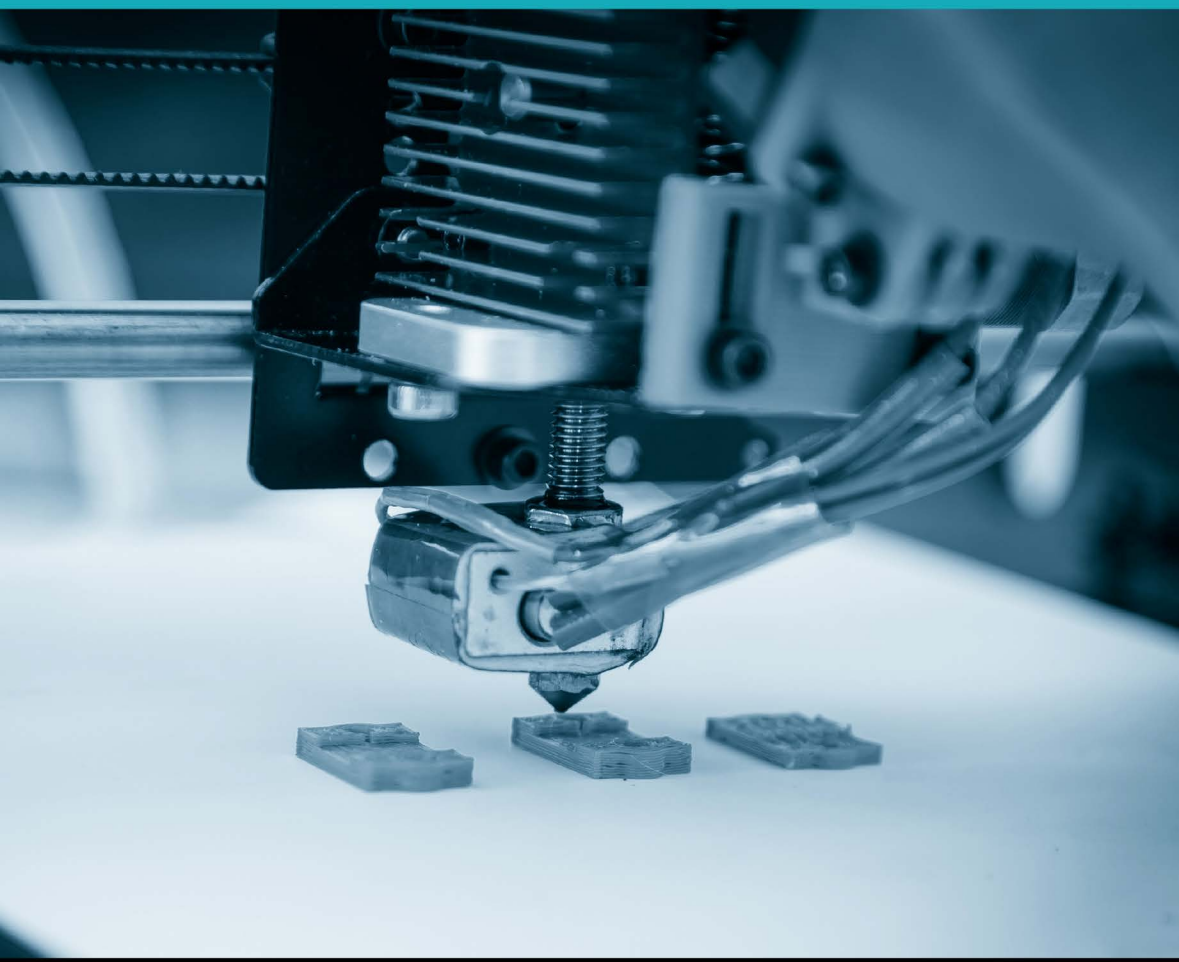


3D Printed Conducting Polymers

Fundamentals, Advances, and Challenges

Edited by Ram K. Gupta

Smart 3D/4D Printing

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3D Printed Conducting Polymers

Conducting polymers are smart materials that possess unique and tuneable electrical, optical, and electrochemical properties. 3D printing technology is rapidly advancing, and using conducting polymers for this process can lead to many emerging applications as it can print complex structures cost effectively, though many challenges need to be overcome before this technology can be used on a large scale. *3D Printed Conducting Polymers* highlights the state of the art of these materials, the basics of additive printing, and the role of conducting polymers in additive manufacturing. It also discusses applications in energy, sensors, and biomedical areas.

- Covers fundamentals, synthesis, and various applications of conducting polymers.
- Discusses basics of energy devices, sensors, and materials technology for emerging applications.
- Explores new approaches for the synthesis of conducting polymers and composites for 3D print technology.
- Details future applications and challenges.

Offering direction to researchers and advanced students to better understand the chemistry and electrochemical properties of conducting polymers and technologies for 3D printing, this book advances the science and technology of this emerging field for readers in materials and chemical engineering, biotechnology, energy, and related disciplines.

Ram K. Gupta is an associate vice president for research and support and a professor of chemistry at Pittsburg State University. Gupta has been recently named by Stanford University as being among the top 2% of research scientists worldwide. Before joining Pittsburg State University, he worked as an assistant research professor at Missouri State University, Springfield, Missouri, then as a senior research scientist at North Carolina A&T State University, Greensboro, North Carolina. Dr. Gupta's research spans a range of subjects critical to current and future societal needs, including semiconducting materials and devices, biopolymers, flame-retardant polymers, green energy production and storage using nanostructured materials and conducting polymers, electrocatalysts, optoelectronic and photovoltaic devices, organic-inorganic heterojunctions for sensors, nanomagnetism, biocompatible nanofibers for tissue regeneration, scaffold and antibacterial applications, and biodegradable metallic implants. Dr. Gupta has mentored 10 PhD/post-doc scholars, 76 MS students, and 58 undergraduate/high school students. Dr. Gupta has published over 290 peer-reviewed journal articles (9600+ citations, 57 h-index, 207 i10-index); made over 420 national/international/regional presentations; chaired/organized many sessions at national/international meetings; written several book chapters (100+); worked as an editor for many books (50+) for the American Chemical Society, CRC, Springer, Elsevier, and so on; and received several million dollars for research and educational activities from external agencies. He also serves as Editor, Associate Editor, Guest Editor, and Editorial Board Member for various journals.

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Dedicated to Dr. Shawn Naccarato for his inspiration, innovation, and motivation. Thank you for championing research and educational advances.


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Preface

Conducting polymers are some of the smart materials used in many applications. They possess many unique and tuneable electrical, optical, and electrochemical properties. The variation in synthesis provides many unique architectural characteristics, making them very suitable for energy and sensor applications. Their properties can be further improved by doping and making composites. A fundamental understanding of the charge-transport mechanism in conducting polymers and their composites is very important to use them for emerging applications. On the other hand, 3D printing technology is rapidly advancing, and using conducting polymers for this process can lead to many emerging applications, as they can print complex structures cost-effectively. However, there are still many challenges that need to be overcome before using this technology on a large scale.

This book provides state-of-the-art knowledge in conducting polymers, the basics of additive printing, and the role of conducting polymers in additive manufacturing. The applications of conducting polymers in the energy, sensor, and biomedical areas are attractive. This book covers the basics and workings of many energy generation and production devices. This book also explores new approaches for the synthesis of conducting polymers and composites for 3D print technology. The future applications and challenges in 3D print technology are also explored. All the chapters are by experts in these areas, making this a suitable textbook for students and researchers.

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1 3D-Printed Conducting Polymers
An Introduction

S. Kalaiarasi, V. Sreeja, P. Karpagavinayagam, and C. Vedhi

1.1 INTRODUCTION

Conducting polymers are attractive substances applied for a wide range of uses, including energy storage, flexible electronics, and bioelectronics. However, traditional methods of conducting polymer fabrication, such as ink-jet printing, screen printing, and electron-beam lithography, have hampered rapid innovation and broad applications of conducting polymers. For conducting polymer three-dimensional (3D) printing, a high-performance 3D-printable conducting polymer ink based on poly (3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) has been presented. As an outcome of the improved printability, conducting polymers can be easily formed into high-resolution and high–aspect ratio microstructures, which can then be integrated with other materials such as insulating elastomers using multimaterial 3D printing. The conducting polymers created by 3D printing can also be converted into highly conductive and soft hydrogel microstructures.

1.1.1 Properties and Applications

Conductive polymers are guaranteed as antistatic components and have been used in commercial displays and batteries. According to the literature, they are also promising in organic solar cells, printed electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, chemical sensors, chemical sensor arrays, and biosensors [1], as well as flexible transparent displays, electromagnetic shielding, and possibly as a replacement for the popular transparent conductor indium tin oxide. Microwave-absorbent coatings, especially radar-absorptive coatings on stealth aircraft, are another application. Conducting polymers are rapidly gaining popularity in new applications due to their raised processability, improved electrical and physical properties, and lower costs. With their higher surface area and better dispersibility, the new nano-structured forms of conducting polymers contribute to this field. According to studies, nanostructured materials conducting polymers in the form of nanofibers and even nanosponges have considerably greater capacitance [2, 3].

PEDOT and polyaniline have achieved a few large-scale uses due to their abundance of solid and consistent dispersions. While PEDOT is primarily used in

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antistatic applications and as a transparent conductive layer in the form of PEDOT: PSS dispersions (PSS = polystyrene sulfonate), polyaniline is frequently employed in electronic board manufacturing facilities in the final finish to protect the copper from corrosion and to prevent solderability [4]. Polyindole is also gaining popularity for a variety of applications due to its higher redox activity, thermal stability, and slower degradation than competitors polyaniline and polypyrrole.

Conducting polymers (CPs) are organic materials that are currently used in a variety of applications such as energy storage, flexible electronics, and bioelectronics. They have the distinct advantage of combining conducting or semiconducting properties in addition to unique optoelectronic properties, with some organic polymer properties. CPs are a type of macromolecule with unique physical and chemical characteristics; their mechanical properties differ significantly from those of thermoplastic polymers. The majority of CPs are insoluble, infusible powdery materials that are difficult to process. Only in a few cases does the inclusion of dissolving chemical features to the primary link backbone allow the use of traditional thin film deposition methods, such as solvent casting or spin-coating, to process CPs into functional devices. As a result, applying additive manufacturing (AM) techniques to conducting polymers has proved more challenging than applying AM methods to other polymer families [3].

Various AM technologies have become known as exciting manufacturing techniques over the past years; their main benefit is the ability to fabricate multi-material objects. Metals, polymers, ceramics, and other materials can be 3D printed with various sections in a single printing process to meet specific requirements such as chemical, mechanical, thermal, and electrical properties. Several papers were published over the past decade concerning metals or ceramic materials 3D printed alongside organic polymers. In fact, a significant migration of equipment from traditional two-dimensional (2D) thin films to shape variable three-dimensional structures has started to occur in the design of electronic devices.

1.1.2 3D Printing

Due to its design versatility and capacity to effectively construct advanced structures, 3D printing has attracted investigators from a wide range of subjects in the past few years [5, 6]. Design ideas can be turned into products using direct digital manufacturing without the use of dies or molds. Subtractive lithography-based processing and patterning processes are currently employed for the fabrication of most devices. They are capable of fabricating intricate structures at high rates yet frequently generate significant amounts of waste [7, 8]. Aside from these benefits, additive manufacturing techniques enable the integration of modules into a single element with less assembly required [9]. These advantages are appealing to a wide range of industries, such as biomedical devices, the aerospace sector, power, and vehicles [10, 11]. Figure 1.1 depicts a 3D direct ink writing printer.

1.1.3 Properties of 3D-Printed Conducting Polymers

3D-printed conducting polymers have electrical conductivities that exceed 155 S/cm in the dry state and 28 S/cm in the hydrogel state, which is comparable to previously

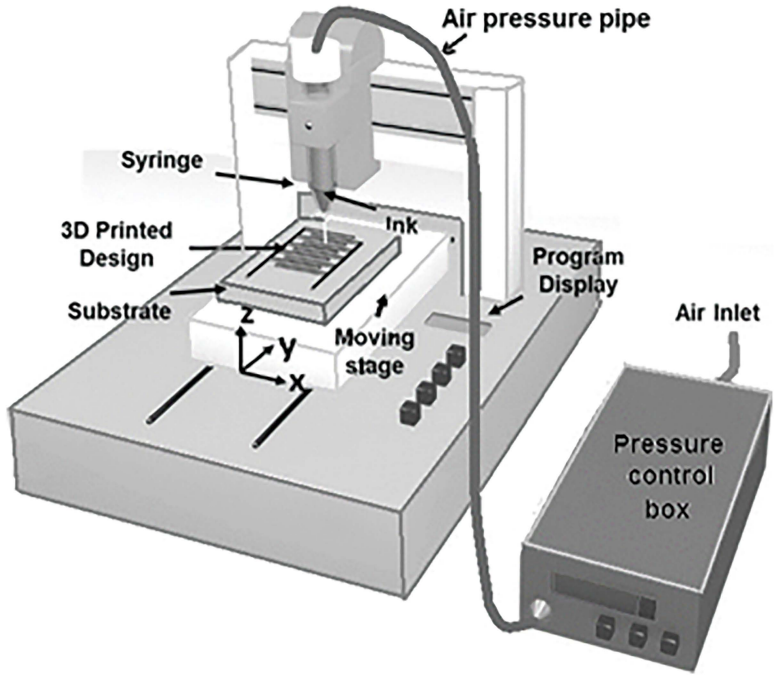


FIGURE 1.1 Direct ink writing printer in 3D representation.

established powerful conducting polymers [12–14]. Notably, a smaller nozzle diameter results in improved electrical conductivity for the created conducting polymers, possibly due to shear-induced improvements in the PEDOT: PSS nanofibril alignment [15]. Mechanical bending with a maximum strain of 13% in the dry state (65 m radius of curvature with 17 m thickness) and 20% in the hydrogel state (200 m radius of curvature with 78 m thickness) is possible with no failure due to the flexibility of 3D-printed conducting polymers. To examine the effect of physical bending on electrical wiring performance, Gladman et al. characterized the electrical conductivity of 3D-printed conducting polymers (100-m nozzle, 1 layer) on versatile polyimide substrates as a function of bending radius and bending cycle. In both dry and hydrogel, the electrical conductivity of 3D-printed conducting polymers changes only slightly (less than 5%) across a wide range of tensile as well as compressible bending circumstances (radius of curvature, 1–20 mm). Furthermore, after 10,000 cycles of repeated bending, 3D-printed conducting polymers can maintain high electrical conductivity (over 100 S/cm in the dry state and over 15 S/cm in the hydrogel state).

1.1.3.1 Electrical Properties

The electrical properties of 3D-printed conducting polymers (100-m nozzle, 1 layer on Pt) are investigated using the technique of electrochemical impedance spectroscopy (EIS). The EIS data are fitted to the equivalent circuit model, where R*e* denotes the electrical resistance, Ri denotes the ionic resistance, Rc denotes the total ohmic

resistance of the electrochemical cell assembly, and CPEdl and CPEg denote the constant phase elements (CPEs) that correspond to the double-layer ionic capacitance and geometric capacitance, respectively [16, 17]. The semicircular Nyquist plot shape indicates the presence of comparable ionic and electronic conductivity in the 3D-printed conducting polymer hydrogels, which is supported by the extracted fitting parameters of the equivalent circuit model, which demonstrate similar magnitudes of ionic and electronic resistances (Ri = 105.5 and Re = 107.1).

The cyclic voltammetry (CV) results show that 3D-printed conducting polymers (100-m nozzle, 1 layer on Pt) have a height control storage capability (CSC) when compared to typical metallic electrode materials such as Pt, with remarkable electrochemical stability (less than 2% reduction in CSC after 1000 cycles). The CV of 3D-printed conducting polymers also exhibits broad and stable anodic and cathodic peaks at varying potential scan rates [18], implying non-diffusional redox processes and electrochemical stability of the 3D-printed conducting polymer.

1.1.3.2 Mechanical Properties

Nanoindentation of the mechanical characteristics of 3D-printed conducting polymers was carried out. In the dry state, 3D-printed conducting polymers have a relatively high Young's modulus of "1.5–0.31 GPa", which is comparable to previously reported values for dry PEDOT: PSS [19]. In contrast, Young's modulus, or the modulus of 3D-printed performing plastics in the hydrogel state, is reduced by three orders of magnitude to "1.1–0.36 MPa", which is comparable to soft elastomers such as polydimethylsiloxane (PDMS) (Young's modulus, 1–10 MPa). The softness of 3D-printed conducting polymer hydrogels can provide beneficial long-term biomechanical interactions with biological tissues, which may be especially useful in bioelectronic devices and implants [20–22].

1.1.4 3D Printing of Conducting Polymer Devices

Enabled by superior 3D printability and properties, 3D printing of conducting polymer ink can offer a promising route for easy and streamlined fabrication of high-resolution and multi-material conducting polymer structures and devices. Highly reproducible 3D printing of conducting polymers in high resolution allows the rapid fabrication of over 100 circuit patterns with less than 100 μm feature size on a flexible polyethylene terephthalate (PETE) substrate by a single continuous printing process with a total printing time of less than 30 min. The resultant 3D-printed conducting polymer electronic circuits exhibit high electrical conductivity to operate electrical components such as a light-emitting diodes (LEDs). This programmable, high-resolution, and high-throughput fabrication of conducting polymer patterns by 3D printing can potentially serve as an alternative to ink-jet and screen printing with a higher degree of flexibility in the choice of designs based on application demands [23, 24].

1.1.5 3D-Printable Conducting Polymer Ink

Conducting polymers are typically used in the form of a liquid monomer or polymer solution whose fluidity prevents their direct use in 3D printing [12, 20, 25].

In order to endow the rheological properties required for 3D printing to conducting polymers, Y. Wang et al. developed a simple process to convert a commercially available PEDOT:PSS aqueous solution to a high-performance 3D printable ink. The pristine PEDOT:PSS solution exhibits a dilute dispersion of PEDOT: PSS nanofibrils with low viscosity (below 30 Pa s). Inspired by the 3D printability of concentrated cellulose nanofiber suspensions [14, 26], B. Lu et al. hypothesized that a highly concentrated solution of PEDOT:PSS nanofibrils can provide a 3D printable conducting polymer ink due to the formation of entanglements among PEDOT:PSS nanofibrils (Figure 1.2). First isolated PEDOT:PSS nanofibrils by lyophilizing the pristine PEDOT:PSS solution. In order to avoid excessive formation of PEDOT-rich crystalline domains among PEDOT:PSS nanofibrils due to slow ice crystal formation during lyophilization at high temperature [27], we perform lyophilization in cryogenic conditions (i.e., frozen in liquid nitrogen). The isolated PEDOT:PSS nanofibrils are then re-dispersed with a binary solvent mixture (water:DMSO = 85:15 v/v) to prepare concentrated suspensions.

With increasing concentration of the PEDOT: PSS nanofibrils, the suspensions gradually transit from liquids to thixotropic 3D-printable inks due to the formation of reversible physical networks of the PEDOT: PSS nanofibrils via entanglements within the solvent. The small-angle X-ray scattering (SAXS) and rheological characterizations quantify microscopic and macroscopic evolutions of the conducting polymer ink with varying concentrations of the PEDOT: PSS nanofibrils, respectively. The SAXS characterizations show that the average distance between PEDOT-rich crystalline domains L (d-spacing calculated by the Bragg expression $L = 2\pi/qmax$) decreases with an increase in the concentration of the PEDOT: PSS nanofibrils (16.1 nm for 1 wt% and 7.0 nm for 10 wt%), indicating closer packing and a higher degree of interactions between the adjacent PEDOT: PSS nanofibrils in more concentrated inks.

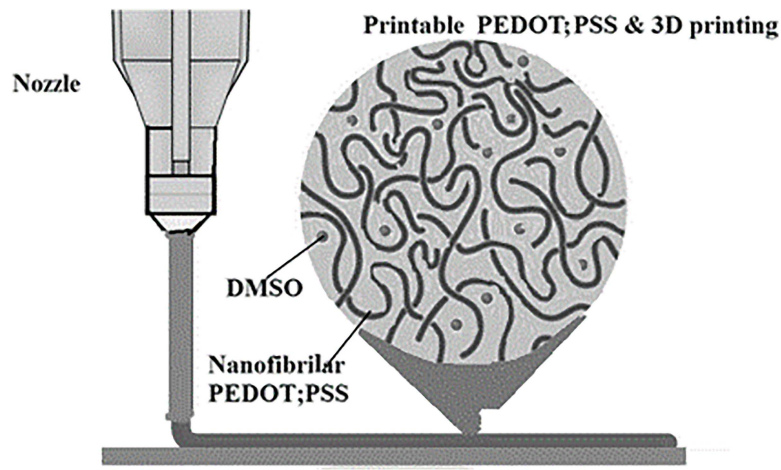


FIGURE 1.2 Printable conducting polymer ink (PEDOT: PSS).

The 3D printing process requires a computer-aided design (CAD) model sliced into a series of 2D digital models by specialized software. Computers manage the 3D printer, which realizes objects by adding each 2D layer onto the prior layers (i.e., layer-by-layer). In this process, a series of layers of materials is laid down in complex shapes or structures. This 'bottom up' manufacturing, conceptually different from traditional manufacture through 'cutting and drilling', can efficiently reduce the cost of production and prevent the waste of expensive advanced materials, meanwhile simplifying the design of microstructures and reducing post-processing (i.e., shaping, heating processing, and assembly). This technology has been extensively applied to jewelry, footwear, industrial design, pre-product models, engineering, automotive, aerospace, biomedical applications, dental, and medical industries. The two main technologies used for 3D printing are: (1) extrusion, the most common and probably the simplest 3D printing technique, where the main printing material is a plastic filament, which is heated, melting in the printing head of the 3D printer, and (2) laser stereolithography (SLA) or direct laser printing (DLP), which use photochemical processes by which light causes chemical monomers and oligomers to cross-link together to form polymers. Among the different 3D printing technologies, the photochemical approach is attractive since the choice of materials can be more ample, and the photopolymerization reactions of monomers is a tool with intrinsic environmental, economic, and production benefits. In SLA or DLP, printable materials are mainly composed of mono/multifunctional monomers, photoinitiating systems, and various additives. When the resin is exposed to UV light, the photoinitiators decompose into free radicals that react with the monomers, causing them to form cross-linked polymer chains. Absorbing additives are commonly used to adjust the horizontal and vertical resolutions.

1.1.6 3D Printing of Conducting Polymers

The superior printability of conducting polymer ink allows various advanced 3D printing capabilities, including printing of high-resolution, high–aspect ratio, and overhanging structures. The favorable rheological properties of the conducting polymer ink further enable the fabrication of multi-layered high–aspect ratio microstructures (100-μm nozzle, 20 layers, as well as overhanging features. 3D-printed conducting polymer structures can readily be converted into dry and hydrogel forms without loss of the original microscale structures, owing to the constrained drying (while attached to the substrate) and swelling property of the pure PEDOT:PSS hydrogels [15]. Furthermore, 3D-printed conducting polymer hydrogels exhibit long-term stability in physiological wet environments without observable degradation of microscale features (e.g., high aspect ratio and overhanging structures) after storage in PBS for 6 months.

1.1.7 Additive Manufacturing Techniques for 3D Printing of Electrically Conductive Polymer Composites

Despite recent developments in electrical CPCs, traditional manufacturing procedures are still mostly used in the fabrication of structures and devices based on

conductive polymer composites [28, 29]. These manufacturing and fabrication methods are often limited to low-resolution (>100 mm), in-plane patterning (low aspect ratio), and intricate and expensive procedures [30]. Compared to traditional methods, 3D printing gives the potential to create microscale or even nanoscale structures in a way that is programmable, simple, and flexible while allowing for creative freedom in three dimensions. The technologies for the additive manufacture of polymers can be categorized as follows: vat photopolymerization (VP), material jetting (MJ), binder jetting (BJ), material extrusion (ME), and powder bed fusion (PBF). The basic and material requirements of each technique are different, and the choice of process would rely on the kind of conductive polymeric material employed and the required electrical qualities of the printed component.

3D printable conducting polymer ink can be readily incorporated into the multi-material 3D printing processes together with other 3D printable materials. For example, we fabricate a structure that mimics a high-density multi-electrode array (MEA) based on multi-material 3D printing of the conducting polymer ink and an insulating polydimethylsiloxane ink with a total printing time of less than 30 min. The 3D-printed MEA-like structure shows a complex microscale electrode pattern and a PDMS well that are comparable to a commercially available MEA fabricated by multi-step lithographic processes and post-assembly [31].

1.1.8 Main Additive Manufacturing and 3D Printing Technologies Used for Conducting Polymers

3D printing is the manufacturing of a structure with a specific design using computer-aided design and computer-aided manufacturing (CAM) software. Depending on the source, 3D printing methods can be classified as follows:

1. inkjet printing that uses controlled pulses for material deposition,
2. extrusion-based printing, where the source can be considered a mechanical movement,
3. electrohydrodynamic printing, which employs a controlled electric field for the deposition process, and
4. light-based printing, where lasers or light-emitting diodes are used for the curing/printing process [32, 33].

This section collects the 3D printing processing of the current most relevant conducting polymers.

1.1.8.1 Inkjet Printing

Inkjet printing operates through the same mechanism as inkjet office printers, which means that material droplets are ejected from a cartridge due to the pressure generated from the formation and collapse of microbubbles inside the nozzle. The bubbles can be generated from a thermal, piezoelectric, or electromagnetic stimulus, and the material in the form of droplets is deposited on a surface [34]. In contrast to extrusion-based printing, inkjet inks should be not viscous to ensure proper deposition and minimize the shear forces experienced by the material when it is ejected from

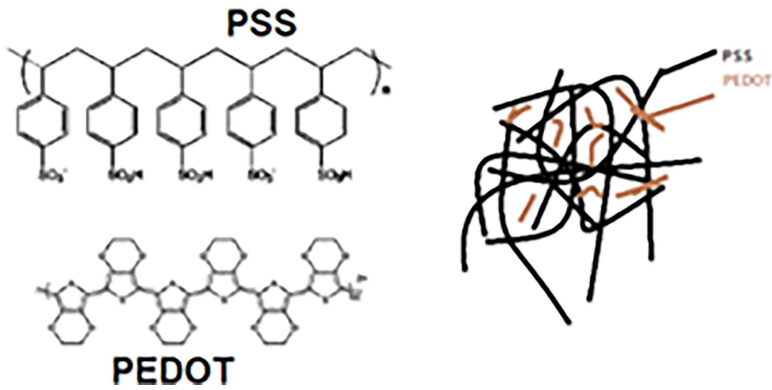


FIGURE 1.3 Inkjet printing using PEDOT: PSS.

the nozzle. Therefore, a viscosity lower than 100 mPa·s is recommended for inkjet inks [32]. This opens the possibility for CPs to be formulated into solvent- or water-based inks for inkjet printing. However, the low solubility of CPs brings difficulties in ink formulations. Nowadays, PEDOT is the most successful commercial CP in the (bio)electronics field due to its inherent properties, such as high conductivity, optical transparency in the form of thin films, and thermal and electrochemical stability [33, 35]. Moreover, PEDOT properties can be tuned using counterions and secondary dopants as well as by polymer blending, processing, and posttreatment methods [36] The most successful commercial PEDOT material is an aqueous dispersion of poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonate) [34, 37]. The different processing methods of this PEDOT:PSS dispersion (Figure 1.3) and the combination with other polymers and conducting fillers allow for tuning the electrical, conducting, mechanical, and biological properties of the resulting materials [38, 39].

1.1.8.2 Extrusion-Based Printing

Extrusion-based printing consists of the layer-by-layer deposition of a material through a movable nozzle, which follows a specific shape previously programmed using software. There are two main extrusion printing methods that differ in the way to drive down the polymer. On the one hand, fused deposition modeling (FDM) uses a polymer in the form of a filament moved throughout a gear mechanism straight to a hot end, where the polymer is melted. On the other hand, direct ink writing (DIW) uses polymers that are semi-melted, in solutions or pastes, which are driven down by the action of current, air, pistons, or screws. Both FDM and DIW methods require the employment of polymers with a specific rheological behavior and viscosity values lower than 104 Pa·s for low shear rates ($10^{-1}s^{-1}$) and 101 Pa·s for high shear rates (102 s^{-1}) to be printable as well as to retain the desired shape after printing [40–45].

1.1.8.3 Electrohydrodynamic Printing

Electrohydrodynamic printing (EHD) is based on the deposition of a material dissolved in a polarizable liquid, which is subsequently evaluated for accessibility using

an electric field that is typically placed between the nozzle and the grounded substrate. The EHD printing method possesses high resolution and overcomes the limitation related to the nozzle in the inkjet printing methodology. It can be used in pulsating or jet mode, creating dots or continuous fibers, so the deposition modulates the resolution at the micro- or nanoscale domain.

The printing quality is affected by the ink properties, such as viscosity, surface tension, electrical conductivity, or dipole moment, and the process-related factors, including the applied voltage, pressure, and flow rate. Overall, at low applied voltages and low ink viscosity, a dripping mode is observed at the apex of the Taylor cone. By increasing the voltage and keeping a low ink viscosity at low flow rates, the droplet size is much smaller than the nozzle size, giving rise to microdripping mode. An increase of the flow rate under these latter conditions makes the ink eject like a column, generating spindle mode. The employment of high-viscosity inks and high voltages generates a thin liquid jet at the apex of the cone known as cone-jet mode. In this way, by increasing the voltage and flow rate up to very high values, the unstable and uncontrollable multijet mode will be achieved. Among these jetting modes, microdripping and cone-jet provide the required printing process controllability for precision manufacturing. Moreover, electrodes can be located around the nozzle, which controls the deposition trajectory, achieving a sub-micrometer printing resolution.

1.1.8.4 Light-Based 3D Printing

Light-based 3D printing is based on the photopolymerization of a prepolymer or monomer in a liquid state placed inside a vat through partially controlled solidification in a specific shape, forming the 3D structure [46]. Two main methods are employed, stereolithography and digital light processing. SLA photocures resin by a laser beam controlled under a deflection mirror, and the liquid is solidified on the surface where the light spot was scanned. Regarding DLP, a digital micromirror device (DMD) formed by millions of mirrors is used to directly project a 2D image onto the photosensitive material. Moreover, SLA occurs in the top part of the vat, photocuring the resin point-by-point through the laser beam, whereas in the case of DLP, the light source projects the entire slice in the bottom part of the vat, where the photopolymerization takes place [47]. Besides these two methods, selective laser sintering (SLS) can be considered a light-based printing technique, where a photo-cross-linkable prepolymer in a powder is mixed with other polymers, metals, or ceramics to form composites that can be sintered by the action of a high-power laser [48]. However, CPs are rarely obtained by photopolymerization, which limits the applicability of light-based printing to inks where the CP is dispersed with a light-sensitive curable material.

1.1.9 Challenges

An important challenge in the field of additive manufacturing or 3D printing (Figure 1.4) is the lack of advanced polymer materials and available nanocomposites to match the performance and fabrication requirements. Thus, research efforts at academic, government, and industrial institutions have been focused on developing

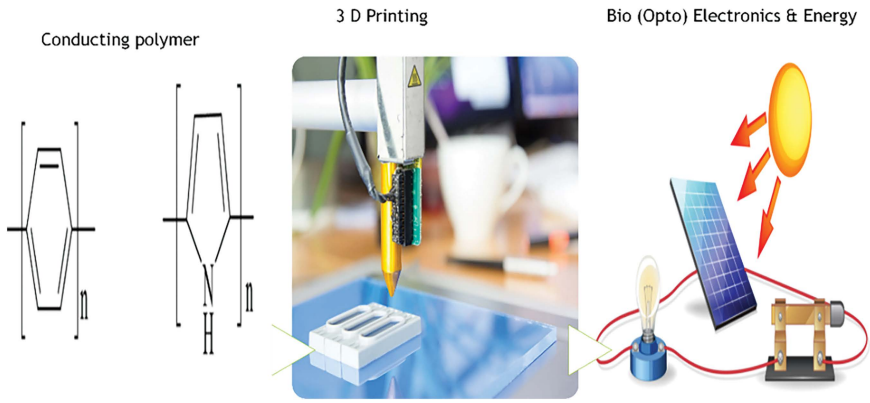


FIGURE 1.4 Challenges of 3D-printed conducting polymers.

new high-performance materials, improving the efficiency and speed of the process, and widening the range of its properties and applications [49]. The introduction and development of novel polymers, additives, and other thermoplastic composites for AM aims to extend the impact of AM on the fabrication of end-product components [50] and real part replacement.

A common issue in using commodity thermoplastic products in AM is their lack of strength and functionality as high load-bearing parts. The use of engineering plastics and high-performance polymers (HPPs) is desirable, but the cost and requirements for more demanding processing conditions (such as higher temperatures) present a challenge, especially if high build volumes are desired. Common matrix materials used in AM are thermoplastic material formulations. Traditional polymer blending has been used to combine the strength of two polymers or reinforce a weaker polymer with a high-performance polymer. It can also be done with the use of compatibilizers, telechelic copolymers, plasticizers, and other synergistic additives [51]. In a review by Dizon et al. (2017), it was emphasized that the mechanical properties of 3D-printed parts are indeed affected by the intrinsic material properties (before printing), the chosen manufacturing method, and build orientation, among many other factors. Thus, it is essential to constantly focus on improving the intrinsic properties of polymer materials from the molecular to the macroscopic level [52].

1.2 CONCLUSION

Three-dimensional printing methodologies have experienced explosive growth in the last decades; such growth has stimulated the interest of research groups. Among different CPs used for 3D printing, PEDOT is the most studied, especially the commercial dispersion PEDOT:PSS, which has resulted in the preferred material for different authors. The additive manufacturing of CPs presents great opportunities in the design of new devices and applications in the (bio)electronic field. However, CPs show important limitations in terms of processability. Therefore, their combination with other polymers and nano additives that improve their processability while keeping

high conductivity is needed for their processing by additive manufacturing methods. In this regard, the 3D printing of CPs has started to be explored very recently and portrays a field with a huge number of possibilities and applications in the future.

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