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Experimental and numerical analysis of the selective laser sintering (SLS) of PA12 and PEKK semi-crystalline polymers

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Abstract

A dual experimental-numerical approach was carried out to estimate thermal cycles and resulting fusion depths obtained during the selective laser sintering (SLS) of two polymers: PA12 and PEKK. The validation of thermal cycles was obtained by considering fusion depths on single layers for different experimental conditions and temperature measurements with IR thermal camera. It was shown that a simple Beer–Lambert’s heat deposit equation incorporating an extinction coefficient determined experimentally and an efficiency ratio including both laser absorption and diffusion in the powder bed were sufficient for determining accurately fusion depths, and heat cycles for the two polymers. This allowed determining optimum process conditions for manufacturing additive layers on a specifically-designed SLS set-up.

1. Introduction

The selective laser sintering (SLS) or selective laser melting (SLM) technique has now become a viable technique for producing parts of short series of complex shapes, not only on metals but also on polymers as shown by Kruth et al. (2007), Pham et al. (2008), or Goodridge et al. (2012). Many industrial machines already exist that allow fabricating solid thermoplastic polymer components, either on rather low fusion temperature polymers like PA6 (Pham et al., 2008) and PA12 (Dupin, 2012) polyamides, or amorphous polymers (Childs et al., 1999). Other works have focused on more technical polymers such as PEEK Schmidt et al. (2007) or PEKK (Dumoulin, 2014). When applied to semi-crystalline polymer materials, the SLS technique requires a high temperature maintain at \( T_0 \) level, comprised between the crystallization temperature start \( T_{cs} \) and the melting temperature start \( T_{ms} \). Too low temperatures (below \( T_{cs} \)) promote thermal shrinkage during crystallization and layer deformation, which is unacceptable for additive manufacturing. In turn, a small work temperature range WTR (\( \Delta T = T_{ms} - T_{cs} \)) can be a very limiting factor for a given polymer, because a precise control of the temperature becomes a critical point (Fig. 1). Crystallization rates should also be maintained at a low level during the whole process, and especially during the spreading stages, in order to limit extensive distortion that prevents stable layer addition. Other critical aspects of the SLS process come from the thermo-physical properties of polymers, especially their high viscosity (nearly \( 10^6 \) times the viscosity of metals) that limits polymer flow, and resulting densification rates. However, as reminded by (Kruth et al., 2007), the reason why specific polymers such as polyamides PA sinter well compared with other polymers is not fully clear yet, even if low viscosities and molecular weights are usually considered as beneficial for enhancing powder beds densification. Although the SLS process has many industrial applications, the physical processes involved during the laser–polymer powder layer interaction are not well described because industrial set-ups do not favor physical instrumentations. Consequently, there is a real need for understanding the basic phenomena involved in the SLS process, considering more simple and opened set-ups than industrial machines. This includes the determination of laser–polymer layer coupling (absorptivity, extinction coefficients), temperature profiles \( T = f(t) \) on molten layers, and densification kinetics.

Previous publications have proposed macroscopic thermal numerical models for the SLM or SLS process like the 3D SLS model by Dong et al. (2009), the 3D SLM model of Hussein et al. (2013), or more microscopic models considering powder densification at a local scale like the recent work by (Defauchy, 2013). However, most of these numerical works, and especially those carried out at a macro-scale or meso-scale on commercial codes did not systematically validate their results with experimental data, and most of all did not characterize laser–powder bed interaction. Recently, Franco and Romoli (2012) have addressed laser–polymer powder interaction on single sintered lines, with the objective of analyzing...
In another rather pioneer work by (Tolochko et al., 2000), the laser laser beam radius at 1/e² (m) was investigated, but without considering in-depth transmission aspects. In this context the current work, carried out in the frame of a French national research project (FUI Fadiplast) was focused on three objectives: (1) to develop a small SLS prototype with dedicated diagnostics to carry out instrumented SLS tests, (2) to investigate laser–powder bed interaction, (3) to carry out numerical simulations to validate laser-material coupling and address the influence of process parameters on the thermal cycles experienced by surface layers. Two polymers have been investigated: a PA12 polyamide, and a more technical PEKK (polyetherketoneketone) with different thermo-physical properties (Table 1).

2. Materials, experimental, and numerical conditions

2.1. The polymers

Two semi-crystalline polymers have been investigated: a polyamide (PA12) and a PEKK, which differ mainly by their melting and crystallization temperatures (Table 1), resulting in smaller WTR for PEKK (≈29 K) than for PA12 (≈17 K), and by their viscosity η (higher for PEKK). Moreover, the PEKK is expected to be usable at much higher temperatures (up to 570 K) than the PA12 (320 K). Powder grain diameters were in-between 30 and 70 μm for the PA12 polyamide and in-between 10 and 90 μm for the PEKK (average value D50 = 50 μm for both), with a more spherical shape for the PA12 powders than for the PEKK.

2.2. The experimental SLS set-up

A specific SLS system was fully designed and manufactured in order to investigate basic phenomena involved in the selective laser sintering of polymers. This system is composed (Figs. 2 and 3) of:

1. Two plateaus (a manufacturing plateau, and a powder feeding plateau), with a stainless steel knife as layering device, allowing to spread layer thickness of less than Δh = 0.1 mm height with a ±0.005 mm accuracy;
2. Two heating systems: a resistive-heating (Joule’s effect) positioned below the two plateaus, and a radiant system composed of six high power infra-red (IR) radiant lights operating in the 0.7–2 μm wavelength range, to record the temperature of the powder layer (30–80 μm thickness) is spread on the building plateau at 0.7–2 μm wavelength range, and located on top of the building plateau. This heating system is different from those available in industrial machines, but allows nearly identical thermal rise and fall;
3. A laser system composed of a 50 W CO₂ laser (ULR40, Continental) working in pulse width modulation mode (PWM: see Section 3.3.1) at 5 kHz frequency at λ = 10.6 μm, a beam expander, a scanning head, and a 300 mm focal f-theta lens;
4. Different diagnostics: a pyrometer operating in the 8–14 μm wavelength range, to record the temperature of the powder layer on a 5 mm diameter area, a SC4000 FLIR thermal camera with a 320 × 240 pixels sensor, working in the 2–4 μm wavelength range, and a fast camera (Pixel Link) with a 200 Hz maximum frequency rate.

A SLS experiment can be summarized as follows: (1) a powder layer (30–80 μm thickness) is spread on the building plateau at average spreading temperatures of 373 K (for PA12) and 373–473 K (for PEKK), (2) after a few tens of seconds of IR heating, the powder layer surface reaches its optimum processing temperature T₀ (controlled by the pyrometer) comprised within the WTR, and the CO₂ experimentally the laser energy consumption through the determination of geometrical features of fusion lines. However, they did not consider a combined numerical and experimental approach.

In another rather pioneer work by (Tolochko et al., 2000), the determination of normal spectra absorptance of a large range of metals and polymer powders under Nd:YAG or CO₂ laser irradiation was investigated, but without considering in-depth transmission aspects.

![Fig. 1. DSC profile of a semi-crystalline polymer (from Defauchy, 2013)—On PA12, the rather large WTR (≈29 K) favors the SLS process.](image-url)
Table 1
Thermo-physical properties of dense thermoplastic polymers Dong et al (2009), Dupin (2012), Defauchy (2013). Temperature data have been determined by DSC experiments detailed in (Defauchy, 2013).

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (K)</th>
<th>$T_s^m$ (K)</th>
<th>$T_s^c$ (K)</th>
<th>WTR (K)</th>
<th>$\Delta H_m$ (J/kg)</th>
<th>$C_p$ (J/kg K)</th>
<th>$\eta^*$ (Pa s)</th>
<th>$\sigma$ (N/m)</th>
<th>$k_0^*$ (W/m K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA12</td>
<td>325</td>
<td>448</td>
<td>419</td>
<td>29</td>
<td>1030</td>
<td>245000</td>
<td>1090</td>
<td>1100</td>
<td>0.024</td>
</tr>
<tr>
<td>PEKK</td>
<td>423</td>
<td>600</td>
<td>583</td>
<td>17</td>
<td>1300</td>
<td>43000</td>
<td>1340</td>
<td>1500</td>
<td>0.032</td>
</tr>
</tbody>
</table>

Viscosity values have been identified by rheology tests carried out just above $T_m$.

Fig. 2. Experimental SLS set-up–(a) side view, (b) top view (1) 50 W CO2 laser, (2) Scan head, (3) IR Heating radiants, (4) Powder feeding plateau, (5) Powder spreader (knife), (6) Building plateau (positioned below radiants on the picture).

Fig. 3. Simplified scheme of the SLS device.

[Text]

2.3. Numerical conditions

3D Numerical calculations of laser-heating were carried out on a laptop computer equipped with a four-core processor of 1.6 GHz frequency and 1600 MHz random access memory, using COMSOL Multiphysics™ 4.2 software, and more specifically its thermal module. The meshed volume considered for the thermal simulation was a 5 mm x 4 mm x 1 mm body (Fig. 4). Linear hexahedral elements were considered, with a mesh refinement in the laser path.

The heat equation was numerically solved in transient conditions Eq. (1), with heat losses considered in terms of natural convection and radiative losses. In the equation of heat capacity Eq. (2), the energy of solid-liquid change $\Delta H_m$ is distributed, through a Gaussian law (Bonaccina et al., 1973), between the fusion start $T_m^s$ and fusion finish $T_m^f$ temperatures ($\Delta T = T_m^f - T_m^s$). Last, the laser heat deposit $Q_v$ was considered as a volume input, following a Beer’s Lambert attenuation law (see Section 3.1.2).

$$\rho C_p \frac{\partial T}{\partial t} = \nabla (k \nabla T) + Q_v$$  \hspace{1cm} (1)
where, \( k \) is the thermal conductivity assumed to be constant with temperature, \( Q_0 \) the heat source (W m\(^{-3}\)), and \( C_p^* \) the modified heat capacity integrating solid–liquid phase transformation as follows:

\[
C_p^* = C_p(T) + \frac{\Delta H_m}{\pi(T_{mf} - T_{ms})^2} \frac{\exp\left(\frac{-(T - T_{ms})^2}{(T_{mf} - T_{ms})^2}\right)}{\left(T_{mf} - T_{ms}\right)^2}
\]

where, \( T_{ms} \) is the temperature at the melting point (K), \( T_{mf} \) and \( \Delta H_m \) the temperatures of fusion start and finish respectively, \( T_{ms} \) the enthalpy heat of fusion, \( C_p(T) \) considered as a constant value.

The thermal conductivity \( k \) of the powder bed was simply taken into account by considering a porosity ratio \( \delta \) as follows Dong et al. (2009):

\[
k = k_0(1 - \delta)
\]

The tapped powder porosity ratio was estimated to be around 70% (\( \delta = 0.70 \)) for PA12 and 75% (\( \delta = 0.75 \)) for PEKK. This was evaluated considering the change of volume after melting-solidification, and the resulting displacement of the free surface.

Boundary and initial conditions were considered as follows: Initial conditions were applied as a uniform temperature and the resulting displacement of the free surface.

Once laser beam distribution was characterized, it became important to investigate laser transmission through the powder bed. As no surface deformation (volume shrinkage) was assumed in this model, the calculation of fusion zones was only carried out considering the first molten layer. It has also to be noticed that thermo-physical properties were kept unchanged after melting (no variation of \( C_p, k, \rho \)) were considered after fusion.

3. Results

3.1. Experimental analysis of the laser beam/powder coupling

3.1.1. Experimental determination of laser power spatial distribution

During a SLS process, the spatial distribution of CO\(_2\) laser beam power is of rather high importance, while it directly influences local temperatures experienced by powder grains. For instance, considering similar laser power, non-uniform laser distributions, which are usual for CO\(_2\) lasers generate much higher thermal cycles and different powder grains. For instance, considering similar laser power, non-uniform laser distributions, which are usual for CO\(_2\) lasers generate much higher thermal cycles and different powder temperatures experienced by powder grains. For instance, considering similar laser power, non-uniform laser distributions, which are usual for CO\(_2\) lasers generate much higher thermal cycles and different powder grain temperatures. For instance, considering similar laser power, non-uniform laser distributions, which are usual for CO\(_2\) lasers generate much higher thermal cycles and different powder grain temperatures.
layers to be able to estimate a reliable analytical heat input for numerical calculations.

For this purpose, a specific device was developed, allowing measurement of the transmission of various powder layer thicknesses, in order to determine the power versus depth attenuation law. The experimental set-up is shown in Fig. 6a. The tapped powder layers, with various thickness obtained using thin foils in the lateral part of the set-up, were spread on a 5 mm–thick NaCl window, allowing 95% transmission of the CO2 laser beam. Assuming that no transmission difference exists between ambient and pre-heated powder bed, such measurements were useful data for numerical calculations. Results (Fig. 6b) indicate a fast in-depth attenuation of the transmitted laser beam. This attenuation (and in-turn the laser absorption–diffusion in the powder layer) is shown to follow a Beer-Lambert’s equation Eq. (7), which is even more pronounced for PA12 than for PEKK. This results in a higher extinction coefficient for PA12 (9000 m−1) than for PEKK (7500 m−1).

\[ Q(z) = Q_0 \exp(-\alpha z) \]  \hspace{1cm} (7)

where, \( \alpha \) is the extinction coefficient and \( Q_0 \) (x,y) the surface heat deposit (W/m²).

3.2. Experimental determination of fusion depths

SLS tests were carried out on single layers to determine the evolution of molten depths with experimental parameters. Scanning speeds \( V \) in the 0.1 m/s–1 m/s range were considered, together with laser power \( P_0 \) in-between 1.7 W and 7 W for both PA12 and PEKK powder layers.

Prior to laser-melting tests, powder layers (5 mm thick to limit thermal gradients) were pre-heated up to a \( T_0 \) temperature (440 K on PA12, and 600 K on PEKK) by using thermal resistances and IR radiant light sources (0.75–2 μm). The surface temperature was controlled by an IR pyrometer, and regulated by a PID system, that allows limiting local thermal variations to less than ±2 K. The thermal gradient on the building plateau was near 10 K between the edges and the center of the powder bed.

For each condition, optical microscopy was used to estimate fusion depths \( h \) (Fig. 7), without taking into account non-melted agglomerated particles. The variation of molten depths was shown to follow a linear dependence versus \( P_0/V^{0.5} \) on the two powders investigated so far (Fig. 8).

3.3. Numerical simulation of the SLS process

The numerical description of SLS was considered through the following three aspects:

- The analysis of the PWM regime in order to check the ability of a numerical continuous heat deposit to reproduce a pulsed laser irradiation;
- The FE calculation of fusion depths and thermal cycles induced by SLS;
- The influence of layer deposition on thermal stability of the powder bed.

3.3.1. Numerical analysis of the pulse width modulation (PWM) regime

The CO2 laser used for SLS experiments operates in pulsed regime at \( f = 5 \) kHz maximum frequency (period \( T_{\text{laser}} = 0.2 \) ms) and delivers a peak power of \( P_{\text{peak}} = 50 \) W. Like most of the CO2 lasers for SLS applications, it adjusts the mean output power \( P_0 \) by multiplying a constant output peak power value \( P_{\text{peak}} \) by a duty cycle value \( dc = \tau f \) (with \( \tau = \text{laser pulse duration}, f = \text{pulse frequency} \) Eq. (8)). For instance, a 10% \( dc \) is required to obtain a \( P_0 = P_{\text{peak}} \cdot dc = 5 \) W value, starting from a 50 W peak power (Fig. 9a). This configuration is known as pulse width modulation (PWM) mode.

In PWM regime, low \( dc \) values can promote discontinuous laser melting when the scan speed is higher than a scan speed threshold \( V_{\text{max}} \). This \( V_{\text{max}} \), which enables an overlap between laser spots (Fig. 9b), was calculated by Eq. (9). Considering an average power \( P_0 = 5 \) W and a laser radius \( r_{\text{laser}} = 125 \) μm, a \( V_{\text{max}} = 1.56 \) m/s was found. Above \( V_{\text{max}} \), laser impacts do not intersect at all.

\[ P_0 = P_{\text{peak}} \cdot \tau = P_{\text{peak}} \cdot \tau f \hspace{1cm} (8) \]

\[ V_{\text{max}} = \frac{2r_{\text{laser}}}{(r_{\text{laser}} - \tau)} = \frac{P_{\text{peak}} \cdot 2r_{\text{laser}}}{P_{\text{peak}} - P_0} \hspace{1cm} (9) \]

FE simulations of the SLS process reported in the literature Dong et al. (2009) usually consider a continuous laser irradiation, even if lasers operate in a PWM regime.

To further investigate this aspect, and determine the range of applicability of the cw assumption, 2D simulations were carried out to calculate thermal cycles \( T = t(t) \) induced by either a pulsed laser...
mode ($P_{\text{peak}} t_{\text{laser}}$) or the corresponding cw regime ($P_0 = P_{\text{peak}} t_{\text{laser}}$). The pulsed regime was simulated by considering rectangular laser pulses of $t_{\text{laser}}$ duration. Numerical results (Fig. 10) confirm that for $V < V_{\text{max}}$, the temperature profile, and especially the maximum temperature induced by the real pulsed mode and the equivalent cw regime are nearly the same (maximum variation = $\pm$10 K), whatever the position considered. Considering laser radii $r_{\text{laser}}$ equal to 120 $\mu$m and frequencies equal to 5 kHz, a fully continuous laser melting was only obtained for $V < 0.5 V_{\text{max}}$ corresponding to an inter-spot distance near $r_{\text{laser}}$ (Fig. 9b). Above this value ($V > 0.78$ m/s), more pronounced thermal variations occur (up to $\Delta T = 50$ K), the surface melting becomes heterogeneous, and a cw irradiation cannot be considered anymore for the simulations. Consequently, experimental conditions have been restricted to scanning speeds below $V = 0.78$ m/s.

In Fig. 10, the calculated time maintain above $T_0$ (=520 K) is approximately 0.1 s, which is far from providing a full densification of polymers. Indeed, according to (Frenkel, 1945) the time for densification of polymers $t_d$ can be estimated by Eq. (10) where, $\eta$ = dynamic viscosity (Pa s), $D_{50}$ = average grain size (m), $\sigma$ = surface tension (=0.003 N m$^{-1}$ on the two polymers). This makes $t_d = 18$ s on PA12 and $t_d = 25$ s for PEKK, with physical data from Table 1.

Fig. 6. Experimental measurement of the laser/tapped power transmission (a) Experimental set-up (a defocused laser beam is transmitted through a power bed layer, below which a power measurement is carried out), (b) results obtained on PA12 and PEKK powders for a 1.8 W incident power.

Fig. 7. Determination of fusion depths for a single pass melting of (a) PA12 powder bed ($P_0 = 2.5$ W, $V = 0.3$ m/s, $T_0 = 440$ K), (b) PEKK powder bed ($P_0 = 3$ W, $V = 0.3$ m/s, $T_0 = 600$ K).
Such large densification times justify afterwards why SLS machines operate at a temperature level above the crystallization temperature, and maintain this temperature a long time after the laser switch-off.

\[
t_d = \frac{\eta D_{so} T_0}{\alpha}
\]  

(10)

3.3.2. Numerical calculation of single fusion lines

In a second step, numerical calculations of fusion depths were carried out for the two polymer powders. As extinction coefficient \(\alpha\) (m\(^{-1}\)) and spatial distribution \(P = f(x,y)\) have been experimentally determined (Section 3.1), the only adjustable factor is the \(K\) value Eq. (7), which corrects heat input by considering reflectivity and Mie diffusion losses through the powder bed.

![Fig. 8. Variation of experimental molten depth with the laser process parameter \(P_0/V^{0.5}\) (Preheating temperatures \(T_{0\text{ PA12}} = 440\text{ K}\) and \(T_{0\text{ PEKK}} = 600\text{ K}\)).](image)

![Fig. 9. (a) Basics of the pulse width modulation (PWM) regime: the laser operates at \(f\) frequency and \(t\) pulse duration, (b) Optimization of the scanning speed in PWM regime: for scanning speeds above \(0.5V_{\text{max}}\), a discontinuous SLS is obtained.](image)

![Fig. 10. Thermal simulation of the CO\(_2\) laser heating in PWM mode–Comparison with the equivalent cw heating (PEKK powder, \(T_0 = 520\text{ K}\), \(P_0 = 5\text{ W}\), \(P_{\text{peak}} = 50\text{ W}\), \(f = 5\text{ kHz}\), \(V = 0.5\text{ m/s}\)).](image)
The numerical model was shown to reproduce correctly fusion depths on PEKK layers with the use of a $K=0.4$ factor (Fig. 11), which indicate afterwards that approximately 60% of the incident power is lost by reflection or diffusion processes, whereas only 40% contributes to the polymer melting.

However, on PA12 fusion lines, the experimental $\alpha$ value (9000 m$^{-1}$) was shown to underestimate the real variation of fusion depths. For this reason, alpha was slightly decreased down to 7500 m$^{-1}$, which is coincidently the same value than for PEKK, in order to provide a better fitting with experiments. Consequently, similar $K$ and alpha coefficients were numerically identified on PA12 or PEKK polymer layers.

This allowed us estimating numerically the maximum temperatures carried out during the SLS process (Fig. 12). For instance, for a 0.6 m/s scanning speed (Fig. 12), maximum calculated temperatures, averaged on a 0.1 mm diameter around the laser, were comprised between 690 K and 875 K for increasing laser powers.

Even if the cooling part of $T(t)$ curves could be correctly reproduced (Fig. 13), the comparison of simulated and experimental $T(t)$ thermal profiles was not very successful. Simulations indicate a 740 K maximum temperature, whereas the thermal measurement indicated maximum temperatures near 635 K. Two explanations are possible: (1) the lack of spatial resolution of the thermal camera sensor (1 pixel = 180 $\mu$m $\times$ 180 $\mu$m) which averaged thermal measurements in the laser-powder bed interaction zone, and lowers maximum determined temperatures, (2) a change of emissivity of PEKK above $T_m$ (with a $\kappa$ decrease), which would minimize the apparent temperature.

On a given powder bed, numerical simulations indicate a quasi-linear variation of surface temperatures with $P_0$ (Fig. 14). By comparing calculated temperatures, with the surface morphology and the color of the powder bed, temperature thresholds assumed to provoke the thermal degradation (thermo-oxidation) of the polymer were determined. Above 760 K, the first deterioration traces (black spots) are visible on the PEKK surface, and above 825 K, most of the polymer surface is degraded. Such modifications of the polymer surface are mostly due to the limited gas shielding used in the process (the $O_2$ content was lowered to near 5% due to Argon flow, but was somewhat superior to $O_2$ levels in industrial machines). However, the model is assumed to allow predicting correctly degradation thresholds.
3.3.3. Influence of layer deposition conditions on powder bed 
temperature

One of the main technical issues of SLS is to maintain stable 
temperature levels during the SLS process in order to: (1) limit 
thermally induced deformations and stresses (dependent on ther-
mal gradients G (K/m)) and (2) favor densification Eq. (10). Such 
deformations are particularly important during crystallization i.e., 
when the local temperature becomes lower than the crystallization 
temperature Tc.

Excessive cooling rates are susceptible to occur during layer 
deposition, because of the lower temperature of the spread powder 
layer which induces a thermal sinking effect.

A specific numerical approach has been proposed to estimate 
 optimum layer deposition conditions (thickness of deposited pow-
der layer Δh(powder, temperature of the deposited powder T(powder, 
deposition speed Vsp)) allowing maintaining the temperature of 
powder beds above Tc.

Basically, the numerical model uses a time-dependent Heaviside 
Step function f(t) included in COMSOL MultiphysicsTM a time 
variation k(x, y, z, t) of thermal conductivity Eq. (11) to simulate 
the layer deposition sequence, as already used by Peyre et al. (2008) 
for the DMD process. This function simulates a continuous tran-
sition from a k=0 W/m K state (the air) to the k(T) state (the deposited pow-
der bed). With such an approach, it becomes possible to estimate 
the local time-temperature cycle T = f(t) of the powder bed surface 
during layer deposition, and to evaluate the influence of various 
deposition parameters on fused powder thermal stability.

\[ k(T, t, x, z) = k(T)(1 - f(t)2hs(x - x_0 - Vt, x_{scale})) \]  

(11)

where, \( f(t) \) = Heaviside step function, \( x_{scale} \) = transition interval, \( x_0 \) = initial positions, \( V \) = scanning speed (m/s)

In Fig. 15, the influence of powder layer thickness on surface 
temperature is reported, considering a powder layer deposited at 
373 K on a pre-fused powder bed with a 610 K stabilized temper-

ture following laser surface melting (Fig. 12). A rather low effect 
is shown on minimal temperatures (5 K), indicating that sinking 
effects are only a little dependent on powder layers thickness. For 
this specific configuration, the minimum temperature reached on 
the molten layer is 565 K, which level is expected to be below the 
crystallization start on PEKK.

Considering similar calculations, a processing map for powder 
deposition conditions (Fig. 15b) was established, allowing the 
selection of optimum process parameters. This map includes fac-
tors such as: the temperature of deposition (= T_{ext}), the temperature 
of the molten powder bed surface T_{surf} before spreading and the 
powder layer thickness. As shown in Fig. 15a, this last factor has 
almost no effect on thermal–microstructural transitions. Similarly, 
the spreading speed V_{spread} (considered between 0.5 mm/s and 
10 mm/s) did not have significant influence on the processing map.

Transitions were considered according to the crystallization peak 
of PEKK (crystallization start at 590 K, crystallization peak at 580 K, 
crystallization ends at 570 K). Consequently, with the use of such 
a processing map, one can select optimum powder spreading con-
ditions. For instance, for an external temperature T_{ext} (=powder 
layer temperature) of 480 K, the temperature of the molten pow-
der bed before deposition should be superior to 605 K to fully avoid 
crystallization. On the other hand, considering a surface tempera-
ture before deposition of 590 K, a full crystallization will necessarily 
occur for T_{ext} < 440 K.

3.4. Selective laser sintering of additive polymer layers

Examples of multi-layers PA12 samples are shown in Fig. 16, for 
various process conditions applied on five additive layers of sim-
ple squared geometries. For low P/V\(^{0.5}\) ratios, incomplete melting 
occurs (right sample from Fig. 16), whereas excessive P/V\(^{0.5}\) val-
ues provide thermal distortions (left sample on Fig. 16). Finally, 
opimum process conditions were found (0.2 m/s, 1.6 W) where the 
density, estimated by a double weighing technique (Dumoulin, 
2014), was shown to be approximately 95%, which is rather sat-
factory. However, overheating effects at the edge of the samples 
were evidenced, which have been attributed to a slowing down of 
the scanning head at the beginning and the end of each fusion lines. 
This caused a thermally induced curvature of the samples (Fig. 17), 
despite a pyrometer control of the surface temperature of the
powder bed, which was stabilized to $T_0 = 440 \pm 5$ K during the whole process.

On PEKK powder beds, thermal distortions were even more pronounced on PEKK samples than on PA12 specimens, for similar $P/V^{0.5}$ ratios (Fig. 18, Fig. 19). Some degradations were also confirmed for similar $(P_0, V)$ thresholds than those determined on single fusion lines (Fig. 14). However, optimum porosity rates were shown to be near 15% on PEKK, especially due to a lack of re-melting of interlayer zones. The reason why porosity rate could not be reduced was attributed to the geometrical deformation of the samples during the SLS process that necessitated increasing $-z$ shift values between each layer to avoid contact between the

Fig. 15. Numerical calculation of the thermal influence of layer deposition on PEKK. (a) Influence of spread powder layer thickness ($\Delta h = 100 \mu m$ to $500 \mu m$, $T_{\text{powder}} = 370$ K) on fused powder cooling rates (molten layer temperature $= 610$ K), (b) numerical processing map considering the temperatures of spread layers ($y$) and molten layer ($x$).

Fig. 16. SLS Fabrication of squared PA12 samples obtained with various process conditions ($T_0 = 440$ K, five layers).

Fig. 17. Cross section of a squared PA12 sample obtained with five additive layers, ($T_0 = 440$ K, $P$= 1.6 W, $V$= 0.2 m/s). Fused layer thickness $h$ is near 150 $\mu m$, and a $-z$ shift of $-120 \mu m$ of the building plateau has been used to carry out additive layers.

Fig. 18. SLS Fabrication of squared PEKK samples for different experimental conditions ($T_0 = 600$ K, $P$= 3.1 W scan speeds $V$ between 0.1 m/s and 0.8 m/s). A clear polymer degradation is evidenced below 0.3 m/s scan speed.
powder scraper and the fused sample. Such extended deformations were due to the combined effect of: (1) the limited work temperature range for PEKK that makes difficult avoiding crystallization, (2) overheating effects near the samples edges due to non-constant scan speeds.

For instance, on the PEKK sample shown in Fig. 19, the measured layer thickness $\Delta h$ is 160 $\mu$m, but lower $z$-shift values could not be used to ensure re-melting of previous layers because of the thermal deformation of the specimen edges that provoked contact with the spread knife. In turn, a 180 $\mu$m $z$-shift was used, which was not sufficient to ensure full re-melting of interlayer zones.

Oncoming developments will focus on the galvanic head system and software with the objective of ensuring more stable scan speeds all along the fusion paths, for limiting overheating effects and associated thermal deformations.

4. Conclusion

The use of combined experimental and numerical developments has been shown to provide useful information concerning laser-matter coupling, molten polymer characteristics and damage thresholds during the SLS process. For the two polymer powders investigated on a specifically designed SLS set-up, transmitted power measurements allowed determining the powder transmission law, which was used as a volume heat source for numerical calculations. Such numerical calculations were shown to reproduce correctly experimental fusion depths with the use of a $K = 0.4$ absorption coefficient, which indicates that most of the incident laser light (60%) is either reflected or diffused in the powder bed. Last, time-temperature profiles were numerically estimated on the PEKK powder, and allowed us determining thermo-oxidative degradation thresholds. In turn, this numerical approach allowed selecting adequate parameters for limiting degradation, and ensuring optimum fusion depths.

In the last stage, the manufacturing of additive layers was shown to be problematic due to non-constant scan speed values along the fusion paths. This provoked local overheating and extensive deformations that impeded a full densification of the SLS parts.

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