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3D Printing Gets a Boost and Opportunities with Polymer Materials

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ABSTRACT: 3D printing has recently gained much attention from media and the scientific community, touted as a replacement for traditional manufacturing and a potential to change the way we develop, produce, market, and distribute all sorts of products. With a short introduction to the general idea and initial development of rapid prototyping, we have a look at the prevalent technologies which are now summarized as 3D printing, each with its specific properties and reliance on the materials adapted to the automated application process. Polymers in various forms, reactive, liquid solutions, or as thermoplastic melts, play a key role in many applications and the further expansion toward manufacturing robust, real end use products.

What exactly is 3D printing, the "new manufacturing process" which draws so much attention in the press and research institutions lately? There is nowadays so much attraction and momentum for these technologies that you often see the question "is it a real revolution or just hype?". If we consider that some of the basic technologies like stereolithography (SL) or selective laser sintering (SLS) have been demonstrated roughly 30 years ago and were commercially available in the late 1980s, we can ask ourselves why they have so long only been known to a few specialists and engineers. They have always been attractive to these select groups and seen gradual growth over the years but rarely the long predicted "exponential rise" of other inventions like the personal computer or mobile telephones.

After following the technology, markets, and publications over several years, it appears that now we are in a period where many decisive actors in industry, media, and research and even finance advisors realize that the traditional area of prototyping is expanding more and more into manufacturing,[1] and this will have a significant impact on many areas of our lives and probably induce a spectacular growth of the 3D printing industry.[2]

For a more detailed consideration of this "3D printing" topic we have to look at a description of the numerous technologies and their features and also what they have in common; we will focus our attention on the methods which have made it to the commercial stage and survived to this day−without pointing to specific brand names, which can be found on the web[3]—and within the scope of this journal see how polymer materials are used as an essential element in all these processes. Besides the basic function of these materials in each printing process, there is a constant effort to develop new formulations to improve properties and functions, as they often appear as the limiting factors when new applications or higher performance are desired.

There has been substantial discussion on the nomenclature which migrated from rapid prototyping (RP), including rapid manufacturing (RM),[4,5] toward additive manufacturing (AM), which is now an accepted standard (ASTM F2792) by the organization.

There are many descriptions of these AM technologies, as, e.g., in the recent textbook of Gibson et al.:[6]

Additive manufacturing is defined by a range of technologies that are capable of translating virtual solid model data into physical models in a quick and easy process. The data is broken down into a series of 2D cross sections of a finite thickness. These cross sections are fed into AM machines so that they can be combined, adding them together in a layer-by-layer sequence to form the physical part.

In a somewhat official and more detailed way, the ASTM F2792-12 standards text[7] summarizes the dominant technologies as follows:

Photopolymerization Process: An additive manufacturing process in which liquid photopolymer in a vat is selectively cured by light-activated polymerization. Stereolithography is an example of this process.

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Material Jetting: An additive manufacturing process in which droplets of build material are selectively deposited. Objet's PolyJet is an example of this process.
Binder Jetting: An additive manufacturing process in which a liquid bonding agent is selectively deposited to join powder materials. The ZPrinter (ProJet x60) line uses this process.
Material Extrusion: An additive manufacturing process in which material is selectively dispensed through a nozzle or orifice. Stratasys' FDM technology is an example of this process.
Powder Bed Fusion: An additive manufacturing process in which thermal energy selectively fuses regions of a powder bed. EOS' direct metal laser sintering is an example of this process. (This also includes Selective Laser Sintering).
Sheet Lamination: An additive manufacturing process in which sheets of material are bonded to form an object. The Mcor Technologies printers use this type of process. (This also includes ultrasonic additive manufacturing, such as Fabrisonic).
Directed Energy Deposition: An additive manufacturing process in which focused thermal energy is used to fuse materials by melting as they are being deposited. The Optomec LENS systems are an example of this process.

This shows that a large number of these additive manufacturing processes have been developed, based on the same fundamental principles; the ones listed here are still being used and commercially available, and we will see that there are so many characteristics and parameters to select that they have their specific application fields and niches so that they can continue to coexist, especially now in a globally expanding 3D printer market.

Depending on the technical execution of the processes, we can divide these production methods into two distinct groups, depending on the step which defines the shape of each cross section.

As a summary we can describe the *first group* as a repetitive process of:

- apply a “fluid” material as a thin layer on a workpiece (or fluid bed) under construction;
- induce a selective phase change (solidification) on the current cross section of the workpiece;
- lower the workpiece (on a platform) into the fluid bed by one layer thickness; then repeat.

The *second group* combines the “imaging” step with the addition of the material of a full cross section:

- dispense a liquid or liquefied material as small droplets or filament onto the preceding cross section of the workpiece
- solidify the new cross section
- optionally equalize the new layer to a defined thickness; then repeat.

In general, the parts are built and attached to a platform and in many cases separated from the latter by a support structure, which is built simultaneously with the part in the same process; the support can be built with the part material or a specific support material. The processes which have a powder bed as the build envelope can use this powder (which is reusable) as a support.

As we mentioned before, the majority of these processes uses or produces polymers in the part formation, as these offer various possibilities of the required phase change and also offer a vast palette of material properties for the supports and finished parts. So let us look at the dominant 3D printing processes and some of the materials employed there, along with process-related requirements.

A fairly large number of methods are established on a commercial level and can exist in parallel, as they are differentiated in many aspects and have each their strengths and limitations which make them useful for different application domains. We will briefly summarize these characteristics and preferred applications for each of the methods described below, shown with simplified process schematics (pictures courtesy of Ed Grenda, Worldwide Guide to Rapid Prototyping Web site, Copyright Castle Island Co., All rights reserved).

For the first group of processes, we have the traditional photopolymer process, stereolithography (ASTM: Photopolymerization Process); the starting material is a liquid mixture of monomer and oligomer components with a viscosity range of ∼100−2000 cP, which is rapidly solidified by a scanned laser beam, as depicted in Figure 1. One essential requirement is a photopolymerization sensitivity which is tuned to the UV wavelength of the laser light of the machine; current printers use the frequency tripled output of Nd-crystal-based lasers at 355 nm. Two other process-related requirements are a specific UV absorption to catch the majority of the laser light within the desired layer thickness (typically around 0.1 mm) and a fast solidification of the resin near ambient temperature. The machines are manufactured in a range of sizes, where the most popular size of the ∼250 mm cube is surpassed by industrial machines up to more than 1 m part size.

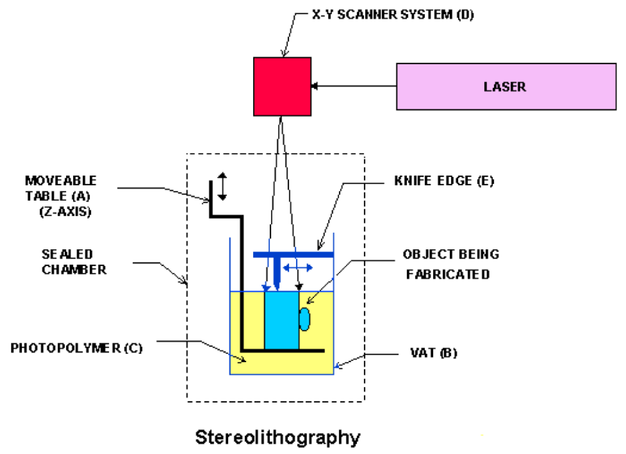

Figure 1. Schematic of the stereolithography process; the part being built is immersed in the liquid photopolymer bath and the top layer cured at the surface.

On the other hand, a very fast reaction, along with the virtually inevitable cure shrinkage and some thermal effects, will induce stress in the parts, which builds up from layer to layer and can lead to significant curl and warping. Most of the current stereolithography materials avoid these effects with a well-balanced cure and solidification rate, further optimized by specifically tuned exposure strategies and parameters, the so-called build styles.

The rapid solidification of a slightly viscous liquid to a stable solid is achieved with a highly cross-linked polymer network. The above conditions were met after years of development and optimization with special blends of acrylate and epoxy resins, combined with the respective photoinitiator for each system.

Stereolithography parts are generally of high accuracy and resolution and can be produced in a large variety of material properties. The tight and variable focusing of the UV laser beam allows us to realize small features and skins. The materials generally have the properties of cross-linked epoxies, which can approach some aspects of engineering thermoplastics, although their structure is fundamentally different and prevents them from melting or dissolution.

Around the same time as stereolithography appeared another process in the first group (ASTM: Powder Bed Fusion) called selective laser sintering (SLS) also appeared. This technique uses a bed of fine powder, which can be sintered to solid layers with brief heating to a high temperature. The localized energy is supplied by a focused IR laser beam, as shown in Figure 2,

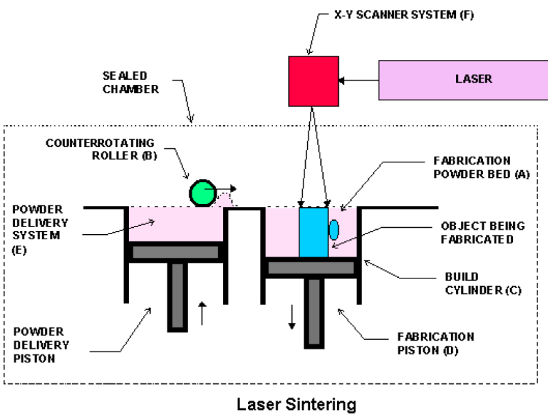

Figure 2. Principal elements of a laser sintering or laser melting machine; powder is spread in thin layers from the supply tank to the build tank, then fused to the part by a powerful IR laser.

which is scanned across the powder surface in the shape of each cross section; this process requires significantly higher laser power than stereolithography, typically some tens of watts, because this is the essential source of energy. The photopolymer processes, on the other hand, use the chemical energy of the monomers, and the UV laser is only the trigger.

Excessive deformation of parts after the large temperature jump due to the laser heating is controlled by bulk heating of the build chamber with the powder bed well above room temperature, and chemical stability of the powder is maintained by inert gas purging.

The majority of the applications of SLS use thermoplastic materials for the powder bed, notably different types of polyamide (PA11, PA12), but the process also works with different metal alloys and even mineral materials (sand) for foundry molds or cores. With an engineering thermoplastic as the base material, these parts have good mechanical properties and thermal resistance and are mostly used for rigorous testing of prototypes, but increasingly also for real end use parts.

These machines are rather complex and require appropriate facilities, which designate them primarily for industrial and production environments; they are also popular in Service bureaus for the supply of custom parts on demand.

The third method in the group of "imaging" on a bulk material uses (ink)jet technology on a powder bed (ASTM: Binder Jetting) to solidify the loose powder with a liquid solution, which dries or reacts to agglomerate the powder particles at the specified locations of each layer. This method was originally coined with the name "3D Printing" by MIT but is now used alongside the other techniques with the same designation.

Here again the palette of materials can be very large, as so many solid materials can be supplied as a powder and then be bonded by an organic or even inorganic "glue", as long as the latter can be supplied in a liquid, jettable consistency. Some embodiments of this techniques have used the well-developed ink jet technology to build medium-sized machines at moderate cost which can print parts at higher speeds than most of the competing devices. In a more advanced generation of machines, multiple print heads are used with colored binders. With the appropriate software, multicolor parts, a unique feature of this technique, can be built in a remarkably complete gamut for very realistic object representations. As this process produces parts from the powder structure and only a minor amount of binder, they have a certain porosity and limited mechanical robustness; for enhanced properties, infiltration of the finished parts with a reactive resin is available, which makes them solid and seals their surface.

Recent developments extend the availability of colors with this process also to polymer materials, which allows us to produce more robust parts without infiltration or other post-processing steps.

If we look at the second group of technologies where we use addition of the material for each full cross section, without a separate imaging step, we have two major processes, which dominate the market by machine numbers: (multi)jet printing of reactive resins or molten wax (ASTM: Material Jetting) and extrusion of molten thermoplastics (ASTM: Material Extrusion).

The processes coined as Multijet Modeling or Polyjet use a print head similar to inkjet printers to deposit exactly shaped layers of a photopolymer resin and normally a support material to partially surround it, which is then immediately cured with an UV lamp. To maintain exact layer thickness and compensate for small variations of droplet size, current machines use a mechanical planarizer, which removes excess material on each pass of the print head (see Figure 3).

These machines can process robust resin objects—generally complex acrylate formulations—with high accuracy and resolution and do not require complex lasers and beam scanners. Some limitations related to materials relate to the (low) viscosity requirements of the jetting process; often the

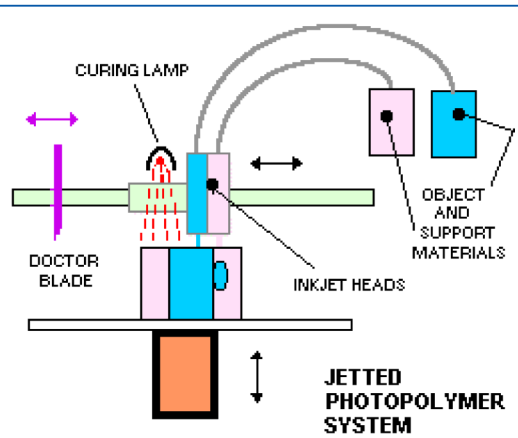

Figure 3. Simplified presentation of a polymer jetting 3D printer with separate support and build material channels; each layer is planarized and cured by UV exposure immediately after its deposition.

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viscosity is reduced by heating the print head and nozzle plate. This heating is also required in machines which are processing wax materials to produce patterns for investment casting, in jewelry and dental restoration applications notably.

A recent development adds machines with multiple print heads or channels, again similar to color inkjet printers, which can deposit selected mixtures of different materials. Besides a palette of colors, this also allows us to assign different material properties, essentially modulus of elasticity, to different regions of a part. It is another step to replace assemblies of several components and fasteners with a single part, which is generally an advantage of additive technologies.

The last technique we look at is based on the original process of fused deposition modeling (FDM) and also relies on a rather simple buildup of an essentially standard thermoplastic material (ASTM: Material Extrusion).

The concept of melting a "standard" plastic material and extruding it through a thin, heated nozzle seems quite straightforward, as shown in the schematic of Figure 4; the extruded melt can then be spread in a controlled *X*−*Y*-movement onto the previous layer of the part being built. Obviously the processing temperature has to be adapted to the melting point of the specific material and well controlled, and thermal shrinkage after deposition can be reduced by heating the build platform or even the complete build chamber.

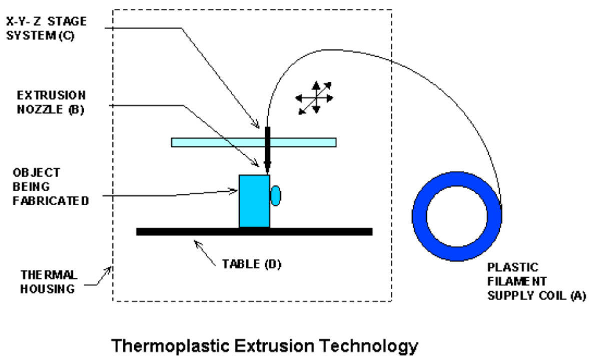

Figure 4. Principle of the popular FDM process, using an *X*−*Y*−*Z*-mobile extrusion head to apply lines of thermoplastics.

Originally developed and implemented as an industrial quality process with larger size machines and a selection of thermoplastic polymers, the scope has now grown into the widest palette of smaller and low cost machines. Some of these machines are even offered as kits to be built or assembled by the user. In recent times this type of machine has become very popular and also has the largest number of manufacturers of quite similar devices, mostly with rather small build volumes of roughly 100−200 mm on each side. While the simple machines just have one extrusion head and filament spool, many of the newer developments have multiple heads and can extrude support and part material for good accuracy and complex shapes or to combine different colors in a single part.

The most popular polymers in this process are ABS and polylactide, which is also offered on almost every entry level printer, but higher-grade machines can also process engineering materials like polycarbonate, polyamide, or even polyphenyl sulfone. As the starting material in this process already is a thermoplastic polymer, the mechanical properties of parts approach those of traditionally molded or machined products, similar to SLS, but using a significantly simpler machine.

The extrusion type machines are a specific example to demonstrate the accelerated progress in the development toward a wide availability of 3D printers at affordable cost, relying on the assembly of readily available core components like precision rails, servo drives, and control electronics modules, including computers and software which can handle the complex geometry data. The latter is also essential for the design of the 3D model data based on CAD programs or object scanners, and not the least is the declining cost of computers to handle all these data and control the machine components.

Another early method which uses paper or other thin films of material, which are stacked up, bonded together, and cut to shape, was called layered object manufacturing (LOM) and has now been revived (ASTM: Sheet Lamination) with the possibility to use standard office paper sheets. Whereas the original version used an IR laser to cut the individual layers, the more recent devices cut the paper with a stencil, and a special option allows one to print onto the sheets with an office printer, which then creates fully colored parts. Whereas paper is a well-known standard build material, the pressure- or heat-sensitive adhesives which hold the sheets together are specially developed to fit the process.

We can see there is a vast choice of 3D printing methods available, many with a variety of materials to choose from, and generally a large range of possible or preferred applications. Technically the possibilities are almost without limits, and on top of the thousands of applications which are being realized today, there is also a lot of speculation about imminent replacement of current production technologies with these new 3D printers. In commercial reality, the majority of users still applies these methods to produce prototypes of all kinds, unique parts and new designs, including architectural models and display objects. On the other hand, there are some areas where 3D printing is quite competitive with the cost and speed required for a specific set of products, and the available materials meet specifications. Today these applications are mostly in the medical field for personalized prostheses, in the aeronautical business for low volume production of special parts, or complex shaped tools and fixtures for traditional manufacturing. The benefits are particularly high for complex parts which can often replace an assembled device with a single printed part. The user community is constantly expanding the limits toward manufacturing by 3D printing, and with progress on the machine side, improved reliability, increased build speed, and intuitive user interfaces, the range of these applications keeps growing steadily. Besides that effort, there is a lot of development in materials to expand the scope of manufacturing, notably by the machine manufacturers, by independent materials supply companies, and at research institutions.[8] Processing conditions with the required phase change are a substantial challenge for the development of radically new materials; therefore progress is currently rather incremental, while new chemistries or some sort of fiber reinforcement may come along. Other developments tend toward multicolored parts, either by "assembling" sections of several defined colors or by jetting the basic colors for a full palette. By extending this principle, different materials can be blended from a set of print heads to achieve different material properties within one single part; eventually this principle can be extended to produce graded material properties, e.g., from soft to rigid within the part.

This quest for better materials[9] is also true in the realm of low cost printers, which are affordable for individuals and

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schools at higher levels; hobby designers, artists, and researchers can turn their ideas and creations into solid plastic parts. There is notable interest in creating toys, accessories for personal electronics, or sometimes even replacements for broken parts.

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Notes

The authors declare no competing financial interest.

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