Additive manufacturing technologies: an overview of challenges and perspective of using electrospraying

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ABSTRACT

Additive manufacturing (AM) is integrated into almost every industry, with an objective to improve product functionality and decrease costs. Ever since from its introduction four decades ago, AM technologies have used numerous kinds of materials in polymers and composite materials to create complex 3D structures which were almost impossible to manufacture through conventional techniques. However, many concerns remain for widespread applications of 3D-printed materials, which include inhomogeneous distribution of particles, unavailability of spherical particles, poor surface finish, inadequate accuracy, shrinkage in the material, and mismatch in desired mechanical properties. To meet the high standards of part quality, immediate emphasis should be given to these pertaining issues and challenges needs to addressed from the grassroots level. It is understood that, electrospraying, a powder particle production technique, may hold great potential to address these challenges and needs of AM by synthesizing fine spherical particles of any material with high scalability and reproducibility. A comprehensive review has been done to discuss the necessity of electrospraying for AM by providing an extensive summary/insight in current material advances and also attempted to bring the connection between the electrospraying and commercialized AM methods. This article also encourages the readers in obtaining an understanding the leading-edge technology electrospraying and makes them to contribute toward the future generations more effectively.

GRAPHICAL ABSTRACT

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1. Introduction

Since its introduction in the 1980s, additive manufacturing (AM) or three-dimensional (3D) printing or rapid prototyping (RP) or solid free form fabrication has opened new horizons in design and construction of various 3D objects in aerospace industry, manufacturing sectors, dental/orthopedic implants, biomedical devices, drug delivery and tissue engineering [1–5] (Figure 1(a)). The major contribution from each mentioned sector is referred in Figure 1(c). This unique method represents a technology that is simple and inexpensive way to fabricate any given complex structure with different materials such as metals, ceramics, polymers, composites, and biological systems.

AM is guided by computer-aided design (CAD), by creating finite two-dimensional (2D) layers that are joined together to form a 3D structure without any part-specific tooling. The steps involved in 3D object development using AM is shown in Figure 2.

Figure 1. Timeline showing additive manufacturing advances in respective areas: Biomedical—prosthetic leg (2008), functional kidney (2002), heart valves (2012), prosthetic jaw printed and implanted (2012), titanium full implants (2013), vascular grafts (2014); Aerospace—SULSA-robotic aircraft (2011), fuel nozzle LEAP engine (2012); bearing of jet engine (2014); Automotive—bike frame (2014), Urbee, Worlds first prototype car (2010), fully functional car (2015); Architecture—wall clock (2009), guitar (2012), canal house (2013), apartment building (2015). (b) The total number of publication distribution in last 12 years in electrospraying/electrospinning and additive manufacturing (2018—as on October 31st, 2018, SCOPUS). (c) Contribution of each sector in additive manufacturing (as on October 31st, 2018, SCOPUS Database).
The process starts with designing a required part/model in a CAD software which is subsequently exported to a .stl file. The model divided into a 'series of slices' containing the object information in vertical/horizontal cross-sections. Depending on the AM technology, various kind of energy sources are applied to the resin where solidifying of each layers occurs at a specific location.

Vat polymerization, sheet lamination, powder bed fusion, and material extrusion are among some printing technologies/process of AM, which have been widely used in the corporate and technological fields. There are wide range of tools sectioned under the shadow of these AM technologies, all with their own processing capabilities, advantages, and limitations. Few of them are stereolithography (SLA), digital light processing (DLP), fused deposition modelling (FDM), multijet modelling (MJM), selective laser sintering (SLS), selective laser melting (SLM), electronic beam melting (EBM), laminated object manufacturing (LOM), direct ink writing (DIW), and inkjet printing. These technologies can be conventionally categorized into four groups namely liquid based (SLA, MJM and RFP), powder based (SLS, EBM, 3DP and LOM), solid sheet based (LOM), and filament based (FDM and FEF). The details of each AM technologies (Figure 3), its working principles and typical materials used have been summarized in Table 1.

Apart from the extensive availability of AM techniques, there are still questions in early detecting of low-quality parts, processing concerns and post treatment of 3D printed objects. In some cases, widespread outreach of AM adoption in commercial sectors, for example, aerospace, biomedical, and daily consumers is deteriorated because some of the part properties in AM were not enough to meet the stringent requirements by these sectors. To overcome this, the issues at the elemental level need to be addressed. The most fundamental requirement of a material powder to qualify for AM is that it should be with a uniform/spherical geometry with homogenous particle distribution without any agglomeration. The details about the issue with non-spherical structures are described in Figure 4. In view of this, there is an urgent need of technique which can generate particles with accurate spherical morphology for various AM technologies. One possible solution is to investigate the next generation systems and concentrate on single technique where the user obtains material (polymers, ceramics, composites, and metals) with spherical geometry.

Electrospraying, liquid atomization by means of electrical forces, can able to create narrow size distributions of spherical micro-nanoparticles with limited or no agglomeration. The technique has unwrapped new ways in producing particles and revolutionized the fields of modern material technologies, microelectronics sectors, and biomedical (polymeric and biomaterial nano-microparticles). A variety of organic/inorganic materials, polymers, ceramics, composites, metals and range of different morphologies viz. nanocups, nanobeads, microspheres, have been formulated via electrospraying [6–12]. The practice of using microparticles by electrospraying in AM may be a one-stop solution and has a huge prospect in overcoming many impediments to provide better 3D printed objects in future. As indicated by SCOPUS database, there is an incredible increase in the number of publications in AM and electrospraying in past 12 years (Figure 1(b)).

2. Industrial problems and challenges associated with AM

As of today, and as mentioned earlier in Section 1, many AM techniques have proved to be a better alternative when compared to commercial CNC machining. But, many fundamental research
challenges that need to be addressed before taking the prototype to end product and to commercialization. At present, many 3D printed products are being stalled at the prototype stage without accomplishing to the final finished product. Mechanical properties are always not critical for the parts created for prototypes, but when it comes to commercialization, it becomes vital for engineers to match the mechanical properties with the desired application. It should be also noted that, under similar ambient conditions, different AM processes can result in the variation of built-in part dimensions. Also, production of accurate parts is hindered due to shrinkage of the material (3–4% approx.) that occurs during crystallization [58].

First and foremost, the strength and stiffness of the object made from 3D printed polymer. In most cases, the properties (strength and stiffness) are much inferior to the conventional made objects. Recent developments have improved the properties by adding/doubling specific strength of a polymer feedstock material and by adding additional filler materials such as glass, carbon fiber, etc. to the polymer.

Secondly, accessibility of material in powdered form with desired particle size is the main obstacle in AM. Majority of materials which are commercially available are not shaped directly in fine powdered form. These materials are further altered to a suitable particle size by mechanical procedures which results in deformed/irregular shape. It has been reported that the particles with smaller diameter will enable smooth flow, have greater homogeneity, and have larger surface area to volume ratio. These unique particle size properties support in improving capability of the part and provides greater surface quality [59]. Many fabrication techniques which are currently adopted to produce microparticles for AM lack homogeneous distribution, unique size dispersion, spherical morphology and lack of batch to batch reproducibility. Most of the particles that are generated are uneven spherical shape, angular, rounded, acicular, flakes, spongy,
| Printing processes | Method | Principle | Advantages | Issues | Feature resolution | Typical materials | Ref. |
|-------------------|--------|-----------|------------|--------|-------------------|------------------|------|
| VAT photopolymerization | Stereolithography (SLA) | Uses UV laser beam as an energy source to solidify repeating photo resin layers on the surface. | 1. Large objects with good surface finish can be achieved up to 4000 dpi. 2. No need of external support. 3. High level of precise internal designs and exact external architecture can be achieved. | 1. Low mechanical properties. 2. Post-curing is must. 3. Limited availability of materials. 4. External support is must, it may be sometime difficult to remove it. | 50 – 100 µm | Acrylics and epoxies, PPF ceramics hydro-gels, cells | [13-16] |
| Digital light processing (DLP) | Digital light projector below the resin instead of UV lasers. | 1. Wide selection of materials. 2. Most complex objects are easily created at a very fast rate. 3. Thermal distortion in polymers. | 1. Porosity and rough surface finish. 2. Complex operational system. 3. Changeover in the material system is sometimes difficult. | 50 – 100 µm | Nylon, PEEK, PLGA, PCL, PLA, PVA, HA | [17, 18] |
| Powder bed fusion | Selective laser sintering (SLS) | The CO2 laser beam is utilized to sinter powder particles by atomic diffusion. | 1. Overall production rate is very high. 2. High quality parts with excellent mechanical properties. 3. Highly complex accurate metal objects for biomedical applications. | 1. Balancing behaviour issue in non-ferrous metals. 2. Molten pool instability. 3. Relatively slow in creating 3D objects. | 30 – 150 µm | Starch, cellulose, PLGA, PCL PLA Al2O3, and shape-memory alloys | [19-23] |
| 3D printing (3DP) | Binding of particles | 1. Rapid verification. 2. No need of external support. | 1. Anisotropic mechanical properties can be achieved. | 100 µm | Starch, cellulose, PLGA, PCL PLA Al2O3, and shape-memory alloys | [24-27] |
| Selective laser melting (SLM) | The generated laser beam will melt the particles in definite locations on a bed of metallic powder until fully melted and fused together. | 1. Overall production rate is very high. 2. High quality parts with excellent mechanical properties. 3. Highly complex accurate metal objects for biomedical applications. | 1. Works only with a limited set of metals. 2. Requires vacuum incurs cost in production. 3. Manufactured parts require lot of post processing. 4. No good surface finish. | 20.3–25.4 µm with a minimum feature size: 0.1 mm | Ti-6Al-4V, Co-Cr-Mo, Cp-Ti, Ti-6Al-4V, aluminum, and ceramics | [28-30] |
| Electron beam melting (EBM) | Electron beam which is generated in high vacuum will be used to melt the metal powders. | 1. Very high density, greater than 99% can be achieved. 2. Compared to SLM, parts have less thermal stress. 3. Fast and less support structure. 4. Vacuum environment eliminates impurities such as oxides and nitrrides. | 1. High degree of accuracy is attained in less time. 2. Sharp internal corners and difficult geometries can be produced with ease. 3. Superior mechanical properties for aerospace applications. | 89–97 µm | Ti-6Al-4V, Co-Cr | [31-33] |
| Direct metal laser sintering (DMLS) | Similar to SLS, but uses metal alloy powders instead of plastic powders. | 1. Overall production rate is very high. 2. High quality parts with excellent mechanical properties. 3. Highly complex accurate metal objects for biomedical applications. | 1. Only very small to medium sized parts are produced. 2. Extensive post processing is required even for small parts. | 40 µm with an accuracy of 0.1–0.3 mm | Ti-6Al-4V, Co-Cr | [34, 35] |
| Material jetting | Continuous printing (CIJ) | Droplets are formed via continuous breakup of a stream liquid. | 1. High quality surface finish and greater accuracy. 2. Offers more than 100 digital material combinations. | 1. Limited materials - only wax like materials and polymers used. 2. Parts are sometimes being fragile. | 40 µm with an accuracy of 0.1–0.3 mm | PCL ABS, polyamide, PLA and their composites | [36, 37] |
| Material jetting | Drop-on-demand (DOD) | Droplets are generated when required. | 1. High quality surface finish and greater accuracy. 2. Offers more than 100 digital material combinations. | 1. Limited materials - only wax like materials and polymers used. 2. Parts are sometimes being fragile. | 40 µm with an accuracy of 0.1–0.3 mm | PCL ABS, polyamide, PLA and their composites | [36, 37] |
| Printing processes | Method | Principle | Advantages | Issues | Feature resolution | Typical materials | Ref. |
|--------------------|--------|-----------|------------|--------|-------------------|-------------------|-----|
| Binder jetting     | Binder jetting | Prints the binder fed onto the powder bed of raw material | 1. Parts in different colors are possible. 2. Any material which is in powder form can be fabricated. 3. Relatively cheap. | 1. Fragility in parts with limited mechanical properties. 2. Structural parts cannot be fabricated. 3. Additional processes like casing or sintering is required after fabrication. | 25 µm | Steel, polymers and BiTiO₃ intermetallics, solid oxide fuel cells, magnetic materials, shape memory alloys, biodegradable alloys | [38-42] |
| Material extrusion | Direct ink writing (DIW) | Deposition of colloidal- or polymer-based inks layer by layer | 1. Mild processing conditions. 2. Possibility of incorporation of drugs and biomolecules. 3. High quality porous structures for biomedical application can be created. | 1. Postprocessing is required for few materials. 2. Limited resolution. 3. Very slow processing. 4. Unfavorable mechanical properties. | 20 µm lateral | PCLHA, zirconia, aerogels bioactive glasses | [43-48] |
| Fused deposition modelling (FDM) | Extrusion of molten of thermoplastic filament layer by layer through a fine nozzle | 1. Variety of materials can be used. 2. No support structures are required. 3. Economical set-up. 4. No post-curing is required. | 1. Porosity and rough surface finish. 2. Weak Z-directional finish. 3. Very difficult to remove support parts. 4. Takes time fabricate large parts. | 100–150 µm | ABS, polyamide, PLA and their composites | [49-51] |
| Sheet lamination | Lamination | Laminated object manufacturing (LOM) | 3D object is formed by cutting, sequentially laminating, and bonding | 1. Producing good bonds between layers is always a challenge. 2. Hallow parts are difficult to manufacture. 3. Decubing, which requires a lot of labor and time consuming. | 200–300 µm | Ceramics, aluminum, stainless steel, copper, titanium, plastics, fabrics, synthetic materials, and composites | [52] |
| Directed energy deposition | Laser-engineered net shaping (LENS) | Object is fused together with laser | 1. Part fabrication is not limited by direction or axis. 2. Single point deposition rates are possible. 3. Can be applied to pre-existing part features also. | 1. Lower resolution. 2. Final machining of object is always required. 3. Heat treatment for metal objects is required. | 10 – 120 µm | Metals, permalloys, magnetic alloys, Ti-tungsten alloys | [53-57] |
| Electron beam additive manufacturing (EBAM) | Electron beam is used to create an object | Electron beam is used to create an object | 1. Dual wire feed system, implies 2 metal alloys can be combined. 2. Wide range of metal alloys | 1. Operational difficulties. | 90 µm | SS, cobalt alloys, nickel alloys, copper nickel alloys, tantalum, titanium alloys | [58-62] |
and potato-shaped particles. The details of powder particles used and their possible consequences in AM were explicated in Figure 4. Except for spherical particles, it is understood that, any other shaped particles mentioned above are mostly inadequate for AM industry because of their poor powder flowability. It is also understood that, majority of cases fail to achieve the required surface dimensions, surface finish and finally end up in a weak condensed part with extremely low density and inadequate properties.

Also, by employing irregular and non-uniform particles, components of AM will tend to reduce the accuracy and 3D part features such as surface roughness, minimum feature size, and porosity gets affected [60]. To an extent, this leads to complications in removing the un-sintered powders. Lack of these unique features hinders the idea of prototype and its conversion to an end-product. Therefore, it is a necessity to use accurate particle size and desired morphology in AM. The optimum size of a particles for macro sized parts is usually around 45–90 µm [61]. There are some instances where particle size of 150–200 µm (PLA) and 212–380 µm (HDPE) were used to create substrates for the biomedical application where a rough surface is more preferred than smooth surface for enhanced implant-bone interlocking [62].

Atomization (water atomization and gas atomization), mechanical (ball milling) and chemical reduction (electrolytic deposition) are the three most common techniques used for particle production for AM. Particle characteristics for each process vary. For example, in chemical reduction, there is a high probability of obtaining irregular shape particles, large surface area with substantial internal porosity. Whereas in electrolytic deposition, high purity of particles can be achieved but with dendritic morphology. In case of mechanical processing, there is always a high risk of potential contamination in the system with irregular shaped particles. Water atomization and gas atomization are other methods, where particles are obtained with no internal porosity but with irregular and spherical shape respectively. With these kind of drawbacks, flow time and packing density can be affected very severely in 3D printing. The increase in flow time and decrease in the packing density occurs due the irregular particles size and agglomeration. Overcoming these issues will require advances in both process control approaches and material selection.

Finally, another main challenge to address in AM is anisotropy. When the layer-by-layer deposition occurs to build an object, the effective strength in Z-direction (build direction) is always lower than x and y directions because of controlling difficulties in Z-directions. But, recently, detailed studies were underway to increase the strength in Z-direction.

From the above mentions, it can be understood that the different process/technology were incorporated to supply various kinds of powders to AM technologies. But, electrospraying is a single step technology where all the raw material (polymers, ceramics, composites, metals and bioinks) needed for AM industry can be supplied with better properties and dimensions. If used efficiently, electrospraying can possibly solve all the affecting issues in AM. As mentioned, till date, various kinds of materials such as polymers, ceramics, metallic particles, nano-composites, and bioinks have been electrosprayed.
for different kinds of applications like aerospace, wound dressings, tissue engineering scaffolds and drug delivery systems.

3. Current polymers and composite materials for AM

Polymers are of great interest and are critical for AM because they represent the largest market penetration and user accessibility since its introduction. Layer-by-layer manufacturing of polymers has a quick potential to assist manufacturing of lightweight intricate structures that can impact a wide range of manufacturing industries. AM technology is mainly applied to polymers initially but is later expanded to ceramics, metals, and composites by changing its feedstock. SLS, SLA, FDM, and 3DP are some AM technologies which uses polymers/plastics such as acrylonitrile butadiene styrene (ABS), polyactic acid (PLA), polyvinyl alcohol (PVA), polycarbonate (PC), and polyamide (PA) to create complex net-shaped objects. Table 2 summarizes the list of various polymers used in AM with their typical sizes and supplier information. In SLS process, photo curable polymer polyamide (also known as nylon), in FDM process ABS, PLA, and in 3DP process waxes, elastomeric, and starch-based polymers are used most extensively [63–67].

Apart from well-established thermoplastic and thermoster polymers, for biomedical applications, biocompatible and biodegradable polymers such as poly-e-caprolactone (PCL) [23], polyetheretherketone (PEEK) [22], poly (lactide-co-glycolide) (PLGA), and other starch based polymers [70] have also been broadly studied with the SLS, FDM, and 3DP processes respectively. The typical morphologies of these polymers used in AM are shown in Figure 5.

Table 2. Different kinds polymers used for additive manufacturing.

| Sl. no | Polymer | Technology | Advantages | Source | Size | Ref |
|-------|---------|------------|------------|--------|------|-----|
| 1     | ABS     | FDM        | High impact resistance, high toughness even at low temperatures, dimensional stability, and chemical resistance | P400 ABS | – | [49] |
| 2     | PA-Nylon| FDM        | Excellent resistance to most chemicals, High temperature tolerance, dimensional stability | Taulman | 2.85 mm | [72] |
| 3     | PLA and its copolymers | 3DP | Biodegradable, easily forms co-polymers. High specific strength and modulus have shown significant increase with filler materials | Sigma Aldrich | – | [76] |
| 4     | PVA     | Inkjet printing | Biodegradable and water soluble. Can easily blends with other biopolymers and co-polymers | PVOH Polymers Ltd, UK | – | [82] |
| 5     | PC      | FDM        | Biocompatible polymer with a combination of good heat resistance, moisture absorption capability, impact strength, rigidity, and high toughness | – | – | [88] |
| 6     | Polyethylene | SLS | Can be reused after initial use and can be recycled easily | Oritex | 231 μm | [69] |
|       |         | SLS        | Lightweight and durable | HD7555 Ipiranga | 106–125 μm | [62] |
| 7     | PCL     | Material Jetting | Biodegradable polymer, better mechanical properties, good biocompatibility, degradation rate >24 months | Sigma-Aldrich, Inc | 40 μm | [86] |
| 8     | PEEK    | SLS        | Thermoplastic polymer with high tensile strength and stiffness with excellent dimensional stability | PEEK 150PF | 56 μm | [22] |
| 9     | PLGA    | 3DP        | Biodegradable, biocompatible, and FDA approved polymer | Birmingham Polymers, AL, USA | 10–200 μm | [98] |
PA, commonly known as nylon is a semi-crystalline thermoplastic polymer broadly used for powder bed process and making up close to 95% of the current market [71]. Despite of various developments in material choice over the past few years, PA remains by far the most appropriate polymer for many AM parts. PA offers exceptional strength and stiffness, decent chemical resistance with excellent long-term consistency in material properties. Both renowned companies in AM, 3D Systems and EOS, offer a wide range of nylons based on the application viz. polyamide-12 [PA2200 (PA12)], glass-bead filled polyamide-12 [PA3200], carbon-fiber filled polyamide-12 [PA CF], flame retardant nylon 12 [PA 2241 FR], and aluminum-filled polyamide PA12 powder [Alumide™]. On the other hand, ABS, an another commonly used polymer in FDM. The properties of ABS include, high temperature heat resistant, durable, high tensile strength, impact strength, process ability and low cost of making the material makes it ultimate choice for production of complex structures for many applications. ABS plus, ABS-M30, ABS-M30i, ABSi, PC-ABS are some commercially available trade names of ABS.

PC, a low weight thermoplastic polymer with excellent physical and mechanical properties which is capable enough to replace glass or metal in many commercially available products. The properties include high heat resistance, good impact strength, rigidity, and toughness. PLA is a biodegradable semi-crystalline thermo-softening aliphatic polyester, primarily obtained from renewable resources like corn starch or sugarcane. PLA is probably the most dominating material used in AM for biodegradable medical devices and implants. Choice of manufacture (used as either a resin or filament), environment friendly, stress-free to work, easy to blend with other polymers, controlled degradation, and diversity of color printing make PLA a great choice for AM. PLA has a melting point of 180–220°C and a glass transition temperature of approximately 60–65°C making it much harder material and brittle than its competitor ABS. Commercially available PLA is largely in co-polymers of poly-L-lactic acid (PLLA), poly-D-lactic acid (PDLA), and poly-DL-lactic acid (PDLLA) which are synthesized from L-lactides, D-lactides and DL-lactides, respectively.

In biomedical engineering, fabricating a new scaffold to patient-specific defect tissue with adequate mechanical properties, controlled biodegradability, and large pore size with interconnectivity and superior bioactivity to stimulate tissue regeneration is still a major challenge. Upon the introduction of 3D printing in the biomedical field, many of the issues were addressed and precise reproducible architectures are made possible. PCL is a one of the widely used FDA approved semicrystalline (56%) biodegradable polymer with good mechanical properties, biocompatibility, and stretched degradation period close to 24 months. If PCL scaffolds are to be effectively applied for bone repair, they must be precisely constructed from CAD, should have exact mechanical properties within an appropriate physiological range, and support the in-growth of bone tissue. By acknowledging these factors, many fabricating techniques, such as FDM, SLS, 3DP and SLA [88, 91, 93, 94, 96] have been proposed to fabricate PCL scaffolds to engineer bone tissue regeneration.
Composite materials represent an innovative design of new class of materials or compounds which have resolved many academic and industrial problems in past years. Polymer nanocomposites, i.e. composites of polymers filled with nanoparticles have become a dynamic substitute material to conventional micro-composites by enhancing complete performance of a material at all intervals. As compared to other equivalent materials, polymers in current form show lower thermal and mechanical properties. Thus, for enhancement of properties, polymers are typically blended with other polymers, or forms nanocomposites with filler/additives or copolymerize with other biopolymers.

In AM, polymer matrix composites (PMC) are the most noticeable materials which bind the matrix through liquid phase sintering. It is a known fact that filler materials can easily agglomerate and get inclined to give poor dispersion in polymeric matrix. The degree of dispersion and distribution of the filler material in the polymer matrix is critical as this have a significant effect on many physical, chemical, and mechanical properties of PMC. The different polymer and ceramic composites with diverse geometrical 3D structures that have been reported for AM have been summarized in Table 3 with their typical morphologies is shown in Figure 6.

In this regard, in AM, polymer nanocomposites have attracted substantial attention in research community in developing composites with different raw materials significant to a variety of morphologies and characteristics. The noticeable unique characteristics capabilities include better biocompatibility, superior mechanical strength, better wear properties, and improved bio mimicking of tissues scaffolds. At the moment, SLS and FDM are two main AM techniques have been explored for the fabrication of composite materials [102-115]. It is understood that many degradable/non-degradable, natural and synthetic polymers such as PA, ABS, PCL, PEEK, PLA and their copolymers have been extensively studied for 3D printing for various kind of applications [51, 100,112,124]. Composite parts with complex geometry are essential for cell proliferation for tissue growth. Even though FDM is capable of fabricating intricate structures at macro level, for biomedical application, this technique is limited. FDM, as the process is dependent in several external processing conditions such as diameter of filaments, raster gap, road width, and slice thickness.

4. Perspective of using electrospraying for AM technologies

As mentioned in Section 2, one of the main issues in 3D object fabrication process is inhomogeneity of the particle size. Depending on process, this defect leads to clogging of particles at the nozzle. To avoid this, printing precursor needs to have homogenous distribution of particles all the time. Electrospraying is a well-known single-step established technique (Figure 7) to prepare ultra-fine particles with controlled dimensions up to 100 nm, from a very fine liquid spray through electrostatic charging [7]. The mechanism for droplet formation has been theoretically established by Lord Rayleigh in 1882 [131], further developed by Zeleny in 1917 [132] and advanced by Sir Taylor in 1964 [133]. There are many instances especially where electrospraying technology was referred to electrostatic inkjet printing or electro-hydrodynamic inkjet printing [134, 135] for generating core-shell structures for biomedical, solar cells, electronic circuits, piezoelectric devices and texturing [136-138].

Inkjet printing comes under AM technology which uses piezoelectric technology to jet the material onto a build platform layer-by-layer. The working principle of material jetting is similar to electrospraying, i.e. based on Rayleigh’s theory of droplet development from a fluid. In this process, the droplets of material are initially deposited from the print head onto surface and solidify to make up the first layer. Further layers are built on top of the previous layers. The material layers are then cured or hardened using UV light. Details of schematics of material jetting are shown in Figure 3(c). Several investigations have been carried out on two modifications of ink-jet printers, namely, continuous inkjet printing (CIJ) and drop-on-demand (DOD). The unique difference between CIJ and DOD is the timing of generating droplets. In DOD, droplets are generated when required, whereas in CIJ, the droplets are generated by breaking up the continuous stream of droplets through an ejection nozzle. Materials such as ABS, polyamide, PLA and their composites are commonly used for printing of 3D objects by CIJ and DOD.

Where as in electrospraying, a high voltage, around 5-40 kV, is applied to a drop of the polymer solution which is held by its surface tension at the end of capillary tube. When the applied voltage is gradually increased, the surface of the droplet undergoes distortion to form a conical shape, known as the Taylor cone. Once the voltage surpasses a critical threshold limit, electrostatic force between droplet and the target overcomes the surface tension of solution and a stable spraying occurs from cone tip. As the jet travels in air to reach the target, solvent evaporation and polymer diffusion occurs simultaneously, leaving behind ultrafine particles which are collected on an electrically grounded target. It can be noticed that, except for grounded
Table 3. Additive manufacturing technologies to produce composites.

| Sl. no. | Material     | Method   | Binder | Supplier                          | Size         | Ref.   |
|---------|--------------|----------|--------|-----------------------------------|--------------|--------|
| 1       | PA-Nylon     | SLS      | HDPE   | PA2200 (EOSINT) HD 7555 (Ipiranga S.A.) | 60 and 150 μm | [21]   |
|         | SLS Al₂O₃    |          |        |                                    | 50 μm        | [100]  |
|         | SLS Silica   |          |        |                                    | 106–150 μm   | [101]  |
|         | SLS Al₂O₃    |          |        |                                    | 0.3 μm       | [102]  |
|         | SLS Al₂O₃    |          |        |                                    |              |        |
|         | SLS SIC      |          |        |                                    |              |        |
| 2       | Polystyrene  | SLS      | Nano-Al₂O₃ | Wuhan Chemical Co., China Jiangsu Hehai | 50–60 μm     | [110]  |
| 3       | Polyethylene | SLS      | HA     | Rigidex HD5226EA P218R, Plasma Biotal Ltd., UK | 3.80 μm      | [111]  |
| 4       | Polypropylene| FDM      | βi-TCP | Phillips Sumika Polypropylene, Houston FCC IV Grade, Rhodia | –           | [112]  |
| 5       | PCL          | 3DP      | PVA    | Solvay Caprolactone (Cheishire, UK) Nippon Gohsei, Singapore | 150–212 μm   | [92]   |
|         | SLS HA       |          |        | Solvay Caprolactones, UK Plasma Biotal Ltd. | 106–150 μm   | [113]  |
|         | SLS HA       |          |        | Sigma Aldrich Chemical Co. Plasma   | <100 μm ~5 μm | [114]  |
|         |              |          |        | Biotal Ltd.                       | 125 μm 38 μm |        |
| 6       | ABS          | FDM      |       | Montmorillonite Qimei Stock Company, China Nanocor, with tradename as PGW | –           | [115]  |
| 7       | PLA and its copolymers | SLS | βi-TCP | –                                   | –            | [116]  |
|         |              | SLS HA   |        |                                     | –            | [117]  |
|         |              | Robocasting 4555 Bioglass | – | Ecorene NW51-100, ICO Polymers | –           | [44]   |
|         |              | FDM TCP  |        | Biovision, Wiesbaden, Germany Karl | <90 μm       | [118]  |
|         |              | SLM βi-TCP |       | Leibinger Medizintechnik, Mühlheim, Germany | –           |        |
|         |              | SLS HA   |        | Plasma Biotal Limited (UK) Purasorb L, PURAC, Netherlands | 111 ± 5 μm   | [119]  |
|         |              |          |        |                                   | 163 ± 5 μm   |        |
| 8       | PVA          | 3DP      | Calcium polyphosphate | – |                                      | [120]  |
|         |              | SLS HA   |        | Aldrich Chemical Company Inc. Cam Implants BV, Netherlands | 50–100 μm 60 μm | [121] |
|         |              | SLS HA   |        | Aldrich Chemical Company, Inc Cam Implants BV, Netherlands | 42–372 μm 56 μm | [122] |
| 9       | PEEK         | SLS HA   |        | VircettPlc, Lancashire, UK Cam Implants B.V., Netherlands | 25 and 60 μm | [123]  |
|         |              | SLS HA   |        | VircettPlc, Lancashire, UK Cam Implants B.V., Netherlands | 25 and 60 μm | [124]  |
| 10      | PMMA         | SLS      | βi-TCP/HA | Monsanto Inc. Union Carbide Corporation | 1–2 μm       | [125]  |
| 11      | PLGA         | 3DP      | TCP    | Birmingham Polymers Inc., AL Sigma, St. Louis, MO | 38–150 μm   | [126]  |
| 12      | Titanium nickel-ide (NiTi) | SLS | HA     | Gdroskaiap-GAP85d grade | –           | [127]  |
| 13      | TiC          | LENS     | Cp-Ti  | Atlantic Equipment Engineers Pyrogenesis company | 45 and 150 μm | [128]  |
| 14      | Al₂O₃        | SLM      | ZrO₂   | INNALOX bv, Netherlands | –           | [129]  |
| 15      | SiO₂         | DIW      | CaCO₃  | Industrie Bitossi, Italy Aerosil R106, Evonik Germany | <10 μm     | [43]   |
| 16      | Wollastonite (CaO·SiO₂) | DIW |         | Wacker-Chemie GmbH, Munich, Germany | <100 μm | [47]   |
methods, in electrospraying, particle size and morphology can be effortlessly controlled by altering the solution parameters (concentration, solvent type, viscosity, and conductivity), processing parameters (flow rate, tip to target distance, capillary size, and applied voltage) and polymer properties (molecular weight). Apart from this, particle agglomeration can also be controlled to a larger extent by using different types of grounded collectors, as these particles are electrically charged, results in self-dispersing in space with great uniformity [139].

This review is an attempt to provide an overview and possibility of incorporating of electrosprayed nanostructures into AM. As mentioned above, several researchers have demonstrated promising results on utilizing regular spherical particles into AM and witnessed improved dimensional accuracy and superior mechanical properties. Electrospraying can be a one-step solution for synthesizing spherical particles from micro to nano size and have an advantage of uniform particles generation. Many properties of the 3D printed objects can be tunable and material properties can be expanded for greater application by bringing electrospraying and AM together.

Another major advantage which is unlike in any other equipment is the freedom of changing regime. In the same equipment, one can change to the electrospinning regime (fiber) from electrospraying regime (particle). These morphology conversions from particles to fiber i.e. from electrospraying to electrospinning is mainly accredited to the variations in polymer concentration and changes in molecular weight. These events are the most fundamental mechanisms in the modification of chain entanglement numbers which subsequently causes changes in solution viscosity and separate solutions as dilute, semi-dilute unentangled and semi-dilute [140–142]. So, technically anything which can be electrospinnable can be electrosprayable by changing these parameters as well.

A research study with PA as a polymer, Ojha et al. demonstrated that at 10 wt% of polymer concentration particles like morphology is formed. Whereas, when the molecular weight and concentration is increased to 15 wt%, nanofibers with many beads were obtained [144]. Interestingly, Felice et al. [145] had assessed the change in morphology by varying PVA molecular weight and concentration. The authors demonstrated that low molecular weight PVA always generates particles irrespective of concentration, while at high molecular weight PVA, particles were generated when the concentration is below 0.05 g mL$^{-1}$. In another study, PLGA microspheres with spherical shape with mean diameter of 3.963 μm has been reported by Nath et al. The authors have showed that, at a certain concentration of 6 wt%, spherical shape has been obtained. Other concentrations of 4, 8, and 10 wt% yielded irregular, not perfectly spherical and various shapes, respectively [146].

Solvent properties such as evaporation rate, boiling point, electrical conductivity and surface tension can also play a significant role in particle formation. Many studies have demonstrated that solvents with
high evaporation rates produces porous, hollow, and even fragmented particles whereas low evaporation rate of a solvent hinders complete evaporation, which gives enough time for a complete rapid polymer diffusion of a particle that ensures the generation of dense inhomogeneous semi-solid particles [147]. In few instances, fast evaporation solvents can even result in cup like morphology which may occur due to the contraction of the polymer at a faster rate after solidifying the outer surface layer. Kranthi et al. demonstrated that cup morphology of TiO$_2$ is attributed to the fast evaporating solvents [6].

Based on the chain entanglements in the polymer, Figure 8 shows the series of events that can be normally observed during formation of the electrospayed particles. Figure 8(A) illustrate establishment of polymer particle where concentration is not enough to create a significant degree of chain entanglement. Morphologies shown in Figure 8(B) are not desirable as it is a non-reproducible morphology which typically occurs when insufficient evaporation happens. Figure 8(C) shows the desired electrospaying regime where significant degree of entanglement within the polymer is observed and dense, solid and reproducible particles are produced. If excessive cohesion in the polymer happens, fibers with beads or fibers without beads are formed (Figure 8(D)).

4.1. Electrospun polymeric and nanocomposite particles for AM

It remains a great challenge to generate novel materials with low cost without any restrictions in surface characteristics. Production of polymeric particles by electrospaying for AM may evidently overcome the basic restrictions of particles created by other conventional process. Electrospaying has great potential to produce high yields of monodisperse distributions of submicron polymeric particles, with limited or no agglomeration [7]. Examples of ultra-fine micro/nanoparticles prepared by electrospaying technique are shown in Figure 9. As of today, close to 100 different types of polymers, structures and morphologies have been produced by electrospinning/electrospaying including the polymers used to AM such as nylon, polyester, polycarbonate, and polystyrene, PCL, PLGA, PVA(150). It can be acknowledged that an electrosprun fiber can be electrospayed to particles by decreasing the polymer concentration [8] and also adjusting voltage and flow rate. Commercially pure polymers that are shaped by electrospinning/electrospaying with solvent used, processed parameters and size are listed in Table 4.

Polyamide 6 (nylon 6) is most widely researched polymer for electrospinning but the synthesis of nylon submicron particles by electrospaying is rarely reported in the literature. Nylon-6,66,1010 nanofibers were synthesized for the first time by using 2,2,2-trifluoroethanol (TFE) as a solvent by Li et al. [151] and reported that crystallinity of synthesized membranes are much poorer than that of the corresponding casting films. The authors reported that the polymer concentration with 14 wt% solution demonstrates the best mechanical properties. Tsou et al. studied the effect of solution concentration and temperature on electrospun

![Figure 8](image_url)

Figure 8. Top row: physical representation at the molecular level of various entanglement regimes obtained for different polymer concentrations. $R_g$ is referred as the radius of gyration. Bottom row: examples of corresponding scanning electron micrographs of dried PCL microparticles. PCL concentration in chloroform was: (A) 5%, (B) 7.4%, (C) 8.7%, (D) 9.6% (w/v). Electrospaying conditions were 26 G for needle gauge, 20–25 cm for tip-to-collector distance, 0.5 mL/h for flow rate and 10 kV for voltage. The molecular weight of PCL on average was 130 kg/mol with a polydispersity index of 1.45. Scale bar is 10 $\mu$m [148,149]. (Images are reproduced with permission from Elsevier.)
nylon 6 nanofibers with formic acid as a solvent and established that minimum of 8 wt% of polymer is required to obtain round fibers whereas lower the concentration will lead to ribbon-like fibers with widths of 2–3 μm [152]. Ultra-high molecular polyamide 6 (UHMW-PA6) porous fibers by electrospinning were reported by Zhang et al. by using a solvent mixture of formic acid and acetone [153].

Even though PCL is preferred over many biodegradable polymers, only very few reported the production of electrospayed PCL particles. Wu et al. investigated the effect of atmospheric pressure on PCL particle morphology by using dichloromethane (DCM) as a solvent. It is been reported that, uniform spherical PCL particles were obtained at a polymer concentration of 5 wt% and at a pressure 150 mmHg [157]. The authors also studied the effect
of particle morphology with change in the polymer concentration. At 7 wt% particles were formed along with fibers and at 3 wt% aggregation of particulate microstructure was produced. Precise control over PCL polymer microspheres can be achieved by using chloroform as a solvent. Detailed analysis is being done on by varying PCL polymer concentrations (5, 7.5, 9 and 10g), tip-to-target distance (15, 20 or 25 cm), gauge diameter (21 or 26-gauge) and flow rate (0.2 or 0.5 mL/h) to study the effect of these parameters on the final morphology of PCL microspheres by electrospinning [154]. It has been concluded that at any point of time chloroform did not act as a plasticizer and can be removed completely after drying. Hwang et al. prepared polystyrene core PCL shell (PS@PCL) and polymethylmethacrylate core PCL shell (PMMA@PCL) by using coaxial electrospinning of concentrated polymer solution and studied the effect of polymer concentration on the morphology of the microcapsules on PCL [163]. PCL particles were synthesized by electrospinning and loaded with anti-cancer drug taxol to study the mean morphology and encapsulation efficiency of taxol-loaded PCL particles in PBS saline [156].

Xie et al. has successfully electrospayed PLGA particles of size 200–900 nm for controlled drug delivery. Solvent acetonitrile was varied with the paclitaxel drug, surfactants and organic salts to study size and morphology of PLGA particles with different concentration. It has been found that polymer concentration had a minimal effect on the size of the particles unless the concentration is greater than 10%. Non-agglomerated particles were obtained when the amount of drug loaded in higher
and smoother surface is formed when the polymer concentration is greater than the obtained level [155]. Electrospinning of PLGA microparticles of size 600 nm to 36.10 μm were successfully employed by Yao et al. [159] in a shuttle chamber by using dichloromethane (DCM) and ACN as the organic solvents. With a primary focus on electrical current, it has been demonstrated that the PLGA particles size is found to shrink gradually with decreasing the tip to target distance. Because of the strong cooling effect, PLGA particles with DCM as a solvent were found to be with smooth spherical shape whereas in microparticles with ACN (minor cooling effect) as a solvent found to have in less spherical in shape. Recently, PLGA particle morphology, size and shape were studied by varying the different molecular weights of the polymer (20,000–30,000 g mol⁻¹ and 9000–124,000 g mol⁻¹) and nozzle diameter (21–27 G) with different solvents (DMF, THF, EtOH, water) has been reported by Nodoushan et al. [10].

Antimicrobial activity of PC nanofibers has been studied against Staphylococcus aureus, Escherichia coli, and Klebsiella pneumoniae bacteria by Kim et al. by using chloroform as a primary solvent. The authors reported that, at polymeric concentrations below 10% resulted in large particles size of 50 μm whereas at 16 wt%, fibers with average diameter 15.4 μm were produced [177]. Another research group [178] studied that electrospun PC nanofibers as a function of the solvents (chloroform, tetrahydrofuran (THF) and N,N-dimethyl formamide (DMF)) and the applied voltage [179].

Polylactic acid and its copolymers (PLAs) are extensively used for encapsulation of drug molecules because of their superior biocompatibility and for controlled biodegradation. PLA has a very slow degradation rate stretching from 10 to 48 months due to hydrophobic methyl group on its backbone. Many research studies have been done in this context to explore the possibility of electrospinning/electrospraying of PLs particles for drug delivery. Hirvonen et al. synthesized PLA microparticles of with narrow size distributions of 200 nm and encapsulated hydrophilic drugs and poorly-water soluble drugs into the polymeric nanoparticles with entrapment efficiency more than 50% [167]. Effect of different solvents and role of their evaporation rates have been studied by Ciach et al. on the morphology of PVA particles by electrospraying [173].

Unlike other conventional process, in electrospinning solvent evaporation leads to an additional solidification of a polymer solution which determines the particle morphology and its size. Also, the droplets/particles are of self-dispersing nature in space. Hence, achieving particles with low standard deviation is much easier than other conventional mechanical atomizers. Motion of the charged particles can be easily controlled by changing the voltage of the set-up and can be easily adapted for AM technologies. The nanocomposite materials of polymer and additives prepared by electrospinning/electrospraying are of exceptional importance since they can combine and retain the core properties of polymer as well as additives. As far as nanocomposites are concerned, a wide range of techniques have been explored to fabricate micro-nanocomposites with enhanced physical, chemical, and mechanical properties. Electrospinning and electrospraying has gained wide popularity and became a single-step methodology for developing various hybrid nanocomposite materials comprising of two or more components. Figure 10 shows SEM images of polymer composite particles obtained by electrospaying and the list of all electrospayed composite particles is listed in Table 5. Now-a-days, the most promising method for incorporating nanoparticles (metal or ceramic) within electrospun nanofibers is by dissolving synthesized nanoparticles into the polymeric solution before the electrospinning.

Electrospaying of PVA polymer is comparatively easy due to its high hydrophilicity and processability. Due to this, PVA is used as an organic phase of many polymer-ceramic hybrid fibers and particles. Zhang et al. reported the fabrication of PVA/Ag composite nanofibers by mixing Ag nanoparticles into PVA solution consisting of tannic acid and water as a reducing agent and solvent respectively. PLA and its co polymers, mostly electrospunned for interim applications in for its rapid biodegradation. PLA nanocomposites with ZnO have been reported by Virovska et al. [202] and assessed the photocatalytic and antibacterial activity of PLA/ZnO nanocomposite mats. It is reported that ZnO particles deposited ‘on’ PLA fibers surface are more efficient against microbiological tests than that of type ‘in’ mats which were mainly seen in the fibers bulk. Zhou et al. [201] found that PLA/CDHA coatings performed by electrospraying are PLA/CDHA coatings are favored by osteoblast cells and promoted bone formation while delivering the drugs locally. With PLA/HA as electrospun nanocomposites, Prabhakaran et al. [170] have studied and demonstrated that ECM production, mineralization and subsequent tissue regeneration properties have improved to a larger extent.

PA or nylon, a synthetic polymer with major application in textile industry and electronics, is usually known for its excellent mechanical properties. Nylon and its composites, specifically when dissolved in highly polar solvents such as formic acid, HFP and TFE have been electrospun to nanoscale...
materials. Yanilmaz et al. [196] evaluated the electrospun SiO\textsubscript{2}/nylon nanomembranes for separators in Li-ion batteries. The authors reported that SiO\textsubscript{2}/nylon 6,6 nanofiber with 12 wt% SiO\textsubscript{2} had a great effect on cycling and C-rate performance. Apart from SiO\textsubscript{2}, several additives such as carbon nanotubes, MgO and Ag were also used to improve the mechanical properties whereas HA is used as an additive filler to improve surface wettability for bone tissue engineering [194].

By having precise control over the process, electrospaying of this polymeric solution with small amounts nanoparticles can have a substantial influence on the physical, chemical and mechanical properties of nanocomposites. Besides, the recent developments in electrospaying technologies have
made to improve any material properties by addition of nanoparticles meant for its high surface to volume ratio.

5. Challenges and future directions

By bringing a first thorough literature overview of current knowledge in the field of electrospraying and their applicability, this present state of the art technology may be mapped to AM in many ways. Using a well-established technology for particulate production for AM with low cost production for highly abundant materials could be a promising approach for future industries. Irrespective on the way in which it is employed (initial or later stages), electrospraying may present attractive results, which tend to elevate in the long-term. The real success of incorporating this novel technique electrospraying to AM depends very much on the upcoming start-ups. It is not easy to persuade the established firms where the end customer is always interested in the final product rather than the process.

Current modifications in the fundamental electrospraying setups allow the production of many biodegradable nano and microparticles with encapsulation of other particles too. Due to these unique advantages, electrospraying is being extensively applied to engineering processes and technical instrumentations. These features allow for the formulation and manufacture of highly novel products, which can greatly increase compliance of the material. It can be safely assumed that, by incorporating electrospraying in AM, 3D printing for practical uses can be more exciting in near future. Maybe in next decade, as predicted, 4D printing can become a succeeding frontier in this swiftly evolving field with an ability to self-assemble, self-repair and respond to the environmental cues such as heat, water and pressure.

On contrary, even though many penetrating issues of AM can be resolved by introducing electrospraying, yet significant amount of work remains to be fully understood. For example, metal nanoparticles by electrospraying are still in early stage. Clogging of the solution at the nozzle, agglomeration of the particles on the target are some of the own inherent limitations of electrospraying. Overcoming these process and material boundaries will dictate the execution AM with electrospraying. Overall, we find it interesting to join electrospraying and AM together for greater cause.

Disclosure statement

No potential conflict of interest was reported by the authors.

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