3D Printing and advance material technology

[1]Dr. Nilesh Ghongde, [2]Amit Sachdev

[1]Associate Professor, [2]Research Scholar
M.H.Saboo Siddik College of Engineering
Mumbai-400008

***Abstract*: Three-dimensional (3D) printing an additive manufacturing technique which has been around for few decades but it's capabilities to produce complex structures as required by consumer and industries from a 3D computer-aided design model without the need of any tooling, dies and heavy machinery makes it a step-up to the present manufacturing techniques. In the world of developing technologies, 3D printing will soon be replacing our conventional manufacturing system consisting of casting, forging and will also be able to deliver better results then CNC machining. With extreme versatility, ease of manufacturing, rapid process and accelerate innovation, reduced energy and material consumption, this automated manufacturing process is being currently incorporated into industries like Prototyping, Automobile, Medical, Aviation and space exploration industry. Additive manufacturing has also reduced the need for human resources, huge capital investment and need for additional framework. For more than 25 years a concentrated research, development and use of additive manufacturing has resulted into a fully mature manufacturing techniques with endless capabilities. Through this article the latest research trends in advance printing techniques such as SLS, DLP, LOM are reviewed along with their future prospects. The article also presents a study on different materials available for printing application as per the end product requirements. Finally, this paper gives a brief description of some advance developing materials such as composites (ABS with Chopped/Continuous carbon fire or Graphene) and Nanocomposites incorporation Carbon nanotube (CNTs). A detailed comparison of advantages and drawbacks along with their properties of different materials is bestow for the readers.**

***Keywords*: Additive manufacturing [AM]; Computer-aided Design [CAD]; 3D printing; Polymers; Nanocomposites; Carbon Nanotubes.**

1. INTRODUCTION:

In the Industrial revolution 4.0 there has been a search for advance manufacturing technologies to find the solution for the quickly changing market which impose high demand for variability, efficient supply chain and optimized energy consumption. As a result, the further growth of industry is supported by the modern manufacturing technologies to increase production capabilities [1]. In the context to the smart manufacturing methods, improvements in the optimizing labor, energy and materials to produce a high-quality product is required.

Of the many production technique, rapid prototyping or additive manufacturing has been developed to be the most suitable manufacturing practice for the current industry type [2]. This technology has substantially improved in the recent years and has evolved as a useful tool for many fields like research and development, manufacturing, designing and engineering. With the benefits of the reduced manufacturing and development time of products, also the variability in terms of the shape and size and almost zero waste material in production.

Additive manufacturing or commonly known as 3D printing has become an innovative and promising method of manufacturing [3]. Additive Manufacturing (AM) is a collection of versatile techniques of rapid prototyping that allows material to be designed in 3D digital models before manufacturing [4]. Additive Manufacturing is a technology that produces parts from 3D models one superfine layer at a time. The process consists of bondage of successive layers to the preceding layer. Through this approach complex and low batch number parts can be easily manufactured under the control of a computer. The difference between traditional manufacturing and 3D printing is that the 3d printer involves additive approach but most of the traditional manufacturing processes involve subtractive approach that includes a combination of grinding, bending, forging, moldings, cutting, gluing, welding and assembling [6].

In the recent years a lot of research and development has gone in advancement of Additive Manufacturing (AM) in terms of the materials used as well as the techniques used to manufacture products, all have been covered in this paper with more emphasis on the advancement made in the materials for future use.

2. 3D Printing Process:

The first robotic 3D printer was developed by Charles W. (Chuck) Hull in 1984. But it was first in 1990 when the plastic extrusion process for manufacturing was used with the term "3D printing" was invented by Stratasys by the name fused deposition method (FDM). However, it wasn't till 2009 when the patent for FDM printers expired and there was a drop in the prices from $10,000 to $1,000. This was the time when many manufactures paved their way into making commercial printers for the usage of rapid prototyping and the growth of 3D printed parts in the market was sensed. Since then there has been a lot of development in the field of additive manufacturing ranging from metal 3D printing to desktop manufacturing for prototyping.

With the current growth rate of additive manufacturing technique, it is estimated that the worldwide market for 3D printed products and services is anticipated to exceed 40 billion U.S dollars by 2024. The industry is expected to grow at a compound rate of 29 percent between 2020 and 2024.

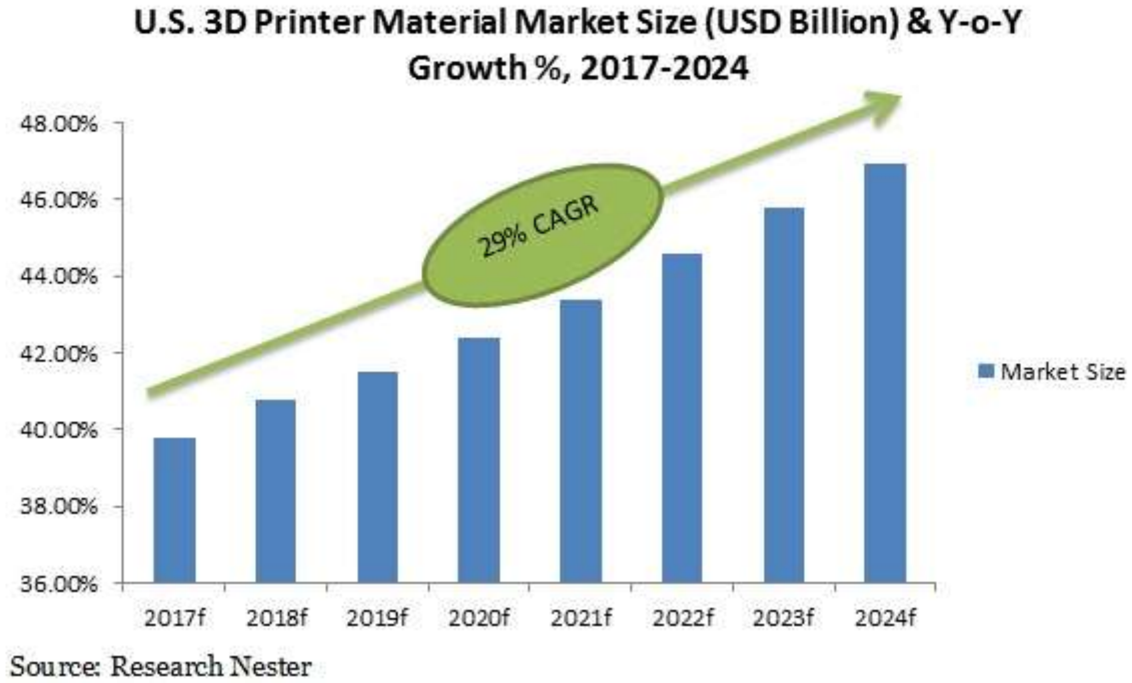

Figure 1: Growth of 3D printing market [7]

3D printing process is generally done in the same way as mentioned. Firstly, the modeling is done with the help of the CAD tolls and then the printing is done. These steps are explained in detail below and also shown in the flow diagram in fig 2.

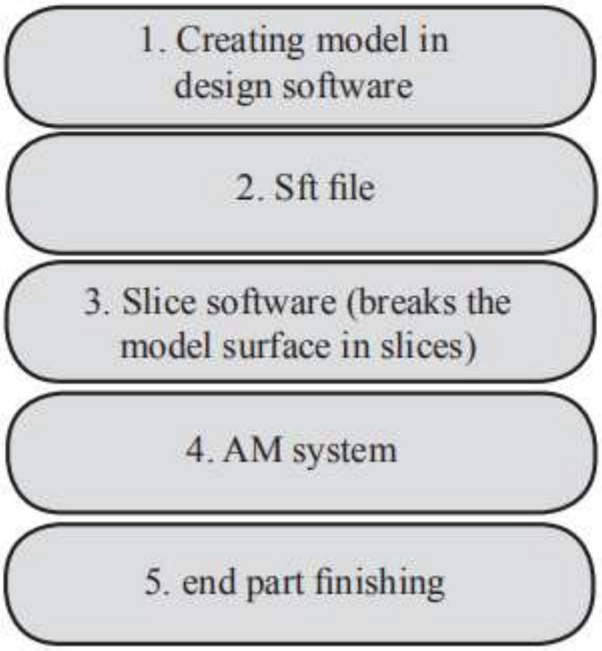

Figure 2: Process steps in 3D printing [6]

a) **Modelling**: The first step in printing 3D models is to create a model of exact dimensions as the part to be printed with the help of computer-aided design (CAD) package or via a 3D scanner. 3D models created by with CAD software have less errors as compared to the other methods. 3D scanning is an emerging technology to produce models by collecting digital data on the shape and appearance of real objects. CAD models are saved as stereolithography file format (STL) for additive manufacturing that stores data based on the triangulation of the surface of CAD models. SLT files have large file sizes due to large number of surfaces involved which make it not suitable for additive manufacturing. However, to deal with this problem a new CAD file format is introduced in 2011 i.e. Additive Manufacturing File Format (AMF) which stores information using curved triangulation.

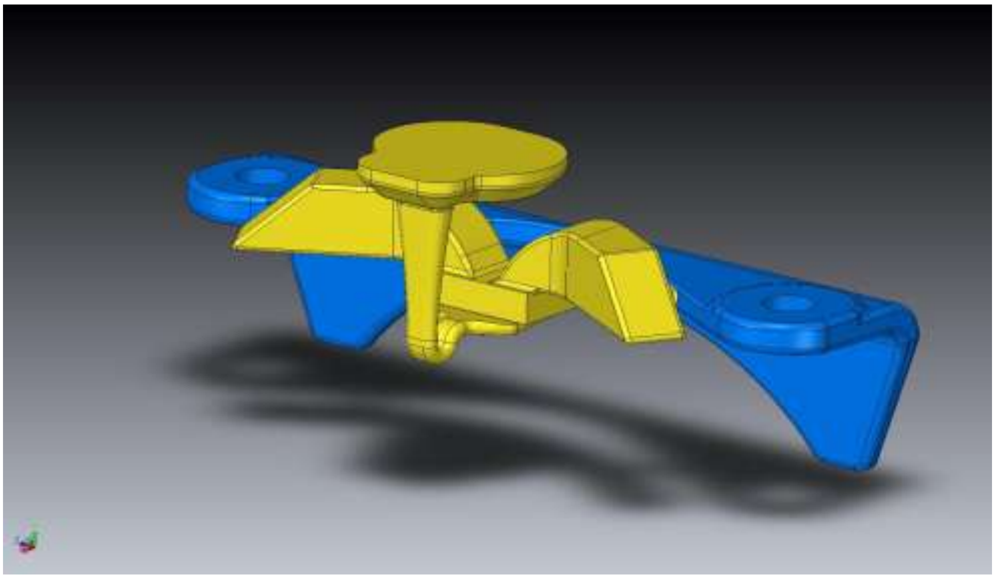

Figure 3: CAD model prepared for 3D printing [8]

b) **Printing:** Before printing the 3D model from the STL file we have to check for the errors in the file or the model. After corrections the file is fed to a software know as slicer, which converts the model into thin layer or slices to produce a dG-code file containing instructions for the 3D printer. This G-code file is then loaded into the 3D printer to print the parts as per the instructions.

Figure 4: Printing process using the G-code file. [9]

The figure 4 shows a 3D printer in action and is using the G-code file to print the part. The G-code file is nothing but a set of instructions derived from the slicer software which instructs the printer to print on a layer-by-layer basis. The G-code as shown in above figure always consists of the coordinate instruction for the printer in all three plain (X, Y and Z) and also the layer thickness.

c) **End Part Finishing**: Even though the 3D printer produces high resolution parts those are strictly according to the sizes mentioned for a part. But sometimes greater accuracy can be achieved by printing a slightly over-sized parts and then removing excess material by using a higher-resolution subtraction process. [8]

As additive manufacturing technique works on layered structure this leads to generation of a stair-steeping effect on the parts surface. This steeping effect can curve or tilted to the building platform and has to be rectified while finishing process for a smoother surface. Printable materials such as ABS can have their surface finish smooth and improved with chemical vapor processes based on acetone or similar solvents.

There are many methods for the post-processing of the parts to have the desired dimensions and surface finish. Most commonly used in industry are sanding, Bead blasting, tumbling, Vapor smoothing and Plating [10]. The figure 5 we can sum-up the printing process as explained above.

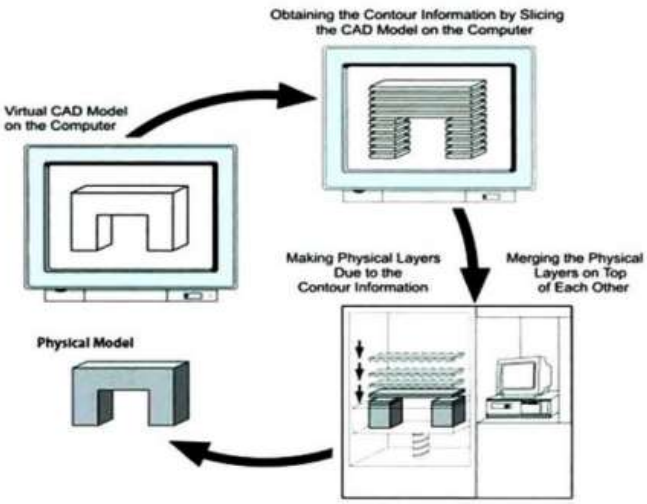

Figure 5: Overview of Printing process. [11]

3. 3D printing techniques:

Since the introduction of 3D printer in 1970, a lot of research and development has gone into the search of better and efficient technology to replace conventional manufacturing method. Earlier 3D printers were large and very expensive as compared to the parts they produce. So, with recent advancement many additive manufacturing techniques have been developed each having its own advantages. Some methods use melted or soften materials to lay layers to form the parts e.g.: Selective laser melting (SLM), selective laser sintering (SLS), Fused deposition method (FDM), while some techniques make parts directly from liquid material such as stereolithography (SLA) and laminated object manufacturing (LOM).

Some 3D printing techniques are specifically designed and developed for some particular material or application such as: - [12]

- For printing **plastic or Alumide**: Fused deposition (FDM) or SLS technology is used.
- For printing **Resin or wax**: Stereolithography (SLA) or Digital Light Processing (DLP) or Continuous Liquid Interface production (CLIP)
- For print printing parts using **Metal**: Direct Metal laser Sintering (DMLS), DLP, Electron Beam Melting (EBM).

The list of 3D printing technologies and processes continues to grow as 3D printing is an emerging technology with advancement made every day. The 3D printing industry continues to innovate its hardware as well as the materials and processes to create objects or parts. There is a total of 11 types of 3D printing techniques that have been developed and are used today. All these techniques are briefly explained in this section.

3.1 Stereolithography (SLA):

SLA is rapid prototyping technique which uses melted or semi melted polymer plastic to make a 3D printed part. This technology was introduced as early as 1970 and today is being widely used by engineers to produce prototypes of the final product with accurate dimensions and precision.

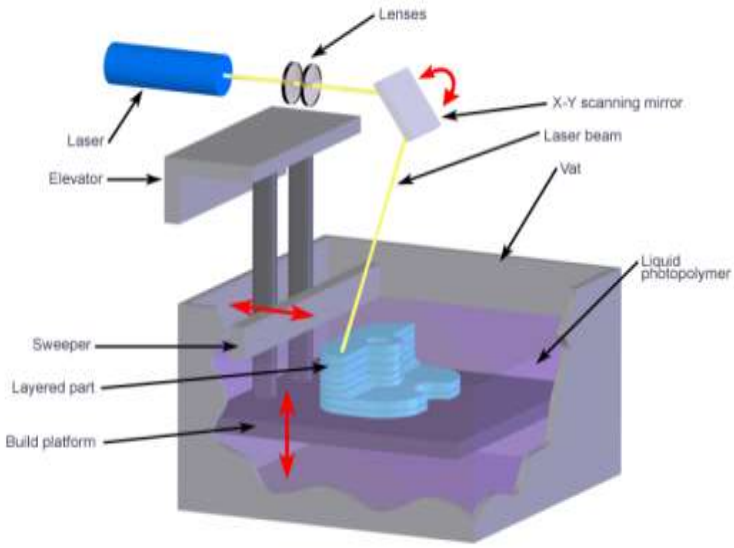

Figure 6: Stereolithography (SLA) setup.[11]

Observing the above figure 6 Stereolithography process setup can be understood. Liquid resin (liquid photopolymer) is placed in a vat having a transparent bottom. Liquid photopolymer (a special type of plastic) is the name given to the liquid used in this technique as this material can solidified to create 3D parts. In this technique a UV (Ultraviolet) laser traces a pattern on the liquid resin from the bottom of the vat. The resin is first heated into a semi-liquid form and then it solidifies. [13]
So, layer-by-layer the resin is solidified to form the desired structure and once completed the solidified structure is carefully separated from the platform. After the printing stage, the parts usually go for a chemical bath to remove any excess resin and then straight into an ultra violet oven for post-cure procedure. SLA has come up as a favored economical choice for industrial application. Some application of this technique has found its way into automobiles, medical, aerospace, entertainment and also in consumer products.

3.2 Digital Light Processing (DLP) Technology:

DLP technology to print 3D printed parts is one of the oldest techniques used in this field. DLP was introduced back in 1987 by a person named Larry Hornback. DLP printing technology is very similar to the SLA technology as discussed above in terms of working and construction. The only key difference between two technologies is that DLP uses different light source than the SLA technology. DLP uses more conventional light source i.e. Digital light projector and the light is controlled using micro mirrors that controls the light being incident on the surface of the object being printed.

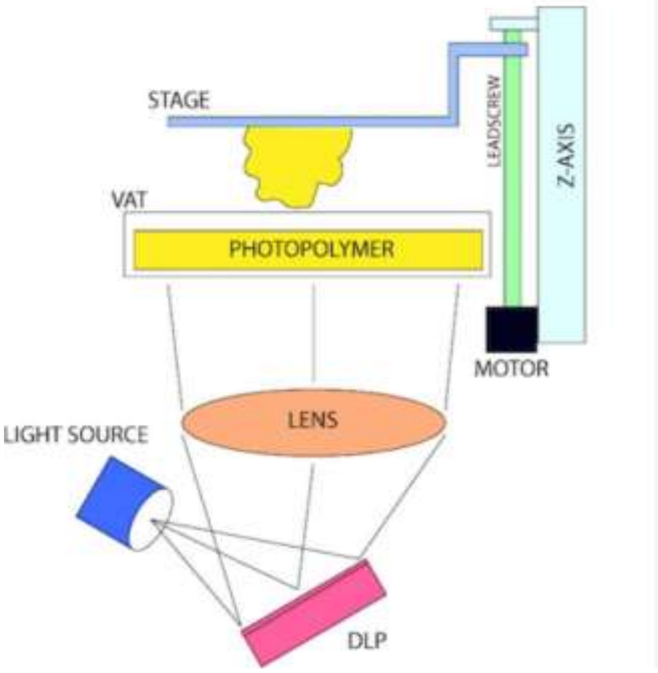

Figure 7: Digital light processing (DLP) setup. [14]

In DLP process of printing the light flashes and crystallizes layers instead of single points made by laser in SLA. Through the figure 7, the set-up of DLP technique to print parts can be observed. The liquid plastic resins used to make 3D object goes into a translucent resin container and light is used to harden the resin just as in SLA.
But there are sone advantages to DLP technology over SLA: -

- Better printing speed
- DLP setup is robust as well as economical at the same time.
- DLP always produces high resolution models.
- The material wastage is also less and parts produced using DLP are also cheaper in manufacturing.

3.3 Fused Deposition Modeling (FDM):

FDM is the most commonly used 3D printing technology these days and was developed by Scott Crump and then implemented by Stratasys Ltd. In **1980**. After the patent to this technology ended in **2009** there was a sudden surge in large open source, community and commercial development of 3D printers using this FDM technology. This development made this technology available to the masses and now it is the most preferred choice of the industries for rapid prototyping. This printing technology is now also available in form of the desktop printer having small sizes.

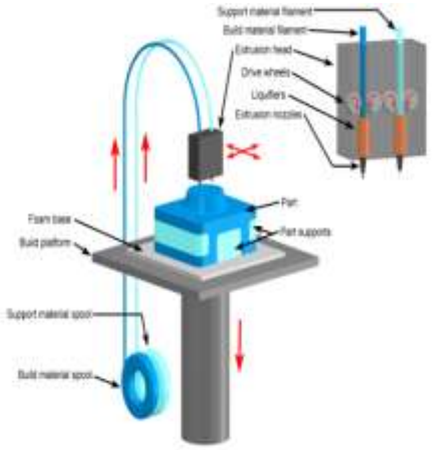

Figure 8: Fused Deposition Modelling (FDM) setup. [11]

With the recent year development in FDM technology and mass production has led to significant drop in its prices since its creation. Referring to figure 8, the construction and setup layout for FDM 3D printing can be observed. The major parts of the system are the material in form of thin wires, the melting extrusion tip and the controlling unit to read the G-code. In this technique, the model is produced by extruding small beads of material which harden to form layers.
The melting of the material takes place at the nozzle and the directional accuracy to lay the material is done by Stepper-motor to move the nozzle in all 3-directions. The head can be moved in both horizontal and vertical directions, and control of the mechanism is done by a computer-aided manufacturing (CAM) software package running on a microcontroller.

3.4 Selective Laser Sintering (SLS) Technology:

SLS technique to print 3D objects was introduced in mid-1980s by a man named DR. Carl Deckard. He developed and patented this technology which was further used to establish a company named DTM. By year 2001, DTM was acquired by their competitor 3D Systems. DTM had a patent on Deckard's selective laser issued in January 1997 and expired in January 2014.

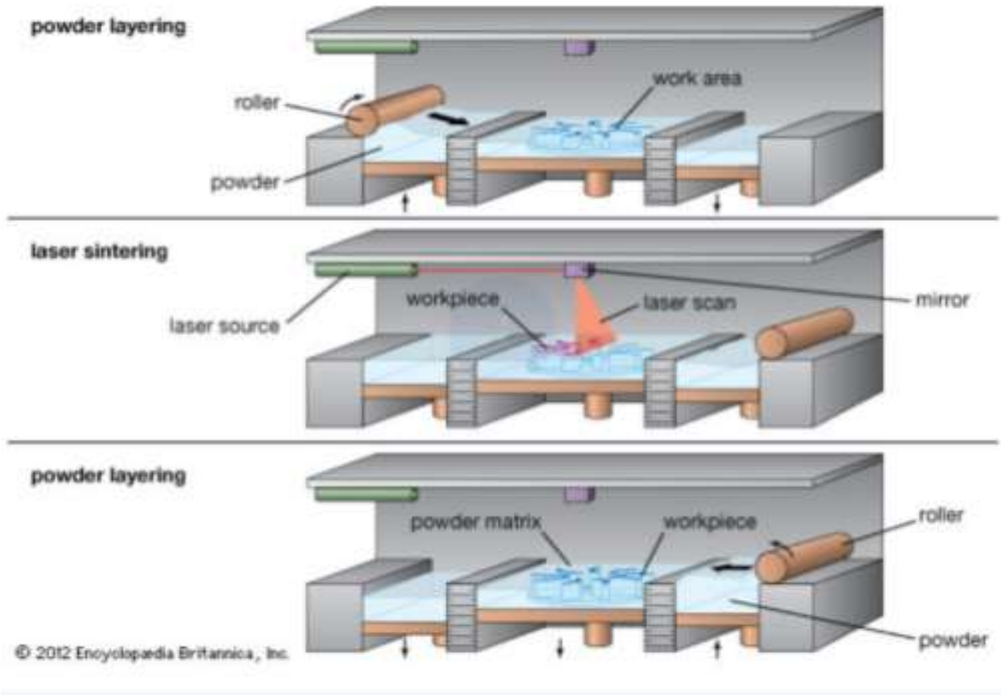

Figure 9: Selective Laser Sintering (SLS) [13]

From the above figure 9, it can be observed that SLS technology also used the concept of SLA technology in a modified way. SLS technology however uses pondered material along with CO2 lasers to fuse the particles together to make 3D objects. In the process of printing parts, the powdered material is placed in vat and according to the G-code file layer-by-layer the material is solidified to give shape to the object.

3.5 Laminated Object Manufacturing (LOM):

This technology was first developed by a Californian company called Helisys Inc. (now Cubic Technologies). The patent of this technology is on name of a US design engineer called Michael Feygin.

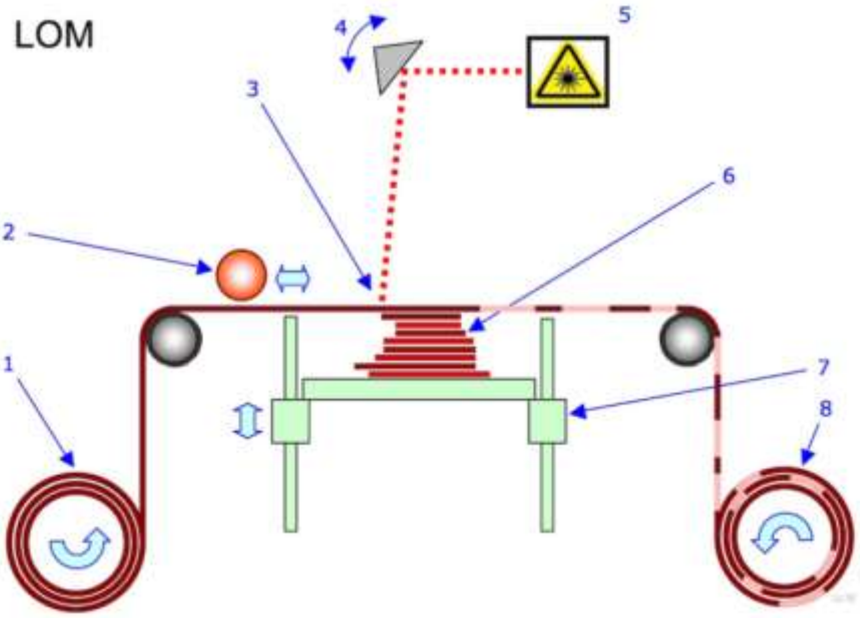

Figure 10: Laminated Object Manufacturing setup [14]

LOM is a rapid prototyping system in which layers of adhesive-coated paper, plastic or metal laminates are fused or laminated together by applying heat and pressure and cut as per design by a computer-controlled blade or laser cutter to give the desired shape to the 3D printed part. For the printing process of combining many layers of the laminate together every time when a layer is applied the platform on which the part rest is moved down by about 1/16th of an inch, ready for the next layer. The printing process can be easily understood by observing the figure 10.

Following are the major parts depicted in the figure 10: -

- Roll of thin layer material of which the part is being made
- Heating roller which heats the adhesive on the sheet to make the layer stick together
- Platform on which the part is printed.
- Adjustable mirror to focus the laser cutter as per design requirements
- Laser generator
- Printed part
- The mechanism that moves the platform lower once a layer is laminated
- Rolled material that can be reused by meting to make new rolls.

4 Materials used for 3D printing: -

Material and printing technique are the most important parameter that has to be determined before printing a part by 3D printing technology. This can only be done by carefully observing the parts functionality and applications requirements. As we discussed in the last section about the different 3D printing technologies available today and anyone can be chosen as per requirement on basis of cost, material or no. of parts to be produced.

Coming to choosing material for 3D printing, the sky is the limit and researchers are working rigorously to make new 3D printable material. When 3D printing an object, choosing the correct material for the application is just as critical as choosing the best printing technology. With the advancement in 3D printing technologies new materials as well as more advance 3D printing machines are been developed with enhanced technology.

In the coming section more information on materials available or are in development stage are discussed: -

❖ Most of the 3D printable material available today can be categorized into the category of Polymers, Metals or composites.

4.1 Polymers: -

The most commonly used material these days for rapid prototyping are the Polymers. These polymers can be biological or inorganic in nature, Plastics are also commonly referred as polymers.

Figure 11: Polymers material. [15].

These compounds are made of synthetic or semi-synthetic compounds that are malleable in nature (capable of changing shape) and are thermoset in nature. The synthetic polymers are generally derived from petrochemicals but, due to environmental concern nowadays plastics are derived from renewable material. The ease of availability and cost effectiveness' of these synthetic polymers are the root cause of the growth of the 3D printing industry. Figure 15 shows filament type polymer and the final product.

Fused Deposition technology is the most popular and affordable 3D printing technology in market today and prints by the process of extrusion of plastic filaments. So, a material is required that can be formed in filament form and then can be easily thermoset to form different structures. Even though FDM is widely used but, in terms of accuracy and finish of the final product it is no way near to other advanced technologies such as SLS or SLA. As discussed earlier all advance technologies used lasers or special Photo-resins or powered materials to achieve higher accuracy or finish. So according to the requirement and part quality the 3D printing process or material can be selected as per convince. Through past R&D many forms of polymers have been developed and some of which are discussed in brief below:

All plastics used for additive manufacturing are either in filament or power form, the plastic melts and solidify to form the structure layer-by-layer. In resin or liquidly form the resin should solidify to form the object. Figure 12 shows the available forms of polymers.

Figure 12: Common forms in which polymers are available.

A comprehensive guide to polymers is given below: -

4.1.1 ABS:

Acrylonitrile butadiene styrene (ABS) it is a terpolymer compound fabricated by polymerizing styrene and acrylonitrile with polybutadiene. ABS is the most commonly used material to make 3D parts. ABS because of its versatility and cheap price is preferred by many to make 3D parts. ABS is available in filament, powder as well as liquid form for FDM, SLS and SLA printing process respectively.

Figure 13: Common available form of ABS material [16].

4.1.2 PLA:

Polylactic Acid (PLA) has gained popularity for being the best bioplastic in world i.e. it's biodegradable. PLA is prepared from renewable, organic resources as corn starch or sugarcane. PLA is one of the easiest materials to work with as it doesn't shrink on solidifying, environmentally friendly, available in variety of colors and is available in resin/filament form. PLA is generally used to make food packaging and biodegradable medical devices and implants.

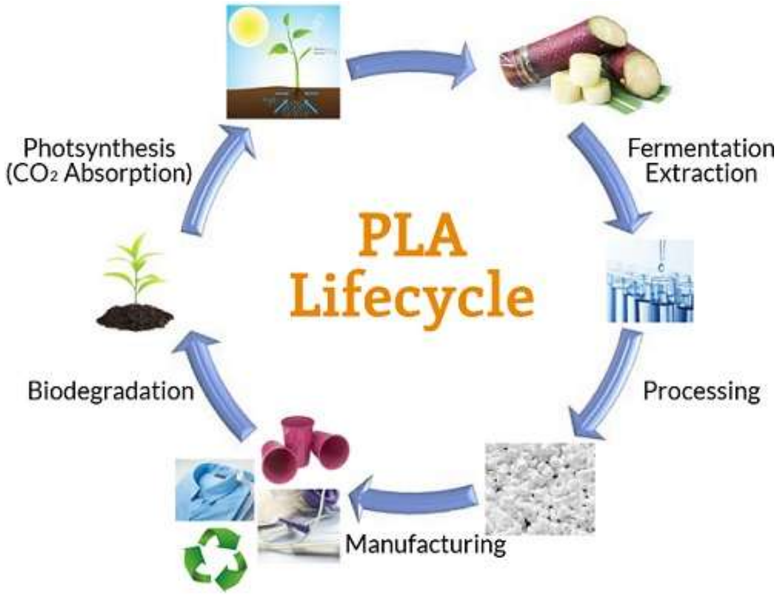

Figure 14: PLA extraction process. [17]

PLA extraction process is easy and eco-friendly as shown in figure 14. PLA can form some issues while printing due to its high cooling and solidification speed. Moreover, the parts made by this material deteriorates when in contact with water.

4.1.3 PVA:

PVA and HIPS (high impact Polystyrene) are special types of Polymers that are printed with the intention of being dissolved in the future stages of manufacturing process. These two soluble filament materials, HIPS in association with ABS can be dissolved with limonene. Whereas, the most common and applicable soluble material PVA can be dissolved in water easily.

Figure 15: Final product after using PLA as the support structure [19].

PVA are hydrophilic, water soluble, biodegradable thermoplastic polymer synthesized by the hydrolysis or alcoholysis of poly (vinyl acetate) (PVAc) due to the instability of its vinyl alcohol monomer.

PVA (Polyvinyl alcohol) being dissolvable in water is being used extensively as to make support structures as shown in figure 15. Support structures are necessary when printing 3D parts with notable overhang. PVA works best with printers with duel extruders. PVA is non-toxic and biodegradable and also need low temperature 190°C – 220°C. With PVA complex geometric water-soluble structures can be produced. The figure 16. shows the step by step printing process of such a part.

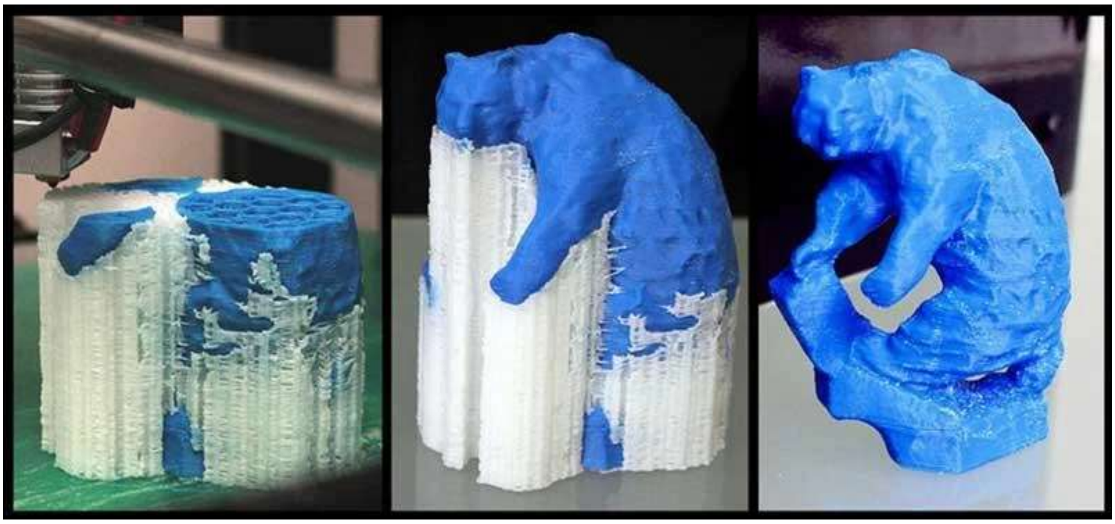

Figure 16: Printing process in duel extruder 3D printer. [20]

When PLA is used as the support material any complex shape with details as shown in figure 16 can be produced easily. The support to the part is printed in PVA and at end part finishing stage the PVA material is dissolved in water, leaving only the ABS or other material art in place. Other than support material PVA is also used as a thickener in paper adhesive, in personal hygiene products, as a mold-release agent and for freshwater fishing products.

4.1.4 Thiol-Ene and Thiol-Yne:

These polymers are available in resin form only and is popularly used for stereo-lithography and inkjet printers in which UV light is used to solidify the resin to form the part structure. When parts are manufactured by SLA technique they are subjected to ambient air and immediately shrinks after coming out of the vat. But as thiols are reactive to carbon-carbon double bonds they are inhibited by molecular oxygen. This compound has clear advantage over (meth)acrylate-based resin material. During printing process acrylates undergo a radial chain growth formation as shown in figure 15.

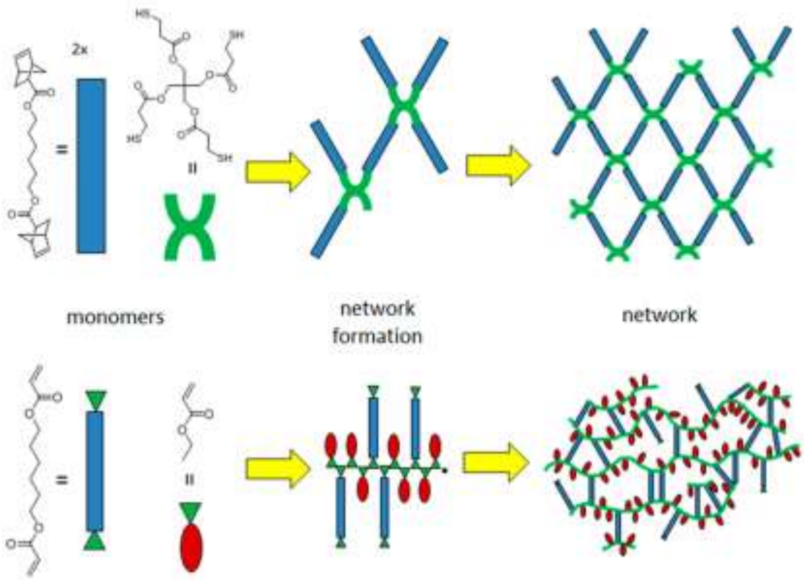

Figure 17: Thiol-Ene and Thiol-Yne chain formation. [18]

A quick comparison of the most commonly used polymers is shown in figure 16. So to conclude the Polymer section all the polymers are compared on parameters that are important for any 3D printed part. Observing the image, it would be easy to understand which material is better for an application and which one is better suited for another applications.

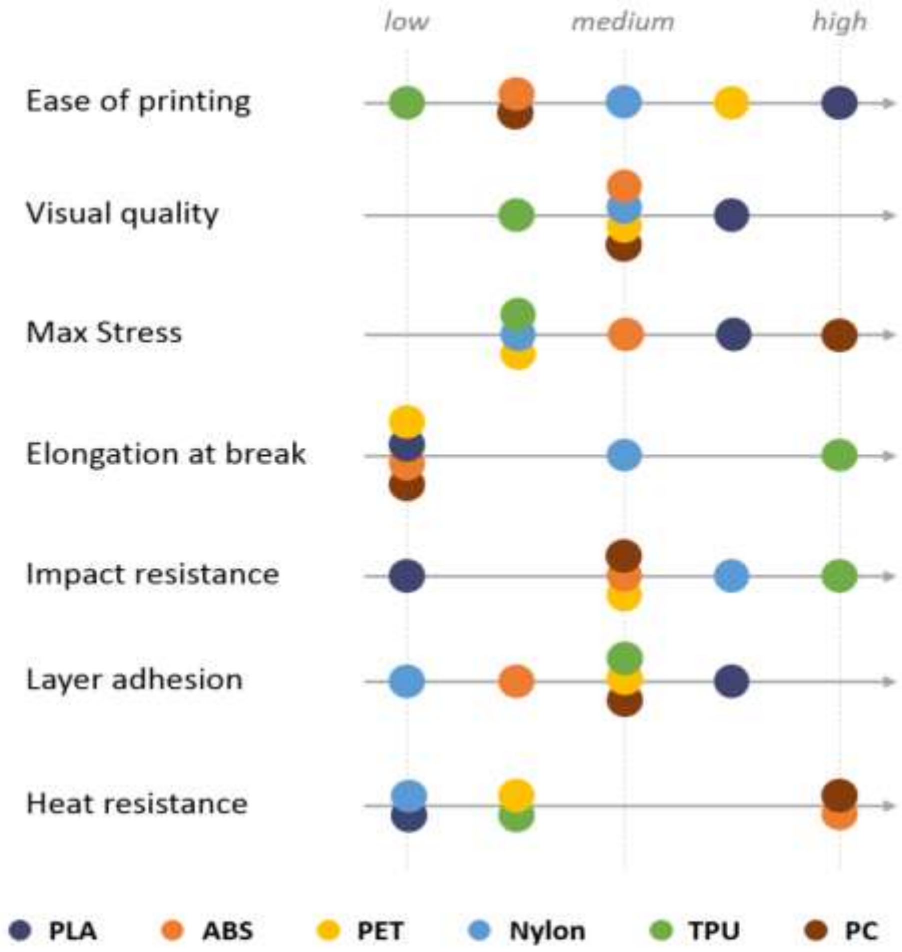

Figure 18: A comparison of 6 polymers. [19]

After going through figure 16, it is clear that **PLA** is the easiest polymer to print and also provides good visual quality. The parts made by PLA are also rigid and strong but the con to this material is that it has low humidity resistance. Looking at the **ABS** plots it is clear that it has higher temperature resistance and higher toughness as compared to PLA. The only drawback to ABS is that it is sensitive to UV and high fumes are released while printing it. **PET** is an all-rounder in every department with some additional benefits such as high chemical resistance, recyclable and good abrasive resistance. **Nylon** possesses some great mechanical properties and the best impact resistance. However, it does face some issues of moisture absorption and difficulty in layer adhesion while printing. Thermoplastic polyurethane (**TPU)** is the most flexible of the all and also possess high impact resistance property. Polycarbonate **(PC)** is the strongest of the all material in terms of heat resistance, impact resistance and max stress capacity.

4.2 Metals: -

The next category of 3D printing material having the highest potential in coming future is metal 3D printing. For many centuries we have been using metals for various applications where plastics or polymers are not a suitable option such as making tools, car parts those are subjected to very high stresses. With limited resources and need for light weight & high strength metal parts. 3D printing of metal parts has shown a great potential to achieve lighter parts than casting with similar strength and at the cost of less material usage and less pre & post-manufacturing processes.

Metals have become the 2nd most popular material in 3D printing industry after Plastic printing for rapid Prototyping. Many researchers and manufactures are using plastics to print the parts as prototypes and study its ergonomics & feel to further improve the design. Then the final product is being manufacture by metal 3D printing by this approach in the recent years there has been improvement in speed of R&D department and less usage of metal and associated parts & machinery required to make products.

Metal 3D printing is finding its newer application in various industries day-by-day such as in the Medical field to produce stunts for heart, Automobile industry to produce parts having less material but the same strength as casted parts or the jewelry industry to make more complex art pieces. All this have been possible due to newer technologies in printing techniques as well as the material that are available to print.

To 3D print the metals there are several methods to do so same as in case of the polymers or plastics. The metal 3D printing processes can be classified in basic two forms such as: -

a) **Powder bed process**: SLM/SLS, DML, LMF and EBM
b) **Additive procedure**: LMD, DED, DMD, Laser cladding and MPA.

❖ The most commonly used techniques to 3D print metals is briefly explained below: -

1) SLM – Selective Laser Melting

SLM as well as Direct Laser Sintering process both are additive manufacturing processes that belong to the powder bed fusion manufacturing process. Before going deep into the concept and procedure it is good to know more about the powder bed fusion technique. In which a slider is used to lay down thick layer of the powdered metal on the building platform and simultaneously the laser or electron beam melts and fuse the particles together to form the desired structure.
The process visual of SLM or Direct Metal Fusion Sintering (DMLF) can be seen figure 19. As shown in the picture the printing process is done in a chamber filled with inert gas (for example argon) to minimize the oxidation of the metal powder. On every layer built the slider lays another layer of the powder material to be fused and also the building platform keeps on moving one step downward. Once the scanning is done the part is removed from the powder bed and excess powder is manually removed. The final product is heat treated while still being attached to the building platform to relive any residual stresses. And finally, the part undergoes post printing finishing stage via cutting, machining or wire EDM and is detached from the build plate.

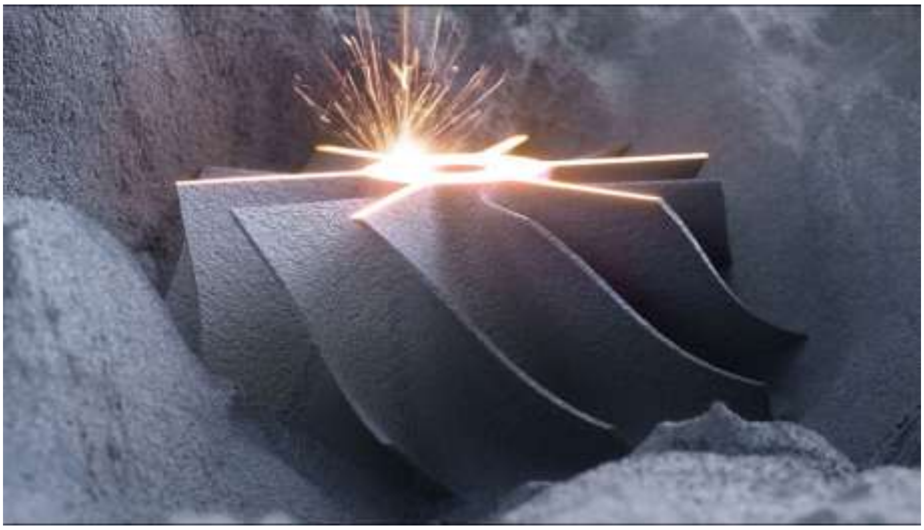

Figure 19: 3D printed part with SLM process. [21]

SLM and DMLS processes can produce parts from a large range of powdered metals and metal alloys including **aluminum, stainless steel, titanium, cobalt chrome and Inconel**. These materials cover most of the industrial needs from aerospace to medical. Precious metals such as **gold, platinum, palladium and silver** can also be processed. The average powder size is **20 to 50 µm**, but also particles of up to **100 µm** can printed. The printing space is preheated to just below the melting temperature of the material, minimizing the energy consumption of the laser and preventing distortion of the component.

2) LDM – Laser Deposition Welding

The above discussion gave clarity about the powder bed technique for metal 3D printing. But the LDM, Direct Energy Deposition (DED), Direct Metal Deposition (DMD) or laser Cladding all are the additive manufacturing techniques. As discussed in previous section the additive manufacturing process is one in which the parts are produced one layer at a time which is laid directly by the nozzle same as the Fused Deposition Method (FDM) used in printing polymers. This approach saves the material usage as well as due to the increased accuracy in terms of the dimensions of the part the post-manufacturing finishing process is also shortened as compared to SLM or DMLS 3D printing techniques.

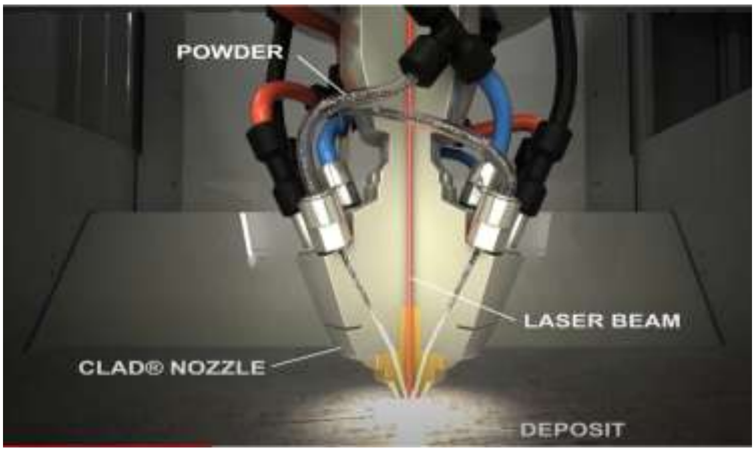

Figure 20: LDM or Laser cladding process. [22]

Seeing the figure 20, it can be observed that the powdered metal material is passed through pipes to the nozzle and the laser melts the metal to make fuse between the particles. The positioning for the laying the successive layers is determined by the G-code file as well as the software controlling the nozzle. During the printing process the material in powder form is sprayed into the protective gas stream in the pipes to the nozzle and the material particles can be within the range of particle size of 40 to 90 µm. This technique is well suited for the low feed rates as small particles and high feed rate might block the laser or nozzle making the process less efficient and degrades the quality of the product.

This technique is logical further development of conventional deposition welding and is suitable for repairs, coating work, joining processes or making components out of alloys just by supplying different metal powder to the nozzle.

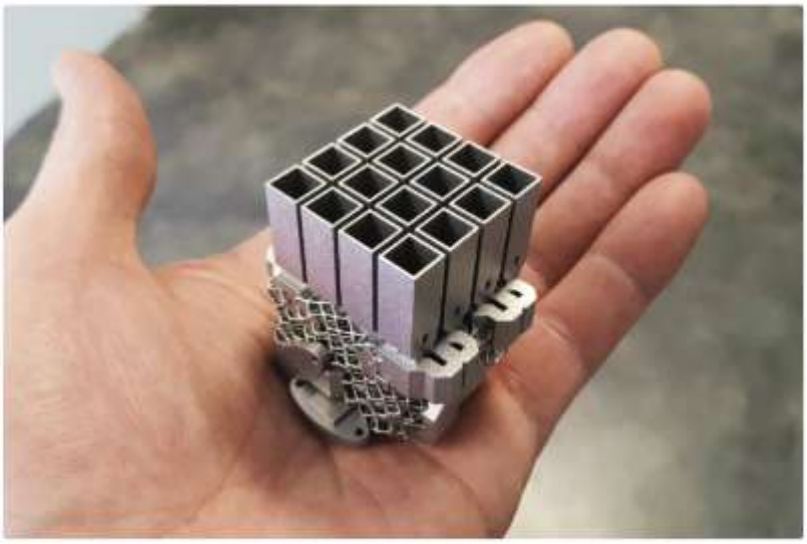

Figure 21: Metal 3D printed part. [23]

Commonly used 3D printable metals and a general comparison is given in table no. 1 to choose the best one suitable for the desired results.

Table no. 1: Commonly used metals for 3D printing.

Material	Properties
Aluminum alloy	Good mechanical & thermal properties Low density Good electrical conductivity Low hardness
Stainless steel & tool steel	High wear resistance Great hardness Good ductility and weldability
Titanium alloys	Corrosion resistance Excellent strength-to-weight ratio

	Low thermal expansion Biocompatible
Cobalt-Chrome superalloys	Excellent wear & corrosion resistance Great properties at elevated temperatures Very high hardness Biocompatible
Nickel superalloys (Inconel)	Excellent mechanical properties High corrosion resistance Temperature resistant up to 1200ºC Used in extreme environments
Precious metals	Used in jewelry making Not widely available

4.3 Composite:

The next and emerging type of material for printing 3D parts with special properties & characteristics is composites materials. **Composite** is a synthesized material made from two or more constituent material with significantly different physical or chemical properties, that are combined to produce material with characteristics different from the individual components. Composites can be broken down into two categories: the **matrix (binder) and the reinforcement**. The matrix serves as support to the reinforcement material by surrounding it so that it can maintain its relative position. Sometimes composite materials are made by mixing small amount of additive in large portion of a particular material, to improve or enhance the properties of the material for good. The simplest example to the above statement can be concrete. Concrete mainly consists of rock, sand and mud with the binding agent such as water and Portland cement. Looking at the individual components no one can say that they can have such high resistance to sheer stress of the building, neither rocks or sand are capable to hold that amount of pressure without crumbling. But when combined together with binding agents and made a composite material it can produce some marvelous structures.

Composite material has clear advantage over some traditional materials and is being extensively used for many applications. Researchers are going all out to develop new & more acceptable composite materials. In recent years many composite materials have been developed and much emphasis is been given in this age to develop new ones. In this section an extensive explanation on how composites will change the future of manufacturing and also some important & most potential composites are discussed.

With the development of new technologies and techniques to produce more enhanced material for special applications. Researchers have been developing ways to produce more acceptable and easily manufacturable products from these special materials. The need for newer materials with enhanced properties and characteristics over traditional materials has been felt by almost every industry. Taking into account the automobile industry, earlier the lightest material available for use was aluminum or alloy steel having tensile strength of 570 & 1275 MPa respectively. But when manufactures felt the need for more light & stronger material, composite material like carbon fiber (epoxy composite) was developed and used as a replacement to traditional material. Carbon fiber not only was lighter than any material available, but also provided increased tensile strength of 2550 MPa. Carbon fiber was quickly accepted by many industries for example to make aircraft parts, car parts, as a heat resistant material and much more.

Composites materials have also seen a growth in usage in **3D printing industry** as technologies have been developed to print these materials at a faster and in more affordable way. Use of composite fibers has shown excellent results in terms of strength, stiffness, heat resistance and durability of the 3D printed parts. Composites have shown clear advantage over traditional thermoplastics like ABS or PLA. The parts that are printed with composite material have better sheer strength and are also more resistant to heat as compared to low melting point thermoplastic materials. According to a study done by **IDTechEx** the composite 3D printing market is expected to worth $1.73 billion in the next ten years.

Seeing to this growth rate many big players have entered to the composite material field releasing their own composite material printers as well as materials. The **Markforged** company is the company that has been continuously working towards developing new composite material and it also makes advance printers to match the materials.

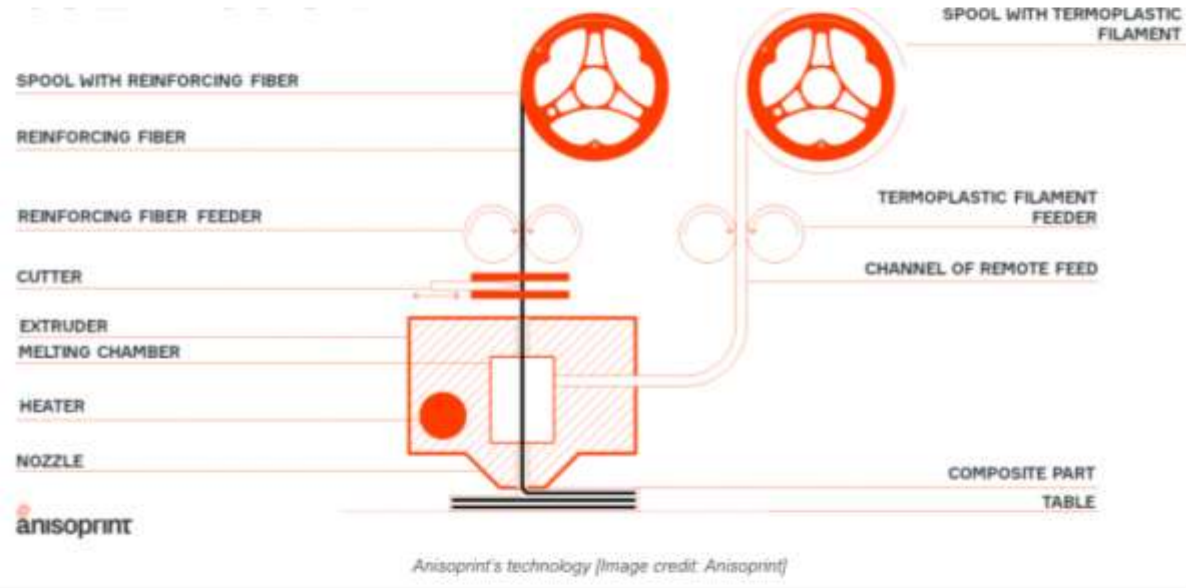

Figure 22: Anisoprint's Composite Fiber Coextrusion technology. [25]

A similar company like Markforged, Anisoprint a Russian and Luxembourg start-up has developed an extrusion-based process that the company calls **Composite Fiber Coextrusion (CFC)**. As the name suggests CFC allows user to print parts of required material along with stands of carbon fiber in it continuously without any pre-printing processes.

From the discussion above the concept of what composite materials are, how they are composed (matrix & reinforcement) and what additional benefits they provide over tradition material is discussed. Coming to the composite material prepared for 3D printing most of the materials are produced with **reinforcing fibers**. Most commonly used reinforcing fibers that are mixed with our traditional materials are **Carbon fiber, Fiberglass and Kevlar.**

All the fibers available are thin, brittle and easy to snap if bent. All the fibers are never used by themselves to produce parts, they are usually woven into sheets, wrapped into rods or formed into custom molded shapes are per requirement with help of a matrix material. As we discussed above about the available reinforced fibers available to make composite materials, Carbon fiber has been accepted more widely for making reinforced fiber parts and components. Carbon fiber has come out to be the one of the highest strength-to-weight ratio material. More details about the most valuable fiber i.e. carbon fiber is given below with explanation about the process to introduce this fiber to traditional materials.

4.3.1 Carbon fiber:

Carbon Fiber are made up of carbon atoms organized into a crystalline structure to make up thin filament aligned into strands, making strands incredibly strong. Carbon fiber as discussed above also has a flexural strength of 540 MPa with almost 3-4 higher than many traditionally used materials. Its tensile strength is 800 MPa i.e. twice the ultimate tensile strength of aluminum 6061. In general application thermoset resins are used as the bonding agents to set these fibers into desired shape, making sandwich panel having foam in between. Through figure 23 a comparison of properties of material reinforced with carbon fiber to our traditional material like Nylon, ABS and PLA is depicted.

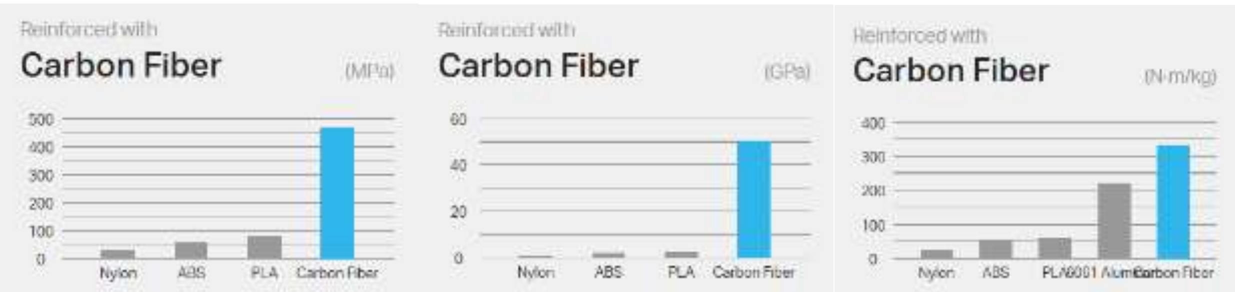

Figure 23: The first graph compares CF material to other material on ground of Flexural strength, in 2nd on flexural stiffness and in last on basis of strength to weight. [27]

❖ For use in printing 3D printed parts and components, carbon fiber can be introduced to the material in 3 different forms: -

(a) Chopped Fiber material:

The term chopped fiber refers to short-length fibers chopped into segments less than a millimeter in length and mixed with traditional thermoplastics material like ABS, PLA and Nylon to form what is called filled plastics. Filled thermoplastic are traditional plastics having a small number of additives (in this case Chopped fibers) to enhance its properties. The major advantage of the composite materials is that the concentration of the additive can be altered as per requirement. These altered thermoplastics can be easily printed with an FDM printer.

Figure 24: Chopped Carbon fiber to be added to thermoplastic. [30]

The figure 23 shows the chopped small pieces of carbon fiber stick that will be added to the thermoplastic structure at time of printing to make the structure strong and durable in long-run. The next figure 24 shows end result of adding carbon fiber pieces to the part. Each strain of carbon fiber provides excellent tensile strength to the part.

Figure 25: Part made with chopped carbon fiber pieces. [31]

The most common application of this material is **carbon fiber reinforced nylon,** a nylon-based thermoplastic having microscopic pieces of carbon fiber. By adding carbon fiber to nylon transforms it from a niche plastic to a superplastic. The fiber boost strength, stiffness, heat resistance and also increases the dimensional stability of the material. The addition of carbon fiber to any material is a very important factor, the right amount of carbon fiber increases strength and stiffness but when nylon is overfilled with carbon fiber a completely different material is obtained. Overfilling does affect the stiffness but also makes printing of part difficult and yields poor quality parts having visible defects & rough surface texture. The figure 25 shows a comparison between nylon plastic to its composite material having carbon fiber and to the overfilled version.

Figure 26: Comparison of properties of Nylon, Filled CF Nylon and Over-filled CF nylon. [27]

Through figure 25, it is observed that Carbon filled nylon has clear advantage over singular nylon thermoplastic in terms of part quality, strength, stiffness and heat resistance. But when the carbon content is increased further to achieve overfilled version of the thermoplastic. There is an increase in the strength, stiffness and durability but at the cost of part quality as discussed above. Overfilling of carbon fiber makes the binding thermoplastic difficult to flow through the printing system that causes poor results when printed.

(b) **Continuous Fiber Fabrication (CFF) 3D printing material**:
The next type of material that can be generated by adding reinforcing fiber is continuous fiber composite. Through the discussion above it has been observed that chopped carbon fiber remarkably increases the strength of the material to which they are added but, when CFF structure of composite is used it further adds more strength to the part.

CFF material are produced by laying down long strands of fiber reinforcement in conventionally printed thermoplastic parts. To print and achieve steel like strength through this composite the extrusion-based printing technique is used same as above. But the major difference lies in the printing layout, chopped fiber composite was layer to make structures using only one nozzle printers whereas the continuous fiber composite requires two nozzle printers. The first nozzle lays layers of traditional material like ABS, Nylon or PLA and the second nozzle iron down the strands of carbon fiber above the first layer creating a structure of high strength and better composition. This process structure is called Continuous Fiber Fabrication (CFF). The CFF structural layout can easily be understood by observing figure 27. It shows a CFF structure in which the outer and inner most shell is laid out in Nylon. But to provide the strength and stiffness to the part an additional core having long strands of carbon fiber is also layer between the honeycomb structure and the outer shell.

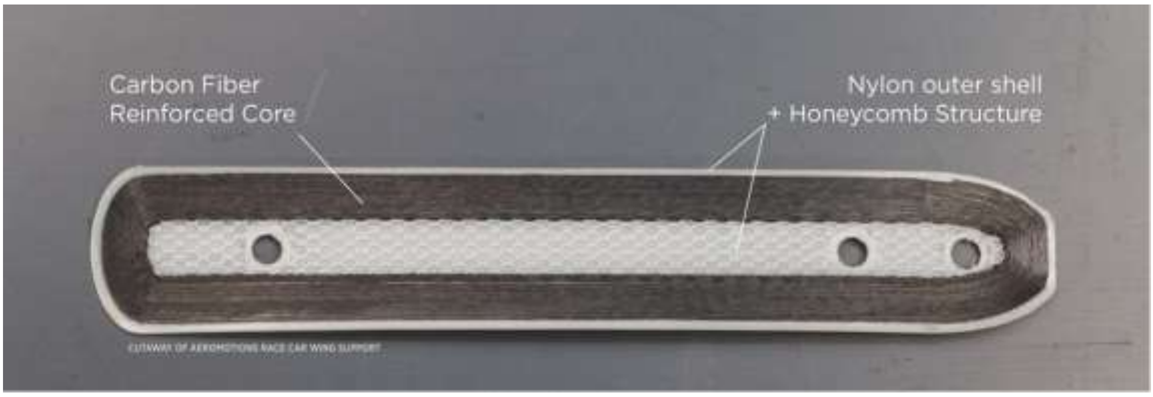

Figure 27: Continuous Fiber Fabrication structure. [32]

After observing the above figure, it can be seen that the main structural strength to CFF structure is from the continuity of the strands. On a comparison basis continuous strands can absorb and distribute load more efficiently across their surface than the chopped fiber particles. So, when the parts are printed the thermoplastic filament is melted and layered by one nozzle at the desired position. As the fibers are very heat resistant, they do no melt instead they're captured by the thermoplastic matrix, making a firm

bond and incorporating the fiber into the structure giving higher strength to handle higher loads and absorb larger impacts. The fiber acts as the backbone of the part and as a result part are an order of magnitude stronger, stiffer and more durable than plastic (filler or not) and maintain the heat resistance, chemical resistance and print quality also increases.
In figure 28 a general comparison on several characteristics of the normal thermoplastic to the filled and continuous fiber version is depicted.

Figure 28: Comparison of properties of Nylon, Filled CF Nylon and Continuous Fiber. [27]

By observing the figure 28, it is very easily noticeable that why continuous fiber has so much importance as compared to the filled CF thermoplastics. Continuous fiber gives a significant increase in the strength, stiffness and durability over the filled and non-filled thermoplastics.

4.4 Nanocomposites:

As discussed in the above section about the composite materials, CM are prepared from the combination of two or more different materials with different chemical or physical characteristics. The composite materials discussed were chopped carbon fiber and Continuous Fiber Fabrication (CFF) which provided the strength & advancement in mechanical properties. In recent times, there has been huge demand in materials that can have distinctive properties that are well suited as per the application.
For the search for better material that can be printed to form parts and objects, researchers have been working on nano-composite materials. This search has taken us to our last section on materials for 3D printing and major research is being done in this context. Over the last few years there has been a surge in the papers published on the nano-composites, nanotechnology, nano-materials, nanoscience etc.

Nanocomposites can be described as the composite materials having a composition of two or three materials in matrix. The only difference between composite and nano-composites is of the size of the additive particulate. In nano-composite materials the base material PLA or ABS is combined with particulate materials at nano-scale having a dimension in nm regime (i.e. between 1 and 100 nm). Addition of nano particles to the material induces change in its overall macroscopic properties and helps to achieve superior materials properties when compared with macro composites. Nano-composite materials can be broadly classified in to polymer based or non-polymer-based nano-composited. The researchers are continuously exploring the nano-composite materials and studying the effectiveness of nano-composites in materials is normally only between 0.5 and 5% by weight.

Nano-composites are prepared from bulk matrix material and nano-dimensional phase which gives extremely high surface to volume ratio which drastically improves their properties when compared to its bulk sized equivalents. The dimensional range for the nano particles to be added has been researched intensively and has been concluded to provide the desired properties as discussed in table 2.

Table 2: Feature size for significant changes in properties of nano-composite materials. Size limits to have the desired properties has been examined. [33]

Properties	Feature size (nm) at which changes might be expected
Catalytic activity	**<5 nm**
Making hard magnetic materials soft	**<20 nm**
Refractive index changes	**<50 nm**
Super-paramagnetic & electromagnetic phenomena	**<100 nm**
Modifying hardness and plasticity	**<100 nm**

In mechanical terms, nano-composites differ from conventional composite materials due to the exceptional high surface to volume ratio of reinforcing or it's exceptionally high aspect ratio. The high aspect ratio or volume to surface ratio means that a relatively small amount of nanoscale reinforcement can have an observable effect on the macroscale properties of the composites as presented in table 2. Nano-composites have been declared as novel materials because of additional improvements in properties of the materials such as: -

1. Mechanical properties- Strength, flexibility, modulus and dimensional stability.
2. Increase in electrical conductivity
3. Decrease in gas, water and hydrocarbon permeability
4. Improvement in flame retardancy, thermal stability and chemical resistance
5. Better surface appearance of the printed parts
6. Optical clarity

After discussing the benefits of addition of nano-particles to the materials, some **advance manufacturing technologies to produce and incorporate nanoparticles to the material** can be discussed. The reinforcing material or nano-composites can be manufactures by addition of types of materials such as particles (e.g. minerals), sheets (e.g. exfoliated clay stack) or fibers (e.g. carbon nano tubes or electropunk fibers).

Synthesis of nanocomposite material mainly depends on the matrix material that's being added to the filler material. According to the matrix material added the nanocomposites can be classified into three different categories:

1) Ceramic Matrix Nanocomposites (CMNC)
2) Metal Matrix Nanocomposites (MMNC)
3) Polymer Matrix Nanocomposites (PMNC)

The table 3 gives the examples of the matrix materials that can be used to produce the above nanocomposites categories.

Table 3: Different types of nanocomposites. [36]

CLASS	Example
Metal	Fe-Cr/AL_2O_3, Ni/Al_2O_3, Co/cr, Fe/Mgo, Al/CNT
Ceramic	Al_2O_3/SiO_2, Sio_2/Ni, Al_2O_3/TiO_2, Al_2O_3/CNT
Polymer	Thermoplastic/thermoset Polymer/layered silicates, polyester/TiO_2, polymer/CNT, polymer/ layered double hyfroxides.

From all the discussed nanocomposites in the above table 3. The polymer-based composites are novel materials, having only a less than a decade of history and a promising future. The polymers are used every day in 3D printing and the improvement by the addition of the various filler materials (in terms of electrical conductivity and colloidal stability) has led to a lot of research of newer & better polymer-based materials. There has been a big leap in the material sciences to produce materials having biodegradable properties, crystallization & melt rheology, layered, particulate and fiber materials.

4.4.1 Production techniques to manufacture nano-composite materials:

The use of nanocomposite material to produce 3D printed parts is usually in the form of filaments. The filaments usually consist of the matrix and filler composition to provide addition chrematistic properties to the matrix material. Filament production is very important procedure to produce the raw materials acceptable by the 3D printer, also to vary the %composition of the materials and to recycle or reuse the material left in the last production stage. For production of the filaments there are specials machines called extruders as shown in figure 29.

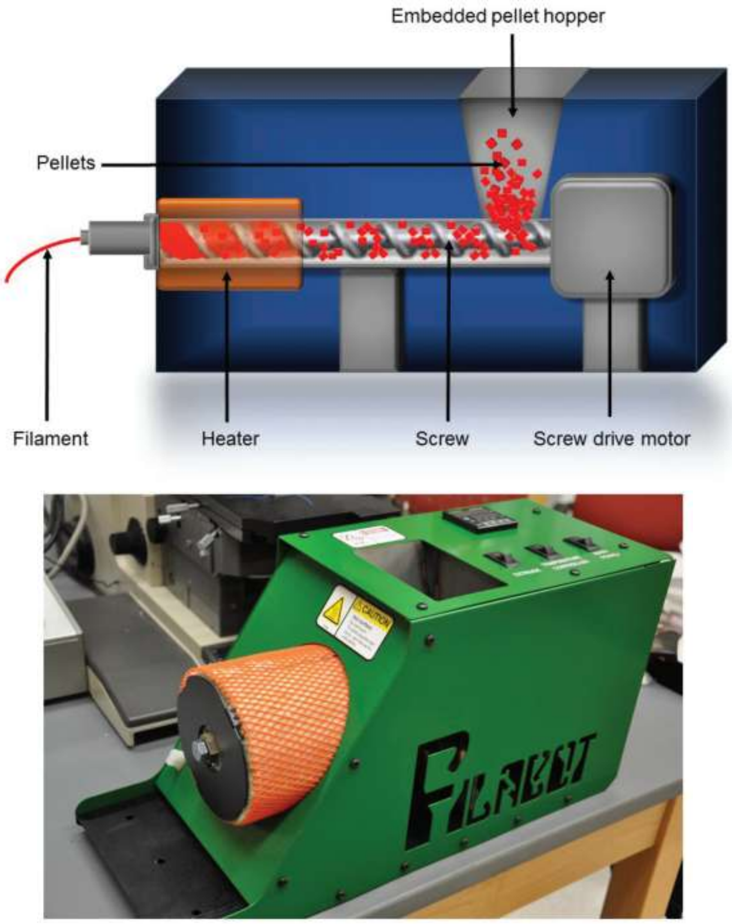

Figure 29: The internal diagram of a filament maker and a picture of the "Filabot-Original" used for producing filament for FDM

As seen in the above diagram the internal of a filament producing machine can be seen having an opening to introduce the pellets of the filler and matrix material that can be extruded out from the machine by passing through the heater. The heater melts the pellets and filament of small diameter is extruded out from the nozzle. The extruded filament is rolled on a cooling drum/spool that can detached from the machine and directly feed to the FDM printer.

Researchers have been using the filament and pellet formation technique at its best to produce materials with different composition of the filler materials. Not only the composition of different materials, the variation of different nozzle diameters, layer diameter, screw drive motor speed, different extrusion temperature produces materials/parts with different characteristic properties.

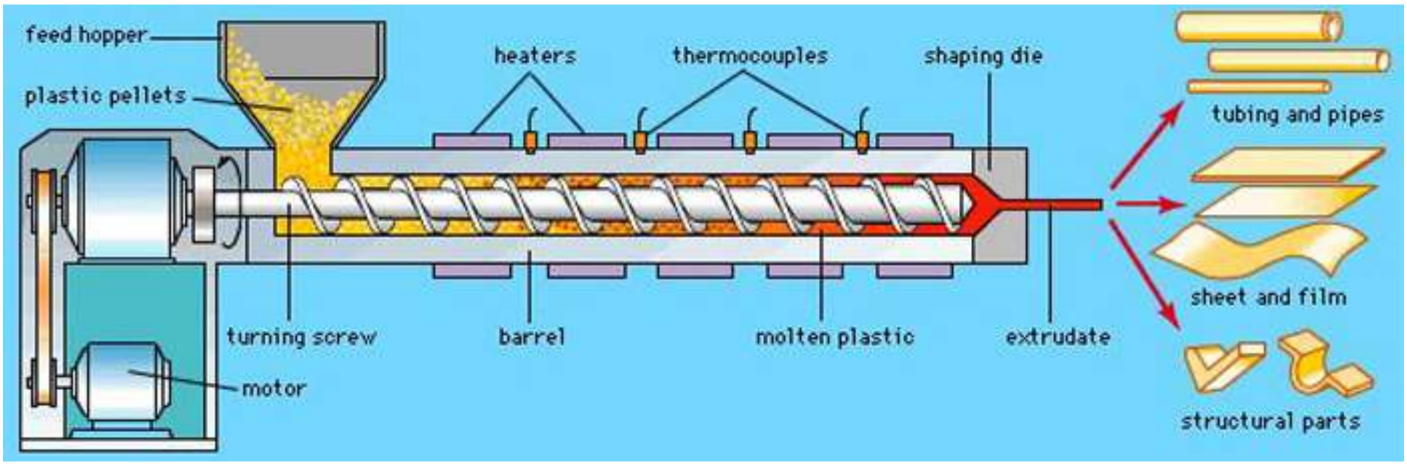

Figure 30: Extrusion process to manufacture different nanocomposites materials.[37]

From the table 3, of all the nanocomposites materials know to us the Carbon-nano tube (CNT) since their discovery in 1991 and its ability to significantly enhance material properties. In the recent years Nanocomposite materials have emerged as a suitable alternative to overcome limitations of micro composites and monoliths. In this next section recent research on CNTs conducted by researchers is concluded.

4.4.2 Carbon Nanotubes (CNTs):

While discussing about the composite materials, we discussed about the reinforced fiber such as Continuous Fiber Fabrication and Chopped Carbon filler materials to be added to polymers to make composites/micro-composite materials. But with further advancement in nano-technology and need for more advance materials for production of parts and components with desired properties, with this requirement researchers are set to introduce some advance materials that will have tweakable properties. One of such materials is CNTs which is being excessively researched on and shows the results of a promising future.

Since the discovery of CNTs in 1991 by Iijima, a whole new field of material science also took birth called Nanoscience. Carbon Nanotubes as the name suggests are made up of carbon particles (graphene) rolled-up sheets forming a tube-like structure having a diameter of less than 1 nanometer. CNTs just like their building block graphene, they are chemically bonded with sp^2 bonds which is one of the strongest forms of molecular interaction. Along with strong molecular interaction these particles are naturally inclined to rope together via van der Waals forces, which when incorporated into the object gives ultra-high strength and light weight due to its tube-like structure [38].

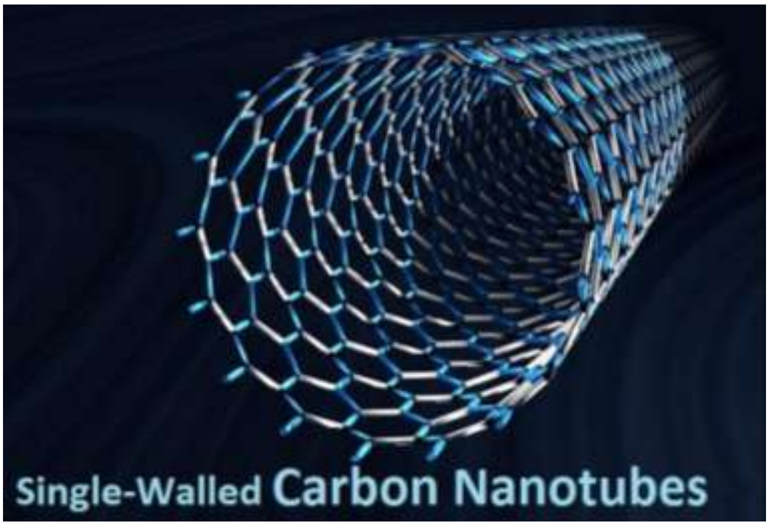

Figure 31: Nano-structure of Single-walled Carbon Nanotubes. [39]

As seen in the figure 31, the nano-structure of CNTs and the strength of the bonds between the carbon atoms have resulted to produce a material that is 100 times stronger than steel at the molecular level at one-sixth the weight. Due the above mentioned different between steel and CNTs, CNTs have been considered more useful in various applications and more research as well as commercial application are in development [40]. Very recently a 4^{th} state of matter having water trapped inside carbon nanotubes has been discovered, this material doesn't act as a solid, liquid or gas [40].

Along with exceptional strength qualities, the rolled-up structure of graphene layers in CNTs gives the ability of conducting heat and electricity similar to copper without oxidative concerns. Carbon nanotubes can have different structure, length, thickness and number of layers. Any change in one parameter mentioned results in different structural or molecular properties.

The structure of a single-walled carbon nanotube can be best visualized as one-atom-thick layer of graphene of a regular hexagonal lattice wrapped onto an infinite cylindrical surface. The carbon nanotubes are laid down in zigzag and armchair configurations. In terms of nanoscience, the zigzag configuration can be explained as a path of graphene lattice that turns 60 degrees alternatively left and right, after stepping through each bond as shown in figure 31. Whereas the armchair structure can be defined as a path of graphene lattice that makes two left turns of 60 degrees followed by two right turns every four steps as shown in figure 33 [41].

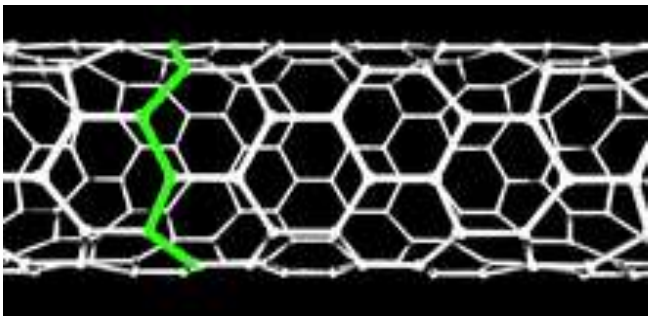

Figure 31: Zigzag configuration of CNTs [41]

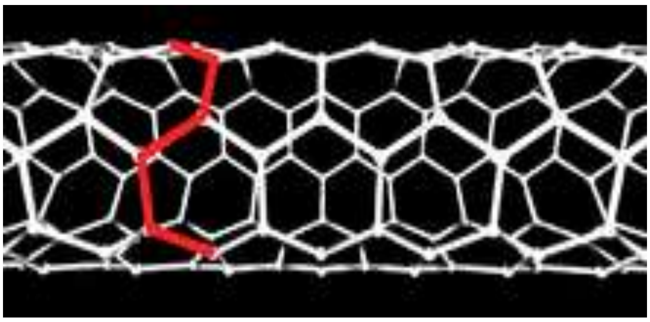

Figure 32: Armchair configuration of CNTs [41]

From the above structures it can be seen that in zigzag configuration there is a closed zigzag path that goes around the tubes and in armchair configuration the tube is instead encircled by a closed armchair path [41]. The armchair path has identical chiral indices and are highly conductive in nature whereas the zigzag CNT are less conductive i.e are semiconductors.

❖ CNTs are available in the following forms
a) Single-walled CNTs
b) Double-walled CNTs
c) Multi-walled CNTs

Single-walled CNTs has already been discussed above and when 2 concentric nanotubes (SWCNT) are stacked inside one-another they form the double-walled CNT structure. This configuration gives a lot of flexibility in terms of properties desired depending on the chiral angle of nanotubes during the synthesis. These material (DWCNT) have improved lifetime and are highly stable under chemical, mechanical and thermal treatment without the loss of flexibility as observed in SWCNTs. The nano structural configuration DWCNTs can be observed in figure 32.

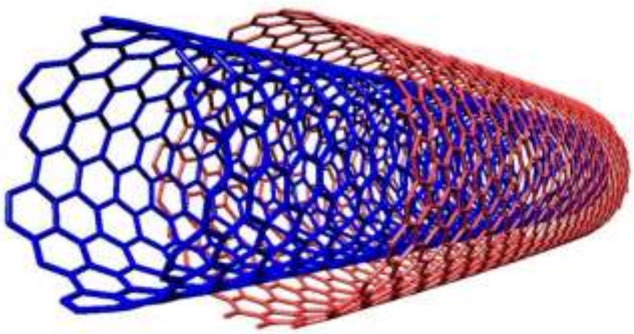

Figure 32: Structure of Double-walled CNTs. [42]

Coming to the Multi-walled CNTs they can be easily recognized because of their more complex array structures. MWCNTs consists of multiple rolled layers of concentric tubes of graphene. Multi-walled nano tubes are unique material because of their complex array of form and each nano-tube can have different structure/arrangements. MNCNT due to their varied properties and different configuration is the most valuable of the three types. MNCNT can also be found in two layouts in which one can be understood as stacking of multiple individual nano-tube to form a structure and the other one can in form of a Parchment model. In Parchment configuration a single sheet of graphite is rolled around itself like a rolled newspaper [41].

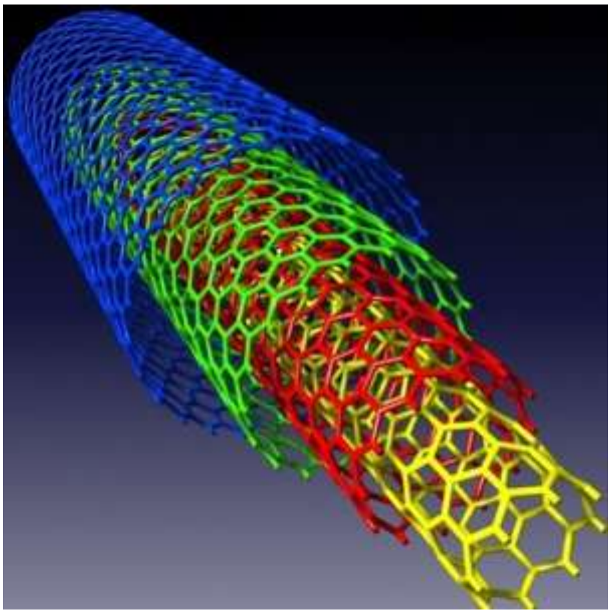

Figure 33: Representation of MWCNTs structure. [43]

With the development of different structures and continuous improvements in the department of nanoscience, a lot can be said on the properties and application of CNTs in this recent age. Apart from the electric conductive properties inherited from graphene, CNTs have always surprised us with unique thermal, mechanical and optical properties. With the above properties CNT are virtually suitable for any application requiring high strength, electric & thermal conductivity and light weight properties. CNTs are available in powder form to be used as an additive to the conventional materials to add additional benefits mentioned above along with increased wear resistance and breaking strength.

While addition of the CNTs to the substrate i.e. a plastic material, there should a formation of chemical bondage between the two. The ease of formation of nanocomposite material with exceptional properties as compared to the conventional material has led to whole new wave of applications, that will be benefitted by these enhanced properties of CNTs. CNTs are being popularly used as a Catalyst in many relevant chemical processes, for next-generations of advance transistors, for development of electrochemical nano-sensors and in the nanomedicine & biotechnology [38].

CNTs have also found it way in 3D printing technology and that to even in the most basic & most commonly used technique to print 3D parts i.e. Fused Deposition Modelling. Materials used in FDM has shown exceptional improvement in properties when infused with CNTs and graphene. CNTs has come-up as a need for today's material market and many companies have started producing commercial CNT infused materials. 3DXTech is one of such company which provides ABS filament containing MWCNTs. The filament is available with diameters of 1.75mm and 2.85mm, produced using MG-94 Premium ABS, mixed with MWCNTs and process/dispersion modifier. Table 4 exhibits the study of 3DXNano™polymer.

Table 4: Study of 3DXNano™polymer [44]

Polymer	Extrusion Temp.	FDM Platform Temp.	Surface Resistance	Tensile Strength
3DXNano ™	220 to 240°C	100 to 110°C	107 to 109 Ω	42 MPa

With the benefits of the CNTs infused in the materials there has been a lot of discussion on the optimum amount of CNTs to be added to the polymer. The theoretical concentration of carbon nanotubes required to reach the electrical percolation threshold for a CNT/Polymer composite can be obtained, as a first step, by the use of the power law:

$\sigma \infty (\varphi-\varphi_c)^{\alpha}$

Where σ is the electrical conductivity, φ is the MWCNT volume concentration in the nanocomposites, φ_c is the critical MWCNT volume concentration at electrical percolation and α is a critical exponent. So, to conclude the material topic a discussion on **production of CNTs infused material**, a comparison on what **wt% of CNT in a material** does and what has been the best concluded **proportion of CNT in plastic to achieve the best property material.**

4.4.3 Manufacturing of CNT infused material: -

Amorphous thermoplastic teracrylonitrile-butadiene-styrene (ABS) is most commonly used material in FDM process due to its wide availability and various application. ABS with CNT and Graphene as additive in 3D printing is a light-weight, rubber-toughened thermoplastic with low temperature toughness and is stronger than polystyrene. CNT as discussed above are available in the powder form and can be incorporated with the plastic in following ways:

1) **Hot Melt Extrusion process**:

As seen above in the composite section this process is widely used for the production of filaments for FDM 3D printing process. Due to its process simplicity and adaptability for the commercial production of thermoplastic polymer/MWCNT nanocomposites [45]. This process of manufacturing is most suitable for polymers that cannot be processed with the solution processing approach due to its inability to dissolve in commonly employed solvents.

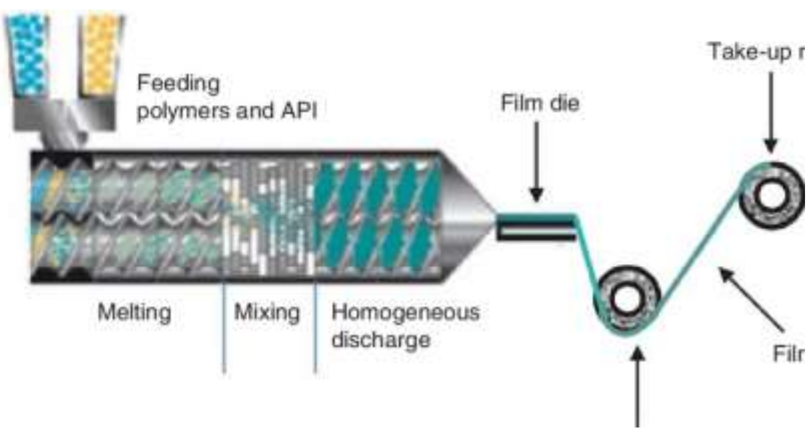

Figure 34: Representation of Hot melt extrusion process

The high magnitude of shear during the melt process facilitates the breakup of the CNT agglomerates followed by dispersion and distribution of tubes in the polymer melt. In this technique to acquire the optimum results the following parameters can be easily configured such as screw speed, barrel temperature, weight % of additive and screw position. Through the melt extrusion process first the pellets of MWCNTs dispersed in ABS are obtained and have to be feed to the filament producer to make usable filament for FDM process. The ABS dispersed with MWCNT pellets can be observed in figure 35.

Figure 35: ABS dispersed with MWCNT pellets.[45]

2) ABS filaments with MWCNT coating and Micro-sintering:

3D printed parts with conventional materials are often hindered by the weak weld between printed filament which results in delamination and mechanical failures. By infusing these nanotubes having dimensions in nm and having strong bondage with the atoms to the material bring additional improvement in the properties of the material. These nanotubes having a unique response to the microwaves that they heat up quickly and melt, used to weld and provide strength to the successive layers of the parts. The ABS material does not heat-up so quickly and remain intact till the CNTs infuse with the plastic to provide additional strength. The similar structure as described above is shown in figure 36.

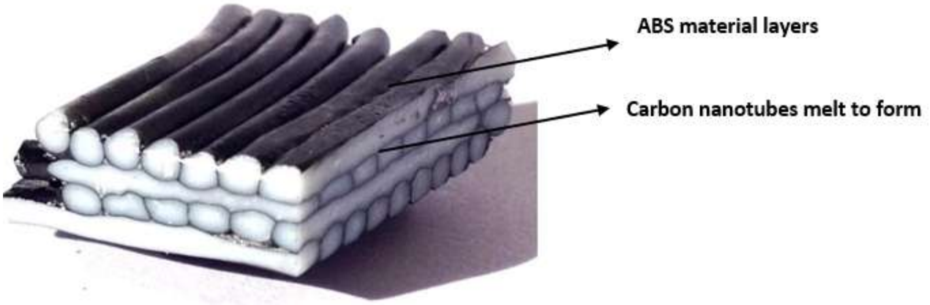

Figure 36: Layers of ABS having coating of CNTs. [46]

The manufacturing of these materials is followed by fist coating MWCNTs by spray deposition on the polymer (ABS) filament. The coating process is done with MWCNT dispersed in proprietary solvent filled in the fluid cup of an airbrush and sprayed homogeneously on the surface of the ABS filament. The proprietary solvent is there to enhance the bonding capacity of the MWCNTs on the ABS filament when exposed to the air.

In the next step the sensitivity of CNTs to microwaves is take advantage of i.e. when CNTs are exposed to the microwaves they heat-up quickly whereas, the ABS filaments are relatively insensitive to the microwaves. This melting of CNTs by the microwaves help to establish strong filament-filament interaction as shown in figure 36.

In the final step, the MWCNT coated ABS filament is placed together in a cross-hatched structure followed by ~20 second of exposure to microwaves. This step sinters the filament by reducing the air gap between intra adjacent filament in stage 1 and 2 [45].

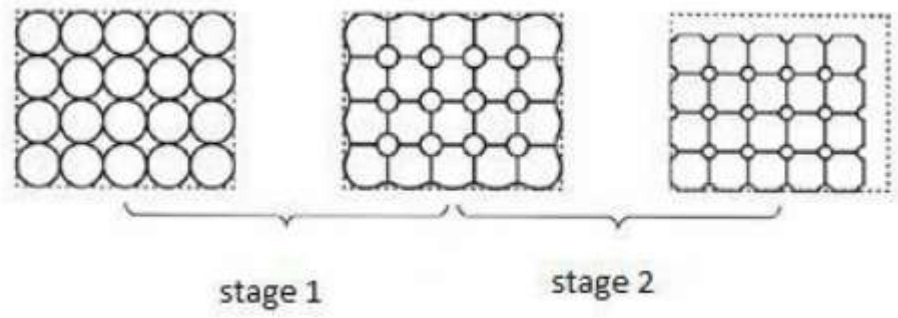

Figure 37: Nanostructure of the filament during stages 1, 2 and 3. [45]

As discussed above the there are two commercially viable manufacturing techniques to produce ABS infused with Carbon nano-tubes. So as per [45], a comparison of the parts produced by conventionally used ABS filament, filament of CNT infused in the ABS material and CNT coated ABS is given.

Table 1: Test results of average of 5 test specimens.

Property	Standard	Unit	MWCNT mixed ABS	MWCNT coated ABS	ABS
Tensile'Strength'(Yield)	ASTM'D638	MPa	51.5	62	41
Tensile'Modulus	ASTM'D638	MPa	2125	2350	1955
Tensile'Elongation	ASTM'D638	%	5.65	4.5	4.1
Flexural'Strength	ASTM'D790	MPa	80	89	68
Flexural'Modulus	ASTM'D790	MPa	2385	2182	1950
Izod'Impact, 'Notch	ASTM'D256	Ft-lb/in	9.5	12	3.75
Izod'Impact, 'NONotch	ASTM'D256	Ft-lb/in	18	21	9
HDT'(@66psi)	ASTM'D648	°C	125	113.5	97.5
Surface'Resistance	ASTM'D257	Ohms	105-107	107-109	>1013

After studying the above table, it can be easily observed the how addition of CNTs to ABS material provided major improvements in tensile strength, tensile elongation, flexural strength and heat resistance. On comparing the test results for the MWCNTs mixed and coated over ABS, it can be observed that coated ABS perform better in tensile test. The same can be observed with the stress-strain graph as shown in figure 38.

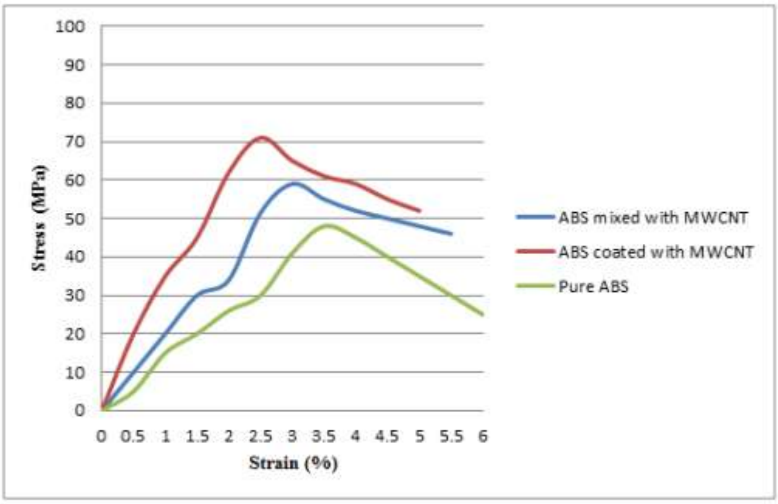

Figure 38: Tensile test results for Pure ABS, ABS coated with MWCNT and ABS mixed with MWCNT [45]

Also comparing both coated and mixed materials, it can be observed that ABS coated with MWCNT are stiffer material having less tensile elongation as compared to ABS mixed with MWCNTs. The flexural strength is slightly higher in ABS coated materials as compared to ABS infused with CNTs. A illustration of a compression test done with pure plastic and plastic having CNT conducted is shown in figure 39.

Figure 39: Compression test on Pure ABS and ABS material having CNT infused in it. [47]

In the above section we discussed about the different manufacturing techniques and how the properties of material differ when produced as mixed or coated in nature. Now we can examine some factors that affect the ABS material property when infused with the CNT. The other parameter that affect the material property other than manufacturing technique is the %wt of CNT added to the pure material. A lot of research has been done in this domain and is briefly concluded in this section.
According to the research conducted by [48] various samples of ABS mixed with CNTs were prepares in the filament extruder machine by also varying the machine dynamics during each process. The following can be observed in the table given below.

Samples	Pressure (bar)	Torque (Nm)	Screw Speed (rpm)	Collection Rate (m/min)	Output (g/h)
ABS	16.9	40.4	5	1.00	137.6
CNT1	17.1	38.4	5	1.00	134.6
CNT2	21.7	45.9	5	1.00	137.7
CNT4	28.0	66.8	5	1.00	138.6
CNT6	44.2	100.1	5	1.15	139.6
CNT8	45.7	119.6	4.5	0.88	122.1

In the table, ABS denote filament of pure matrix and CNT (1-6) indicates nanocomposite filament having 1-6 wt% of CNT in pure ABS matrix.

In [48] after conducting tests on the materials indicated in table 6. The test series conducted on all the material were density measurement of CNTs, melt flow index analysis of extruded filaments, scanning electron microscopy, thermogravimetric analysis, differential scanning calorimeter, creep test, dynamic mechanical thermal analysis and electrical resistivity test. After conducting all those test the following conclusion was obtained that the optimum CNT fraction for Fused deposition modelling was found to be 6% wt [48].
In another research conducted and published in journal of manufacturing processes [49]. They used ABS (Specific gravity 1.05 g/cm^3) as the base material and MWCNTs (9.5 nm dia., 1.5um length and 250-300 m^2/g surface area) as the filler material. They used a twin-screw micro extruder (DSM Xplore) to make filaments having CNTs imbedded into ABS. They made 4 different nano-composite samples with different loading having 1, 3, 5, 7 and 10 wt% of CNT in ABS. the composition of these material is given in table 7.

No	MWCNT (g)	ABS (g)	Ratio (wt.%)
1	0.15	14.85	1
2	0.45	14.55	3
3	0.75	14.25	5
4	1.05	13.95	7
5	1.50	13.50	10

On the above-mentioned materials, they conducted the following test tensile stress test, Raman spectroscopy, electric conductivity test, melt flow index, scanning electron microscopy (SEM) and the following conclusion was obtained. The tensile stress test gave the following results as shown by the graph in the figure 40.

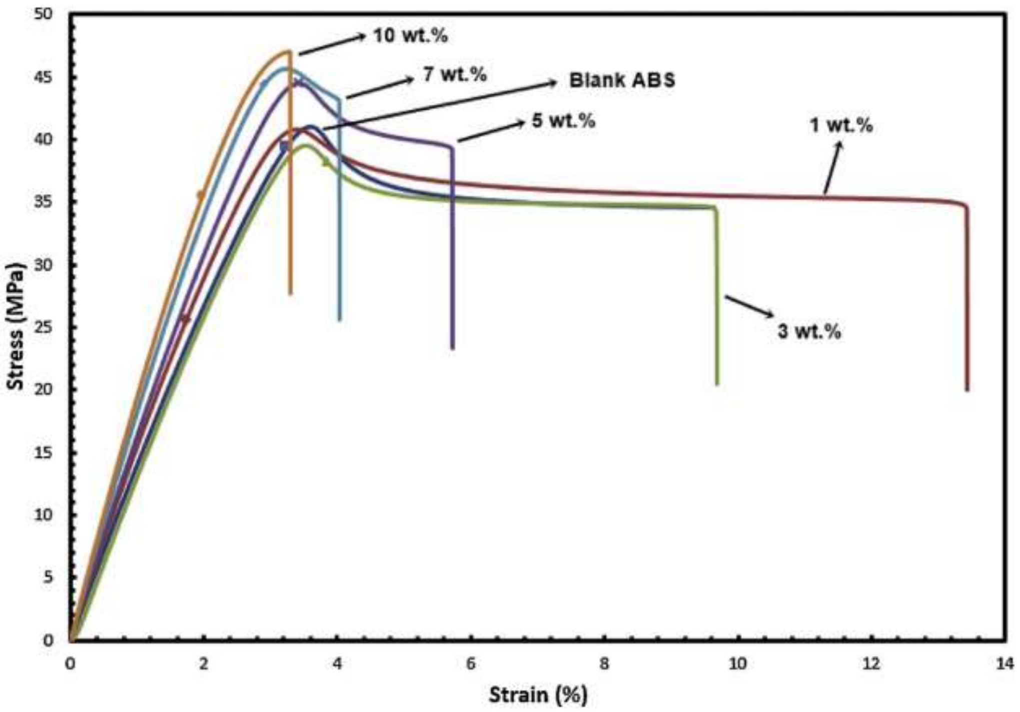

Figure 40: Tensile test on ABS material infused with 1,3,5,7 and 10 wt% of CNT [49]

The tensile test results clearly suggested that specimen with higher MWCNT content are stronger than specimen with lower content. This conclusion was further confirmed by Raman Spectroscopy test. In the electric conductivity test also, the highest conductivity was achieved with %10 sample of 232 e^{-2} S/cm while the Melt flow index test indicated a dramatical decline for %10 sample indicating that this material will have some issues in printing as well as can create nozzle clogging problem. The optimum %wt of MWCNT in ABS was again confirmed to be in the range of 6-7%.

CONCLUSION and FUTURE DEVELOPMENT

Even though 3D printing or additive manufacturing technique is an emerging technology and new discoveries are being done in this domain every passing day. The paper presents a technological roadmap to this emerging manufacturing technique giving detailed explanation on its discovery, past development and current scenario. 3D printing technique has shown it's worth with its versatility, cost saving and impowering advancement nature. Various 3D printing techniques have been developed in all sizes ranging from small household desktop printers to very large-scale printers as used by NASA to print space shuttle parts/body. 3D printing techniques has led us to discovery of new materials to print our structure with such as metals alloys (aluminum) can be easily printed to desired structure with techniques such as Laser deposition Welding (LDM) and Selective laser Melting (SLM) can print parts from metal alloy powder. The paper also gives a detailed analysis on some developing materials to make our end product more usable, light, strong and less expensive, Nanotechnology has been started on the foundation layed by additive manufacturing technique. Composites and Nanocomposites will be the future in manufacturing replacing our depleting, hazardous, harmful conventional materials for good to both mankind and to nature. 3D printing will not only change the future of manufacturing, it is going to have a big impact on the technological impact also with more and more products prototyped and released into the market for the consumers. Furthermore, the paper provides deep analysis and information of current research going on in additive manufacturing domain.

REFERENCES

[1] Mehrpouya, M., Dehghanghadikolaei, A., Fotovvati, B., Vosooghnia, A., Emamian, S. S., & Gisario, A. (2019). **The Potential of Additive Manufacturing in the Smart Factory Industrial 4.0: A Review**. Applied Sciences, 9(18), 3865. https://doi.org/10.3390/app9183865

[2] Der Klift, F. V., Koga, Y., Todoroki, A., Ueda, M., Hirano, Y., & Matsuzaki, R. (2016). **3D Printing of Continuous Carbon Fibre Reinforced Thermo-Plastic (CFRTP) Tensile Test Specimens**. Open Journal of Composite Materials, 06(01), 18–27. https://doi.org/10.4236/ojcm.2016.61003

[3] Der Klift, F. V., Koga, Y., Todoroki, A., Ueda, M., Hirano, Y., & Matsuzaki, R. (2016). **3D Printing of Continuous Carbon Fibre Reinforced Thermo-Plastic (CFRTP) Tensile Test Specimens**. Open Journal of Composite Materials, 06(01), 18–27. https://doi.org/10.4236/ojcm.2016.61003

[4] Der Klift, F. V., Koga, Y., Todoroki, A., Ueda, M., Hirano, Y., & Matsuzaki, R. (2016). **3D Printing of Continuous Carbon Fibre Reinforced Thermo-Plastic (CFRTP) Tensile Test Specimens**. Open Journal of Composite Materials, 06(01), 18–27. https://doi.org/10.4236/ojcm.2016.61003

[5] What is Additive Manufacturing? | GE Additive. (2020). GE Additive. https://www.ge.com/additive/additive-manufacturing
[6] **A Comprehensive Study on 3D Printing Technology**. Medhavi Kamran M.Tech Scholar Mechanical Engineering Department, AKGEC, Ghaziabad, U.P., India
[7] Research Nester. (2019). US 3D Printing Market Size: Industry Demand, Growth, Share & Forecast 2024. https://www.researchnester.com/reports/us-3d-printing-market-analysis-opportunity-outlook-2024/88
[8] Gupta, H., Chaudhary, G., & Malik, K. M. S. |. . D. K. |. . A. (2018). Enclosure Design for 3D Printing. International Journal of Trend in Scientific Research and Development, Volume-2(Issue-4), 618–623. https://doi.org/10.31142/ijtsrd13023
[9] Wikipedia contributors. (2004, December 21). 3D printing. Wikipedia. https://en.wikipedia.org/wiki/3D_printing#Modeling
[10] 3d printing g code - Google Search. (2016). Google. https://www.google.com/search?q=3d%20printing%20g%20code&tbm=isch&hl=en&hl=en&tbs=rimg%3ACUdmy-
[11] Chen, A. (2014). How to surface finish 3D printed parts. CMAC. https://www.cmac.com.au/blog/how-to-surface-finish-3d-printed-parts
[12] A Result Paper on 3D Printing and Technologies Used for Developing 3D Models. (2017). International Journal of Recent Trends in Engineering and Research, 3(12), 98–105. https://doi.org/10.23883/ijrter.2017.3542.jufft
[13] 3D Printing Technologies and Techniques. (2019, November 5). Sculpteo. https://www.sculpteo.com/en/3d-printing/3d-printing-technologies/
[14] TechPats. (2017, April 27). 3D Printing | An Overview of 3D Printing Technologies. https://www.techpats.com/3d-printing-technologies-overview/
[15] Types of 3D Printers: Complete Guide - SLA, DLP, FDM, SLS, SLM, EBM, LOM, BJ, MJ Printing. (2018, April 10). 3D Insider. https://3dinsider.com/3d-printer-types/
[16] 3D printing & 3D printers: Prices, News, Interviews, Tests. (2020, January 6). 3Dnatives. https://www.3dnatives.com/en/
[17] 3d printing filament - Google zoeken. (2019, January 1). Google. https://www.google.com/search?q=3d+printing+filament&rlz=1C1SQJL_enIN894IN894&sxsrf=ALeKk03b4n9T0sv_4JnCrFKgUiRxzbFgnA:1597579752981&source=lnms&tbm=isch&sa=X&ved=2ahUKEwjV1LSt2J_rAhUPxDgGHXZsDjkQ_AUoAnoECBAQBA&biw=748&bih=712
[18] Polylactic Acid or Polylactide, PLA Plastic, Lactic Acid Polymer Guide. (2015, October 5). Omnexus. https://omnexus.specialchem.com/selection-guide/polylactide-pla-bioplasticPolymers for 3D Printing and Customized Additive Manufacturing Samuel Clark Ligon,*,†,‡ Robert Liska,‡ Jurgen Stampfl,§ Matthias Gurr,∥ and Rolf Mulhaupt*,⊥
[19] Materials Archives. (2018, October 5). 3Dnatives. https://www.3dnatives.com/en/category/materials/
[20] eSUN PVA Water Soluble 3D Filament 0.5kg. (2016, December 15). Cubic Technology. https://www.cubictech.com.au/products/esun-pva-filament-0-5kg
[21] Direct metal laser sintering. (2018, October 5). 3Dnatives https://www.3dnatives.com/en/direct-metal-laser-sintering100420174-2/
[22] BeAM Machines. (2016, January 15). How Does It Work - BeAM Metal 3D Printing. YouTube. https://www.youtube.com/watch?time_continue=22&v=Pjqysyy1ySs&feature=emb_title
[23] Introduction to metal 3D printing. (2018, June 20). 3D Hubs. https://www.3dhubs.com/knowledge-base/introduction-metal-3d-printing/
[24] 3D Printing Carbon Fiber and Other Composites | Markforged. (n.d.). Markforged. Retrieved June 20, 2020, from https://markforged.com/learn/3d-printing-carbon-fiber-and-other-composites/#:%7E:text=Carbon%20fiber%2C%20fiberglass%2C%20and%20Kevlar,easy%20to%20snap%20if%20bent.
[25] Complete guide 3D printing composites. (2018, October 5). 3Dnatives https://www.3dnatives.com/en/complete-guide-3d-printing-composites-280120204/
[26] Composite materials. (2019, August 10) https://make.3dexperience.3ds.com/materials/composite-materials-for-3d-printing-processes
[27] 3D Printer Continuous Carbon Fiber Filament Material | Markforged. (n.d.). Markforged. Retrieved June 20, 2020, from https://markforged.com/materials/carbon-fiber/
[28] https://www.3dnatives.com/en/complete-guide-3d-printing-composites-280120204/
[29] https://markforged.com/learn/3d-printing-carbon-fiber-and-other-composites/#:~:text=Carbon%20fiber%2C%20fiberglass%2C%20and%20Kevlar,easy%20to%20snap%20if%20bent.
[30] https://www.tradekorea.com/product/detail/P692623/Chopped-carbon-Fiber.html
[31] https://www.stratasys.com/manufacturing/3d-print-strong-parts-carbon-fiber-advanced-materials
[32] https://3hti.com/3d-printing/mark-one-3d-printer-faq-printing-material/
[33] https://en.wikipedia.org/wiki/Nanocomposite#:~:text=Nanocomposite%20%2D%20Wikipedia-,Nanocomposite,that%20make%20up%20the%20material.
[34] https://www.scielo.br/scielo.php?script=sci_arttext&pid=S1516-14392009000100002
[35] https://www.azonano.com/article.aspx?ArticleID=1832
[36] Carbon Nanotubes and Graphene as Additives in 3D Printing Lara A. Al-Hariri University of Massachusetts Amherst Branden Leonhardt Florida State University Mesopotamia Nowotarski Florida State University.
[37] https://www.google.com/url?sa=i&url=https%3A%2F%2F3dprintingindustry.com%2Fnews%2Fsculptifys-flex-flees-filament-favour-pellets-

27618%2F&psig=AOvVaw0p99Cm2uq6zXNRYXTqhsnU&ust=1593589756084000&source=images&cd=vfe&ved=0CAMQjB1qFwoTCOD2782GqeoCFQAAAAAdAAAAABAD

[38] https://www.nanowerk.com/nanotechnology/introduction/introduction_to_nanotechnology_22.php

[39] https://www.openpr.com/news/1856453/single-walled-carbon-nanotubes-market-profiling-players

[40] https://www.cheaptubes.com/carbon-nanotubes-history-and-production-methods-2/

[41] https://en.wikipedia.org/wiki/Carbon_nanotube#Structure_of_single-walled_tubes

[42] https://nanografi.com/blog/doublewalled-carbon-nanotubes-overview/

[43] https://www.indiamart.com/proddetail/multi-walled-carbon-nanotubes-21117659412.html

[44] A REVIEW ON STUDY OF POLYMERS AND RECENT DEVELOPMENTS AND FUTURE CHALLENGES IN MATERIALS FOR ADDITIVE MANUFACTURING-3D PRINTING. Dattaji K. Shinde1

[45] **ABS Nano Composite Materials in Additive Manufacturing** Eshwar Reddy Cholleti1, Ian Gibson2 1 M.Tech Thermal Engineering, Co - Founder of 3D Srishti Pvt Ltd, Telangana, India. 2Professor, Head of School at Deakin University, Highton, Victoria, Australia**.**

[46] https://3dprint.com/4517/carbon-nanotube-3d-print-filament/

[47] https://3dprint.com/4517/carbon-nanotube-3d-print-filament/

[48] **Filaments Production and Fused Deposition Modelling of ABS/Carbon Nanotubes Composites** Sithiprumnea Dul ID, Luca Fambri and Alessandro Pegoretti *

[49] FDM 3D printing of MWCNT re-inforced ABS nano-composite parts with enhanced mechanical and electrical properties, H. Kürşad Sezer