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CHARACTERIZATION OF BICOMPONENT 3D PRINTING TECHNOLOGIES OF BIODEGRADABLE MATERIALS

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Abstract: Reducing the effect of human activities on the environment, natural resources and public health has become one of the essential concerns of researchers around the world. Biodegradable materials are suitable alternatives to petrochemical-derived materials and have essential roles in environmental protection due to reduced use of fossil-based raw materials and decreased carbon dioxide emissions. Therefore, there is a growing interest in biodegradable materials, which degrade faster than conventional materials. The current study aims to analyze the use of biodegradable polymer materials in Additive Manufacturing, through bi-component 3D printing. In Additive Manufacturing-AM, parts are manufactured layer by layer with minimal allocation for finishing operations. Because AM enables greater material savings than traditional processes, 3D printing can be considered a distributed manufacturing technology to improve sustainability and the circular economy worldwide.
Key words: bi-component 3D printing, biodegradable matherials, additive fabrication.

1. INTRODUCTION

In recent years, interest in protecting the environment not only by using products made from renewable natural resources, but also products that break down into ecological constituents has grown steadily and rapidly. Green movements, initiatives and regulations have emerged in almost every developed country to reduce the volume of solid polymer waste generated by consumers each year. Consumers have also expressed a desire for products that are eco-friendly while providing the same results as products made from synthetic material. However, consumer preferences for organic products may be hindered by the higher cost and inferior properties of these products compared to synthetically derived products, [1].
Additive Manufacturing (AM), from its early days of single-material rapid prototyping, is currently undergoing a huge transition into multi-material printing with unprecedented design opportunities. Together with different printing technologies, digital computer-aided manufacturing (CAD) for physical 3D objects is achievable in a short period of time. Multi-Material Additive Manufacturing has created a new possibility, which enables one-step production of 3D printed composite materials. Unlike traditional manufacturing processes, which could only produce simple geometry, 3D printing has greatly expanded its capacity for design complexity. Multimaterial AM includes several metals, ceramics, and polymers. It also involves cross-materials such as metal and ceramic. However, multi-material printing is still in its infancy compared to single-material printing technology, [2].
The need for multi-materials in structural applications: In recent advances for specific application-oriented functional needs, there is an increasing need for excellent tooling techniques and manufacturing techniques used for specific purposes. To make a particular application, tooling and testing require more time and multiple tools that cannot be activated for different processes while it was selected new advanced machining techniques. Thus, the new 3D printing technique has given us a wide range of material selection or processing techniques that can be solved. In addition, very specific applications such as spacecraft, aerospace, automotive structures, biomechanics, electronic components need a wide range of materials to be processed or incorporated into a single material, which eliminates the number of components to be manufactured. Especially in biomechanical applications, various tissues, muscles, blood vessels, bones are incorporated into a single substitute for various operations and muscle tears required by the surgeon, and in electronic components, various chips and motherboards require separate fabrication or placement different sensors to be placed this multi-material

printing reaches us a new way to print single embedded plates and robotic structures are enabled.
The bioplastic term is often used loosely and synonymously with biodegradable. While some bioplastics are indeed biodegradable, some are not. Bioplastics should be designed as polymers that meet either of two criteria: the polymer is bio-based; the polymer is biodegradable. Biomass means that the polymer is obtained either wholly or partly from biomass, i.e. from any type of renewable organic material of biological origin, as well as from organic waste. Biodegradable means that the material can break down into natural substances such as carbon dioxide, water and biomass due to the action of microorganisms. In a more specific sense, a biodegradable plastic is a plastic material that meets certain official standards of biodegradability, where a certain amount of degradation must be scientifically observed within a certain time frame and under specific conditions, [3].
Bioplastics form three broad groups of polymers: those that are both bio-based and biodegradable, those that are only bio-based, and those that are only biodegradable. Some prime examples of bioplastics that are both bio-based and biodegradable are polylactic acid (PLA), polyhydroxyalkanoates (PHAs) and bio-polybutylene succinate (bio-PBS), as well as starch-based plastics, cellulose, lignin and chitosan.
Examples of bioplastics that are bio-based but not biodegradable are bio-polypropylene (bio-PP), bio-polyethylene (bio-PE), bio-polyethylene terephthalate (bio-PET), etc. Finally, examples of biodegradable bioplastics that rely on fossil resources are polybutylene succinate (PBS), polycaprolactone (PCL), polyvinyl alcohol (PVA) and polybutylene adipate terephthalate (PBAT). In addition, polymers such as bio-PE, which are bio-based and chemically identical to their fossil-based counterparts, are commonly referred to as drop-in polymers, [3].
A wide range of materials such as metals, polymers, ceramics and concrete are used in the additive manufacturing process. Polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS) are the main polymers used in 3D printing of composites. Advanced metals and alloys are commonly used in the aerospace sector because traditional processes are longer, more difficult and more expensive. Ceramics are mainly used in 3D printed scaffolds and concrete is the main material used in additive manufacturing of buildings. However, the inferior mechanical properties and anisotropic behavior of 3D printed parts still limit the potential of large-scale printing, [4].
Apart from PLA, other biodegradable plastics used for FDM filaments are polyhydroxyalkanoates (PHA), polyvinyl alcohol (PVA), polyethylene terephthalate (PET) and high impact polystyrene (HIPS).

2. CURRENT MULTI-MATERIAL ADDITIVE MANUFACTURING PROCESSES

2.1 Advantages and disadvantages

Additive Manufacturing of Multi-Material (MMAM) technology is becoming increasingly popular in the industrial and research communities. Layer by layer, material is added to build the desired structure to form a solid 3D model. Raw materials used to produce parts include metals, thermoplastics, hydrogels, ceramics, composites, hybrids, and functionally graded materials in liquid, powder, and solid forms. MMAM has several advantages over traditional manufacturing processes, including minimal material waste, easy manufacturing, low-cost processes, and its ability to easily manufacture complex shapes, in addition to being affordable and environmentally friendly. Each MMAM technology has its own advantages and disadvantages, including low dimensional accuracy, limitation of component sizes, limited range of materials, required post-processing, inefficiency for large volumes, and requirements for specific environments. MMAM technology is relevant in various applications for industrial sectors such as aerospace, automotive, healthcare, construction and food processing, as well as in research and academic institutions. Broadly speaking, MMAM technology is divided into seven categories: Material Extrusion, Vat Light Curing, Powder Bed Fusion, Material Jetting, Direct Energy Deposition, Sheet Lamination, Binder Jetting and Hybrid Additive Manufacturing, [5].

Material Extrusion

Material Extrusion is one of the most well-known additive manufacturing processes that uses various materials such as thermoplastics, composites, metal-filled thermoplastic filaments, and flexible elastomers to make components in a layer-by-layer fashion, [5]. The basic principle of material extrusion technologies is that any material that is in paste or semi-liquid form can be extruded through a nozzle and used to build a 3D model layer by layer.
Depending on the temperature required or suitable for extrusion, it can be classified into two main subgroups: Filament Extrusion Fabrication (FFF) or Thermoplastic Extrusion Molding (FDM) for extrusion of molten thermoplastic polymers and Direct Ink Writing (DIW) for extrusion without melting. Material extrusion technology can easily be extended to multi-material 3D printing by using multiple nozzles, [6].

Fused Filament Fabrication (FFF)

Filament Extrusion Fabrication (FFF) technology uses thermoplastic polymer filaments that are melted and extruded through a nozzle onto the desired substrate, layer by layer. Figure 1 provides a schematic representation of the Filament Extrusion Fabrication (FFF) process. The filament material is melted inside the extrusion head and deposited onto a build plate using a pearl-by-pearl and layer-by-layer technique. The main advantage of this process is the availability of a large selection of materials and the easily customizable process to produce tailored multi-material structures. The development and advancement of modern technologies make it possible to manufacture parts from several materials in a single manufacturing process, [5].

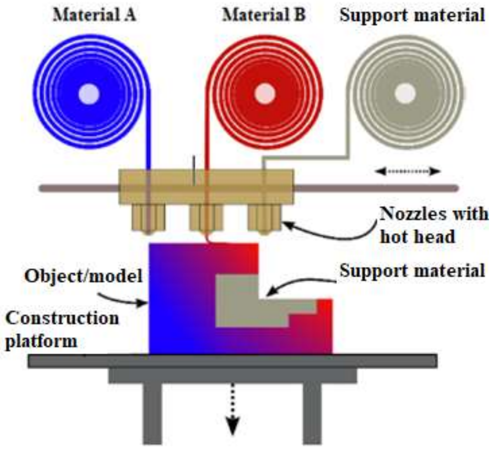


Fig. 1. Description of the Fused Filament Fabrication-FFF process, [5]

Dual or multi-extruder printheads are often used in material extrusion systems to print parts with multiple materials simultaneously. However, dual and multi-extruder printers usually come with a few limitations: the presence of the additional extruder (second or more) will reduce the print area that would be available for printing with a single extruder; the chances of leakage and stringing become greater; and eventually layer-shifting defects may be observed if one of the extruders causes the material deposited by the other to deform, [6].

Direct-Ink-Writing (DIW)

Direct Ink Writing (DIW) technology is one of the simplest and most accessible processes among MMAM methods. This process allows the use of a wide range of materials to fabricate multi-material structures with low manufacturing and material costs. Although the process operation is similar to FFF, DIW uses a heating source to produce parts. The materials used in this process are introduced in liquid rather than solid form. The material is mixed using a rotating impeller and passes through the nozzle when pressure is applied. Figure 2 shows a schematic description of the DIW process.

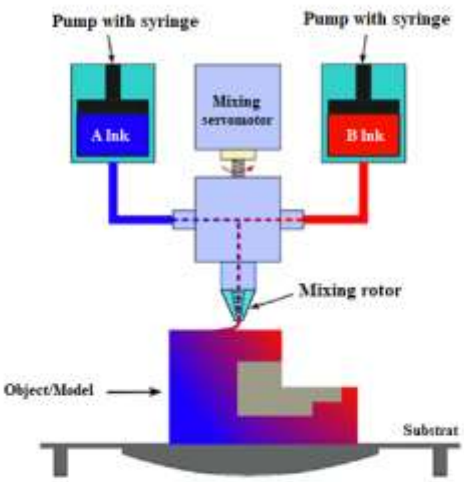


Fig. 2. Description of the DIW process, [5]

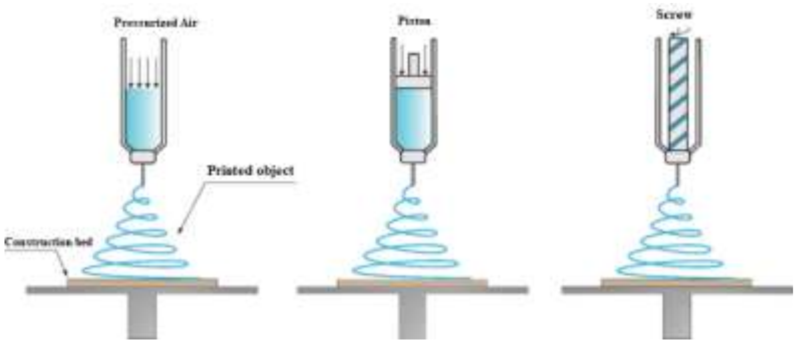


Fig. 3. DIW printers use pressurized air, a piston, or a screw to extrude materials, [6]

The material filament is deposited using dispensers (usually pneumatic dispensers) that are mounted on a motion-controlled positioning stage or a dispensing robot (Figure 3), [6].
Printing materials such as epoxy resins, however, require certain viscoelastic and rheological characteristics to be smoothly extruded from the print head. Most ink solutions made using such materials exhibit shear-thinning rheological behavior, characterized by a decrease in viscosity with increasing shear rate, [6].
The benefit of this process is the availability of a large selection of materials, including materials with biological, structural and electrical properties. The disadvantage of the DIW technique is the use of a sequential manufacturing process for each material, which slows down the entire manufacturing time. To overcome this challenge, a single-nozzle DIW system was recently developed. Enables fabrication of multi-material structures using a single nozzle extrusion head based on adjustable material deposition ratio. Moreover, the material mixing process can be improved by adding the mixer in the extrusion head, which can increase the homogeneity and uniformity of the material mixtures. This allows the operator to quickly change the mixing ratio of the material during the deposition process. The mixing ratio of the materials can also be varied, which allows the deposition of Functionally Graded Materials (FGMs) with tailored thermo-mechanical properties, [5].
VAT photopolymerization
A vat of liquid photopolymer (resin) is used by photopolymerization in the vat, and the pattern is printed layer by layer using some types of light sources. Stereolithography (SLA), Digital Light Exposure (DLP) and Continuous Digital Light Exposure (CDLP) are the three main vat light curing techniques. The vat photopolymerization process is generally not a candidate for multi-material 3D printing. It builds parts of a vat of photopolymers, and therefore the use of multiple materials in the vat photopolymerization presents difficulties in controlling contamination between each vat, [6]. However, automation of this technique has recently been proposed to facilitate the fabrication of parts using multiple materials. In this process, the change between materials was automated using a rotating carousel system. Several vats filled with liquid resin were mounted on a rotating platform. At the time of material change, the required tray is rotated to the manufacturing platform, where the laser power is used for further processing. The advantages of this process include the high dimensional accuracy of the final component and the manufacture of transparent material. Major disadvantages of this process include the need for additional time to change between materials, limitation to photopolymers only, contamination of the material, and possible waste in the process, [5].
Stereolithography (SLA)
The stereolithography (SLA) VAT process uses photopolymer resin to fabricate materials with high resolution and better surface quality compared to other AM processes. Photopolymerization is the curing process that occurs when UV light is exposed to the deposited material and cross-links develop between the polymer chains, causing the deposited material to transition from a liquid or semi-solid state to a solid state. Figure 4 shows a schematic description of the VAT photopolymerization process. Manufacturing multi-material parts using this method requires a material exchange from one liquid resin to another within the vat. This process increases manufacturing time and is extremely labor intensive, [5].

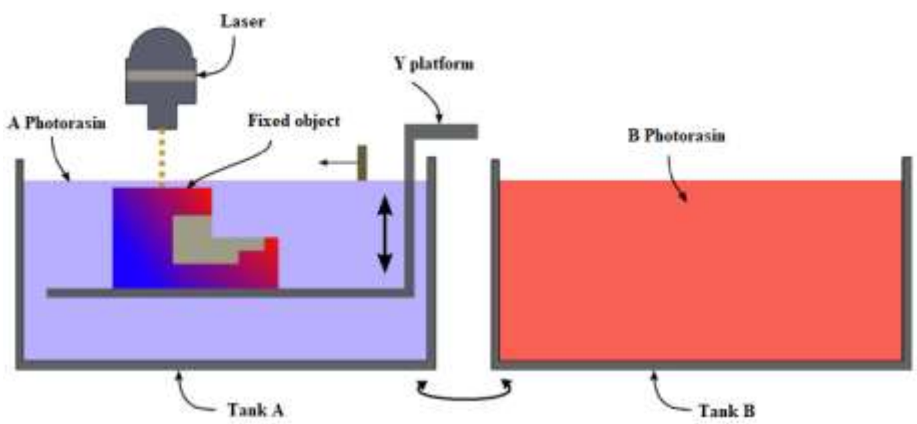


Fig. 4. Description of the VAT photopolymerization process, [5]

Powder Bed Fusion (PBF)
Powder Bed Fusion (PBF) is an AM technology where a heat source (eg laser, heated print head) is used to solidify a material powder to form 3D parts. The heat source is applied to the powder particles which gradually index as each layer is finished and new powder is spread over the build area. One of the advantages of multi-

material 3D printing compared to standard single-material printing is the possibility of less powder cohesion, which usually leads to inaccurate part dimensions and poor surface finish. Therefore, a process in which a "built" powder (eg, a polymer) is co-deposited with a non-fusible "support" powder (eg, a different polymer or ceramic) would completely avoid this problem. With multi-material powder deposition, expensive polymer powders could be placed only where needed, and inexpensive, fully reusable ceramic powder would form the surrounds to provide mechanical support during the build process. It is clear that such a process could significantly reduce powder waste, [6].

One of the major disadvantages of current powder bed fusion methods is that they are inherently monomaterial. The current objective of AM is to simplify and streamline manufacturing, enabling the production of functional, geometrically complex parts that can effectively replace entire assemblies made of many simple components. Such assemblies are often made of a variety of materials. Therefore, a future direction for metal AM should be to produce parts from multiple materials. Currently, the patented spatially selective multi-powder deposition system of Aerosint SA (Belgium) appears to be the only available multi-material 3D printing system based on powder layer fusion technology adaptable to metal, ceramic and polymer powders (see Figure 5), [6].

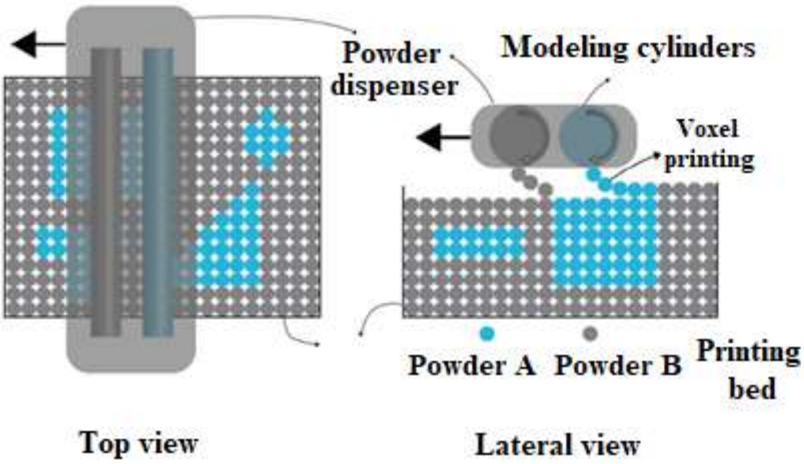


Fig.5. A selective powder coating technology belonging to Aerosint SA, [6]

Material Jet (MJ)

Material jetting is one of the most efficient and accurate AM methods. The working principle of MJ is the same as conventional printing machines. The microdroplets are deposited layer by layer on the build platform. Fabrication of multiple materials in a single structure is well established in the MJ process. In this process, several photopolymer materials are processed using a jet head. Each of these heads has many tiny nozzles, which allow printing multiple materials simultaneously with high resolution. The MJ process allows the production of high-resolution materials, which is one of the main limitations of other AM processes. Figure 6 shows a schematic description of this method.

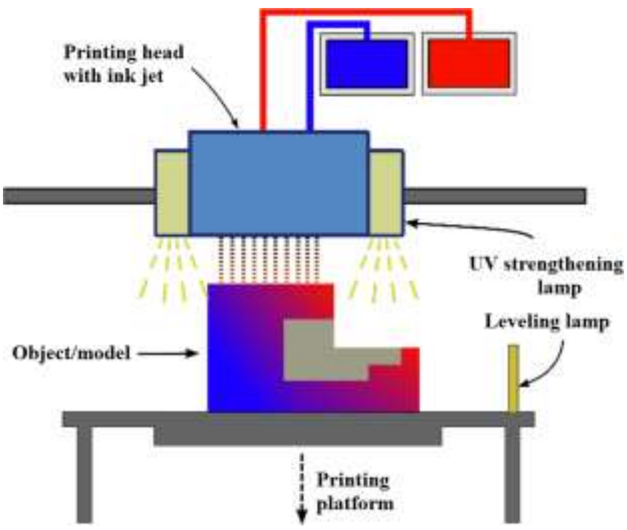


Fig. 6. Description of the MJ process, [5]

PolyJet (Stratasys Ltd., USA) is probably the most common multi-material jetting process commercially available. In this system, nozzles can switch between different materials, including backing material. The scheme of the material jet is presented in Figure 7 with the print tray and the corresponding movement of the print head, [6].
Advantages of this technology include easy fabrication of complex geometries, faster multi-material printing time, high dimensional accuracy, parts can be built in a variety of materials with multiple inkjet nozzles, multiple materials can be fabricated with higher resolution, parts have homogeneous mechanical and thermal properties, reduced material waste due to precise casting, etc. Disadvantages of this method refer to the high cost of this process, limited selection of materials, higher material cost, poor mechanical properties of the materials, UV-activated photopolymers lose their mechanical properties over time and can become brittle, most parts still require support materials, mainly used for non-functional prototypes etc., [5].

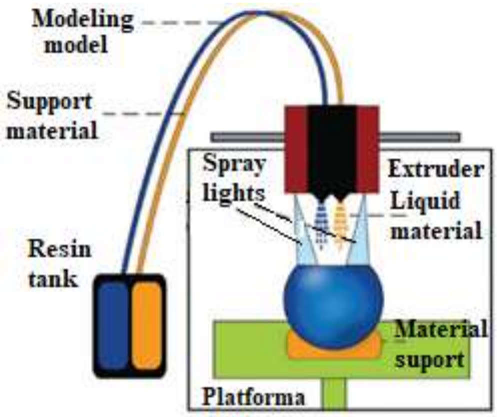


Fig.7. Schematic of the material jet process, [6]

Direct Energy Deposit (DED)
Lately, metal-based AM methods have evolved to produce direct fabrication of heterogeneous components with full spatial material distributions. DED is one of the MMAM methods that fall into different processing categories such as laser metal deposition (LMD), laser engineered network patterning (LENS) and direct metal deposition (DMD). In this process, the material is used in the form of wire or powder. Materials are melted using laser, electron beam or plasma arc energy sources in the controlled region. In this process, inert gas is used to prevent oxidation of the molten pool. In the DED process, the powder material is blown through deposition nozzles where it is melted and deposited layer by layer onto the substrate, which then solidifies. The nozzle has a multi-axis arm and moves around the object. This procedure includes the use of a variety of materials such as metal wire and powder, ceramics, functionally graded materials (FGM), metal matrix composites (MMC) and coatings. In this technique, powders are deposited at a specific time of construction by dynamically changing types. Figure 8 shows the schematic description of the DED process with multi-material capability. The advantage of this process is the ability to change the powders at any time during the manufacturing process. Additional premixed powders can also be added without interrupting the manufacturing process. Another benefit of the DED technique is the possibility of gradual changes in the material deposition process, which allow the creation of FGM structures with customization, [5].
Research studies have shown that laser engineering techniques can be used to produce multi-material metal parts with high strength and good surface quality. The main advantage of the DED process is the availability of a wide range of materials, and the material interfaces can be produced with high strength. Disadvantages of this process include the low dimensional accuracy of printed parts, residual thermal stress, the requirement for atmospheric control, and the machining process, which is important for part finish, [5].

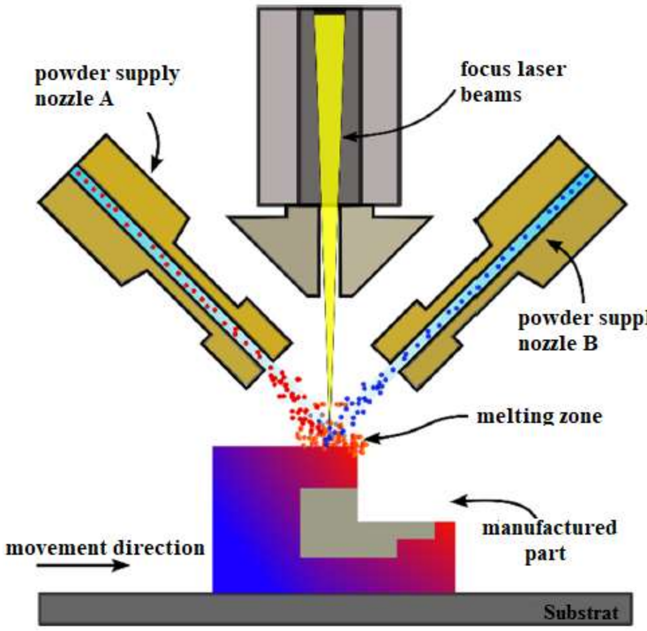


Fig.8. Description of the process of submitting multiple materials using the DED process, [5]

Lamination of sheets

In the sheet lamination process, the raw material is added together to form the final product in the form of sheets. The raw materials (worksheets) are cut by laser or cutter according to the geometry before the lamination process. The sheets are stacked layer by layer, and the stacked sheets have been diffusion bonded instead of melting. Laminated object manufacturing (LOM) and ultrasonic additive manufacturing (UAM) are the main techniques belonging to this process. Various materials such as polymer, ceramic, paper and metals can be used in this sheet lamination process. The main advantages of this process are the integration as a hybrid manufacturing system, working with ceramic material and composite fibers, and without the need for support structures. The limitation of this process is the availability of limited materials and the removal of excess materials after lamination, [7]. Compared to other methods, the waste is high in the sheet lamination process. In addition, bond strength is based on the lamination technique, and in some cases adhesive bonds will not be sufficient for the required long-term strength and integrity, [7].

In Figure 9 an overview of the manufacturing technology of laminated objects is presented, [8].

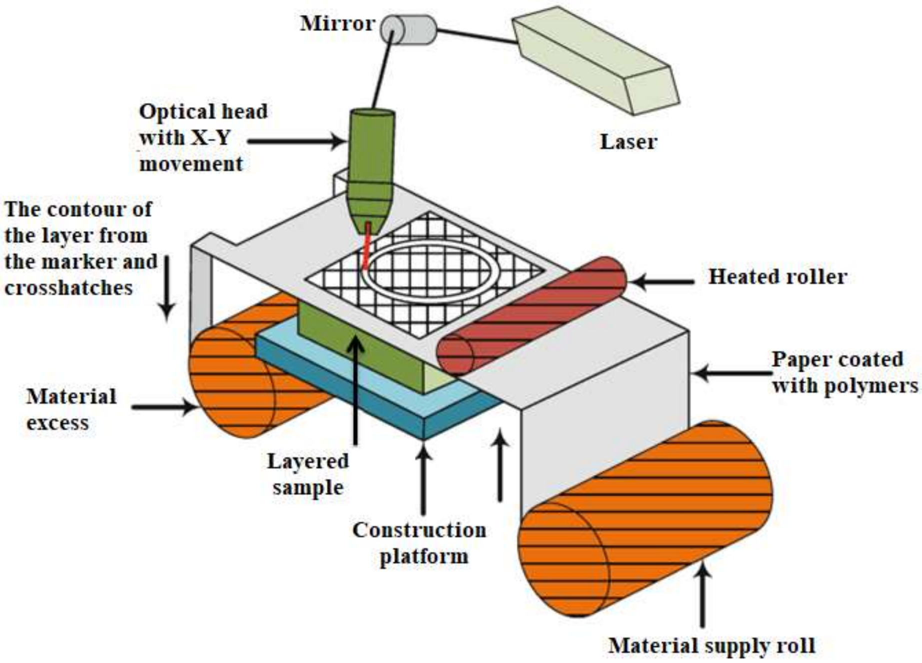


Fig.9. Overview of sheet lamination technology, [8]

Binder Spray (BJ)
During the binder jet 3D printing process, the 3D print head moves across the build platform depositing droplets of binder, printing each layer in a similar way to 2D printers printing ink on paper. When a layer is complete, the powder bed moves down and a new layer of powder is spread over the build area. The process is repeated layer by layer until all parts are complete. After printing, parts are in a green or unfinished state and require additional post-processing before they are ready for use. Often an infiltrating substance is added to improve the mechanical properties of the parts. The infiltrated substance is usually a cyanoacrylate adhesive (in the case of ceramics) or bronze (in the case of metals). Another strategy is to introduce the workpiece, in the green state, inside a furnace to achieve a sintering of the matter granules. Figure 10 presents the binder spray technique, [9].
Binder jet is best suited for large-scale printing and low-cost metal component production. Binder jetting takes place at ambient temperature, which avoids warping and curling problems. Powder size, layer thickness during bonding, bed part orientation, heater power, roll speed, curing temperature, curing time, sintering time, sintering temperature and sintering medium are examples of these. To investigate the impact of each of these factors and their interactions would require a massive experimental design with hundreds of samples and tests, [10].
The binder jet has advantages such as: relatively fast and cheap technique; the pieces can be made in different colors; can use several materials: metals, polymers and ceramics; usually faster than other processes; and two materials methods can realize a large number of binder powder combinations with different mechanical properties. This process is excellent for applications that require good aesthetics and form, such as architectural models, packaging, toys and figurines, [11]. It is generally not suitable for functional applications due to the fragile nature of the parts, [9].
However, they have some problems in this technology, such as: due to the use of adhesive materials, it is not always suitable for structural parts; additional post-processing can increase the time of the whole process; the successful realization of this process not only involves the printing process itself but also a proper post-processing procedure, both of which have a huge influence in determining the mechanical performance of the manufactured part and this technology is mostly used for conceptual realization, [11].

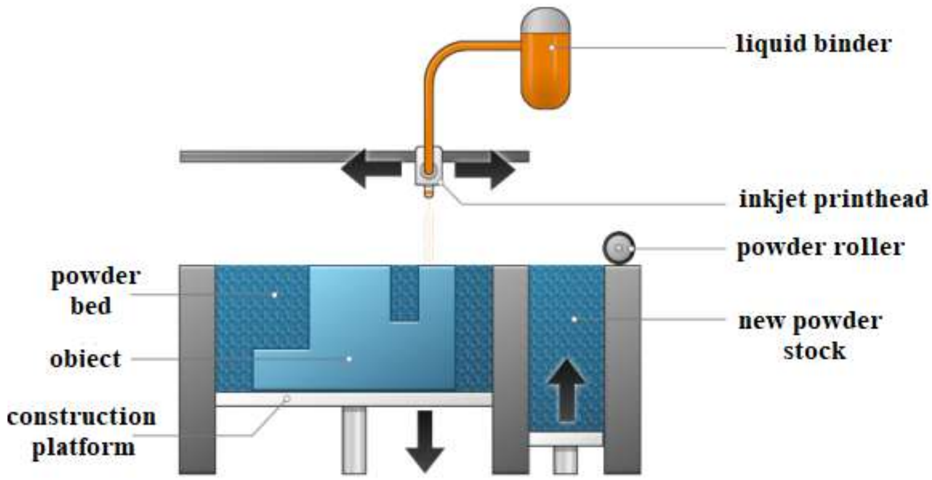


Fig. 10. Schematic of binder jet printing, [9]

3. HYBRID ADDITIVE MANUFACTURING

The term hybrid manufacturing (HAM) describes the combination of two or more different processes and machines. The main purpose of this method is to overcome the limitations of the MMAM technique and to improve quality and productivity. Figure 11 presents the AM technique combining FFF, DIW and MJ.

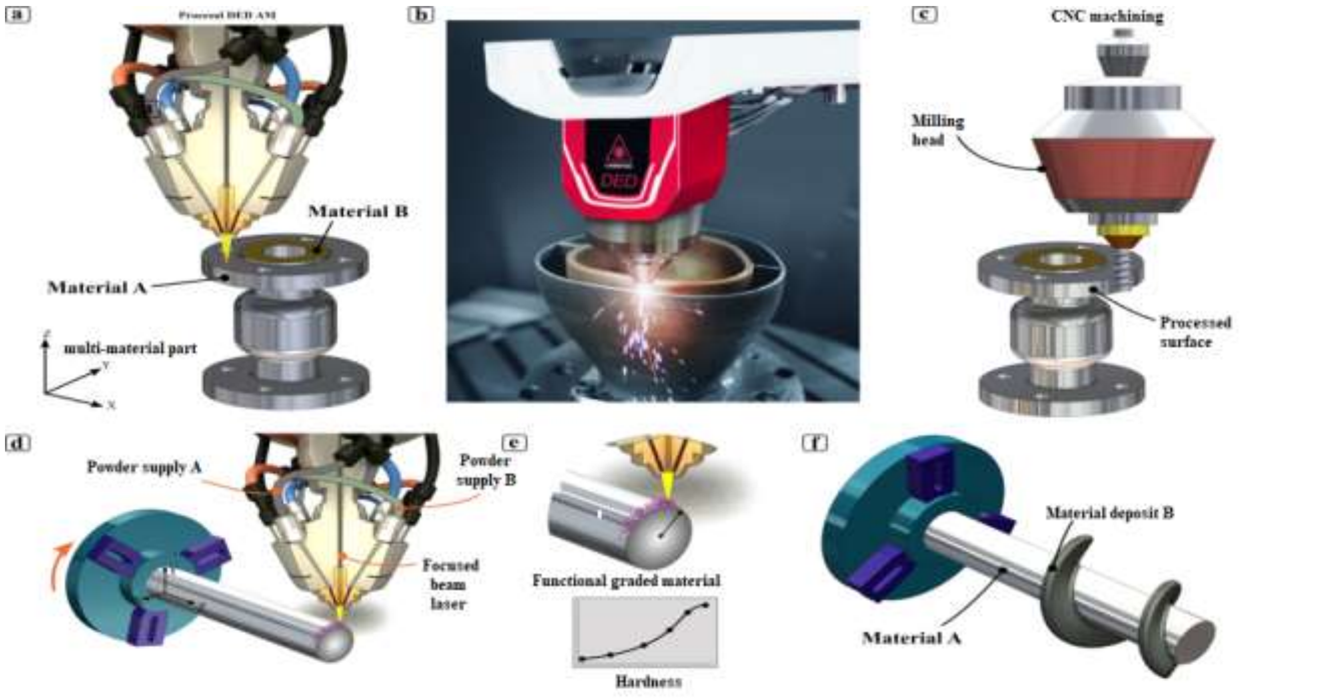


Fig.11. Hybrid AM system combining DED and CNC machining processes: (a) multi-material part manufacturing using DED process, (b) multi-material heat exchanger manufactured by Lasertec 125 by DMG MORI, (c) CNC machining process to increase surface quality of the part, (d) performing the DED process on the shaft to fabricate functionally graded material, (e) FGM fabricated part with different hardness properties, (f) depositing a second material during the turning process, [5]

Generally, HAM combines the cost-saving AM process with a dimensionally accurate subtraction process such as CNC machining. Because extensive material waste occurs during the CNC machining process, HAM allows material waste to be reduced while maintaining the dimensional accuracy of the workpieces. In HAM techniques, first the AM process (DED process is mainly used) is used to manufacture a part, and then conventional manufacturing techniques are used to increase the surface quality of the final part. Recently, DMG MORI's Lasertec 125 3D hybrid system was launched, which is a HAM process that creates, maintains and repairs workpieces up to 1250 mm wide and 750 mm high, weighing up to 2000 kg. This system uses a five-axis material manufacturing process and a five-axis milling process within the same machine. It is worth noting that the automatic switching between laser deposition welding and simultaneous five-axis milling in a single manufacturing process reduces the manufacturing time by up to 80%. Another HAM machine was introduced by Optomec, which uses CNC milling, turning, robotic operation and more in one process, creating high-quality components, providing precise motion control during the manufacturing process. The limitations of this process are the use of CNC machining operations in the surface areas of the printed parts, the time required for tool changes, and the huge amount of preprocessing considerations.

3.1 Functional graded additive manufacturing (FGAM)

Functionally graded additive manufacture (FGAM) is a layer with layer that intentionally changes the processing parameters and gradually modifies the spatial distribution of the material in a component to perform the desired function. The main purpose of the use of FGAM is to produce free -based components based on performance, determined by the gradual change of the properties of the material. In the case of FGM, they are manufactured with the FFF process. The additive manufacture with multiple materials (multi -material Addive Manufacturing - MMAM) is revolutionary because its applications offer new opportunities for the FGM in the aerospace, car and medical industry. The interface of the structures with several materials can be manufactured by varying the volume concentrations of the materials in a continuous stage using a single machine that allows the manufacture of composite parts directly from the design stage to functional parts. The materials are combined in a single process to produce polymer-polymer, metal and polymer-composite combinations in the desired locations, [5].

Currently, the manufacture of parts with several materials using separate nozzles for each material limits the printing capacity of FGM components due to the direct transition of the interface. Because a sudden transition to materials can present high concentrations of voltage, the piece will present weaknesses in different demand states. This limitation is controlled by using an extruder with a single nozzle that allows the continuous change of the composition during printing based on the adjustable ratio of the extruder engine.

The advantage of the FGAM process to AM conventional is the change of materials without changing the extrusion head. Figure 12 Describe the entire FGAM workflow from designing FGM components to their manufacturing and characterization stage, [5].

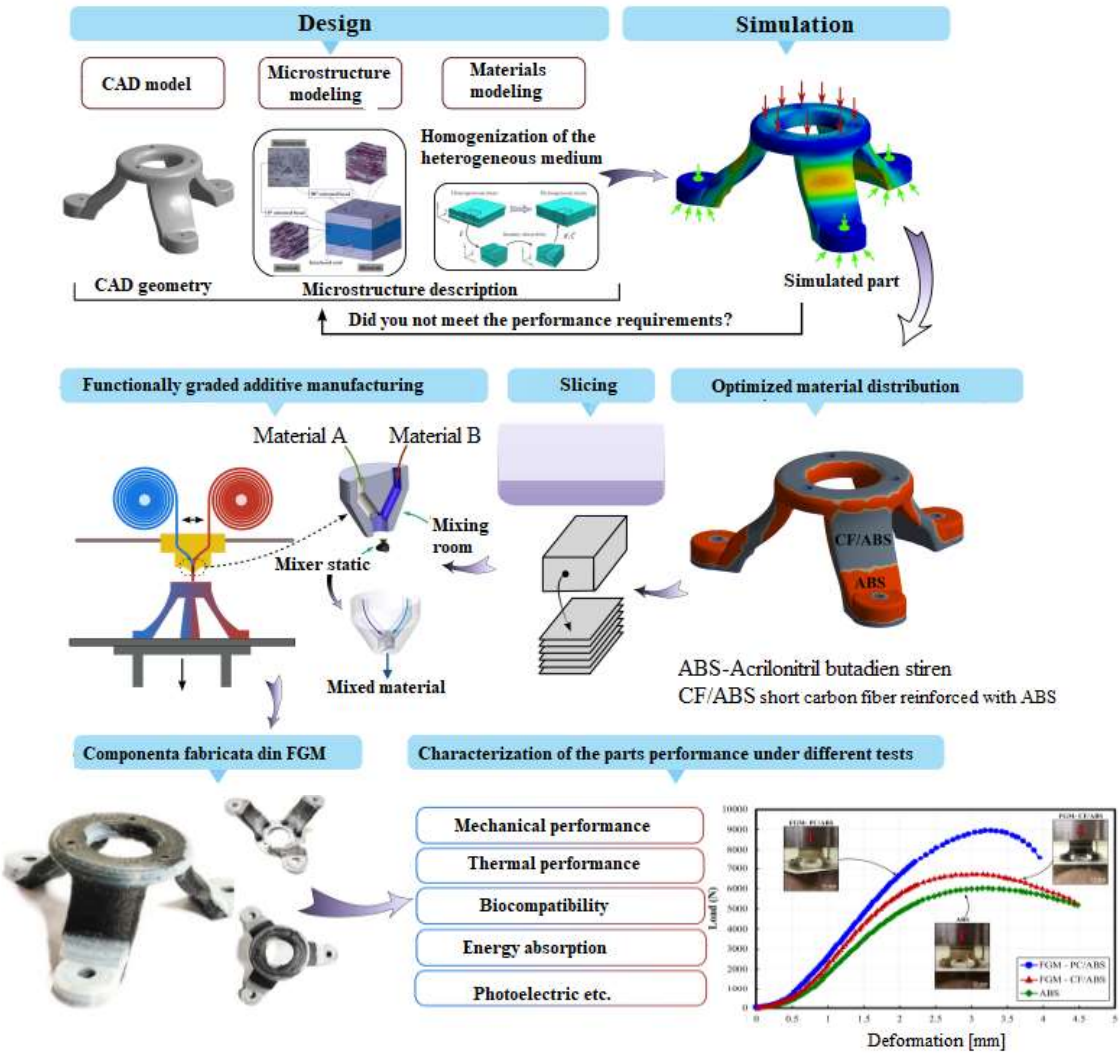


Fig. 12. Functionally graded additive workflow, [9]

The working flow of the FGAM process involves several steps, including design modeling (geometric modeling, microstructural modeling and material modeling), simulation, optimization of material distribution, slicing and generating the tool route, 3D printing, characterizing the material and performance analysis. Because most of the parts manufactured by AM have anisotropic material properties due to the heterogeneities created during the manufacturing process, it is necessary to homogenize the properties of the material. This must be done in the initial stage of the material design process. Another important step is to cut and generate the tool route, which involves the conversion of a small -voxels model for allocating the material characteristics and cutting the tool route. After the manufacture of the piece, different test methods are applied to characterize the performance of the piece for the desired functionality, [5].

The processing capacities of the processes AM requiring the improvement of existing CAD programs to evaluate the optimal allocation and distribution of materials in the MMAM parts. The typical CAD work flow is most suitable for conventional production, which requires the basic use of modification forms and processes to create 3D objects. However, in the components with several materials, a dedicated CAD package is required to explicitly allocate the materials in the desired locations in the volume of the piece to adapt their functionality, [5].

Grammacad is a CAD program developed by Computer Graphics Research of the Fraunhofer Institute for Multi-Material pieces with local defining materials.
As an interactive graphic tool, it is used for amplifying 3D models that arise from CAD commercial systems with FGM information to be manufactured with the appropriate technology. It also exceeds the current limitations of many CAD systems that are based on limits representations and provides an easy -to -use interface to add FGM information inside CAD geometry. Moreover, Fraunhofer conducts research in alternative volumetric representation schemes to integrate geometric modeling and simulation (IgA) and 3D printing with multiple materials. Figure 13 It presents a sample piece, with an interface designed to order, from hard to soft material, designed using grammacad and manufactured with 3D with several materials.

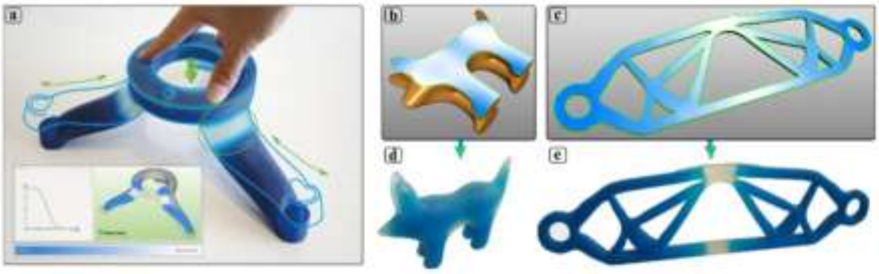


Fig. 13. The CAD models can be increased with transitions of functional graduated materials (for example, from rigid to flexible): (a) the support produced by the multimaterial 3D print The model optimized Cayote and Topology, respectively (green lines are cutting contours), (d, e) objects made with gradient material interfaces based on volumetric models, [5]

3.2 FDM technology with multiple materials

Invented by Scott Crump in 1989, modeling by thermoplastic extrusion produces 3D objects by depositing, layer by layer, of thermoplastic materials that have been heated to their semi -pointed state before extrusion to the dosage nozzle. Once deposited, the material solidifies by creating a uniform hard layer that is stacked above the anterior layer according to the sliced model. Today, this method is the most common 3D printing technology due to the simplicity and availability of cars at affordable prices. Thermoplastic materials such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), polycarbonate (PC), polyamide (PA), etc. are usually used and supplied in the form of a filament (as power coils), Figure 14. Different nozzles with different materials can be used simultaneously during a single print process, creating structures with multiple materials. The materials can also be used as a support or sacrifice structure that will later be removed from the finished object.

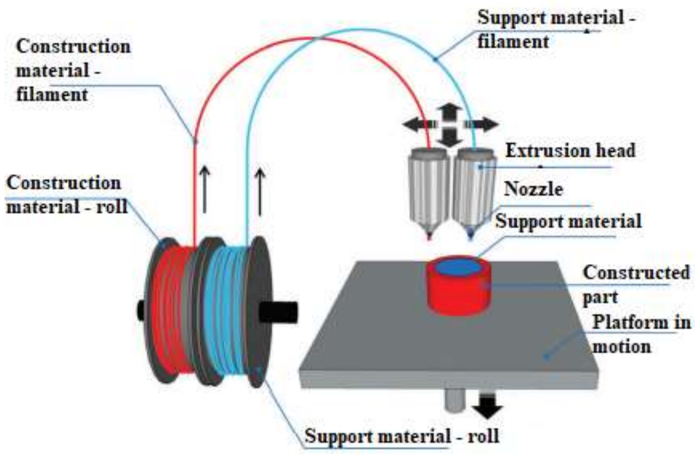


Fig. 14. Schematic diagram of FDM printing technology. A nozzle fed with a thermoplastic thread is moved in three dimensions on the construction platform on which the melted voxels of a polymer are applied, [12]

Multimaterial additive manufacture (multi-material addesive Manufacturing-MMAM) was implemented by modeling by thermoplastic extrusion (FDM), usually by equipping FDM cars with two or more extrusion nozzles. The typical FDM process with several materials can be easily found as extruding two discrete materials: a material serves as a structure material, while the secondary material is often a soluble material used to build temporary support structures, [13].

The performance of an extrusion nozzle in 3D FDM printing allows the capabilities to build more materials, improve new products and improve the mechanical properties of a certain component. The concept of thermoplastic extrusion of the multiple material (Fused of multi -material - FDMM) can be classified into two main subgroups, as shown in Figure 15, single multimaterial mixing nozzle and multimaterial multiple nozzles, [14].

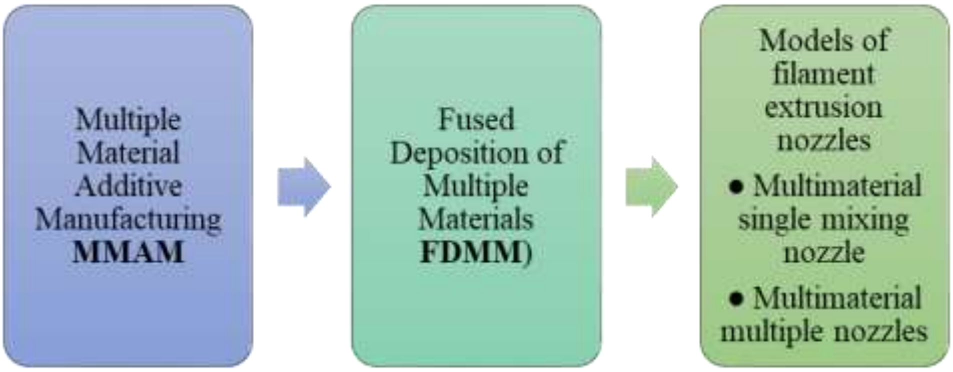


Fig. 15. Classification of Multi-Material FDM nozzles, [14]

A unique multimaterial mixing nozzle allows the extrusion of several colors and materials with the same nozzle and obtaining mixed filaments and produces gradient materials. Either the single-mixed nozzle uses the same working temperature to melt several input filaments or within a range of temperatures between different polymers. Otherwise, it will generate a final contaminated product. For this reason, the materials must have a close relationship at their melting point in order to obtain an efficient and quality glue in different parts of a print. The author suggests that small temperature changes between filaments can be done during the printing tower print or using the filling. This approach reduces the transition of the material after each change of the filament. The advantages of using a unique multimaterial mixing nozzle are that for each basic layer, there are no calibration defects when depositing the material, [14]. In order to print a high quality object using this method, the model must be precisely divided into parts and then in different printing stages, the machine must be interrupted to change the filament. There are few studies on the properties of 3D-printed multi-materials that have been printed by a single nozzle print, [15].

Extrusion -based systems usually use two or more separate nozzles mounted side by side on the same stroller to build multicolored and multimaterial components. The use of multiple nozzles can facilitate the production of several printing parts by increasing the processing speed through a continuous operation. One of the main challenges that use the multi -nozzle arrangement comes with calibration and drainage problems due to inactive extrusion. This last problem is generated when the next nozzle is heated and reaches the melting temperature of the polymer, causing drops of material during printing. Requires deactivation of one of the Hot End nozzles while the other prints. In order to solve this problem, a route planner has thought to be introduced to optimize the orientation of the piece and the movements to reduce or hide the flaws. Another approach to mitigate this problem is to activate the filament withdrawal for each polymer before printing, in addition to the printing tower print when moving on to another material to print a section. The advantages of using several nozzles allow to place nozzles with different diameters in the same stroller. These different dimensions allow the models to be printed quickly or with fine details, to easily replace the clogged nozzles or to build layers of materials with different thicknesses depending on a certain application. These benefits can improve the resolution, functional and mechanical properties within the same piece, [14].

It has been shown that the multiple nozzle achieves better performance during construction, while the single nozzle has a greater consistency in the manufacture of high quality materials, [16].

3.3 Available solutions of extrusion heads

There are many solutions available. Due to the characteristics of the Reprap project, many users adjust or create extruder according to their needs and publish their solutions on the Internet. The most common extrusion head models are listed below. It should be noted that solutions are often combined. One of the criteria for dividing extrusion into categories is the filament means using the supply mechanism in the hot part of the extrusion head. The vast majority of extruders that use a printing wire to use one of the following supply solutions:

- extrusion with gears;
- extrusion with direct drive;
- Bowden extrusion, [17].

Extruders with gears use a reduced gear supply mechanism to feed the filament. For this reason, these extrusion offers couples larger than direct extruders and are therefore mainly suitable for printing larger diameter (3 mm). However, the disadvantage is the slightly more robust structure and dimension. An example of this extruder is presented in Figure 16, [17].

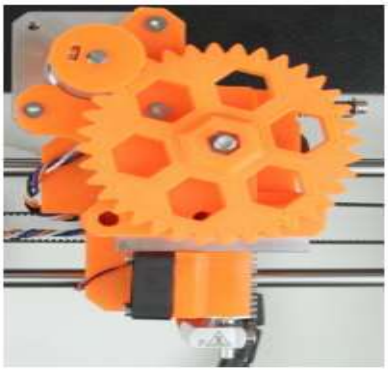
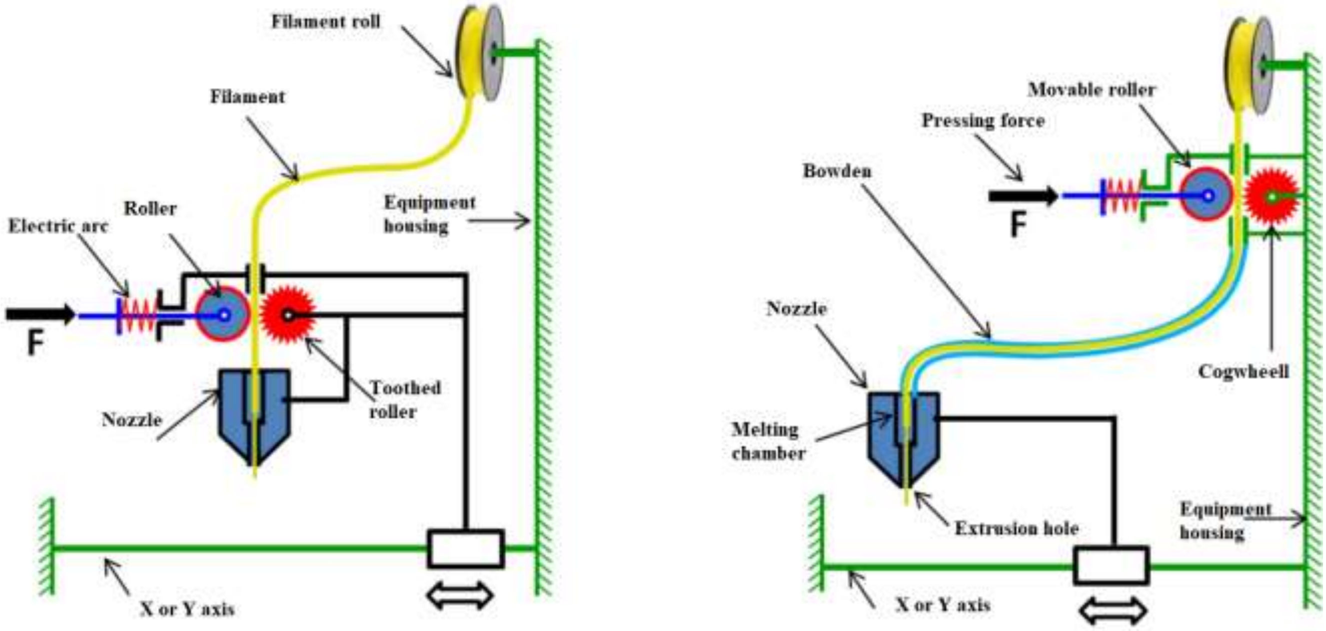


Fig. 16. Example of extruder with gears, [17]

Direct actuating extruders are characteristic by the fact that their power wheel is directly attached to the step -by -step engine shaft. Unlike the previous solution, the supply mechanism is not engaged and offers a smaller couple, which is, however, sufficient for the filament with a diameter of 1.75 mm, [17].
The *Bowden extruder* is one of the special cases. The specificity consists in the fact that the power mechanism is not located in the head together with the hot part (see Figure 17), but is mounted on the printer. The filament is fed to the hot side through a tube. Filament supply can be direct or transmitted. The advantage of this solution is to ease the moving parts, thus allowing faster printing and quieter leadership, [17]. Also, this intelligent solution offers a larger volume of construction and is very adaptable for making a multi-extruder system. By implementing multiple-no-nozzles, materials of different or multicolored, simultaneously or alternatively, automatically and without interruption of the printing process, can be supplied, [18]. The disadvantage of the Bowden extrusion consists in the less precise supply of the material at the beginning and the end of the material due to elasticity the material and the bowden. Some of the more flexible materials cannot be used at all for printing with this type of extruder [17].

Fig. 17. Example of Bowden extruder, [17]

Most 3D FFF printers belong to the direct extrder type. In this type of extruder, the mobile parts include the nozzle, the heater and the engine. The engine pulls and drives the filament directly from the cold end to the hot end. For the type of extruder Bowden, the training parts are separated from the hot end and is the only difference between the direct extruder and Bowden. The Bowden extruder FFF printer has a flexible cable connected between two separate parts. The cable is known as Bowden cable or sometimes it is also called Teflon tube (because of the material used). The thermoplastic filament is driven inside the tube to obtain a permanent supply of the material to the hot end, [19].



(a) (b)

Fig. 18. Basic diagram of FDM3D printer extruder: (a) direct extruder, (b) bowden extruder, [18]

For the direct extruder (Figure 18(a), the exit of the filament is arranged directly in front of the entrance of the hot terminal, at a very small distance. The two systems are buried and form a very compact block mounted on the X or Y axis with a sliding connection. In the case of the Bowden (Figure 18(b)), the supply system is fixed on a well -chosen place of the 3D printer frame, very far from Hot End. In order to properly guide the filament from the exit of the supply system at the entrance of the hot end (to avoid the flamboyant without the effective movement of the wire), a flexible tube with the appropriate interior diameter ensures the interior slipping. clearance, [18].

The design of available FDM printers offers different technical solutions for multimaterial/multicolored extruder. Although in the literature there are several classifications of extruders, it is very interesting to classify them according to the relevance of the additional functions it offers for the initial extrusion system, mainly the multi-material/multicolored function. Multicolored/multimaterial extrusion can be classified in two families: mosaic printing model and complete mixing model.

In the print model with mosaic, the object is discredited with large patterns that share the same color or material, while the complete print print is modeled by the continuous degradation of the color or color (Figure 19), [18].

The most classic color/mosaic material systems are based on the duplication of the extruder and works according to the same principle as a single extruder, so that the head trolley becomes equipped with many identical extrusions. The first units arising are dual extruders that can be used for dissolvable or removable supports to keep some regions of the piece that are in console and to escape them intelligently without affecting the fineness of the final surface. The multiple standard extrusion can be of parallel or independent type, as illustrated in Figure 20, [18].

In the standard parallel extruder, two or more nozzles are incorporated on the same body (print head). Then they are forced to describe parallel routes, while in the independent double extruder, two print ends move independently on the X axis. The advantages and disadvantages of each solution are summarized in Table 1, [18].

The number of components added is a multiple of the uses of the extruder to be implemented. This type of design disappears due to its very limited advantages (extrudes work only separately); It is very bulky and adds additional weight and also increases the price of the car. Because these extrusion works alternatively, some designers have optimized the weight and space occupied by this extrusion system by using a single -wire drive system (step -by -step engine power mechanism). This coupling/decoupling process, similar to that of the clutch gearbox, allows the application to be selected or not the pressing force against the filament. The advantage of having several independent nozzles is the possibility of printing various materials with different temperatures and colors, [18].

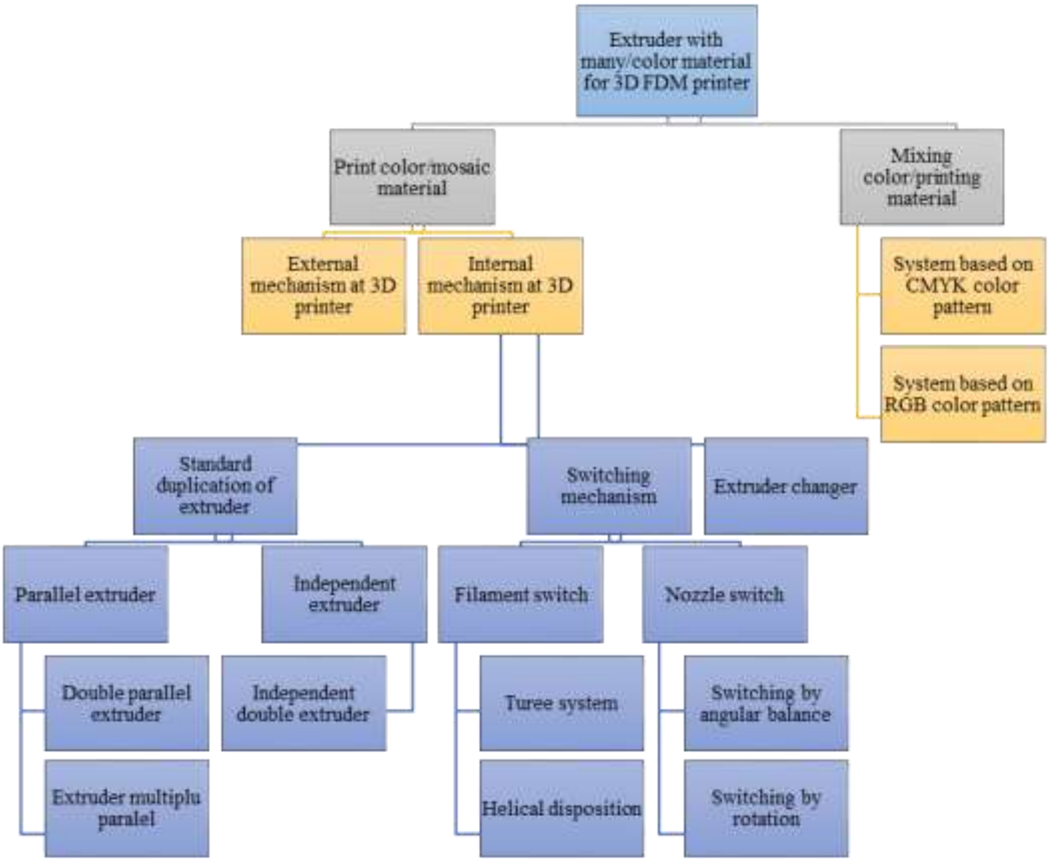


Fig. 19. Classification of multicolored/multi-material extruder of 3D printing by merging modeling (FDM), [18]

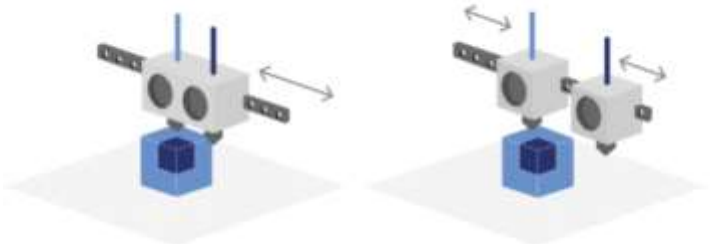


Fig. 20. Types of standard extrusion systems: (a) parallel: two or more print ends placed together in the same trolley; (b) Independent: Two or more printing ends that move independently on the same X axis, [18]

Table 1. The advantages and disadvantages of the double parallel and independent extruder, [18]

Performances	**Double parallel extruder**	**Independent double extruder**
Productivity	Unchanged because only an extruder is active on print	It can clone the piece and also print distinct objects. Then the production capacity is doubled
Precision	The large mass of two printing ends involves high inert when moving at high speed to another, which leads to lower accuracy	Design and operating regime are identical to those of a single extruder
Calibration	Special calibration is not required	Difficult calibration if it is intended to work simultaneously on the same slicing of the same piece
Print quality, compared to a single extruder	The inactive nozzle can escape melted plastic while waiting	The same as a single extruder
3D printer workspace	Nu este afectat	Is divided between independent extrusion

An independent extruder is another class of multiple nozzles with a different vision to treat distinct materials and increase productivity. The design of this class generally limits the number of extrusion to two (dual extrusion) due to the complexity of their implementation and the difficulty of calibration. Dubbing extruders, which divide and independently divide the same space, will considerably reduce the volume of printing of the parts and increase the probability of collision if no measure is taken, [18]. This type of system is simple and easy to use, and two materials with a big difference of melting temperature can also be easily printed and also avoid starting and stopping the printer while changing the duty by reducing the time of non -functioning. While the limitations of this system reduce the printing surface of the printer, the offset of both nozzles should remain constant even after a change in temperature appear various defects, such as leaking, striving and moving the layer, which prevents the quality of the product and the tower. of purification must be printed, [20].
By using a single-nozzle multi-extrusion system, it is assumed that several filaments go through the same hole, which solves most of the problems mentioned in classic or independent extruders (compact design, without calibration and reducing the number of extrusion), [18].
The design of a multi-material system differs greatly from that of a multicolored, because each material has its proper characteristics and its own melting temperature. Therefore, it has become clear that we cannot divide the same nozzle for different printers. This is especially the case when it was intending to increase productivity, so the increase in the number of extrusion becomes a persistent need. The current solutions for submitting several materials, have only partial advantages and, therefore, remains a lot of insurance work for designing an optimal technical solution. Figure 21 summarizes some of the new functions that can be added by reviewing the filament extrusion system, [18].

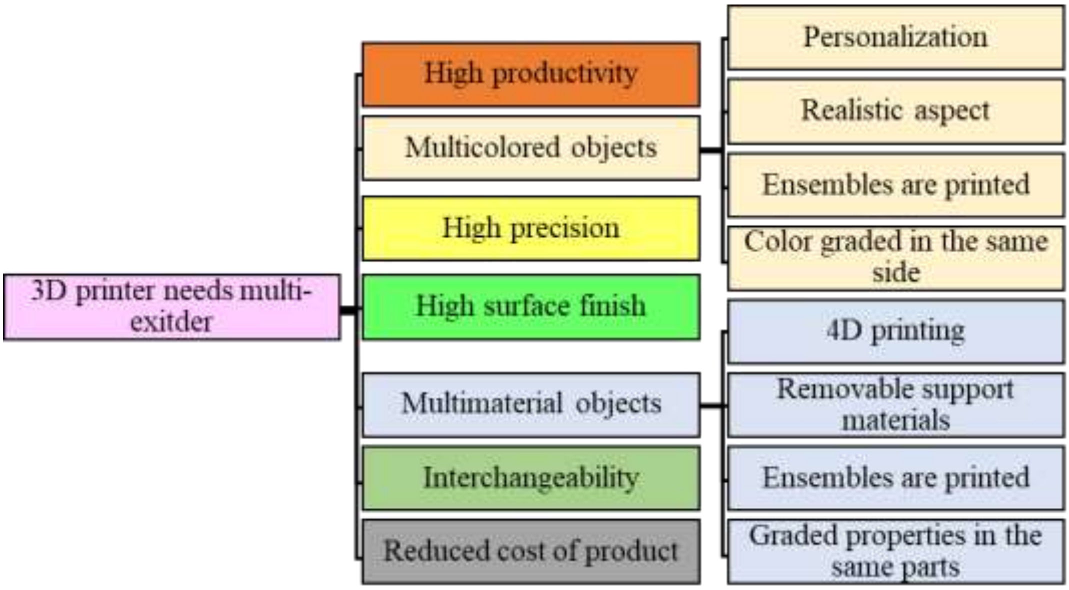


Fig. 21. Some of the generated functionalities resulting from the addition of
a multi-exitder system to the 3D FDM printer, [18]

Multimous extrusion systems offer the possibility of depositing multimaterials regardless of their melting temperatures, but they are less suitable for the mixing operation and are very cumbersome and their balancing is very difficult. On the other hand, a single -nozzle system is very compact and makes it possible to obtain colored objects with surprising degradation, but being equipped with a single source of heating, forces the use of materials of the same quality. However, the two classes of extrusion systems are far from satisfying the needs of the industry in terms of productivity, which stimulates us to look for a new design with technical solutions adapted for the emergence of different characteristics for 3D printing of different materials types, [18].

3.4 Limitations of the multi-material 3D printing process based on extrusion
The issues related to "equipment"
The limitations of the equipment -related process are mainly two:
1. Reducing the available area of printing and calibration of extrusion ends
The first is a direct consequence of the space required to host the head/ends of extra extrusion (E), usually side by side in a direct training system (most compatible with flexible filaments). Therefore, this type of constructive

solution results in a reduction of the available construction space, in proportion to the distance between the extrusion nozzles and the dimensions of the extrusion ends. Without changing the printer frame, this limitation is impossible to bypass and its magnitude depends on the dimensions and appearance of the extrusion ends used. As an alternative, a few multi-material kits for printers are based on the Bowden extrusion variant, in which the filament training is carried out far from the hotnd. This saves weight and space at the head of the printer, but is usually not compatible with flexible materials, which tend to stretch before reaching the hotnd, [21].

2. The need to ensure/maintain a precise alignment of the two or more extrusion heads during the printing process

This is a time -consuming precision operation, which could involve some tests of testing, printing and evaluation, to ensure an appropriate macroscopic continuity of the printed object whenever the active extrusion head. Independent of the quality of the calibration procedure, a switch in the active extrusion head generates a special interface called - limit interface. It is no longer of the type inherent in the process, formed between the neighboring extruded filaments of the same material. In contrast, this is formed between different materials at the geometric limit of the different sections of the object that involves discontinuity in the printing process. Therefore, at these special interfaces, a severe harmful effect on the mechanical performance of the printed piece is expected. For this reason, the design of the piece will consider this problem, offering the overlap of the two materials, [21].

The problems related to the "design of the piece"

The geometry of the limits between the different sections of materials is an important problem of design design. Another problem related to the "design of the piece" is the lack of control over the residence time of the filament inside the hotnd. Unlike what happens in a single piece of material, the specific design/geometry of one with several materials dictates the residence time of each material filament in the appropriate hotel. Therefore, the residence time cannot be optimized by flow, as in the process with a single extrusion head. Thus, there is a greater tendency of the polymer to flow, as is the case in the extrusion of plastics, which can negatively affect the uniformity of the extrusion/deposit process. This problem cannot be bypassed but can be minimized by:

- avoiding the use of the upper limit of the extrusion temperature range;
- avoiding the use of filaments with low molecular weight additives in their formulation, among other factors identified to favor the occurrence of flow;
- withdrawal of the filament, whenever the extrusion head is not active, to shorten its residence time at the place place;
- activation of the main pillar, which first prints a pillar when changing between nozzles to ensure that the active nozzle is primed before printing the piece, [21].

Chemical -related problems/formulation of materials used in the same print

Finally, probably the hardest to systematize, are the problems related to the chemical nature/formulation of the materials used in the same circulation. If they are different, they can generate problems associated with their possible different thermal expansion coefficients and, therefore, different contraction values, leading to the distortion of the part/low dimensional accuracy or the formation of gaps at the interface. Another problem is the reduced mechanical integrity expected at the interfaces between the different materials printed when they are chemically incompatible or have low chemical affinity. The existence of interfaces is an inherent disadvantage of all 3D printing processes, but the severity of its negative effect will increase if beyond its physical origin, there is a chemical one. Given this, choosing the pairs of materials that will be used simultaneously must be done carefully. Whenever possible, the same basic material should be used, ie the use of the same material with different colors or composites having a common polymer matrix, [21].

4. CONCLUSIONS

In order to reduce the consumption of petrochemical resources, alternative solutions are constantly sought. An example in this regard implies the use of bioplastic and biocomposites in the 3 D Printing Printing in order to improve the technical-functional properties to compete with the oil-based plastic materials. The method of multi-material additive manufacture is a revolutionary approach because it offers a wide range of implementations in areas such as the aerospace industry, car, medical, electronics, food, etc. Terminal extrusion modeling technology can be considered a suitable method in the multi-material 3D printing due to the main advantages such as low price, simplicity of technology, efficient laying of layers, etc.

Following the revision of the specialized literature in terms of multimaterial 3D printing, the following can be learned:

- the most common technique for multi-material printing is the double extruder that has advantages such as simplicity and ease of use; However, the offset of both nozzles should be taken into account, which is preferable

to remain constant;
- the performance of 3D prints with several materials depends largely on how different materials interact with each other;
-the most important process parameters that influence the inter-layered and intra-stretched bonding of the deposited states are the extrusion temperature and the supply speed;
- the choice of the bi-component material is usually done taking into account the properties of the materials; Thus, most of the times a first material with high properties is chosen that can compensate for the weaker performance of the second material;
- the proportional control of the Bi-Compont material can be done by adjusting the technological parameters;
- the mechanical performance of the parts manufactured additive with several materials is usually better compared to those printed by printing with a single material;
- the interface formed between different materials is dependent on the properties of the materials involved and the printing conditions;
- Consider the manufacture of multi-material parts functionally graded to increase their performance by controlling the processing parameters.

An interesting combination of biodegradable and biocompatible materials is that of polylactic acid (PLA, melting temperature of 180°C) with polyprolactone (PCL) that has a melting temperature of 60°C. The bending module of the PLA material is much larger than that of the PCL material. Thus, the introduction of PLA filaments as a reinforcement material during the multimaterial FDM process with PCL materials can significantly increase the stiffness of PCL parts. On the other hand, the presence of PCL materials can provide a certain elasticity to composite parts (made of PLA materials and PCL), [22].

Following the revision of the "Espacenet" database it was founded that there is a wide variety of patents belonging to the field of 3D Bi-Component printing, each having an important role in developing this vast domain. It was noticed that the extrusion system plays the most important role in the multimaterial 3D printing, which is why it is aimed at its continuous embodiment and innovation in order to increase the performance of the printed product. As a general conclusion, it is necessary to continue to carry out research because there is no comprehensive model for the quantitative understanding of the Multimaterial FDM parts binding mechanism. Also, new materials can be studied to find those compatible with each other so that, after combining their performance, they increase.

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