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A REVIEW ON PRINTING MATERIALS OF ADDITIVE MANUFACTURING

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ABSTRACT

Additive Manufacturing is emerging as an enabling technology for a wide range of new applications. From fundamentals point of view, the available materials of Additive Manufacturing printing processes must be considered for each specific application. This review provides a basic understanding of Additive Manufacturing printing materials used in various additive manufacturing technologies such as smart materials, ceramic materials, electronic materials, biomaterials and composites. It should be noted that the versatility of 3D printing materials comes from the variety of 3D printing systems, and all the new printers or processes for novel materials have not gone beyond the seven categories defined in ISO/ASTM standard. However, 3D printing should never be seen as a standalone process, it is becoming an integral part of a multi-process system or an integrated process of multiple systems to match the development of novel materials and new requirements of products.Various factors mostly generated to materials themselves, which make further improvement in prototype printing. Mostly processes are built-up around an ideal material that responds to a narrow range of temperature inputs or light frequency. Using heat or light, printers often liquefy or solidify substances to manipulate the material into specific forms.

Keywords: *Additive Manufacturing, 3D Printing, printing materials, smart materials, ceramic materials, electronic materials, biomaterials and composites.*

I. INTRODUCTION

Additive Manufacturing (AM), commonly known as 3D printing, can be defined as the "process of joining materials to make parts from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing and formative manufacturing methodologies". Additive Manufacturing (AM) is already being adopted for rapid prototyping and soon rapid manufacturing. This review provides a brief discussion about AM and also the most employed AM technologies for polymers. Additive Manufacturing has emerged as a leading manufacturing technology all over the world. The development of new method does not affect only quality of the end product but it also opens new markets and influences on the price of used materials. The success of additive manufacturing is depended on fine-tuning materials to the needs of each application. This fine-tuning process is involved on the type and the quality, strength and costs of materials. There are many materials that can select when it comes to additive manufacturing. However it's often tough to decide on the right one. The various materials can be adopted for additive manufacturing based on the needs of market.

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No single technology can print in every material. Some of them support a wide range of materials whereas some others can work with only one specific material. In the following lists you will find the most popular technologies today for both metal and non-metal additive manufacturing. The idea behind this seemingly arbitrary division is to minimize overlapping capabilities. Simply put, if one technology of one group is ideal for a certain job, the others in the same group may do reasonably well whereas the technologies in the other group will be probably unsuitable or highly impractical.

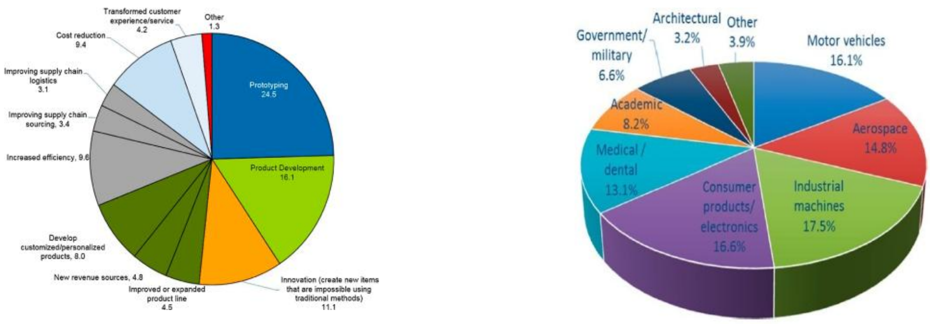

Fig.1. Reasons for pursuing Additive Manufacturing techniques [1].

II. MAIN NON -METAL ADDITIVE MANUFACTURING TECHNOLOGIES

FDM (Fused deposition modelling): Most common type of consumer-grade additive manufacturing. The material comes in filament form and is fused and deposited on the 3D space of the building box. Also referred as **FFF** (Fused Filament Fabrication).

SLS (Selective Laser Sintering): One of the most popular options for large scale production. The material comes in powder form and is sintered layer by layer with an infrared laser[2].

SLA (Stereolithography): The oldest additive manufacturing technology, it uses a LED or laser UV light source to solidify a liquid photo-curable resin.

DLP (Direct Light Processing): Similar to SLA but replacing the LED or laser with a projector. Thus it can generate a complete layer in a single step instead of scanning the layer's surface.

PolyJet: Tiny photo-curable resin droplets are jetted by the printer and quickly solidified with light. This technology developed by Objet (Stratasys) can mix and jet different resins during the printing process, allowing multi-material objects.

MultiJet: Analogous to Polyjet but developed by 3D Systems. Some differences in the cleaning process.

ColorJet: This technology involves two major components, a core powder (plaster-like) and a multicolour binder. Layer by layer the binder glues and gives colour to the powder particles.

MCor Paper 3DP: Regular paper sheets are printed on full colour, glued and stacked. The shape of each layer is also cut with a blade so the final object can peeled away, discarding the excess paper all around.

III. MAIN METAL ADDITIVE MANUFACTURINGTECHNOLOGIES

DMLS (Direct Metal Laser Sintering): Analogous to SLS additive manufacturing but using metal powder instead of plastic powder. As expected, the laser is also significantly more powerful in order to reach the sintering temperature of the metal particles.

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SLM (Selective Laser Melting): Similar to DMLS but reaching higher temperatures in order to melt the powder metal particles instead of just sintering them. Laser power is even higher than on DMLS, reaching the 1000W mark.

EBM (Electron Beam Melting): This technology works similarly to SLM but it uses an electron beam instead of a laser. This change allows for higher energy transfer, reaching melting temperature faster and thus 3D printing (generally) faster than SLM.

BJ (Binder Jetting): This is a multi-step process that starts gluing metal powder together with a jetted binder. The resulting object, still fragile, is cured in an oven, removed from the powder box and then infiltrated with bronze in a furnace. Similar to powder bed fusion, binder jetting selectively binds particulate materials in a layer-by-layer fashion[3].

IV.PRINTING MATERIALS

We have grouped all 3D printing materials into 4 categories:

1) POLYMERS 2) RESINS 3) METALS 4) OTHERS MATERIALS

1) POLYMERS:

Polymers are the most used materials in the 3D printing world. This is not coincidental, the extremely wide variety, relative low cost of the material and compatibility with even the most inexpensive printers have made of it one outstanding option for multitude of projects and the number one choice for both enthusiasts and professionals.

POLYAMIDE (PA): More commonly known as Nylon, polyamide objects are created from either an extruded filament or sintered fine powder. The material is rigid and strong but flexes under high loads. PA12 and some dry blends based on PA12 are today the materials which are used to generate almost all commercial SLS parts[4].Thanks to its widespread use it is one of the cheapest materials available for 3D printing. The advantages of PA material are toughest plastic material, bends without snapping, relatively inexpensive, high chemical resistance, and Food compatible, high softening temperature. And the disadvantage is found as, Nylon filaments are prone to absorb humidity fast and need to be properly stored.

ALUMIDE: Alumide is a mix of Polyamide 12 and Aluminium that comes in powder form for SLS printers. It is produced by German e-manufacturing company EOS (Electro Optic Systems).The advantages of Alumide are stiffer than Polyamide, Aluminium gives metallic shine to the surface, and high softening temperature. The drawback is it only comes in grey colour (but can be dyed).

POLYLACTIDE (PLA): Polylactide or Polylactic acid is one of the most popular materials for consumer-grade 3D printers. Corn-starch based, is also one of the most eco-friendly and that along with its ease of use have made it a great replacement for previously ABS users. PLA is seriously eye catching on dark places and available on several colours. But temperature variations during printing can slightly change the colour of the layer. Finding calcium carbonate in the PLA is significant due to the fact that PLA can also be used as support structure material for growing cells, and calcium is a required element for the growing cells[5].PLA is of special interest due to its biocompatible, biodegradable, non-toxic, non-immunogenic, and non-inflammatory properties, making the material usable in medical applications[6].

CARBON FIBER PLA: Carbon composites are always awesome and all the advantages they offer had to arrive to 3D printing at some point. This reinforced PLA material has up to 20% (by weight) of tiny carbon fibres that give structural rigidity to your prints. The advantages are increased stiffness and light-weight. The disadvantages are it is more brittle than regular PLA, the fiber can lead to clogging nozzles, especially on smaller sizes and it is expensive.

WOOD PLA: This material has up to 30% of real wood particles and fibres mixed with PLA plastic that give the characteristic colour, texture and even smell that resembles a wooden object. It is the only option to quickly produce a convincing wood-like object. Printing with this material can be a bit tricky and not the cheapest material.

BAMBOO PLA: Bamboo PLA is another great example of recent development in 3D printing materials. Similar to Wood PLA but with the characteristic bamboo colour. It provides unique bamboo effect. Printing with this material can be a bit tricky and material is expensive.

COPPER PLA: With a genuine reddish colour brought by the copper particles in the mix, this material not only looks metallic after polishing but it's also heavier than most 3D printing materials, making the metallic effect more realistic. The advantages are it can be polished to achieve a metallic look and way heavier than regular PLA, feels like a real copper. The drawback is expensive.

BRONZE PLA: As one the first metal-plastic filament materials, Bronze-PLA lead the way for more and more complex compounds designed for FDM printers. Similarly to Copper-PLA above, this material looks its best after is polished, revealing a unique metallic appearance. The advantages are it can be polished to achieve a metallic look and way heavier than regular PLA, feels like a real copper. The drawback is expensive.

ACRYLONITRILE BUTADIENE STYRENE (ABS): ABS is extremely common thermoplastic polymer and one of the 2 or 3 most used materials for 3D printing, as well as one of the first to be used on FDM printers. The fact that it's among the cheapest 3D printing materials and is compatible with even the most basic and affordable FDM printers make it a good alternative for enthusiast with a limited budget. Several studies have been carried out to evaluate various mechanical parameters of acrylonitrile butadiene styrene (ABS), including tensile, compressive, flexural and impact strength[7]. The advantages arestronger than PLA, gives long lifespan, Inexpensive, wide variety colours available and LEGO® uses this plastic so it must be good. The disadvantages are warping can be an issue, not biodegradable, it can shrink significantly when it cools down, unpleasant and toxic fumes will be released when printing. Also, iron particles filled ABS and copper particles filled ABS is successfully developed for direct application in Fused Deposition Modelling rapid prototyping process[8].

THERMOPLASTIC POLYURETHANE (TPU): TPU is another material that found its way into multiple 3D printing technologies as is one of the favourite options for flexible prints. On FDM printers the surface will have a more shiny, layered texture whereas SLS prints will have a more homogeneous and granular texture. It is the perfect material to give some movement to your designs and prototypes.

HIGH IMPACT POLYSTYRENE (HIPS): HIPS is a mix of polystyrene and polybutadiene that has become particularly interesting not because of its mechanical properties but because it can be dissolved in Limonene solution. This combination allows for its use as support material, which can be easily removed without having to cut, force, sand or break parts of the print, resulting a cleaner and better looking object. It's easy to print, inexpensive and it comes in a wide range of colours.

POLY VINYL ALCOHOL (PVA): PVA is another widely used filament, mainly as support material since it can be dissolved using just water. Just as with HIPS, to make the most of this material, a dual extruder FDM printer is necessary.

POLYETHYLENE TEREPHTHALATE (PET): PET is another popular material that found its way to 3D printing. Commonly used for plastic bottles, objects printed with this material will be stiff, lightweight and colourless. It's also really strong and, as you can guess, food compatible. Printing PET can be a bit tricky for beginners. Some suppliers even offer bottles-based recycled material.

GLYCOL MODIFIED PET (PETG): PETG is an inexpensive, naturally transparent, flexible and durable material that has found its way to FDM 3D printers aiming to match the strength of ABS plastic with the ease of use of PLA plastic. Its low shrinkage makes prints less prone to warp and detach form the printing bed. Although PETG filament is pretty new in the market it is already gathering a lot of attention. Some suppliers of this material are Taulman3D, eSun and Airwolf3d.

POLYCARBONATE (PC): Polycarbonate is another type of thermoplastics that is widely used in all sort of objects from water bottles to CDs and safety goggles. It is really strong, impact and temperature resistant and has recently started to be used in consumer grade 3D printers. Several colours are already available but it's still recommended only for experienced users that have high-temperature extruders. Some suppliers of this material are Polymaker, Gizmodorks and Ultimachine.

THERMOPLASTIC ELASTOMER (TPE):TPE or Thermoplastic elastomer is a rubber-like material with good abrasion resistance ideal to print any kind of flexible object. It is usually not as flexible as other materials like TPU. Available in several colours for FDM printers and just natural colour for SLS printers. Some suppliers of this material are Verbatim, NinjaFlex(FDM), EOS and 3DSystems(SLS).

Fig.2. Objects printed with different materials.

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2) RESINS:

After plastics, resins are used extensively for 3D printing. When Additive Manufacturing was born, a resin was the first material to be there creating stuff for us. Today, several 3D printing technologies use resins and they are mostly used to achieve superior printing quality and maximum resolution. More often than not, this requires paying a premium but the results are likely to be worth it. For some specific applications, they can even be the only way to go. There are lots of resin suppliers and resin compositions, and similar looking resins may be really different at a chemical level so the following categorisation is just a way to present resins in a simplified form. When working with resins some precautions must be taken as they can be irritating, or even toxic. Always wear gloves and eye protection. Resins are definitely among the coolest materials for 3D printing. The technologies that evolved around resins are today the ones that offer the highest quality and this make it a great choice for professional applications, important product presentations, small objects, etc.

TRANSLUCENT RESIN: Translucent resins offer a similar transparency to what could be obtained with plastic printing but with the typical superior quality of resin-printing technologies. It has a “frosted” appearance that is difficult to replicate with any other material without some sort of post processing. This is a wonderful material to create objects that will interact with light as a skilled designer can play and control the way light propagates within the material but is scattered in the surface. Translucent objects lighten up with LEDs looks phenomenal in the dark.

TRANSPARENT RESIN: This kind of resins are the only 3D printing materials that can print objects that are transparent enough and with a smooth enough surface to manufacture optical devices. From a simple magnifier glass to waveguide to a see-through mechanism or virtually unlimited decorative objects, this material will look amazing. Just as with translucent resins, if you add some lights to your project printed with this material you will definitely grab people’s attention.

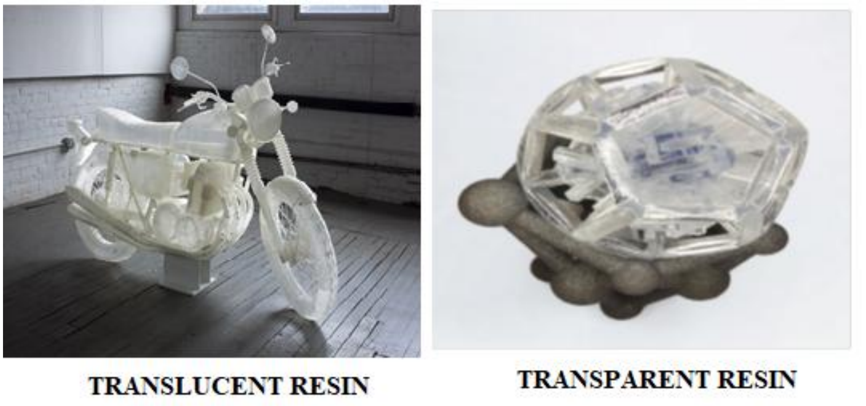

Fig.3. Objects printed with resins

3) METALS:

One could say that metal 3D printing is a world by itself. And one which is evolving faster than ever pushed by humongous industries like aeronautics, space and the military. It is also a very complex one as handling, mixing and building with metals is significantly more challenging and expensive than doing so with plastics or resins. On the bright side, the outcome of all this investment of resources is also huge and not only for 3D printing users like engineers, artists or enthusiasts but also for people that travel by airplane or need a prosthesis among many other indirect beneficiaries.

SILVER	GOLD	STAINLESS STEEL
BRASS	BRONZE	TITANIUM

SILVER: Silver 3D printing is one of those materials that is pretty much focused on one type of application which is jewellery. This is not to say that it can be used for other purposes but the metal cost itself plus the indirect production process that requires a good amount of manual labour make this material best suited for small precious objects[9]. Considering that silver objects were never particularly cheap, having the ability to personalize or even design a unique piece of jewellery from scratch can result in a truly astonishing gift. It simply looks amazing, safe to wear and can be polished to a mirror-like surface.

GOLD: Unsurprisingly for some people metals like silver are not premium enough and they feel like stepping up the game. For them, there is gold 3D printing. Needless to say, when you decide to print something in gold you know it probably won't be cheap, but that's kind of the idea. At least you can feel confident that a personalized 3D printed gold gift will definitely be remembered.

STAINLESS STEEL: Stainless steel 3D printing would be the entry level alternative for metal printing. Because its mechanical properties and chemical resistance are greatly surpassed by other metals, it is mostly used for decorative elements. Stainless steel is inexpensive raw material, can be post-processed with a thin coating of several other metals completely changing its appearance, can be polished and heat resistant. The drawback is depending on the technology the surface quality may not be that good and BJ technology imposes some important design limitations.

BRASS: Brass is an alloy of copper and zinc has been used extensively in objects like musical instruments, coins and jewellery among many others. Today with 3D printing this material is mostly used for the jewellery since the typical since in this field is something than most 3D printers can handle. This metal can be a great substitute for those who don't want to spend a lot more for gold, or perhaps to run a test print before 3D printing in gold.

BRONZE: Bronze is an alloy that consists primarily of copper and about a 10% of tin. Thanks to this relatively small addition the new material is stronger than copper alone making it more suitable for a wide range of applications. When it comes to 3D printing this material is most commonly used for jewellery, miniatures and small decorative items.

TITANIUM: Among all the metals that current technologies are able to 3D print, Titanium is the first choice by some the biggest players using metal 3D printing: aeronautic, space, automotive, military and medical

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industries. Although one could 3D print a cool ring or a miniature, most importantly this material is currently being used to 3D print rockets, jet engines, medical implants, F1 car parts and many other key elements for the most advanced technology in existence. The advantages of titanium are highest strength to density ratio of any metallic element, highly resistant to corrosion, biocompatible, strongest material you can currently 3D print.

Fig.4. Objects printed with different metals.

4)OTHERS MATERIALS

The purpose of prototyping is to test part functionality, verify a design, and communicate a concept before moving into manufacturing when money and time are limited resources. There are a variety of materials can be used for this purpose, such as metals, photopolymers, thermoplastics, and others, but we will only focus on digital materials and smart materials for 4D printing as shown in Fig.5, in which a 4D printed flower self-opens upon heat stimulation.

4.1. Digital materials

A digital material is an advanced composite material that consists of two or three photopolymers in specific microstructures and ratios. It can be used to create a functional prototype with tunable characteristics, such as superficial hardness, colours and textures. For example, the latest Stratasys J750 can incorporate over 360,000 colours and load up to six materials at once without swapping canisters in a single build process. In addition, digital materials can simulate various elastomers, mimic standard plastics, produces photorealistic details for different kind of applications, such as functional prototyping, manufacturing tooling, medical models and communication models. Hiller et al. studied the design of digital materials for physical 3D voxel printing. The practical implication is that digital material provides the possibility of fabrication of multi materials objects with micro-scale accuracy using spherical voxel.

4.2. Smart materials for 4D printing

Smart materials are defined as those materials have the capability to transform their geometry under the influence of external stimuli. 4D printing is an emerging topic in the field of 3Dprinting, where the fourth dimension is time and the basic concept of 4D printing is based on the 3D printing of programmable smart materials that can gradually change the shape over time under external stimuli, such as water and heat. Ge et al. applied the concept of 4D printing to the design and fabrication of active origami, where a flat sheet with active hinges can fold into a 3Dcomponent[10]. Rajiv et al. reported a new design of complex self-evolving structure that can transform into a pre-determined shape based on the concept 4D printing. Recently, Ge et al. introduced a new 4D printing approach that can create multi material architectures using shape memory polymer. This approach is based on the projection micro stereo lithography that belongs to vat photo polymerization. Recently, Gladman et al. published a paper about bio-mimetic 4D printing as shown in Fig.6 Composite hydrogel architectures that are programmed with anisotropic swelling behaviour controlled by the alignment of cellulose fibrils along prescribed four-dimensional pathways are reported in this paper[11]. It is important to realize that the efficacy of this bio-mimetic printing concept can only be realized based on the local control of the orientation of cellulose fibrils within the hydrogel composite.

Fig.5. 4D printing of smart materials.

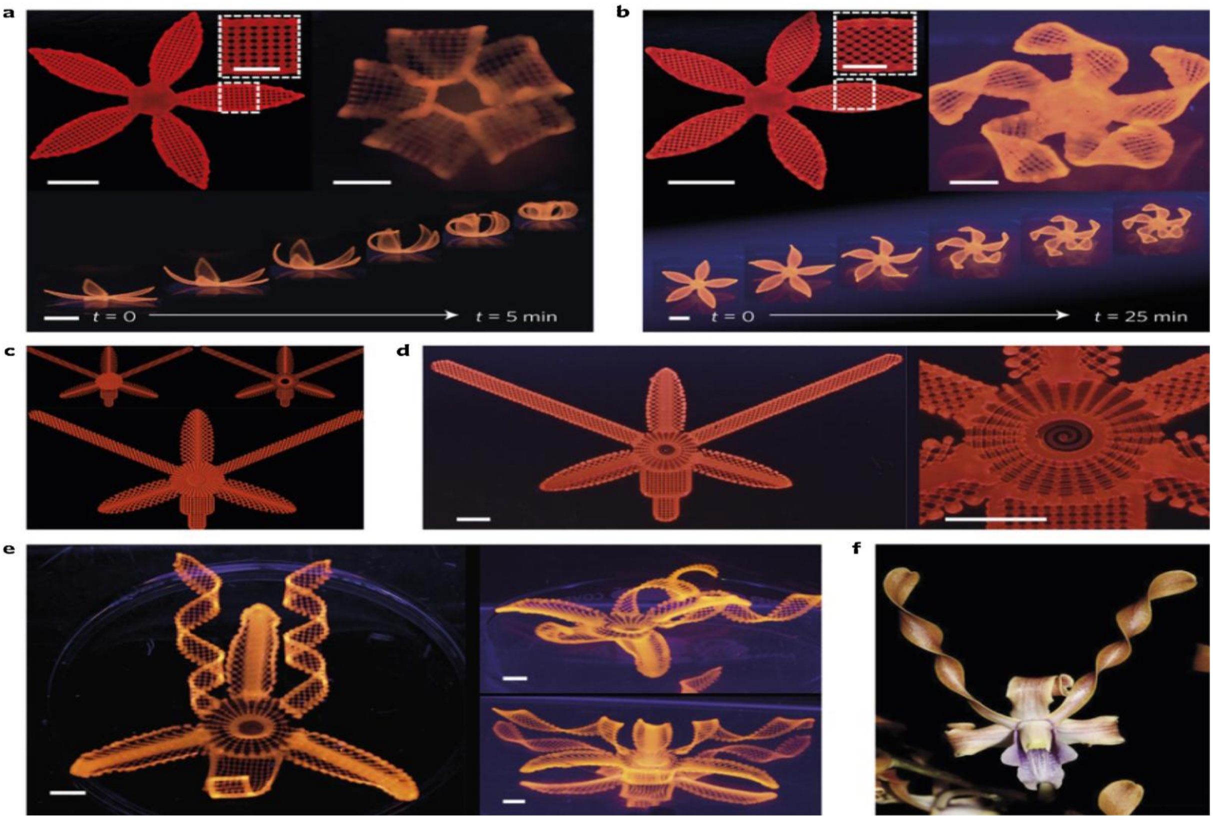

Fig.6. Biomimetic 4D printing.

4.3 CERAMIC MATERIALS

Certain materials, such as ceramics and concrete, are not suitable for 3D printing because the individual powder cannot be fused together by applying heat to their melting point. In contrast, metals and polymers can fuse together by applying heat to their glass transition temperature or melting temperature. Comparing with metals and polymers, the extremely high melting point of ceramics materials is one of the most critical challenges in the field of additive manufacturing. Deckers et al. reviewed the methods of additive manufacturing using ceramics materials. Current AM methods can produce ceramics parts without any cracks or large pores through optimization of the parameters of AM process and their mechanical properties are similar to those of traditionally fabricated ceramics parts. It is also possible to produce pore-free ceramics parts through incorporating colloidal processing techniques in the AM process or performing extra densification steps after the AM process. It is important to highlight that indirect AM processes that involve multiple steps are more suitable to fabricate different kinds of ceramics while direct AM processes that involve only single step are more appropriate to produce ceramics parts in shorter time.3D printing ceramic is a pretty complex multi-step process that impose several limitations to the design process. Despite its modest use, this material has a few great uses: 3D printing the coolest personalized coffee cups and mugs, tableware items and pottery designs. To address the challenges of ceramics in AM process, Eckel et al. reported a novel way to fabricate a 3D printed ceramics parts using specific pre-ceramics monomers mixing with UV photo-initiator as shown in Fig. 7

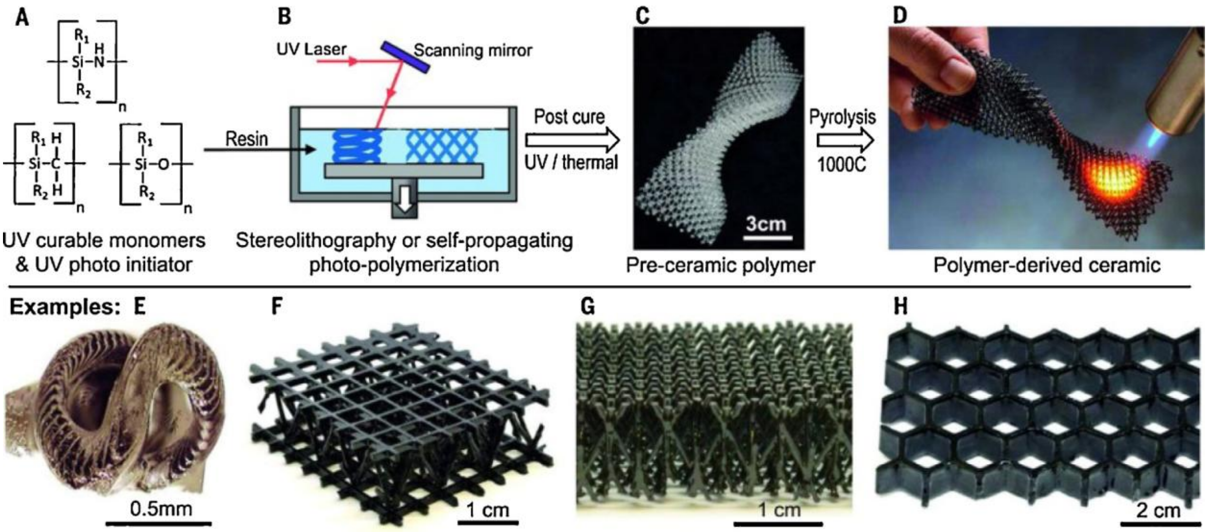

Fig.7. Additive manufacturing of polymer-derived ceramics.

4.4 Electronic Materials

In the past decades, there have been significant advancements in electronics materials in the field of additive manufacturing. One interesting research question that arises is whether3D printing of fully functional electronic devices is the best approach for fabricating mass-customized electronics. Cur-rent AM technologies allow fabrication of functional electronics, such as antenna, capacitors, resistors and inductors, in a single step without any post-processing. Aerosol jet printing and inkjet printing are two of the most common technologies use in this field and they can be classified as non-contact printing due to their nozzles will not in direct contact with the 3D printed electronics. Kimet al. reported the fabrication of thin-film transistors, which are flexible on plastic substrates using self-synthesized silver ink. Jung et al. demonstrated a method to print resistors on a plastic substrate, which can achieve higher resistance value with high repeatability using conducting polymer. Kong et al. showed that five different materials: (1) quantum dot nano-particles; (2)an elastomeric matrix; (3) conducting polymers; (4) metal leads;(5) a UV-adhesive transparent substrate layer, can be 3D printed and fully integrated into device components with active properties. The 3D printed quantum dot-based light emitting diodes (QD-

LEDs) and it exhibits pure and tunable colour emission properties. Based on these papers, it is concluded that 3D printing is a versatile method to fabricate electronic devices and is capable of integrating many distinct classes of materials.

4.5 Biomaterials

Recent developments in biocompatible materials have enabled 3D bio-printing of functional living tissues, which can be applied to regenerative medicine to address the need for organs transplantation. The materials have to be biocompatible, whereby it evokes host responses appropriate in a specific application with minimal non-specific activity; bio restorable, where the degradation rate is proportional to the regenerating rate of the target tissues/organ; and can withstand medical sterilisation procedures to prevent infection [12].Generally speaking, the materials of 3D bio printing is very limited, mainly natural polymers and biocompatible synthetic polymers such as modified diblock copolymers, sodium alginate, chitosan and acrylates-based polymers but the material selection is one of the most critical steps in 3D bio printing. 3D bio-printing usually consist of alginate or fibrin polymers that have been integrated with cellular adhesion molecules, which support the physical attachment of cells. Bio-printing of several materials including hydrogels and embedded filaments would increase the mechanical stability of the constructs[13].These polymers are specifically designed to maintain structural stability.

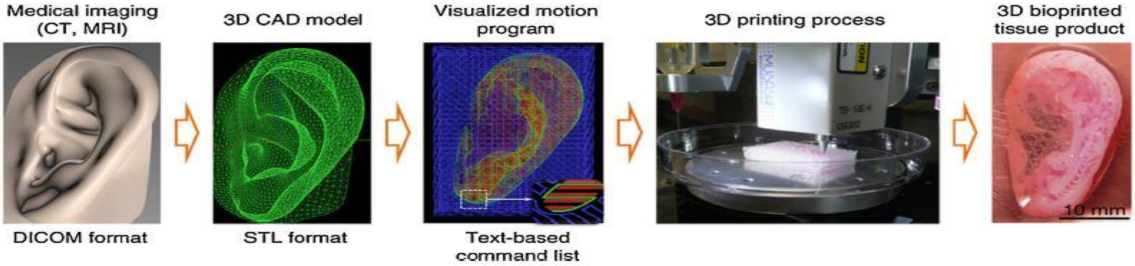

Fig. 8. Integrated tissue–organ printer (ITOP) system.

4.6 CASTABLE WAX

This material has been designed to manufacture small metal objects with exceptional precision using the lost-wax casting process. This is essentially a middle step to 3D print metals such as silver, gold, bronze or brass, among many other metals. Wax prints are used to create the mould that will later hold the molten casting material. Gives brave enthusiast and professionals the chance to create sophisticated metal objects in the most affordable way. Requires some additional skills and knowledge and equipment to cast an object with the wax print and Wax prints are very fragile and temperature sensitive.

Fig.9. Object printed with castable wax.

V. VARIOUS PROCESSES USED FOR DIFFERENT MATERIALS.

Table.1. Materials used for different technologies[13].

Technology	Polymers	Metals	Ceramics	Composites
Stereolithography	●			●
Digital light processing	●			
Multi-jet modeling (MJM)	●			●
Fused deposition modeling	●			
Electron beam melting		●		
Selective laser sintering	●	●	●	●
Selective heat sintering	●			
Direct metal laser sintering		●		
Powder bed and inkjet head printing	●	●	●	●
Plaster-based 3D printing			●	●
Laminated object manufacturing	●	●	●	●
Ultrasonic consolidation		●		
Laser metal deposition		●		●

Table.2. Materials Used for different Additive Manufacturing Processes

PROCESS NAME	MATERIALS
FDM	ACRYLONITRILE BUTADIENE STYRENE (ABS),THERMO PLASTIC POLYURETHANE (TPU),ASA, Nylon 12, PC,PPSF/PPSU, POLYAMIDE (PA), POLYLACTIDE (PLA), HIGH IMPACT POLYSTYRENE (HIPS), POLY VINYL ALCOHOL (PVA), POLYETHYLENE TEREPHTHALATE (PET), GLYCOL MODIFIED PET (PETG), POLYCARBONATE (PC), THERMOPLASTIC ELASTOMER (TPE)
SLS	POLYAMIDE (PA), ALUMIDE, THERMOPLASTIC POLYURETHANE (TPU), THERMOPLASTIC ELASTOMER (TPE)
SLA	RESIN, CASTABLE WAX
DLP	RESIN, CASTABLE WAX
POLYJET	RESIN, Digital ABS, Fullcure RGD 720, Rubber-like material, Dental material
LWC	GOLD, SILVER, BRASS, BRONZE
DMLS	STAINLESS STEEL, TITANIUM
SLM	STAINLESS STEEL, TITANIUM
EBM	STAINLESS STEEL, TITANIUM
BJ	STAINLESS STEEL,TITANIUM,CERAMIC BEADS,INCONEL ALLOY,IRON
MULTIJET	CASTABLE WAX

VI. CONCLUSION

This review summarizes the fundamental aspects of AM processes and materials. An effort is made to list the types of materials available and which is used for different AM technologies. 3D printing is versatile in terms of materials and the versatility of 3D printing material comes from system variety but for each specific applications such as bio-printing, the biocompatible materials are still limited and further development of materials are still required. All the new printers or processes for materials have not gone beyond the seven categories and most still work with a single material with limited industrial applicability. The development of smart materials should be in parallel with advances in 4D printing techniques.

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