A REVIEW ON 3D PRINTING OF POLYMERIC NANOCOMPOSITE MATERIALS UTILIZING STEREOLITHOGRAPHY.

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ABSTRACT

This review encompasses recent trends and progress in the field of 3D printing technology. 3D printing technology is one of the emerging and very much applicable field of research. In this review special literature survey is carried out for 3D printing of materials based on polymeric nanocomposites utilizing stereolithography due to very important and interesting applications of these new materials on industrial scale. 3D printing technology utilizing interesting, materials like polymer composites have revolutionized this field because of the production of scaffolds for biomedical applications. The review also extends its literature survey about progress in the field of bioprinting technologies utilizing biopolymer materials as inks.

Keywords: Stereolithography, Polymeric Nanocomposites, 3D Printing, Bio Printing.

1. INTRODUCTION

The review presented here shall cover almost all the aspects related to technological advancements in 3D printing, various materials used for 3D printing with special emphasis on polymeric nanocomposite materials, applications so far and future potentials of 3D printed materials. 3D printing is associated with the fabrication of complex 3D solid objects utilizing a digital file and electronically handled printer. The technique is also referred as additive manufacturing because an object is fabricated and printed in form of successive layers which are added smoothly sharply unlike traditional fabrication techniques which involve cutting and drilling processes and are thus subtractive techniques. The ultimate quality of the 3D printed object is dependent on many factors like the type of material, printer type, and its speed and specially the manufacturing process used [1]. These 3D printers can produce objects from simple to complex in a short span of time. For example, objects like gear usually take less than an hour to be fabricated [2].

The major advantage of 3D printed materials over conventional subtractive technologies is that this technique is cost-effective and timesaving. 3D printing never uses expansive tools particularly for small scale production of objects. This provides the basis for profitable consumption of the technique for functional markets in the world. Another functional advantage of 3D printing material which further adds to its cost-effectivity is the 95 % - 98% recycling possibility of the waste materials produced [3]. In addition to cost effectivity, 3D printing technology has the tendency to produce products more quickly as compared to other cutting machinery techniques. Moreover, 3D printing technology is a quick source of sharing ideas and designs of objects using software programs all over the world. One can easily design a product in his home and office and can share it with the customers all around the world for 3D printing. For instance, a mechanical engineer designed a device and posted its prototype on a social website as a design for 3D printing. It was not more than a few hours various customers interested in 3D printing all over the world downloaded that design for fabricating that tool [4].

2. EVOLUTION OF 3D PRINTING

The very first idea bout fabrication of 3D objects came into sight by a patent put by Chuck Hull in 1986 [5]. A similar patent was produced by Sachh et al [6] for the fabrication of a 3D component utilizing powdery porous material along with binder layer by layer. With the passage of time, this technology has gone through various stages of evolution. These phases can be summarized as a prototype designing phase, the creation of finished goods and the final consumer phase.

Most of the 3D printing still keenly depends on its phase which involves the fabrication of a prototype of new designs by artists and architects. This is because the 3D printers have tremendous capability to duplicates them with the lowest cost and keeping in view privacy considerations [7]. Low cost for the fabrication of prototypes is attributed to the use of less expensive materials like plastics and various resins as test materials. These materials can then be replaced with metals for actual objects Figure 1. Moreover, the time for fabrication of prototypes is also reduced without need of any other tools and dyes which can save millions of dollars [8].

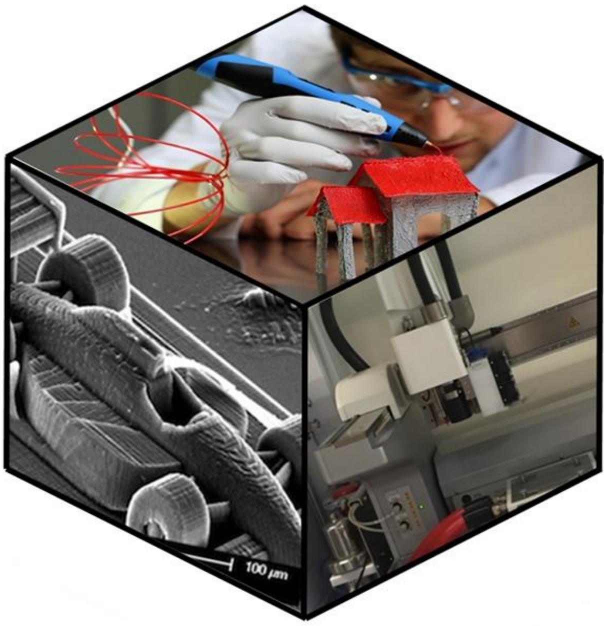

Fig. 1 3D Printing Technology Utilization

In the second phase of evolution, direct digital manufacturing yields finished goods to be used in the market for a test. The test marketing utilizes prototypes of various sizes, colours, styles and shapes to be tested for their applications. The utilization of such firm specializations in 3D printing for the production of finished goods based on prototypes could exceed with the passage of time [9].

The last phase of evolution involves especially the fabrication of arts, crafts and replacement parts to produce coloured figures, replacement of knobs in cooking ranges and fabrication of chess pieces. In short, the third phase comprises the future of 3D printing technology when it shall be possible for consumers to use 3D printers just like conventional desktop printers for fabricating objects themselves in homes and offices. According to a view in the near future people will go online and download what they need and print it out for them instead of going to market [10]. Similarly, according to an engineer by virtue of the 3D printers in our home in the near future we shall be able to fabricate parts of cars, other household machinery parts, knobs, etc. In simple one would have a small factory of his own at home [11].

3. DIVERSITY IN 3D PRINTING MATERIALS

A variety of materials have been in practice for fabrications of the prototypes using 3D printers. The choice of the material depends upon the technique used to print out objects and the overall chemistry of the finished object. Almost all the techniques used for 3D printing utilizes an external source of energy in form heat, light, laser, and other-directed energies. The selection of the materials used to print out objects by virtue of 3D printers is highly related to the form of energy used [12]. A diversity in 3D printing material does also exist with respect to their physical characteristics from powdery to filaments and granular to viscous resins. The choice of which depends on the final applications of the object. Moreover, from time to time many other materials are still under research to have properties which could be addressed in many active applications like bio-medics and energy.

In this part of the review, we shall address the common materials in practice so far for the fabrication of objects using 3D printing techniques with special emphasis on polymeric nanocomposites as the 3D printing materials of the future.

3.1.POLYMERS

Thermoplastics polymers are the most common type of materials practiced and studied for additive manufacturing technique. The use of thermoplastics is frequent because of the ease of manipulation, low cost and little heat for moulding. Many prototypes have been reported by various researchers utilizing the most common thermoplastic materials like acrylonitrile-butadiene-styrene copolymer (ABS) [13], polyesters [14], polyurethanes [15], polyformaldehydes [16], rubbers [17] and polyphenylenesulfide [18]. All of these and other such thermoplastic materials have certain promising properties for many applications of 3D printed objects. For instance, nylon or polyamides are flexible, strong and durable while ABS is strong and available in various colours. In contrast to them, polylactides are nor much strong but have very good transparency and can be used in a variety of colours. PLA finds its wide applications in the medical field because of its properties such as biocompatibility, biodegradability and non-toxic, non-immunogenic, and non-inflammatory nature [19].

3.2.METALS

Different metals are used in 3D printing technology. Some of the metals used in pure form are gold, copper, niobium, tantalum, titanium, alloys in powdered form are aluminum-based, cobalt-based, copper-based, iron-based, nickel-based, and titanium-based [20]. Stainless steel in grinded form is one of the most preferred materials for the sintering/melting/electron beam melting processes of 3D printing. It is widely used in jewellery where its silver colour can be plated with other metals to give different colours such as gold, bronze, etc [21]. Alloys of cobalt can be used in the field of dentistry for the purpose of 3D printing because of their properties such as heat-treated conditions, high specific strength, resilience, elongation and high ability to recover [22]. Nickel-based alloys are being used for the production of aerospace parts by 3D printing [23]. Nickel is highly resistant to heat (up to 1200°C) and corrosion [24]. Furthermore, Titanium alloys can also be used for printing of objects using 3D printing technology due to their outstanding resistance to corrosion and oxidation. They also have low density and good ductility and are useful in high operating temperatures and high-stress environments, for instance in the aerospace industry [25] and biomedical field [26]. Metals have excellent physical properties and they can be used from the biomedical field to the aerospace industry hence, they are widely used in every field.

3.3.INORGANIC CERAMICS

Ceramics have excellent properties due to which they are widely used in the industry. They have high-temperature resistance, mechanical strength and are light in weight. Ceramics were first introduced into 3D technology by Marcus et al [27] Marcus et al [28] in the 1990s. Plausibly, rigid and solid bulk ceramics with high densities, very homogeneous microstructure, high compression strength, and bending can be manufacture with the help of Stereolithographic Ceramic Manufacturing (SLCM). In a similar way, for the first time in the year 2012, the probability of bioactive glass powders to be operated by SLCM was substantiated. Some of the ceramic materials used are zirconia (ZrO_2), alumina (Al_2O_3), tricalcium phosphate (TCP), bioactive glasses and silicate bioceramics (e.g. glass-ceramics) [29,30]. The ceramics should possess some properties so that they can be used in 3DP. They should have suitable rheological behavior, long-term stability, and suitable viscosity. Along with this ceramic suspension in the required medium must be homogenous, stable (long period of time) and should not segregate otherwise it would form inhomogeneity in the fabricated parts [31]. For example, Alumina powder has the ability of undergoing 3D technology. It finds its uses as catalyst, adsorbent and in microelectronics, chemical, aerospace and other high-technology industries [32]. Alumina has a high green density which is helpful in 3D printing of complex-shaped alumina parts [33]. Weng et al. observed that the tensile strength and modulus of the 3D printed products increase by 20.6% and 65.1% respectively, if 5% w/w of SiO_2 is added to commercial SLA feedstock [34].

3.4.BIOMATERIALS

Materials of biological origin instead of fossil fuels are called as biomaterials [35]. Biomaterials may be called cell-encapsulating inks, or bioinks, and acellular inks, depending on the presence of living cells [36]. Some of the properties which should be considered regarding biomaterials are; surface chemistry, surface reactivity, surface roughness, surface charge, contact angle, and rigidity [37]. These characteristics lead to some cell-biomaterial interactions and cell-cell interactions which play an important role in cell attachment, viability, and differentiation in case cells are present in the biomaterial. They determine the success of the product. Apart from properties, there are some important prerequisites for biomaterials are; cell survival support, biodegradability, mechanical strength, biocompatibility, adaptability in fabrication procedure, cell adhesion and response, directional stability [38]. Biomaterials can be natural and synthetic. Some natural biopolymers are collagen, chitosan, hyaluronic acid, alginate, etc. synthetic non-degradable biopolymers include as polyethylene derivatives, poly(tetrafluoroethylene), poly(methyl)acrylates, polyacrylamides, polyethers, polysiloxanes, and polyurethanes on the other hand degradable biopolymers includes polyesters, poly(α-hydroxy acids), polylactones, polyorthoesters, polycarbonates, polyanhydrides, and Polyphosphazenes [39]. Bioceramics are also in use due to their biocompatibility and bioactivity. Some are obtained from biological sources like demineralized bone matrix [40]and coral [41], and other are synthetic which include hydroxy apatite (HA), β-tricalcium phosphate (β-TCP), α-tricalcium phosphate (α-TCP) [42] bi-phasic calcium phosphate (BCP—a mixture of β -TCP and HA) [39] calcium sulfate (CS) [43], calcium silicates and bioactive glasses [44]. Some examples of the use of biomaterials in 3D printing are; Gaebel et al. used laser-based 3D technology in bioprinting for the regeneration of cardiac tissue. They transferred human umbilical vein endothelial cells and human mesenchymal stem cells on a specified area on polyester urethane urea cardiac patch for the regeneration of cardiac tissues. The printed product was incorporated into the infected heart of a rat and vessel development of printed tissue was observed [45].

3.5.POLYMERIC NANOCOMPOSITES

Polymers have become part and parcel of the industry as they are used in the manufacturing of toys, tools, bottles, bags, electronics and transportation accessories [46]. The importance of polymer is due to their excellent properties i.e. easy processing, light in weight, durability, and ductility [47]. But due to significantly less modulus, dielectric constant and mechanical strength, polymers are not used alone or in a pure state as compared to ceramics and metals [48-51]. To overcome problems associated with polymers, some other materials such as metal ceramic or polymers in the form of fibers, pallets, whiskers or particles are added in the polymer [52, 53]. The host polymer is known as a matrix and the addition of any inclusion makes it a composite [54]. It is normally called a polymer matrix composite [55]. When polymer matrix composites are formed by adding Nano-sized inclusions it gives nanocomposites which means that PMCs have constituents with at least one phase in nanometer range [56]. Traditionally PMCs were formed by the addition of any additive of micro-size [57] but the trend has shifted towards the addition of additives of Nano-size with an average size range of [58,59] 1nm-100nm. Polymer nanocomposites can be prepared in several ways. Some of them are; One of the processes is adding Nano inclusion to the polymer solution and using the process of sonication in the Nano-inclusion-polymer suspension to disperse the additive. In another process, a monomer is polymerized after the addition of nanoparticle in accordance with the nature of the monomer as well as nanoparticle [60].

Adding Nano inclusions to the polymer enhances its mechanical [61], electrical [62], thermal [63], flame retardance [64] and optical [65] properties. In addition to this, additives also improve the UV and radiation resistance [66–68], and anti-fouling properties [69–71]. For instance, a nanoparticle of silver (Ag) behaves differently towards electrons and photons as compared to bulkier silver [72]. Additives can be silica [73, 74] organoclay, carbonaceous Nano-fillers (carbon nanotubes (CNTs), graphene-based fillers, carbon black (CB), carbon nanofibers (CNF) and metallic nanoparticles [75-77]. But carbon tubes [78,79] graphene [80] and graphite [81,82] are widely used as inclusions. Polymer-metal composites are also being used [83] for example, polymer with metal oxide nanoparticles like TiO_2 or MoO_3 were printed by 3D technique and checked for antimicrobial and antifungal characteristics [84]. Graphene oxide (GO), an oxidized form of graphene which is said to be 1000 times more conductive as compared to copper and 200 times stronger than steel, is one of the outstanding nanofiller (additive) due to its unique characteristics of mechanical strength thermal and electrical conductivity, and antibacterial and biocompatibility [85-90]. Lin et al. printed a photopolymer loaded with 0.2% w/w graphene oxide which showed a 62.2% increase in the tensile strength [91] and. Manapat et al. observed a 673.6% increase in the tensile strength because of the addition of 1% w/w graphene oxide [92].

4. PRINTING TECHNOLOGY

3D printing also is known by many other names such as Rapid Prototyping, Additive Manufacturing, Additive Technique and many more names [93] is a process of creation of physical products from a geometrical blueprint by addition of materials successively [94]. This process allows the production of products within hours and minutes by using CAD software and raw materials [95,96]. This technology became famous in the 1990s [97] but soon afterward many new 3D printing technologies were introduced [98]. Now there are different types of printing technologies available which are classified on the basis of materials used, mechanism and characteristics of the product. The American Society for Testing and Materials (ASTM) divides 3D printing/ Additive Manufacturing into seven classes shown in Table 1 [99].

Table 1. Classification of additive manufacturing

ASTM Category	**Technologies**	**Substrate**	**Mechanism of Layering**
Binder jetting	Powder bed inkjet printing S-printing M-printing Theriform™ ZipDose®	Solid particles (plastic, metal, sand, ceramics, and polymer)	A liquid binding material is particularly settled to bind powder materials
Vat polymerization	Stereolithography (SLA) Digital light processing (DLP) Continuous layer interface production (CLIP)	Liquid (photopolymer)	Liquid photopolymer in a vat is particularly treated with light-activated polymerization

Powder bed fusion	Selective laser sintering (SLS) Direct metal laser sintering (DMLS) Selective laser melting (SLM) Electron beam melting (EBM) Concept laser	Solid particles (metal, plastic, polymer)	Regions of powder bed are fused particularly by thermal energy
Material extrusion	Fused deposition modeling (FDM) Gel/paste extrusion	Filament (thermoplastic polymers e.g. ABS; PLA; PC; ULTEM™ resin)	Material is particularly distributed through an opening or aperture
Material jetting	printing Poly jet Thermo jet	Liquid (acrylic-based photopolymers, Elastomeric photopolymers, wax-like materials)	Drops of formed material are particularly settled
Directed energy	Electron beam direct Manufacturing	Wire (metal)	Pointed thermal energy is concentrated on fusing

deposition	Direct metal tooling (DMT) Be additive manufacturing (BeAM)		materials to deposit them as they melt
Sheet lamination	Laminated object manufacturing (LOM) Selective deposition lamination (SDL) Ultrasonic additive manufacturing (UAM)	Sheets	Object is made by joining sheets of material

5. STEREOLITHOGRAPHY

Stereolithography is an additive manufacturing technology that involves the fabrication of a model or sample or prototype [100-102] in a complex shape by depositing layers of the polymer through the process of photopolymerization with the help of computer-aided design (CAD) [103]. Dr. Hideo Kodama developed stereolithography (SLA) for the first time in 1981 when he saw it as a speedy and inexpensive process as an alternative for holographic technology [104]. Later, in 1986 Charles W. Hull patented the first SLA printer [105]. Figure 2.

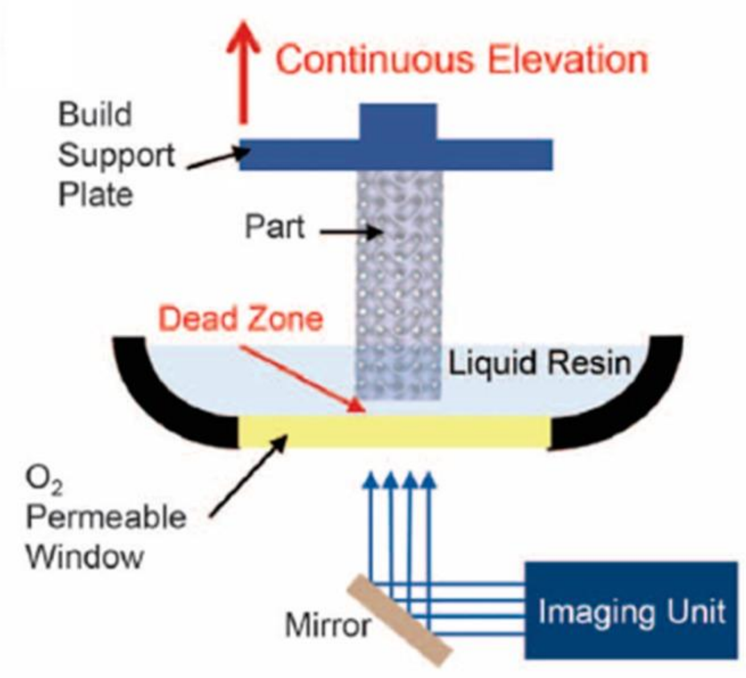

Fig. 2 Schematics of a 3D Printer

Generally, a stereolithography apparatus has the following parts.

- A photopolymer (clear liquid) in a tank.
- An ultraviolet laser (high-powered)
- A platform is submerged in a tank (it can move up or down in accordance with the printing process being used)
- A software/ computer interface to handle and monitor platform and laser[106].

The basic principle behind the working of stereolithography is photopolymerization [107] i.e. solidifying a photosensitive polymer with the help of a light, laser or an ultraviolet (UV) source [108]. This procedure involves the use of CAD software to store information and instructions for the object to be printed. In the very first step, a model is prepared in CAD which is converted to an STL file (Standard Tessellation Language). An STL file is a system of coordinates (x, y, z), triangles and vectors which are responsible for the 3D designed structure. The right-hand rule is used for determining interior and exterior surfaces. The designed structure is cut into pieces/layers ranging from 25-100 µm which consists of information. During this cutting/slicing process additional edges are introduced but due to the replacement of continuous contour with discrete stair steps because of the algorithm can cause inaccuracy in the slicing procedure. This inaccuracy can be treated by creating multiple STL files and then combining them. Also, the dimension in z coordinate should be such that it is the multiple of layer thickness value. There many other file formats as well such as stereolithography contour (SLC), Hewlett-Packard graphics language (HPGL) and initial graphics exchange specifications (IGES), etc. The information in the STL file is used in the stereolithography apparatus for the 3D printing process. Other than CAD software, the stereolithography apparatus consists of a tank containing liquid polymer and a platform, used to hold and support the structures being printed. A light source such as laser light or a UV laser (computer-controlled) is directed on the photosensitive polymer to solidify it at particular places on each layer. Then after solidification of one layer, the platform is again lowered, and the process is repeated. The thickness and resolution of the layer is dependent upon the instrument [109-115].

There are a number of resins that can be used in SLA. Resin is a liquid that solidifies upon curing with the laser light [112]. Many of the resins present for stereolithography are low in molecular weight and have multifunctional monomers. They can be glassy, hard and rigid and brittle. There are some resins which are high molecular weight (1-5 kg/mol) and can give elastomeric products. They are mostly combined with non-reactive diluents like N-methylpyrrolidone (NMP) or water to decrease the viscosity of the resin [116-118]. Photoinitiator and UV absorbers can be added to resin for the adjustment of the depth of polymerization that occurred [119]. A number of photoinitiators (PI) and its nature can affect the reaction kinetics, required light amount, conversion, cross-linking density and up to some mechanical strength of the product [120-122]. Light absorber acts as a shield and controls the penetration of light in the resin. It decreases and prevents the deep penetration of light until the curing of the resin. This is important for complex geometries to have a predetermined curing depth so that additional and over curing in the direction of z-coordinate and feature development loss can be avoided [123-125]. One of the UV absorbers which can be used are derivatives of benzotriazole [126]. Along with other properties such as laser power, scan speed, and UV exposure time, depth of polymerization also act as quality determining a property of the final product [127].

Stereolithography can be done in three different modes or routes given below:

- Aces Mode.
- Quick Cast
- Solid Weave

In the ACES route, the products have additional strength and are as transparent as crystal. It is an incomparable mode of stereolithography when it comes to the products with high visual quality and excellence e.g. lenses and optics. On the other hand, Quick Cast gives 80% hollow product i.e. it produces quasi-hollow parts through a robust honeycomb interior in the hollow form. Then after doing rapid prototyping, metal parts can be completed within 3-5 days. Solid weave has the fastest reversal time. It does not compromise on strength and precision of product along with this it is also in-expensive of all of the three modes. [128].

Stereolithography is no more limited to the use of only liquid resin or polymer. New materials have been used in stereolithography. A brief account of which is given below:

5.1.METAL STEREOLITHOGRAPHY

Metal stereolithography deals with the use of powdered metal instead of the liquid polymer as a resin along with LASER as a source of light. This is extensively being used in industries for daily life accessories

5.2.CERAMIC STEREOLITHOGRAPHY

Ceramic materials have always been used conventionally but now they are being used in stereolithography as a resin. LASER acts as a light source [128]. Photopolymerization in ceramic resin occurs only in the organic part i.e. in organic monomer because ceramic particles are neutral and inert to laser [129]. It has become a common technique by now [128]. Graham and Holloran used a slurry system instead of a resin-based system. The slurry was composed of a suspension of ceramic particles. Micro/nanometer size, light-sensitive monomers, and a photoinitiator were added to the suspension. This ceramic suspension (alternative of the resin-based system) when exposed to the Laser light became solid by the process of the photo-polymerization mechanism [130]. Materials other than ceramic which were added to slurry helped the ceramic particles to get stabilized and avoid agglomeration and settling down [131]. Phenomena of light scattering is the main difference between conventional SLA and Ceramic SLA [130, 132].

Apart from this SLA has also a new type of process called micro stereolithography. This process has very high resolution and it can give layers with a thickness of less than 10 µm. [113].

SLA has extensive and widespread applications and is successfully being applied in every field. Its widespread use includes applications in the field of fabrication of implantable devices [133], tissue engineering [134,135], tissue scaffolding [136,137], production of highly elastic silicones for use in soft robotics [138], high-strength thermally post-cured epoxy resins [139], dentistry [140] and many more such as in oral surgery [141, 142] and preparing moulds by utilizing data from CT scans to prepare implants in cranial surgery [143, 44].

SLA has a preference over other 3D printing processes because of its high-resolution printing. High resolution can be determined by the number of photons to be applied since one photon can generate a polymerization process. There is a possibility that localized polymerization initiation can help in achieving resolution even higher than 100 microns. High resolution enables the printing of objects which are highly complexed and advance [145]. Whereas Formlabs Form2 SLA3D can have a resolution (layer thickness) of about 25 microns [146]. SLA process also has one more advantage i.e. it does not have an issue of blockage or clogging because it does not use nozzles [145]. However, cytotoxicity due to utilizing photoinitiators and radicals during the SLA process entrapped unreacted monomer and an unused photoinitiator, and incompetency of creating a compositional gradient in the direction of horizontal planes are some of the challenges [147]. The high cost of the SLA-based 3D printing system is an additional problem manufacturing industry [148,149].

5.3.PHOTOPOLYMER JETTING

Photopolymer jetting is known as the advanced type of inkjet printing technique in which many print nozzles efficiently spray small drops of liquified photopolymer or any other material as an alternative of ink for printing [150]. It works on the principle of inkjet printing which can be stated as that different substances like photocurable polymers [151], ceramics [152] and metallic nanoparticles [153] can be liquified, converted to droplets and are then allowed to deposit on surfaces like polyimide [154] and alumina [155]. The droplets of the substance to be used are utilized using a thermal or piezoelectrical drop-on-demand device, deposited on a particular place at the substrate and finally it is converted to solid with the help of chemical or thermal process like curing or sintering [156]. Photopolymer jetting works on the same principle i.e. use of liquified droplets instead of ink. In the process of photopolymer jetting more than one printing heads are used which move backward and forward in the x-y direction. These printing heads spray the small drops of liquified photopolymer on the substrate according to the STL file. Multiple jetting heads are used for the printing of the desired product and for the support of materials as well. The function of support material (wax-like) is to keep the material together, stabilize them in the direction in which object is building, filling the empty spaces and holes that are present in digital design, which can be removed by using a high-pressure water jet or chemical procedure at the end of the printing process. [157-161]. Cazon et al used different types of processes at the end of printing on the products from polyjet printing. They used processes like a matte or glossy option, water pressure to remove the supporting material, and caustic soda bath at the end of the printing process. These processes did not affect any quality of the product like tensile strength but have some effect on the property of roughness [162]. The layers formed by the tiny droplets of photopolymer are then cured using an ultraviolet (UV) lamp [163]. When one layer of deposited photopolymer is cured with the help of an ultraviolet lamp then the new layer is cured and hardened on previous by lowering the platform. Moreover, using more than one jetting head can give different coloured objects in one structure [161].

Poly jetting is an advance and advantageous process. Some of its advantages are the high resolution of 16 µm thickness (smaller than human RBC) within the range of accuracy of 0.1mm, multi-coloured products, a smooth and clean process with no need of post-curing, support multi-materials at the same time which can increase yield, and ability to print complex structures in a fine and smooth way with smallest details [158,161,164-166]. Table 2 [163] shows some of the facts of poly-jet technology. Poly-Jet printing with Stratasys J750 system is said to have the capability of producing tiny objects which have layers 14 µm thick with the resolution parameters as 600 dpi in X and Y direction, and 1800 dpi in Z direction [167]. However, print jetting heads have high price value and are expensive in comparison to others. Apart from this as they are needed to be replaced on a regular basis, so they also have maintenance costs too which makes them further expensive [168].

Table 2. Poly-jet technology

Material type	**Liquid (photo polymer)**
Material	Photopolymer resin
Maximum part size	19.30 x 15.40 x 7.90 in.
Min feature size	0.006 in.
Min layer thickness	0.0006 in.
Tolerance	0.0010 in.
Surface finish & Build speed	Surface finish is smooth and build speed is fast
Applications	Very detailed parts, Rapid tooling patterns, Presentation models, Jewellery and fine items.

6. FUSED DEPOSITION MODELLING

Fused deposition modelling (aka FDM) is an additive 3D extrusion-based technique that is commonly used to print fibre reinforced polymer composites [169,170]. Crump et al. first time patented it (FDM) in 1989 [171] whereas Stratasys Inc. has the credit of commercializing it in the year 1990 [172]. Stratasys Inc. is called as pioneers of the 3D AM technique of FDM and is known for creating 3D models via FDM and work for its development [173].

The general principle of FDM is the extrusion of molten material and its deposition, with the help of a feeding mechanism e.g. by using a pressure system, on some substrate in layers to create a 3D product [174, 175]. In the FDM process, a filament of material is added to the extrusion head where it is heated above its melting point and forms a viscous liquid. It is then extruded through a nozzle to create layers. The layer formed is solidified quickly. The platform on which the deposition occurs on the substrate is run through the same process again to form another layer in the same way, but the previous layer is cooled and solidified properly before the deposition of a new layer. A CAD software acts as a brain of the process since it controls and design the operation and is responsible for creating a layer-by-layer model used for deposition and printing. The 3D printed product is, in fact, the translation of sliced layers of digital data from CAD software. There is a different range available for the thickness of sliced layers i.e. it can be from 0.178 mm – 0.356 mm but is not static as it can be changed according to the need. During the process, the size of the extrusion head/nozzle is important since it determines the thickness which is responsible for vertical dimensional resolution [60,161, 176-179].

There are different types of materials which can b used in FDM process, but the material used must be of excellent qualities since the mechanisms such as pressure systems, tension and compression and heating are used during FDM, therefore, the material used must be mechanically and thermally so that it can bear stress and heat [145]. Thermoplastics are a good option for FDM and are widely used as their melting temperature is low and have a better ability to flow which is important for the printer to be accurate and functional [140,156]. Some of thermoplastics are polylactide (PLA) [180, 181], polyacrylonitrile butadiene styrene (ABS) [182,183], polyamide (PA) [184], Polycarbonate (PC), polyphenylsulfone (PPS) [185], and (PC/ABS) blends [186]. However, one way to increase the stability of thermoplastics is by incorporating fillers [60]. Fillers like metal particles or carbon nanotubes can be incorporated into thermoplastics for use in FDM [187,188]. To print thermal devices, enhanced thermal conductivity and stability are needed which can be achieved by using thermal conductive fillers such as graphene, boron nitride (BN), and CNTs [189, 190]. For instance, the thermal stability of ABS is enhanced by using copper powders [191]. Peng and co-workers printed a heat sink via FDM by utilising graphite flake-based [189].

Fused deposition modelling is a useful and advantageous technology. Krejcova et al. utilized polylactide to print a microfluidic chip which can be used for electrochemical analysis of the influenza virus with the help of CdS quantum dots [192]. FDM is also being used in the medical field for the printing of cells such as corneal stromal cells, dermal fibroblasts [193], and fabricating in vitro pharmokinetic [194].

FDM is not only a low-cost and simple process but it is also capable of printing at high speed [195,196]. Apart from this FDM can also add more possible functions to the materials like polymer-based composites in different ways such as blending functional particles with polymer filaments [197], and use of multiple nozzles and heating heads for printing different materials i.e. printing composites of multiple materials with various functions [198]. However, limitation of availability of materials [199], the product being porous i.e. increased porosity [200] and weak interfacial bonds [201] are some of its weaknesses. The heating and cooling process which must be quick and immediate also affects the thermal and mechanical properties [202].

7. BIOPRINTING

Bioprinting is one of the AM techniques which is said to have been helpful in overcoming the shortage of organs for transplant. It can be defined and explained in a number of ways. Bioprinting in 2010 was explained as a process which uses CAD for designing and combining living and non-living substances in a specific fashion in order to get biologically engineered products which can be helpful in regenerative medicine, pharmacokinetic and basic cell biology studies [203]. In another way, it is defined as a process that uses different materials and techniques to construct a biological structure that has tissue cells and biomolecules which perform biological functions in the specific organization [204]. In simple words, it is a process in which AM techniques are used to print a 3D object by using biological materials and CAD which can resemble or replicate a functional tissue or organ [205,206]. Figure 3.

Fig. 3 3D Printed human mandible

Bioprinting is a stepwise process in which a biologically active substance is printed on some substrate [207]. The assembly for bioprinting consists of a bioprinter, bioink (living or non-living material used for printing), biogel (gel/liquid used for support of bioink/cells) [208]. In the stepwise, the first step is to construct a CAD model of the object and then bioinks are added in the printer heads which deposits the layers of bioinks on some base or substrate until many layers are formed which are allowed to dry and mature in an incubator for a time period of one day to a week depending upon the material. In this way, a 3D object is printed [209].

There are different techniques used for bioprinting which are micro-extrusion, inkjet printing, and laser-assisted printing [210]. A brief description of these methods for bioprinting is given below.

7.1.MICRO-EXTRUSION BIOPRINTING

Micro-extrusion bioprinting is based on the use of pneumatic pressure, plunger-screw based pressure or robotic power. In this method, a CAD model is first constructed which defines the directions for the bioinks. The extrusion of bioink occurs first with the help of any of the pressure mechanism on some substrate through a micro-size nozzle or a standard micro extrusion needle. The extrusion occurs in the x, y, z planes as directed by a CAD software. Layers of bioink are formed dried matured and treated until a complete 3D product is printed [211, 212]. The phase of the bioink, its viscosity are important factors in extrusion-based printing [213]. Biomaterials in solutions, pastes, or dispersions form which has a viscosity between 30 mPa/s-6$\times 10^7$ mPa/s and are suitable for micro-extrusion process [214, 215]. Aortic valves [216], tumour models [217] and vascular tissues [218] have been printed by using the micro-extrusion process. However, increasing printing resolution and speed are the drawbacks [219].

7.2.INKJET BIOPRINTING

Inkjet bioprinting is the same as conventional inkjet printing in which droplets of bioink are deposited on some substrate by using CAD software [220]. The bioprinters which were initially utilized for bioprinting were the modified form of 2D ink-based printers [221,222]. In inkjet bioprinting, acoustic and thermal forces are used for the ejection of bioink on a substrate [223]. Inkjet printers working on thermal technology uses electrical heat energy to produce droplets which are forced out of nozzles with pressure [212, 224]. On the other hand, an acoustic force can be created in two ways i.e. with the help of air bubbles or piezoelectric actuators [225]. The piezoelectric actuator uses short-lived pressure to produce drops of bioink [212]. Bioinks like synthetic and natural-derived polymeric solutions which have low viscosity can be utilized for inkjet printing [226, 227]. Although regeneration of functional skin [228] and cartilage in situ [229] have been achieved via inkjet bioprinting but it is confined to low cell densities to prevent clogging of nozzles and to decrease shear stress [208].

7.3.LASER-ASSISTED BIOPRINTING

Laser-assisted bioprinting (LAB) is based on the principle of Laser-Induced Forward Transfer (LIFT) in which bioink is deposited on the substrate by using a laser pulsed beam [219, 230]. LAB assembly is made up of a pulsed laser beam, a focusing system, an absorbing layer, and a substrate for the bioink. The pulsed laser beam is used for stimulating the transmission of bioink, the focusing system is used to help laser in focusing, absorbing layer is a gold or platinum ribbon. Initially, a high-pressure bubble from a bioink layer is created. It can be created by focusing a laser beam on an absorbing layer which is gold or platinum ribbon. This ribbon creates the high-pressured bubble which is used to transmit the bioink on the substrate [219]. LAB technology gives resolution at a single cell per droplet [231] whereas resolution is dependent on various factors such as laser energy, the air gap between the absorbing layer and substrate, nature of the substrate surface, surface tension and viscosity of the bioink [232]. Moreover, this system does not require any nozzles so clogging of materials is no problem here [219].

Other than these three methods of bioprinting given above there are also some other newly developed methods such as integrated tissue organ printer (ITOP) and robotic bioprinting [219]. Table 3 [219,233,234] gives a comparison of different bioprinting techniques.

Bioprinting has opened new opportunities and horizons in the field of technology. Various tissues, nerves [212], blood vessels [235], hearts [236], bone [237], cartilage [238], kidneys [239], skin [240] have been printed via bioprinting technology. Cooper et al. printed a bone using DermaMatix and BMP-2 (Bone Morphogenetic Protein-2) which has been helpful in curing a calvarial defect in a mouse model [241].

Table 3. Various bioprinting techniques

Nature	**Micro extrusion**	**Inkjet printing**	**Laser assisted bioprinting**	**ITOP**	**Robotic bioprinting**
Viscosity	6–30×10^7 mPa/s	3.5–12mPa/s	1–300mPa/s	N/A	N/A
Cell density	High	Low < 10^6 cells/mL	Medium, 10^8 cells/mL	High	High High
Cell viability	40–80%	85%	>95%	>90%	>90%
Resolution	100 µm millimetre	75 µm	10 – 100 µm	2–50 µm	N/A
Print speed	100 µm/s	1–10000 drops/s	2–1600 mm/s	N/A	N/A
Nozzle size	20 µm-millimetre	20–150 µm	Nozzle-less	50 µm	N/A
Working principle	Contact	Non-contact	Non-contact	Contact	Contact
Mechanical integrity	High	Low	Low	High	Medium
Purchase cost	Low	Low	Medium	High	High
Reference	[219]	[219]	[219]	[233]	[234]

8. APPLICATIONS OF 3D PRINTING

3D printing is used in a wide variety of fields and this can be put into some exceptional uses. Many people and scientists have found different uses to make products by 3D printing that just not only shuns the use of plastic made products, but it also has made the material useful that is commonly considered as non-traditional and unavailable to print objects [242]. In developing countries, the technology of 3D printing is limited only to engineering departments of universities and workshops which are dedicated to such critical work such as Fabrication Laboratories [243]. A factory that is small-scale and is equipped with tools and software of electronics and fabrication of industrial-grade which used by specialist individuals to manufacture prototypes. These labs are being adopted in countries that are developing [244]. 3D printing has found usages in different areas such as research, in manufacturing of artistic items, visual aids, covers of devices, custom parts, presentation models, functional models and patterns and series production [245]. In today's world, rapid prototyping has spread its roots in broad domains. It is being used in different industries, factories and educational institutions which involves from basic level to higher level and for individual use as well [246].

3D printing technology is being used in making hearing aids [245]. Organs and parts of body printing is being done using this technology [247]. Parts of body such as titanium pelvic, plastic tracheal splint, titanium jaws using 3D technology have been printed [245]. 3D blood vessels have been printed because this technology has found remarkable advances in Tissue Engineering [248]. In developing countries like Uganda and South-Sudan, this technology is being used to produce 3D printed Prosthetic limbs [245]. To print cartilage and bone, used to replace the bone and cartilage that has bony voids caused by trauma or disease [249]. Customized 3D printed teeth are provided to the individuals [250]. Before this technology, fake teeth were of one universal size for all age people, but now this technology has made it possible to customize implant teeth, that is suited to a particular person [245].

This technology is used in the construction industry for either printing of the entire building or creation of the construction component. The development in the business Information Model will help facilitate the improved use of 3D printing [251]. A digital demonstration of physical and functional characteristics that can give the knowledge of 3D printing is Building Information Modelling. This can provide a dependable source for decisions during the cycle of its life that includes basic or initial concepts to its destruction for the building design [252]. It is predicted that in the future, we might be living in 3D printed houses. It is claimed by the researcher at the University of Southern California to have designed a 3D printer that has the ability to print an entire house in one day. The base elements used in this conceptual model was concrete to duplicate the computer programs of the house. To ensure the compatibility of the house with plumbing and electrical gadgets, layered fabrication tech called 'Contour Craft'' is used [242]. One-story house has been built in one day in China by this technology [253].

Decorative and Ornamental objects such as pendants, rings and plastic toys can be printed at the domestic level. People in the future would be able to print the goods on their own instead of buying them from markets [254,255].

For the food industry, the doors have been opened by 3D printing technology. The demand for the production of customized dietary food for a special group of people such as children, pregnant women, athletes' patients and so on is increasing that requires the more amount of healthy ingredients and reduction in the amount of unhealthy and unnecessary ingredients [256]. NASA is also putting attention on food printing and doing funding research to provide food to astronauts in space [242].

Industry of Art and Fashion have started getting the benefits of 3D printing. Artists have got to know more easy and straight ways of carrying out ideas to reality and fashion designers are using this technology to make shoes, luggage and other fashion accessories. [257]. 2012 Vapor Laser Talon football shoe by Nike [258] and for athletes New Balance custom-fit shoes by using 3D prototype has been made [259] on the commercial scale[245].

In learning processes and curriculum, with the help of applications from models of printed molecules to plastic gears, 3D technology is used [260]. It helps students in practical learning because now they can print prototype models in 3D [245].

The aerospace industry is among one of the areas that first used 3D technology to create a prototype [257]. In this industry, it is applied to make parts which lighter in weight, enhanced and complicated geometries, that minimize the use of resources and energy [261]. It not only saves the fuel but minimizes the usage of materials to produce parts of aerospace. This technology has been applied to produce spare parts for components of aerospace like engines [262].

3D printing has dramatically changed the automotive industry that designs, develop and makes new things. It is used in a process that gives new shines, for lighter and complicated structures in real quick time. 3D-printed electric car in 2014 had been printed by this technology. 3D printing technology broad range of applications has been extended by Local Motors by manufacturing a 3D- the printed bus that is electric can run without a driver, a recyclable and extremely smart bus called OLLI. Moreover, Ford is a leader in using this technology to make parts of the engine and prototype [263]. Parts of cars and airplanes are being printed efficiently and in a fast manner which contributes greatly to the value chain [264]. Figure 4.

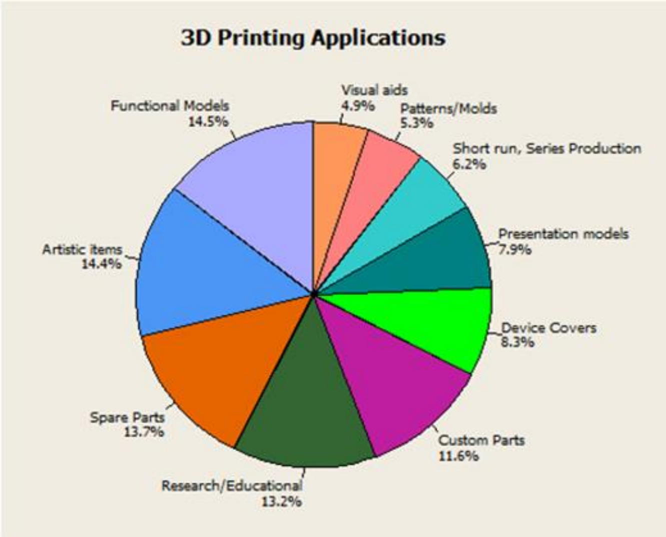

Fig. 4 Applications of 3D printing

9. CONCLUSION

3D printing is fastest growing and diverse field of research for scientists with endless applications. Steriolithography results in prototypes with finely finished prints. The degree of error in these prints is minimum. Moreover, polymer and polymer-based inks used for in 3D printer can be used to produce valuable products with applications in the field of biomedical and energy.

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