 nm and 7.6 μm, respectively [57].

1.2.3 Cleaning/Welding of silver nanowires

The polyol method, one of the most widely used methods to synthesize silver nanowires, most commonly utilizes PVP as a stabilizer and structuring substance in the reaction, which also prevents the aggregation of the nanowires during storage [58]. As such, the AgNWs produced by this method are wrapped in PVP (Figure 2), which has an isolating effect on the nanowire junctions in the resulting films, increasing their resistance [58]. There are many methods to enhance the conductivity of AgNW films through the removal of PVP and/or the welding of the nanowires, such as electrochemical processes, thermal annealing, immersion in solutions, or utilizing light.

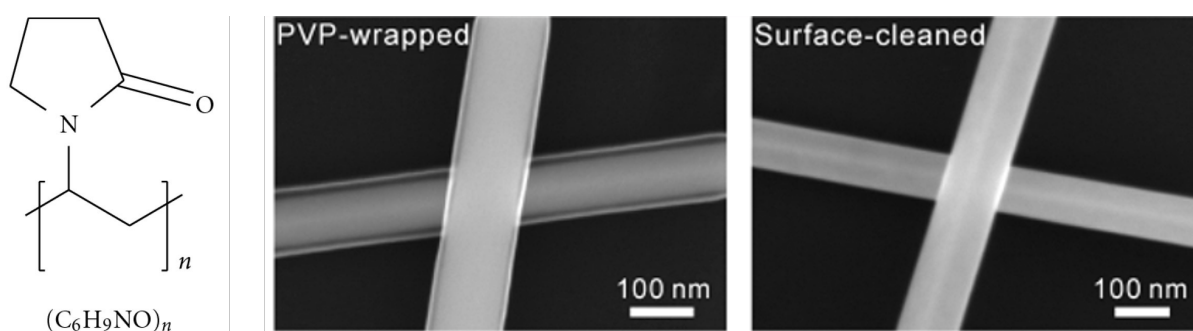


Figure 2: PVP's chemical structure, PVP-wrapped and PVP-free silver nanowires. Adapted from [59, 60].

Electrochemical cleaning and welding of silver nanowires were reported, for instance, in 2019, by Ge et al. In that work, the cleaning was carried out in a three-electrode configuration in which the AgNW films on PET were used as the working electrodes, and the counter and reference electrodes were a platinum wire and a mercury/mercurous sulfate electrode (Hg/Hg₂SO₄), respectively. A potential of -85 V vs. standard reversible hydrogen electron (RHE) was applied for 15 seconds, in an electrolyte of 0.5 M aqueous solution of sodium perchlorate (NaClO₄). The resistance of the films was reduced four times due to the adsorption of hydrogen atoms on the surface of the nanowires, which would remove the PVP, and the further formation of hydrogen gas which also aided in its removal [60]. The same method was utilized, by Zhang et al., in 2022, to reduce the resistance of AgNW films by 45.5% on average. The electrochemical reactions took

place in an electrolyte composed of 0.5 M of NaClO_4 and 0.1 M of NaCl . AgNW films on PET, a platinum wire, and a silver/silver chloride (Ag/AgCl) reference electrode were used as the working, counter, and reference electrodes, respectively. The films were oxidized at 0.3 V vs. the reference for 50 seconds and then reduced at -0.15 V for 100 seconds, which promoted the removal of PVP through the formation of AgCl , and the further deposition of silver, respectively, which effectively welded the nanowires at the junctions [61].

Furthermore, annealing can be used for this purpose as well. In 2014, for instance, Giusti et al. studied the effects of different temperature values in the thermal annealing of AgNW films on glass. The resistance of the films decreased for temperature values up to 310°C , likely due to the removal of substances left from the synthesis of the silver nanowires, especially of PVP at around 150°C , and the welding of the nanowire junctions at temperature values between 225 and 300°C . Higher temperatures resulted in the degradation of the nanowires, which increased the resistance. The optimal resistance was achieved through annealing at 200°C for 2 hours, although for AgNW films with different densities, this temperature may vary [62]. In the following year, Oh et al. tested the effect of thermal annealing for 60 seconds at temperature values between 150 and 300°C on the conductivity of AgNW films on glass. Even though at 150°C the nanowires would already start welding, the most significant enhancement in the conductivity was obtained for temperature values between 225 and 250°C , which would weld sufficient AgNWs to decrease the resistance by around 50%, while only decreasing the transmittance slightly. For higher temperature values, the degradation of the nanowires would decrease the conductivity and the transmittance of the films [63].

Moreover, the immersion of AgNW films in solutions has also been used to increase their conductivity. In 2020, for instance, Liu et al. studied the effect of immersing AgNW films on PET in three different surfactant solutions of cetyltrimethylammonium chloride (CTAC), cetyltrimethylammonium bromide (CTAB), or octadecyltrimethylammonium chloride (OTAC) with concentrations 0.01 M. The resistance of the films was shown to decrease in all cases, with an optimal decrease of 63.1% for treatment with CTAC, while the transmittance only decreased slightly. CTAC showed the best results among the three surfactants used, followed by CTAB and OTAC. The enhancement of conductivity was due to the promotion of the formation of silver halide on the surface of the nanowires by the surfactants in the solutions, which would displace PVP [64]. In 2018, Ge et al. studied the effects of immersing AgNW films on PET on solutions of sodium borohydride (NaBH_4) with different concentrations and for varying time periods, concluding that immersion in a 0.5 M NaBH_4 solution of ethanol and water for 30 seconds would effectively remove the PVP from the nanowires by breaking the bonds between oxygen present in PVP's carbonyl group and silver, and substituting them with bonds to the hydrogen ions from the sodium borohydride. The resistance of

the films was decreased by more than half, while maintaining the transmittance above 90%. The films were further treated with dodecanethiol, which formed a protective layer on the films, making them more stable [58]. In 2014, Ni & Hong studied the welding of silver nanowires and the removal of PVP through immersions in different solutions. An aqueous solution of 6mM of AgNO₃ and 36 mM of ethylenediamine (EDA) was mixed with an aqueous solution of 70 mM of potassium sodium tartrate and 74 μM of 3,5-diiodotyrosine (DIT). AgNW films immersed in the resulting solution for 2 minutes allowed the deposition of silver mainly on the junctions between nanowires, which decreased the resistance of the films as far as three orders of magnitude, while decreasing the transmittance only by 9%. The selectivity of the silver deposition was attributed to the presence of PVP wrapped around the nanowires, given that PVP-free films obtained through thermal annealing showed a homogenous silver deposition. Additionally, the removal of PVP from AgNW films immersed in an EDA solution of concentration 16.7 mM for different times was also studied. The resistance of the films decreased due to the formation of silver and EDA compounds, which displaced PVP from the AgNWs' surfaces. However, for treatment times higher than 15 minutes, a significant loss of silver from the nanowires and a consequent decrease in the conductivity was verified. Furthermore, the removal of PVP through immersion in ammonium hydroxide solutions was studied, and the lowest resistance was observed for a solution with a concentration of 16.7 mM and a treatment time of 2 minutes. For both PVP removal methods, the resistances decreased by two orders of magnitude. Finally, treatment in an ammonium hydroxide solution with further immersion in the silver-depositing solution was used to remove PVP and then weld the nanowires. This process resulted in a film with the lowest resistance (lower than 20 Ω/sq) and highest transmittance (83%) among all the utilized methods [65].

Moreover, light has been used to remove PVP and weld silver nanowires in AgNW films as well. In 2012, for instance, Garnett et al. tested the effect of different time exposures to a tungsten-halogen lamp in the welding of silver nanowires, a process that takes advantage of the small distance between AgNWs intersections due to the wrapped PVP, resulting in a concentration of light at the nanowire junctions, which increases their temperature. A light treatment of 60 seconds with a power density of around 30 W/cm² was sufficient to weld the nanowires, reducing the resistance of the films by more than three orders of magnitude, and higher exposure times did not increase the conductivity further [66]. Wang et al. reported, in 2022, a study with different UV light powers, wavelengths, and treatment times in the welding of silver nanowires. An optimal resistance decrease of more than half was obtained for a UV light treatment of 60 W/cm² for 3 minutes and for a wavelength of 380 nm, which corresponds to the AgNW's absorption of the UV light [67]. In both these methods, the resistances decreased until they reached a constant value, showing a self-limiting behavior in the welding of the nanowires, which is an advantage against the

thermal annealing and immersion methods, which can increase the resistance of AgNW films if applied for too long.

Chapter 2

Films for heating systems

Heating systems, especially flexible and transparent ones, have gained importance due to their many potential applications, including in defrosting windows, thermochromic displays, and sensors [2]. Conductive thin films have been widely studied for this purpose because they can be deposited on transparent substrates such as glass and on flexible transparent materials like polyethylene terephthalate (PET) or polyethylene naphthalate (PEN). Additionally, thin films offer the advantage of adjustable resistance and transmittance through various methods, such as solvent addition, post-treatments, or modifications in thickness or concentration. For instance, the addition of silver nanowires to PEDOT:PSS can enhance film conductivity while maintaining the transmittances at high values.

The increase in temperature of films when used as heaters is attributed to the Joule effect, in which the heat (H) produced by a flowing current is proportional to the square of the applied voltage (V) and the time (t), and inversely proportional to the resistance of the films (R) (2.1) [2]. Therefore, films with lower resistances show better performance, making it the main objective of many studies to decrease the resistance of the films as much as possible in order to maintain the input voltage at adequate values for further applications.

$$H = \frac{V^2 t}{R} \quad (2.1)$$

In this context, PEDOT:PSS films with silver nanowires (PEDOT:PSS/AgNW films) have been used to fabricate conductive, transparent, and flexible electrodes. In 2011, for instance, Gaynor et al. utilized AgNWs deposited on PEDOT:PSS to produce transparent PET and glass electrodes. Compared with similar ITO electrodes, these showed lower transmittances but also lower resistances and better stability. PEDOT:PSS/AgNW and ITO films on PET and glass were further applied in a photovoltaic cell and showed the same efficiency [68]. In the following year, Choi et al. reported the fabrication of transparent films with better performance than ITO's in terms of resistance and transmittance. PEDOT:PSS treated with DMSO was spray-coated on a previously spray-coated AgNW film and further laminated, which flattened the silver nanowires, resulting in a less rough film and in a decrease of 28% in the resistance. Annealing

of the AgNW films at 140°C for 20 minutes before PEDOT:PSS deposition was able to further decrease the resistance of the PEDOT:PSS/AgNW film by almost 28% [7].

The applicability of transparent and flexible PEDOT:PSS/AgNW electrodes on heating systems has been studied as well. In 2014, for instance, Ji et al. tested the heating of PEDOT:PSS/AgNW films on PET produced through doctor blading of AgNWs and further doctor blading or spin coating of PEDOT:PSS diluted in isopropanol. The films showed transparencies around 90% and good stability, and reached uniform temperature values above 100°C for an input voltage of 6 V. The PEDOT:PSS/AgNW films were deposited on glass and compared to ITO films on the same substrate, showing a shorter response time and needing less input voltage to reach the same temperature. Further tests showed that this film was able to defog a window in 40 seconds [5]. In 2017, He et al. studied the effects of different concentrations of silver nanowires added to PEDOT:PSS on the heating of the resulting films, which were deposited through screen printing on PET, an easily reproducible technique. The temperature could be homogeneously increased up to 99°C with the application of 40 V for films with a AgNW concentration of 12 mg/mL and transmittances around 74% [1]. In 2021, Zheng et al. reported the fabrication of a PEDOT:PSS/AgNW film through the spray-coating of a solution of PVP-free silver nanowires, DMSO and PEDOT:PSS on PEN. Both additives to PEDOT:PSS enhanced the conductivity of the resulting films enough to achieve an optimal temperature of almost 115°C throughout the film with an input of 7 V [6]. In 2023, Rezvani et al. reported the heating of PEDOT:PSS/AgNW films on PET treated with an intense pulsed light, which increased the conductivity of the films through the removal of PSS from the PEDOT:PSS, the removal of PVP from the nanowires, and the welding of AgNW junctions. The treated samples were able to increase their temperature by up to 50% [69].

Furthermore, other films with silver nanowires, such as films of AgNWs and poly(p-phenylene vinylene) [70], carbon nanotubes [2], PEDOT:PSS and ITO [71], cobalt nanoparticles [55], polyimide [72], polyvinyl alcohol (PVA) [73, 74], or polymer composites [75, 76] have also been studied for possible applications in heating systems, showing a wide range of maximum temperature values between around 75 and 350°C, depending on the film and the applied voltage.

In this work, the main goal is the production of a heating system, produced by the screen printing technique, that operates at low values of tensions applied (low power consumption) with a great temperature gradient and transmittance of visible light.

Chapter 3

Materials

Commercial PEDOT:PSS ink was acquired from Saralon. PVP, silver nitrate, glycerol, sodium chloride, methanol, sodium borohydride, PVA, CTAB, and PEG of molecular weight 2000 g/mol were obtained from Merck/Sigma Aldrich. DMSO was acquired from Thermo Fisher. Commercial silver nanowire ink was obtained from Dycotec Materials Ltd, and the ionic liquid 1-Ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]) was acquired from Iolitec-Ionic Liquids Technologies GmbH. The substrates used - polyethylene terephthalate (PET), polyimide (Kapton) and polycarbonate (PC) - were obtained from Mitsubishi Polyester Film GmbH, DuPont, and AGI, respectively.

Chapter 4

Experimental methods

4.1 Synthesis of silver nanowires

Silver nanowires were produced according to the polyol method. For that, AgCl was first synthesized. An aqueous solution of 1 M of sodium chloride and an aqueous solution of 0.5 M of silver nitrate were prepared. 5 mL of the NaCl solution were added to the same volume of the AgNO₃ solution under magnetic agitation for 1 minute and protected from light. The mixture resulted in the formation of silver chloride (AgCl) and the supernatant was removed. To produce the silver nanowires, 0.34 g of PVP were dissolved in 20 mL of glycerol and heated to 160°C in a closed vessel. While maintaining the temperature and agitation, 25 mg of AgCl were added to the solution. After 3 minutes, 0.11 g of AgNO₃ were also added, turning the solution yellow due to the formation of silver nanoparticles. The solution was left to react for 15 minutes, developing a dark gray green color, which indicates the formation of the silver nanowires. This process is schematized on Figure 3, while Figure 4 shows the setup (left) and the AgNW ink obtained after the synthesis (right).

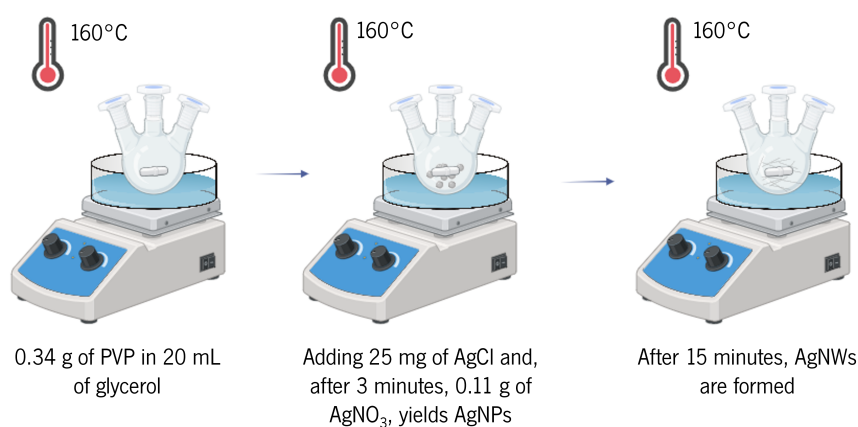


Figure 3: Synthesis of silver nanowires.

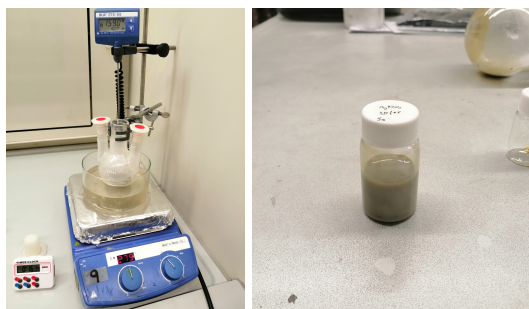


Figure 4: Laboratory setup for the synthesis of AgNWs (left) and the final result of the reaction (right).

The obtained silver nanowires in glycerol were used without any modification or diluted with 40 or 55% (w/w) of methanol in an attempt to increase their adhesion to PEDOT:PSS, while potentially improving the conductivity of the films.

4.2 Film deposition/printing

4.2.1 Deposition/printing methods

In this work, three methods were utilized to produce films: screen-printing, doctor blading, and spin coating (Figure 5). Screen-printing is a reproducible method that results in uniform films [1], as such, it was used to print films of the best approaches throughout the experiments. In this process, the ink is first spread on a screen with a certain mesh size and with a predefined pattern. Then, the screen contacts the substrate and the ink is transferred to it through the passage of a squeegee that pushes the ink through the mesh [77]. The films are formed after curing. Doctor blading is a manual technique for the deposition of films in which a blade or squeegee is used to spread a solution in a substrate, occasionally in the presence of a mask. This results in a thin layer of the solution on the substrate, which forms the film after the evaporation of the solvents. Finally, spin coating is a simple method of depositing films in which a solution is placed on the substrate, which is spun at high velocities for a short period of time, spreading the solution. The thickness of the film obtained after evaporation of the solvents depends on the velocity of the deposition and on the viscosity of the solution utilized [78].

In this work, the use of these diverse deposition methods resulted in films with varying thicknesses, namely in a range between 0.0030 and 0.0110 mm.

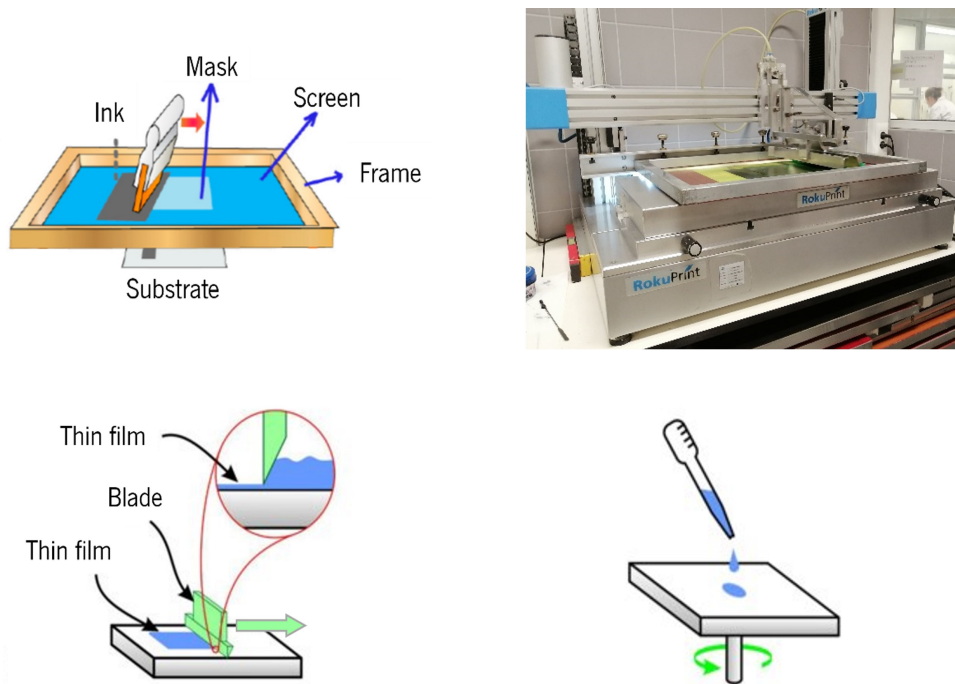


Figure 5: Methods of deposition: Screen-printing schematic and machine used in this work (top), doctor blading and spin coating schematics (bottom). Adapted from [1, 79].

4.2.2 Silver nanowire films

Initially, films of just silver nanowires were prepared. AgNWs in glycerol with 55% (w/w) of methanol were spin coated at 1000 RPM for 40 seconds on PET and PC but showed no effective adhesion to the substrates. Trying to improve the adhesion, the same solution was spin coated on PET, Kapton and PC previously subjected to a 40 W/cm UV treatment mat for two consecutive times, at velocity 0.022 m/s. However, that process did not increase the adhesion of the films to the substrates. Consequently, two layers of commercial AgNW ink were deposited on PET and Kapton using the doctor blade method and dried at 110°C in an oven. Furthermore, as Kapton is more resistant to higher temperature values than PET, two films of this substrate were thermally annealed at 225°C for 1 hour.

4.2.3 PEDOT:PSS and AgNW films

Films of PEDOT:PSS, modified PEDOT:PSS, and PEDOT:PSS with silver nanowires were fabricated on substrates of PET, Kapton, and PC using the three previously mentioned techniques. Each layer was cured at 110°C, and occasionally overnight at 60°C or at room temperature, until the film was visibly dry. Furthermore, several films containing silver nanowires were thermally annealed at 225°C for 1 hour and at 180°C for 5 hours. Table 1 shows the PEDOT:PSS solutions that were used to produce films and the

corresponding deposition methods, the characteristics of the silver nanowire solutions that were utilized to deposit a AgNW film on top of the PEDOT:PSS, unless otherwise specified, and additional information, namely the annealing of some of the samples.

Table 1: Films of PEDOT:PSS, modified PEDOT:PSS and PEDOT:PSS with AgNW deposited through doctor blading, screen-printing or spin coating.

Sample	Deposition of PEDOT:PSS solution	Silver nanowires	Deposition of AgNWs	Additional information
PEDOT:PSS	Doctor blading	AgNWs in glycerol and 55% (w/w) methanol	Spin coating of two layers	
Two layers of PEDOT:PSS	Doctor blading, screen-printing	AgNWs in glycerol and 55% (w/w) methanol	Spin coating	Annealing of some samples for 1 h at 225°C and/or 5 h at 180°C
Three layers of PEDOT:PSS	Screen-printing	AgNWs in glycerol and 55% (w/w) methanol	Spin coating	
Two layers of PEDOT:PSS with an intercalated layer of AgNWs	Doctor blading, screen-printing	AgNWs in glycerol and 55% (w/w) methanol	Doctor blading, spin coating	
Two layers of PEDOT:PSS with 30 or 50 w/w% in water	Doctor blading	AgNWs in glycerol and 55% (w/w) methanol	Doctor blading, spin coating	Annealing of some samples for 1 h at 225°C and/or 5 h at 180°C
PEDOT:PSS aqueous solution of concentration 0.2 g/mL with 4% (V/V) of PEG	Doctor blading	AgNWs in glycerol	Doctor blading	
PEDOT:PSS aqueous solution of concentration 0.2 g/mL with 2.5% (V/V) of AgNWs in glycerol and 4% (V/V) of PEG	Doctor blading			
One or two layers of PEDOT:PSS with 4% (w/w) of PEG and 5% (w/w) of glycerol	Doctor blading	AgNWs in glycerol and in glycerol with 40 or 55% (w/w) methanol	Doctor blading	

PEDOT:PSS glycerol solution of concentration 0.2 g/mL with 10% (V/V) of methanol	Doctor blading	AgNWs in glycerol with 40 or 55% (w/w) methanol	Doctor blading
PEDOT:PSS glycerol solution of concentration 0.4 g/mL with 5% (V/V) of methanol	Doctor blading	AgNWs in glycerol with 40 or 55% (w/w) methanol	Doctor blading
PEDOT:PSS aqueous solution of concentration 0.2 g/mL with 5% (V/V) of glycerol and 10 or 50% (V/V) of methanol	Doctor blading	AgNWs in glycerol and 55% (w/w) methanol	Doctor blading
PEDOT:PSS aqueous solution of concentration 0.2 g/mL with 5% (V/V) of AgNWs in glycerol, and 10% (V/V) of methanol	Doctor blading		
One or two layers of PEDOT:PSS with 10 or 40% (w/w) of DMSO	Doctor blading	AgNWs in glycerol and in glycerol with 40 or 55% (w/w) methanol	Doctor blading

4.2.4 Treatment of films with methanol or DMSO

Initially, films with just one layer of PEDOT:PSS on Kapton were immersed in methanol and DMSO for 5, 20, 40 and 60 minutes to evaluate the effect of different treatment times on the conductivity.

Furthermore, films with PEDOT:PSS on PET, Kapton and PC were also treated with methanol or DMSO after the deposition and curing of each PEDOT:PSS layer. Treatments with methanol were done following two different methods: dropping a methanol drop on the films followed by its evaporation at 110°C in an oven or in a hotplate at 140°C, or immersion in methanol, followed by the same curing processes. Treatments in DMSO consisted in simply immersing the films in it and drying them at 110°C in an oven. Afterwards, a AgNW film was deposited on top of each the treated films, except for the films fabricated with silver nanowires already in solution with PEDOT:PSS. Table 2 and Table 3 detail the characteristics of the films treated with methanol and DMSO, respectively, specifying the PEDOT:PSS solutions used, their deposition method, the type of treatment, the silver nanowire solutions used, their method of deposition, and additional information, namely the annealing and/or other immersion treatments of some of the samples.

Table 2: Characteristics of films with PEDOT:PSS treated in methanol.

Sample	Methods of deposition of PEDOT:PSS solution	Methanol treatment	Silver nanowires	Methods of deposition of AgNWs	Additional information
One or two layers of PEDOT:PSS	Doctor blading	Drop of methanol or drop of methanol followed by immersion for 10 minutes	AgNWs in glycerol and in glycerol with 40 or 55% (w/w) methanol	Doctor blading	
Two layers of PEDOT:PSS	Doctor blading, screen-printing	Immersion for 20 minutes	AgNWs in glycerol and 55% (w/w) methanol	Doctor blading, spin coating	
One or two layers of PEDOT:PSS with 4% (w/w) of PEG	Doctor blading, screen-printing	Immersion for 20 minutes	AgNWs in glycerol and in glycerol with 40 or 55% (w/w) methanol	Doctor blading, spin coating	Annealing of some samples for 1 h at 225°C and/or 5 h at 180°C
Two layers of PEDOT:PSS with 4% (w/w) PEG with an intercalated layer of AgNWs	Doctor blading	Immersion for 20 minutes	AgNWs in glycerol and 55% (w/w) methanol	Doctor blading	
One or two layers of PEDOT:PSS with 25% (w/w) of glycerol	Doctor blading	Drop of methanol or drop of methanol followed by immersion for 10 minutes	AgNWs in glycerol and in glycerol with 40 or 55% (w/w) methanol	Doctor blading	
PEDOT:PSS with 30% (w/w) of AgNWs in glycerol with 55% (w/w) methanol	Doctor blading	Immersion for 20 minutes			

Table 3: Characteristics of films with PEDOT:PSS treated in DMSO.

Samples	Methods of deposition of PEDOT:PSS solution	DMSO treatment	Silver nanowires	Methods of deposition of AgNWs	Additional information
One or two layers of PEDOT:PSS	Doctor blading, screen-printing	Immersion for 30 minutes	AgNWs in glycerol and in glycerol with 40 or 55% (w/w) methanol	Doctor blading, spin coating	Annealing of a set of samples for 1 h at 225°C and/or 5 h at 180°C
Two layers of PEDOT:PSS with an intercalated layer of AgNWs	Doctor blading	Immersion for 30 minutes	AgNWs in glycerol and 55% (w/w) methanol	Doctor blading	
Two layers of PEDOT:PSS with an intercalated layer of AgNWs	Doctor blading	First layer of PEDOT:PSS immersed for 30 minutes	AgNWs in glycerol and 55% (w/w) methanol	Spin coating	
Two layers of PEDOT:PSS with 4% (w/w) of PEG	Doctor blading, screen-printing	Immersed for 30 minutes	AgNWs in glycerol and 55% (w/w) methanol	Doctor blading	
PEDOT:PSS with 4% (w/w) of PEG and 30% (w/w) of AgNWs in glycerol and 55% (w/w) methanol	Doctor blading	Immersed for 30 minutes			
PEDOT:PSS	Doctor blading	Immersed for 30 minutes			Immersion in AgNWs in glycerol and 55% (w/w) methanol for different times

4.2.5 Films with cleaned AgNWs

Silver nanowires obtained from the synthesis were cleaned through centrifugations in ethanol and water, three times each, at 6000 RPM for 10 minutes. The resulting AgNWs powder was added to PEDOT:PSS

after drying but did not disperse in it well.

Trying to overcome this problem, the silver nanowires were instead centrifugated in acetone and water as well, in the same conditions, yielding a higher amount of AgNWs. The resulting nanowires were dispersed through magnetic agitation and ultrasonication in IPA and acetone in equal volumes, resulting in a concentration of approximately 0.6% (w/w). This dispersion was spin-coated on PEDOT:PSS films, showing no adhesion. Subsequently, 0.2 g/mL of PEDOT:PSS was added to it, and the resulting mixture was deposited through spin coating on PET, showing no adhesion as well. Finally, this last mixture was added dropwise to 2 g of PEDOT:PSS until an ink was obtained, which corresponded to the addition of 2 mL. The resulting solution was doctor bladed on PET and cured at room temperature.

Furthermore, the AgNWs obtained after centrifugations in acetone and water were dried and sintered at 250°C for 10 minutes to remove any substances left from the synthesis. These AgNWs were further dispersed in water at a concentration of approximately 0.4% (w/w), added to PEDOT:PSS, and deposited through doctor blading, but did not adhere to the substrate. Moreover, this AgNW dispersion was spin-coated on top of PEDOT:PSS films of two or three layers previously screen-printed on PET or Kapton, which were cured overnight at 60°C in an oven. Finally, AgNWs were mixed, in the same concentration, with ethanol and water at a volume proportion of 3:1 and added to 2 g of PEDOT:PSS until an ink was formed, which corresponded to 2 mL. This solution was doctor bladed onto PET and dried at 110°C in an oven.

4.2.6 Treatment of films with CTAB or sodium borohydride

For a further attempt at increasing the conductivity of the films, a few of the previously mentioned films with PEDOT:PSS and silver nanowires on PET and Kapton were treated with CTAB or sodium borohydride (NaBH_4). The films were soaked in a 0.01 M aqueous solution of CTAB for 3 minutes, rinsed with water, and dried at room temperature. Additionally, as PEDOT:PSS is soluble in water, the same process was applied to identical films, but they were rinsed with ethanol instead. For the borohydride treatment, films were immersed in a 0.5 M solution of equal parts of ethanol and water for 30 seconds, cleaned with water and ethanol, and dried at room temperature. Table 4 displays the characteristics of the films, as well as the treatment they were subjected to.

Table 4: Films treated with CTAB or sodium borohydride.

Sample	Methods of deposition of PEDOT:PSS solution	PEDOT:PSS's layers' treatment	Silver nanowires	Method of deposition of AgNWs	Treatment of the final film
Two layers of PEDOT:PSS	Screen-printing	None	AgNWs in glycerol and 55% (w/w) methanol	Spin coating	CTAB
Two layers of PEDOT:PSS with an intercalated layer of AgNWs	Screen-printing	None	AgNWs in glycerol and 55% (w/w) methanol	Spin coating	CTAB
Two layers of PEDOT:PSS	Screen-printing	Immersion in methanol for 20 minutes	AgNWs in glycerol and 55% (w/w) methanol	Spin coating	CTAB
Two layers of PEDOT:PSS with 4% (w/w) of PEG	Screen-printing	Immersion in DMSO for 30 minutes	AgNWs in glycerol and 55% (w/w) methanol	Spin coating	CTAB
Two layers of PEDOT:PSS	Doctor blading	None	AgNWs in glycerol and 55% (w/w) methanol	Spin coating	NaBH ₄
Two layers of PEDOT:PSS with an intercalated layer of AgNWs	Doctor blading	None	AgNWs in glycerol and 55% (w/w) methanol	Doctor blading	NaBH ₄
Two layers of PEDOT:PSS	Doctor blading	Immersion in methanol for 20 minutes	AgNWs in glycerol and 55% (w/w) methanol	Doctor blading	NaBH ₄

4.2.7 Ionic liquid and PVA

An ionic liquid was used to enhance the conductivity of some of the already deposited films. With that purpose, the ionic liquid 1-Ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]) was spin coated on three films: PEDOT:PSS, two layers of PEDOT:PSS with one layer of AgNWs in glycerol and 55% (w/w) methanol, and two layers of PEDOT:PSS with an intercalated layer of the same AgNW solution, all deposited

through doctor blading. As another treatment, films identical to the last two previously mentioned were immersed in the ionic liquid for 10 minutes. In both treatments the films were further dried at 110°C. Additionally, PEDOT:PSS with approximately 30% (w/w) of [EMIM][BF₄] was spin coated on PET and cured at room temperature.

Furthermore, given PVA's very high transparency and flexibility, it was utilized alongside the ionic liquid to produce films with PEDOT:PSS and silver nanowires. First, a solution of 1.5 g of PVA and 10 mL of water was prepared and left in magnetic agitation for 1 hour at 90°C, to which the ionic liquid was added, at room temperature, in a ratio of 0.8:1 relatively to PVA's weight. Then, 1.5 mL of this solution were poured on a Petri dish and left to form a film at room temperature. Solutions with 5 mM and 10 mM of silver nitrate were further prepared by adding the AgNO₃ to the previous solution and agitating for an additional hour at 90°C, and films were formed using the same method. Additionally, the solution of PVA, ionic liquid, and 5mM of AgNO₃ was spin coated on PEDOT:PSS, or added to it in concentrations of 20, 50, and 80% (w/w), and films were doctor bladed on PET and left to dry at room temperature. Furthermore, the same processes were followed but with ionic liquid in a ratio of approximately 3:1 in comparison to PVA's weight.

Moreover, a film of PVA and AgNWs was also produced. For that, 1.5 g of PVA were dissolved in 10 mL of water and agitated for 1 hour at 90°C. 10 mL of AgNWs in IPA and acetone of concentration 0.6% (w/w) were added dropwise while maintaining agitation and the temperature. 1.5 mL of the solution were deposited on a Petri dish and the film was left to form at room temperature.

4.3 Characterization of the films

Aliquots of the silver nanowires' synthesis were taken at 5 minute intervals, diluted in water and characterized by UV-Vis. UV-Vis characterization (absorption) of AgNWs solution ($\approx 10^{-6}$ M) was performed with a diode array spectrophotometer by the Agilent 8453 UV-Vis spectroscopy instrument (PerkinElmer, Lambda 35). The experimental spectra were recorded over the range of 200–800 nm at 298 K.

The films deposited throughout all the experiments had their resistances measured with a Fluke or Keysight digital multimeter.

An Insize digital micrometer with range 0 – 25 mm was used to measure the thickness of films, allowing for a comparison between the doctor blade and screen-printing techniques.

A FLIR ThermoVision A320 infrared camera and the ThermaCAM software were used to observe the changes in the average temperature of films on Kapton, PET and PC substrates with the application of a

voltage of 12 V by a power source.

Finally, the morphology of the different films was analysed by high-resolution scanning electron microscopy (SEM, FEI Nova 200 (FEG/SEM) instrument) at the Serviços de Caracterização de Materiais da Universidade do Minho (SEMAT) services. SEM micrographs were acquired using the secondary electrons detector (SED). The acceleration voltage was 10 keV, while an in-lens detector was employed with a working distance of about 10 mm.

Chapter 5

Results and discussion

5.1 UV-Vis characterization of silver nanowires

Figure 6 displays the results from the UV-Vis characterization for aliquots taken at 5 minute intervals from the synthesis of the silver nanowires, showing the emergence of an absorption peak at around 370 nm and a much weaker peak at around 350 nm, which are associated with the presence of silver nanowires [80] at the end of the reaction.

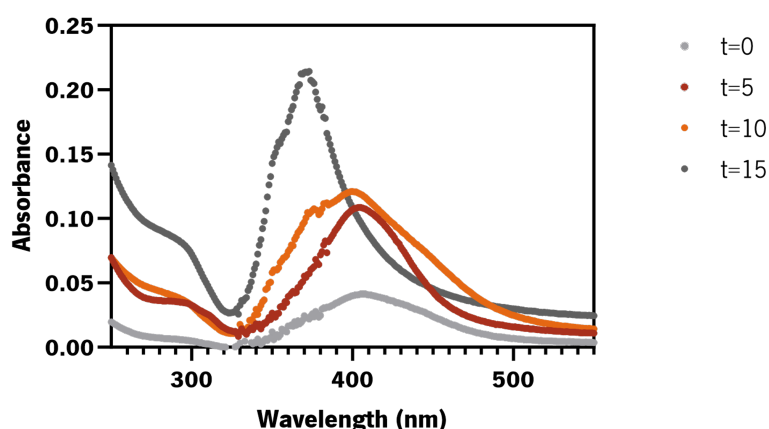


Figure 6: Ampliation of the UV-Vis characterization of the synthesized silver nanowires for wavelengths between 250 and 550 nm.

5.2 Film designs

Four different designs were used for the deposition of the films throughout the experiments. In the following results and discussion, they will be labeled as the preliminary design and the 1st, 2nd and 3rd designs according to their length, as shown in Figure 7. These designs had areas of approximately 4, 6, 8, and 12 cm², respectively.

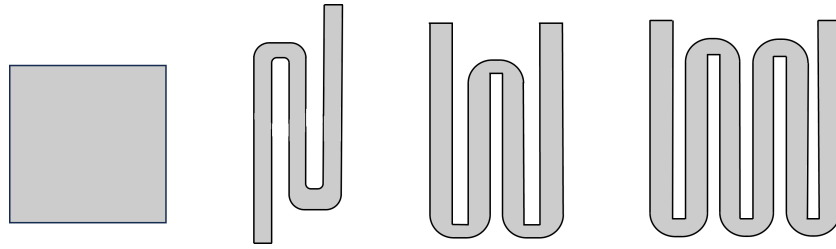


Figure 7: Preliminary, 1st, 2nd, and 3rd designs, in this order.

5.3 Silver nanowire films

Figure 8 shows the resistance of films with one and two layers of commercial silver nanowire ink deposited through doctor blading onto Kapton and PET substrates. While the deposition of one layer originated films with low resistances, the addition of another layer increased the resistance to hundreds of millions of ohms, likely due to a considerable increase in the number of junctions between AgNWs, which have high resistance. Furthermore, two films were subjected to annealing, which substantially decreased their resistance to values around 5 k Ω . Some reports refer that the annealing allows a better electrical conductivity performance [60, 61, 62, 63].

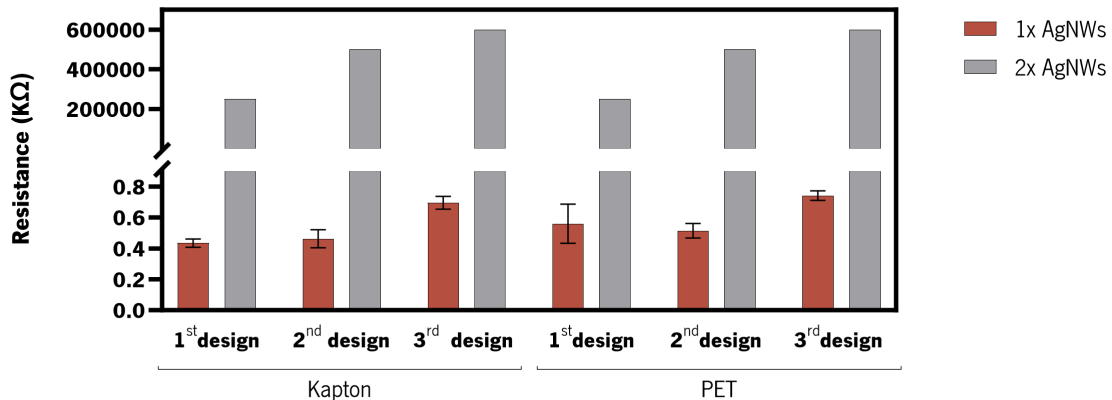


Figure 8: Resistance of films with one and two layers of commercial silver nanowire ink.

5.4 PEDOT:PSS and AgNW films

5.4.1 Effect of number of layers of the PEDOT:PSS films

Initially, PEDOT:PSS films were deposited through doctor blading on PET and as-synthesized AgNWs in glycerol and 55% (w/w) methanol were spin coated on top, which resulted in a decrease in the electrical

resistance. Additionally, another layer of AgNWs was deposited with the same method, which increased the conductivity of the film further. Figure 9 demonstrates the resistance's variations with the addition of each layer.

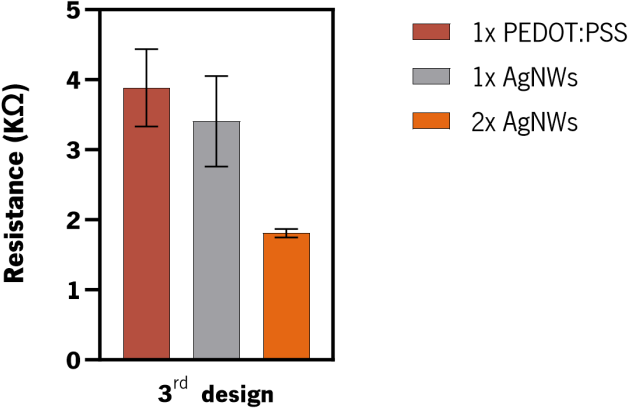


Figure 9: Resistance for films with subsequential layers of PEDOT:PSS and AgNWs.

The effect of the number of PEDOT:PSS layers and their thickness was further studied.

Films with two layers of PEDOT:PSS and one layer of the same solution of AgNWs deposited through doctor blading and spin coating, respectively, demonstrated similar final resistances to the previous approach (Figure 10), although the second layer of PEDOT:PSS caused a higher decrease in the resistance than the first AgNW layer in the previous film. Additionally, the thermal annealing of the films in Kapton resulted in a decrease in their conductivity. It seems that the effect of the one layer of AgNWs deposited in one layer of PEDOT:PSS is explained by an increment of thickness.

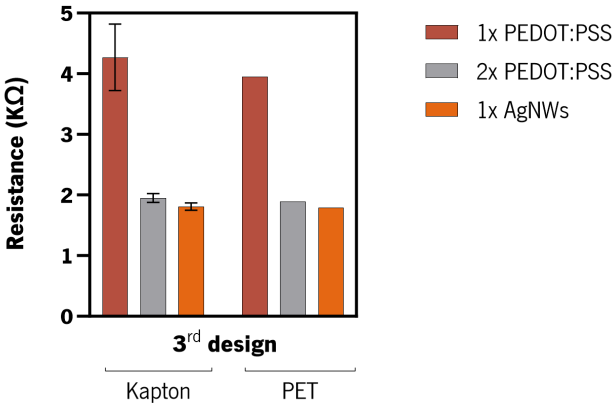


Figure 10: Resistance variations for films with two layers of PEDOT:PSS and one layer of AgNWs in glycerol with 55% (w/w) methanol.

The same solutions were used to produce films on PET through the screen-printing of the two PE-

DOT:PSS layers, while the AgNWs solution was deposited through spin coating. Figure 11 shows the resistance associated with the addition of each layer to the film. Even though screen-printing is a more reproducible technique, the resulting films have higher resistance due to the thinner PEDOT:PSS layers. In comparison to the average (0.0050 ± 0.0009) mm thickness obtained by the doctor blading method, screen-printed layers had an average thickness of (0.0030 ± 0.0002) mm.

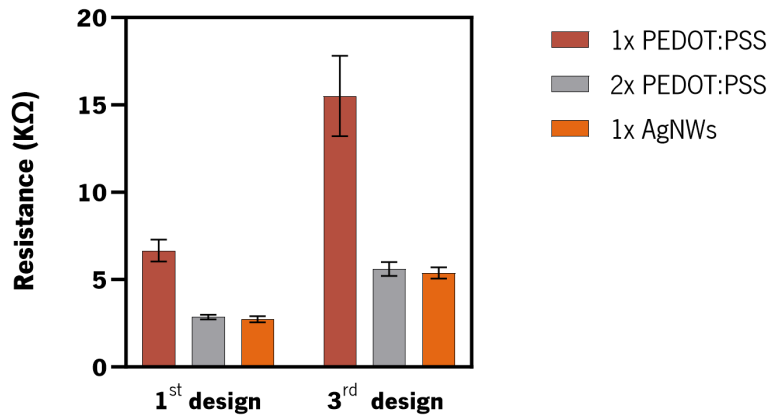


Figure 11: Resistance variations for films with two layers of screen-printed PEDOT:PSS and one layer of AgNWs.

Figures 12 and 13 show photographs of samples obtained by this approach without and with the AgNWs layer, respectively, on the left, and their corresponding SEM images on the right. Figure 13 reveals the even dispersion of the as-synthesized AgNWs across the PEDOT:PSS film. It demonstrates the quality of the AgNW synthesis process given that the AgNWs had consistent dimensions, and that the nanowires stayed on PEDOT:PSS' surface and did not penetrate it, which can be attributed to the film's homogeneity and compactness.

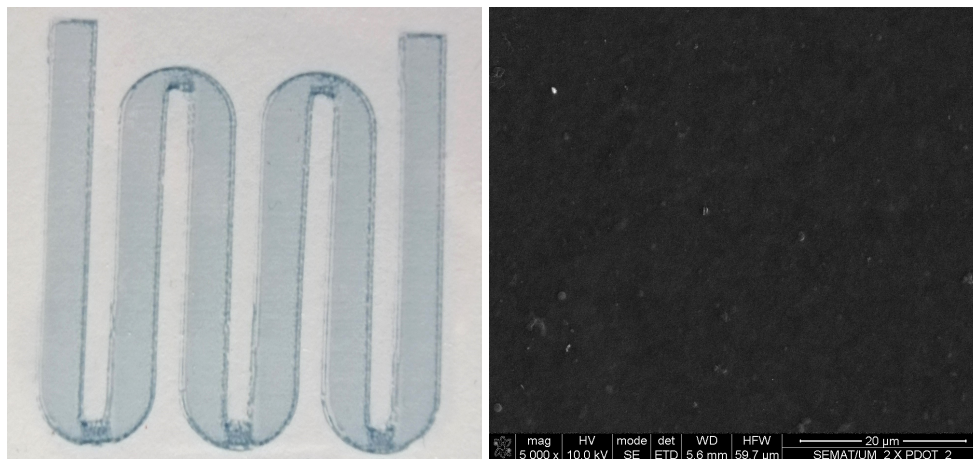


Figure 12: Photograph (left) and SEM image (right) of two layers of screen-printed PEDOT:PSS.

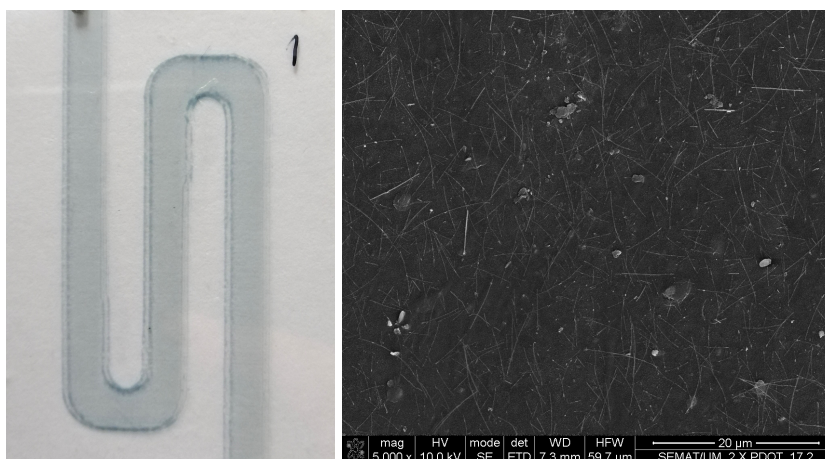


Figure 13: Photograph (left) and SEM image (right) of a film with two screen-printed layers of PEDOT:PSS and one layer of AgNWs.

To further test the influence of the thickness of the layers, this process was exceptionally repeated with a screen-printing mesh of bigger size, which resulted in the passage of more ink onto the PET substrate and consequently in thicker films, of average (0.0110 ± 0.0006) mm. Figure 14 shows the resistances of the last PEDOT:PSS layer and of the final film (with AgNWs). Even though the resistances of the PEDOT:PSS layers were lower than in all of the prior films, the addition of the silver nanowires did not decrease them significantly. This approach showed the highest increase in temperature among all films throughout this work, likely due to also having the highest thickness.

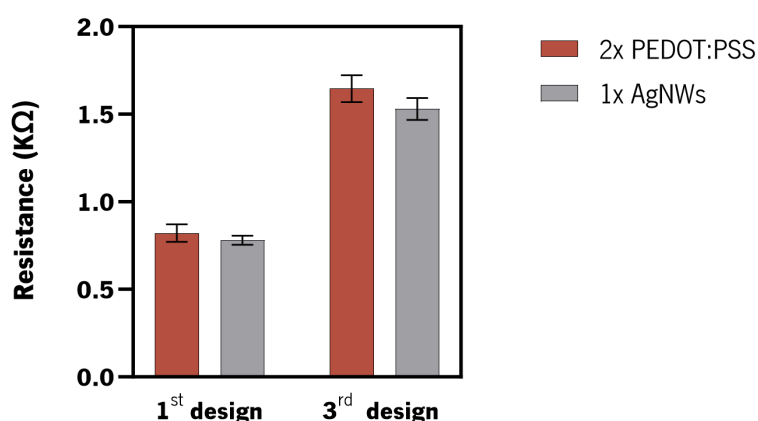


Figure 14: Resistance variations for films with two layers of PEDOT:PSS and one layer of AgNWs. The screen-printing of the PEDOT:PSS layers was carried out with a bigger mesh size, which resulted in thicker films.

Figure 15 shows a photograph of a film obtained with this approach, as well as its SEM image, in which it is noticeable the non-uniform distribution of the AgNWs, which could be due to the difference in

the roughness of the film. Furthermore, the scarce dispersion of the nanowires does not allow for the creation of a AgNW network, which could result in higher conductivities. This, alongside the fact that the AgNWs are only on the film's surface, corroborates the presumption that the lower resistances of the films were mainly due to their higher thickness and not due to different interactions between the nanowires and the underlying PEDOT:PSS.

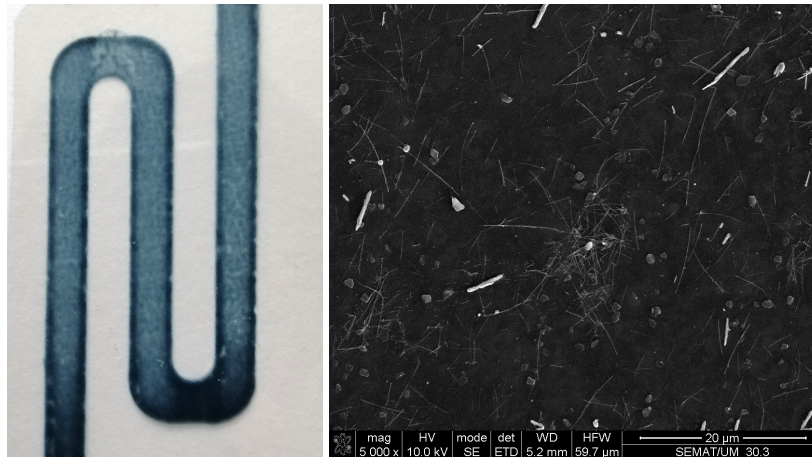


Figure 15: Film with two layers of screen-printed PEDOT:PSS with bigger mesh size and one layer of AgNWs and its corresponding SEM image.

Additionally, Figure 16 shows two infrared pictures of films obtained with this approach at the highest temperature they could reach, which corresponded to average increases in the temperature values of (4.8 ± 0.1) and $(2.0 \pm 0.1)^\circ\text{C}$ for the 1st and 3rd designs, respectively.

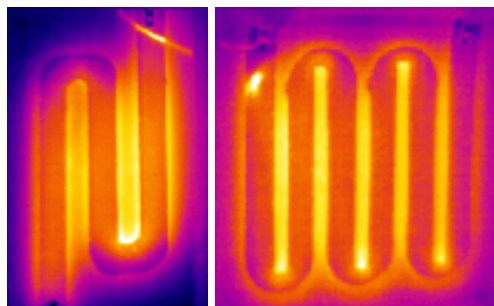


Figure 16: Infrared pictures of heated films of two screen-printed layers of PEDOT:PSS with a bigger mesh size and one layer of AgNWs.

Furthermore, films with three layers of PEDOT:PSS were screen-printed on PET, and a layer of the same AgNWs solution was spin coated on top. Figure 17 displays the variation in resistance caused by the addition of each layer. Although the layer of silver nanowires did not significantly reduce the resistance, the third layer of PEDOT:PSS decreased it considerably. With an average thickness of (0.0050 ± 0.0005) mm,

these films showed conductivities similar to the films with two layers of doctor bladed PEDOT:PSS, likely due to the identical thicknesses, but lower than the films with two screen-printed layers of PEDOT:PSS with bigger mesh size, which were thicker.

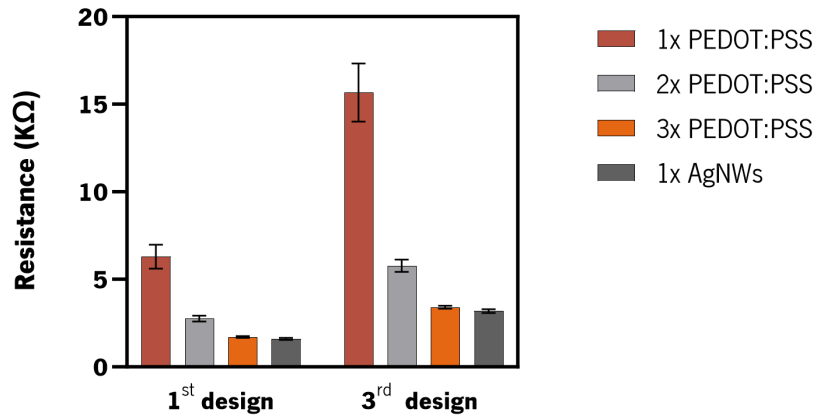


Figure 17: Variation of the resistance for films with three layers of screen-printed PEDOT:PSS and one layer of spin-coated AgNWs.

A photograph of a film obtained with this approach is shown in Figure 18, along with its SEM image. Similar to other films, the AgNWs had an even dispersion, even though it was scarce, which could explain the lack of effect of the AgNW layer on the resistance of the film.

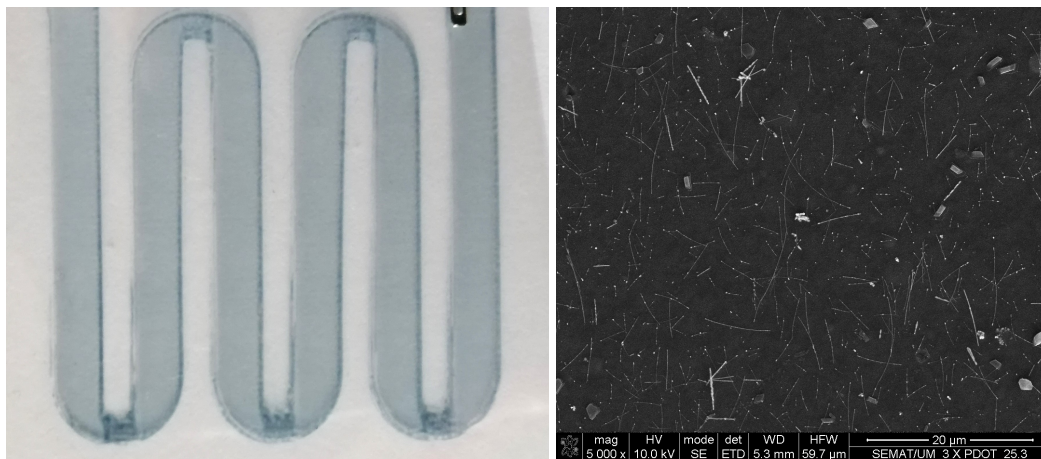


Figure 18: Photograph of a film with three layers of screen-printed PEDOT:PSS and one layer of AgNWs, and its SEM image.

Finally, films with intercalated silver nanowires and PEDOT:PSS were produced. Figure 19 shows the variation of the resistance for PEDOT:PSS deposited through doctor blading with intercalated spin-coated as-synthesized AgNWs in glycerol and 55% (w/w) methanol on Kapton, and for the same approach but with

screen-printed PEDOT:PSS on PET. These films had average thicknesses of (0.0050 ± 0.0020) and (0.0040 ± 0.0004) mm, respectively. The similar thicknesses could explain the similar conductivities between films of screen-printed PEDOT:PSS with intercalated and non-intercalated AgNWs shown previously.

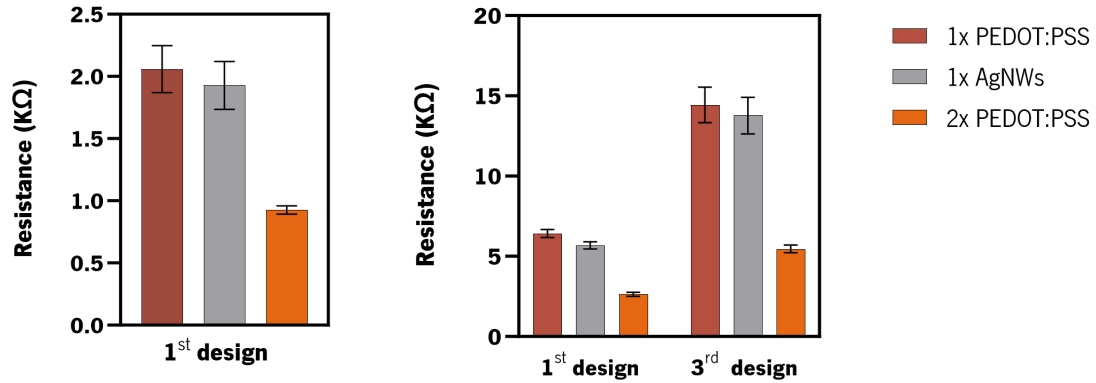


Figure 19: Resistance fluctuation for films with a AgNW layer intercalated in PEDOT:PSS layers deposited through doctor blading (left) and screen-printing (right).

In essence, these results are in accordance with the previously mentioned works developed by He et al. [1], Ji et al. [5], and Rezvani et al. [69], in which the resistance of films of PEDOT:PSS and AgNWs was lower than films of just one of the substances. The thickness of the films seemed to be the main factor in their final resistance, while the addition of a layer with silver nanowires usually decreased it only slightly. A future study using different AgNWs concentrations should be performed.

Table 5 shows the temperature variation of these films when subjected to an input voltage of 12 V. Most of the films increased their temperature insignificantly, except for the film with screen-printed PEDOT:PSS with the bigger mesh size which, due to having the lowest resistance, increased its temperature the most, by almost 5°C.

Table 5: Resistances and increase in temperature for films with PEDOT:PSS and AgNWs.

Sample	Design	Average Resistance (k Ω)	Average temperature increase ($^{\circ}\text{C}$)
1x PEDOT:PSS	3 rd	1.810 \pm 0.035	1.1 \pm 0.3
2x PEDOT:PSS (doctor blading)	3 rd	1.765 \pm 0.025	1.3 \pm 1.1
2x PEDOT:PSS (screen-printing)	1 st	2.733 \pm 0.085	1.3 \pm 0.1
	3 rd	5.380 \pm 0.0147	0.5 \pm 0.1
2x PEDOT:PSS (screen-printing - bigger mesh)	1 st	0.781 \pm 0.011	4.8 \pm 0.1
	3 rd	1.530 \pm 0.026	2.0 \pm 0.1
3x PEDOT:PSS	1 st	1.598 \pm 0.024	2.2 \pm 0.1
	3 rd	3.188 \pm 0.048	0.9 \pm 0.1
Doctor bladed PEDOT:PSS with an intercalated layer of AgNWs	1 ^s	0.926 \pm 0.017	2.9 \pm 0.2
Screen-printed PEDOT:PSS with an intercalated layer of AgNWs	1 st	2.634 \pm 0.056	1.1 \pm 0.1
	3 rd	5.464 \pm 0.110	0.3 \pm 0.2

Furthermore, Figure 20 shows how the average temperature of the films increased approximately linearly with the inverse of their resistance. Thus, the lower the resistance of the films the higher the increase in their temperature.

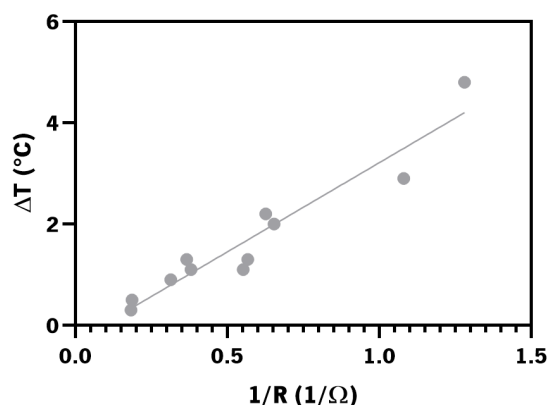


Figure 20: Average temperature increase (ΔT) for the inverse of the resistances ($1/R$) of the films discussed in this section.

5.4.2 Films with modified PEDOT:PSS

In an effort to obtain films with better conductivities, different solvents were added to PEDOT:PSS. According to the aforementioned reports by Wang et al. [31], Mengistie et al. [32], Li et al. [33], and

Snaith et al. [27], the addition of PEG, glycerol, or both, to PEDOT:PSS decreases the resistance of the resulting films. Furthermore, in the previously mentioned works by Alemu et al. [28], Jikei et al. [29], and Lingstedt et al. [30], for instance, the combination of methanol or DMSO with PEDOT:PSS can also enhance the conductivity of films. As such, all of these approaches were taken in this work, and the results are displayed henceforth.

Initially, films of PEDOT:PSS with two layers were doctor bladed onto Kapton and PET in the preliminary design with the aim of having another benchmark for the following results. Films with one layer had an average resistance of $(0.365 \pm 0.005) \text{ k}\Omega$, while the addition of the second layer lowered the resistance to an average of $(0.185 \pm 0.005) \text{ k}\Omega$.

Figures 21 and 22 show the variation of the resistance for films with two doctor bladed layers of PEDOT:PSS with 30 or 50% (w/w) of water, as well as an additional spin-coated layer of as-synthesized AgNWs in glycerol and 55% (w/w) methanol. Films with more water had PEDOT:PSS layers with higher resistances, likely due to its dilution, which was reflected in their final resistance. These results demonstrate that water could break the interaction between PEDOT and PSS monomers, leading to a decrease in conductivity. The silver nanowires layer decreased the resistance only slightly, which could be explained by the weak dispersion and alignment of the nanowires between PEDOT:PSS chains. Furthermore, the thermal annealing of random samples of both approaches, at 225°C for 1 hour and at 180°C for 5 hours, resulted in a decrease of the conductivity of the films.

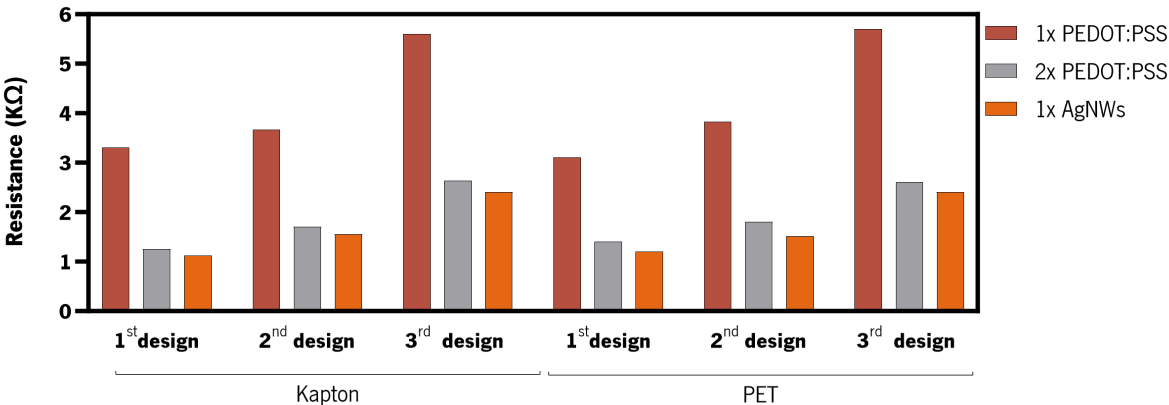


Figure 21: Resistance for each layer of films with PEDOT:PSS with 30% (w/w) of water. Films in the 1st design had lower resistances probably due to their smaller area.

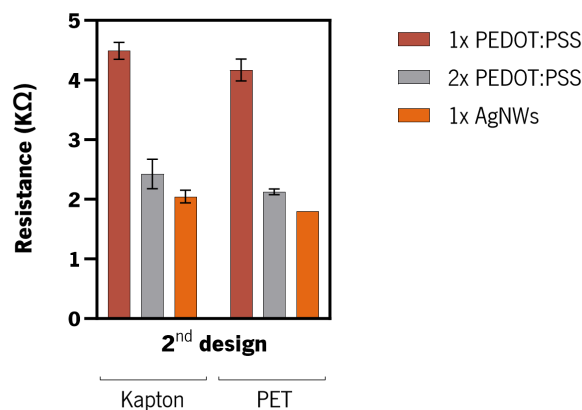


Figure 22: Resistance variation for films with PEDOT:PSS with 50% (w/w) of water.

PEDOT:PSS modified with PEG was also utilized for the production of films. For that, an aqueous solution of PEDOT:PSS with PEG and an additional layer of as-synthesized AgNWs in glycerol were deposited through doctor blading on Kapton. However, for both of these layers the resistances were higher than 600 MΩ. Moreover, the same method was used to deposit a solution of the same concentrations but with an additional 2.5% (V/V) of as-synthesized AgNWs in glycerol. Nevertheless, this also resulted in films with resistances of millions of ohms, which were not applicable in the objective of this work.

Furthermore, films of PEDOT:PSS treated with PEG and glycerol were produced on Kapton substrate. Figure 23 displays the variation of the resistances with the addition of each layer, for films with one or two layers of PEDOT:PSS with PEG and glycerol and another layer of as-synthesized AgNWs, all deposited through doctor blading. AgNWs in glycerol (GLY) or in glycerol with 40 or 55% (w/w) of methanol (MeOH) were used due to potential interactions between methanol, glycerol and PEG, as they are all polyols (all have an OH group). The results demonstrate a lack of uniformity, as the resistances of the first PEDOT:PSS layer were significantly different, even though they were deposited by the same method, and the addition of the same AgNWs solutions did not have similar effects in both types of films.

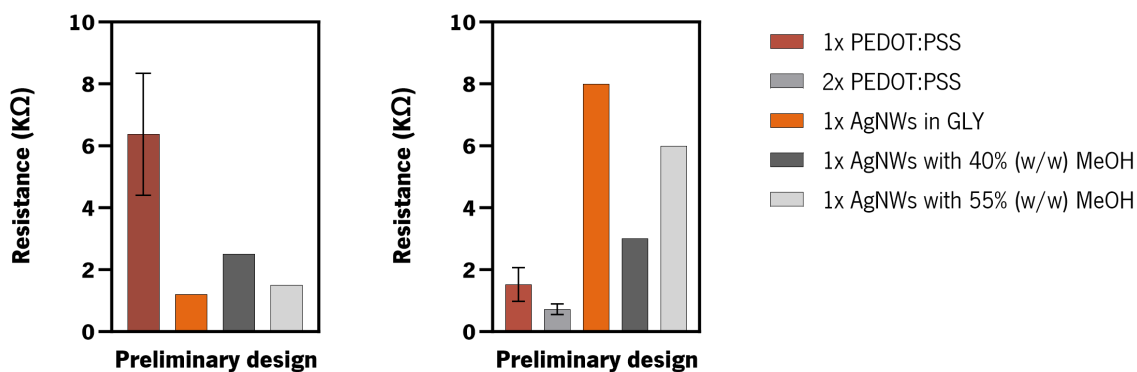


Figure 23: Resistance of films with one or two layers of PEDOT:PSS with PEG and glycerol, and one layer of AgNWs.

Moreover, glycerol solutions with PEDOT:PSS and methanol were also used to fabricate films. First, a PEDOT:PSS glycerol solution of concentration 0.2 g/mL with 10% (V/V) of methanol was deposited on Kapton, as well as an additional layer of as-synthesized AgNWs in glycerol, or in glycerol with 40 or 55% (w/w) of methanol, both through the doctor blading method. In this approach, the resistances were inconsistent for both layers, ranging from hundreds of thousands to hundreds of millions of ohms, which represented a too low conductivity for the application studied in this work. Additionally, the same methods were used for the fabrication of films of a PEDOT:PSS glycerol solution of concentration 0.4 g/mL with 5% (V/V) of methanol, with further deposition of similar AgNWs layers, in the same substrate. Although the average resistance did not variate consistently, as seen in Figure 24, for individual samples the application of a layer of AgNWs in glycerol with 55% (w/w) of methanol did result in a slight decrease of the resistance. The same solvents systems in PEDOT:PSS and AgNWs seemed to work better.

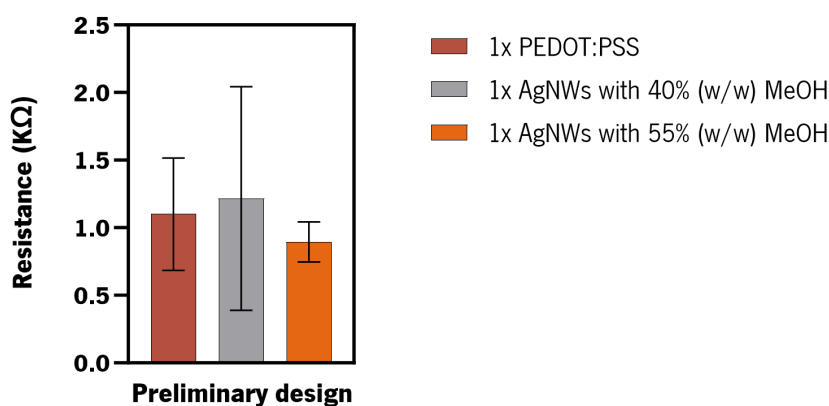


Figure 24: Resistance variation of films with one layer of a PEDOT:PSS glycerol solution of concentration 0.4 g/mL with 5% (V/V) of methanol and another layer of AgNWs.

Based on these results, PEDOT:PSS aqueous solutions with glycerol and different concentrations of methanol were further used to produce films. These solutions were doctor bladed on Kapton, as well as an additional layer of as-synthesized AgNWs in glycerol with 55% (w/w) methanol. The results are displayed in Figure 25, which shows that a higher percentage of methanol resulted in films with substantially greater resistances as well as leading to an abnormal increase of the resistance with the addition of the AgNW layer. This increase in the resistance is explained by the strong interaction of water and methanol. The presence of water reduced the effect of methanol.

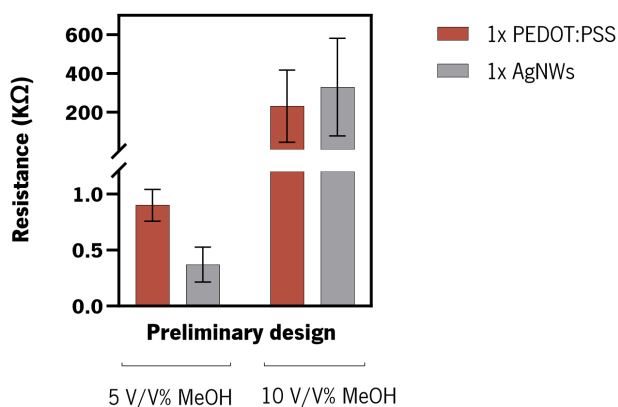


Figure 25: Resistances for films of PEDOT:PSS aqueous solutions with glycerol and 5 or 10% (V/V) of methanol, and one layer of AgNWs.

As a result of these findings, a similar PEDOT:PSS solution with 10% (V/V) of methanol and as-synthesized AgNWs in glycerol in the same concentration as the glycerol in the previous solution was doctor bladed on Kapton in the preliminary design. The resulting films had an average resistance of (1.333 ± 0.816) kΩ, which was higher than that of the separated layers of the previous approach. The alcohols caused a misalignment of the PEDOT and PSS chains, leading to a decrease in the electrostatic interactions and a decrease of electrical conductivity.

Furthermore, PEDOT:PSS was modified with different concentrations of DMSO. Films of one or two layers of PEDOT:PSS with 10 or 40% (w/w) of DMSO were doctor bladed on Kapton, as well as another layer of as-synthesized AgNWs, whether in glycerol or in glycerol with 40 or 55% (w/w) of methanol. Figure 26 shows the resistances of films with 10% (w/w) of DMSO. Despite the inconsistency of the results, the films had a low final resistance.

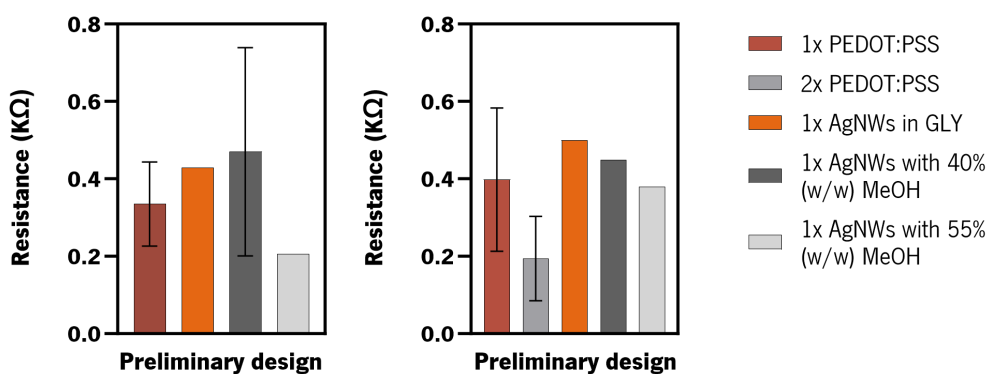


Figure 26: Resistance variation with each layer for films with one or two layers of PEDOT:PSS with 10% (w/w) DMSO and one layer of AgNWs.

Figure 27 shows the results obtained for PEDOT:PSS with 40% (w/w) of DMSO. In this case, the addition of a second layer of the PEDOT:PSS solution produced a significant decrease in the resistance, while a slight decrease was caused by the silver nanowire layer. Nevertheless, these films showed similar resistances to the ones obtained by the previous method. These results confirm the effect of DMSO in PEDOT:PSS, already reported in [29] and [30], for instance. In fact, contrary to other solvents, DMSO tends to align the PSS monomers in the PEDOT chains, increasing the electrostatic interactions and enhancing the electrical conductivity.

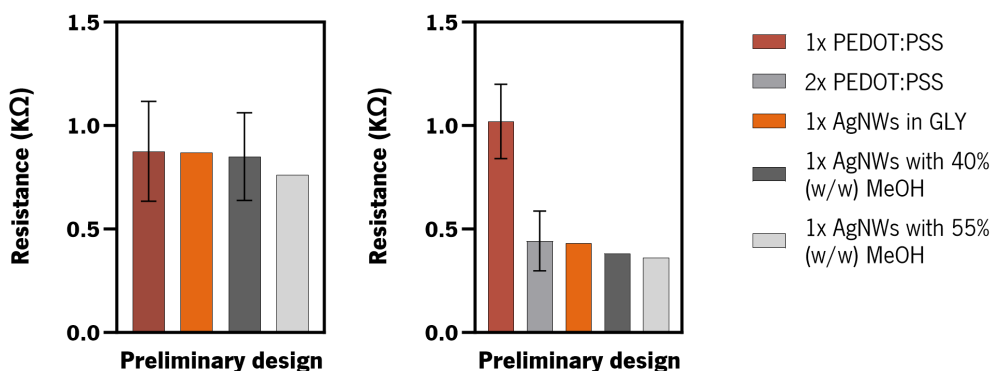


Figure 27: Resistance variation with each layer for films with one or two layers of PEDOT:PSS with 40% (w/w) DMSO and one layer of AgNWs.

Table 6 summarizes the results presented in this section.

Table 6: Summary of the results obtained for films with modified PEDOT:PSS.

Sample	Design	Average resistance (kΩ)	
2x PEDOT:PSS with 30% (w/w) in water	1 st	1.160 \pm 0.040	
	2 nd	1.530 \pm 0.020	
	3 rd	2.400	
2x PEDOT:PSS with 50 % (w/w) in water	2 nd	1.960 \pm 0.160	
1x PEDOT:PSS with PEG	Preliminary	Millions of Ω	
1x PEDOT:PSS with PEG and 2.5% (V/V) of AgNWs in glycerol	Preliminary	Millions of Ω	
1x PEDOT:PSS with PEG and glycerol	Preliminary	AgNWs in GLY	1.200
		AgNWs with 40% (w/w) MeOH	2.500
		AgNWs with 55 w/w% MeOH	1.500
2x PEDOT:PSS with PEG and glycerol	Preliminary	AgNWs in GLY	8.000
		AgNWs with 40% (w/w) MeOH	3.000
		AgNWs with 55% (w/w) MeOH	6.000
1x PEDOT:PSS glycerol solution of concentration 0.2 g/mL with 10% (V/V) methanol	Preliminary	Millions of Ω	

1x PEDOT:PSS glycerol solution of concentration 0.4 g/mL with 5% (V/V) methanol	Preliminary	AgNWs with 40% (w/w) MeOH	1.215 ± 0.585
		AgNWs with 55% (w/w) MeOH	0.895 ± 105
1x PEDOT:PSS with glycerol and 5% (V/V) methanol	Preliminary		0.370 ± 0.110
1x PEDOT:PSS with glycerol and 10% (V/V) methanol	Preliminary		Millions of Ω
1x PEDOT:PSS with AgNWs in glycerol and 10% (V/V) methanol	Preliminary		1.333 ± 0.816
1x PEDOT:PSS with 10% (w/w) DMSO		AgNWs in GLY	0.430
	Preliminary	AgNWs with 40% (w/w) MeOH	0.470 ± 0.155
		AgNWs with 55% (w/w) MeOH	0.207 ± 0.030
2x PEDOT:PSS with 10% (w/w) DMSO		AgNWs in GLY	0.500
	Preliminary	AgNWs with 40% (w/w) MeOH	0.450
		AgNWs with 55% (w/w) MeOH	0.380
1x PEDOT:PSS with 40% (w/w) DMSO		AgNWs in GLY	0.870
	Preliminary	AgNWs with 40% (w/w) MeOH	0.850 ± 0.150
		AgNWs with 55% (w/w) MeOH	0.760 ± 0.140
2x PEDOT:PSS with 40% (w/w) DMSO		AgNWs in GLY	0.430
	Preliminary	AgNWs with 40% (w/w) MeOH	0.380
		AgNWs with 55% (w/w) MeOH	0.360

5.4.3 Treatment of films with methanol or DMSO

Still following the works by Alemu et al. [28] and Lingstedt et al. [30], in which films were also post-treated with methanol or DMSO, respectively, these methods were also utilized in an attempt to increase the conductivity of films with PEDOT:PSS and silver nanowires. After curing, each layer of PEDOT:PSS was treated using a drop of methanol, by immersion in methanol, both, or simply by immersion in DMSO.

Initially, films with one layer of PEDOT:PSS on Kapton were immersed in methanol or DMSO for different

periods of time, and the effects of these treatments on the resistance of the films are shown on Figures 28 and 29, respectively. Both techniques resulted in practically no variation of the resistance of the films, independently of the treatment time.

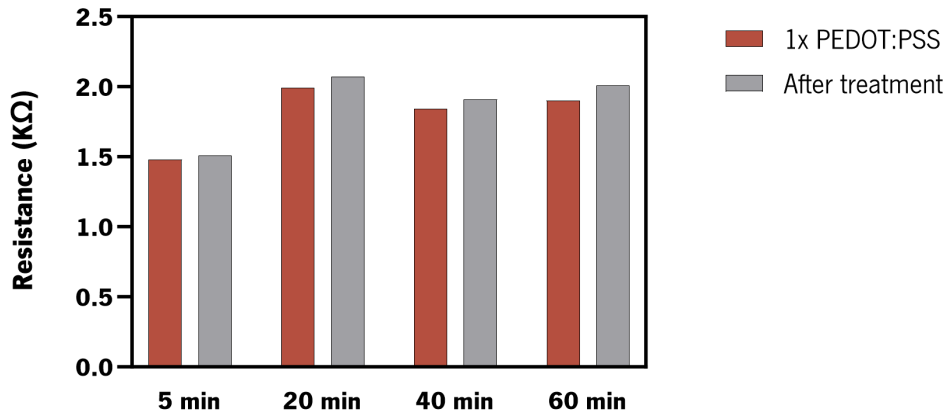


Figure 28: PEDOT:PSS films treated with immersion in methanol for different times.

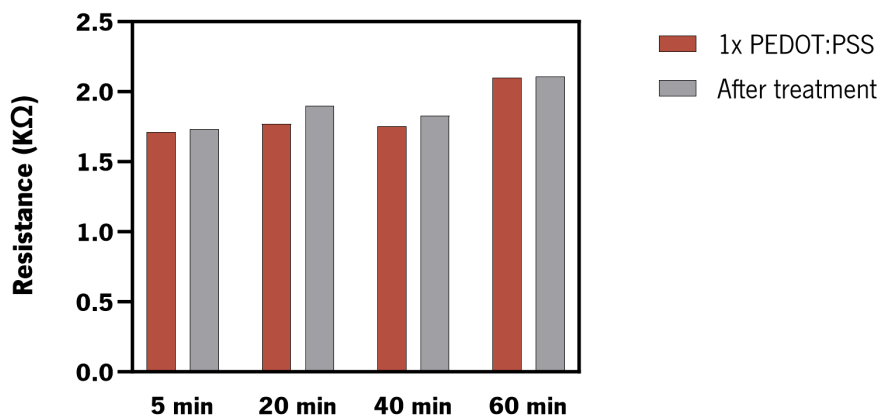


Figure 29: PEDOT:PSS films treated with immersion in DMSO for different times.

Nevertheless, films with PEDOT:PSS and AgNWs were still subjected to these treatments. Since the treatment time seemed to have a minimal impact on the final resistance of the films, the treatment with methanol was applied for the time reported in the work by Alemu et al. [28], 10 minutes, or for 20 minutes, while the immersion in DMSO was carried out for the same time as in the work by Lingstedt et al. [30], 30 minutes.

Initially, films of one or two doctor bladed PEDOT:PSS layers on Kapton were treated with a drop of methanol. A layer of as-synthesized AgNWs in glycerol or in glycerol with 40 or 55% (w/w) of methanol was subsequently doctor bladed on the films. The results associated with these films are shown in Figure

30. As in previous approaches, the addition of a second layer of PEDOT:PSS caused a decrease in the resistance, which was reflected in the final resistance of the films, even though the addition of the AgNWs did not lead to a significant change in the resistance. Furthermore, in the case of films with just one layer of PEDOT:PSS, there was a considerable uncertainty associated with the resistance of the film after the deposition of AgNWs in glycerol.

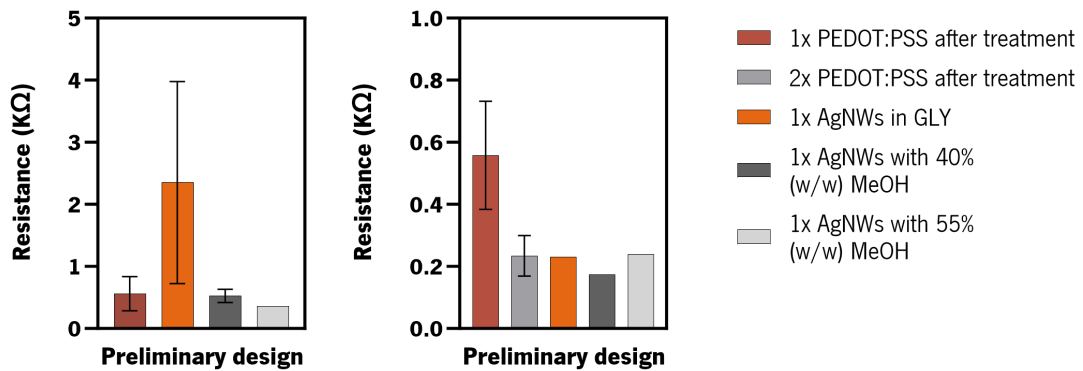


Figure 30: Resistances for films with one or two layers of PEDOT:PSS treated with a drop of methanol and further deposition of AgNWs.

Afterwards, identical samples were treated with a drop of methanol followed by immersion in it. Figure 31 displays the variations in the resistance with the addition of each layer. As in the previous method, for films with one layer of PEDOT:PSS, the resistance associated with addition of a layer of AgNWs in glycerol had a high uncertainty, and the film with the double layer of PEDOT:PSS showed better conductivity. Furthermore, this treatment resulted in films with lower resistances than the previous one.

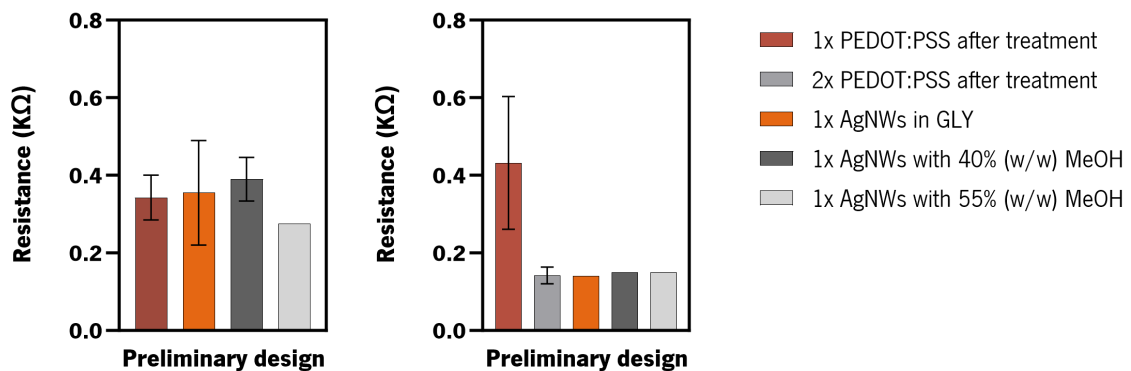


Figure 31: Variations in the resistance for films with one or two layers of PEDOT:PSS treated with a drop of methanol followed by immersion, and an additional layer of AgNWs.

As the immersion seemed to have a more significant effect on the resistance of the films, films with two

layers of PEDOT:PSS were treated with this method, followed by the deposition of as-synthesized AgNWs in glycerol with 55% (w/w) of methanol. Figures 32 and 33 show the resistances associated with each step of the process for films with doctor bladed or screen-printed PEDOT:PSS, respectively, and spin-coated AgNWs, on PET. In both cases the treatment resulted in practically no variation in the resistance, especially when compared to the effect of the addition of the second layer of PEDOT:PSS. As in previous approaches, the screen-printing technique originated films with lower conductivities, presumably due to their smaller thickness, (0.0040 ± 0.0005) mm, when compared to the thickness of the doctor bladed films, (0.0050 ± 0.0006) mm.

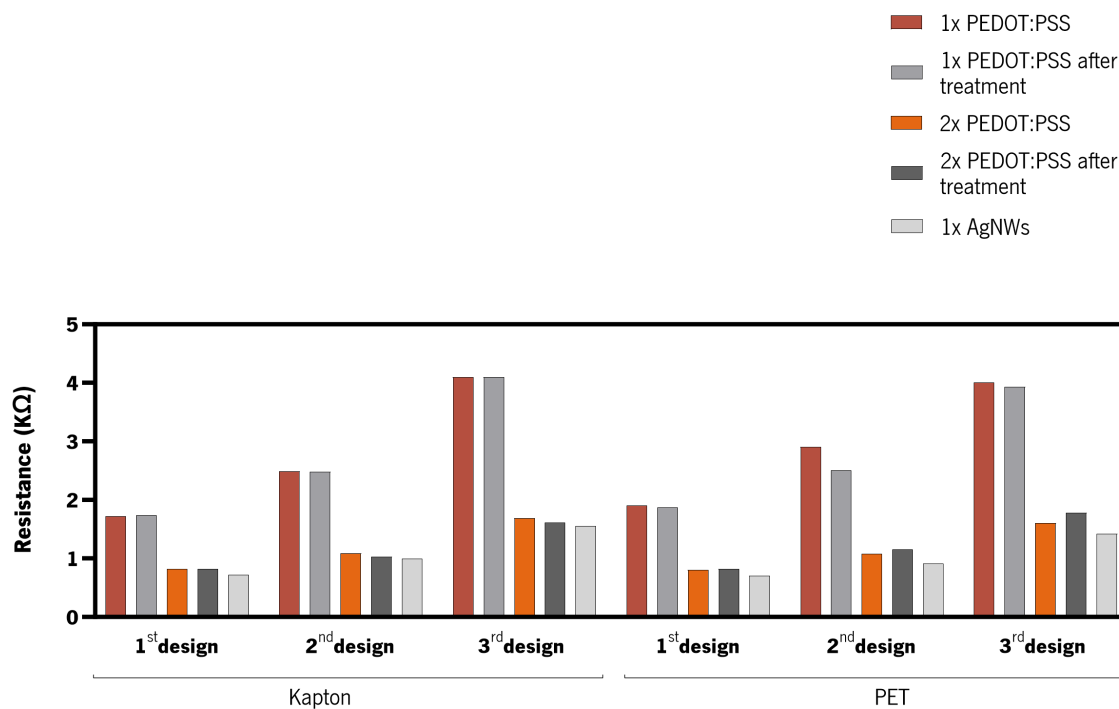


Figure 32: Resistances for films with two layers of doctor bladed PEDOT:PSS immersed in methanol and one layer of AgNWs.

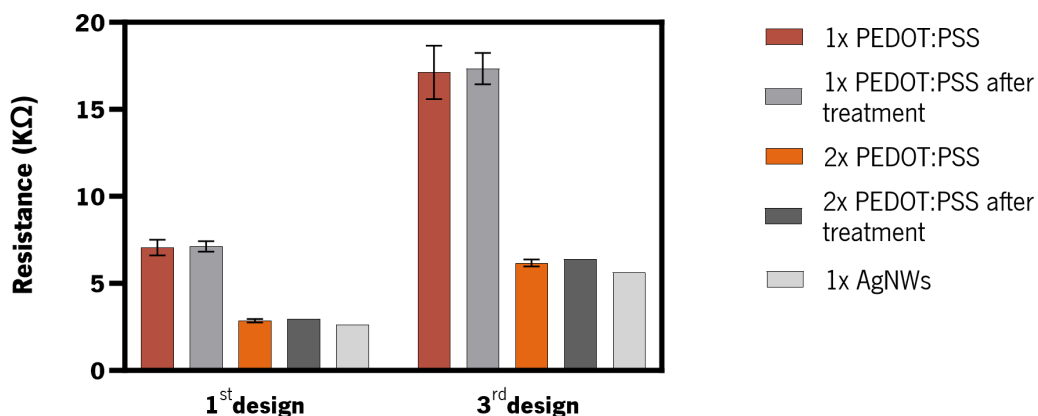


Figure 33: Variation of the resistance for films with two layers of screen-printed PEDOT:PSS immersed in methanol and one layer of AgNWs.

Despite the inefficiency of the treatment, the films with the two doctor bladed layers of PEDOT:PSS immersed in methanol and another layer of AgNWs showed the best results among all films deposited by that method throughout this work. Figure 34 shows a film obtained with this approach, as well as its corresponding SEM image. Like in previous films, the AgNWs were evenly dispersed, albeit sparsely, which could be the reason for their minimal impact on the resistance of the films.

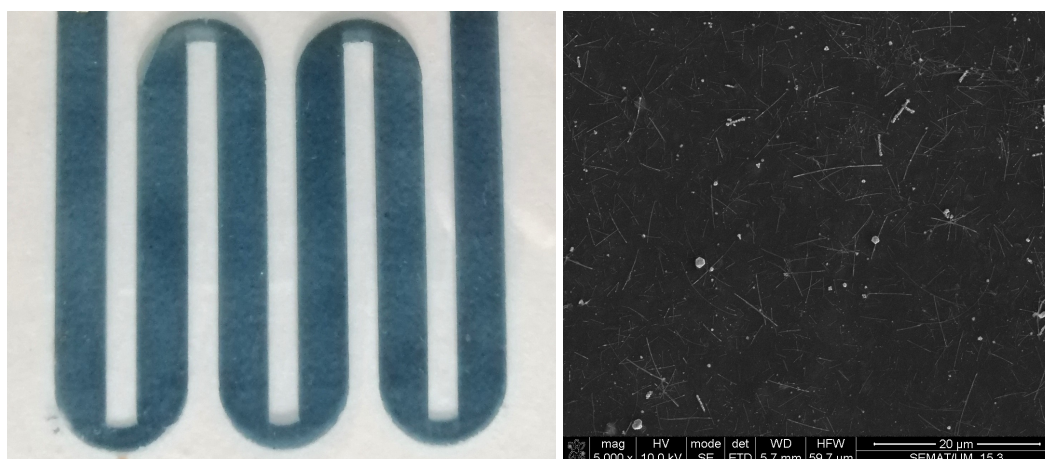


Figure 34: Film with two doctor bladed layers of PEDOT:PSS immersed in methanol and one layer of AgNWs, and its SEM image.

Furthermore, films with one or two layers of PEDOT:PSS modified with PEG were also soaked in methanol. Figure 35 shows the resistance variation for one or two layers of PEDOT:PSS with PEG immersed in methanol with an additional layer of as-synthesized AgNWs in glycerol or in glycerol with 40 or 55% (w/w) of methanol. The films were deposited through doctor blading on Kapton. As was the case

in previous approaches, films with two layers of PEDOT:PSS had lower resistances, while those with one layer showed a high uncertainty associated with the deposition of AgNWs in glycerol.

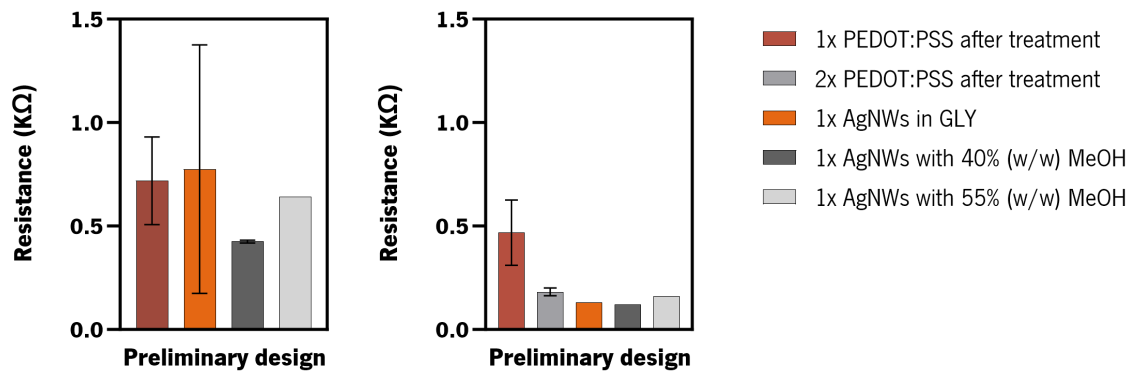


Figure 35: Resistances for films with one or two layers of PEDOT:PSS with PEG and another layer of AgNWs in glycerol with different methanol concentrations.

Following these results, two layers of PEDOT:PSS with PEG were screen-printed and as-synthesized AgNWs in glycerol and 55% (w/w) of methanol were deposited through spin coating. As seen on Figure 36, the treatment of the first PEDOT:PSS layer had an inconsistent effect on the resistance or even increased it. On the contrary, the immersion of the film with the double layer of the polymer resulted in similar or slightly lower resistances. In comparison to the doctor bladed films, of average thickness (0.0070 ± 0.0010) mm, the screen-printed films were less conductive, likely due to its lower thickness, of average (0.0040 ± 0.0010) mm. Additionally, these films had higher resistances than non-modified PEDOT:PSS films deposited by the same method. Furthermore, some samples were annealed at 225°C for 1 hour and at 180°C for 5 hours, which increased the resistance of the films by one or two orders of magnitude.

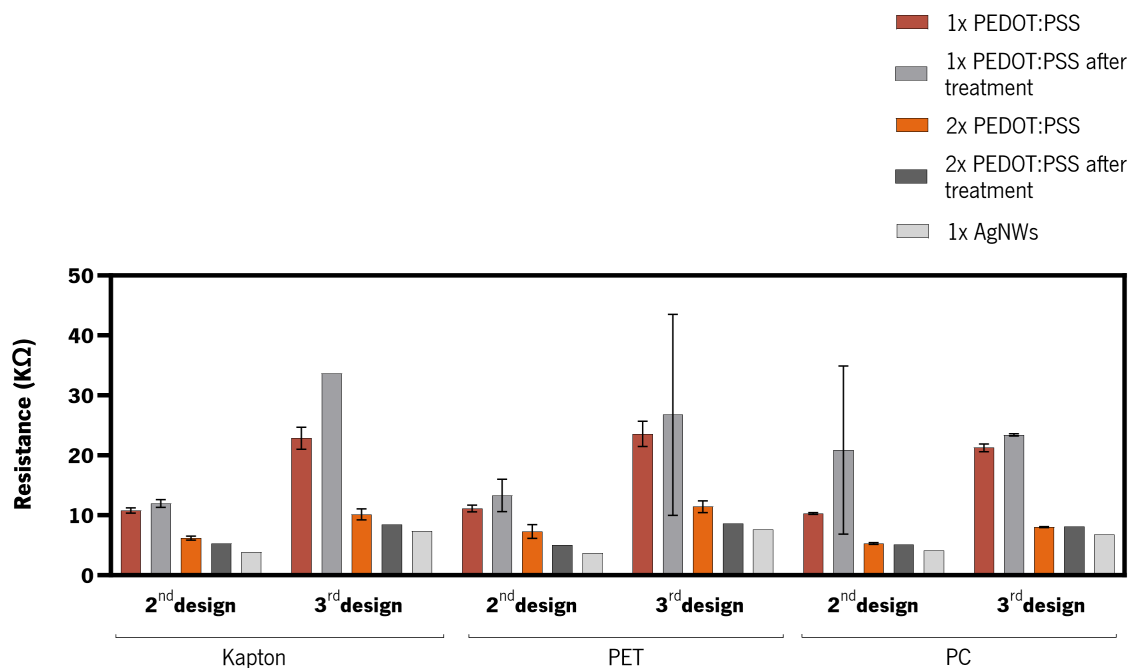


Figure 36: Resistance variations for screen-printed PEDOT:PSS with PEG and spin-coated AgNWs in glycerol and 55% (w/w).

Furthermore, PEDOT:PSS modified in the same way was used to produce films with intercalated AgNWs in glycerol with 55% (w/w) of methanol, in which all layers were deposited by doctor blading on Kapton. Figure 37 displays how the treatment was able to decrease the resistance of both PEDOT:PSS layers. The films obtained with this approach had a slightly lower average resistance than the non-intercalated films deposited by the same method.

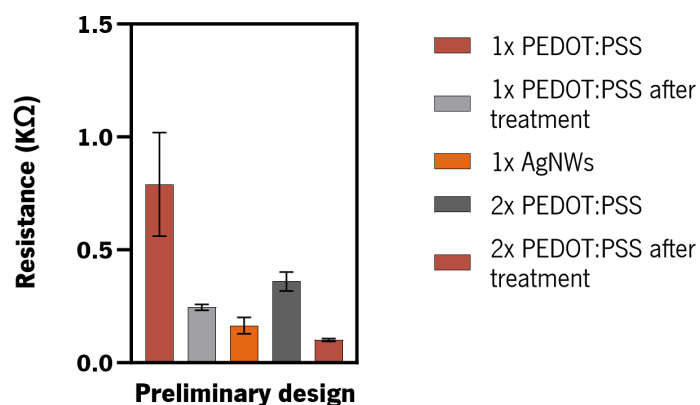


Figure 37: Resistances for films with two treated layers of PEDOT:PSS and one intercalated layer of AgNWs.

Moreover, films with one or two layers of doctor bladed PEDOT:PSS with glycerol on Kapton were also

treated with methanol. Additionally, as-synthesized silver nanowires in glycerol with different concentrations of methanol were deposited through the same method. Figure 38 shows the resistances for films of one or two layers treated with a drop of methanol, in which the effect of the second layer is noticeable. The uncertainties and differences in the resistance of the first layer may be attributed to the inconsistency of the deposition method.

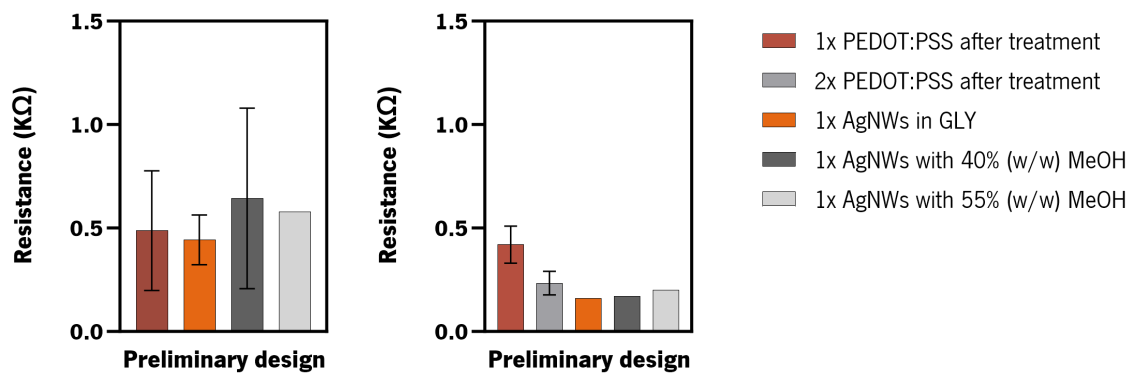


Figure 38: Resistance fluctuation for films with one or two layers of PEDOT:PSS with glycerol treated with a drop of methanol and one layer of AgNWs.

Similar films were also treated with an additional immersion in methanol. Figure 39 displays the results obtained with this approach. In this case, there was also a considerable uncertainty in the resistance of the first layer of PEDOT:PSS, and the final resistances were similar to the ones obtained by the previous drop treatment.

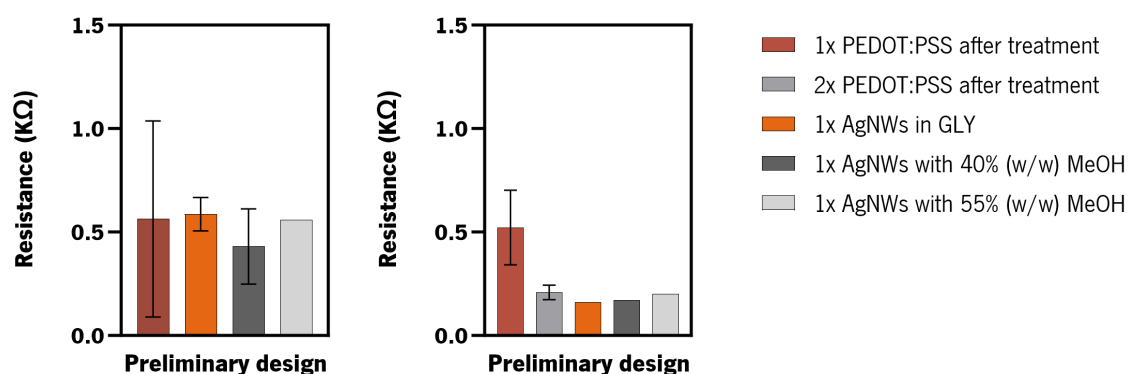


Figure 39: Resistance for films with one or two layers of PEDOT:PSS with glycerol treated with a drop and immersion in methanol and one layer of AgNWs.

Finally, a solution of PEDOT:PSS with AgNWs in glycerol with 55% (w/w) methanol was used to produce films by doctor blading. The results of their treatment in methanol are presented in Figure 40, which shows

that the immersion was not effective in this case.

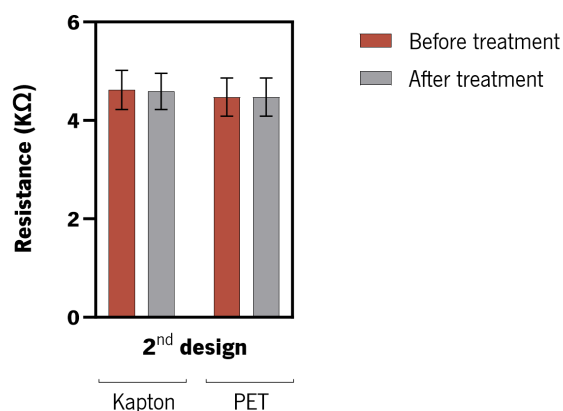


Figure 40: Resistance variation for a film of PEDOT:PSS with AgNWs in glycerol and methanol treated with immersion in methanol.

Table 7 summarily presents the results for films treated with methanol. In comparison with non-modified PEDOT:PSS films, most of the treatments did not result in films with lower resistances. Nevertheless, films with two doctor bladed or screen-printed layers of PEDOT:PSS treated with immersion in methanol had slightly lower or similar resistances to simple PEDOT:PSS films, respectively. Films of PEDOT:PSS with PEG and an intercalated layer of AgNWs seemed to be the best approach for utilizing methanol immersion as a treatment. Furthermore, the screen-printed films were characterized in terms of the increase in temperature when a voltage of 12 V was applied. Additionally, the films with two layers of PEDOT:PSS deposited through doctor blading and immersed in methanol, as they had the lowest resistance for the films with the “final” designs, were also characterized. Finally, the film with two layers of PEDOT:PSS with an intercalated layer of silver nanowires, all deposited by doctor blading, was also characterized given the results obtained. All films showed a lower increase in the temperature than the films with the double doctor bladed PEDOT:PSS layer in the 1st and 2nd designs, which could elevate their temperature on average more than 4 and 3°C, respectively.

Table 7: Summary of the results obtained for films treated with methanol.

Sample	Design	Average resistance (kΩ)	Average temperature increase (°C)
1x PEDOT:PSS treated with a drop	Preliminary	AgNWs in GLY	2.350 \pm 1.150
		AgNWs with 40% (w/w) MeOH	0.525 \pm 0.075
		AgNWs with 55% (w/w) MeOH	0.365 \pm 0.115
2x PEDOT:PSS treated with a drop	Preliminary	AgNWs in GLY	0.230
		AgNWs with 40% (w/w) MeOH	0.175
		AgNWs with 55% (w/w) MeOH	0.240
1x PEDOT:PSS treated with a drop and immersion	Preliminary	AgNWs in GLY	0.355 \pm 0.095
		AgNWs with 40% (w/w) MeOH	0.390 \pm 0.040
		AgNWs with 55% (w/w) MeOH	0.275 \pm 0.075
2x PEDOT:PSS treated with a drop and immersion	Preliminary	AgNWs in GLY	0.140
		AgNWs with 40% (w/w) MeOH	0.150
		AgNWs with 55% (w/w) MeOH	0.150
2x PEDOT:PSS treated with immersion (doctor blading)	1 st	0.713 \pm 0.010	4.3 \pm 1.1
	2 nd	0.955 \pm 0.041	3.3 \pm 0.9
	3 rd	1.485 \pm 0.065	1.3 \pm 0.6
2x PEDOT:PSS treated with immersion (screen-printing)	1 st	2.634 \pm 0.047	1.3 \pm 0.2
	3 rd	5.622 \pm 0.072	0.3 \pm 0.0
1x PEDOT:PSS with PEG	Preliminary	AgNWs in GLY	0.775 \pm 0.425
		AgNWs with 40% (w/w) MeOH	0.425 \pm 0.005
		AgNWs with 55% (w/w) MeOH	0.640 \pm 0.150

		AgNWs in GLY	0.130	
2x PEDOT:PSS with PEG (doctor blading)	Preliminary	AgNWs with 40% (w/w) MeOH	0.120	
		AgNWs with 55% (w/w) MeOH	0.160	
2x PEDOT:PSS with PEG (screen-printing)	2 nd	3.885 ± 0.057		0.7 ± 0.1
	3 rd	7.421 ± .180		0.3 ± 0.1
2x PEDOT:PSS with PEG and an intercalated layer of AgNWs	Preliminary		0.101 ± 0.003	0.3 ± 0.1
1x PEDOT:PSS with glycerol treated with a drop	Preliminary	AgNWs in GLY	0.443 ± 0.069	
		AgNWs with 40% (w/w) MeOH	0.643 ± 0.252	
		AgNWs with 55% (w/w) MeOH	0.580 ± 0.185	
2x PEDOT:PSS with glycerol treated with a drop	Preliminary	AgNWs in GLY	0.160	
		AgNWs with 40% (w/w) MeOH	0.170	
		AgNWs with 55% (w/w) MeOH	0.200	
1x PEDOT:PSS with glycerol treated with a drop and immersion	Preliminary	AgNWs in GLY	0.587 ± 0.047	
		AgNWs with 40% (w/w) MeOH	0.430 ± 0.105	
		AgNWs with 55% (w/w) MeOH	0.560 ± 0.172	
2x PEDOT:PSS with glycerol treated with a drop and immersion	Preliminary	AgNWs in GLY	0.160	
		AgNWs with 40% (w/w) MeOH	0.170	
		AgNWs with 55% (w/w) MeOH	0.200	
1x PEDOT:PSS with AgNWs	2 nd		4.533 ± 158	

The first films treated with DMSO were films of one or two layers of PEDOT:PSS. Figure 41 shows the resistance associated with the doctor blading and treatment of each layer of PEDOT:PSS and the further deposition of as-synthesized AgNWs in glycerol or in glycerol with 40 or 55% (w/w) of methanol on a Kapton

substrate. Films with the double layer of the conducting polymer originated films with higher conductivities, especially those with silver nanowires with methanol.

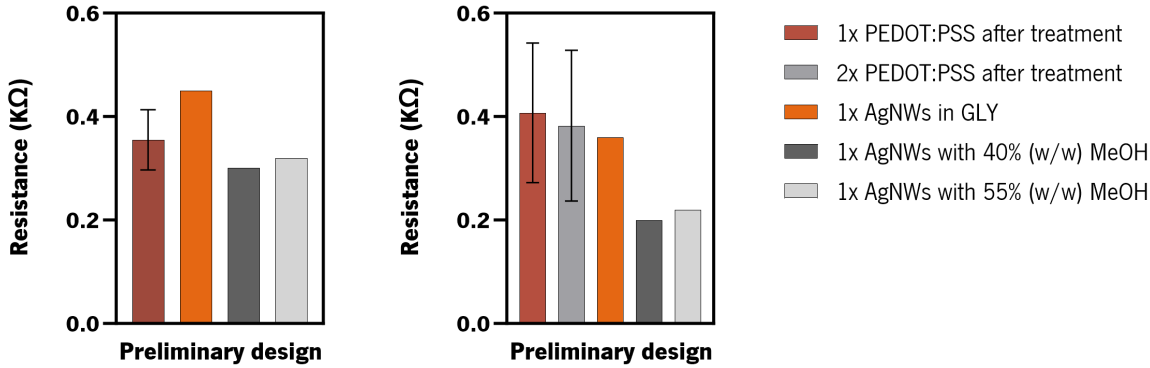


Figure 41: Resistances for films with one or two layers of PEDOT:PSS treated with DMSO and one layer of AgNWs.

Following these observations, films with two layers of PEDOT:PSS were screen-printed on Kapton and PET and soaked in DMSO. However, as a consequence of this treatment, films on PET lost their adherence to the substrate. As such, Figure 42 presents the results for films on Kapton with an additional layer of as-synthesized AgNWs in glycerol and 55% (w/w) of methanol deposited through spin coating and doctor blading, in which it is observable that the DMSO treatment increased the resistance of the films, even if only slightly. Once more, the screen-printing method resulted in higher resistances than the doctor blading, even though in this case the average thicknesses measured were identical: (0.0040 ± 0.0003) mm. Additionally, a few samples of this approach were annealed at 225°C for 1 hour and at 180°C for 5 hours, all of which had their conductivity decreased.

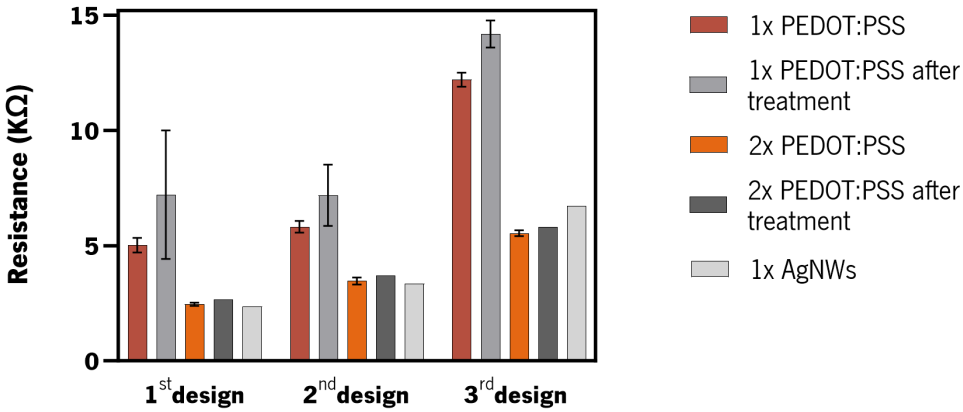


Figure 42: Resistances for screen-printed PEDOT:PSS layers treated in DMSO and one layer of AgNWs.

Furthermore, this treatment was applied in PEDOT:PSS layers of films with an intercalated layer of as-synthesized AgNWs in glycerol and 55% (w/w) of methanol, all doctor bladed on Kapton. Figure 43 displays the resistance fluctuations in this process, in which it is possible to notice effective treatment of the first layer of PEDOT:PSS. Nevertheless, the final resistance obtained with this approach was the same as the one with the non-intercalated layers deposited by the same method.

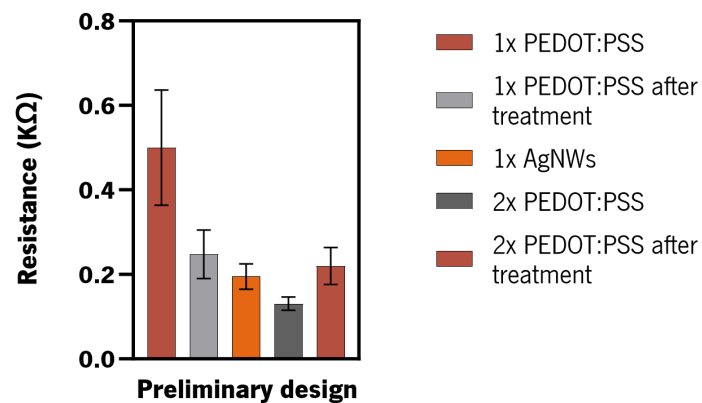


Figure 43: Variation in the resistance for films with PEDOT:PSS treated with DMSO and an intercalated layer of AgNWs.

Following these results, the same approach was taken without treatment of the last layer of PEDOT:PSS. The conductive polymer was doctor bladed on Kapton and the same silver nanowire solution was deposited through spin coating. As shown in Figure 44, the resistance followed the same trend as in Figure 43.

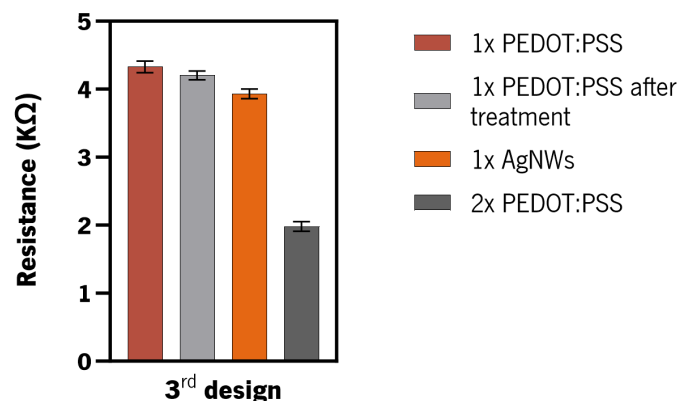


Figure 44: Resistance for films with one layer of treated PEDOT:PSS, one intercalated layer of AgNWs, and one untreated layer of PEDOT:PSS.

Moreover, PEDOT:PSS modified with PEG was doctor bladed on Kapton and immersed in DMSO. An additional layer of as-synthesized silver nanowires in glycerol and 55% (w/w) of methanol was deposited

using the same technique. Figure 45 displays how the treatment effectively reduced the resistance of the first layer and slightly affected the resistance of the second. In comparison with the previous approach with non-modified PEDOT:PSS, the films obtained with this method had slightly lower resistances.

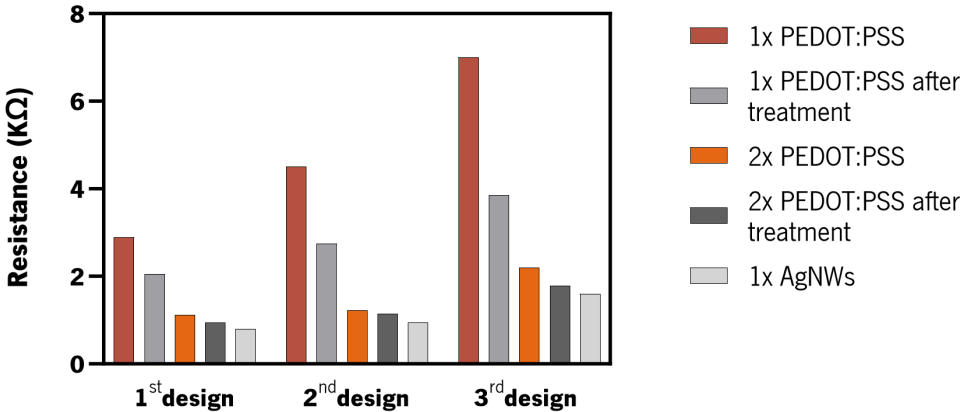


Figure 45: Variation in resistance with each layer of films with two treated layers of PEDOT:PSS with PEG and one additional layer of AgNWs.

Similar PEDOT:PSS films were further deposited on the same substrate by screen-printing of the PEDOT:PSS layers and spin coating of AgNWs. Figure 46 displays the variation of the resistance for each step of the process, showing how the treatment was only lightly effective. The screen-printed films' thickness was on average (0.0030 ± 0.0004) mm, approximately half of the average thickness of the doctor bladed films, (0.0060 ± 0.0010) mm, which resulted in lower conductivities. The effect of the immersion was minimal when compared to the films' thickness.

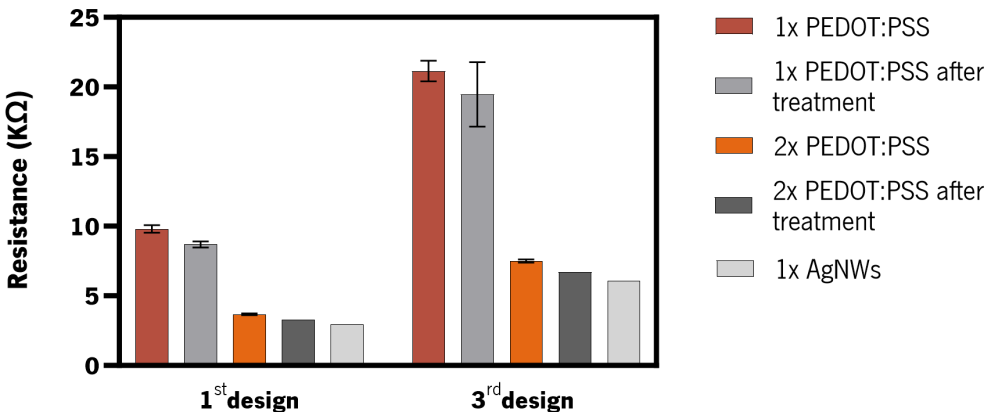


Figure 46: Resistance fluctuation for films with two screen-printed layer of PEDOT:PSS with PEG further treated in DMSO, and one layer of spin-coated AgNWs.

Furthermore, a solution of PEDOT:PSS with PEG in the same concentration as the previous approaches

and with as-synthesized AgNWs in glycerol and 55% (w/w) of methanol was doctor bladed on Kapton and immersed in DMSO. Figure 47 demonstrates how the treatment was able to reduce the average resistance more than half, even though it was still higher than in previous approaches that utilized the same deposition method.

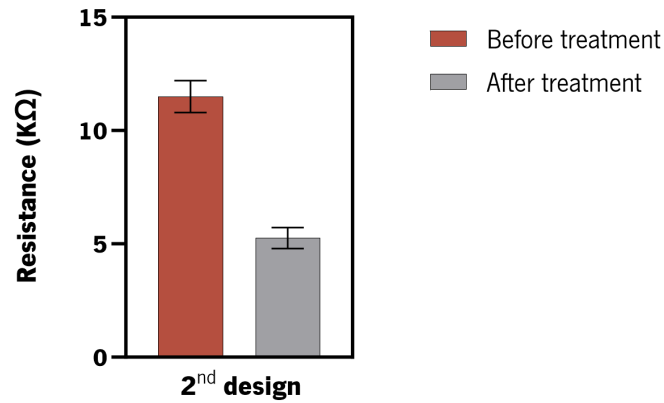


Figure 47: Resistance for a film of PEDOT:PSS with PEG and AgNWs treated in DMSO.

Finally, films of doctor bladed PEDOT:PSS were treated in DMSO and further immersed in the previously mentioned silver nanowire solution for different times. Figure 48 shows how the DMSO treatment was not effective in this instance and that the longer the immersion in the AgNWs solution, the lower the conductivity of the film. These results could be explained by the great affinity of the sulfonic groups to silver, which could allow a degradation of the nanowires.

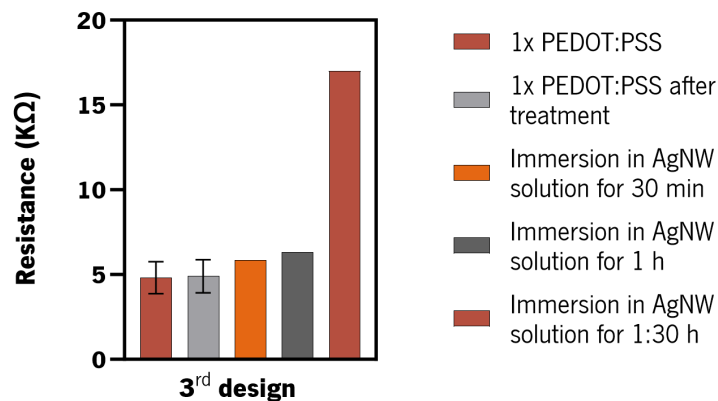


Figure 48: Resistance associated with DMSO treatment of PEDOT:PSS films followed by immersion in a AgNW solution.

Table 8 recapitulates the results of this section. Overall, immersion in DMSO resulted in a decrease in the resistance of the films. Nevertheless, in some cases its effect was slight or even detrimental. It

is hypothesized that, as DMSO has a higher boiling point than the temperature at which the films were dried, the longer the films took to dry the more DMSO was evaporated, thus reducing the resistance of the films more effectively. Films with screen-printed layers of PEDOT:PSS were characterized with an input of 12 V, as well as the films with doctor bladed PEDOT:PSS with PEG, given that they had the best conductivities of the films produced in the “final” designs. While films produced by the first method increased their temperature less than or around 1°C, films deposited through the second could increase their temperature up to 2.7°C, likely due to their higher thickness and consequent lower resistance.

Table 8: Summary of the results for films treated in DMSO.

Sample	Design	Average resistance (k Ω)	Average temperature increase ($^{\circ}$ C)
1x PEDOT:PSS	Preliminary	AgNWs in GLY	0.450
		AgNWs with 40% (w/w) MeOH	0.300
		AgNWs with 55% (w/w) MeOH	0.320
2x PEDOT:PSS (doctor blading)	Preliminary	AgNWs in GLY	0.360
		AgNWs with 40% (w/w) MeOH	0.200
		AgNWs with 55% (w/w) MeOH	0.220
2x PEDOT:PSS (screen-printing)	1 st	2.365 \pm 0.095	1.1
	2 nd	3.353 \pm 0.211	0.7
	3 rd	6.737 \pm 1.014	0.5
2x PEDOT:PSS with an intercalated layer of AgNWs	Preliminary	0.220 \pm 0.022	
2x PEDOT:PSS with an intercalated layer of AgNWs (last layer of PEDOT:PSS not treated)	3 rd	1.980 \pm 0.050	
2x PEDOT:PSS PEG (doctor blading)	1 st	0.800	2.7
	2 nd	0.953	2.3
	3 rd	1.600	1.2
2x PEDOT:PSS PEG (screen-printing)	1 st	2.960 \pm 0.033	1.3 \pm 0.1
	3 rd	6.104 \pm 0.108	0.4 \pm 0.1
1x PEDOT:PSS with 4 w/w% of PEG and 30 w/w% of AgNWs in glycerol and 55 w/w% methanol	2 nd	5.255 \pm 0.325	
1x PEDOT:PSS immersed in AgNW solution	3 rd	Immersion for 30 min	5.860
		Immersion for 1 h	6.320
		Immersion for 1:30 h	17.000

5.4.4 Films with cleaned AgNWs

Given that using AgNWs in glycerol and in glycerol with different concentrations of methanol seemed to have only a slight effect on the films, the as-synthesized AgNWs were cleaned, sintered, and dispersed

in different solutions in an attempt to further study the effect of AgNWs on the films, and to potentially obtain films with better conductivities.

First, a solution of PEDOT:PSS with AgNWs in equal volumes of IPA and acetone was doctor bladed on PET in the 1st design, resulting in films with an average resistance of (11.00 ± 3.00) k Ω .

Afterwards, sintered AgNWs at 250°C for 10 minutes were dispersed in water and spin coated on screen-printed PEDOT:PSS films of two or three layers and the corresponding resistances are shown in Figures 49 and 50, respectively. As expected, films with more layers of PEDOT:PSS had higher conductivities. The addition of the AgNWs generally decreased the resistance only slightly.

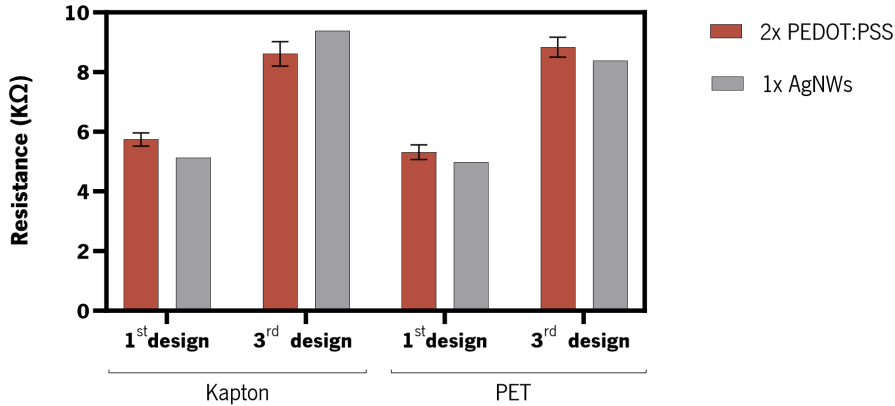


Figure 49: Resistance variation for the addition of sintered AgNWs in water to a film of two screen-printed layers of PEDOT:PSS.

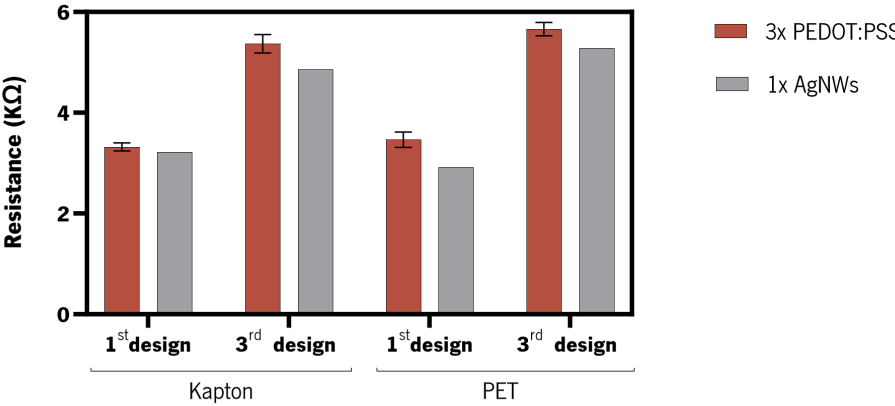


Figure 50: Resistance fluctuation with the addition of sintered AgNWs dispersed in water to a film of three layers of screen-printed PEDOT:PSS.

Finally, sintered AgNWs in water and ethanol were added to PEDOT:PSS and doctor bladed on PET in

the 1st and 3rd designs, resulting in films with average resistances of $(5.050 \pm 0.050) \text{ k}\Omega$ and $(8.975 \pm 0.375) \text{ k}\Omega$, respectively.

Table 9 summarily presents the results of this section. The addition of a layer of AgNWs overall slightly increased the conductivity of the films, while the addition of AgNWs to a PEDOT:PSS solution resulted in films with higher resistances than simple PEDOT:PSS films of the same number of layers. Given the ineffectiveness of this approach, the films were not tested for their heating abilities.

Table 9: Summary of the results for films with cleaned silver nanowires.

Sample	Design	Average resistance (k Ω)
1x PEDOT:PSS with AgNWs in IPA and acetone	1 st	11.00 ± 3.00
2x PEDOT:PSS, 1x AgNWs in water	1 st	5.055 ± 0.075
	3 rd	8.885 ± 0.495
3x PEDOT:PSS, 1x AgNWs in water	1 st	3.070 ± 0.150
	3 rd	5.070 ± 0.210
1x PEDOT:PSS with AgNWs in ethanol and water	1 st	5.050 ± 0.050
	3 rd	8.975 ± 0.375

5.4.5 Treatment of films with CTAB or sodium borohydride

As an attempt to increase the conductivity of films, a treatment reported by Liu et al. [64] was used. With that purpose, the following previously deposited films were treated in CTAB (cetyltrimethylammonium bromide):

- (A) Two layers of screen-printed PEDOT:PSS and one layer of spin-coated AgNWs in glycerol and 55% (w/w) of methanol.
- (B) Two layers of screen-printed PEDOT:PSS with an intercalated spin-coated layer of AgNWs in glycerol and 55% (w/w) of methanol.
- (C) Two layers of screen-printed PEDOT:PSS immersed in methanol and a layer of spin-coated AgNWs in glycerol and 55% (w/w) of methanol.
- (D) Two layers of screen-printed PEDOT:PSS with PEG immersed in DMSO and a layer of spin-coated AgNWs in glycerol and 55% (w/w) of methanol.

Figure 51 shows the changes on the resistance caused by this treatment. For all films the immersion in CTAB followed by rinsing with water and drying at room temperature increased their resistance substantially, while rinsing the films with ethanol resulted in similar resistances for all of them, which were still higher than the initial resistances.

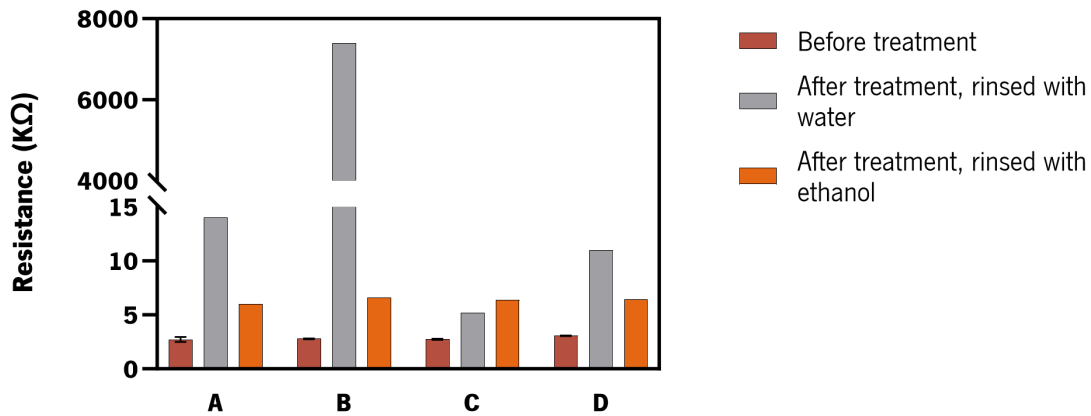


Figure 51: Effects of CTAB immersion on films with PEDOT:PSS.

Furthermore, prompted by the work reported by Ge et al. [58], the following previously mentioned films were immersed in NaBH_4 :

- (A) Two layers of doctor bladed PEDOT:PSS and one layer of spin-coated AgNWs in glycerol and 55% (w/w) of methanol.
- (B) Two layers of PEDOT:PSS with an intercalated layer of AgNWs in glycerol and 55% (w/w) of methanol, both doctor bladed.
- (C) Two layers of PEDOT:PSS immersed in methanol and a layer of AgNWs in glycerol and 55% (w/w) of methanol, both doctor bladed.

For films treated with NaBH_4 , which results are shown in Figure 52, the treatment decreased the conductivity in all cases, contrary to the reported by Ge et al. [58]. This could be due to reactions between the sodium borohydride and the remaining glycerol and methanol from the AgNW solution, which formed hydrogen bubbles [81, 82] that damaged the films, as seen in Figure 53.

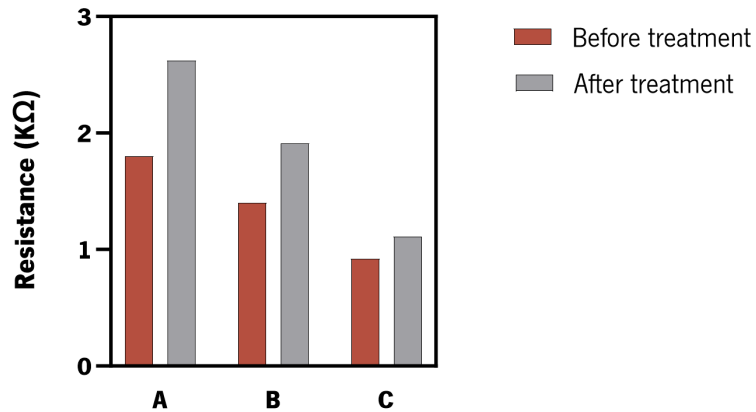


Figure 52: Variation in the resistance of films with PEDOT:PSS immersed in sodium borohydride



Figure 53: Photographs of the damaged films after immersion in NaBH_4 .

5.4.6 Ionic liquid and PVA

Given the high conductivity associated with ionic liquids and PVA's very high transparency and flexibility, and while drawing inspiration on the previously mentioned works by Yemata et al. [35], Imae et al. [36], Lan et al. [73], and Kaikanov et al. [74], these substances were used in an attempt to obtain films with low resistances. While the ionic liquid may increase the conductivity of the films through the formation of PEDOT and PSS-rich zones, while substituting PSS for other anions [35, 83], PVA might improve films' flexibility and mechanical stability while maintaining their transparency [73].

The following previously doctor bladed films were modified with ionic liquid:

- (A) Two layers of PEDOT:PSS immersed in methanol and a layer of AgNWs in glycerol and 55% (w/w) of methanol.
- (B) Two layers of PEDOT:PSS with an intercalated layer of AgNWs in glycerol and 55% (w/w) of methanol.
- (C) One layer of PEDOT:PSS.

Figure 54 shows the effects of spin coating a layer of ionic liquid on the films (left) or immersing them in it (right). For both treatments the resistances did not decrease, which rendered these treatments ineffective.

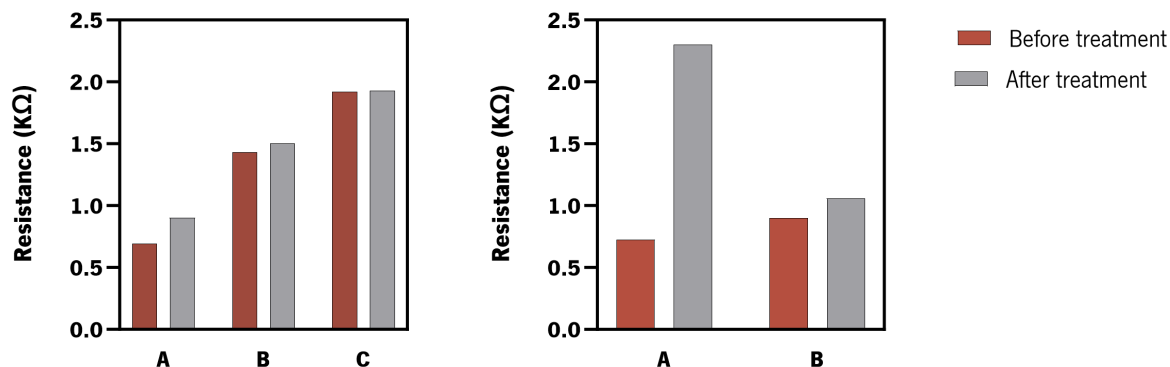


Figure 54: Variation in the resistance of films modified with ionic liquid by spin coating (left) or immersion (right).

Furthermore, solutions of ionic liquid and PVA in a ratio of 0.8:1 were used. The deposition of this solution originated a film with resistance $36.5 \text{ M}\Omega$, while adding 5 mM or 10 mM of silver nitrate resulted in films of $800 \text{ k}\Omega$ or $61.2 \text{ M}\Omega$, respectively. Figure 55 shows the final aspect of the films, in which the effect of the silver nitrate on the color and transparency is notorious.



Figure 55: Films formed on Petri dishes: ionic liquid and PVA in a ratio of 0.8:1 (left), with 5 or 10 mM of AgNO_3 (center and right, respectively).

The PVA, ionic liquid, and 5mM of AgNO_3 solution was spin coated or added to PEDOT:PSS in concentrations of 20, 50 and 80% (w/w), and the variations of the resistances associated with these processes are shown in Figure 56 and 57, respectively. The presence of PVA lead to an increment of electrical resistance.

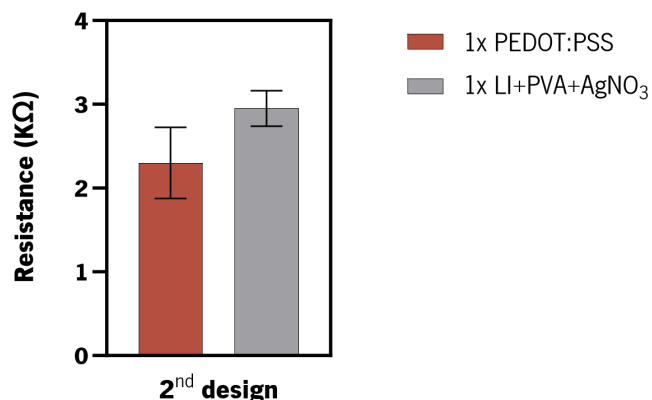


Figure 56: Resistance for a spin-coated layer of ionic liquid with PVA and AgNO₃ on doctor bladed PEDOT:PSS.

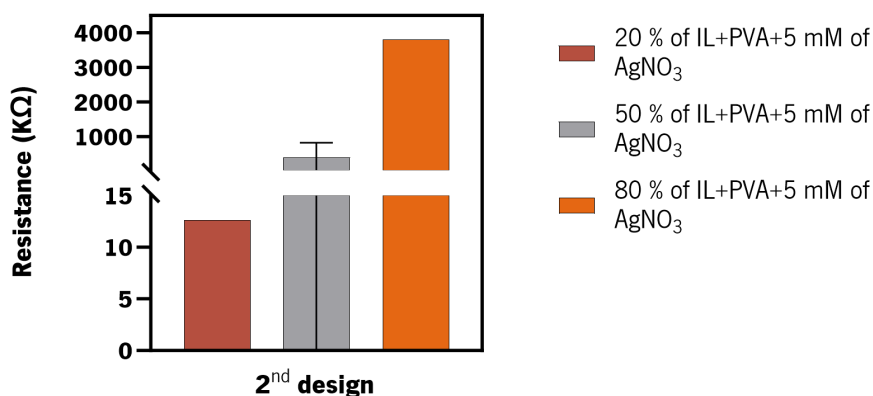


Figure 57: Resistance for different concentrations of the solution of ionic liquid, PVA and AgNO₃ added to PEDOT:PSS.

Moreover, a solution of ionic liquid and PVA in a ratio of 3:1 was used. The deposition of this solution originated a film with 1.26 MΩ of resistance, while the addition of 5 mM or 10 mM of silver nitrate produced films with resistances of 1.02 MΩ or 3.5 MΩ, respectively. Figure 58 shows the final films. For this ratio, the difference in color and transparency is only observable for the highest concentration of AgNO₃.



Figure 58: Films deposited on Petri dishes: ionic liquid and PVA in a ratio of 3:1 (left) with 5 or 10 mM of AgNO_3 (center and right, respectively).

Figures 59 and 60 show the resistance of films with a spin-coated layer of the ionic liquid, PVA and 5 mM of AgNO_3 solution, and of films resultant from adding this solution to PEDOT:PSS in concentrations of 20, 50 or 80% (w/w), respectively. The presence of PVA lead to an increment of electrical resistance.

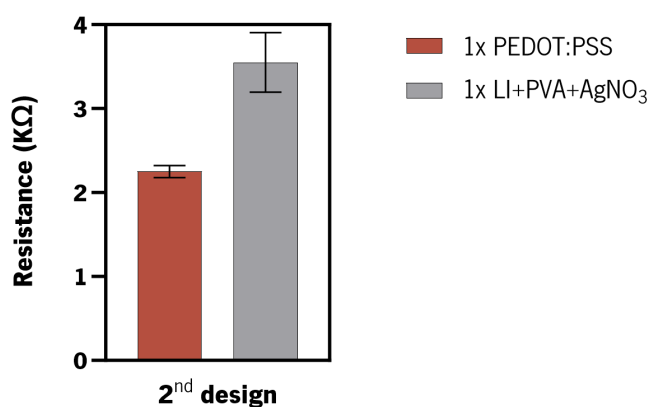


Figure 59: Resistance for films of one doctor bladed layer of PEDOT:PSS and one spin-coated layer of a solution of ionic liquid, PVA and 5 mM of AgNO_3 .

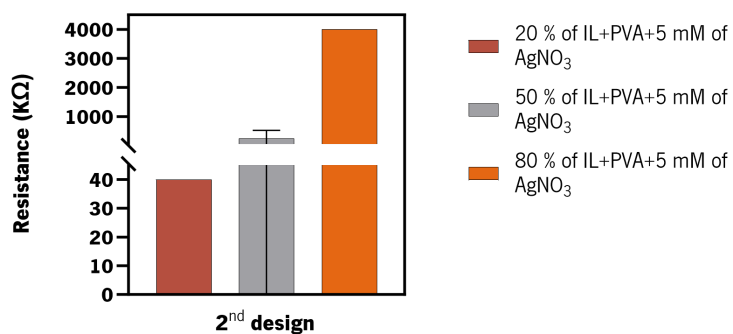


Figure 60: Resistances for films of PEDOT:PSS with different concentrations of a solution of ionic liquid, PVA, and AgNO_3 .

For solutions with both ratios between ionic liquid and PVA, with AgNO_3 , spin coating a layer on top of PEDOT:PSS films increased their resistance, which was also verified for films in which the solutions were added to PEDOT:PSS. For these films, the lower the concentration of PEDOT:PSS, the lower the conductivities of the films.

Finally, a solution of silver nanowires in IPA and acetone with PVA was used to produce a film as well, which had no conductivity.

Given that the modifications to PEDOT:PSS films using the ionic liquid and PVA increased the resistances of the films, and that the films produced with these reagents and AgNO_3 and the film with PVA and AgNWs all showed high resistances, it was concluded that utilizing this ionic liquid and PVA was not an effective method to increase the conductivity of the films.

The average results displayed graphically throughout this chapter are further elaborated in the appendices of this work, providing detailed values for a more comprehensive understanding of the results.

Chapter 6

Conclusion and future work

In this work, films were produced and studied with the objective of using screen-printing as a reproducible technique to produce flexible and transparent heating systems that would operate efficiently with low input voltages. Given that the heating mechanism is inversely proportional to the resistance, the main intention throughout this work was to obtain films with the lowest resistance possible.

With that purpose, films of the conducting polymer PEDOT:PSS with silver nanowires were fabricated. Silver nanowires were synthesized through the polyol method and modified with the aim of improving their adhesion and conductivity when utilized with PEDOT:PSS. PEDOT:PSS was modified and its films were post-treated with different solvents with the goal of reducing their resistance. The approaches with the highest conductivities were then screen-printed on different substrates, and the films had their temperature analyzed with an infrared camera when subjected to an input voltage of 12 V.

With the obtained results it was possible to conclude that the addition of a layer of as-synthesized silver nanowires, whether in just glycerol, directly from the synthesis, or with different concentrations of methanol, generally had only a slight effect on the resistance of the films. This was likely due to the sparse dispersion of the nanowires on the films, which was observable in SEM images and might be improved by increasing the AgNWs' concentration. The addition of PEDOT:PSS layers, however, did originate considerable decreases in the resistances of the films, likely due to an increase in their thicknesses.

Furthermore, modifying PEDOT:PSS with water, PEG, glycerol, glycerol and PEG, glycerol and methanol, or with DMSO did not result in films with lower resistances.

Moreover, films post-treated with methanol overall did not show lower resistances than untreated films. However, films with two doctor bladed layers of PEDOT:PSS immersed in methanol with an additional layer of silver nanowires had slightly lower resistances than simple PEDOT:PSS films and showed the highest temperature increase for films produced by this method. On the contrary, post-treatment with DMSO was generally effective, but the temperature increase was only slight.

Additionally, utilizing silver nanowires that had been previously sintered was not an effective approach

at increasing the conductivity of films.

Furthermore, treating films with immersion in CTAB or sodium borohydride solutions did not decrease their resistance either.

Finally, utilizing an ionic liquid and PVA was not an effective approach to obtaining films with high conductivity as well.

With these results, it was concluded that the determining factor for reducing the final resistance of the films seemed to be their thickness. In agreement with that assumption, the thicker films produced, with two screen-printed layers of PEDOT:PSS with a bigger mesh size and an additional layer of spin-coated AgNWs, showed the highest average increase in temperature, of almost 5°C.

All films produced throughout this work were flexible and had varying levels of transparency. However, the better-performing films were the less transparent ones, since the lower resistances were observed for thicker films.

For films with this range of temperature increase, applications can include window defogging or textile implementations, for instance.

Future work in this area may include the utilization of other solvents to modify or post-treat PEDOT:PSS and/or silver nanowires with the main objective of obtaining reproducible films with low resistances and simultaneously high flexibility and transmittance of visible light. Additionally, the synthesis of PEDOT:PSS and silver nanowires can be improved to achieve better compatibility in films, which might increase their conductivity and thermal stability. Finally, future work in this field can be focused on creating deposition methods that are more efficient and easily reproducible at a larger scale with the aim of commercially utilizing heating systems with films of PEDOT:PSS and silver nanowires.

Bibliography

- [1] Xin He, Ruihui He, Qiuming Lan, Weijie Wu, Feng Duan, Jundong Xiao, Mei Zhang, Qingguang Zeng, Jianhao Wu, and Junyan Liu. Screen-printed fabrication of PEDOT: PSS/silver nanowire composite films for transparent heaters. *Materials*, 10(3), 2017.
- [2] Jeung Choon Goak, Tae Yang Kim, Dong Uk Kim, Ki Soo Chang, Churl Seung Lee, and Naesung Lee. Stable heating performance of carbon nanotube/silver nanowire transparent heaters. *Applied Surface Science*, 510(November 2019):145445, 2020.
- [3] Yoon Soo Kim, Min Hwa Chang, Eun Jong Lee, Dae Woo Ihm, and Jin Yeol Kim. Improved electrical conductivity of PEDOT-based electrode films hybridized with silver nanowires. *Synthetic Metals*, 195:69–74, 2014.
- [4] Hui Shi, Congcong Liu, Qinglin Jiang, and Jingkun Xu. Effective Approaches to Improve the Electrical Conductivity of PEDOT:PSS: A Review. *Advanced Electronic Materials*, 1(4):1–16, 2015.
- [5] Shulin Ji, Weiwei He, Ke Wang, Yunxia Ran, and Changhui Ye. Thermal response of transparent silver nanowire/PEDOT:PSS film heaters. *Small*, 10(23):4951–4960, 2014.
- [6] Boda Zheng, Qingsheng Zhu, and Yang Zhao. Fabrication of high-quality silver nanowire conductive film and its application for transparent film heaters. *Journal of Materials Science and Technology*, 71:221–227, 2021.
- [7] Dong Yun Choi, Hyun Wook Kang, Hyung Jin Sung, and Sang Soo Kim. Annealing-free, flexible silver nanowire-polymer composite electrodes via a continuous two-step spray-coating method. *Nanoscale*, 5(3):977–983, 2013.
- [8] Magatte N. Gueye, Alexandre Carella, Jérôme Faure-Vincent, Renaud Demadrille, and Jean Pierre Simonato. Progress in understanding structure and transport properties of PEDOT-based materials: A critical review. *Progress in Materials Science*, 108(September 2019):100616, 2020.

- [9] Takakazu Yamamoto and Mahmut Abila. Synthesis of non-doped poly(3,4-ethylenedioxythiophene) and its spectroscopic data. *Synthetic Metals*, 100(2):237–239, 1999.
- [10] Junyan Yang, Karen Lipkin, and David C. Martin. Electrochemical fabrication of conducting polymer poly(3,4- ethylenedioxythiophene) (PEDOT) nanofibrils on microfabricated neural prosthetic devices. *Journal of Biomaterials Science, Polymer Edition*, 18(8):1075–1089, 2007.
- [11] Elena Poverenov, Mao Li, Arkady Bitler, and Michael Bendikov. Major effect of electropolymerization solvent on morphology and electrochromic properties of PEDOT films. *Chemistry of Materials*, 22(13):4019–4025, 2010.
- [12] Hyo Joong Lee, Joowook Lee, and Su Moon Park. Electrochemistry of conductive polymers. 45. Nanoscale conductivity of PEDOT and PEDOT:PSS composite films studied by current-sensing AFM. *Journal of Physical Chemistry B*, 114(8):2660–2666, 2010.
- [13] Yuhei Seki, Momoko Takahashi, and Masayuki Takashiri. Effects of different electrolytes and film thicknesses on structural and thermoelectric properties of electropolymerized poly(3,4-ethylenedioxythiophene) films. *RSC Advances*, 9(28):15957–15965, 2019.
- [14] Shisong Nie, Zaifang Li, Yuyuan Yao, and Yingzhi Jin. Progress in Synthesis of Conductive Polymer Poly(3,4-Ethylenedioxythiophene). *Frontiers in Chemistry*, 9(December):1–8, 2021.
- [15] Bjørn Winther-Jensen and Keld West. Vapor-phase polymerization of 3,4-ethylenedioxythiophene: A route to highly conducting polymer surface layers. *Macromolecules*, 37(12):4538–4543, 2004.
- [16] Xiaoxue Wang, Xu Zhang, Lei Sun, Dongwook Lee, Sunghwan Lee, Minghui Wang, Junjie Zhao, Yang Shao-Horn, Mircea Dincă, Tomás Palacios, and Karen K. Gleason. High electrical conductivity and carrier mobility in oCVD PEDOT thin films by engineered crystallization and acid treatment. *Science Advances*, 4(9):1–10, 2018.
- [17] Meysam Heydari Gharahcheshmeh, Charles Tai Chieh Wan, Yasser Ashraf Gandomi, Katharine V. Greco, Antoni Forner-Cuenca, Yet Ming Chiang, Fikile R. Brushett, and Karen K. Gleason. Ultrathin Conformal oCVD PEDOT Coatings on Carbon Electrodes Enable Improved Performance of Redox Flow Batteries. *Advanced Materials Interfaces*, 7(20):1–11, 2020.
- [18] Jörgen Metsik, Martin Timusk, Andris Šutka, Marek Mooste, Kaido Tammeveski, and Uno Mäeorg. In situ investigation of poly(3,4-ethylenedioxythiophene) film growth during liquid phase deposition polymerization. *Thin Solid Films*, 653(July 2017):274–283, 2018.

- [19] Jianxiong Li, Meijuan Zhang, Jie Liu, and Yaxiao Ma. Effect of attached peroxyacid on liquid phase depositional polymerization of EDOT over PI film with adsorbed ferric chloride. *Synthetic Metals*, 198:161–166, 2014.
- [20] Jianxiong Li and Yaxiao Ma. In-situ synthesis of transparent conductive PEDOT coating on PET foil by liquid phase depositional polymerization of EDOT. *Synthetic Metals*, 217:185–188, 2016.
- [21] L. Groenendaal, Friedrich Jonas, Dieter Freitag, Harald Pielartzik, and John R. Reynolds. Poly(3,4-ethylenedioxythiophene) and its derivatives: past, present, and future. *Advanced Materials*, 12(7):481–494, 2000.
- [22] Ivan Karbovnyk, Igor Olenych, Olena Aksimentyeva, Halyna Klym, Orest Dzendzelyuk, Yuri Olenych, and Oksana Hrushetska. Effect of Radiation on the Electrical Properties of PEDOT-Based Nanocomposites. *Nanoscale Research Letters*, 11(1):1–5, 2016.
- [23] Lin Hu, Jiaying Song, Xinxing Yin, Zhen Su, and Zaifang Li. Research progress on polymer solar cells based on PEDOT: PSS electrodes. *Polymers*, 12(1), 2020.
- [24] Yow Jon Lin, Fu Ming Yang, Chi Yen Huang, Wei Yang Chou, Jay Chang, and Yi Chun Lien. Increasing the work function of poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) by ultraviolet irradiation. *Applied Physics Letters*, 91(9), 2007.
- [25] J. Huang, P. F. Miller, J. C. De Mello, A. J. De Mello, and D. D.C. Bradley. Influence of thermal treatment on the conductivity and morphology of PEDOT/PSS films. *Synthetic Metals*, 139(3):569–572, 2003.
- [26] T. P. Nguyen, P. Le Rendu, P. D. Long, and S. A. De Vos. Chemical and thermal treatment of PEDOT:PSS thin films for use in organic light emitting diodes. *Surface and Coatings Technology*, 180-181:646–649, 2004.
- [27] Henry J. Snaith, Henry Kenrick, Marco Chiesa, and Richard H. Friend. Morphological and electronic consequences of modifications to the polymer anode 'PEDOT:PSS'. *Polymer*, 46(8):2573–2578, 2005.
- [28] Desalegn Alemu, Hung Yu Wei, Kuo Chuan Ho, and Chih Wei Chu. Highly conductive PEDOT:PSS electrode by simple film treatment with methanol for ITO-free polymer solar cells. *Energy and Environmental Science*, 5(11):9662–9671, 2012.

- [29] Mitsutoshi Jikei, Takahiro Yamaya, Shintaro Uramoto, and Kazuya Matsumoto. Conductivity enhancement of PEDOT/PSS films by solvent vapor treatment. *International Journal of the Society of Material Engineering for Resources*, 20(2):158–162, 2014.
- [30] Leona V. Lingstedt, Matteo Ghittorelli, Hao Lu, Dimitrios A. Koutsouras, Tomasz Marszalek, Fabrizio Torricelli, N. Irina Crăciun, Paschalis Gkoupidenis, and Paul W.M. Blom. Effect of DMSO Solvent Treatments on the Performance of PEDOT:PSS Based Organic Electrochemical Transistors. *Advanced Electronic Materials*, 5(3):1–8, 2019.
- [31] Tiejun Wang, Yingqun Qi, Jingkun Xu, Xiujie Hu, and Ping Chen. Effects of poly(ethylene glycol) on electrical conductivity of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonic acid) film. *Applied Surface Science*, 250(1-4):188–194, 2005.
- [32] Desalegn Alemu Mengistie, Pen Cheng Wang, and Chih Wei Chu. Effect of molecular weight of additives on the conductivity of PEDOT:PSS and efficiency for ITO-free organic solar cells. *Journal of Materials Chemistry A*, 1(34):9907–9915, 2013.
- [33] Yang Li, Xinda Li, Shiming Zhang, Leslie Liu, Natalie Hamad, Sanyasi Rao Bobbara, Damiano Pasini, and Fabio Cicoira. Autonomic Self-Healing of PEDOT:PSS Achieved Via Polyethylene Glycol Addition. *Advanced Functional Materials*, 30(30):1–9, 2020.
- [34] Liangqi Ouyang, Chiara Musumeci, Mohammad J. Jafari, Thomas Ederth, and Olle Inganäs. Imaging the Phase Separation between PEDOT and Polyelectrolytes during Processing of Highly Conductive PEDOT:PSS Films. *ACS Applied Materials and Interfaces*, 7(35):19764–19773, 2015.
- [35] Temesgen Atnafu Yemata, Yun Zheng, Aung Ko Ko Kyaw, Xizu Wang, Jing Song, Wee Shong Chin, and Jianwei Xu. Binary treatment of PEDOT:PSS films with nitric acid and imidazolium-based ionic liquids to improve the thermoelectric properties. *Materials Advances*, 1(9):3233–3242, 2020.
- [36] Ichiro Imae, Hiroki Uehara, Keiichi Imato, and Yousuke Ooyama. Thermoelectric Properties of Conductive Freestanding Films Prepared from PEDOT:PSS Aqueous Dispersion and Ionic Liquids. *ACS Applied Materials and Interfaces*, 2022.
- [37] Zeng Fan, Pengcheng Li, Donghe Du, and Jianyong Ouyang. Significantly Enhanced Thermoelectric Properties of PEDOT:PSS Films through Sequential Post-Treatments with Common Acids and Bases. *Advanced Energy Materials*, 7(8), 2017.

- [38] Falin Wu, Pengcheng Li, Kuan Sun, Yongli Zhou, Wei Chen, Jiehao Fu, Meng Li, Shirong Lu, Dongshan Wei, Xiaosheng Tang, Zhigang Zang, Lidong Sun, Xixia Liu, and Jianyong Ouyang. Conductivity Enhancement of PEDOT:PSS via Addition of Chloroplatinic Acid and Its Mechanism. *Advanced Electronic Materials*, 3(7):1–10, 2017.
- [39] Zhimeng Yu, Yijie Xia, Donghe Du, and Jianyong Ouyang. PEDOT:PSS Films with Metallic Conductivity through a Treatment with Common Organic Solutions of Organic Salts and Their Application as a Transparent Electrode of Polymer Solar Cells. *ACS Applied Materials and Interfaces*, 8(18):11629–11638, 2016.
- [40] Xin Li, Zhen Liu, Zekun Zhou, Haiyang Gao, Guodong Liang, Daniel Rauber, Christopher W.M. Kay, and Peng Zhang. Effects of Cationic Species in Salts on the Electrical Conductivity of Doped PEDOT:PSS Films. *ACS Applied Polymer Materials*, 3(1):98–103, 2021.
- [41] Yijie Xia and Jianyong Ouyang. Anion effect on salt-induced conductivity enhancement of poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) films, 2010.
- [42] Kholoud M.M. Abou El-Nour, Ala'a Eftaiha, Abdulrhman Al-Warthan, and Reda A.A. Ammar. Synthesis and applications of silver nanoparticles. *Arabian Journal of Chemistry*, 3(3):135–140, 2010.
- [43] Rebeca G. Melendez, Karla J. Moreno, Ivana Moggio, Eduardo Arias, Arturo Ponce, Irantzu Llanera, and Sergio E. Moya. On the influence of silver nanoparticles size in the electrical conductivity of PEDOT:PSS. *Materials Science Forum*, 644(March):85–90, 2010.
- [44] Jae Hee Jung, Hyun Cheol Oh, Hyung Soo Noh, Jun Ho Ji, and Sang Soo Kim. Metal nanoparticle generation using a small ceramic heater with a local heating area. *Journal of Aerosol Science*, 37(12):1662–1670, 2006.
- [45] Mohammad Zamakhsari Alhamid, Beny S. Hadi, and Ali Khumaeni. Synthesis of silver nanoparticles using laser ablation method utilizing Nd:YAG laser. *AIP Conference Proceedings*, 2202(August 2018), 2019.
- [46] Farid Bensebaa. *Wet Production Methods*, volume 19. 2013.
- [47] Bolla G. Rao, Deboshree Mukherjee, and Benjaram M. Reddy. *Novel approaches for preparation of nanoparticles*. Elsevier Inc., 2017.

- [48] Mingliang Tian, Jinguo Wang, James Kurtz, Thomas E. Mallouk, and M. H.W. Chan. Electrochemical growth of single-crystal metal nanowires via a two-dimensional nucleation and growth mechanism. *Nano Letters*, 3(7):919–923, 2003.
- [49] Mladen Barbic, Jack J. Mock, D. R. Smith, and S. Schultz. Single crystal silver nanowires prepared by the metal amplification method. *Journal of Applied Physics*, 91(11):9341–9345, 2002.
- [50] Heebo Ha, Chiara Amicucci, Paolo Matteini, and Byungil Hwang. Mini review of synthesis strategies of silver nanowires and their applications. *Colloids and Interface Science Communications*, 50(June), 2022.
- [51] Jun Jie Zhu, Qiao Feng Qiu, Hui Wang, Jian Rong Zhang, Jian Ming Zhu, and Zhi Qiang Chen. Synthesis of silver nanowires by a sonoelectrochemical method. *Inorganic Chemistry Communications*, 5(4):242–244, 2002.
- [52] Xiangqin Lin and Shuqing Wang. Electrochemical generation of silver nanowires. *Indian Journal of Chemistry - Section A Inorganic, Physical, Theoretical and Analytical Chemistry*, 44(5):1016–1018, 2005.
- [53] Xiao Jun Zheng, Zhi Yuan Jiang, Zhao Xiong Xie, Shu Hong Zhang, Bing Wei Mao, and Lan Sun Zheng. Growth of silver nanowires by an unconventional electrodeposition without template. *Electrochemistry Communications*, 9(4):629–632, 2007.
- [54] Jixiang Fang, Horst Hahn, Ralph Krupke, Frank Schramm, Torsten Scherer, Bingjun Ding, and Xiaoping Song. Silver nanowires growth via branch fragmentation of electrochemically grown silver dendrites. *Chemical Communications*, (9):1130–1132, 2009.
- [55] Bharat Sharma, Jung Sik Kim, and Ashutosh Sharma. Transparent AgNW-CoNPs conducting film for heat sensor. *Microelectronic Engineering*, 205(November 2018):37–43, 2019.
- [56] T. K. Lahane, J. Agrawal, and V. Singh. Optimization of polyol synthesized silver nanowires for transparent conducting electrodes application. *Materials Today: Proceedings*, 59:257–263, 2022.
- [57] Yafei Shi and Jixiang Fang. Large-Scale Synthesis of High-Purity Silver Nanowires with Reduced Diameters by the Polyethylene Glycol-Assisted Polyol Method. *Journal of Physical Chemistry C*, 126(46):19866–19871, 2022.

- [58] Yongjie Ge, Xidong Duan, Meng Zhang, Lin Mei, Jiawen Hu, Wei Hu, and Xiangfeng Duan. Direct Room Temperature Welding and Chemical Protection of Silver Nanowire Thin Films for High Performance Transparent Conductors. *Journal of the American Chemical Society*, 140(1):193–199, 2018.
- [59] Masoud Negahdary, Gholamreza Mazaheri, Somyeh Rad, Mohammadreza Hadi, Roya Malekzadeh, Mohammad Mahdi Saadatmand, Saeed Rezaei-Zarchi, Fariba Pishbin, and Mojdeh Khosravi-anhemami. Direct Electron Transfer of Hemoglobin on Manganese III Oxide-Ag Nanofibers Modified Glassy Carbon Electrode. *International Journal of Analytical Chemistry*, 2012(March 2014):1–7, 2012.
- [60] Yongjie Ge, Jianfang Liu, Xiaojun Liu, Jiawen Hu, Xidong Duan, and Xiangfeng Duan. Rapid Electrochemical Cleaning Silver Nanowire Thin Films for High-Performance Transparent Conductors. *Journal of the American Chemical Society*, 141(31):12251–12257, 2019.
- [61] Wang Zhang, Jiashuan Bao, Chenhui Xu, Pengfeng Zhu, Xiangliang Pan, and Rui Li. Electrochemical Redox In-Situ Welding of Silver Nanowire Films with High Transparency and Conductivity. *Inorganics*, 10(7), 2022.
- [62] G. Giusti, D. P. Langley, M. Lagrange, R. Collins, C. Jimenez, Y. Bréchet, and D. Bellet. Thermal annealing effects on silver nanowire networks. *International Journal of Nanotechnology*, 11(9-11):785–795, 2014.
- [63] Jong Sik Oh, Ji Soo Oh, Jae Hee Shin, Geun Young Yeom, and Kyong Nam Kim. Nano-welding of Ag nanowires using rapid thermal annealing for transparent conductive films. *Journal of Nanoscience and Nanotechnology*, 15(11):8647–8651, 2015.
- [64] Li Liu, Jianchun Jiang, Zhan Xu, Jiahang Zhou, and Yunbo Li. Enhanced electrical conductivity of PEDOT-encapsulated silver nanowire film pretreated with surfactants. *Colloid and Polymer Science*, 299(4):595–601, 2021.
- [65] Chih Jui Ni and Franklin Chau-Nan Hong. Electroless nanowelding of silver nanowires at room temperature. *RSC Advances*, 4(76):40330–40338, 2014.
- [66] Erik C. Garnett, Wenshan Cai, Judy J. Cha, Fakhruddin Mahmood, Stephen T. Connor, M. Greyson Christoforo, Yi Cui, Michael D. McGehee, and Mark L. Brongersma. Self-limited plasmonic welding of silver nanowire junctions. *Nature Materials*, 11(3):241–249, 2012.

- [67] Shengyong Wang, Huan Liu, Yongqiang Pan, Fei Xie, Yan Zhang, Jijie Zhao, Shuai Wen, and Fei Gao. Performance Enhancement of Silver Nanowire-Based Transparent Electrodes by Ultraviolet Irradiation. *Nanomaterials*, 12(17), 2022.
- [68] Whitney Gaynor, George F. Burkhard, Michael D. McGehee, and Peter Peumans. Smooth nanowire/polymer composite transparent electrodes. *Advanced Materials*, 23(26):2905–2910, 2011.
- [69] Sina Rezvani, Hong Seok Jo, and Simon S. Park. Flexible transparent electrodes based on intense pulsed light treatment of silver nanowires/PEDOT:PSS composites. *Organic Electronics*, 116(February):106776, 2023.
- [70] Hyewon Lee, Weontae Oh, Choonghyun Sung, Hyoung Seok Moon, and Jong Seong Bae. Heating characteristics of transparent thin films prepared with silver nanowire and conducting polymer. *Thin Solid Films*, 753(April):139262, 2022.
- [71] Juhung Park, Dongjun Han, Seunghwan Choi, Yunkyung Kim, and Jeonghun Kwak. Flexible transparent film heaters using a ternary composite of silver nanowire, conducting polymer, and conductive oxide. *RSC Advances*, 9(10):5731–5737, 2019.
- [72] Dhriti Sundar Ghosh, Tong Lai Chen, Vahagn Mkhitarian, and Valerio Pruneri. Ultrathin transparent conductive polyimide foil embedding silver nanowires. *ACS Applied Materials and Interfaces*, 6(23):20943–20948, 2014.
- [73] Wei Lan, Youxin Chen, Zhiwei Yang, Weihua Han, Jinyuan Zhou, Yue Zhang, Junya Wang, Guomei Tang, Yupeng Wei, Wei Dou, Qing Su, and Erqing Xie. Ultraflexible Transparent Film Heater Made of Ag Nanowire/PVA Composite for Rapid-Response Thermotherapy Pads. *ACS Applied Materials and Interfaces*, 9(7):6644–6651, 2017.
- [74] Marat Kaikanov, Bauyrzhan Amanzhulov, Gulzat Demeuova, Gulnur Akhtanova, Farabi Bozheyev, Aidar Kemelbay, and Alexander Tikhonov. Modification of silver nanowire coatings with intense pulsed ion beam for transparent heaters. *Nanomaterials*, 10(11):1–9, 2020.
- [75] Aekachan Pichitpajongkit, Hyeonjin Eom, and Inkyu Park. Joule Heating of Metallic Nanowire Random Network for Transparent Heater Applications. *Journal of Sensor Science and Technology*, 29(4):227–231, 2020.

- [76] Junpeng Li, Jiajie Liang, Xiang Jian, Wei Hu, Juan Li, and Qibing Pei. A flexible and transparent thin film heater based on a silver nanowire/heat-resistant polymer composite. *Macromolecular Materials and Engineering*, 299(11):1403–1409, 2014.
- [77] M. Sauer, S. Meilchen, A. Kalleder, M Mennig, and H Schmidt. Screen Printing. In *Sol-Gel Technologies for Glass Producers and Users*, pages 117–122. 2004.
- [78] Nam-Trung Nguyen. *Fabrication technologies*. 2012.
- [79] Diógenes Frederichi, Mara Heloisa Neves Olsen Scaliante, and Rosangela Bergamasco. Structured photocatalytic systems: photocatalytic coatings on low-cost structures for treatment of water contaminated with micropollutants—a short review. *Environmental Science and Pollution Research*, 28(19):23610–23633, 2021.
- [80] Mohammad Reza Azani and Azin Hassanpour. Synthesis of Silver Nanowires with Controllable Diameter and Simple Tool to Evaluate their Diameter, Concentration and Yield. *ChemistrySelect*, 4(9):2716–2720, 2019.
- [81] Vesna Stanic. Reactions of Chemical Hydrides with Polyhydroxyl Compounds for Onsite Hydrogen Production. *The Electrochemical Society*, 16:2145–2153, 2008.
- [82] Chih Ting F. Lo, Kunal Karan, and Boyd R. Davis. Kinetic studies of reaction between sodium borohydride and methanol, water, and their mixtures. *Industrial and Engineering Chemistry Research*, 46:5478–5484, 2007.
- [83] Hatim Machrafi, Fabio Iermano, Souhail Tamsamani, Ilija Bobinac, and Carlo S. Iorio. Enhanced electrical conductivity and stretchability of ionic-liquid PEDOT:PSS air-cathodes for aluminium-air batteries with long lifetime and high specific energy. *Scientific Reports*, 12(1):1–12, 2022.

Appendices

A Silver nanowire films

Tables A.1, A.2, and A show the resistance in $k\Omega$ of films with one and two layers of commercial silver nanowire ink deposited through doctor blading on PET and Kapton.

Table A.1: Resistance of films with one and two layers of commercial silver nanowire ink in the 1st design.

Substrate	Sample	1 layer	2 layers
Kapton	1	0.430	
	2	0.460	
	3	0.400	250 $M\Omega$
	4	0.450	
PET	1	0.550	
	2	0.390	
	3	0.690	250 $M\Omega$
	4	0.610	

Table A.2: Resistance of films with one and two layers of commercial silver nanowire ink in the 2nd design.

Substrate	Sample	1 layer	2 layers
Kapton	1	0.400	
	2	0.490	
	3	0.530	500 $M\Omega$
	4	0.430	
PET	1	0.580	
	2	0.520	
	3	0.480	500 $M\Omega$
	4	0.480	

Table A.3: Resistance of films with one and two layers of commercial silver nanowire ink in the 3rd design.

Substrate	Sample	1 layer	2 layers
Kapton	1	0.650	600 M Ω
	2	0.730	
	3	0.730	
	4	0.670	
PET	1	0.740	600M Ω
	2	0.760	
	3	0.700	
	4	0.770	

B Effect of number of layers of the PEDOT:PSS films

Tables B.1 through B.7 show the values of the resistances in k Ω obtained in the study of the effect of the number of layers of PEDOT:PSS on the resistance of the films. The deposited as-synthesized AgNWs were in glycerol with 55% (w/w) methanol.

Table B.1: Resistance for films with subsequential layers of doctor bladed PEDOT:PSS and spin-coated AgNWs in the 3rd design on PET.

Sample	1x PEDOT:PSS	1x AgNWs	2x AgNWs
1	4.410	3.930	4.150
2	3.310	2.970	3.100

Table B.2: Resistance variations for films with two doctor bladed layers of PEDOT:PSS and one spin-coated layer of AgNWs in the 3rd design.

Substrate	Sample	1x PEDOT:PSS	2x PEDOT:PSS	1x AgNWs
Kapton	1	4.140	2.030	1.850
	2	3.800	1.930	1.840
	3	4.870	1.890	1.740
PET	1	3.950	1.890	1.790

Table B.3: Resistances for films with two layers of screen-printed PEDOT:PSS and one layer of spin-coated AgNWs in the 1st and 3rd designs, on PET.

1 st design			
Sample	1x PEDOT:PSS	2x PEDOT:PSS	1x AgNWs
1	7.540	3.020	2.830
2	6.500	2.820	2.660
3	6.000	2.690	2.530
4	6.240		
5	7.030	2.900	2.910

3 rd design			
Sample	1x PEDOT:PSS	2x PEDOT:PSS	1x AgNWs
1	17.90	6.270	5.910
2	13.77	5.300	5.330
3	12.80	5.340	5.080
4	17.75	5.460	5.140
5	15.30	5.690	5.440

Table B.4: Resistances for films with two screen-printed layers of PEDOT:PSS with a bigger mesh size and one spin-coated layer of AgNWs on PET.

1 st design		
Sample	2x PEDOT:PSS	1x AgNWs
1	0.755	0.739
2	0.795	0.770
3	0.875	0.810
4	0.861	0.798
5	0.860	0.795
6	0.783	0.771

3 rd design		
Sample	2x PEDOT:PSS	1x AgNWs
1	1.568	1.460
2	1.550	1.480
3	1.750	1.600
4	1.685	1.570
5	1.686	1.590
6	1.632	1.480

Table B.5: Resistance for films with three layers of screen-printed PEDOT:PSS and one layer of spin-coated AgNWs on the 1st and 3rd designs on PET.

1 st design				
Sample	1x PEDOT:PSS	2x PEDOT:PSS	3x PEDOT:PSS	1x AgNWs
1	6.000	2.650	1.670	1.560
2	6.120	2.720	1.700	1.580
3	5.790	2.680	1.700	1.590
4	6.060	2.670	1.660	1.570
5	7.500	3.050	1.790	1.690

3 rd design				
Sample	1x PEDOT:PSS	2x PEDOT:PSS	3x PEDOT:PSS	1x AgNWs
1	14.30	5.530	3.370	3.15
2	13.76	5.390	3.290	3.040
3	16.05	5.830	3.450	3.230
4	16.37	5.790	3.410	3.190
5	17.85	6.300	3.530	3.330

Table B.6: Resistances for films with a spin-coated AgNW layer intercalated in doctor bladed PEDOT:PSS layers in the 1st design, on Kapton.

Sample	1x PEDOT:PSS	1x AgNWs	2x PEDOT:PSS
1	2.160	1.950	0.900
2	1.800	1.680	0.895
3	2.230	2.150	0.962
4	2.040	1.930	0.948
5	17.85	6.300	3.530

Table B.7: Resistances for films with a spin-coated AgNW layer intercalated in screen-printed PEDOT:PSS layers, on PET.

1 st design			
Sample	1x PEDOT:PSS	1x AgNWs	2x PEDOT:PSS
1	6.480	5.700	2.580
2	6.730	5.870	2.780
3	6.270	5.520	2.490
4	6.540	5.920	2.750
5	6.080	5.410	2.570

3 rd design			
Sample	1x PEDOT:PSS	1x AgNWs	2x PEDOT:PSS
1	14.14	13.33	5.610
2	16.15	15.53	5.790
3	13.09	12.62	5.340
4	14.15	14.22	5.430
5	14.62	13.14	5.150

C Films with modified PEDOT:PSS

Tables C.1 through C.7 show the resistances in $k\Omega$ of films with one or two layers of modified PEDOT:PSS and one layer of as-synthesized AgNWs in glycerol, or glycerol with 40 or 55% (w/w) of methanol, referred to as GLY, 40% or 55%, respectively, on the sample's section of the tables.

Table C.1: Resistance for films with two doctor bladed layers of PEDOT:PSS with 30% (w/w) of water and one spin-coated layer of AgNWs in glycerol and 55% (w/w) methanol.

Substrate	Design	1x PEDOT:PSS	2x PEDOT:PSS	1x AgNWs	Annealing 5h 180 °C
Kapton	1	3.300	1.250	1.120	1.910
	2	3.660	1.700	1.550	2.460
	3	5.600	2.630	2.400	4.000
PET	1	3.100	1.400	1.200	
	2	3.820	1.800	1.510	
	3	5.700	2.600	2.400	

Table C.2: Resistance for films with two doctor bladed layers of PEDOT:PSS with 50% (w/w) of water and one spin-coated layer of AgNWs in glycerol and 55% (w/w) methanol in the 2nd design.

Substrate	Samples	1x PEDOT:PSS	2x PEDOT:PSS	1x AgNWs	Annealing 1h 225 °C	Annealing 5h 180 °C
Kapton	1	4.590	2.250	1.970	10.30	27.00
	2	4.390	2.600	2.120		3.380
PET	1	4.040	2.090			
	2	4.300	2.160	1.800		

Table C.3: Resistance of films with one or two doctor bladed layers of PEDOT:PSS with PEG and glycerol, and one doctor bladed layer of AgNWs. The films were deposited on Kapton in the preliminary design.

1 layer

Sample	1x PEDOT:PSS	1x AgNWs
1	8.000	
2 (GLY)	3.500	1.200
3 (40%)	7.000	2.500
4 (55%)	7.000	1.500

2 layers

Sample	1x PEDOT:PSS	2x PEDOT:PSS	1x AgNWs
1	2.000	0.700	
2 (GLY)	2.000	0.500	8.000
3 (40%)	1.100	0.900	3.000
4 (55%)	1.000	0.800	6.000

Table C.4: Resistances for films with one layer of a PEDOT:PSS glycerol solution of concentration 0.4 g/mL with 5% (V/V) of methanol and another layer of AgNWs, both doctor bladed on Kapton in the preliminary design.

Sample	1x PEDOT:PSS	1x AgNWs
1 (40%)	1.200	630
2 (40%)	1.500	1.800
3	1.100	
4 (55%)	900	790
5 (55%)	1.500	1000
6	400	

Table C.5: Resistances for films of PEDOT:PSS aqueous solutions with glycerol and 5 or 10% (V/V) of methanol, and one layer of AgNWs in glycerol with 55% (w/w) methanol. All layers were doctor bladed on Kapton in the preliminary design.

5% (V/V) of methanol

Sample	1x PEDOT:PSS	1x AgNWs
1	0.800	0.480
2	1.00	0.260

10% (V/V) of methanol

Sample	1x PEDOT:PSS	1x AgNWs
1	345.0	465.0
2	333.0	485.0
3	16.00	38.00

Table C.6: Resistances for films with one or two layers of PEDOT:PSS with 10% (w/w) DMSO and one layer of AgNWs, all doctor bladed on Kapton in the preliminary design.

1 layer

Sample	1x PEDOT:PSS	1x AgNWs
1	0.340	
2 (GLY)	0.460	0.430
3 (40%)	0.200	0.170
4 (40%)	0.410	0.690
5 (40%)	0.490	0.550
6 (55%)	0.300	0.150
7 (55%)	0.230	0.220
8 (55%)	0.250	0.250

2 layers

Sample	1x PEDOT:PSS	2x PEDOT:PSS	1x AgNWs
1	0.600	0.300	
2	0.600	0.320	
3 (GLY)	0.260	0.150	0.500
4 (40%)	0.280	0.120	0.450
5 (55%)	0.250	0.080	0.380

Table C.7: Resistances for films with one or two layers of PEDOT:PSS with 40% (w/w) DMSO and one layer of AgNWs, all doctor bladed on Kapton in the preliminary design.

1 layer			
Sample	1x PEDOT:PSS	1x AgNWs	
1	1.200		
2	0.490		
3 (GLY)	0.930	0.870	
4 (40%)	0.890	0.700	
5 (40%)	1.100	1.000	
6 (55%)	0.670	0.620	
7 (55%)	0.850	0.900	

2 layers			
Sample	1x PEDOT:PSS	2x PEDOT:PSS	1x AgNWs
1	1.000	0.600	
2	1.300	0.600	
3 (GLY)	1.000	0.340	0.430
4 (40%)	1.000	0.330	0.380
5 (55%)	0.800	0.340	0.360

D Treatment of films with methanol or DMSO

Tables D.1 through D.20 show the resistances in $k\Omega$ of films with one or two layers of PEDOT:PSS post-treated with methanol or DMSO. In the samples sections of the tables, the references to GLY, 40% and 55% indicate that the AgNW layer was composed of as-synthesized AgNWs in glycerol, or in glycerol with 40% (w/w) or 55% (w/w) of methanol, respectively.

Table D.1: PEDOT:PSS films in Kapton treated with immersion in methanol for different times.

Sample	1x PEDOT:PSS	After treatment	Treatment time (min)
1	1.480	1.510	5
2	1.990	2.070	20
3	1.840	1.910	40
4	1.900	2.010	60

Table D.2: PEDOT:PSS films in Kapton treated with immersion in DMSO for different times.

Sample	1x PEDOT:PSS	After treatment	Treatment time (min)
1	1.710	1.730	5
2	1.770	1.900	20
3	1.750	1.830	40
4	2.100	2.110	60

Table D.3: Resistances for films with one or two layers of PEDOT:PSS treated with a drop of methanol and another layer of AgNWs, all deposited through doctor blading in the preliminary design on Kapton.

1 layer			
Sample	1x PEDOT:PSS after treatment	1x AgNWs	
1	0.450		
2	0.320		
3 (GLY)	1.200	3.500	
4 (GLY)	0.650	1.200	
5 (40%)	0.500	0.600	
6 (40%)	0.450	0.450	
7 (55%)	0.500	0.250	
8 (55%)	0.420	0.480	

2 layers			
Sample	1x PEDOT:PSS after treatment	2x PEDOT:PSS after treatment	1x AgNWs
1	0.640	0.240	
2	0.360	0.180	
3 (GLY)	0.430	0.340	0.230
4 (40%)	0.560	0.230	0.175
5 (55%)	0.800	0.180	0.240

Table D.4: resistance for films with one or two layers of PEDOT:PSS treated with a drop of methanol followed by immersion in it and an additional layer of AgNWs. All layers were deposited through doctor blading in the preliminary design on Kapton.

1 layer		
Sample	1x PEDOT:PSS	1x AgNWs
1	0.290	
2	0.420	
3 (GLY)	0.420	0.450
4 (GLY)	0.260	0.260
5 (40%)	0.320	0.350
6 (40%)	0.340	0.430
7 (55%)	0.370	0.350
8 (55%)	0.320	0.200

2 layers			
Sample	1x PEDOT:PSS	2x PEDOT:PSS	1x AgNWs
1	0.450	0.170	
2	0.230	0.120	
3 (GLY)	0.410	0.160	0.140
4 (40%)	0.370	0.130	0.150
5 (55%)	0.700	0.130	0.150

Table D.5: Resistances for films with two layers of doctor bladed PEDOT:PSS immersed in methanol and another spin-coated layer of AgNWs in glycerol with 55% (w/w) of methanol, in the 1st, 2nd and 3rd designs.

Substrate	Design	1x PEDOT:PSS	1x PEDOT:PSS after treatment	2x PEDOT:PSS	2x PEDOT:PSS after treatment	1x AgNWs
Kapton	1 st	1.720	1.740	0.820	0.823	0.723
	2 nd	2.490	2.480	1.090	1.030	0.996
	3 rd	4.100	4.100	1.690	1.610	1.550
PET	1 st	1.900	1.870	0.805	0.820	0.703
	2 nd	2.900	2.500	1.080	1.150	0.914
	3 rd	4.000	3.930	1.600	1.780	1.420

Table D.6: Resistances for films with two layers of screen-printed PEDOT:PSS immersed in methanol and another spin-coated layer of AgNWs in glycerol with 55% (w/w) of methanol, in the 1st and 3rd designs on PET.

1 st design					
Sample	1x PEDOT:PSS	1x PEDOT:PSS after treatment	2x PEDOT:PSS	2x PEDOT:PSS after treatment	1x AgNWs
1	6.700	6.830	2.800	2.910	2.650
2	6.840	6.830	3.020	3.080	2.770
3	6.900	7.120	2.750	2.850	2.530
4	7.830	7.330	2.820	2.890	2.530
5	7.000	7.500	2.900	3.070	2.690

3 rd design					
Sample	1x PEDOT:PSS	1x PEDOT:PSS after treatment	2x PEDOT:PSS	2x PEDOT:PSS after treatment	1x AgNWs
1	15.86	16.12	6.170	6.630	5.690
2	16.54	17.28	6.500	6.700	5.860
3	17.36	17.95	6.150	6.380	5.610
4	19.67	18.44	6.020	6.240	5.450
5	16.16	16.90	6.000	6.040	5.500

Table D.7: Resistances for films with one or two layers of PEDOT:PSS with PEG immersed in methanol and another layer of AgNWs, all deposited through doctor blading, in the preliminary design, on Kapton.

1 layer

Sample	1x PEDOT:PSS after treatment	1x AgNWs
1	0.960	
2	0.690	
3 (GLY)	1.000	1.200
4 (GLY)	0.410	0.350
5 (40%)	0.600	0.430
6 (40%)	0.550	0.420
7 (55%)	0.640	0.490
8 (55%)	0.900	0.790

2 layers

Sample	1x PEDOT:PSS after treatment	2x PEDOT:PSS after treatment	1x AgNWs
1	0.660	0.190	
2	0.400	0.170	
3 (GLY)	0.400	0.180	0.130
4 (40%)	0.280	0.160	0.120
5 (55%)	0.600	0.210	0.160

Table D.8: Resistance for films with two screen-printed layers of PEDOT:PSS with PEG immersed in methanol and one spin-coated layer of AgNWs in glycerol and 55% (w/w) methanol in the 2nd and 3rd designs.

2 nd design								
Substrate	Sample	1x PEDOT: PSS	1x PEDOT: PSS after treatment	2x PEDOT: PSS	2x PEDOT: PSS after treatment	1x AgNWs	Annealing 1h 225 °C	Annealing 5h 180 °C
Kapton	1	11.20	11.80	6.200	5.180	3.900		
	2	10.90	11.00					
	3	10.20	12.70	5.800	5.300			
	4	10.50	12.40	6.600	5.160	3.760		10.20
	5	11.20	11.84	6.100	5.490	3.880	21.20	54.20
PET	1	5.400	5.30					
	2	10.60	12.40	6.000	5.360	3.780		
	3	10.70	12.08	8.200	5.000			
	4	11.60	17.32					
	5	11.60	11.42	7.700	4.750	3.710		
PC	1	10.40	30.80	5.200	5.200	4.100		
	2	10.20	10.96	5.400	5.060			

3 rd design								
Substrate	Sample	1x PEDOT: PSS	1x PEDOT: PSS after treatment	2x PEDOT: PSS	2x PEDOT: PSS after treatment	1x AgNWs	Annealing 1h 225 °C	Annealing 5h 180 °C
Kapton	1	23.70	12.80	9.800	8.510	7.490	46.40	1400
	2	22.30	21.30	11.30	8.630	7.420		
	3	21.80	19.99	10.40	8.250	7.250		16.80
	4	20.90	14.70	9.100	6.700			
	5	25.60	33.66					
PET	1	25.40	55.30					
	2	21.20	22.00	12.00	8.200	7.100		
	3	21.40	18.10	12.50	8.410	7.530		
	4	24.60	12.20	10.70	9.460	8.340		
	5	25.30	26.16	10.50	8.410			
PC	1	20.80	23.27	8.100	8.140			
	2	21.70	23.56	7.980	8.050	6.820		

Table D.9: Resistances for films with two layers of PEDOT:PSS immersed in methanol and one intercalated layer of AgNWs in glycerol with 55% (w/w) of methanol. All layers were deposited through doctor blading in the preliminary design on Kapton.

Sample	1x PEDOT:PSS	1x PEDOT:PSS after treatment	1x AgNWs	2x PEDOT:PSS	2x PEDOT:PSS after treatment
1	1.100	0.260	0.200	0.400	0.100
2	0.560	0.250	0.190	0.370	0.110
3	0.700	0.230	0.130	0.370	0.096
4	0.800	0.240	0.136	0.300	0.096

Table D.10: Resistances for films with one or two layers of PEDOT:PSS with glycerol treated with a drop of methanol with an additional layer of AgNWs. All layers were deposited through doctor blading in the preliminary design on Kapton.

1 layer

Sample	1x PEDOT:PSS after treatment	1x AgNWs
1	0.800	
2	0.840	
3	0.450	
4 (GLY)		0.450
5 (GLY)		0.560
6 (GLY)	0.330	0.500
7 (40%)		0.230
8 (40%)	1.200	1.100
9 (40%)	0.220	0.220
10 (55%)		0.260
11 (55%)	1.300	0.900
12 (55%)	0.630	0.890

2 layers

Sample	1x PEDOT:PSS after treatment	2x PEDOT:PSS after treatment	1x AgNWs
1	0.540	0.270	
2	0.350	0.220	
3 (GLY)	0.420	0.150	0.160
4 (40%)	0.320	0.230	0.170
5 (55%)	0.470	0.300	0.200

Table D.11: Resistance for films with one or two layers of PEDOT:PSS with glycerol treated with a drop and immersion in methanol and another layer of AgNWs. All layers were deposited through doctor blading in the preliminary design on Kapton.

1 layer			
Sample	1x PEDOT:PSS after treatment	1x AgNWs	
1	0.650		
2	0.600		
3	0.240		
4 (GLY)		0.660	
5 (GLY)	1.000	0.600	
6 (GLY)	0.330	0.500	
7 (40%)		0.540	
8 (40%)	1.700	0.530	
9 (40%)	0.220	0.220	
10 (55%)		0.480	
11 (55%)	0.600	0.310	
12 (55%)	0.630	0.890	

2 layers			
Sample	1x PEDOT:PSS after treatment	2x PEDOT:PSS after treatment	1x AgNWs
1	0.600	0.240	
2	0.390	0.190	
3 (GLY)	0.450	0.190	0.160
4 (40%)	0.800	0.250	0.170
5 (55%)	0.370	0.170	0.200

Table D.12: Resistances for films of PEDOT:PSS with AgNWs in glycerol and methanol deposited through doctor blading in the 2nd design and treated with immersion in methanol.

Substrate	Sample	Before treatment	After treatment
Kapton	1	4.340	4.330
	2	4.900	4.850
PET	1	4.750	4.750
	2	4.200	4.200

Table D.13: Resistances for films with one or two layers of PEDOT:PSS immersed in DMSO and one layer of AgNWs. All layers were doctor bladed in the preliminary design on Kapton.

1 layer

Sample	1x PEDOT:PSS after treatment	1x AgNWs
1	0.320	
2 (GLY)	0.430	0.450
3 (40%)	0.300	0.300
4 (55%)	0.370	0.320

2 layers

Sample	1x PEDOT:PSS after treatment	2x PEDOT:PSS after treatment	1x AgNWs
1	0.600	0.600	
2 (GLY)	0.400	0.330	0.360
3 (40%)	0.330	0.300	0.200
4 (55%)	0.300	0.300	0.220

Table D.14: Resistances for films with two screen-printed PEDOT:PSS layers immersed in DMSO and one layer of spin-coated or doctor bladed AgNWs in glycerol and 55% (w/w) of methanol. The films were produced in the 1st, 2nd, and 3rd designs on Kapton.

1st design

Sample	1x PEDOT:PSS	1x PEDOT:PSS after treatment	2x PEDOT:PSS	2x PEDOT:PSS after treatment	1x AgNWs
1	5.070		2.470	2.600	
2	4.930	10.95	2.500	2.800	2.270
3	4.860	5.400			
4	5.550	7.700	2.500	2.600	2.460
5	4.730	4.800	2.360	2.600	

2nd design

Sample	1x PEDOT:PSS	1x PEDOT:PSS after treatment	2x PEDOT:PSS	2x PEDOT:PSS after treatment	1x AgNWs	Annealing 1h 225 °C	Annealing 5h 180 °C
1	6.200	7.430	3.660	3.600			
2	5.930	6.260	3.300	3.560	3.090	14.10	36.30
3	5.690	6.100					
4	5.730	8.980	3.510	4.000	3.200		
5	5.550	4.700	3.390	3.600	3.770		

3rd design

Sample	1x PEDOT:PSS	1x PEDOT:PSS after treatment	2x PEDOT:PSS after treatment	2x PEDOT:PSS	1x AgNWs	Annealing 1h 225 °C
1	12.60		5.480	6.130		
2	12.36		5.710	5.880	8.450	
3	11.79	13.83	5.550	5.700	4.940	21.01
4	12.07	13.87	5.430	5.540	6.820	
5	12.21	14.86				

Table D.15: Resistances for films with PEDOT:PSS immersed in DMSO and an intercalated layer of AgNWs in glycerol and 55% (w/w) of methanol. All layers were doctor bladed in the preliminary design on Kapton.

Sample	1x PEDOT:PSS	1x PEDOT:PSS after treatment	1x AgNWs	2x PEDOT:PSS	2x PEDOT:PSS after treatment
1	0.600	0.220	0.180	0.112	0.200
2	0.630	0.330	0.240	0.130	0.270
3	0.420	0.200	0.180	0.150	0.240
4	0.350	0.240	0.180	0.130	0.170

Table D.16: Resistances for films with one layer of PEDOT:PSS immersed in DMSO, one intercalated layer of AgNWs in glycerol and 55% (w/w) of methanol, and one untreated layer of PEDOT:PSS. PEDOT:PSS was doctor bladed, while the AgNWs were spin-coated in the 3rd design on Kapton.

Sample	1x PEDOT:PSS	1x PEDOT:PSS after treatment	1x AgNWs	2x PEDOT:PSS
1	4.270	4.160	3.880	2.030
2	4.390	4.250	3.980	1.930

Table D.17: Resistances for films with two layers of PEDOT:PSS with PEG further immersed in DMSO and an additional layer of AgNWs in glycerol and 55% (w/w) of methanol. All layers were doctor bladed in the 1st, 2nd, and 3rd designs on Kapton.

Design	1x PEDOT:PSS	1x PEDOT:PSS after treatment	2x PEDOT:PSS	2x PEDOT:PSS after treatment	1x AgNWs
1 st	2.900	2.050	1.120	0.950	0.800
2 nd	4.500	2.750	1.230	1.150	0.953
3 rd	7.000	3.850	2.200	1.790	1.600

Table D.18: Resistances for films with two layers of PEDOT:PSS with PEG further immersed in DMSO and an additional layer of AgNWs in glycerol and 55% (w/w) of methanol. PEDOT:PSS layers were screen-printed, while AgNWs were spin coated in the 1st and 3rd designs on Kapton.

1st design

Sample	1x PEDOT:PSS	1x PEDOT:PSS after treatment	2x PEDOT:PSS	2x PEDOT:PSS after treatment	1x AgNWs
1	9.400	8.400	3.620	3.150	2.870
2	9.80	8.980	3.700	3.470	2.980
3	10.10	8.590	3.600	3.380	3.070
4	10.00	8.620	3.750	3.280	2.950
5	9.700	8.850	3.680	3.250	2.930

3rd design

Sample	1x PEDOT:PSS	1x PEDOT:PSS after treatment	2x PEDOT:PSS	2x PEDOT:PSS after treatment	1x AgNWs
1	19.90	18.43	7.350	6.390	5.730
2	21.20	18.38	7.500	6.550	6.100
3	21.30	23.61	7.440	7.360	6.370
4	21.40	18.22	7.620	6.690	6.250
5	21.90	18.70	7.590	6.450	6.070

Table D.19: Resistances for films of PEDOT:PSS with PEG and AgNWs in glycerol and 55% (w/w) of methanol doctor bladed in the 2nd design on Kapton and further immersed in DMSO.

Sample	Before treatment	After treatment
1	12.00	4.930
2	11.00	5.580

Table D.20: Resistances associated with DMSO treatment of films of doctor bladed PEDOT:PSS followed by immersion in AgNWs in glycerol and 55% (w/w) of methanol.

Sample	1x PEDOT:PSS	1x PEDOT:PSS after treatment	After immersion in AgNWs solution	Immersion time (min)
1	5.050	5.220	5.860	30
2	3.780	3.800	6.320	60
3	5.610	5.680	17.00	90

E Films with cleaned AgNWs

Tables E.1 and E.2 show the resistances in $k\Omega$ associated with the use of cleaned and sintered as-synthesized AgNWs.

Table E.1: Resistances for the spin coating of sintered AgNWs in water onto a film of two screen-printed layers of PEDOT:PSS in the 1st and 3rd designs.

1 st design			
Substrate	Sample	1x PEDOT:PSS	1x AgNWs
PET	1	5.200	4.980
	2	5.150	
	3	5.600	
Kapton	4	5.630	5.130
	5	6.000	
	6	5.600	

3 rd design			
Substrate	Sample	1x PEDOT:PSS	1x AgNWs
PET	1	9.210	8.390
	2	8.750	
	3	8.560	
Kapton	4	8.950	9.380
	5	8.160	
	6	8.730	

Table E.2: Resistances for the spin coating of sintered AgNWs in water onto a film of three screen-printed layers of PEDOT:PSS in the 1st and 3rd designs.

1 st design			
Substrate	Sample	1x PEDOT:PSS	1x AgNWs
PET	1	3.330	2.920
	2	3.440	
	3	3.630	
Kapton	4	3.400	3.220
	5	3.330	
	6	3.240	

3 rd design			
Substrate	Sample	1x PEDOT:PSS	1x AgNWs
PET	1	5.510	5.280
	2	5.760	
	3	5.710	
Kapton	4	5.180	4.860
	5	5.540	
	6	5.390	

F Treatment of films with CTAB or sodium borohydride

Tables F.1 and F.2 show the resistances in k Ω of the following films treated with immersion in CTAB:

- (A) Two layers of screen-printed PEDOT:PSS and one layer of spin-coated AgNWs in glycerol and 55% (w/w) of methanol.
- (B) Two layers of screen-printed PEDOT:PSS with an intercalated spin-coated layer of AgNWs in glycerol and 55% (w/w) of methanol.
- (C) Two layers of screen-printed PEDOT:PSS immersed in methanol and a layer of spin-coated AgNWs in glycerol and 55% (w/w) of methanol.
- (D) Two layers of screen-printed PEDOT:PSS with PEG immersed in DMSO and a layer of spin-coated AgNWs in glycerol and 55% (w/w) of methanol.

Table F.1: Resistances for films treated with CTAB and rinsed with water.

Film	Before treatment	After treatment
A	2.880	14.00
B	2.760	7.400x10 ³
C	2.700	5.200
D	3.090	11.0

Table F.2: Resistances for films treated with CTAB and rinsed with ethanol.

Film	Before treatment	After treatment
A	2.560	6.000
B	2.810	6.600
C	2.790	6.400
D	3.040	6.430

Table F.3 shows the resistances in $k\Omega$ of the following films treated with immersion in sodium borohydride (NaBH_4):

- (A) Two layers of doctor bladed PEDOT:PSS and one layer of spin-coated AgNWs in glycerol and 55% (w/w) of methanol.
- (B) Two layers of PEDOT:PSS with an intercalated layer of AgNWs in glycerol and 55% (w/w) of methanol, both doctor bladed.
- (C) Two layers of PEDOT:PSS immersed in methanol and a layer of AgNWs in glycerol and 55% (w/w) of methanol, both doctor bladed.

Table F.3: Resistances for films treated with NaBH_4 .

Film	Before treatment	After treatment
A	1.800	2.620
B	1.400	1.910
C	0.919	1.110

G Ionic liquid and PVA

Tables G.1 through G.5 show the resistances in $k\Omega$ for films with ionic liquid and PVA.

Table G.1, specifically, shows the effect of modifying the following doctor bladed films with ionic liquid:

- (A) Two layers of PEDOT:PSS immersed in methanol and a layer of AgNWs in glycerol and 55% (w/w) of methanol.
- (B) Two layers of PEDOT:PSS with an intercalated layer of AgNWs in glycerol and 55% (w/w) of methanol.
- (C) One layer of PEDOT:PSS.

Table G.1: Resistances for films modified with ionic liquid by spin coating or immersion.

Spin coating		
Film	Without ionic liquid	With ionic liquid
A	0.695	0.900
B	1.430	1.500
C	1.920	1.930

Immersion		
Film	Before immersion	After immersion
A	0.723	2.300
B	0.900	1.060

Table G.2: Resistances for a spin-coated layer of ionic liquid with PVA (ratio 0.8:1 in weight) and AgNO₃ on doctor bladed PEDOT:PSS in the 2nd design.

Sample	1x PEDOT:PSS	1x LI+PVA+AgNO ₃
1	2.000	2.800
2	2.600	3.100

Table G.3: Resistances for different concentrations of the solution of ionic liquid, PVA and AgNO₃ added to PEDOT:PSS, for a weight ratio between ionic liquid and PVA of 0.8:1, in the 2nd design.

Sample	Resistance
20 % of IL+PVA+5 mM of AgNO ₃	12.60
50 % of IL+PVA+5 mM of AgNO ₃	700.0 92.00
80 % of IL+PVA+5 mM of AgNO ₃	3800

Table G.4: Resistances for a spin-coated layer of ionic liquid with PVA (ratio 3:1 in weight) and AgNO₃ on doctor bladed PEDOT:PSS in the 2nd design.

Sample	1x PEDOT:PSS	1x PEDOT:PSS
1	2.300	3.300
2	2.200	3.800

Table G.5: Resistances for different concentrations of the solution of ionic liquid, PVA and AgNO₃ added to PEDOT:PSS, for a weight ratio between ionic liquid and PVA of 3:1, in the 2nd design.

Sample	Resistance
20 % of IL+PVA+5 mM of AgNO ₃	40.0
50 % of IL+PVA+5 mM of AgNO ₃	440.0 60.00
80 % of IL+PVA+5 mM of AgNO ₃	4000

