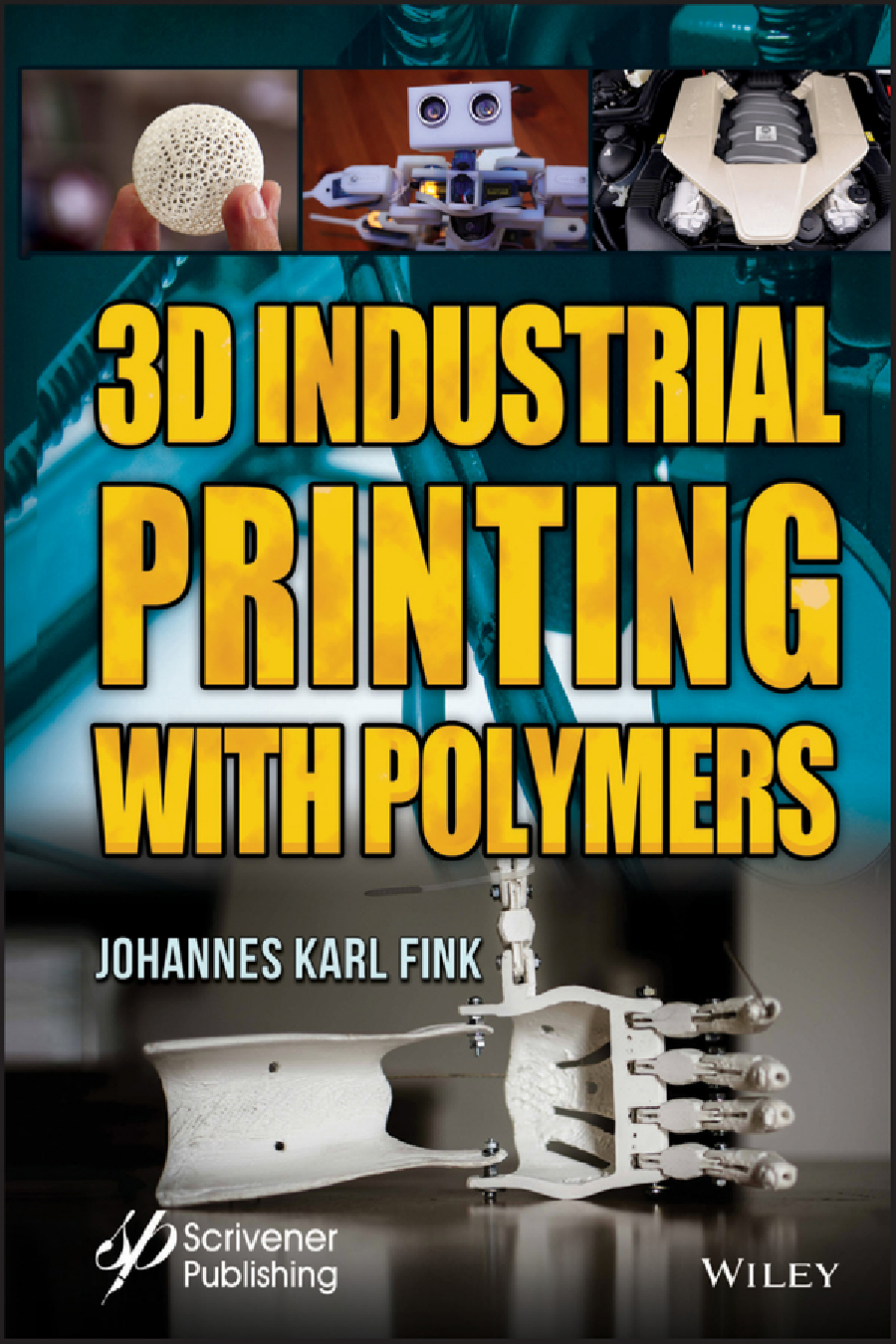

3D INDUSTRIAL PRINTING WITH POLYMERS

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Preface

The scientific literature with respect to 3D printing is collected in this monograph. The text focuses on the basic issues and also the literature of the past decade. The book provides a broad overview of 3D printing procedures and the materials used therein. In particular, the methods of 3D printing are discussed initially. Then, the polymers and composites used for 3D printing are detailed.

Furthermore, the fields of uses are discussed. The main fields are electric and magnetic uses, medical applications, and pharmaceutical applications. Electric and magnetic uses also include electronic materials, actuators, piezoelectricmaterials, antennas, batteries and fuel cells.

A special chapter deals with aircraft and automotive uses for 3D printing, such a in manufacturing of aircraft parts, aircraft cabins, and others. In the field of cars, 3D printing is gaining importance for automotive parts (brake components, drives), for the fabrication of automotive repair systems, and even 3D printed vehicles.

Medical applications include organ manufacturing, bone repair materials, drug-eluting coronary stents, and dental applications. Finally, pharmaceutical applications include composite tablets, transdermal drug delivery, and patient-specific liquid capsules.

How to Use This Book

Utmost care has been taken to present reliable data. Because of the vast variety of material presented here, however, the text cannot be complete in all aspects, and it is recommended that the reader study the original literature for more complete information.

Index

There are three indices: an index of acronyms, an index of chemicals, and a general index. In the index of chemicals, compounds that occur extensively are not included at every occurrence, but rather when they appear in an important context. When a compound is found in a figure, the entry is marked in boldface letters in the chemical index.

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I also want to express my gratitude to all the scientists who have carefully published their results concerning the topics dealt with herein. This book could not have been otherwise compiled.

Last, but not least, I want to thank the publisher, Martin Scrivener, for his abiding interest and help in the preparation of the text. In addition, my thanks go to Jean Markovic, who made the final copyedit with utmost care.

Johannes Fink
Leoben, 16th October 2018

1

Methods of 3D Printing

The issues of 3D printing have been summarized (1). There are recent monographs on 3D printing (2–19). Also, the technical and economic development and the advances of 3D printing have been summarized, as well as detailed examples of applications (20).

Three-dimensional printing can fabricate 3D structures by inkjet printing with a liquid binder solution printed onto a powder bed (21,22)

A wide range of materials could be utilized in printing since most biomaterials exist in either a solid or liquid state. The process begins by spreading a layer of fine powder material evenly across the piston. The X-Y positioning system and the printhead are synchronized to print the desired 2D pattern by selective deposition of binder droplets onto the powder layer (23). The piston, powder bed, and part are lowered, and the next layer of powder is spread. The drop-spread-print cycle is repeated until the entire part is completed. Removal of the unbound powder reveals the fabricated part. The local composition can be manipulated by specifying the appropriate printhead to deposit the predetermined volume of the appropriate binder.

The local microstructure can be controlled by altering the printing parameters during fabrication (24). The incorporation of microchannels effectively distributes additional seeding surfaces throughout the interior of the device, increasing the effective seeding density and uniformity. Patterned surface chemistry potentially offers spatial control over cell distribution of multiple cell types. This technology is limited by the competing needs between printhead reliability and feature resolution, as small nozzles can make finer features but are more prone to clogging. Current limitation in resolution is 100 μm for one-dimensional features (e.g., width of the thinnest printable line), and 300 μm for three-dimensional features (e.g., thickness of thinnest printable vertical walls) (25).

1.1 History

A brief history of 3D printing has been given (26). Also, the history of 3D printing in healthcare has been documented (27). The concept of three-dimensional (3D) printing goes back to Charles W. Hull (28). In 1984 Hull used UV light to harden tabletop coatings and created the term stereolithography (29). This apparatus was the world's first 3D printer. There are monographs dealing with the technology of practical 3D printers (30).

The term *3D printing* originally referred to a process that deposits a binder material onto a powder bed with inkjet printer heads layer by layer (1). More recently, the term is being used in popular vernacular to encompass a wider variety of additive manufacturing techniques. United States and global technical standards use the official term additive manufacturing for this broader sense, since the final goal of additive manufacturing is to achieve mass production, which greatly differs from 3D printing for rapid prototyping (1).

Three-dimensional printing was invented at the Massachusetts Institute of Technology (25). The history of the development of 3D printing is summarized in Table 1.1.

Additive manufacturing of polymer-fiber composites has transformed additive manufacturing into a robust manufacturing paradigm and enabled the production of highly customized parts with significantly improved mechanical properties, compared to non-reinforced polymers (33). Almost all commercially available additive manufacturing methods have benefited from various fiber reinforcement techniques.

The recent developments in 3D printing methods of fiber reinforced polymers, i.e., fused deposition modeling (FDM), laminated object manufacturing, stereolithography, extrusion, and selective laser sintering (SLS), have been reviewed (33).

Table 1.1 History of 3D printing (1,32).

Year	Event 1860–1993
1860	The photosculpture method of François Willème captures an object in 3 dimensions using cameras surrounding the subject.
1892	Blanther proposes a layering method for producing topographical maps.
1972	Mastubara of Mitsbushi Motors proposes that photo-hardened materials (photopolymers) be used to produce layered parts.
1981	Hideo Kodama of Nagoya Municipal Industrial Research Institute publishes the first account of a working photopolymer rapid prototyping system.
1981	In 1981, Hideo Kodama of Nagoya Municipal Industrial Research Institute invented two additive methods for fabricating three-dimensional plastic models (31).
1984	Charles Hull (founder of 3D systems) invents stereolithography.
1984	On 16 July 1984, Alain Le Méhauté, Olivier de Witte, and Jean Claude André filed their patent for the stereolithography process.
1984	Three weeks later in 1984, Chuck Hull of 3D Systems Corporation filed his own patent for a stereolithography fabrication system.
1988	Invention of fused deposition modeling developed by S. Scott Crump
1991	Stratasys produces the world's first FDM (fused deposition modeling) machine. This technology uses plastic and an extruder to deposit layers on a print bed.
1992	3D systems produce the first SLA 3D printing machine.
1992	DTM produces the first SLS (selective laser sintering) machine. This machine is similar to SLA technology but uses a powder (and laser) instead of a liquid.
1993	3D printing commercialized by Soligen Technologies, Extrude Hone Corporation, and Z Corporation.
1993	Dot-on-dot technique introduced by Solidscape.

Table 1.1 (cont.) History of 3D printing (1,32).

Year	Event 1995–2013
1995	Fraunhofer Institute developed the selective laser melting process.
1997	Aeromet invents laser additive manufacturing.
1999	Scientists manage to grow organs from patient's cells and use a 3D printed scaffold to support them.
2000	The first 3D inkjet printer is produced by Objet Geometries.
2000	The first multicolor 3D printer made by Z Corp.
2001	The first desktop 3D printer made by Solidimension.
2002	A 3D printed miniature kidney is manufactured. Scientists aim to produce full-sized, working organs.
2005	The RepRap project was founded by Dr. Adrian Bowyer at the University of Bath. The project was intended as a democratization of 3D printing technology. The open source hardware for the 3D printer can produce a large number of its own parts.
2008	The first 3D prosthetic leg is produced.
2008	The first biocompatible FDM material was produced by Stratasys.
2008	The RepRap Darwin is the first 3D printer to be able to produce many of its own parts.
2009	Expiration date of fused deposition modeling printing process patents.
2009	MakerBot produces a RepRap evolved kit for a wider audience.
2009	The first 3D printed blood vessel is produced by Organovo.
2011	The first 3D printed car is produced (Urbee by Kor Ecologic).
2012	The first 3D printed jaw is produced in Holland by LayerWise.
2013	Cody Wilson of Defense Distributed is asked to remove designs for the world's first 3D printed gun and the domain is seized.

In addition to extra strength, fibers have also been used in 4D printing to control and manipulate the change of shape or swelling after 3D printing, right out of the printing bed (33). Although additive manufacturing of fiber-polymer composites is increasingly being developed and is under intense scrutiny, there are some issues that need to be addressed, including void formation, poor adhesion of fibers and matrix, blockage due to filler inclusion, increased curing time, modeling, and simulation.

1.1.1 Recently Developed Materials for 3D Printing

According to International Data Corporation (IDC), the global amount spent on 3D printing technologies is expected to reach nearly $12 billion in 2018 (34). As 3D printers become more popular in the enterprise, there is an increased need for materials that can be used throughout the entire product development cycle.

The use of improved-performance thermoplastics in 3D printing has potential in almost all manufacturing environments. It has major uses especially in electronics, automotive and aerospace industries.

High-end 3D printing of polymers is seeing an important convergence between additive manufacturing and specialty polymers technology. This requires a collaboration between the manufacturers of 3D printing machines and speciality materials suppliers (34).

Several recently developed materials and their manufacturers have been reviewed (34,35).

These materials include poly(ether ether ketone) and PPSU filaments, nanodiamonds, and others (34).

1.1.2 Shrinkage Compensation

To predict the final product shape in 3D printing, finite element analysis (FEA) can be employed, for example, to simulate the structural shrinkage using a linear elastic model (36), or the complete photopolymerization, mass, and heat transfer process through a comprehensive kinetic model (37).

However, the finite element analysis method may be limited by inadequate physical understanding and a trade-off between accuracy and computational complexity (38). In addition, a large number of model parameters can be difficult to acquire accurately in practice and model complexity can reduce its practicality in direct and efficient control of shape accuracy.

Empirical models have also been developed to reduce the shrinkage through optimization of process parameters such as light intensity, exposure time, and layer thickness. Response surface modeling was adopted to optimize shrinkage at different directions (39), or to optimize the building parameters to achieve the trade-off between accuracy, building speed, and surface finish (40).

Designed experiments were used to decrease distortion and increase flatness (41). However, this approach may only control or reduce the average shape shrinkage (38).

Controlling the detailed features along the boundary of the printed product changed the CAD design to compensate for shrinkage, and polynomial regression models are used to analyze the shrinkage in X, Y, and Z directions separately (42,43). However, the prediction of deformation based on the shift of individual points can be independent of the geometry of the product, which may not be consistent with the physical manufacturing process (38).

To summarize, part shape deformation due to material shrinkage has long been studied, e.g., in casting and injection molding processes. Strategies and methods that have been developed to prescale design parts for shrinkage compensation can be classified as follows (38):

1. Machine calibration through building test parts: Similar to the calibration of computer numerically controlled machines, the additive manufacturing machine accuracy in x, y, z directions can be calibrated through building test cases (42–44).

   The dimensional accuracy of the additive manufacturing products is anticipated to be ensured during full production. However, the position of additive manufacturing light exposure may not play the same dominant role as the tool tip position of computer numerically controlled machines. The part geometry and shape, process planning, materials, and processing techniques jointly can have complex effects on the profile accuracy. The calibration of the additive manufacturing machine can therefore mostly be limited to the scope of a family of products, specific types of materials and machines, and process planning methods.

2. Part geometry calibration through extensive trial and error build: Besides machine calibration, another strategy is to apply either a shrinkage compensation factor uniformly to the entire product or different factors to the computer-aided design for each section of a product (45).

   However, it can be time-consuming to establish a library of compensation factors for all part shapes. The library may therefore not be inclusive. In addition, interactions between different shapes or sections may not be considered in this approach. Preliminary research shows that the strategy of applying section-wise compensation may have detrimental effects on the overall shape due to *carryover effects* or interference between adjacent sections.
3. Simulation study based on first principles: Theoretical models for predicting shrinkage could potentially reduce experimental efforts. Models have been developed, e.g., in a powder sintering process (46, 47) and in metal injection molding (48). Although numerical finite element model simulation can be developed to calculate the impact of shrinkage compensation, three-dimensional deformations and distortions in additive manufacturing processes can still be rather complicated. Improving part accuracy based purely on such simulation approaches can be far from effective, and may seldom be used in practice (49).

A data processing system has been presented that may minimize errors caused by material phase change shrinkage during additive layer 3D printing (38).

Information indicative of the shape of a layer of a 3D object that is to be printed may be received. A shape that most closely corresponds to the shape of the layer may be selected from a library of shapes. Each shape in the library may have shrinkage information associated with it that includes, for each of multiple points that define a perimeter of the library shape, a radial distance to the point from an origin of a coordinate system, an angle the radial distance makes with respect to an axis of the coordinate system, and information indicative of an anticipated amount by which the point will deviate from its specified location when the shape is printed due to shrinkage.

The closeness between two shapes may be measured by the L_2 distance between the multiple points on the perimeters of two shapes. Compensation for anticipated shrinkage of the layer when printed may be calculated based on the shrinkage information that is associated with the selected shape from the library. The information indicative of the shape of the layer to be printed may be modified to minimize errors cause by shrinkage of the layer when printed based on the calculated compensation.

After the layer is printed using the selected shape with the modified shape information, error information from a user indicative of one or more size errors in the layer caused by shrinkage may be received. A new shape that is closer to the shape of the layer than the selected shape may be created and added to the library based on the selected shape and the error information from the user.

The shrinkage information in the library with the new shape may include, for each of multiple points that define a perimeter of the new shape, a radial distance to the point from an origin of a coordinate system, an angle the radial distance makes with respect to an axis of the coordinate system, and information indicative of an anticipated amount by which the point will deviate from its specified location when the shape is printed due to shrinkage.

The radial distances of at least one shape in the library may not all have a common origin. For each common origin, however, there may only be a single point at each angle.

The shrinkage information for at least one of the points in at least one of the shapes in the library may include a location-dependent and a location-independent component.

Calculating compensation for anticipated shrinkage may include computing a Taylor series expansion of the shrinkage information that is associated with the selected shape from the library. Calculating compensation for anticipated shrinkage may include calculating compensation for each point in the selected shape. A deviation may be determined between each point that defines a perimeter of the selected shape and a corresponding point on the to-be-printed layer. For each point that defines a perimeter of the selected library shape, the information of the anticipated amount by which the point will deviate from its specified location may be adjusted to include the determined deviation between the point and the corresponding point on the to-be-printed layer.

A non-transitory, tangible, computer-readable storage medium containing a program of instructions may cause a computer system running the program of instructions to implement all or any sub-combination of the functions of the data processing system that are described herein (38).

1.2 Basic Principles

The use of an inkjet-type printhead to deliver a liquid or colloidal binder material to layers of a powdered build material is involved in 3D printing (50). The printing technique involves applying a layer of a powdered build material to a surface typically using a roller. After the build material is applied to the surface, the printhead delivers the liquid binder to predetermined areas of the layer of material.

The binder infiltrates the material and reacts with the powder, causing the layer to solidify in the printed areas by, for example, activating an adhesive in the powder. The binder also penetrates into the underlying layers, producing interlayer bonding. After the first cross-sectional portion is formed, the previous steps are repeated, building successive cross-sectional portions until the final object is formed.

The apparatus for carrying out 3D printing typically move the printheads over the print surface in raster fashion along orthogonal X and Y axes. In addition to the time spent printing, each printhead move requires time for acceleration, deceleration, and returning the printhead to the starting position of the next move (50).

In design-related fields, 3D printing is used for visualization, demonstration and mechanical prototyping. It may also be useful for making patterns for molding processes. In addition, 3D printing is useful in the field of medicine (51).

The 3D printing process can be quicker and less expensive than conventional machining of prototype parts or production of cast or molded parts by conventional hard or soft tooling techniques (51).

1.2.1 4D Printing

With its additional dimension, 4D printing is emerging as a novel technique to enable configuration switching in 3D printed items (52).

Four major approaches, i.e., self-assembly of elements, deformation mismatch, bi-stability, and the shape memory effect, were identified as the generic approaches to achieve 4D printing.

The main features of these approaches were briefly discussed (52). Utilizing these approaches either individually or in a combined manner, the potential of 4D printing to reshape product design has been demonstrated by a few example applications.

1.3 Uses and Applications

1.3.1 Heat Exchangers

An overview of the most common polymer additive manufacturing processes has been presented, including vat photopolymerization, material jetting, sheet lamination, powder bed fusion, and fused filament fabrication (53).

The general strengths and challenges of the common methods were discussed (53). In particular, methods to increase the thermal performance of polymers used with the various manufacturing methods have been highlighted.

Heat exchangers enabled by polymer additive manufacturing were reviewed to assess novel designs in metal, ceramic, and polymer heat exchangers which can be made possible by the unique properties of certain polymers and the advantages offered by additive manufacturing (53).

1.3.2 3D Plastic Model

A method for the automatic fabrication of a 3D plastic model has been described (31).

The solid model is fabricated by exposing a liquid photocurable polymer of 2 *mm* thickness to UV radiation, and subsequently stacking the cross-sectional solidified layers.

1.3.3 Gradient Refractive Index Lenses

Gradient refractive index (GRIN) optical structures are composed of an optical material whose index of refraction, n, varies along a spatial gradient in the axial and/or radial directions of the lens (54). They have many useful applications such as making compact lenses with flat surfaces.

There are several known techniques for fabricating GRIN lenses. One approach is to press films of widely varying refractive indices together into a lens using a mold, e.g., as described before (55). This process, however, is expensive to develop (54).

A second approach for fabricating GRIN lenses is to infuse glass with ions at varying density. This approach has reached commercial production, but it is also expensive and effectively limited to small radially symmetric lenses by the depth to which ions will diffuse into glass.

A third approach for fabricating GRIN lenses is to use 3D printing technology with inks composed of a polymer matrix doped with particles which change the index of refraction of the matrix. Each printed droplet has a distinct refractive index controlled by the concentration of dopants in the polymer material. This approach has been described (56, 57).

The key physical characteristics of matrix materials and dopants have been specified that are sufficient to provide all the important properties suitable for 3D printing of high quality GRIN lenses (54). Also, a variety of specific examples of such ink compounds have been detailed. These inks have the following key physical characteristics:

The matrix material is a monomer that is UV crosslinkable with 20% or less shrinkage to minimize the strain and subsequent deformation of the optical structure. The matrix material has a transmittance of at least 90% (preferably at least 99%) at the wavelengths of interest, and the viscosity of the matrix in its monomer form is less than 20 *cPoise* so that it can be inkjet printed. The matrix material is doped with nanocrystal nanoparticles at a loading of at least 2% by volume. The nanocrystals are selected such that a difference in index of refraction between the doped and undoped matrix material is at least 0.02, i.e., $\Delta n \geq 0.02$.

The nanocrystal sizes are sufficiently small that they do not induce

Mie or Rayleigh scattering at the wavelengths of interest (e.g., less than 50 *nm* in size for visible wavelengths, less than 100 *nm* for IR wavelengths). The nanocrystal material, as well as the doped matrix material, preferably has a transmittance of at least 90% (more preferably, at least 99%) in a predetermined optical wavelength range (e.g., visible spectrum). The nanocrystals are functionalized with silane ligands. In some embodiments, the ligands are less than 1.2 *nm* as measured radially from the nanoparticle core. Some of the ligands attach to the nanoparticle core at their anchor end and have a buoy end. The buoy end is either reactive to the monomer or non-reactive to the monomer. A plurality of ligands can be used with different functionalization based on anchor and buoy ends.

The matrix or host polymer is 1,6-hexanediol diacrylate, and the nanoparticle is an organometallic compound. 1,6-Hexanediol diacrylate is a well-known material for the fabrication of clear coatings. It has a low viscosity of 7.9 *cP* making it amenable towards dispensing using drop-on-demand techniques such as inkjet printing. It also has a large spectral window in which greater than 99% transparency is observed, making it ideal to construct lensing material. 1,6-Hexanediol diacrylate also has an index of refraction of 1.456. By using an organometallic compound having an index of refraction different from that of 1,6-hexanediol diacrylate, using drop-on-demand techniques such as inkjet printing, gradient refractive index lenses may be fabricated having control of the index of refraction in three dimensions.

Ligand functionalization of clear, transparent metallic salts provide matrix compatibility with 1,6-hexanediol diacrylate, allowing high density loading of the organometallic salt into the matrix. Furthermore, due to a difference of index of refraction between undoped 1,6-hexanediol diacrylate and 1,6-hexanediol diacrylate doped with the functionalized metallic salt, GRIN lenses may be formed using drop-on-demand printing techniques such as inkjet printing. The metallic salts interact favorably with a host matrix material such that greater than 90% transparency is obtained in the spectral region spanning 375 *nm* through 1600 *nm* (54).

1.3.4 *Photoformable Composition*

A method for fabricating an integral three-dimensional object from layers of a photoformable composition has been presented (58).

A semi-permeable film can be used, which is impermeable to the photoformable composition but is permeable to a deformable-coating-mixture that is non-wetting and immiscible with the photoformable composition.

The deformable-coating-mixture passes through the membrane by diffusion and forms a thin, slippery surface on the photoformable composition side of the membrane, thereby eliminating any adhesion forces caused by chemical, mechanical or hydrogen bonds.

The following steps comprise the method for fabricating an integral three-dimensional object from successive layers of a photoformable composition (58):

1. Positioning a transparent, semi-permeable film,
2. Contacting an interface with a gaseous oxygen-containing atmosphere,
3. Allowing gaseous atmosphere to permeate through the film and also partially permeate into a photoformable composition layer,
4. Exposing the photoformable layer to radiation imagewise through the film, thus making a photoformed layer and a release coating,
5. Sliding the formed film from the photoformed layer,
6. Positioning the film in order to form a photoformable layer between the previously made photoformed layer and the other surface, and
7. Repeating the previous steps until all the layers of the three-dimensional object are formed.

1.3.5 *Comb Polymers*

Suspensions stabilized by comb polymers may serve as colloid-based inks for fabricating three-dimensional structures.

In such applications, the improved dispersion of nanoparticles that is yielded by comb polymers has proven to be advantageous (59,60).

Such inks enable the production of three-dimensional structures with feature sizes as small as 100 μm (61).

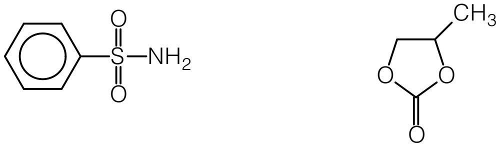
Preferred comb polymers contain two types of side chains and are water soluble. The first type of the side chain has moieties that ionize at the pH of the colloidal suspension. The second type of side chain is nonionizable. Comb polymers from poly(acrylic acid) and poly(ethylene oxide) have nonionizable side chains, in addition to ionizable side chains (62).

1.3.6 Post-Processing Infiltration

Printing processes may include a post-processing infiltration step in order to increase the strength of the printed article using two-component casting resins or adhesives or one-component cyanoacrylate adhesives to achieve greater durability in a three-dimensional article (63).

Furthermore, they may be infiltrated with a liquid plasticizer to obtain strengths comparable to that of articles formed with cyanoacrylate adhesive.

The usage of infiltrant materials for plasticized sintering may provide some advantages over conventional methods. The plasticizer may be ethanol, benzene sulfonamide or propylene carbonate. These compounds are shown in Figure 1.1.



Benzene sulfonamide

Propylene carbonate

Figure 1.1 Plasticizers.

An extremely high solubility of the polymer in plasticizer may be undesirable because it may result in over-plasticization or the dissolution of the thermoplastic additive. In that case, the glass transition temperature may be close or below room temperature, which may cause distortion and weak particle bonding. The plasticizer material may be preferably selected from materials that have low solubility at room temperature but greater solubility at higher temperatures. To reduce the solubility, the plasticizer may be diluted either by a solvent that is removed after sintering or an inert solid material that may remain in the three-dimensional article after cooling.

Using two-component casting resins, such as epoxy-amine, isocyanate-amines, or isocyanate-polyol systems, decreases the ease of use for the end-user by incorporating extra mixing steps, imposing pot-life constraints, and giving rise to safety, health, and environmental issues.

One-component cyanoacrylate adhesives typically offer better ease of use because these materials do not require mixing, but they may create safety, health, and environmental issues such as fumes, irritation, and adhesion to skin, and may not be stable when exposed to the open atmosphere for long periods of time.

The plasticized assisted sintering of a material consisting of a thermoplastic particulate increases ease of use by offering a method in which the process can be automated, whereby the article is immersed in a stable, one-component liquid medium for a predetermined amount of time and allowed to cool to a handling temperature (63).

The steps of a plasticizer-assisted sintering process are (63):

1. A layer is formed of a substantially dry particulate material containing thermoplastic particulate, a plaster, or a water-soluble polymer such as a water-soluble adhesive,
2. An aqueous fluid binder is applied to the layer of the dry particulate material in a predetermined pattern to cause binding in the areas to which the binder is applied,
3. The previous steps are repeated sequentially to form a three-dimensional article,
4. After complete setting of the polymer, the three-dimensional article is removed from the build.
5. Then the three-dimensional article is submerged in the plasticizer solution, and
6. Optionally, the particulate material may be exposed to additional energy in the form of conventional heat, visible or infrared light, microwave, or radio frequency, for additional sintering of particulate material.

1.3.7 Sensors and Biosensors

Applications of 3D printing in analytical and bioanalytical chemistry have been on the rise, with microfluidics being one of the most represented areas of 3D printing in this chemistry branch (64).

Most stages of the analytical workflow comprising sample collection, pretreatment and readout, have been enabled by 3D printed components. Sensor fabrication for detecting explosives and nerve agents, the construction of microfluidic platforms for pharmacokinetic profiling, bacterial separation and genotoxicity screening, the assembly of parts for on-site equipment for nucleic acid-based detection and the manufacturing of an online device for *in-vivo* detection of metabolites are just a few examples of how additive manufacturing technologies have aided the field of (bio)analytical chemistry.

The most relevant trends of 3D printing applications in the abovementioned fields have been reviewed (64).

1.3.7.1 Fluidic Control

The synthesis and assembly of a diverse range of materials, including spray-based synthesis of inorganic nanoparticles and conductive filaments, extrusion-based fabrication of hydrogel fibers and sheets, and the preparation of composite solid films have been reported (65). In the reported studies the properties of these composites were examined and potential applications of these materials were shown. Also, the advantages of material fabrication in 3D printed microfluidic devices were highlighted.

The most representative use of 3D printing technologies in bioanalytical chemistry is based on fluidic control. In 2015, Gowers *et al.* developed a flow microfluidic device for *in-vivo* monitoring of lactate and glucose in people while cycling (66). They printed a microfluidic chip with channels in the range of 520 μm to 1000 μm in height and 520 μm to 550 μm in width, using 3SP technology (photopolymerization). The metabolites were extracted directly from the individuals with a FDA-approved dialysis probe. The dialysate liquid was pumped into the microfluidic chip where two needle electrodes, each functionalized with the specific enzyme for each analyte, were held within a soft structure printed with a multimaterial stereolithography (SLA) printer (64). This method allowed the