Consolidation & Factors Influencing Sintering Process in Polymer Powder Based Additive Manufacturing

Sagar M B, K Elangovan
Assistant Professor, CMR Institute of Technology, Bangalore
Dean Research & Development, Cambridge Institute of Technology, Bangalore, India.

Abstract: Additive Manufacturing (AM) is two decade old technology; where parts are build layer manufacturing method directly from a CAD template. Over the years, AM techniques changes the future way of part fabrication with enhanced intricacy and custom-made features are aimed. Commercially polymers, metals, ceramic and metal-polymer composites are in practice where polymers enhanced the expectations in AM and are considered as a kind of next industrial revolution. Growing trend in polymer application motivated to study their feasibility and properties. Laser sintering, Heat sintering and Inhibition sintering are the most successful AM techniques for polymers but having least application. The presentation gives up selective sintering of powder polymers and listed commercially available polymer materials. Important significant factors for effective processing and analytical approaches to access them are discussed.

Keywords: Additive Manufacturing, Laser sintering, Heat Sintering, Inhibition Sintering, polymer powder, powder properties.

1. INTRODUCTION

AM is constructive technique, parts are constructed layer upon layer method and capable to transfer CAD template into physical model [1]. Laser sintering (LS), Inhibition Sintering (IS) and Heat sintering (HS) are falling under Layer upon Layer manufacturing technique. Polymer powder consolidation by means of heat energy shows immeasurable options give way to build custom parts with freedom of complexity [2]. Laser Sintering is most promising technique to build complex parts and it becomes a prompt technique for varied polymers [3]. Upon serial experimentation on varied polymer powders results Nylon based composites showing higher wear rate and chemical resistance and it became industry standard to produce prototype or functional parts [4]. All polymers are classified based upon two basic polymers: polyamide 12 and its relative polyamide11 [5]. Advanced research shows that Polycaprolactone and hydroxyapatite materials are used to fabricate bone and cartilage engineering [6]. Recent status, few materials are available for SLS & SLM to process like nylon graded polyamide-12, polycarbonate and polystyrene.

Attempt focuses on consolidation of polymers by Laser & IR sintering and the paper is ordered into categories based on materials. Paper shows different polymer classes, it’s processing and important significant factors for effective processing and analytical approaches to access them are discussed.

2. POLYMER CLASSIFICATION

Polymers have long-chain molecules formed mainly by carbon to carbon bonds, though most of the RP technologies are processed by polymer materials. Even the consolidations of polymers are possibly still amongst the least implicit [7]-[9]. Wide variety of indigenous polymers are processed by heat
sintering, in which some materials can sinter when heat is applied and some are having low sintering properties, can be sintered by using binder having lower melting point with the main materials. Thermoplastic, thermostable and elastomers are the common processing types of polymers. Thermoplastics change its state from solid to liquid then into viscous when they heated up high temperature and are different in temperature at which those transitions occur. Thermoplastic are most extensively used in LS process because they can be easily recycled and are clearly distinguished given in Figure 1,

- Crystalline thermoplastics – Molecules are ordered in a random manner like PC.
- Amorphous thermoplastics - Molecules are ordered in an orderly like Nylon.

Semi-crystalline polymers depict clear melting temperature $T_m$ ranging from $100^0C$ to $400^0C$ and glass transition temperature ($T_g$) is between $-100^0C$ to $50^0C$. Consolidation of these polymers happens above melting temperature $T_m$, because they have high order molecular structure with sharp melt point. A polymer remains hard up to its melting temperature, and then rapidly reaches viscous liquid. Molten polymers flow in between particles and are fuse together to form solid bonding when they cool down. As the polymers cools down below $T_m$ it recreated and grow, forms the high molecular chain. Polymer above $T_m$ depicts low viscosity, which favors and rates the amount of consolidation. During sintering process, distortion of parts takes place due to gradient freezing shrinkage at upper layer coincides with shrinkage induces warp and dimensional incorrectness and can be avoid by maintaining low crystallization rate. This can be managed by pre-heating the polymers below its melting temperature and keep the polymer to that temperature for some time after consolidation. Shrinkage of final products can be reduced by pre and post heating of polymers up to the temperature between crystallization and melting temperature. To achieve proper crystallization with uniform shrinkage the powder bed has to keep at higher temperature for some time even after sintering is done. All semi-crystalline polymers are not suitable to fabricate working parts. Only Nylon based polymers are best suitable to process by SLS and to produce prototype models; i.e Polyamide (PA) [10]-[14], it crystallize much faster than others. Research work is undergoing on some semi-crystalline thermoplastic polymers: polyethylene (PE), POM, PEEK and PCL [15]-[17].

Amorphous polymer materials do not show clear melting temperature range and depicts $T_g$ lies just about $100^0C$ and above which the material will gradually change to a fibrous and finally liquid state as increase in temperature without depicting any clear transitions. These polymer materials have low degree of consolidation because consolidation takes place at above $T_g$ temperature and they do not depicts accurate melt point but instead it will became soften slowly when rise in temperature. Polymer parts are partially dense but can fabricate models with good accuracy and higher resolution with high surface finish.

**Fig. 1: Thermoplastic materials (Red colored materials used for LS)**

**Fig. 2: Phase & Transition temperature of few polymers**
Figure 2 illustrate the $T_g$ and $T_m$ for the three most important semi-crystalline polymers (PE, PP, PA 6) with three amorphous polymers (PS, PMMA, PC). Amorphous polymers will reaches leathery state ($T_f$) during glass transition phase. This last range ($T_f$) can physically not be defined exactly. $T_g$ and $T_m$ values largely depends on polymers molecular weight. Availability of polymers in powder form is a big challenge and adoption of powder making techniques limits the availability of polymer powder. Powder making techniques like cryogenic pulverization or precipitation process also influences consolidation. Laser heating of powder layer, may leads to evaporation. This is the negative influence on process consistency and economy of the process.

Elastomeric materials are recently released for SLS process; possess a long chain structure and few cross links between them. They are brittle at below $T_g$ temperature but very elastic at above $T_g$ temperature. Recently a new elastomer polymer is released for SLS [22]. Figure 3 shows polyester based elastomer. Significant properties during materials selection are measured & compared with Neoprene, EPDM and rubber. Figure 4 shows comparison between available materials in terms of hardness & elongation at break:

### 3. POLYMER PROPERTIES FOR SINTERING-PROCESSING

It is hard to transfer polymer into sintering powder and depends on polymer properties, are all summarized and categorized. Properties based on its molecular structure like particle and powder can’t be influenced easily. Property like powder production control is mandatory property can have direct influence externally and impossible to achieve for new polymers. Based upon the influence of factors on polymer are mainly classified into Internal and External properties are pictured in figure 5.

### 4. EXTERNAL PROPERTIES

#### 4.1 Particle

During sintering process polymer powder will be distributing over the part bed of a machine by blade, it is needed that powder should possess free flowing behavior and should not go for any additional compaction. To enhance easy flowability of powder particle depends on each particle shape and surface, can be achieved by maintaining particles should be as least feasible as formed spherical. Powder density is allied with final part density and is mainly depends on particle shape, also its free flowing behavior.

![Fig. 3: Elastomers (polyester based) a) Part at low hardness b) Infiltrated with polyurethane](image)

![Fig. 4: commonly used elastomeric mat in sintering process](image)
Different methods are adapted to make polymer materials more suitable for laser and IR sintering processes. Obtained irregular and sharp edge particle shape by cryogenic method and are inadequate for sintering process. Semi-circular shapes of particles are produced by precipitation method, most of the PA series materials are produced by this method. By co-extrusion process spherical shaped particles are formed are shown in figure 6.

Powder with poorer flowability behavior leads to poor part strength and easy approach to determine the flowability of powders is by determination of loose and tapped density and are calculated based on Hausner Ratio (HR).

\[
HR = \frac{\rho_{\text{tapped}}}{\rho_{\text{loose}}}
\]

HR < 1.25 shows powder having free flowing behavior.
HR > 1.4 Shows powder having fluidization properties.

Temperature, humidity (powder fluidity) and oxygen content are the main critical atmospheric controls need to be maintained within the chamber. Polymers like PE and PP are more prone to quick oxidation, thus machine camber will be covered with nitrogen gas and with small amount of oxygen (de-polymerization).

4.2 Powder

Polymer powder with a certain particle size distribution is needed to be processable and particle distribution is favorably range between 20 m and 80 m (Figure 7), induced energy and heating of polymer powder may tends to evaporation and which in turn affects the sintering process. It results negative influence on process consistency and economy by shield off laser and IR heating elements. Added to this forms of dusty atmosphere which prevents good layer consolidation. Figure 8 illustrate two different polymer powder showing good particles distribution by looking at volume distribution and they seems to be processable on LS and IR sintering process but it’s not true, during trial for powder 2 failed and can be identified by number distribution. It has more part of small particles which
may induce stickiness, results enhanced adhesion between particles but affect free flowing behavior of powder and added to this, may form dusty atmosphere which prevents good layer distribution.

5. Internal Properties

5.1 Thermal Behavior

Today, nylon i.e. Polyamide [12], [13, [19], [20] material is best suitable to produce prototype models and also as functional parts by laser sintering method. Serious work is going on other polymer materials like PE [21], [22], POM [18], [19], PEEK [23], [24] and HDPE [25]. It is required to keep knowledge of desired factors of the thermal behavior and their course of action during sintering process. In sintering process, polymer particle melting and deposition on a thin layer is done by laser or IR heating system. Among all semi-crystalline polymers, PA is most extensively used because it sinters well. Some semi-crystalline materials will crystallize at faster rate that results their chain structure. The crystallization rate is maximum in between T_g and T_m temperatures but is minimum at near T_g & T_m. The crystallization rate is maintained relatively as slow as possible, at least few sintered layers in order to avoid part distortion due to shrinkage. Thus processing temperature will be controlled in between melting and crystallization temperatures for any given polymers. Uniform shrinkage and proper crystallization can be obtained by keeping the powder bed at high temperature for some time even after sintering. Figure 9 shows a DSC plot for PA12. Polymer powder depicts slight overlapping peaks during heating and cooling phase of DCS plot figure 10 (a), if operated at slower crystallization rate. If Ps is very close to crystallization, it forces the powder to undergo early crystallization which results curling frame and part will distort after releasing from hot bed. An early crystallization is avoided by maintaining powder temperature is slightly higher during the process but temperature will be too close to melting point. PA2200 depicted larger sintering window than POM and PA12, means larger gap between meting and re-crystallization pecks shown in figure 10 (b) [18].

5.2 Viscosity and Surface Tension

To obtain fully dense part and to achieve complete consolidation within time scale of the process, powder should have lower melt viscosity (\( \eta_0 \)) and lower surface tension. This is essential to produce a satisfactory coalescence of polymer particles. During sintering process, additional compactions will not be provided, thus polymer powder has to posses lower melt viscosity without shear stress and it is ranges up to few thousands for pure polymers to process successfully [6]. Figure 11 shows the effect of rise in melt viscosity of PA12. Left side (fig 10) shows the rough surface finish and imperfections in the part structure morphology as well. Right side (fig 10) part with improved morphology and surface finish for low zero melt viscosity.
Fig. 7: Particle size distribution of PA12

Fig. 8: Powder distribution with similar volume distribution and dissimilar Number distribution.

Fig. 9: DSC plot for melting & crystallization of PA12

Fig. 10: DSC plots a) overlap between melting & re-crystallization peaks, b) for POM & PA
5.3 Optical properties

During sintering process laser beam hits the polymer powder layer obvious three effects are results in principle, absorption, radiation and transmission of energy. Polymer powder absorbs the energy to sinter each partials and it is obvious in all powder sintering methods. Figure 12, depicts the optical conditions of Laser or IR sintering processing effects of reflection and transmission as well. Amount of heat energy transmits into deeper portion of the powder bed to induce satisfactory layer adhesion. If polymer powder results poor absorption and transmission, heat energy power can be augmented to compensate the effects but not too high energy to destroy the powder.

6. CONCLUSION

Additive manufacturing have a potential to produce highly complex parts and it is almost close to become production technique. Polymer powders are becoming a promising material to fabricate working parts by Laser or IR sintering process. Market survey reveals that, few polymers are applicable for this technology. Way of consolidation of such polymer powder into solid parts by Laser or IR sintering is discussed in this paper. The paper includes the important factors that polymer materials have to be fulfilled and make itself suitable for laser or IR sintering process and are discussed as external & internal factors. In powder particles distribution situation each particles shape and surface is outlined, means spherical shaped polymers possess higher flowability and higher density. A thermal property with a specific sintering window is discussed as well as the essential appropriate viscosity and optical behavior.

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Sagar M B is a Assistant Professor in the Department of Mechanical Engineering, CMR Institute of Technology. He obtained his B.E. degree in Mechanical Engineering branch from B.L.D.E.A’s Bijapur and Master’s degree in Product Design & Manufacturing specialization from “Jnana Sangama” VTU Belgaum. Presently pursuing Ph.D degree in the field of Additive Manufacturing.
at VTU-RRC Belgaum. He has published over 5 papers in the proceedings of the National & International Conferences. He has published 5 papers in National & International Journals. He published two books in the field of Manufacturing Process.

**Dr. K. Elangovan** is a Dean – Research & Development, Cambridge Institute of Technology, Bangalore. He obtained his Bachelor's degree in Mechanical Engineering branch from Annamalai University and Master’s degree in Production Engineering specialization from PSG College of Technology, Coimbatore and he received his Ph.D Degree from Anna University Chennai. He has published over 50 papers in the proceedings of the leading National and International Conferences. He has published 20 papers in National and International Journals. Two scholars awarded Ph.D under his guidance and 5 research scholars are currently pursuing Ph.D. programme under his guidance. He is the reviewer of various National and International Journals. He had received funds from various funding agencies like Aeronautical R &D Board, Department of Science and Technology, etc to carryout research projects.