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Chapter 4

Powder bed fusion

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Abstract

This chapter presents the available powder bed fusion technologies for the processing of polymers. Selective laser sintering (SLS) is the most commonly used technique; the process involves the deposition of a powder layer, and the use of a laser to selectively melt the region of interest. The 3D object is therefore produced with a layer-by-layer strategy. The increasing interest of both scientific and industrial communities for this technique has promoted its development, which nowadays is involved for the production of functional prototypes and small series of components. An alternative and emerging technique is multi jet fusion (MJF); differently from selective laser sintering, MJF uses an infrared (IR) radiation to promote the melting of thermoplastic polymers. Both these processes will be discussed in term of required processing conditions, available materials and all the processing aspects which can influence the properties of the final component. Conclusively, some alternative technologies including selective mask sintering (SMS), high-speed sintering (HSS) and selective inhibition sintering (SIS) will be presented.

Keywords

Additive manufacturing, powder bed fusion technologies, polymer powders

4.1 Introduction

Powder Bed Fusion (PBF) process is one of the most popular techniques associated with additive manufacturing. According to ISO/ASTM 52900 [1], PBF includes any technology in which a source of thermal energy is used to selectively fuse a region of a powder bed.

Historically, the first process that shows comparable characteristics with respect to modern PBF technique was proposed by Pierre Ciraud in 1971 [2]. He described a process where particles were used to form a powder layer onto a matrix; then a laser, an electron or a plasma beam locally heated the particles leading to the consolidation of a continuous layer. In 1979 Ross Housholder firstly described a powder laser sintering process in a patent [3]); however, only in 1997 Carl Deckard,

while he was at the University of Texas, filed two patents inherent the description of the method and the first modern PBF apparatus for the fabrication of parts through the deposition and the selectively sintering of subsequent powder layers [4, 5]. Starting from this early system, the evolution of this technology was continuous and nowadays powder bed fusion technology, with particular reference to selective laser sintering, represents one of the most used and widespread 3D printing technology worldwide.

The available polymer-PBF (p-PBF) technologies are selective laser sintering (SLS), which is the most common and investigated from both scientific and industrial communities, multi-jet fusion (MJF), and some alternative PBF techniques specifically designed to increase the process productivity. These last techniques are defined as line-wise and layer-wise PBF processes respectively, and they mainly include selective mask sintering (SMS), high-speed sintering (HSS) and selective inhibition sintering (SIS) techniques.

All PBF processes can be identified by three main steps (powder recoating, energy input followed by coalescence and cooling of the system), as described in the following.

- The *powder recoating* refers to the process of spreading a fixed amount of powder particles to obtain a smooth and homogeneous powder layer. This step plays a fundamental role because it greatly influences both the quality of the deposited layer and the properties of the printed part. Wang et al. [6] underlined that the recoating step affects the density and the homogeneity of the layer of powder; moreover, this initial stage also influences the force which is applied to the underlying solidified part. All these factors contribute to the success and the performance of building process in term of build speed, dimensional accuracy, and part properties.

The deposition of subsequent powder layers occurs using a recoater that generally shows two main geometries, a blade or a roller respectively. Because of the importance of this step, many researchers investigated the interaction between the recoater and the powder as a function of the recoater shape.

Parteli et al. [7] focused the attention on the use of a roller for SLS process, and developed a model which describes the transport of particles using this coating device. The results show that the surface roughness and the packing characteristic of powder layer is greatly influenced by the process speed.

According to Haeri et al.[8] the use of a roller allows obtaining a higher quality powder layer with respect to that produced by a blade. This can be explained by considering the higher contact area of a roller if compared to a blade; the roller promotes the progressive rearrangement of particles during the deposition step forming a homogeneous and uniform powder layer. On the contrary, the slender shape of the blade leads to a limited interaction with the particles inducing a dragging effect; as a consequence, a rough powder layer forms. These considerations induced Haeri [9] to further investigate this issue. A later study evidenced that the optimization of the blade geometry profile in term of width, height and shape can significatively improve the powder bed quality.

Once the region of interest belonging to a single layer is scanned, the powder bed is lowered by a height corresponding to one-layer thickness and a new powder layer is deposited.

- *Energy input* is the thermal source required to induce the fusion of powder particles in a selected area on the powder bed. The most common thermal sources for commercial PBF systems are lasers, able to provide a precise delivery of coherent energy. Through a proper mirror system, it is in fact possible to focus the laser beam on a single powder layer with a high spatial resolution. On the base of the nature of the material to be processed, different lasers can be used. In fact, polymers and metal powders show a significantly different absorption spectrum and moreover they require significantly different amount of energy to melt; therefore, different laser sources are required.

As an alternative, non-laser thermal sources can be adopted such as the high-power electron beam, which is used for the additively processing of metal powders through the so called "electron beam melting (EBM)" technology. The use of this kind of thermal source involves an equipment which is significantly different with respect to a laser sintering machine. Another non-laser thermal source is used in multi-jet fusion technique, where an infrared light selectively heats the region of the powder layer containing a previously dispersed heat-conducting liquid.

- Coalescence and cooling are the two mechanisms that lead to the consolidation of a single layer, and the formation of a bonding with the previously scanned layer. The particle coalescence involves that two or more particles form sintering necks, and bond together thanks to the reduction of their free energy [10]. In polymer-PBF, this mechanism is mainly induced by the temperature increase occurring after the exposure to the energy source and the viscous motion. Then, the polymer solidifies as a consequence of heat loss, and the system cools firstly down to the temperature of the powder bed, and then to the room temperature reached when the object is built.

According to Sillani et al. [11] two of the main factors influencing the coalescence phase are associated with the rheological behaviour of the powder materials to be processed by PBF, namely the viscosity and the surface tension.

4.2 Selective Laser Sintering (SLS)

As previously mentioned, selective laser sintering was the first commercialized PBF process. Once the patents application was filed, Deckard and some of his colleagues founded the company Nova Automation, which was later renamed as DTM Corporation. It developed, manufactured, and put into the market rapid prototyping and manufacturing SLS systems. Although SLS was originally developed for research purposes, the launch of Sinterstation 2000 by DTM in 1993 represented the first example of 3D printer designed for industrial use.

In 2001, DTM Corp was acquired from 3D Systems Inc., which nowadays represents one of the reference points for additive manufacturing field. These emerging technologies have attracted a growing interest not only from the scientific community, but also of the industrial ones. Therefore, in addition to the activities of the american DTM Corporation, new companies progressively born world-wide and started commercializing PBF systems such as EOS GmbH. Although this latter initially focused on stereolithography process and 3D scanning systems, afterwards it extended its interest in PBF process and named it as "laser sintering".

Moreover, thanks to the great versatility of this technology, in few years the selective laser sintering approach, which was originally developed to produced polymer components, was extended to the processing of both metals and ceramics.

Selective laser sintering allows obtaining parts with high dimensional accuracy (higher with respect to other AM techniques such as fused deposition modelling), high productivity and good mechanical properties. The possibility to produce both pure polymeric and composites parts with complex geometry without the need of using neither supports nor moulds, increases the potential applications of SLS at industrial scale. Nowadays SLS represents a cost-effective alternative for the production of functional prototypes and small series with respect to both other AM technologies (such as fused deposition modeling or stereolithography) and conventional ones such as injection moulding [12].

The progressive development of AM technologies with the aim to move from fabrication of prototypes to the production of end-use components inevitably increases the requirements in term of the quality of the printed parts. Therefore the physical, thermal and mechanical properties of AM components have to withstand operational requirements which are comparable to those of parts which are obtained by traditional manufacturing techniques [13].

In recent years, the great efforts and financial resources invested in the development of SLS technology allowed achieving numerous advancements in term of SLS equipment (improvements of used laser system, heating source able to provide high stability of temperature within the building camera during the entire process, recoater system), SLS process (investigation of all involved physical aspects and optimization of process parameters), and characterization of starting material properties. All these issues led to an improvement of SLS performance. However, this technology has not yet achieved the same maturity of conventional thermoplastic manufacturing processes. This is mainly due to limited consistency and reliability of the process that has a great effect on the quality of the final parts [14]. In fact, the residual porosity and the quality of the interfaces between layers, which are intrinsically associated with AM process but not involved in conventional ones, lead to an anisotropy of the mechanical properties of the resultant parts [15, 16]. In addition, the possible thermal distortion can lead to curling and warping of fabricated parts [17]. Therefore, to obtain components which can satisfy the requirements imposed by industrial world, and therefore to widen the SLS applications scale, this technology needs to be further investigated and improved.

The following section will describe the main steps that characterize SLS process as well as the very complex phenomena which are involved.

4.2.1 SLS process technology

The SLS process can be described as the layer-by-layer repetition of three main stages, namely warm up, building and cooling steps respectively. Fig 4.1 illustrates the SLS apparatus and its main components.

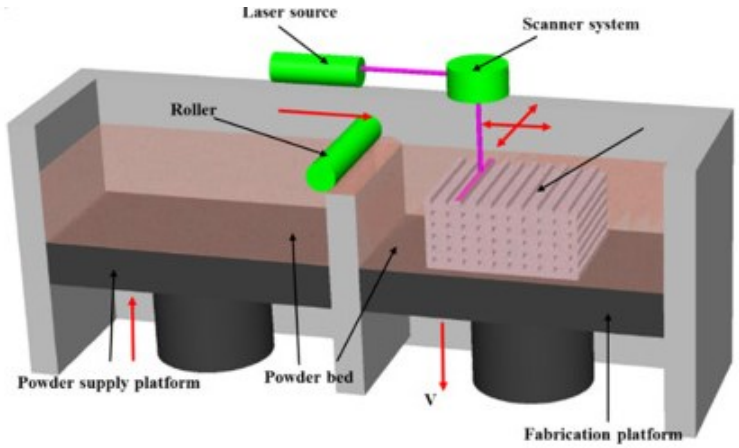

Fig. 4.1 Scheme of SLS equipment. Reprinted with permission from [18]

The warm-up stage is characterized by a preheating of the system up to a defined temperature, referred as powder bed temperature (Tb), which is selected on the base of the powder to be processed and it is maintained during the whole process. Generally, it is set in a range between 40°C and 90°C higher with respect to the material glass transition temperature [19] . The choice of this temperature is crucial because it allows decreasing the amount of energy required to melt the powder when laser scans a layer. At the same time, it must ensure that a homogeneous and uniform powder layer can be obtained during the recoating. In fact, temperature greatly influences the physical properties of the powder and therefore its flowability during the spreading steps.

It is generally accepted that during SLS process, the temperature of powder bed needs to lie between the onset of the crystallization temperature and the onset of the melting one, which can be referred as “processing window” or “sintering window”.

The energy required to increase the temperature of the system up to reach an isothermal condition is usually achieved by using continuous IR lamps and/or resistance heaters placed onto the powder bed.

The building step is the most structured phase of the process because it includes the powder recoating, the laser energy input and the interaction of this heating source with the polymer powder up to achieve its melting, and conclusively the material consolidation.

Firstly, a uniform and controlled-thickness layer of polymer powder is deposited onto the building platform using a blade or a roller. Then, a CO_2 laser placed just above the powder bed, selectively scans the powder surface to induce the melting of polymer particles constituting the area of interest. In fact, by means of a scanning mirror system and based on a previously set computer-controlled model, the laser beam moves across the powder layer, providing to a selected region of the powder bed the extra energy required to locally melt the polymer grains.

After the laser exposure, the molten powder coalesces at a temperature which is close to the polymer melting point; then, the material solidifies upon cooling reaching the bed temperature. During this process, in addition to the increase of the part height of a value corresponding to a layer, the bonding between previously scanned layers is ensured.

When the laser beam heats and melts the polymer grains, these melted grains coalesce and densify. The main driving forces for coalescence and solidification are the viscous flow of the polymer melt and the loss of heat within the powder bed [20].

Zhao et al. [21] described the sintering behavior of two equal size polymer particles using three consecutive, but significantly overlapped, phenomena. Firstly, sintering necks form between particles and progressively grow. The second stage involves the network of channels along the grain edges. In fact, due to the shrinkage of these channels, the grains grow up to reach, in the third phase, the formation of larger spherical particles. In the literature, a large number of models that concern the simulation of sintering process can be found. One of the first one was proposed by Frenkel et al [22], who described the coalescence speed which occurs by viscous flow. This study evidenced that there are two material properties that greatly influence the coalescence step, namely the surface tension and the viscosity respectively. However, this model adequately represented only the first stages of polymer sintering. Pokluda et al. [23] proposed a modified version of Frenkel's model which aims to extend its validity throughout the whole process, but using a limited number of parameters. This last model is based on the equilibrium between the surface tension and the viscous dissipation, considering other possible operating forces as not significant. However, it was found that these models did not fit well the sintering of polymers because they did not include a complete evaluation of their rheological viscoelastic behaviour.

Therefore, further studies elaborated models which take into consideration the importance of these rheological properties such as the viscosity, that can significantly vary as a function of the temperature, the shear rate, and the time.

The model proposed by Bellehumeur et al. [24] in fact, combined the Frenkel's approach with Maxwell equation; the latter introduced the polymer viscoelastic behaviour in the description of sintering process. The validation of this approach through experimental results confirmed the great influence that viscous elastic properties have on polymer particles.

Once the fabrication of 3D objects is completed as a result of the repetition of recoating and building stages, the sintered part is cooled from the bed temperature to the room temperature. This cooling is generally performed in homogeneous conditions in order to avoid the development of residual stresses within the material [22, 25].

After that, the unmelt powder is removed from the powder cake and the final component is recovered.

4.2.2 Materials for SLS

Carl Deckard, creator of SLS technology, did not focus the attention only on the development and commercialization of SLS process and apparatus, but he considered essential the development of materials suitable to be processed with this technology. For this reason, in 2012 he co-founded Structure Polymers, a company with the objective of developing advanced materials for powder fusion technologies.

The rapid evolution of selective laser sintering and the increasing interest in this technology for potential applications at industrial scale make the development of new raw powders that can be processed by SLS necessary, in addition to the optimization of process itself. In fact, it is worth noting that the majority of published studies focused their attention on the optimization of process parameters in order to obtain full dense parts with enhanced mechanical properties or on the study of the variation of mechanical performances of 3D objects as a function of their building orientation [16, 22, 25, 26]. Nevertheless, the key role of starting material and related quality has been recognised as essential for maximising the performance of both SLS process and resultant printed samples [27–30].

Theoretically speaking, any polymer in form of powder can be processed by selective laser sintering if its interaction with a laser beam results in the absorption of an energy amount high enough to cause the full or partial melting of the material [12]. However, some limitations must be considered because some properties of starting powders strongly influence the success of SLS process.

According to Schmid al. [31] some of the most important requirements for a material which make it suitable to be processed by SLS are thermal properties, optical properties, viscosity and surface tension, particle shape and distribution.

Thermal properties.

SLS process involves the heating of powder bed at a not-ambient temperature. Then, an energy source in form of a laser beam provides the extra amount of energy able to melt the polymer particles. Finally, the sintered powders belonging to one layer cool down to the powder bed temperature, while a bond with the previous scanned layer forms. In a process which is so greatly influenced by temperature variations and thermal phenomena, the understanding of the thermal behaviour of starting material during the whole process is fundamental. Therefore, a strict control of operational temperature is required. For semi-crystalline polymers, which are the most used for SLS, the processing temperature has to be fixed in a range between the onset of crystallization and melting point. This thermal range is referred to as "sintering window" and it should be as wide as possible: if the operational temperature is too close to the crystallization one, this latter can be induced when the cooling rate is slow. A premature crystallization can cause the curling or warpage of the parts.

Moreover, thermal conditions which characterize the building chamber during SLS process should be investigated. However, only few studies can be found in the literature on this issue.

Optical properties.

The interaction between the laser beam and the powder particles is one of the key steps of SLS process. This interaction occurs in a very short time, during which the polymer must absorb a sufficient amount of energy to be melted. Generally, SLS systems are equipped with a CO_2 laser: the choice of this energy source is justified

by considering the high absorption of polymers at the wavelength of 10.6 μm, typical of CO_2 lasers. In fact, most polymers are aliphatic compounds containing functional groups that are easily excited in infrared region and therefore, they are able to absorb a high fraction of this radiation.

Viscosity and surface tension.

The key role of these two properties was originally evidenced by Frenkel et al. [22]: a low melt viscosity as well as high surface tension are in fact important to promote a successful coalescence of particles. According to Sillani et al. [11] the polymer melt should have a low value of zero shear viscosity to obtain the full coalescence in the short time expected for the process. Contrary with respect to other processing techniques such as injection moulding, SLS does not involve an additional compacting during the building process; therefore, a low melt viscosity at low shear stress condition is essential [31].

Particle shape and distribution.

The evaluation of both particle shape and size distribution constitutes a standard practice when a new powdered system is going to be processed by SLS. The key role of these two powder properties is due to their impact on the flow behaviour of the powders. In fact, polymer particles must be characterized by a proper geometry and dimensional distribution, that allow a free flow of particles when they are deposited by the recoater, and the formation of a thin and homogeneous layer. Moreover, their size has to be suitable to be easily melt when laser beam is applied.

Polymer powder systems can be produced through different production processes, which strongly influence their shape. There are mainly three particles geometries that can be obtained as shown in Fig. 4.2 [29, 32]. Spherical particles (Fig. 4.2a) can be generated by a co-extrusion process of a mixture of soluble and non-soluble materials. Secondly, particles with the so-called “potato shape” (Fig. 4.2b) are produced through precipitation process; this geometry is the most common for the polyamide 12 (PA12) powders, the most widely used commercial material for SLS. The third possibility involves a shape which is very different with respect to the previously listed ones: cryogenically milled particles (Fig. 4.2c) are in fact characterized by a random and very irregular geometry.

The investigations of many researchers agree that spherical particles are the most suitable for SLS process because they allow obtaining a powder bed showing the highest density and homogeneity [12].

In addition to a spherical geometry, the achievement of powder bed with good quality is obtained by controlling the dimensional distribution of the particle size, taking into consideration that generally the thickness of a deposited powder layer is in the range from 100 μm to 150 μm. Based on the various studies in the literature, however, there are several dimensional ranges that can be considered as suitable for SLS process.

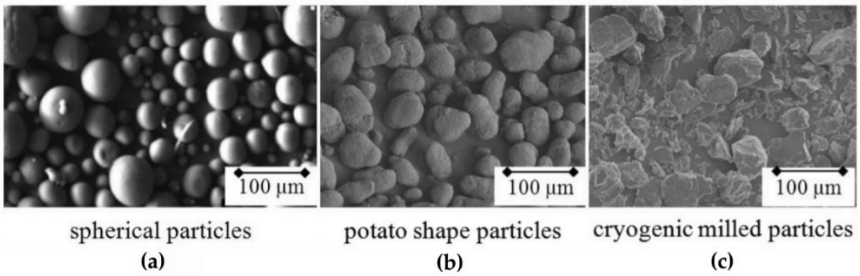

Fig. 4.2 a) Spherical particles obtained by co-extrusion, b) potato-shaped particles obtained by precipitation from ethanol solution, and c) irregular particles obtained by cryogenic milling process. Reprinted with permission from [32]

Wang et al. [33] reported that the optimum particle size distribution (PSD) is in the range between 45 µm and 90 µm, and a narrow distribution is more advisable. A wider range is considered by Chung et al. [34]: on the base of the results obtained in this study, PSD should be slightly smaller with respect to the layer thickness. For this reason, particles with a size from a minimum of 10 µm to a maximum of 150 µm are preferred. However, when using powder with a wide size distribution, the optimization of process parameters requires particular attention [35]. A third approach is used by Schmid et al. [29], who identified as optimal for SLS the powders showing a particle size distribution in the range from 20 µm to 80 µm. Powder systems characterized by a too high fraction of very fine particles show low flow properties, which lead to a low quality powder bed.

The above discussed requirements for SLS powders are quite challenging; this is the main cause of the limited number of materials nowadays available to be processed by this technology. Among polymers, only thermoplastic materials can be considered; on the contrary, thermosetting ones are not suitable because they cannot by melted by the interaction with a laser beam. Moreover, thermoplastic powders can be recycled in subsequent SLS jobs, preventing the material waste.

Thermoplastic can be distinguished between amorphous and semi-crystalline ones, that show very different thermal behaviour caused by a different structure and organization of chain molecules.

The main amorphous materials that can be processed via selective laser sintering include polycarbonate (PC), polystyrene (PS) and styrene-acrylonitrile copolymer.

Thanks to the good mechanical properties and its relative low cost, PC is used in many applications. Denucci [36] was one of the first researchers who produced patterns of investment casting via SLS. It was found that this approach offers numerous advantages when compared to some components produced with more conventional materials such as wax. For this reason, the fabrication of these patterns is nowadays realized mainly using PC. As for other amorphous materials, the thermal behaviour of PC as a function of the thermal conditions involved during SLS required a detailed investigation. Many studies were therefore focused on the development of thermal models describing the SLS process of PC [37–39]. Berzins et al. [39] demonstrated that the variation of material thermal properties as a function of both the temperature and the position of scanned layer which is progressively far from

the platform as the process evolves, are fundamental to effectively predict the heat transfer during sintering.

Moreover, the potential use of PC to fabricate functional components in addition to prototypes, makes the optimization of process parameters to obtain printed parts with good mechanical properties necessary [40].

The investigation of additional amorphous polymers such as polystyrene (PS), high impact polystyrene (HIPS) and styrene-acrylonitrile copolymer was performed using two different approaches, similar to those previously described, which respectively involve the simulation of sintering mechanism as a function of SLS thermal conditions, and the optimization of process parameters to maximize the properties of printed parts [41–44].

However, the literature reveals that SLS processing of amorphous thermoplastics generally leads to parts with very low relative density and therefore poor mechanical properties; on the contrary, components fabricated starting from semi-crystalline polymers exhibit higher relative density and enhanced mechanical performances. As previously discussed, this is mainly due to the organization of macromolecules.

Nowadays thermoplastic semi-crystalline materials are the most used powder systems for SLS, and among them, polyamide 12 was surely the most widely commercialized powder because it can satisfy all the requirements for SLS powders.

From a processability point of view, PA12 shows a wide temperature range between the melting and crystallization onset (detected during the heating and cooling respectively). As previously mentioned, it is generally accepted from scientific community that for semi-crystalline materials, the powder bed temperature should lie in between the sintering window, [45] that should in turn be as large as possible. In addition, it was found that the interaction of CO_2 laser with PA12 involves a reflection of only 5-6 % of the incoming laser energy, and therefore a high absorption coefficient [46]. The good thermal properties, high absorption of infrared radiation, in addition to a proper rheological behaviour [47–49] make PA12 well suitable for SLS. Numerous studies report that the optimization of process parameters leads to obtain PA12 dense parts with high mechanical properties. Caulfield et al. [50] investigated the impact of energy density variation (which is function of the process parameters) obtained by varying the laser power on both the physical and mechanical properties of PA12 specimens. By increasing the energy density, it is possible to obtain parts with higher density, and consequently with enhanced tensile strength and Young modulus. A similar relationship between mechanical performances and provided energy density was observed by Starr et al. [51], who reported an enhancement of tensile properties as a function of increased energy density until a plateau value is reached. On the other hand, according to Vasquez et al. [52], a too much high energy density causes a decrement of mechanical performance probably due to the onset of material degradation, leading to the formation of bubbles and porosity within the obtained parts.

Many of them belong to the family of polyamides (such as PA6 and PA11, and their composites), which are generally used for engineering purposes, where a combination of good mechanical properties and thermal resistance is required. In this context, SLS engineering polymers can be used for replacing conventional materi-

als, exploiting the competitive advantages associated with the lightness of components, and the possibility of easily producing complex shapes or assemblies as a single component.

Recently, an increasing interest arised for the development of SLS high performance polymers belonging to polyaryletherketone (PAEK) group, such as polyetheretherketone (PEEK) and polyetherketone PEK. They show a unique combination of mechanical properties, good chemical and high temperature resistance that guarantees a continuous use of these materials at high temperature (PEEK can be used for applications up to 260°C).

Although the properties of PAEK are very appealing, some drawbacks limit their use such as the high cost, the required high temperature to be processed, and the low resistance to UV light.

Other semi-crystalline commodity polymers include polypropylene (PP) and polyethylene (PE). Although these materials are traditionally used in a wide range of applications fields such as engineering, packaging and medical ones, the study of their processability by SLS requires further investigations. Goodridge et al. [53] successfully produced multilayer structures starting from ultra-high-density polyethylene (UHDPE) via SLS. However, the study revealed that the narrow sintering window of this material greatly limits its processability; the success of the process can be achieved only by strictly controlling the selection of a proper temperature bed, suitable to minimize the thermal gradient during the process. The investigation of these materials is mainly limited to research purposes and specific applications. Salmoria et al. [54] investigated the fabrication of high-density polyethylene (HDPE) scaffold structures that have a potential use in human tissue regeneration; their results show that structures with different porosity degree can be obtained by varying the particle size of starting powders.

4.3 Multi-jet fusion

Multi-Jet Fusion (MJF) is an additive manufacturing technique which was patented by Hewlett-Packard Inc. (HP) in 2014 and introduced into the market two years later. This relative newcomer technology belongs to PBF process family and gets its name from the inkjet heads that distributes multi-agents on selected region of powder layer in order to promote the particles melting. A so conceived printing process shows affinities with metal binder jetting technology, where a liquid binder agent is applied to each powder layer to promote the part consolidation. The use of inks has the aim to enhance optical-to-thermal energy conversion for obtaining an increased production volume and an improvement of both edge-definition and surface finishing.

4.3.1 MJF process technology

The MJF system is constituted by three different units:

- The processing station where the powders are stored and mixed, and the final component is removed after the printing is completed.

- The build unit which is the core of the system because it includes the printing platform where the building process occurs. It is designed to be moved from the processing station to the printer block and vice versa. Here the MJF process occurs.
- The printer unit which is the system where the build unit is placed when a new job is going to start.

Like all AM technologies, MJF process begins with the elaboration of a CAD model, which allows creating the component to be printed with a high design freedom.

As previously mentioned, the material cartridges are inserted into the processing station and then transferred to the build unit through a clean and automated process. When the build unit is placed into the printer, the multi jet fusion process can start leading to the fabrication of 3D parts.

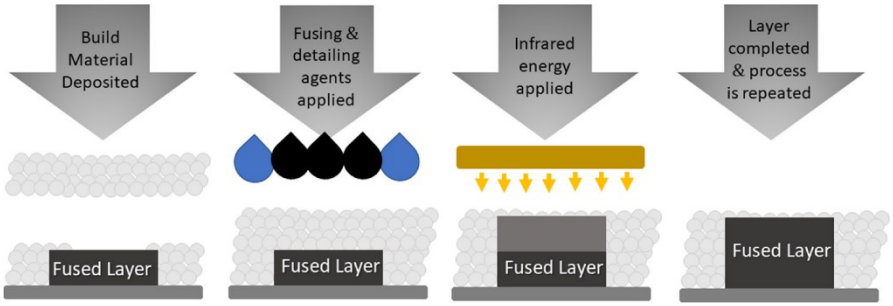

Fig. 4.3 Main steps involved in the multi jet fusion process. Reprinted with permission from [55].

Similarly to the SLS process, a layer of powder is spread onto the powder bed, which is uniformly preheated under a heat lamp system placed over the building platform. However, unlike SLS, the melting of polymer powder is not obtained after the laser scanning, but through the interaction between the powder impregnated with multi-agents and the infrared lamp. In fact, an inkjet head selectively distributes both the fusing and detailing agents on the powder layer (Fig. 4.3): the former is deposited in the selected regions where the particles have to be melted. On the contrary, the detailing agent is spread at their edges in order to prevent the sintering of the neighbour powder, and therefore to delimit the 2D shape of forming layer. The role of this additional agent is important because it allows obtaining a very high dimensional accuracy of the final part, which shows clean contours and very small details, and thus it prevents inaccuracies in specific zones.

Then, an infrared heating source moves across the building platform and promotes the melting of regions where the fusing agent is applied. On the contrary, the areas where the detailing agent has been deposited remain as unmelt particles. In fact, the interaction between the powder filled with fusing agent and the IR source promotes the heating and melting of particles. The liquid inks are known as a radiation absorbing material; however, the chemical composition of these components is generally not reported in the literature because it is considered proprietary. The

material recoating and the process involving both the distribution of multi-agents and the IR heating are carried out by two different heads which move parallel to the powder bed, but in a perpendicular direction one with respect to the other; it allows the operator to optimize both processes as independent steps.

When job ends, the build unit is removed from the printer and transferred into the processing station to let the powder cool down to room temperature. The operator carefully extracts the parts from the build unit and manually removes the remaining powder. The powder which is not involved in the MJF process can be recovered to be used in next jobs providing reusability rates as high as possible. Generally, this unused powder is however mixed with fresh material and used for following jobs.

The fabrication of functional polymeric parts through multi jet fusion technology shows many advantages such as:

- Low cost per part: multi jet fusion has some of the lowest cost per part with respect to any other 3D printing technology; nevertheless, it is not as cheap as a fused deposition modelling 3D printer.
- Fast printing process: one of the main advantages of this technology is the possibility to produce high density parts faster than via selective laser sintering. As underlined by Tey et al. [56] the planar fusion mode strategy involved during MJF allows to significantly reduce the layer processing time, and therefore to increase the overall process production with respect to SLS, which uses a point-by-point time consuming scanning mode. Xu et al. [57] estimated that MJF shows a printing speed almost 10 times higher with respect to SLS.
- It is an environmentally friendly technology: generally, the materials processed by SLS show a reusability ratio of about 50%. On the contrary, powders that are not involved in the building of 3D objects can be recovered and stored in the processing station to be reused in following jobs. According to HP [58] the reusability of MJF materials is not lower than 70% (reported value for PA12 reinforced with glass beads). The most used material, that is PA12, shows a high reusability of 80%; reusability reaches a theoretically value of 100% for polypropylene. The production of lower amount of wasted powder implies a less environmental damage.
- Possibility to print coloured parts. Generally, the polymer AM technologies does not offer the possibility to obtained coloured parts or this possibility is strongly limited, such in the case of stereolithography, which can print few colours. MJF offers a range of powders that allows the processing of parts in full colour, avoiding further post-processing treatments such as painting.
- Good aesthetic finishing. MJF allows obtaining both bulk component and lattice structures with a high level of details and good surface quality.
- MJF processes occur in open air; on the contrary, generally SLS is performed under an inert purge gas.

Although multi jet fusion technology shows the numerous previously mentioned advantages, some drawbacks need to be considered:

- Limited material availability: materials that can be process by MJF are essentially semi-crystalline thermoplastics (PA-based polymers and PP) and thermoplastic elastomers. Nowadays the materials palette includes less than 10 different powdered systems that can be processed by this technology.

- Very high cost for 3D equipment. It represents the biggest limit in using MJF technology because a high initial investment implies long time before any benefit can be obtained.

4.3.2 Materials for MJF

When multi jet fusion technology was developed and commercialized by HP, the only available material was polyamide 12 (PA12). It is the most widely investigated material for both the polymer powder fusion processes of SLS and MJF. As PA12 is a semi-crystalline polymer, when heated to melting temperature the crystal domains go into molten state showing low melt viscosity. The proper fluidity allows filling the pores and thus it results in high density degree of printed parts.

In addition to this suitable thermal behaviour, PA12 shows good mechanical performance, chemical resistance to oil, greases and aliphatic hydrocarbons, thermal resistance in addition to lightness that make it an ideal candidate for a wide range of applications.

Silani et al. [11] selected PA12 powder as reference material to compare selective laser sintering and multi jet fusion additive manufacturing technologies in terms of properties of both starting material and final component. The results show that the experimental conditions involved during SLS and MJF processes respectively can differently modify the properties of starting powders, and therefore can influence their recyclability. In fact, for MJF system, the movement of IR lamp across each layer of powder is faster with respect to the scanning rate of laser in SLS process. The shorter exposure time for MJF process reduces the modification of polymer chains length, favouring the recyclability of powders. The comparison of mechanical properties of samples produced by the two technologies evidences some differences. In fact, the trend of mechanical properties variation is different by considering the two processes. It is worth noting that samples built along z direction (the specimen axis is parallel with respect to the building direction) show lower tensile strength and elastic modulus when processed by SLS. This is due to the weaker interlayer bonding between adjacent layers achieved by this technology. On the contrary, the mechanical performance of z samples fabricated by MJF are higher; the use of fusing agent in combination to the IR radiation seems therefore to favour the interlayer adhesion leading to a final component with better isotropic properties.

The great efforts and huge investments that both scientific and industrial communities put into the development of new solutions made possible the enlargement of powdered materials that are available for MJF processing. Among them there are polyamide 12 reinforced with glass filler, polyamide 11 (PA11) and polypropylene (PP). However, the predominance of polyamide-based materials for MJF greatly limits the potential application fields of this technology. Therefore, two additional materials belonging to a different polymer family have been recently introduced into the market; they are thermoplastic polyurethane (TPU) and thermoplastic amide (TPA), two elastomeric polymers.

The use of glass fillers as reinforcement for thermoplastic material is common for many applications because it increases the load bearing capability in the elastic

deformation range [59]. A composite material constituted by glass beads added to PA12 matrix was therefore developed for MJF process.

O' Connor et al. [60] compared the properties of PA12 and PA12-GB processed by MJF. Although the two materials show similar chemical and thermal properties, basically associated with the common nature of PA matrix, the mechanical performances of printed specimens are reported to vary. The incorporation of glass beads into PA12 matrix leads to a significant increment of elastic modulus (estimated around 85%), while both the tensile strength and elongation at break were found to decrease. The evaluation of flexural properties confirmed this trend. The authors attributed the obtained results to the poor adhesion between the glass spheres and the polymer matrix.

The higher stiffness of PA12-GB composites makes this material ideal for applications such as enclosures, housing and tooling. Moreover, higher dimensional stability of composite was observed with respect to pure matrix, which favours the fabrication of object with bigger size.

Another powdered system that can be processed by MJF is PA11, which belongs to the polyamide family too.

The interest for this material is due to its properties: it is a renewable material coming from castor oil which shows excellent mechanical properties and a good chemical resistance. The impact strength and the elongation at break, higher with respect to PA12, make PA11 ideal for applications such as prostheses, insoles and sport accessories.

As compared to PA12, lower number of papers in the literature deals with PA11, and most of them are focused on the mechanical properties of obtained parts. Wei et al. [56] investigated the mechanical performances of this material in term of tensile and flexural properties; moreover, the study evidenced a strong correlation between these properties and the porosity of the specimens. Lee et al. [61] examined the effect of building orientation on the mechanical behaviour of the material; also in this case, the role of porosity was considered. The mechanical behaviour of PA11 as a function of powder refresh ratio was the object of interest of Pandelidi et al. [62].

Among semi-crystalline thermoplastic polymers, belonging to polyolefins family, polypropylene (PP) is also available as printing material for multi jet fusion. Fused deposition modelling is the most commonly used processing technique for this material. However, its main limits are linked to the tendency of PP to warp during FDM process, and the poor adhesion of the filament with the building platform. However, PP can be also processed by selective laser sintering. Recently, the chemical and thermal properties of this material were found to be compatible with the MJF process. Although the peculiar layer processing approach of MJF technology should allow obtaining a more compact structure with a reduced anisotropy with respect to that observed for other AM technology such as FDM, Safka et al. [58] found that both impact and tensile properties of PP produced via MJF show a significant variation as a function of the building orientation of sample.

In addition to biocompatibility, excellent chemical resistance and low moisture absorption, another interesting property of PP for MJF is associated to the theoretically 100% recyclability declared by HP [58] due to the high thermal stability and

the morphology of PP starting powder. The experimental conditions involved in MJF process do not show a significant impact on the properties of PP.

The versatility of this material allows it to be used in many applications fields such as automotive, industrial and medical ones.

TPUs are linear segmented block copolymers showing hard and soft segments [63]. The former act as tie points serving as physical crosslinks and reinforcing fillers; on the other hand, soft segments form an elastomer matrix and mainly give TPU its typical elastic behaviour. This structure is responsible for the peculiar characteristic of this material, which shows the mechanical properties of a vulcanised rubber and the processability of a thermoplastic polymer. However, a very broad range of properties can be obtained by tuning the composition of the block copolymers, and therefore modifying the relative amount of the two segment fractions.

The high versatility of this material makes it attractive for many applications. Among them, the idea of using the peculiar properties of TPU creating highly customizable components with complex geometry encourages many researchers in investigating the processability of TPU by additive manufacturing techniques.

Before becoming available for MJF, the processing of TPU was possible through selective laser sintering [64–66] or fused deposition modelling (FDM starts from material in form of filament, which is deposited using a layer-by-layer strategy until to the building of 3D object is completed) [67–69]. These studies revealed that TPU can be processed through AM techniques. According to Verbelen et al. [70] the good flowability of powders, their low melt viscosities and low shrinkage upon hardening make TPU a suitable material for multi jet fusion. On the contrary, some issues such as the porosity of obtained parts and the material degradation during the processing need to be further investigated and overcome.

Currently very few papers can be found in the literature about the processing of TPU through multi jet fusion technology. Wei et al. [56] focused the attention on this material by investigating both the properties of starting powders and those of printed specimens. Material anisotropy can be observed from the evaluation of both flexural and tensile properties. Results show that tensile strength and elongation at break are lower for Z samples with respect to X and Y ones. However, the trend is different when flexural properties are determined: flexural strength is higher for samples built with Z orientation with respect to X specimens. This is probably due to the different impact that part porosity has on flexural and tensile properties.

Another elastomeric polymer which can be processed by MJF is the thermoplastic amide (TPA) provided by Evonik. Its flexibility, very low density and good mechanical resistance at low temperature can be exploited in specific applications such as winter sport equipment, car interiors and fluid systems applications.

To authors' knowledge no paper can be found in the literature regarding the characterization of TPA based specimens.

4.4 Alternative p-PBF technologies: line-wise and layer-wise processes.

It is well known that powder bed fusion processes offer the highest flexibility degree among AM technologies, justifying their increasingly wide diffusion in

many applications fields. However, many of these techniques involve the use of expensive laser systems working with a point-by-point scanning strategy, which is a time-consuming approach. From this consideration, an innovative idea of developing a way to fuse “lines” or even “layers” of polymer powder at once was born. The main advantage is associated to the dramatic decrease of processing time making these alternative solutions very interesting for industrial applications.

Gibson et al. [71] report three main processes which were developed to satisfy the previously cited necessity that are selective mask sintering (SMS), high-speed sintering (HSS) and selective inhibition sintering (SIS) processes respectively. The common approach of these systems is the use of infrared energy to promote the fusion of selected areas belonging to each layer. On the contrary, the main difference is associated to the way used to distinguish the areas that need to be molten from the other zones.

Fig. 4.4 illustrates the different approaches of these alternative PBF systems.

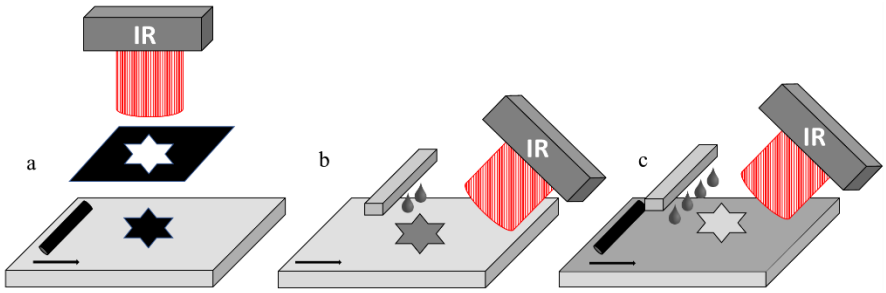

Fig. 4.4: scheme of a) selective mask sintering, b) high-speed sintering, and c) selective inhibition sintering techniques

Speed Part, a company from Sweden, developed a process called selective mask sintering, whose central feature is the sintering of the whole powder layer at one time. For each layer, an IR radiation is applied to the region of interest which is selected by a digitally printed optical mask. Layer-by-layer the shape of the photomask changes as a function of the component slicing. This approach is much faster (layer processing time is estimated to be 5-10 seconds) and cost-effective (the cost of an IR lamp is significantly lower than a laser and galvanometer) with respect to other PBF technologies such as selective laser sintering.

According to Hermann et al. [72] the high speed of the SMS process makes it suitable for all the steps constituting the product life cycle of a polymer part; from the first prototypes, through the production of components, and finally to the “spare parts on demand”. The first material processed by SMS was a nylon reinforced with glass filler.

Later, another company, namely Sintermask Technologies AB, focused its attention on this technology and introduced into the market the first commercially available SMS-machine.

One of the drawbacks of this technology is that the powder needs to absorb and sinter or melt when the IR lamp pass through the powder bed, which involves a very short time. To satisfy this requirement, the powder is generally grey or black; this strongly limits the palette of available colours.

Loughborough University and Sheffield University, both in England, developed another layer-wise process namely high-speed sintering (HSS), that was then commercialized by Factum.

HSS applied a dark liquid ink onto the surface of PA-based powder, which is usually white. The so impregnated areas represent the cross section that will be sintered when an IR radiation scan across the powder bed. The chemical composition of ink allows the absorption of IR radiation. In fact, when the infrared heater irradiates the bed surface, only the regions where the ink is deposited are able to absorb enough energy to sinter. On the contrary, the remaining powder is not involved in the process.

After the sintering completion, the material has not to cool down at temperature lower than its crystallization point in order to avoid the development of residual stresses which cause warping and failure of the object under construction. As discussed for SLS, processable materials need to show a wide gap between melting and crystallization temperature.

According to Ellis et al. [73] the mechanical properties of PA-based samples can be improved by tuning the absorption spectrum of the radiation absorbing ink and the emission spectrum: greater overlap of these spectra leads to a more efficient energy transfer. This should enhance the quality of obtained parts and therefore improve their mechanical properties. The results evidence that a variation of IR radiation exposure time leads to double the elongation at break obtained by processing the same material by SLS.

The third alternative approach is the selective inhibition sintering (SIS) process which was developed at the University of Southern California. In this case, the used approach is opposite with respect to HSS system: in fact, an inhibitor is deposited onto the powder regions where the sinter should be avoided when IR lamp moves across the powder layer. The function of the inhibitor agent is therefore to avoid the sintering of selected areas. Instead of using a chemical product that inevitably contaminates the powders and makes difficult their recyclability, some attempts were pursued using a movable plate hindering the regions that has not to be sintered.

According to Asiabanpour et al. [74] the main advantages of this technique includes low cost, high processing speed (with a required time of few seconds to sinter one layer) and the good quality of parts in terms of dimensional accuracy and surface quality.

The mechanical properties of 3D objects fabricated by SIS mainly depend on the sintering mechanism occurring during the process [75].

4.5 Conclusions

In recent years, as far as the processing of polymers concern, various additive manufacturing technologies have grown and rapidly evolved. Among them, powder bed fusion has enabled the production of high-customized, geometrically complex

and high precision parts that are not technically feasible through conventional manufacturing techniques. PBF includes different processes which share the same basic principles: they make use of a heat source to consolidate three dimensional objects starting from polymer in form of powder, which is homogeneously deposited on a building platform using a layer-by-layer strategy. The two main and investigated polymer-PBF technologies differ in the heat source that is applied to consolidate the powder layer: selective laser sintering (SLS), as suggested by the name itself, works with a laser; on the other hand, infrared lamp is used in multi jet fusion (MJF).

SLS was the first commercialized PBF technique, and nowadays it is also the most popular and widespread one; however, MJF represents a competitive alternative thanks to the improved process productivity it can reach. Both these technologies have been described in term of process conditions and available materials.

Moreover, some additional p-PBF processes were introduced as alternative solutions for industrial applications because they allow to significantly decrease the processing time. These are selective mask sintering (SMS), high-speed sintering (HSS) and selective inhibition sintering (SIS) processes respectively: they use an infrared radiation as heat source, but the adopt different strategies to distinguish the areas to be selectively molten with respect to the others.

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