ABSTRACT: Selective Laser Sintering of polymers has found widespread applications for rapid prototyping and rapid manufacturing. Well known manufacturing applications are the production of hearing aids, by thousands a day, and the series production of design lamp covers. However, the range of polymer materials that can be processed by SLS today is still very limited, restricting most SLS parts to be made from nylon (polyamide). This paper tries to understand the basics of selective laser sintering of polymers. It gives an overview of the materials that were yet successfully processed by SLS or that are being investigated, including reinforced or filled polymers, degradable polymers, biocompatible polymers, etc. It also compares the properties of current SLS polymers to that of injection molded ones.

1 INTRODUCTION
Selective Laser Sintering (SLS) is one of the popular Rapid Prototyping and Manufacturing (RP&M) processes that emerged in the last two decades [39, 45]. It builds 3D objects by applying subsequent layers of powder material on top of each other and by consolidating each layer with a laser beam scanning the powder layer in accordance with the CAD geometry of the part, before the next layer is applied and consolidated (Figure 1).

The main advantages of SLS over other RP&M methods are:
- SLS allows building parts in a wide range of materials, including polymers, metals and various types of composites (e.g. metal-metal, metal-polymer, polymer-ceramic, metal-ceramic composites) [8, 41]. Research is also going on to process pure ceramic parts using SLS [41].
- Parts produced by SLS demonstrates material properties that are very close to the material properties obtained by other manufacturing processes, like injection molded plastic components, or cast and machined metallic parts. The SLS process is indeed not limited to the use of dedicated materials, like photopolymers in stereolithography or wax-like materials in ink-jet printing processes. Theoretically, any material that can be provided in powder form and that melts when rising the temperature (which means almost any material) can be processed by SLS, and as the final part density approaches full density, their properties may reach those of similar bulk material.

Even though SLS theoretically allows to process almost any material and to reach normal bulk material properties, practice is still far from this ideal situation. Depending on the type of laser consolidation applied, the powder may not always be consolidated to full density or may even not be processable. Consolidation mechanisms that could be induced during laser heating are: solid state
sintering, liquid phase sintering, partial melting, full melting (often referred to as Selective Laser Melting or SLM) or chemically induced binding [41]. Solid state sintering is today hardly used, because it would require a very slow scanning process to keep the powder particles at high temperature for a sufficient long time to allow diffusion of atoms to occur, which mainly applies to metals and ceramics, but not at speeds compatible with the demand for economic RP&M. Chemical induced binding is also hardly applied today, leaving mainly two consolidation principles over for current practice: liquid phase sintering or partial melting (commonly referred to as SLS) and full melting (commonly referred to as SLM).

Today, only few powder materials are available on the market for SLS or SLM processing. SLS/SLM of polymers mostly (±95%) involves polyamide-12, i.e. a typical nylon grade. Only few other polymer powders are commercially available today for SLS: limited success was achieved with polycarbonate and polystyrene (see below). SLS and SLM of metals is today also restricted to mainly stainless steel and a few grades of tool steel, while titanium (mainly Ti6Al4V) and aluminum start to reach industrial applications.

This paper focuses on the consolidation of polymers by SLS and SLM. It will also give some examples of other consolidation mechanisms like chemical induced binding or cross linking of polymers. It will describe the fundamentals of polymer processing and describes the various classes of polymers that can be laser processed starting from deposited powder layers.

2 POLYMER CLASSES AND BASIC CONSOLIDATION

Even though polymer is the most processed type of material in SLS/SLM, the consolidation phenomena invoked for polymers are probably still amongst the least understood or at least the least described in literature [6, 54, 64].

Laser consolidation of polymers normally involves melting of thermoplastics (partial-SLS or full-SLM). A clear distinction should be made between (Figure 2):

- (semi-)crystalline thermoplastics
- amorphous thermoplastics.

When heated up from very low to very high temperatures, all those thermoplastic materials will change from a hard (solid and glassy) structure to a softer (tough leathery or rubbery, solid or non-pourable) structure and finally turn into a viscous flowing melt: see Figure 3.

![Figure 3: Phases and transition temperatures of some polymers](image)

Materials however differ in the way and the temperatures at which those transitions occur. Semi-crystalline polymers have a glass transition temperature \( T_g \) that is below or around room temperature (-100° to 50°C) and a distinct melting temperature \( T_m \) that is above 100°C (between 100° and 400°C) at which a significant volume change happens: see Figure 4. Amorphous polymers do not depict a clear melting temperature range. They have a glass transition temperature \( T_g \) that lies around 100°C and above which the material will gradually evolve to a leathery, rubbery and finally liquid state as temperature increases, without clear transitions. Figure 3 indicates the glass transition range (\( \Delta T_g \)) and melting range (\( \Delta T_m \)) for the three most important semi-crystalline polymers (PE, PP, PA 6) and indicates for three amorphous polymers (PS, PC, PMMA) the glass transition temperature ranges (\( \Delta T_g \)) and the temperature range in which the transition to leathery material goes quickly (\( \Delta T_f \)). This last range (\( \Delta T_f \)) can physically not be defined exactly.

Notice also that the \( T_g \) and \( T_m \) values largely depend on the molecular weight (MW) of the polymer. This explains why there might be a significant difference in SLS processability between a low and a high molecular weight PA or PE.
Figure 4: Comparison of relative volume between amorphous and semi-crystalline polymers [6].

The temperature transitions and melting range of polymers can be observed by recording a DSC plot by Differential Scanning Calorimetry analysis. It measures the difference in the amount of heat required to increase the temperature of a sample of the given polymer and of a reference piece or pan as a function of temperature (Figure 5). Both the sample and reference are maintained at very nearly the same temperature throughout the experiment. Figure 6 shows a typical DSC plot of PA 12. It clearly shows a melting peak during the heating cycle and a re-crystallization peak during the cooling cycle of the DSC test. Figure 7 gives the DSC plots of Duraform PA 12 and PA 6 during the heating cycle [58]. Notice that the sign of the differential heat flow may be inverted in the DSC plots. Figure 7 illustrates the much smaller melting range (small width of peak around 187°C) and the smaller melting temperature ($T_m=187°C$) of PA 12 as compared to PA 6 ($T_m=223°C$). This explains, besides viscosity differences (see §3), why PA 12 is more prone to SLS than PA 6 (or PA 66 having $T_m=262°C$ and a wider peak than PA 12).

The laser consolidation of (semi-)crystalline polymer powders will happen by heating above their melting temperature $T_m$. Semi-crystalline materials have a highly ordered molecular structure with sharp melt points. They do not gradually soften with a temperature increase but rather remain hard until a given quantity of heat is absorbed and then rapidly change into a viscous liquid. The molten polymer flows in between the powder particles, forming sintering necks. With enough heat, the complete layer is fully molten and overlaps to the previous layer. As the molten polymer cools down below $T_m$, polymer crystals nucleate and grow, recreating regions of ordered molecular chains (crystallites) mixed up with disordered amorphous regions. Above $T_m$, the polymer depicts a relatively low viscosity, as compared to amorphous polymers, which favors the rate and amount of consolidation. The densities obtained will be close to full density and the mechanical properties will be close to those of molded polymers. However, the freezing of the polymer at $T_m$ coincides with an important shrinkage (phenomenon not occurring with amorphous polymers), that may induce geometrical inaccuracies and distortion of the part (Figure 4). A good way to prevent this is to preheat the polymer powder to a temperature slightly below its melting temperature and keep it there for a certain time after consolidation [66]. Ideally the powder should be preheated and post-heated to a temperature between the crystallization and melting temperature. In such a way, no major shrinkage will occur during laser melting, and localized shrinkage (and hence part distortion) can be avoided: the shrinkage will occur in a uniform way when the part will be slowly cooled down in a uniform way after the whole build is finished. To facilitate the control of pre- and post-heating and of shrinkage, it is recommended to have a certain temperature range between the crystallization and melting peaks in the DSC plot, as depicted in Figure 6 for PA 12 (see further §3).

Figure 5: Differential Scanning Calorimetry analysis [72]

The consolidation of amorphous polymer powder occurs by laser heating above the glass transition temperature, at which the polymer is in a much more viscous state than semi-crystalline polymers at similar temperature. Amorphous polymers have a randomly ordered molecular structure. They do not have a sharp melt point but instead soften gradually as the temperature rises. The viscosity of these materials changes when heated, but they seldom are as easy flowing as semi-
crystalline materials. The flow and sintering rate will be less, resulting in a lower degree of consolidation, higher porosity, less strength, but also a lower shrinkage that is favorable in cases of SLS of patterns for producing mold for molding or casting (i.e. Indirect Rapid Tooling, investment casting patterns, etc.). The higher porosity is also favorable to avoid breaking the ceramic investment casting shell when heating the SLS pattern during the debinding cycle intended to release the mold cavity. In several applications post-infiltration of the pores of the SLS part is applied to consolidate it.

In conclusion for semi-crystalline polymers we rather approach full melting consolidation (even though the parts may still depict some porosity), whereas for amorphous polymers we rather see a partial melting binding mechanism. The former can be called Selective Laser Melting, while the latter coincides with liquid phase Selective Laser Sintering. However, unlike metal powder processing [40], this terminology is rarely used for laser processing of polymer powders: one generally refers all polymer variants as Selective Laser Sintering.

Several researchers tried to analyze and model the complex behavior of polymers during laser sintering, including aspects like viscosity, sintering (neck formation, viscous flow), laser absorption, temperature distribution, thermal conductivity, etc. [8, 13, 34, 42].

The complex thermal behavior of polymers is amplified in SLS processing due to several factors. Among others, the costly pulverization either by cryogenic milling or precipitation-process (Figure 8) limits the availability of polymer powders. The pulverization can influence also the consolidation process: the powder layer's thermal characteristic differs. Moreover, the molecular weight of the polymer will influence the melt viscosity. Characterizing the melt flow index (MFI) of a polymer powder may provide essential additional information to the DSC plots in order to characterize it SLS processability (see below).

![Figure 7: DSC plot of PA 12 (Duraform) and PA 6](image)

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The material is in powder form with a certain particle size distribution (Figure 9) and the induced energy, heating the fine powder particles, may lead to evaporation or disintegration which in turn disturbs the process. It shields off the laser window and the IR heating elements. In short, this has a negative influence on the process consistency and the economy of the process. Further the fine particles may create either a dusty atmosphere or coagulations clustering preventing the homogeneous deposition of layers, thus preventing good layer consolidation.

![Figure 8: Powder particle shapes REM, a) precipitation, b) Cryogenic milling](image)

![Figure 9: Typical particle size distribution of Duraform PA 12 (Source FHSG St. Gallen)](image)

A variety of commercially available technical polymers with excellent properties for SLS have been tuned by blending or by special design of the
chain length (analogy to molecular weight ranges). Often they result in a multi-peak DSC diagram. SLS can handle only one fixed controlled consolidation temperature or several very close peaks (typically 5-10°C difference), which means that polymers with more than one tight melting range are not processable with SLS. Figure 10 demonstrates the DSC-curve of a commercial pulverized blend with no real full melting SLS processability, due to two different melting points at 1780°C and 1850°C.

We can associate seven main SLS polymer powder materials with different application fields.

The four main thermoplastic SLS applications are:

a. SLS of polymer parts: semi-crystalline polymers (§3)
b. SLS of investment casting patterns: amorphous polymers (§4)
c. SLS of metal or ceramic parts using a sacrificial polymer binder: thermally degradable amorphous polymers (§5)
d. SLS of reinforced or filled semi-crystalline polymers for highly loaded parts (§6)

SLS today also allows production of parts using:

e. Flexible elastomeric material parts (§7)
f. Polymer-polymer blends (used in the racing industry) (§8)
g. Thermosetting materials (§9)

Those different material categories are discussed in more detail in following sections.

Figure 10: Commercial pulverized blend with no real SLS processability: melt curve (left) and re-crystallization curve (right)

3 SEMI-CRYSTALLINE POLYMERS

Today, the production of prototypes (RP) and functional parts (RM) by SLS is basically limited to nylon, i.e. polyamide (PA) [2, 11, 12, 13, 36, 78]: Figure 11. Quite some research is going on using other (semi-)crystalline thermoplastics: polyethylene (PE) [55, 57], POM [54, 74], PEEK [52, 53], PCL [70, 71, 75], HDPE [29]. PEEK and PCL are of special interest as biocompatible polymers [52, 65, 75].

The fundamental reason why PA sinters well, while more difficulties are experienced with other polymers is not totally clear yet. Some semi-crystalline polymers are able to crystallize much faster than others, as a result of their chain structure. The rate of crystallization is minimum near Tg and Tm, and reaches a maximum between those two temperatures. Crystallization rate should however be kept relatively slow (relative to the vertical build rate) in order to avoid part distortion due to gradient freezing shrinkage which would be localized in upper layers. Good crystallization and uniform shrinkage is then obtained by keeping the powder bed at high temperature for a sufficient long time after sintering.

Figure 11: Example of PA 12 part produced by SLS

As already introduced in §2, the DSC plot of a well processable thermoplastic material for SLS should depict:

- a narrow melting range (narrow melting peak in heating curve): Figure 7
- non-overlapping melting and re-crystallization peaks: Figure 12, Figure 13, Figure 14
- and should avoid double melting peaks: Figure 10.

Figure 7 already illustrated the difference of PA 12 and PA 6 in terms of melting range.

Figure 12: DSC plots (heating and cooling) of new reinforced PA 12 powder containing elongated rather than spherical beads for better strength

A powder with slow re-crystallization rate, as depicted by non-overlapping or slightly overlapping endothermic and exothermic peaks during the heating and respective cooling phases of the DSC analysis (Figure 12), might result in nearly fully
dense parts with minimal distortion, while highly overlapping peaks will yield bad results (Figure 13).

Figure 14 [74] illustrates that PA2200™ (i.e. a PA 12 powder specially developed for SLS) has more separated melting and re-crystallization peaks, than normal milled PA 12 powder. A larger $dT$ range between those peaks allows for a larger process window in term of fluctuations of temperature in time and space within the processing chamber and build part [54].

![Cooling curve and Heating curve](image)

Figure 13 : DSC plots (heating and cooling) of IP60 powder showing overlap between melting and re-crystallization peaks [US patent 5,648,450]

![DSC plots of PA and POM](image)

Figure 14 : DSC plots of PA and POM

The Chair of Polymer Technology (LKT) of the University of Erlangen successfully produced polyoxymethylene powders (POM) by cryogenically milling for application in SLS. Although the interval between the melting and re-crystallization peaks is smaller than for PA 12/PA2200 (Figure 14), they were able to produce parts in POM and aluminum filled POM (30% Al by volume) that demonstrated good mechanical properties and even better surface quality than commercial PA 12 SLS powders (i.e. PA2200). Figure 15 illustrates the improved surface roughness of POM parts as compared to PA2200 [54]. This figure also illustrates the higher crystalline structure of POM as compared to PA2200, that results in a slightly higher strength (47 vs. 45 N/mm²), higher E-modulus (3071 vs. 1980 N/mm²), but a lower elongation at break (about 3% for POM, compared to 9% for PA2200 and 20% for injection molded POM).

![Transmission light microscopy images](image)

Figure 15 : Transmission light microscopy images of microtome sections of PA (left) and POM (right) [54]

To obtain fully dense parts, the melt viscosity should be low enough to allow complete consolidation within the time scale of the process. Pure polymers with melt viscosity in the range of few tens to few thousands poise (e.g. nylon and waxes) can be processed successfully and reach near full density [6]. However, even for PA 12, the SLS part still contains small amounts of porosity and the process is something between partial and full melting. The densities obtained in SLS of PA 12 are just slightly below those of compression molded parts (0.95-1.00 versus 1.04 g/cm³), yielding very similar mechanical properties under compression, but somewhat lower tensile strength and notched Izod values that are sensitive to small voids.

![Melt viscosity vs. molecular weight](image)

Figure 16 : a) The rise in viscosity of re-used PA 12 material, b) resulting orange peel texture on SLS part

The melt viscosity is linearly related to the molecular weight (MW). For good interfusion of the polymer chains, sufficient to provide particle necking and layer to layer adhesion, a low melt viscosity is desirable. However, low viscosity results in high shrinkage and poor part accuracy. Thus an optimum MW range exists but is not easily controllable, neither at the polymer production nor during aging in process.
In contrast to SLS or SLM of metals, one has to be aware of the thermal degradation of polymer powders over time when re-using the same powder repeatedly. The long exposure to heat leads to chain growth, a rise in MW and so a rise in viscosity. This causes non-constant consolidation conditions and a shift in the melting temperature. The empirical melting temperature ramps up as a function of build height and age of the powder. This results in the decay of the MFI (Mold Flow Index) hence a drop in powder flowability and a rise in melt viscosity preventing proper sintering with reasonable quality. In the limit this can lead to creation of unsmooth patterns on the surface known as “orange peel” texture (Figure 16b) after a certain number of runs (Figure 16a). A drop in mechanical properties can be observed as well.

The consolidation temperature may be raised to compensate for those phenomena, but only in a narrow range and with limited effectiveness. A better way is to limit those problems by always using a mixture of virgin and re-used powder (typically 70% virgin – 30% reused): see below.

Melt Flow Index (MFI) is a critical characteristic. It is the flow in grams that occurs in 10 minutes through a standard die of 2.095 ± 0.005 mm diameter and 8.000 ± 0.025mm in length when a fixed pressure is applied to the melt via a piston and a load of total mass of 2.16 kg at a temperature of 190°C (some polymers are measured at a higher temperature, some use different weights and some even different orifice sizes). MFI is an assessment of average molecular mass and is an inverse measure of the melt viscosity; in other words, the higher a MFI, the more polymer flows under given test conditions. Hence the MFI of a polymer is vital to anticipating and controlling its processing. Generally, higher MFI polymers are used in injection molding, and lower MFI polymers are used with blow molding or extrusion processes.

To achieve functionally strong SLS parts, polymers that have high molecular weights should be favored. High molecular weight can lead to difficulty in placing and forming the material because of the high viscosities, but it can reduce shrinkage and thus improve the dimensional accuracy.

When polymer powder is reused in SLS, the MFI is already about three times lower than the virgin powder (Figure 17). This leads to higher viscosity, and may deteriorate the quality of the product as described above.

With PA 12, process stability and repeatability in the consolidation process can be obtained by keeping the MFI within a constant range by working with an appropriate mix of virgin and recycled powder [43].

All those phenomena are amplified for glass filled PA 12 material, leading to a rapid decline in mechanical properties, a clear evidence of different consolidation conditions (Figure 18).

The aging and the resulting change in consolidation phenomena and final component properties are very minor with amorphous materials like PS and elastomeric polyester based materials that are discussed in sections 4 and 7.

![Figure 17 : Melt flow index of powder as a function of number of builds in which powder is used](Source FHSG St. Gallen)

![Figure 18 : Tensile strength and elongation of PA-GF polymers as function of number of build in which non-refreshed powder is used](PA polymer powders for SLS are normally supplied without additives. Some additives may be added to favor the powder fluidity and powder spreading, but those have no influence on viscosity and sinterability. Some SLS tests have been performed with POM, PE, PBT and PPS having been modified by addition of stabilizers and fillers [54]. The University of Erlangen is also testing PE-UHMW powders that are modified with absorbers and fillers [74]. The use of fillers will be further discussed in §6.

Alternatively, SLS parts in PA 12 and other polymers may be strengthened applying cross-linking agents. Those cross-linking agents are often applied on the finished "green" SLS part by impregnation and by applying high level radiation [74]. The University of Erlangen demonstrated an
increase of E-modulus (from 1650 to 1935 N/mm²) and tensile strength (from 38 to 46 N/mm²), with a drop in elongation at break (from 9 to 4%) [74].

Atmospheric control in the SLS chamber is very critical in terms of temperature (control of sintering and shrinkage), humidity (powder fluidity) and oxygen content (to avoid thermal degradation of the polymer by oxidation resulting in depolymerization). A nitrogen atmosphere is normally used, together with a careful control of the amount of rest oxygen. Typically polymers like PE and PP are more prone to rapid oxidation than aromatic backbone polymers like PET (semi-crystalline) or PC (amorphous).

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Several researchers investigated SLS of biocompatible semi-crystalline thermoplastics like PEEK and PCL (Poly-ε-caprolactone) [5, 51, 53, 60, 65, 71, 75]. PCL is a biodegradable linear polyester, while PEEK is not biodegradable. Their respective melting temperatures lie around 62°C for PCL and 340°C for PEEK. A polymer has never one specific molecular weight, but consists of a mixture of molecules with different chain lengths, and so, different molecular weights. The mean molecular weight and the molecular weight distribution are important properties of a polymer. Typically SLS of PCL with MW of 50,000 g/mol demonstrated good laser sinterability [75], while PCL with a MW of 40,000 g/mol could not be laser sintered well [70, 71] due to big distortions caused by shrinkage. This shrinkage is due to the lower molecular weight of the second PCL powder, and due to the purity differences compared to the first powder.

Powder particle morphology also influences the laser consolidation. Figure 19a shows powder (PA 12) with a near to spherical shape. This yields a lower density during layering because air voids remain (Figure 19b). When no pressure is applied during consolidation (as the one occurring during injection molding), the voids and air traps remain in the solid part. This reduces the effective cross section and the tensile strength compared to molded parts from the same polymer (10-20% reduction). Figure 19b (PA 12) and Figure 20b (PS) depict the tensile break cross section demonstrating a partial melting regime, which is more pronounced in case of the amorphous PS (Figure 20b).

Comparison between SLS and molded parts concerning strength is discussed in §10.

4 AMORPHOUS POLYMERS

Amorphous polymers with strongly temperature-dependent viscosities (or high activation energy for viscous flow) have been readily processed using SLS [6, 7, 24, 32, 49]. Typical examples are polycarbonate (PC) and polystyrene (PS). Depending on the powder size and MW, they are generally pre-heated to a temperature near or even above the glass transition temperature Tₕ and will melt as the temperature further rises above Tₕ. They mainly have the advantage that their volumetric shrinkage, when cooling down, does not show a jump, as it does for semi-crystalline polymers (Figure 4). This fact provides high accuracy with little distortion. However, amorphous polymers show a lower level of consolidation (higher residual porosity) and hence do not reach the strength of their molded equivalent (Figure 20b). The higher degree of porosity, low thermal shrinkage/expansion and high accuracy
makes them well suited for investment casting patterns.

5 THERMALLY DEGRADABLE AMORPHOUS POLYMERS FOR SLS OF METAL OR CERAMIC PARTS

Various SLS applications make use of a powder combining a degradable polymer binder and a structural material (metal or ceramic) that produces a “green part” in which the structural particles are bound into a degradable polymer matrix [9]. These ‘green parts’ are further processed in a furnace to burn out the polymer (“de-binding”) and to consolidate the remaining polymer-free metal or ceramic part by post-sintering, infiltration, or HIPing. The polymers used as the sacrificial binder in those applications are different from the polymers described in the previous and subsequent sections. They should allow de-binding, i.e. thermal de-polymerization. Polymers used for this purpose are PMMA and copolymers MMA-BMA that can be de-bound in a furnace at temperatures around 350-450°C. They should not be water soluble [6, p. 112] and should have sufficient strength, even when heated up in the de-binding furnace, in order to avoid that the ‘green part’ would collapse before some solid state sintering can consolidate the metallic or ceramic particles together. The polymer must also be fully de-bindable (i.e. de-polymerized and sublimated) and should not yield excessive contamination of the remaining part with carbon residuals (important e.g. for steel parts). If the strength of the polymer in the green stage is insufficient, the green part can be consolidated by cross-linking the binder. This can be done by impregnating the green part with a water soluble thermostetting acrylic emulsion and drying it in an oven at 50°C, before it goes to the de-binding furnace [6, p. 139]. Alternatively, a cross-linker can be added into the degradable polymer coating of the powder [6 p. 139]. This will eliminate the step of impregnating the green part.

When using sacrificial binders, care should be taken because de-polymerization could also occur during SLS [6 p. 108, 35, 37]. Indeed, these polymers are deliberately designed to de-polymerize as an aid to their thermal removal in post-SLS processing. Polymers based on copolymers of n-butyl methacrylate (BMA) and methyl methacrylate (MMA) have been observed to also de-polymerize during SLS processing [68, 69].

The polymer binder may be added to the structural material in two ways: mixing [20, 28, 46] or coating [61, 62, 67, 77]. Typical volume of binder in the powder is 5% for mixed powders [20] as well as coated ones [6, p136]. The latter typically corresponds to a 5 µm polymer coating on a 55 µm 1080 carbon steel grain [68].

Figure 21 [78] demonstrates three stages in the SLS process of Apatite-Wollastonite (AW) glass ceramic with 5 wt% MMA-BMA binder:

a) powder mixture before processing (white particles are AW glass ceramic, grey particles are MMA-BMA),

b) highly porous part after SLS processing (The few polymer connections are just enough to give the ‘green' part sufficient strength to be transferred to the post-treatment furnace)

c) 'brown' part after polymer de-binding and 1 hour firing at 1150°C. During firing, AW is partly melted. The part still is not totally dense and may need further densification to convert the brown part into a final one.

Figure 22 : Injection mold made at K.U.Leuven by SLS of polymer-coated steel powder (LaserForm™) and molded connector housings
Figure 22 shows a typical mould made by SLS of a polymer-coated steel powder (LaserForm™). After building the part, the green part was de-binded in a furnace and infiltrated with bronze.

6 SEMI-CRYSTALLINE REINFORCED POLYMER FOR REINFORCED PLASTIC OR COMPOSITE PARTS

Today there exist several SLS powders aimed at production of reinforced polymer parts. Applications include parts made from glass reinforced PA [14, 16], Cu filled PA [10], Al filled PA [1, 22, 47], SiC-PA [27, 33], HA-HDPE, i.e. hydroxyapatite reinforced high density polyethylene [31, 57], HAP-PA [58, 59] and other filled or reinforced polymers [3, 15, 18, 19, 25, 26, 30, 38, 73, 80]. Unlike the sacrificial polymer binders described in §4, the polymers used here should withstand thermal degradation and should be durable. Figure 23 illustrates an injection mold made from Cu reinforced polyamide.

The powder for producing such polymer matrix composite can be provided in 3 different ways:

- The initial powder may be a mixture of polymer particles and reinforcement beads. Figure 24 shows such a mixture of spherical PA and glass particles: on the right side of the picture, the glass particles are colored blue with Prussic ink for better visibility.

- Alternatively, the single powder particles may already be a composite containing of a polymer matrix (typically PA or PE) containing filler particles [57, 58]: see Figure 25.

- A 3rd alternative is to use a polymer-coated metal or ceramic powder [10, 48].

Figure 26 shows the fracture surface of a part made with a popular commercial glass filled nylon powder. One can see that the connection between the glass beads and PA binder was not perfect, that many glass beads have been pulled out and that the PA was stretched during breakage, resulting in a rough spongy surface. Figure 27 shows a new reinforced PA powder having elongated filler beads. This new powder turned out to be better than the traditional GF-PA powder: tensile strength x 1.8; E-modulus x 1.3; elongation x 3.3.

Figure 23: Injection mold made from Cu-filled Polyamide and Polypropylene molded parts (injected at 2.76 MPa and 230°C)

Aluminum filled PA 12 often shows coagulation, since mixing the aluminum and PA powder particles isn’t always very successful. This causes segregation during layering due to the differences in size and specific weight (Figure 28). This fact is even more striking in PA 12-Cu. The inhomogeneous solid with voids creates mechanical defects and deteriorates the tensile strength. The local heat concentration on the filler has a negative influence on the binder polymer causing a very short recycle ability of 2-3 times only (for PA 6-8 times depending on judgment criteria).

Figure 24: Glass-nylon powder mixture (Source: K.U.Leuven)

Figure 25: Cross section of a glass filled nylon part (Source: K.U.Leuven)

Figure 26: PA-12 GF One of the most popular glass beads reinforced HTD materials (Source FHSG St. Gallen)
7 ELASTOMERIC MATERIALS

Elastomeric polymers have a structure with long chains and only few cross-links between them. Below the glass-transition temperature they are brittle, above they are very elastic. When the density of cross-links enlarges, strength and stiffness also enlarge, and ductility lowers.

A new elastomer powder material for SLS was recently released [44]. Figure 29 demonstrates this polyester based elastomer (patent pending). A typical part is depicted in Figure 30. The most significant properties in the thermoplastic material selection were considered and compared with reference to elastomeric materials as Neoprene, EPDM and natural rubber. Figure 31 gives a comparison of the different elastomeric materials for Shore A hardness and elongation at break: materials 1 to 4 are SLS materials.

The influence of laser processing parameters on Shore A hardness and ductility is shown by Figure 32. Clearly the parts processed with higher laser power become more ductile and have a higher Shore A hardness.

The influence of laser processing parameters on elastic modulus $E$ and the tensile strength $R_b$ at rupture is shown by Figure 33.

8 POLYMER BLENDS

Polymeric blends offer an alternative mean to obtain SLS parts with specific structure and properties, permitting the development of new applications. Most polymeric blends are multiphase systems and, therefore, their properties largely depend on their microstructure [17, 76]. Salmoria, for instance, used blends of PA and HDPE (blend ratio’s of 80/20, 50/50 and 20/80 wt%) to achieve dedicated
properties. Depending on the blend ratio, different phases and micro-structures were observed using SEM, EDX and XRD analysis [56]. Others are mixing PS and PA [63].

In a US patent [21] the following is claimed:

A particle for use in selective laser sintering (SLS), including a core (1) formed from at least one first material, and at least partial coating (2) of the core (1) with a second material (further components are optional), the second material having a lower softening point than the first material, wherein the softening point of the second material is lower than approximately 70°C.

The coating (2) generally contains a polymer, preferably a thermoplastic polymer, e.g. a polyvinyl acetal, preferably a polyvinyl butyral. It may consist of alloys with a low softening point which are used e.g. in fuses. Moreover saturated linear carboxylic acids with a chain length of ≥16 (e.g. heptadecanoic acid, melting point 60-63°C.) or polymers in the broadest sense may also be suitable. The softening point of the second material of approximately 70°C or below, allows laser sintering to be carried out at significantly lower temperatures compared to particles which have been used hitherto, and therefore also allows a significantly lower temperature difference between irradiated particles and standard room temperature. Tests have shown that the lower maximum temperature difference also improves the temperature homogeneity of the building space as a whole.

9 THERMOSETTING MATERIALS

Thermosetting polymers can be used in different steps of the SLS process. These materials can be used as an infiltrant [23, 50], because it is a relatively inexpensive path to a fully dense, stiff, net shape, polymer matrix composite part. In addition this is a very useful intermediate step for fully functional materials, as critical surfaces and tolerances may be achieved easily at this stage. An example of infiltration with thermosetting polymers is the production of metal-epoxy molds via SLS indirect processing [6, p143]. In this process, SLS is used to form green mold cavity inserts from metal...
powder that is coated with fusible thermoplastic binder. In subsequent steps, the binder is thermally removed and the metal powder is oxidized to form a porous metal/ceramic cavity that shows little shrinkage and generally excellent retention of geometry, relative to the green part. The cavity is then strengthened and sealed by infiltration and cure of an epoxy tooling resin.

It is also possible to produce metal parts by laser sintering a mixture of metals with thermosetting polymers [46]. When a thermosetting material is exposed by a laser source, the thermosetting material turns into a viscous liquid instantly. When for instance laser sintering an epoxy resin mixture with iron powder, the polar groups (e.g. epoxy group) in the molecule of the resin are activated simultaneously. The liquid flows penetrate the ‘pipes’ made from pores and wet metal particles. As such, they make bridges from one particle to another. The binding effect, depicted in Figure 34, is dominated by the interfacial characteristic between the resin and the iron. Iron surfaces commonly attach some active hydrogen atoms because of its attraction of some molecules such as H₂O and HCl due to its high polarity. Hydrogen bonds occur between the electronegative oxygen atoms in polar groups in resin molecules and the electropositive active hydrogen ones on iron surfaces. Iron particles are strongly bonded because hydrogen bond attraction is more intensive than that of inter-molecular action existing on the interfaces between iron surfaces and other non-polar polymers. The resin viscosity is lowered at higher temperature (i.e., laser energy) and its viscous liquid can spread easily. Thus many more iron particle surfaces can be attached by resin. However, degradation of resin, induced by excessive laser energy, might occur and reduce the bonding capability.

10 PROPERTIES OF MOLDED AND SLS POLYMERS

Although great efforts have been made and some results were achieved, the reasons for the relative few SLS material options are many. In future we would like to have nearly the same choice as e.g. in injection molding. Today we can only compare the differences and compensate for deficits. Figure 35 shows all the commercially available SLS materials (in yellow) in comparison to some molded polymer materials (in blue): the comparison is shown for tensile strength, tensile modulus and elongation. We find some deficits. While some SLS materials have comparable properties to molded ones, none of them is able to reach the highest values of tensile modulus and strength, nor elongation. The low elongation capability can be explained by the many short binding necks creating high stiffness with little elongation.

Figure 34: Binding mechanism for epoxy resin to iron particles

Figure 35: Commercial available SLS materials (yellow) in comparison to some injection polymer materials (in blue)

Figure 36: Boundary between loose powder and solid part
shows the microstructure of a part cross section). Under certain conditions unconsolidated particles may remain in the solid part. This can be overcome easily by proper energy intake settings, correct scan strategies like cross scanning (in X, Y, in X&Y and so on) or multi times scanning of the same layers. The boundary conditions may be partially improved by the so called out-line or skip scanning (i.e. scanning the layer contours separately) imposing a sharper border line between loose powder and consolidated part.

To conclude this paper on polymers, Table 1 gives an overview of some commercial available SLS polymers with their most important properties concerning the SLS process.

Table 1: Overview of commercial available polymers with most important properties for SLS

<table>
<thead>
<tr>
<th>Material</th>
<th>Tg (Glass transition temperature) (°C)</th>
<th>Tm (Melt temperature) (°C)</th>
<th>MW (molecular weight) (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA 6</td>
<td>50</td>
<td>230</td>
<td></td>
</tr>
<tr>
<td>PA 12</td>
<td>(41)</td>
<td>184</td>
<td>9600</td>
</tr>
<tr>
<td>PCL</td>
<td>-65 … -60</td>
<td>58 … 60</td>
<td>40000 … 80000</td>
</tr>
<tr>
<td>PEEK</td>
<td>143</td>
<td>340</td>
<td></td>
</tr>
</tbody>
</table>

11 CONCLUSIONS

This paper has given a survey of ways of consolidating polymer powders into solid material by Selective Laser Sintering. Although a lot has been achieved so far – making SLS of polymers to one of the most popular RP&M techniques – a lot remains to be done to widen the scope of polymers and polymer blends that can be processed by SLS and to improve the properties of resulting SLS parts.

12 REFERENCES

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