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Technoloy-function analysis on Powders of Additive Manufacturing by Patents

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***Abstract*—An analysis of technology-function on powders of additive manufacturing based on patents are presented in this paper. Patent pool is searched and manually screened from official database USPTO, EPO, and JPO. Patent application trend of various materials in these three offices show high increase since 2014. Main applicants are interested in the market of the United States.**

Three materials, plastics, metals, and adhesives in the U.S. are analyzed and showed on technology-function matrix. Major objective functions of metals are mechanical property improvement, fineness improvement, and higher density, plastics are to improve mechanical property, flowability, and precision. The hottest technology of adhesives is to add functional materials.

Keywords— additive manufacturing; patent analysis; technology-function matrix.

I. INTRODUCTION

Additive manufacturing, or 3D printing, is an advanced manufacturing process in the world. The American Society for Testing and Material (ASTM) divides 3D printing technology into seven types, of which the types most relevant to manufacturing industry applications are powder bed melt molding and adhesive injection molding. In these two processes, the most important feature is the use of many different types of powder materials, such as metals, plastics, ceramics, etc.

Market research organization MarketsandMarkets has released a research report on the 3D printing powder market forecast, "3D Printing Powder Market-Global Forecast to 2020". The report states that the global market for 3D printing powder materials will reach sales USD 636.9 million within five years, with a compound annual growth rate of 24.4% from 2015 to 2020. It is obvious that investing in this market in the future can achieve considerable profits.

3D printing technology can be roughly divided into two parts: equipment and materials, which complement each other. In the early stage of technology development, equipment was mainly developed, and materials were relatively less invested. However, until today, device-related technologies have gradually matured, and manufacturers around the world have begun to actively develop materials for 3D printing, especially powder-related materials. Due to the use of powder-related material printing technology, the possibility of applying it to industrial mass production is quite high and has great prospects.

This paper analyzes technical development of multilayer manufacturing powder technology by patents, powders for powder bed fusion and binder jetting, to find out current technology development trend provides the industry as a reference and the basis for subsequent research to facilitate the formulation of research and development directions or patent portfolios, and to occupy a place in this market in the future.

There have been related researches on additive manufacturing, including fundamental patents based on the highest number of citation as prior art by subsequent patents [1], methodology of technological evolution based on International Patent Classification [2], and monitoring the scientific and technological trends in medical applications [3].

Patent documents are important materials to understand the technology development, researches use patent literature to analyze detailed technical development information [4]. Technology-function matrix could be used to show the patent comprehensive or breadth of a company. The occupancy in the matrix can be an indicator of patent comprehensive of an applicant [5][6][7]. This paper focus on technology-function analysis and main applicants on powders of additive manufacturing by patents.

The patents of 3D printing powder-related materials are diversified and are constantly being added. The materials can be divided into the following six types at present, polymers, metals, ceramics, cement, binders, and composite materials.

There are many types of polymers. In 3D printing applications, plastics are the main type. Plastic materials can be applied to a variety of 3D printing manufacturing technologies, such as Material Extrusion or Powder Bed Fusion, etc. However, each technology has different requirements for the form and specifications of plastic. Therefore, it is difficult to directly apply the same kind of materials used in different technologies.

Metal has high strength and therefore an important material for 3D printing. It has a wide range, for example, stainless steel for industrial mold, titanium and titanium-based alloys for aircraft, cobalt-based alloy for medical, aluminum alloy for bicycle or vehicle, copper alloy for boat, precious metals for jewelry, etc.

The main technologies for ceramic materials are Vat Photopolymerization and Binder Jetting. Due to technical constraints, such as the difficulty of heating ceramics, there are currently few applications for powder-related technologies.

In the early days, cement was mainly used for proofing of artwork or industrial samples. At present, the development of such materials has gradually decreased because low strength.

Binders are mainly applied to products whose main powder is metal or ceramic material. Ceramic adhesive is very suitable for displaying aesthetic works or architectural models, etc., but it is not suitable for the manufacture of functional components because it is relatively fragile. Metal adhesive can be for the manufacture of functional components and is more cost-effective, but its mechanical properties are low relative to powder bed fusion technology.

Recently, composite materials has rapid developed. Many carbon fiber composite materials are popular.

II. Methodology and Data

The pool of patents in this study was gotten from official databases by organized search queries. Key words including: (power or grain) in specification, Cooperative Patent classification is B33Y70/00, materials specially adapted for additive manufacturing, the filing date is between 1998 and 2018. And remove some sub-group in B29C64/00, which is additive manufacturing by additive deposition, additive agglomeration or additive layering, e.g. by 3D printing, stereolithography or selective laser sintering.

We manually screen low-related cases, including: Fused Deposition Modelling (FDM) or Stereo-lithography (SLA) related materials, biological cell related materials, liquid and gel materials, film generation or circuit board, main features of apparatus or process. Table 1 is the patent pool in United States Patent and Trademark Office (USPTO), European Patent Office (EPO), and Japan Patent Office (JPO), of in this study.

Table 1 patent pool of this reserch

Patent office	Original	After screen
USPTO	912	502
EPO	154	104
JPO	630	221

III. Illustration

A. Patent application trend chart of various materials

Fig.1 is a patent application trend chard of various materials in USPTO based on filing year. Preparation means to generate grains not limited to any kind of materials, fillers are not limited, either. Observing the horizontal red frame, it can be found that since the early days of development, metal, plastic and adhesive materials are three main materials invested in considerable resources for research and development, and fast growth since 2015. Composites, ceramics, and cement are not so popular. There is a 6 to 18 month delay form patent application to publication, so not all cases filed in 2018 have been published.

Fig.2,3 are patent application trend chard of various materials in EPO and JPO based on filing year. It can be observed that plastics have continued to steadily research and develop, a large number of applications have appeared in all materials since 2014.

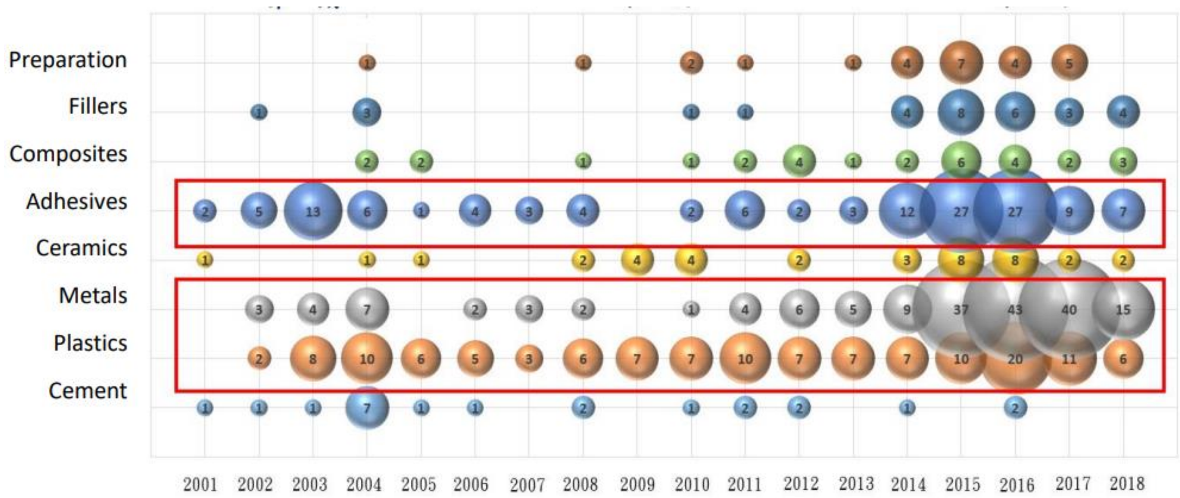


Fig. 1 patent application trend of various materials in USPTO

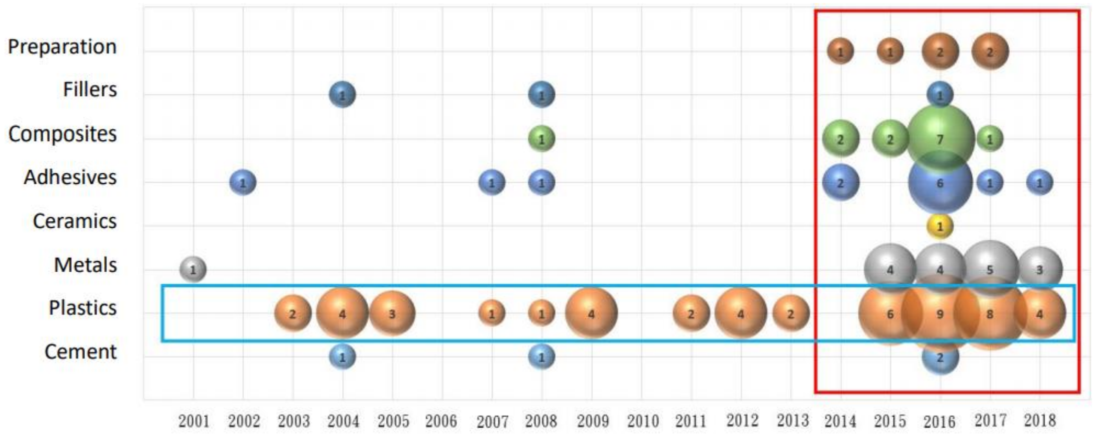


Fig. 2 patent application trend of various materials in EPO

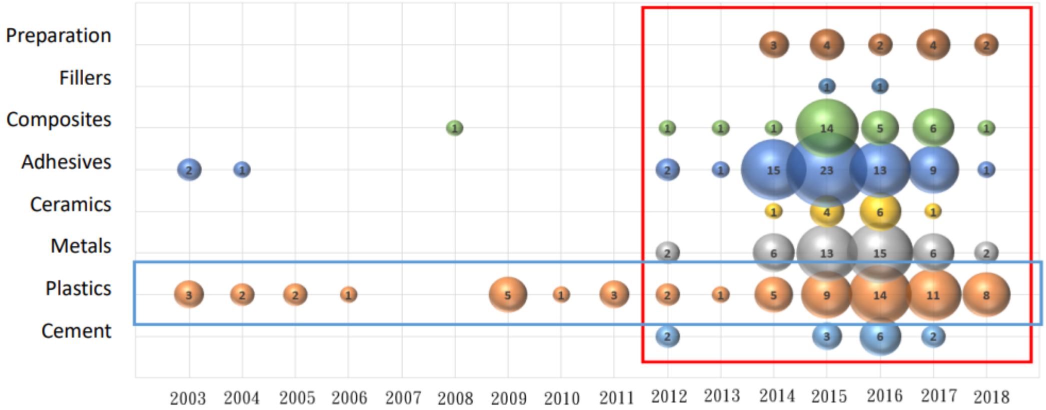


Fig. 3 patent application trend of various materials in JPO

B. Main applicants in various materials

Fig.4 is the main applicants of various materials in USPTO. It can be found that the research and development of the main patentees are concentrated on plastics, metals, adhesives, and composite materials. There are only manufacturers of a single class of materials. Plastics include ARKEMA, SABIC GLOBAL, and DEGUSSA. Metals include ARCONIC, DIAHEN, ANSALDO ENERGIA IP, AIRBUS DEFENCE, and HAMILTON.

Most of them have recently applied for a large number of metal-related patents. Since composite materials are often applied for patents together with other materials, there are no separate manufacturers. From a horizontal perspective, it can be observed that only HEWLETTPACKARD is involved in various materials.

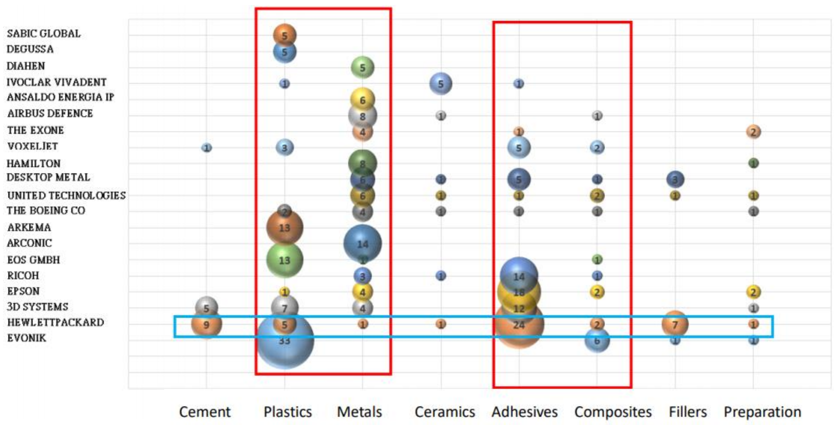


Fig.4 main applicants of various materials in USPTO

Fig.5 is the main applicants of various materials in EPO. It can be found that among the main patentees, no manufacturer has application for cement, ceramics and filler related patents, FUJIMI and ARKEMA have separately applied for composite Materials and plastic patents, other manufacturers are more involved in various materials.

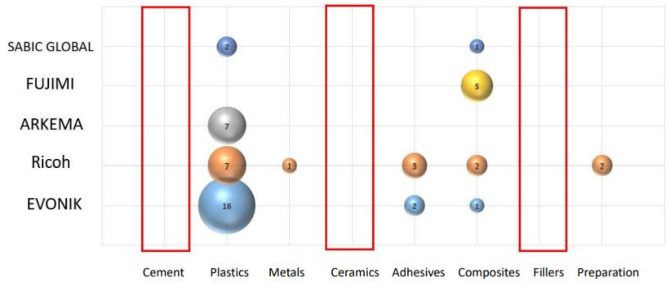


Fig.5 main applicants of various materials in EPO

Fig. 6 is the main applicants of various materials in JPO. Unlike other countries that have a single material R & D manufacturer, the main patentees in Japan have invested considerable resources in various materials.

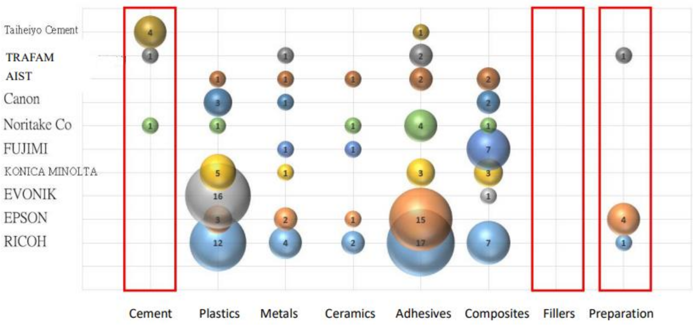


Fig.6 main applicants of various materials in JPO

C. Technology-function anaylysis in USPTO

From the foregoing analysis, the United States is the most important country for main applicants, and metals, plastics, adhesives are three hottest materials of 3D printing. We made technology-function analysis of these three materials in USPTO.

Fig. 7 is a technology-function matrix of metals in USPTO. Eight technologies and nine functions in this figure.

The first technology is particle shape adjustment. The shapes of common particles are spherical, nearly spherical, flake, needle, and other irregular shapes. Irregular particles have a larger surface area, which facilitates sintering. However, it is more suitable for spherical or near-spherical powder in metal 3D printing. Spherical powder has excellent fluidity. It can be spread in the printing process so that the powder can be spread smoothly and densely. The printed product has high density and low porosity. In addition, a small volume shrinkage occurs during the melting process, which improves the fineness of the finished product. The shape of the powder particles is related to the powder manufacturing method. The common manufacturing methods are gas atomization and plasma atomization. One applicant declares that a spherical powder roundness can reach 0.95, which is close to a true circle (US20180104740).

Granularity adjustment is the second technology, granularity refers to the volume percentage of powder particles of different sizes in a certain size range. In addition to 3D printing metal powders being bonded through adhesives, they are mostly melted and sintered by directly absorbing energy during laser or electron beam scanning. Therefore, small granularity has a large surface area, which can directly absorb a large amount of energy, and is easy to heat up for facilitate sintering. One applicant found that when the volume average particle diameter of the particles is 1 μm or more, the fluidity of the powder material is improved, thereby improving the smoothness of the surface of the powder material layer and indirectly increasing manufacturing efficiency (US20180104740).

Surface treatment technology refers to the protection of the base material by modifying the surface of the material or coating a layer of other materials. Most of the damage and failure of materials start from the surface damage, so the surface treatment technology for the materials came into being. For example, coating a carbonaceous material can effectively reduce reflectance (US20170044416), materials have low flammability, low reflectivity, low melting point, and low moisture or pollutant absorption of permetallic powder Coating, such as Mg, W, Fe, Zr, Ti, Si and other materials (US20170368603)

Even with the same material, different lattice structures will exhibit different properties. For example, when pure iron is heated to 912℃, the crystal structure will undergo a phase transition from body-centered cubic (bcc) to face-centered cubic (fcc), which is called austenite transformation. Because the face-centered cubic structure is compact and the body-centered cubic is relatively loose, this explains the phenomenon of iron's volume reduction after heating at 912℃. US20170306449 discloses a new bcc made of titanium, aluminum, vanadium and iron. This new material has a higher β-transition temperature and a narrower freezing range, which can reduce thermal cracks and improve various mechanical properties.

Heat treatment has a very popular application in metallurgy. By heating metal materials to a certain temperature and holding them for a certain period of time, they are cooled to a certain rate or lower at a certain rate, so as to improve the structure of the material and obtain materials with excellent performance. In the production process of ceramics and glass materials, there are often heat treatment procedures.

Add functional materials, for example, adding a specific proportion of rhenium to a nickel alloy, its high temperature ductility can be improved, and rapid cooling can be promoted after heat treatment (US20180037979).

Formula ratio adjustment, as an example, by adjusting the content of carbon, silicon, phosphorus, and sulfur elements in Mar-M-247 alloy, the chemical properties of the alloy can be improved to Solderability (US20180347014).

Process adjustment refers to the adjustment or special improvement of the steps of the manufacturing process, such as sintering energy adjustment, heat treatment time, and steps to increase or decrease. For example, reducing the number of processing steps, and at the same time, it adjusts the processing temperature so that lower-grade raw materials can effectively treat powder Perform modification (US20180117676).

The first function is thermal stability improvement, which refers to the deformation and mechanical properties of the substance under the influence of temperature. The smaller the deformation, the higher the stability. The mechanical properties at high temperatures remain unchanged, and low thermal cracking is the result of high thermal stability. This function is often considered as an indicator of whether it can be applied to aviation and other high-temperature work areas. US20180312946 discloses a new Co-based or Fe-based metal alloy. By reducing the amount of carbon to 0.05% of the total weight, it can be used in molten powder. Prevents or significantly reduces crack formation during layer cooling, overcomes one or more disadvantages of known metal alloys, making it suitable for 3D printing of high temperature machine parts.

Lower cost can be achieved by lower materials cost (US20180105903), reduction of energy consumption required by lower sintering temperature (US20170252807), or reduction of manufacturing time (US20180354032).

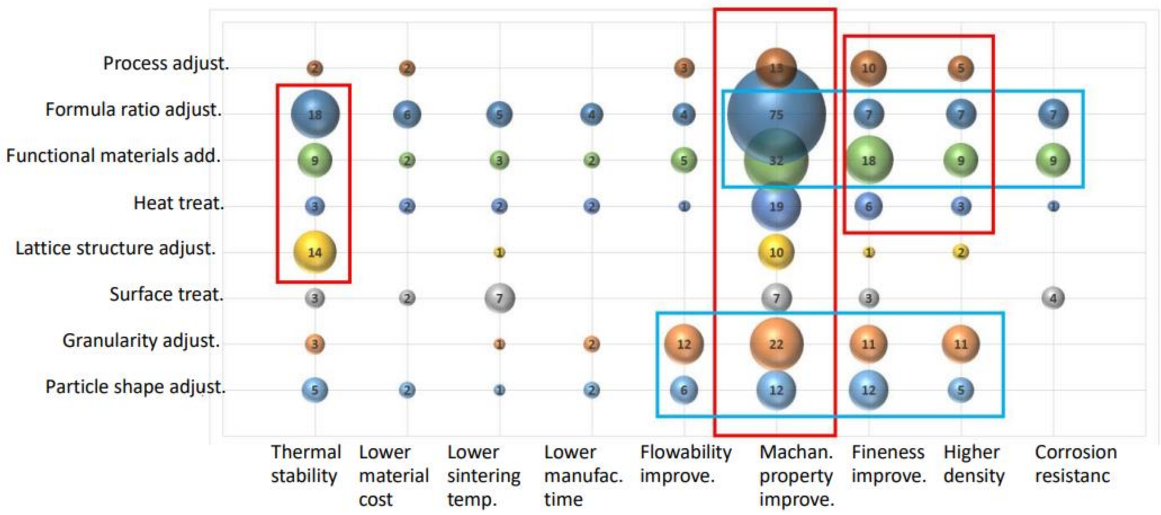
Powder flowability increasing has been the focus of research in recent years. Powder flowability is expressed as the time required for a certain amount of powder to flow through a standard funnel with a defined pore size.

The fluidity will affect the efficiency of the powder coating when filling. Powder flow properties have received much attention in recent years, and various industries have successively invested in research, especially in the two areas of powder metallurgy and pharmaceuticals. The powder metallurgy die-casting process must fill the metal powder into the mold and then die-cast. The solidity of the filling will affect the strength of the cast product. Therefore, it is indispensable to study the relationship between powder flow properties and filling.

The mechanical properties of the material can reflect the relationship between its stress and load and deformation. Mechanical properties generally refer to the mechanical or mechanical properties of a substance, such as the coefficient of friction of a solid, the coefficient of viscosity of a fluid, the density of a substance, the stiffness and hardness of a material, and the properties of materials related to tensile and compression such as impact resistance and fatigue limit.

Fineness improvement is mainly the fineness of the surface of the finished product, such as the fineness of the surface, the degree of shrinkage of the finished product, and the small number of surface microcracks (US20170189960).

The density of the object, such as the density of the material itself, or the number of voids and voids in the finished product, will affect it. The final density and quality of the sintered product depends on, for example, the sintering conditions and powder characteristics (US20170072469).



The ability of a metal material to resist the corrosive damage of the surrounding medium is called corrosion resistance. It is determined by the composition, chemical properties, and morphology of the material. Adding chromium, nickel, aluminum, and titanium that can form a protective film to steel; copper that changes the electrode potential, and titanium and niobium that improve intergranular corrosion can improve corrosion resistance (US20180127854).

It can be observed that most technology-function nodes have been patented, but most of the nodes have fewer than 3 patents. Such nodes are mainly focused on 5 functions, namely reduced material cost, reduced sintering temperature, reduced processing time, and improved corrosion/oxidation resistance.

The vertical red box in Fig.7 is the currently developed objective functions, including thermal stability, mechanical strength, fineness, density improvement. The horizontal blue boxes show hotter technologies, some nodes that have not been patented.

Fig. 8 is a technology-function matrix of plastics in USPTO. All technologies are similar with metal, some functions are different.

the powder provides additional process viscosity stability during repeated printing operations at high temperatures.

Antibacterial is important in food related products and medical engineering. Because they often need to contact the human body and wounds. For example, adding salts such as pure silver, silver nitrate or other silver, silver ions and other substances make it uniformly present in each powder particle, so all surfaces of the object thus manufactured have an antibacterial effect. In the case where the sintered part has a porous structure, since the surface of the cavity wall also has an antibacterial effect, no microorganisms can be deposited in the cavity (US20130273131).

Precision improvement defined here mainly lies in the fineness of the surface of the finished product, such as the surface fineness, the degree of shrinkage of the finished product, and the small surface microcracks.

US20180243978 discloses that its powder contains at least one amorphous polymer binder, which may be one or more semi-crystalline polymer powder binders, which are used to: Along with other additives to adjust the melt viscosity of the system. Amorphous polymer adhesives can produce articles with high dimensional

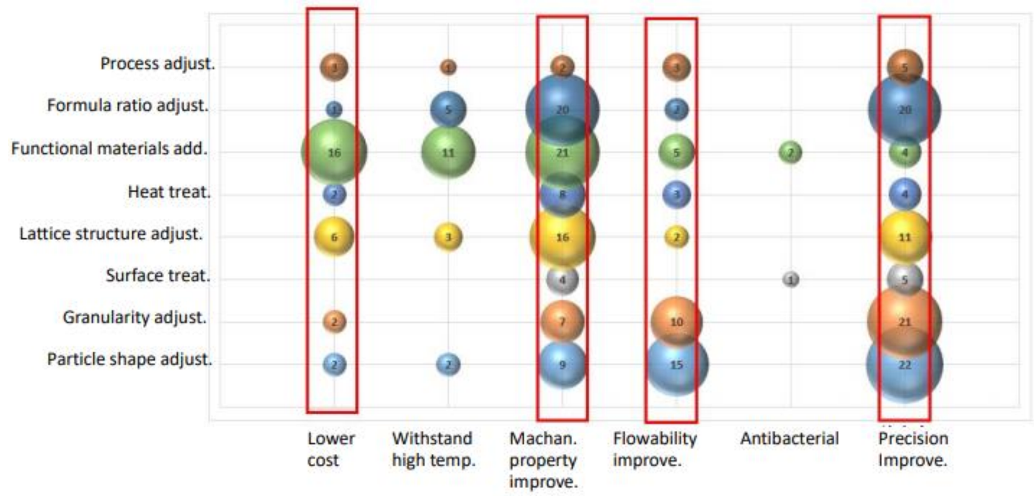


Fig.8 technology-function matrix of plastics

Plastic materials are not like metals that can withstand high temperatures. Excessive heat can easily cause molecular chains to decompose, plastics appear to deteriorate, yellowing, and so on. Such yellowing is usually related to lower mechanical properties because the materials are aging. Examples of significant effects of such aging include embrittlement, damage to tensile strain at break, and impaired notched impact properties. In addition, because plastic is flammable, high temperature may cause fire and burning, so its high temperature resistance is a very important issue in industrial plastic products. US20180009982 discloses a black copolyamide powder with high thermal stability and ease of use, which is composed of aromatic and mixed additives. Due to the addition of phosphorus stabilizers,

It can be observed in Fig.8 that four major functions are hottest in plastics, including lower cost, mechanical property improvement, flowability improvement, and precision improvement. These four functions can be reached by any one of technologies. Fewer nodes in antibacterial and anti-high temperature effects.

Fig. 9 is a technology-function matrix of adhesives in USPTO. Fewer technologies but more functions comparing to metals and plastics.

Mechanical and fineness improvement can be achieved by adhesives. For example, using an organic adhesive having an isocyanate group or an

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epoxy group monomer, the bubbles generated during the removal of the adhesive can be effectively reduced. With black carbon marks, it can effectively improve the bonding strength and mechanical strength (20160325356).

Fineness improvement is the fineness of the surface of the finished product, such as the surface fineness and the reduction of the shrinkage of the finished product. For example, when the viscosity of the adhesive of a specific water-soluble resin is 40 mPa · s or lower, the strength of the powder layer coated with the adhesive can be obtained improve. Therefore, problems such as shrinkage after sintering do not occur, and the dimensional accuracy of the finished product can be effectively improved (US20160368806).

Except for the technology of applying adhesive directly on the powder surface, the other 3D printing technologies using adhesives are mainly spraying adhesives on specific powder areas through printing inkjet heads for adhesion. If the inkjet head is not used for a certain period of time, the adhesive contained in the pipeline is likely to be cured and the pipeline is blocked, or the inkjet is not smooth. Ejection performance can be improved by adding a specific proportion of anti-scaling agent to the adhesive, to prevent the accumulation of scaling in the inkjet head. A suitable anti-scaling agent Examples include oleth-3-phosphate or polyacrylic acid polymer (US20160368806).

Pigment dispersion is also an objective function. In the 3D printing of adhesives, in addition to the coloring function of pigments, more pigments are made by absorbing heat energy to assist the melting and bonding of construction materials. Therefore, uneven dispersion of pigments may easily cause uneven absorption and release, and reduce the quality of the finished product.

US20180320009 discloses that it can be used to help disperse other dyes or pigments by using a high boiling point co-solvent, or to improve the ejection properties of inks. A high boiling point co-solvent Can be present in an amount of about 1 wt% to about 4 wt%.

Because of the chemical nature of the adhesive, most of them have strong volatility, and most of their components are toxic to the human body. Therefore, it is necessary to reduce their toxicity to protect the safety of workers. For example, US20160369116 discloses adhesives contains at least one monofunctional acrylate, at least one polyfunctional acrylate, and at least one chlorinated olefin Structural polymer active energy ray-curable composition. Monofunctional acrylates with excellent solubility generally have a small molecular weight and high volatility, and have problems in skin sensitization. However, the monofunctional acrylate of the present invention is a monomer having excellent ability to dissolve a polymer containing a chlorinated olefin structure, and its skin sensitization test measures a negative SI value.

Improved liquid permeability is also a function of adhesive. After the adhesive is sprayed on the surface of the powder bed, it will penetrate into the powder space for adhesion. At this time, the liquid will have different intermolecular forces due to different material properties, affecting its permeability and poor permeability. The liquid may infiltrate the powder, causing the mechanical strength and accuracy of the finished product to decrease, and excessive permeability may affect the powder bed in unspecified areas due to excessive penetration. For example, US20180178447 discloses a stable liquid functional material, which can effectively prevent excessive penetration of the adhesive.

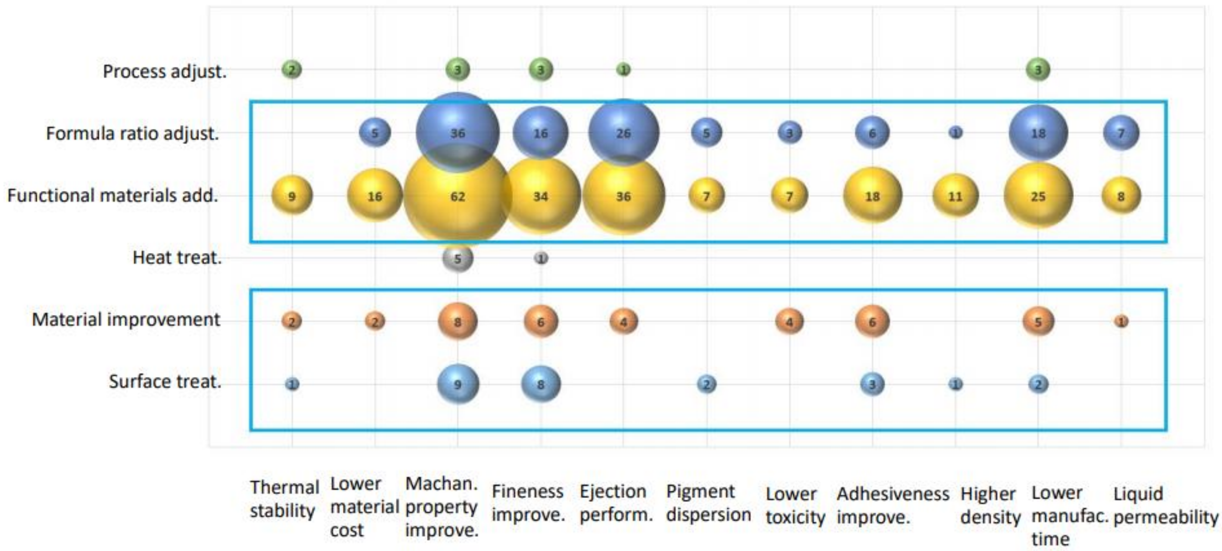

Fig.9 technology-function matrix of adhesives

Observing the horizontal blue box in Fig.9, most of the patents focus on the two types of technology: adjustment of formula ratio and addition of functional materials. Although the number of patents for material improvement and surface treatment technology is relatively low, but it can also achieve more effects. Two functions, mechanical property and fineness improvement, are hot research area for adhesives.

IV. CONCLUSIONS

Plastic materials are one of the materials that were prioritized by a large amount of R&D investment in the early stage of 3D printing and last a long time. The total number of patents held by the top ten patentees exceeds half of the patents for plastic materials, which have been taken the lead by major patentees. However, special effects such as cost reduction and antibacterial, are worth investing in research and development.

The threshold for metal materials is high, R&D investment must be careful. Empty or fewer patents on the nodes of technology-function matrix, particle surface treatment or heat treatment, could be prioritized.

Compared with other plastic and metal materials, adhesives are more worthy of R&D because of low technical threshold. The technology-function matrix of adhesives shows that although most nodes of the matrix are currently occupied, there are not many and few developers.

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