Printing Technologies on Flexible Substrates for Printed Electronics

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Abstract

Printing technologies have been demonstrated to be highly efficient and compatible with polymeric materials (both inks and substrates) enabling a new generation of flexible electronics applications. Conductive flexible polymers are a new class of materials that are prepared for a wide range of applications, such as photovoltaic solar cells, transistors molecular devices, and sensors and actuators. There are many possible printing techniques. This chapter provides an opportunity to review the most common printing techniques used at the industrial level, the most commonly used substrates and electronic materials, giving an overall vision for a better understanding and evaluation of their different features. Several technological solutions (contact/noncontact) and its critical challenges are also presented. Inkjet Printing Technology (IPT) has been receiving a great attention and therefore higher focus is given to this technology. An overview of IPT is presented to evidence its importance and potential as a key-technology on the research field for printed electronics development, as well as on large scale industrial manufacturing. A background and a review on prior work are presented along with used materials, developed applications and potential of IPT technology. The main features of the different printing technologies, advantages and main challenges are also compared.

Keywords: printing techniques, flexible polymers, conductive inks

1. Introduction

When an electrical device is created through a printing process, it is designated Printed Electronics (PE). Over 20 years, the manufacturing industry has been using various printing techniques to produce, e.g., antennas, sensors, membrane switches, etc. [1]. This list is continuously increasing. Today users' demands (for lower cost, flexible and smarter products) are a decisive factor for the selection of PE fabrication technologies, therefore, contributing to novel and better products. The interest on flexible electronic systems to be used, for example, on non-planar surfaces grew tremendously in recent years, [2] in areas such as aerospace and automotive, [3] biomedical, [4] robotics, [5] and health applications [6]. This is possible thanks to the combination of different polymeric materials (compared to traditional silicon substrates) with new coating and printing techniques able to work at temperatures compatible with the polymeric substrate, or even the manufacturing of non-planar surfaces otherwise impossible with old-fashioned fabrication techniques. The use of flexible polymers has many advantages compared to traditional hard substrates including: higher contact area, capability to fold/roll, lightweight, etc., therefore, they have a key role in the development of new conductive circuits.

Thanks to better and flexible materials combined with PE, commercial applications diversity will continue to emerge. According to Markets and Markets latest report, the progress of flexible applications based on PE market will worth $12.1B by 2022. According to Electronics.ca Publications, Printed organic & flexible electronics market will be worth over $73B by 2027.

Each technology is selected according to the type of electronic components or devices (e.g., small, thin, lightweight, flexible, inexpensive and disposable, etc.), the production cost and volume. The essential aspects for the success of any type of PE device is the processability, performance and long-term reliability [1] of the materials used [7]. The pastes, inks or coatings can be based both on organic and inorganic materials [7]. Inorganic inks normally contain metallic (e.g., copper, gold, silver, aluminum) nanoparticles dispersed in a retaining matrix and they are used, for example, in the fabrication of passive components and transistor electrodes [7]. Organic inks are based on organic materials, such as polymers (conductors, semiconductors and dielectrics). The inks based on high conductive polymers are employed in batteries, electromagnetic shields, capacitors, resistors and inductors, sensors, etc., while inks based on organic semiconductors are employed as active layers of active devices such as, Organic PhotoDiodes (OPDs), Organic Light Emitting Diodes (OLEDs), Organic Field-Effect Transistors (OFETs), organic solar cells (OSC), sensors, etc. [7]. Due to the wide range of printing technologies, the materials must meet certain requirements depending on the type of printing being performed and on the application.

PE technologies can be divided in contact and non-contact techniques as shown on **Figure 1**:

- contact techniques (e.g., screen printing, flexography, gravure printing and soft lithography), in which the printing plate is in direct contact with the substrate;
- non-contact techniques (e.g., laser direct writing, aerosol printing, inkjet printing), where only the deposition material get in contact with the substrate.

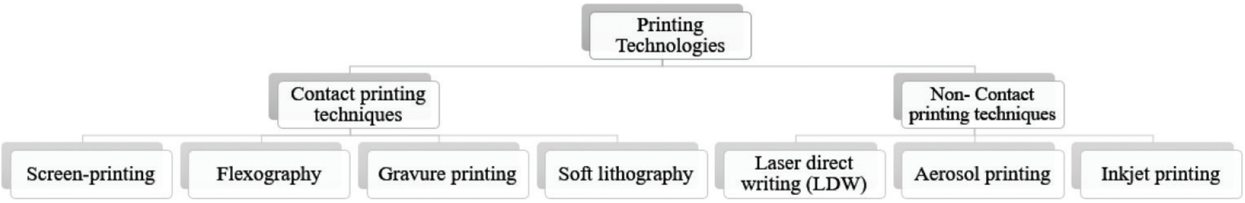

Figure 1. Printing technologies classification.

This chapter reviews simultaneously the most used techniques at the research and industrial level, substrates and electronic materials for an overall vision and a better understanding and evaluation of its different features. Their main features and examples of PE applications are discussed with greater focus on Inkjet Printing Technology.

2. Printing technologies

2.1. Contact printing technologies

The contact printing technologies are the predominant printing processes in the current days. They involve high material waste and limitations around the resolution and range of the materials used (substrates, inks, solvents). Main contact printing technologies are described in the following.

2.1.1. Screen printing

Screen printing (SP) is a mature printing technique that may be performed in a planar system or in a roll-to-roll (R2R) process (**Figure 2**). The planar system uses a SP mesh, which is in direct contact with the substrate; the blade moves, distributes the ink and helps filling the mesh. The ink passes into the standard image in the mesh to the substrate and defines the final image. The substrates could be epidermis [8], paper, glass, metal [9], ceramic, [10] wood, textiles [10], polymers [10]. Webb et al. [11] describes a SP functional ink, comprising a combination of semiconducting acicular particles, electrically insulating nanoparticles and a base polymer ink, that exhibits pronounced pressure sensitive electrical properties for applications in sensing and touch sensitive surfaces.

In the R2R process, the squeegee is replaced by a roller and the ink and the blade are placed inside. The blade forces the ink through the mesh. The process is continuous, contrary to the planar system, allowing high speeds production, although rotary setup is expensive and hard to clean.

SP is a technology that has been often used for PE [12]. This technique produces large waste of production material (including the ink). The biggest limitation is reflected in the level of resolution. Also, the planar system speed is low in comparison to other conventional printing processes [13].

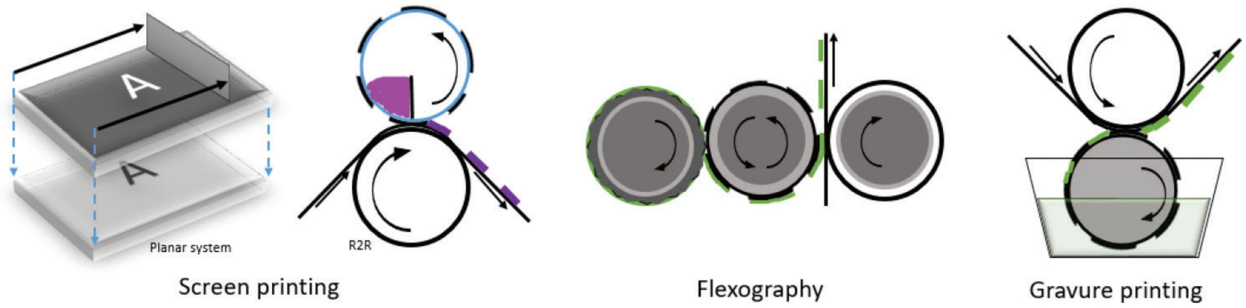

Figure 2. Schematic of contact printing techniques.

2.1.2. Flexography

The flexography is a R2R direct printing technology, where the final pattern stands out from the ink transfer. A ceramic anilox roller, covered with micro-cavities on its surface, allows the collection of ink, and then is transferred to the printing plate cylinder (**Figure 2**). A closed chamber supplies the ink to the anilox roller [13]. A doctor blade removes excess ink from the cylinder and prevents the output from the ink supply chamber. The printing plate continuously rotates in contact with the substrate ensuring a continuous high speed printing process.

However, situations such as the Halo effect (patterns with excess of ink) occur due to the compression between the printing plate and the substrate, despite the low pressure applied. This leads to limitations on image size stability and resolution [13]. This technology is commonly used for the fabrication of on-label battery testers, drug delivery patches, printed batteries and other e-label applications [1]. Julin used flexography to produce flexible piezoelectric pressure sensors [14]. They investigated the suitability of flexography printing and new electrode materials in their manufacture, developing a flexo-printed piezoelectric PolyVinyliDene Fluoride (PVDF) pressure sensor. Although the sheet resistance of the fabricated samples presented high values and a lot of variability, the devices showed a non-uniform structure and some difficulties were reported on achieving a uniform pressure sensor.

2.1.3. Gravure printing

The gravure printing technology is the reverse process of flexography, where the image to be printed is negative (**Figure 2**). The ink is received directly by the ink supplier container or by an additional roller to the gravure plate, where the pattern image is located. A flexible metal blade removes the excess ink. The ink is transferred through capillary action from the small engraved cavities on the cylinder surface to the substrate. This technology is capable of producing high quality patterns in a cost-effective manner and is suitable for printing with inks of low viscosity, and high manufacturing speeds (up to 0.1 m/s [15]) can be achieved. A careful optimization of the process and of the materials is important because the final print quality is highly dependent upon:

- inks properties, i.e., its rheological behavior (viscosity), solvent evaporation rate and curing;
- proper cell spacing (1.06–1.4 μm) for print quality [16, 17];
- feature dimensions on gravure cylinder for proper cell emptying capability [16] are very important;
- shear force in the printing mechanism [17].

Widely used in magazine production, gravure printing is also highly employed for certain electronics products such as medical Electrocardiography (ECG or EKG) pads and high-volume Radio-Frequency Identification devices (RFID) [1], Thin-Film-Transistors (TFT) [16], solar cells [18] and sensors [19]. However, this process presents two main limitations: the printing image is built from separate cells, and when printing a straight line, a jagged line is observed [13], which represents a major obstacle when high resolution is need, e.g., less than 20 μm size is required for electronic structures [15], and the parasitic capacitances are to be avoid; the proper layer deposition alignment, e.g., in electronic applications, repeating conductive film deposition is sometimes required in order to reduce sheet resistance. When it comes to R2R techniques (e.g., screen-printing, flexography and gravure printing) another level of complexity is added to these technologies. Also, frequent replacements of the gravure cylinders are needed, which adds a maintenance cost.

2.1.4. Soft lithography

Soft lithography technology encompasses several printing techniques (**Figure 3**), such as micro-contact printing (μCP) [20], replica molding (REM), micro transference molding (μTM), micro-molding in capillaries (MIMIC), and solvent assisted micromolding (SAMIM) [21]. It provides a convenient, effective method for the manufacturing of high quality micro- and nanostructured systems [22]. In this set of technologies, an elastomeric (commonly of poly (dimethylsiloxane) (PDMS)) stamp or mold with patterned relief structures on its surface is used to transfer patterns and structures with feature sizes ranging from 30 nm to 100 μm [21]. Usually the master is prepared using either e-beam or photolithography. From this master, several stamps can be molded. The material of interest is deposited on the stamp and transferred on the substrate. However, soft lithography does not offer better economic advantages when compared to R2R printing techniques due to the rapid throughput [7]. The fabrication includes several manufacture steps with the involvement of photolithographic technology [5, 23]. Other challenges rely on a proper adjustment of the surface energies of substrates and inks for efficient transfer to the substrate to be printed, on common swelling of transferring materials, resulting on increased features size.

2.1.5. Comparing contact printing technologies

Tables 1 and **2** summarize qualitatively the mechanisms, the process requirements, material and critical limitations of the contact printing technologies, highlighting their main features. These tables also provide the possibility of merging the different techniques in order to combine technologies to overcome one technology limitation with another technology.

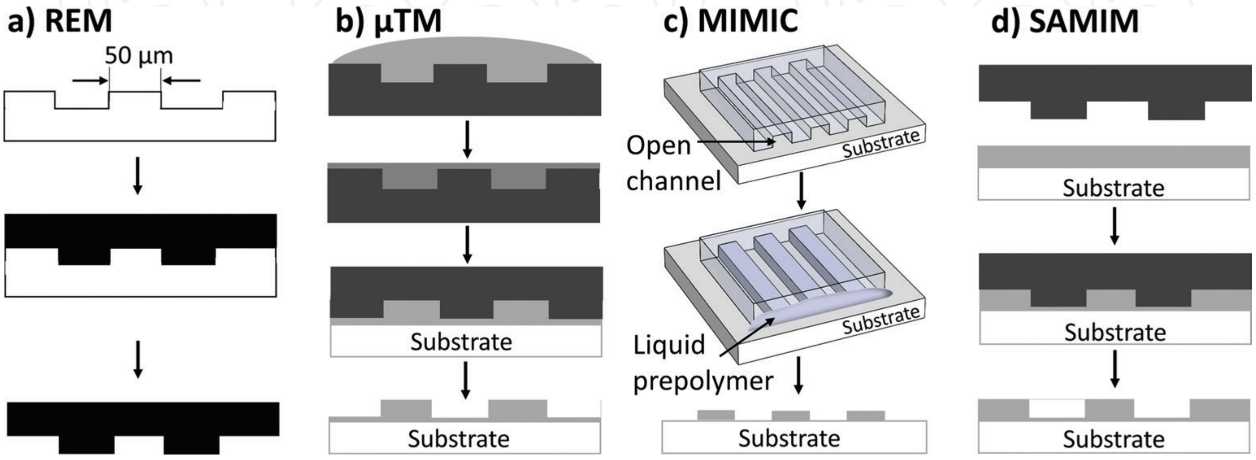

Figure 3. Major steps in soft lithography technologies.

2.2. Non-contact printing technologies

Compared to the contact printing technologies, the non-contact has the advantage of the substrate only getting in contact with the deposition material. This lowers the risks of contamination, of damaging the substrate and the patterns alignment is more accurate. This last issue is an indispensable functionality to pattern multilayered devices. For non-contact printing techniques there is no need for physical mask of the to-be-printed image, only requiring a digital image, simplifying the switching process without no additional cost. However, the non-contact technologies also stumble upon some difficulties when completing multilayered devices [23] are needed. They work with all kinds of substrates, such as, wood, glass, metals and most interesting, rubbers, polymers, which require low processing temperatures, and risk to be damaged and deformed when subjected to thermal stresses and high temperature processes. Main non-contact printing techniques are described in the following.

2.2.1. Laser direct writing

Laser direct-writing (LDW) techniques enable the realization of 1D to 3D structures by laser-induced deposition of metals, semiconductors, polymers and ceramics, without using masks and without physical contact between a tool or nozzle and the substrate material. Operated by a computer, the laser pulses are manipulated to control the composition, structure, and properties of individual three-dimensional volumes of materials, across length-scales spanning six orders of magnitude from nanometers to millimeters [25]. The ability to process complex

Print technique	Mechanisms and features	Challenges
Screen printing [13–15]	Most used and mature printing technique; planar or R2R system; speed and versatile.	Hard to clean; solvents deteriorate mask patterns; high resolution of uniform line patterns are not possible under 30 μm; Unfeasible use of low viscosity inks to prevent spreading and bleed out; material wastage.
Flexography [13]	High speed printing process; low-cost patterns plate; high flexibility and low pressure printing; better vertical and horizontal pattern quality compared to gravure.	Halo effect (patterns with excess of ink) due to printing plate compression to the substrate, despite the low pressure applied; marbling effect; complex multi layers alignment.
Gravure printing [13, 15, 17, 24]	High quality patterns in a cost-effective manner; high speed; low viscosity inks.	Cylinder life and high cost; demanding and careful optimization of the process (several variables) influence final print quality representing a major obstacle where high resolution is required (e.g., PE).
Soft lithography [20–22]	Encompasses several printing techniques (μCP, REM, μTM, MIMIC, SAMIM); fabrication of micro-and nanostructures of high quality; convenient, effective method; mostly used by the biological science area.	Proper adjustment of the surface energies for efficient transfer to the substrate to be printed; common swelling of transferring materials, resulting an increased features size; pattern reproduction and resolution is a challenge due to used forces on stamp; costly solution.

Table 1. Summary of contact printing techniques: mechanisms, features and main challenges.

Technique	Solution types	Solution viscosity (Pa.s)	Print thickness (μm)	Resolution (μm)	Surface tension (mN/m)
Screen printing	Water based, solvent based, UV or electron beam curable	0.1–10	0.02–100 [12, 13]	30–100	38–47
Flexography	Water based, solvent based, UV curable	0.01–0.1	0.17–8	30–80	13.9–23
Gravure printing	Water based, solvent based, UV curable	0.01–1.1 [14]	0.02–12 [13, 24]	50–200	41–44
Soft lithography	Water based, solvent based, UV curable	~0.10	0.18–0.7	0.03–100	22–80

Table 2. Comparison between main contact printing techniques.

or delicate material systems and the achieved resolutions enable LDW to fabricate structures that are not possible to generate using other techniques. Within LDW, there are three writing techniques:

i. LDW addition (LDW+) technique, where the material can be deposited from gaseous, liquid and solid precursors (e.g., Laser Chemical Vapor Deposition (LCVD)) or by transfer, by laser beam, from an optically transparent support onto a parallel substrate (e.g., Laser-induced forward transfer (LIFT) [7], **Figure 4**). These techniques entail high cost due to the sophisticated equipment (e.g., reaction chamber associated with vacuum equipment); it does not allow to deposit organic substrates; and it can only print on flat substrates, parallel to the support material.

ii. LDW subtraction (LDW-) technique, where the material is removed by ablation (e.g., photochemical, photothermal, or photophysical ablation [26], laser scribing, cutting, drilling, or etching [27]). An industrial application example is the high-resolution manufacturing and texturing of stents or other implantable biomaterials.

iii. LDW Modification (LDWM) technique, where the material is modified thermally or chemically [25] (e.g., Laser-Enhanced Electroless Plating, LEEP). The substrate is submerged in a chemical solution that contains the metallic ions required for the deposition. A laser beam is responsible for local temperature rise, decomposing the liquid and leading to the deposition of a metallic layer on the substrate surface. The main disadvantage relies in its disability to create 3D structures.

2.2.2. *Aerosol jet printing*

Aerosol jet printing (**Figure 4**), also known as Maskless Mesoscale Materials Deposition (M3D) is another material deposition technology for printed electronics [28] developed by Optomec [29]. The ink (solutions and nanoparticle suspensions based on metals, alloys, ceramics, polymers, adhesives or biomaterials) is placed into an atomizer where it aerosolizes in liquid

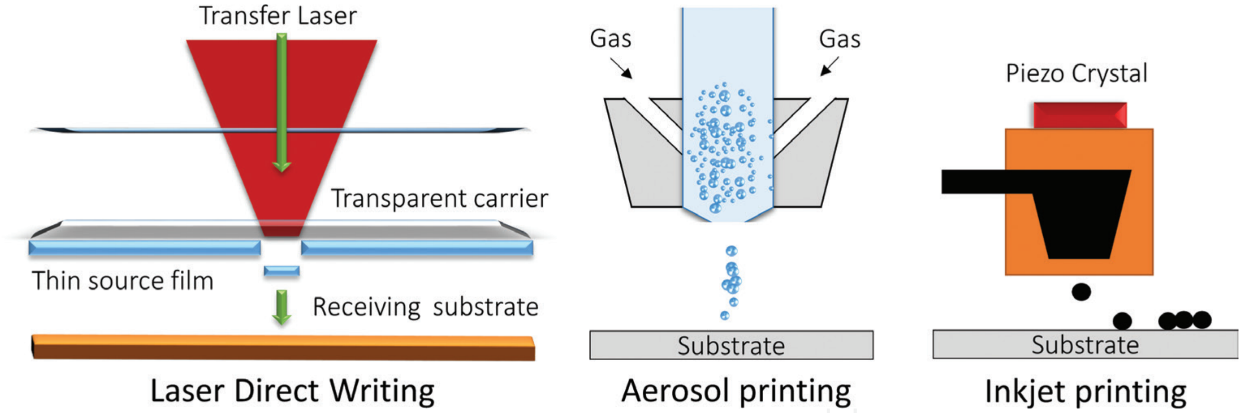

Figure 4. Schematic of non-contact printing.

particles of diameter between 20 nm and 5 μm, depending on the ink viscosity. Then, the ink is transported into the deposition head by a nitrogen flow, the aerosol being focused by jet stream onto the substrate. As being a low-temperature process, many materials and substrates can be handled by Aerosol Jet printing. The technique is also scalable to support high volume production needs. It is suitable for non-planar capability and complex designs could be printed (e.g., displays, thin film transistors, TFT, and solar cells) [29]. Complex conformal surfaces (3D printed electronics) are also possible, thanks to the ability to control the position in z-direction of the writing head over the substrate. This technique also stumbles upon some difficulties. The droplet carrier creates a cloud of powder in the surroundings of the print area. The sheath gas creates a localized crystallization/solidification phase at the trace pattern, reducing the localized bonding layer quality.

2.2.3. Inkjet printing

Inkjet printing is new technology with a grown interest from the scientific community and is considered to be in an early stage of development [2]. In Inkjet printing technology (IPT), a content stored in a digital format is transferred by a direct deposition (from small openings in print-heads, without the use of masks and without contact between the print-head and the substrate) of droplet fluid or powder, proteins or minerals [30, 31], conductive polymers [32], nanoparticles [33, 34] and a wide range of materials (e.g., bioactive fluids, which cannot tolerate exposure to photolithography and etching chemicals present in conventional techniques [32]). Under the print-head ejection, the gravity force, and air resistance, the ink is project into a specified position of the substrate creating the printing patterns (**Figure 4**).

In the case of fluids, it dries through the evaporation of the solvent, by chemical changes (e.g., cross-linking of polymers) or crystallization. Eventually, a post-processing treatment is required, as thermal annealing or sintering [35]. When compared to other deposition methods, IPT is adaptable for patterning on a high variety (rigid or flexible, smooth or rough surfaces [2, 36]) of substrates (glass, plastic [36], paper [37], textile [38], etc.), with low consumption of raw materials [36] and low levels of waste production harmful to the environment [2]. IPT is intended for a wide range of applications: transducers [32], transistors [39], structural polymers and ceramics [30], biomimetic and biomedical materials [31], printed scaffolds for growth of living tissues [30], as well as for building 3D electric circuits [40], MEMS [34], and sensors [37]. No special processing conditions are needed. IPT stands out for being a one-step process, with a simple operating principle, reduced number of manufacturing steps, with the possibility of using low cost raw materials [41]. Thickness around nanometer range is easily achieved by increasing the electric field value along with the distance between the print head and substrate. The used inks have a particular set of physical specifications in particular its viscosity, the superficial tension [36], and the amount of humectant (10–20%) [42]. Sometimes, modifications on the ink viscosity, concentration and solvent system are necessary for proper droplet injection without blocking the nozzle. Although the low process velocity and possible clogging of the nozzles, presenting a challenge to the industrial production, IPT becomes ideal for laboratory research providing innovative fabrication, high quality and low cost productions.

2.2.4. Comparing non-contact printing techniques

Tables 3 and **4** summarize the mechanisms, the process requirements, material and critical limitations of the non-contact printing technologies, highlighting their main features.

2.3. IPT mode technology systems

The IPT can operate in two different modes: Continuous InkJet (CIJ) and Drop-On-Demand (DoD) [36]. The method for controlling the droplet movement is quite different between the two systems.

2.3.1. Continuous inkjet (CIJ) mode

In the CIJ system, the ejection of the droplet is continuous in all nozzles of the printer. In the traditional CIJ, a piezoelectric transducer is coupled to the print head to provide a periodic excitation [38]. After leaving the nozzle, an electric field determines and controls the trajectory of the droplet to the desired position on the substrate (**Figure 5**).

Printing technique	Mechanisms and features	Challenges
LDW [7, 25–27]	1D to 3D structures; nm to mm magnitude; no mask; three writing techniques (LDW+, LDW−, LDWM)	High cost equipment; not possible to deposit organic substrates, printing only on flat substrates, parallel to the substrate
Aerosol [28–43]	Complex design could be printed; complex conformal surfaces; many materials and substrates; non-planar; low-temperature processing, local sintering	Droplet carrier creates a cloud of powder in surrounding printed area; sheath gas creates a localized crystallization/ solidification phase at the trace pattern reducing the quality of the localized bonding layer
IPT [30–42]	Low viscosity; deposition of many types of droplets; droplets ejection through different actuation phenomena; all type of substrates; low material wastage; environmentally friendly	Slow printing speed compared to other techniques; nozzle clogging

Table 3. Summary of non-contact printing techniques and challenges.

Technique	Solution types	Solution viscosity (Pa.s)	Thickness (μm)	Resolution (μm)	Surf. tension (mN/m)
LDW	Solid film (donor substrate)	–	>10	ca. 0.7	–
Aerosol	Solutions and nanoparticle suspensions based on metals, alloys, ceramics, polymers, adhesives or biomaterials	0.001–1	>0.1	10–250	–
IPT	Water based, solvent based, UV curable	0.002–0.1	0.01–0.5	15–100	15–35

Table 4. Comparison between main non-contact printing techniques.

Within this technology, the droplets can be diverted by binary or multiple deflection systems. On the binary systems, the droplets are directed to a single pixel location on the substrate or to the gutter, for later recycling of the ink. In the multiple deflection system, the droplets are charged and deflected to the substrate at different levels, this way creating multiple pixels. Hertz et al. [43] used the binary CIJ and developed a method consisting in the formation of a layer of irregularly droplets of ink size. In the Hertz method, the droplets are dispersed in a straight line to a gutter so as to converge into the recirculation system. This method also introduced a new procedure and methodology relatively to the use of volatile solvents that allows a quick drying of the ink and the adhesion to the substrate materials. The CIJ system benefits from the ability to combine the printing speed (on the order of 25 m/s) with the possibility of achieving extended distances and the ability to divert droplets independent of gravity [44].

CIJ technology is typically used for large industrial productions of bar codes and labels of food products or medicines. This process can be comparatively fast, with the advantage of circumscribing large printing areas with a single pass and its printing heads have a long duration. The droplet size can reach values such as 20 μm, with a standard size of 150 μm [45]. However, in the manufacture of electronic products, the CIJ produces droplets of inadequate resolution due to the long distance between the print-head and the substrate [13]. Other less positive factors are the high cost of initial investment in such equipment, the lower resolution compared to some DoD systems, the need to use low viscosity electrolyte inks (in the range of 3–6 mPa.s), resulting in some final ink waste [46].

2.3.2. Drop-on-demand (DoD) mode

In the DoD system, the print-head ejects a single droplet only when activated (**Figure 5**). The printer is based on several injector nozzles in the print-head and, at each pulse, the droplets are ejected in parallel to each other. The image is constructed from successive pulses, which largely differentiates from CIJ. The DoD is a high speed method, of high scalability that uses high frequency multiple nozzles. The method that is used to generate these pulses defines the subcategories of the primary DoD, namely: the acoustic, the electrostatic, the thermal, the piezoelectric, and an additional method, sometimes controversial, the MEMS [47] method. This last method is more related to the fabrication process, since the drop generation is based on thermal or piezo print-heads.

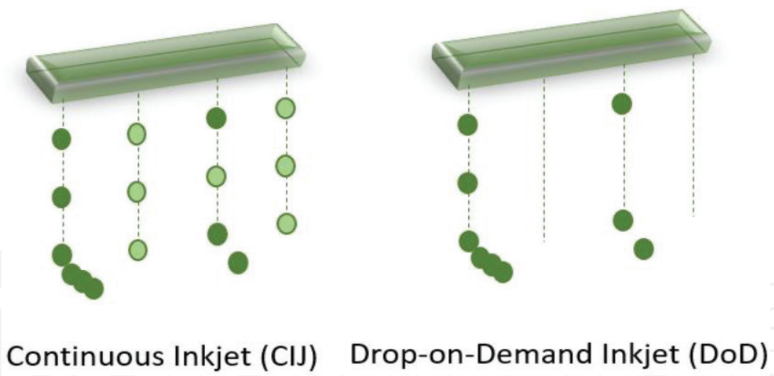

Figure 5. IPT mode technology systems.

2.3.3. Main influencing factors

The control of ink drop, the print-head temperature, the sintering or cure of the ink, and the printing control of each layer are key parameters to ensure the quality of a multilayer printed structure. Also important is to evaluate the properties of the substrate, such as, the service temperature, its barrier properties against humidity, electrical, optical, mechanical and chemical properties. Equally important is consider the receptivity of the ink by the substrate or with previously printed layers, in the case where a different ink has been used. The droplet size can vary depending on the interactions between the ink and the substrate. The droplet size sets the width of the printed line, establishing the pattern space and the electric design limits, and defines the final specifications of the printed pattern and application system (e.g., resolution, bandwidth in the case of a PE). Thereby, during the manufacturing step, the printed pattern characteristics are dependent on the materials and their interaction (i.e., the properties of the ink must be chosen in advance to understand its behavior during and after the printing process over a given substrate). Sintering and cure of conductive materials are essential because it defines its chemical, electrical and physical performance and the reliability of the printed layers over the long term.

3. Printable materials for PE

The printable materials are selected depending on the type of substrate, the type of ink, the type of printing technology and final PE application.

The conductive inks are gathering increasingly attention over the past two decades, and are revolutionizing the industry. Elected due to their attributes, such as, conductivity, suitability for printing substrates, its processing simplicity and mechanical flexibility, but also due to its ability to assign new properties, capabilities and complex functionalities. These emerging inks are penetrating the market with an opportunity to reach $400 m by 2027, according to IDTechEX report “Condutive Ink Market 2017-2027”. A large variety of materials, organic and inorganic, conductors and semiconductors, have been explored for electronics applications. The most common types of inks are water, oil or solvents based. The general form of the ink consist of a mixture of compounds (pigments or dyes, resins, solvents, fillers, humectant and additives), in liquid or solid state, with specific proprieties adapted to the printing technology characteristic, such as viscosity, surface tension, etc., to be easily printed in a large variety of substrates. What makes conductive inks electrically conductive is the fact that it contains in the composition conductive nanoscale particles. The incorporation of conductive polymers [48], carbon (C) [49] or metallic particles (e.g., silver (Ag) [8, 36], copper (Cu) [50], and gold (Au) [51]) are the most common selections. **Table 5** shows the resistivity of the bulk metal particles and the sintered metal ink form. Commonly, the metallic nanoparticles are stabilized in ink solutions by organic ligand shells, i.e., the nanoparticles are encapsulated with an organic material, called a capping agent, to form a uniform and stable dispersion, preventing particles agglomeration. This capping agent can be removed after printing through curing or sintering to allow physical contact between nanoparticles, forming continuous connectivity, i.e., a percolation path for electrical conductivity. Thus, sintering consist on welding the particles to each other below their melting point [2], and this particle welding could be achieved by exposure of the printed pattern to laser sintering [52], to microwave radiation [53], by applying an electrical voltage [54], by a chemical agent at room temperature (RT sintering) [55], or, the most conventional approach, by heating (thermal sintering) [33, 56]. In the case of thermal sintering, the temperature (typically between 100 to 400°C) must be below the softening temperature of the substrate. The presence of a few nanometers organic layer between the conductive particles is enough to block the movement of electrons from one particle to the other [33], thus reducing electrical conductivity. If this happens, the removal of this organic layer is required at high temperatures. For this reason, the sintering temperature of the nanoparticle based inks has extreme importance in plastic electronic applications, where materials, such as polyethylene terephthalate [56] and polycarbonate [56], are widely used as substrates, but have low T_g (98 and 148°C, respectively). The electrical conductivity of a printed nanoparticles based ink layer also depends on the shape and size of the nanoparticles. The amount of sintering temperature and time required depend upon how easy the organic encapsulation breaks, the particle dimensions and upon the thickness of the ink film. The smaller the particle size (2–10 nm) the lower the temperature required to sinter the particles, the short is the process and a higher electrical conductivity is achieved. Typically, the nanoparticle loading inks is higher than 20 wt%. Metal nanoparticles hold the highest electrical conductivity, although, the use of the above categorized precious metals hardly fits in the so called low cost PE.

Conductive polymers are classified into two different categories: extrinsically or intrinsically conductive polymers. The extrinsically conductive polymers normally involve a blend of conductive or nonconductive polymers, and a highly conductive additive (e.g., metallic particles) suspended in the polymer matrix [57], meaning that they are extrinsically enhanced to be conductive. Relatively to the intrinsically conductive polymer, they consist simply in a network

Metal	Ag	Cu	Au
Pure state (Ω.m)	1.59×10^{-8}	1.68×10^{-8}	2.44×10^{-8}
Printed ink (μΩ.cm)*	10–50	5–7	8

*Dependent on sintering temperature and time-higher temperature.

Table 5. Metal resistivity [33].

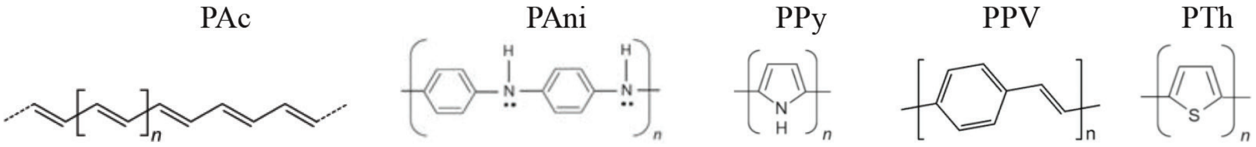

Figure 6. Chemical structure of conductive polymers.

of alternating single and double carbon bonds. It's this alternation of bonds that produces conjugated π-bonds, resulting in an intrinsically conductive material [58]. Polyacetylene (PAc), Polyaniline (PAni), polypyrrole (PPy), polyphenylene vinylene (PPV), polythiophene (PTh) are intrinsically conductive polymers (**Figure 6**).

Within the intrinsically conductive materials, the regioregular PTh has a tremendous potential for applications in flexible organics electronics because of its low cost and specific properties, such us, solubility (thanks to the three-substituents alkyl-chain in the PTh core [59]), spectroscopic and electronic properties, low-temperature process [60], highly ordered structure and semi-crystallinity state in its solid states [61], regioregular compatibility to large-area fabrications and industrial mass production technologies. In the chemical structure of the regioregular PThs, the backbone of the polymer is formed by thiophene rings and a chemical side-chain group can be attached on each thiophene ring along the polymer (**Figure 7**). An end-group or a secondary copolymer chain can be added to each end of the PTh.

Within the PTh and its derivatives, the poly(3-hexylthiophne) (P3HT) and poly (3,4-ethylenedioxythiophene) (PEDOT) [62] are the most well-known. The P3HT is a reference material in organic electronic, physics and chemistry to which any new p-type or donor conjugate molecule should be compared and evaluated. The PEDOT is the most widely used [63] intrinsically conductive polymer. PEDOT stands out for its high transparency [64] when deposited in thin oxidized films, high electrical conductivity [64], very high chemical stability in the oxidized state, processability and simplicity of production [65]. All these features make them suitable for several printing technologies, such as, spin coating [66], screen printing [67] and inkjet printing [68]. These unique properties make intrinsically conductive polymers excellent for various applications, such as, electrochromic devices [69], sensors [60], biosensors [68], actuators [70], capacitors [70], and photovoltaic cells [70], thin film diode [71]; organic thin film transistors (OTFTs) [72], photodiodes, Organic Field-Effect Transistor (OFETs) [52], organic light-emitting diodes (OLEDs) [73], etc., with a growing interest in PE due to its relatively low cost [74].

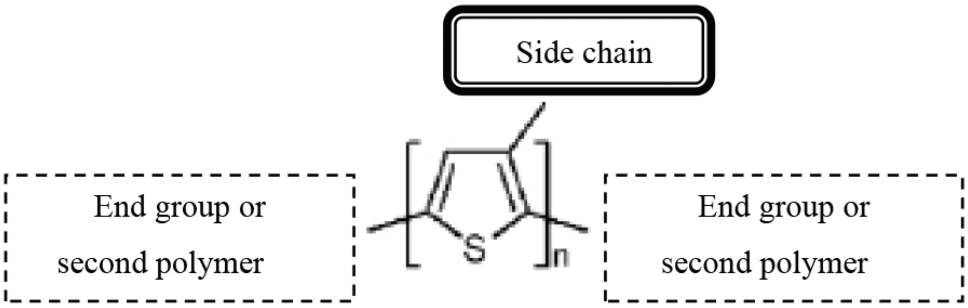

Figure 7. Schematic diagram of a regioregular polythiophene based polymers.

4. Flexible and extensible substrate for PE

There are three types of substrates that may be used on electronic devices: glass; metal and polymers. The first two are rigid material. The glass is non flexible. The metal foil is flexible and sustain high temperature, although, is limited on the freedom of design and is high cost. Polymers composites, such as, glass-reinforced epoxy laminates with flame retardant (FR-4) have been largely used in rigid printed circuit boards (PCB). Non-reinforced polymers are flexible materials, are more economically processed, and gives greater freedom of design, providing studies with increasingly intelligent PE applications, able to be integrated in complex systems and environments [34]. Their major drawback lies on the low surface energy, which, normally requires a prior surface treatment before printing and low processing temperatures. Their selection must meet a series of physical, mechanical, chemical, thermal and optical requirements, and also important, the compatibility with the conductive inks.

Various types of polymers (semi-crystalline and amorphous) have been proposed as flexible substrates (e.g., polyimide [5, 12, 74], polyethylene terephthalate [11], polyethylene naphthalate [75], PVDF [14], polycarbonate [14]), and both flexible and extensible substrates (e.g., poly (PDMS) [4, 5, 75, 76], polyurethane [76], thermoplastic polyurethanes (TPU) [77, 78]), etc. **Table 6** shows the main properties of flexible polymeric substrates.

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

Tg – glass transition temperature, Tm – melting temperature, CTE – coefficient of thermal expansion.

Table 6. Comparison between flexible polymeric substrates.

5. Printing technologies challenges

Understanding the printing process and relationships between process parameters and printing quality (e.g., print resolution, uniformity and electrical conductivity of printed layer) is necessary for process optimization, as well as the suitability of the selected material in terms of adhesion and final applications; the appropriateness of the printed technology and ink properties, the process deposition rate, etc. It will be a commitment between several criteria that will allow achieve the desired PE performance, functionalities and requirements. The main challenges are summarized in **Table 7**.

5.1. Compatibility between printable material and substrate

Most polymers have low surface energy (SE). The transfer and distribution of the ink on a substrate depends on the wettability and adhesion capabilities. The adhesion between two materials is the sum of a number of mechanical, physical, and chemical forces between them, at the interface, and depend on the mechanism of adhesion involved, that include mainly:

- Substrate properties (chemical composition, surface topography and porosity, etc.).
- Conductive ink properties (chemical composition, rheological behavior, the rate of solvent evaporation, etc.).
- The superficial tension (ST) of the ink and the SE of the substrate that will receive the ink, i.e., the difference between them.
- Functional groups and their intermolecular forces present in the ink/polymer system.

Surface wettability, spreadability and adhesion are the most important requirements in the printing process, and both are directly dependent on the fluid contact angle (**Figure 8**). When a fluid spreads evenly over the surface without the formation of droplets, the surface is said to be wettable. When a droplet is formed, the surface is said to be non-wettable, implying that cohesive forces associated with the fluid are greater than the forces associated with the interaction of the fluid with the surface. ST refers to the amount of cohesive forces between liquid molecules. The SE describes the degree of energy with which the molecules of the surface of a solid draw and allow adherence of a fluid. Often, ST and SE are interrelated, since both measure the ability of molecules to attract and to adhere to each other. In IPT, the spheroidal shape of the liquid emerging from the nozzle is defined by the ST of the liquid. The adhesion between two surfaces (ink, substrate) occurs when these droplets come into contact and develop strength in order to maintain a stable interface solid–liquid. Adhesion between a solid and a liquid exists when the solid SE exceeds the liquid ST.

The polymer low SE represents a great challenge in PE. In this situation, surface treatments are required to increasing the SE of the polymer, although implies an extra step in the

Flexible substrates	Printable inks	Equipment
• Flexible substrates encapsulation • Cost effective barrier encapsulation material • Scalability to large area (e.g., OLEDs) • Adhesion • Long time reliability	• Development of new inks formulation • Adhesion • Scalability to large area • Lifetime and stability	• Appropriate, affordable • High volumes • Resolution

Table 7. Main challenges.

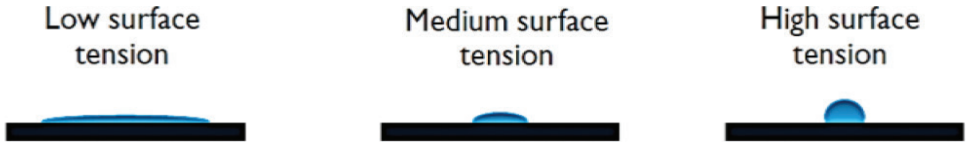

Figure 8. Ink behavior on a substrate.

manufacturing process, increases the time and cost of production. Adhesion-enhancing techniques such as: chemical [79] or mechanical induced roughening of the surface [77], or resorting to a primer (e.g., silane coupling agents [80]), corona discharge [81], plasma treatment [82], and flame treatment [81] are some examples. The most common techniques are plasma, flame and chemical treatment. With plasma and flame treatment, the substrate SE is changed by creating functional groups on the surface and eliminating surface contaminants. Although, the surface treatment is temporary, i.e., the treatment enhances the compatibility of the surface with the ink, but the exposure to air induces hydrophobic recovery [83]. Therefore, it is recommended to print after surface treatment. Chemical treatment is another option. The chemical treatment changes the surface characteristics (physical and chemical) by increasing the total area of interface between both layers leading to structural changes (by increasing the interface roughness) and interactions between the fluid molecules and the substrate.

5.2. Printable materials compatibility

Another aspect that can pose a problem during printing is the incompatibility between different inks used in multilayered structures or between layers of the same ink, which can cause dissolution or resuspension of the previously deposited layer of ink, depriving uniform and uncontaminated layers [42]. The morphology and uniformity of the printed pattern depends on the contained deposited drop in the determined spatial printing area.

The optimization of the ink and interaction between ink and the substrate strongly affects the final resolution and constitutes a main research challenge in order to achieve repeatability of printed patterns and devices. An optimized ink formulation, according to equipment and target application, as well as the substrate treatment processes constitute the main successful factors to achieve high resolution and repeatability of the printed patterns and devices.

Equally relevant are the different post-processing treatments, such as, sintering, annealing or simply drying in air required for each ink, which defines the final morphology and uniformity of the printed pattern and the manufacturing time [32].

6. Applications of IPT to flexible PE

The increase of the printing resolution leads to an increased number of applications. Lee et al. [84] developed a flexible capacitive pressure sensor for plantar pressure measurement, using a flexible printed circuit film as a sensor substrate and PDMS as dielectric layer. Cheng et al. [5] developed a tactile sensor with PDMS using a highly reliable capacitive mechanism. However, the required manufacturing process involved multiple factoring steps and the use of several material layers, which consequently leads to time consumption, large material waste and high manufacturing costs, preventing the process automation to an industrial level. When the goal is large area sensing platforms, manufacture premium prices constitute a problem. In recent years, the interest for IPT to sensor fabrication has attracted attention [39, 85]. First IPT prototypes start to appear and has already been selected to step in the production of several devices, such as, integrated circuits [30, 33], transistors [32, 86], conducting polymer devices [30], structural polymers and ceramics [85], biomaterials, and printed scaffolds for growth of living tissues [30, 31]. In the field of flexible sensors, IPT it is just taking the first steps. IPT of an intrinsically conducting polymer [87] onto a flexible substrate for humidity and gas sensing applications [88] are two of many of the rapidly emerging IPT examples. Only a few examples of IPT sensors combining IPT polymer conductive ink (PEDOT:PSS and P3HT) [79, 89] or silver ink [90], printed on polymer substrate have been reported so far. Someya et al. [91] has developed flexible pressure sensors with a complex designed structure using OFET active matrices manufactured by IPT and screen printing technology. Basiricó et al. [92] have proposed a totally IPT flexible OFET assembled on plastic films as sensors for mechanical variables using a PEDOT:PSS as electrodes and a P3HT as a semiconductor. The results obtained were promising despite the lower charge carrier mobility measured. Cruz et al. [89] have developed a inkjet printed pressure sensing platform capable of measuring the central plantar pressure (CPP). The use of PEDOT:PSS for definition of the electrodes over a TPU substrate resulted in pressure sensors with higher sensitivities and better linearity. Good performance results (comparable with existing solutions) were achieved, with the particularity of offering a low-cost alternative. The printed substrate presented high flexibility, was able to follow and deform along with the substrate, without breaking or losing adhesion and its conductivity properties. The ink piezo-resistive effect and high gauge factors (>300) were demonstrated (higher than the typical value of flexible metallic strain gauges) showing the potential of the material to be used in several sensing applications [79].

7. Final remarks

The PE technology is not a replacement for conventional electronics, however, allows free design and unlimited applications areas. The PE benefits from new printing technologies, new material solutions, and by the combination of other manufacturing processes. The increase of research and development is reflecting a growing interest in the new generation of flexible and PE applications for, space and weight reduction. The PE had an undeniable impact on the electronic industry, economics and on the human life, revolutionizing the electronic applications, otherwise impossible to achieve with the conventional techniques and materials.

This chapter made an overview of the most important printing techniques and material solutions for the PE, with particular attention to the IPT. For the different printing technology, the process requirements, the materials and their critical limitations, highlighting their main features, were summarized. The possibility of combining technologies to overcome one technology limitation with another technology was also presented. Moreover, IPT is a promising technology which main advantages lies on its simplicity and low cost operating principle, overcoming the flaws of traditional technologies. Also, the main printing challenges are addressed, in terms of compatibility between printable material and substrate. At the end, examples of IPT flexible PE are presented. A breakthrough is expected in the next years which potentially will reduce cost with mass production applications. So far, there are other issues that need to be discussed and practical questions start to arise once the industry gets more involved and focused in developing commercial products, such us, market trend, recycling, and return of the investment.

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