

Three dimensional (3D) printing

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The following article introduces technologies that build 3 dimensional (3D) objects by adding layer-upon-layer of material, called also additive manufacturing technologies. Furthermore most important features supporting the conscious choice of 3D printing methods for applications in micro and nanomanufacturing were covered. The micromanufacturing method covers photopolymerisation based methods such as Stereolithography (SLA), Digital Light Processing (DLP), Liquid Crystal Display – DLP coupled method, Two-Photon Polymerisation (TPP) and Inkjet based methods. Functional photocurable materials, with magnetic, conductive or specific optical applications in the 3D printing processes were also reviewed.

1. Introduction

Three dimensional (3D) printing is currently an extremely important branch of Research and Development (R&D) departments. This is because of its rapid prototyping, swift elimination of design errors, and improvements of the product at the prototyping stage. This approach significantly accelerates the implementation of new solutions without incurring significant production costs and eliminating in-production testing of underdeveloped models. Thanks to 3D printing techniques, making a prototype with complex geometry has become possible in a short time with unprecedented precision ^[1].

Progressive computerization of manufacturing processes introduces us to a new era called Industry 4.0. This level of smart production was enabled by significant breakthroughs in artificial intelligence, robotics, nanotechnology, and 3D printing observed in the twenty-first century. Thanks to the extreme customization and personalization of production technologies, the practice of Industry 4.0 is an observed phenomenon in every section of manufacturing processes. The application of artificial intelligence (AI) algorithms for the preparation and transformation of 3D models significantly quickens and improves the quality of 3D figures. All has been successfully applied in printability checking, slicing acceleration, nozzle path planning, and, among others, cloud service platforms ^[2]. Evolution of industry models are presented in Figure 1.

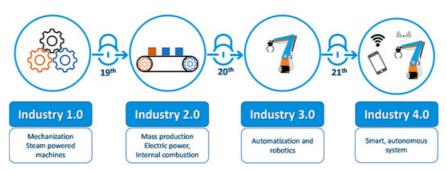


Figure 1. Industrial revolution—from Industry 1.0 to Industry 4.0. The concept of Industry 4.0 is based on encompassing a combination of traditional manufacturing and industrial platforms and practices with the latest smart technologies.

The industry has just begun to adopt additive manufacturing methods, which they use mainly to prototype and produce individual items. With Industry 4.0, 3D printing methods will be widely used to produce small batches of made-to-order products that offer construction advantages, such as complex, lightweight designs ^[3].



The flexibility of 3D printing opens the way for sharing production capacities between diverse companies for better utilization of assets and supporting growth and will also open up opportunities to share production capacities between different companies, thereby better utilizing these assets ^[4]. Research projects such as Horizon 2020 are focused on creating such business models in industry.

Manufacturers have implemented 3D printing technologies through seven different additive manufacturing processes: powder bed fusion, vat photopolymerization, binder jetting, material extrusion, directed energy deposition, material jetting, and sheet lamination. Each method is achieved through a different variation of 3D printing technology, which varies based on its material state, sources of light or heat, print axes, feed systems, and post-production processing ^[5].

- Powder bed fusion: It works by melting powder to fuse particles together. It is ideal for most types of manufacturing [6].
- Vat photopolymerization: It uses a liquid instead of a powder or filament in its build platform and is a light-activated process. It is ideal for low-run injection molds [7][8].
- Directed energy deposition: It uses highly focused thermal energy delivered via a laser, electron beam, or plasma art to melt and fuse material. It is used exclusively in metal additive manufacturing ^{[9][10]}.
- Material jetting: Tiny nozzles dispense droplets of a waxy photopolymer, layer by layer, which is hardened via UV light. It is ideal for items requiring high detail and high accuracy [11][12].
- Binder jetting: It is similar to material jetting but instead uses a powdered material and a binding agent. It is primarily used in furniture design models ^{[13][14]}.
- Material extrusion: A thermoplastic filament is extruded through a heated nozzle onto the build platform, which solidifies as it cools. It is the most commonly referred to additive manufacturing method when someone is discussing 3D printing [15][16].
- Sheet lamination: Ultra-thin layers of solid material are bonded by alternating layers of adhesive. It is best used for non-functional models ^[17].

The history of 3D printing in its extremely turbulent beginnings revealed many ideas and solutions that have been verified by the market over time ^[18]. Among the ideas that have been developed for commercialized technologies based on the polymerization of liquid resin are thermal processing of thermoplastic materials, melting/sintering of metals, and methods creating prints from composite materials or rubber. The list of methods that should be highlighted in the topic of 3D printing is presented below ^[19]:

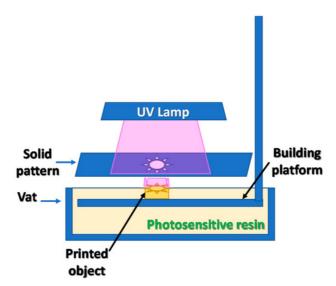
- Photopolymerization of liquid resin:
 - SLA-stereolithography
 - DLP-digital light processing
 - MJP-multijet printing
 - BJ—binder jetting
 - CAL-computed axial lithography
 - SGC—solid ground curing
 - CLIP—continuous liquid interface production
- Thermal processing of thermoplastic polymers:
 - FDM—fused deposition modeling
 - BPM-ballistic particle manufacturing
 - LS-selective laser sintering
- Metal structure fabrication:
 - DED-directed energy deposition
 - DMLS/SLM-direct metal laser sintering
 - EBM—electron-beam additive manufacturing
 - MBJ-metal binder jetting
- Other methods:



- LAM—liquid additive manufacturing deposits a liquid or highly viscous material (e.g., liquid silicone rubber) onto a build surface to create an object, which is then vulcanized using heat to harden it
- LOM—laminated object manufacturing patented by Michael Feygin—printers that cut cross-sections out of special adhesive coated paper using a carbon dioxide laser and then laminate them together
- CFF-continuous filament fabrication

2. Photopolymerization-Based 3D Printing Methods

In the very beginning of 3D printing, photopolymers were applied for manufacturing designed structures^[20]. To produce a three-dimensional element, flat templates with a shape corresponding to the element's cross-section were used, through which the photosetting resin was illuminated ^[21]. The depth of the element was obtained in the same way as in today's printers—by maneuvering the printer table up and down. The template-based solution found little widespread interest due to the limited possibilities of the formation of shapes, and the length of the process. A scheme of the machine used in this approach is presented in Figure 2. It became necessary to find a solution to obtain objects with a more complex geometry ^{[22][23]}.





3. Resolving power in the 3D printing processes

The use of a laser wavelength corresponding directly to the absorption of the photoinitiator limits the maximum print resolution according to the Abbe diffraction limit. The minimum resolvable distance d can be calculated from the Abbe diffraction limit ^[24]:

$$d = \frac{\lambda}{2 \cdot NA}$$

 $\label{eq:Where:} Where: $$NA$ - the numerical aperture of a laser optical system $$\lambda$ - wavelength of the laser $$$

In the case of photopolymerisation, where a high intensity of light is required to start the process, this condition can be overcome because polymerisation starts effectively only in the centre of the laser beam, where light intensity is highest [25].

4. Two-photon polymerisation (TPP) as a high-resolution 3D printing process

In order to bypass the restrictions in resolving power resulting from the use of light with a wavelength of near UV and



the lower range of visible light, it was proposed to use the two-photon absorption effect ^[26]. In the process of onephoton absorption, the absorbance of material is linearly dependent on the intensity of lighting, while in the case of two-photon absorption, the dependence of absorption on the square of the intensity is observed. Due to this effect, in the focus of the laser beam, only a small central area is characterised by an intensity capable of initiating two-photon polymerisation. The area with decent light intensity is therefore much smaller than when using one-photon absorption, which allows a significant improvement in resolution.

Due to the fact that the two-photon process is mediated by passing through a virtual electron state, which means that there is no energy state in the molecule corresponding to the absorption of a single photon, absorption of two photons must occur simultaneously. This means that the efficiency of the two-photon absorption process is very low. The phenomena of two-photon absorption can occur only when the sum of the energy of absorbed photons coincides with the energy difference between energetic levels of the absorbing medium. Therefore, the two-photon absorption process requires a very high intensity of lighting, and certain wavelengths with energy equal to half the energy of a single photon absorption band are favoured ^[26]. The basic TPP scheme is shown in figure 3.

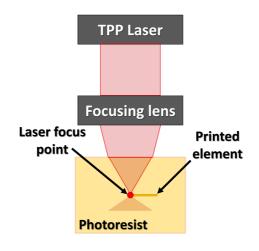


Figure 3. The two-photon polymerisation for direct writing in photoresist scheme

Using traditional broad-spectrum light sources, providing such high energy concentrated in a small area resulted in thermal destruction of the sample, which is why pulse lasers were used for TPP processes. The use of lasers with a nano or even femtosecond pulse provides the sample with an effective dose of radiation, capable of initiating the TP polymerisation process, with a small amount of total energy transferred to the sample. This allows the photopolymerisation process to take place without overheating of the sample ^[27]. The introduction of two-photon polymerisation into the 3D printing process makes it possible to obtain 3D objects with a size equivalent of almost 1/100 of the wavelength of the light used. However, small changes in the regularity of photosensitive material and fluctuations in the intensity of the laser beam make it difficult to obtain such small objects. The development of special two-photon polymerisation initiators allows obtaining an 80 nm resolution using an 808 nm infrared laser. A reduction in the laser wavelength to 532 nm with a combination of the special initiating system, contributes to a further increase in resolution to about 60 nm ^[23].

5. Conclusions

Additive manufacturing methods are widely used in all industries requiring rapid prototyping. Thanks to the implementation of 3D scanning and computer-aided design methods, translation of the computer project into a real 3D printed model is now easier than ever before ^[28]. Prototype or 3D printed product development is now possible on a scale from several nanometers up to multimeter 3D prints. Depending on chosen method, fabricated objects will differ in shape accuracy and general resolution starting from methods with low resolution methods like FDM with up to 100 µm resolution, to SLA and DLP method with accuracy up to of several micrometers, and to nanoscale 3D printing with TPP techniques. On the other hand with rising accuracy, printing speed slows down to level of days needed for fabrication of tiny element with nanoscopic resolution. Thanks to recent development in two photon polymerization, printing speed can be radically shortened by fabrication of multiple objects simultaneously, but for now, this approach demand more expensive and more powerful light sources, and advanced optics.



The methods of 3D printing allow models to be made from materials as diverse as flexible rubber-like materials to specific materials with conductive, magnetic or specialized optical properties, and the range of available materials rises annually. During the development of additive methods, materials with possible biological applications and hydrogel materials were also obtained. The major advantages and disadvantages of each described method are presented in <u>Table 1</u>. The choice of method used to make the appropriate model brings the consequences of an indirect selection of material resources, printing accuracy, maximum resolution, and the need for printing support structures, as well as printing time and the physical properties of the finished model.

Table 1.	Comparison	of described	methods.
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Family	Method (Light Source)	Advantages	Disadvantages
Stereolithography	Direct SLA (laser 365 to 405 nm) [<u>26]</u>	Oldest and well-developed method with multiple materials available. Fair resolution.	Low printing rate, resolution limited by the size of the laser beam and further with Abby diffraction limit
	SLA–TPP (laser 532– 1064 nm) [28][29]	Great resolution. The rising availability of materials.	Slow process—even the smallest models created in days.
	SLA-TPP with a dichromic layer (laser 532-1064 nm) [30]	Outstanding resolution of prints (a few nm).	Slow process—even the smallest models created in days. The necessity for the application of an additional photochromic layer on top of the photoresist.
	SLA–STED (laser 532– 1064 nm) [<u>26][31]</u>	Outstanding resolution of prints (few nm).	Slow process—even the smallest models created in days. Tailoring of initiating– inhibiting systems needed for all materials.
	SLA-TPP- DMD (laser 532-1064 nm) [<u>32]</u>	Great resolution. Possible fabrication of multiple objects at the same time.	Underdeveloped method.
	SLA–TPP– Liquid crystal devices (laser 532–1064 nm) [33]	Outstanding resolution. Possible fabrication of multiple objects at the same time. Faster than SLA-TPP-DMD	Underdeveloped method.
Fused deposition modeling	FDM (-) ^[34]	Great availability of filaments, moderate mechanical properties of printouts.	Low-resolution method. Can cause deformation of printouts during the process.
Digital Light Processing	DLP-DMD projector (HID lamp/LED lamp) ^[35]	High resolution for small models. High precision for small models.	Bigger models decrease resolution.
	LCD-DLP (405-450 nm LED lamp) ^[20]	High resolution. Resolution independent on model size	Low light intensity reaching resin vat, only highly reactive resins can be used.
Inkjet	Binder Jetting (HID Iamp/LED Iamp) ^[36] [<u>37][38]</u>	Numerous materials available, relatively quick printing process.	Low resolution. Poor mechanical properties of green printouts.
	Inkjet(HID lamp/LED lamp) ^[36]	High resolution, multiple materials available. Smooth surface finish.	The high cost of printer and materials. Only low viscous materials can be printed.
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Family	Method (Light Source)	Advantages	Disadvantages
	Multijet (HID lamp/LED lamp) ^[23]	High resolution, multiple materials available. Possibility of printing with multiple materials at the same time. Possible creation of colorful printouts. Smooth surface finish.	The high cost of printer and materials. Only low viscous materials can be printed.

Fair resolution—hundreds of micrometers to tens of micrometers. High resolution—tens of micrometers to micrometers. Great resolution—single micrometers to hundreds of nanometers. Outstanding resolution—tens of nanometers to several nanometers.

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Keywords

3D printing; High-resolution; Additive manufacturing; Photopolymerization; Industry 4.0; Stereolithography; Two-photon polymerisation



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