Prediction of SLS parts properties using reprocessing powder

Ana C. Lopes
IPC – Institute for Polymers and Composites, University of Minho, Guimarães, Portugal and
DONE Lab – Advanced Manufacturing of Products and Tools, University of Minho, Guimarães, Portugal
Álvaro M. Sampaio
IPC – Institute for Polymers and Composites, University of Minho, Guimarães, Portugal;
DONE Lab – Advanced Manufacturing of Products and Tools, University of Minho, Guimarães, Portugal and
Lab2PT, School of Architecture, University of Minho, Guimarães, Portugal, and
Cátia S. Silva and António J. Pontes
IPC – Institute for Polymers and Composites, University of Minho, Guimarães, Portugal and
DONE Lab – Advanced Manufacturing of Products and Tools, University of Minho, Guimarães, Portugal

Abstract

Purpose – Owing to the operating principle of powder bed fusion processes, selective laser sintering (SLS) requires effective management of the mixture ratio of processed material previously exposed to the high temperatures of processing with new virgin material. Therefore, this paper aims to fully understand the effect that the successive reprocessing has in the powder material and to evaluate its influence on the properties of SLS parts produced at different building orientations.

Design/methodology/approach – Polyamide 12 material with 0%, 30% and 50% of virgin powder and parts produced from them were studied through five consecutive building cycles and their mass, mechanical, thermal and microstructural properties were evaluated. Then, the experimental data was used to validate a theoretical algorithm of prediction capable to define the minimum amount of virgin powder to be added on the processed material to produce parts without significant loss of properties.

Findings – Material degradation during SLS influences the mass and mechanical properties of the parts, exhibiting an exponential decay property loss until 50% of the initial values. The theoretical algorithms of reprocessing proved the appropriateness to use a mixture of 30% of virgin with 70% of processed material for the most common purposes.

Practical implications – This paper validates a methodology to define the minimum amount of virgin material capable to fulfil the operational specifications of SLS parts as a function of the number of building cycles, depending on the requirements of the final application.

Originality/value – The use of theoretical models of prediction allows to describe the degradation effects of SLS materials during the sintering, ensuring the sustainable management of the processed powder and the economic viability of the process.

Keywords Polymers, Selective laser sintering, Material properties, Powder recycling

Paper type Research paper

1. Introduction

Selective laser sintering (SLS) is an additive manufacturing technology that allows the production of polymeric parts through the successive deposition of layers of powder material in a building platform within a closed and controlled chamber (Gibson *et al.*, 2010; Dastjerdi *et al.*, 2017). The loose powder which is not directly sintered by the laser beam, typically between 80% and 90%, acts in the process as a support for subsequent layers (Pham *et al.*, 2008; Dotchev and Yusoff, 2009; Gibson *et al.*, 2010). In a theoretical perspective, all processed powder could be reused in successive building cycles; however, the real process involves a complex gradient of temperatures for long periods of time, which can irreversibly modify and deteriorate the structural and morphological nature of the material and, ultimately, compromise its flowability and the resulting quality of the parts produced (Pham *et al.*, 2008; Gibson *et al.*, 2010). Although several investigations have been conducted to comprehend the mechanisms of powder degradation in SLS, the topic is still not completely understood, and therefore, it is recognized as a significant impairment for the full widespread of the technology comparing to other additive manufacturing

---

Rapid Prototyping Journal
27/3 (2021) 496–506
© Emerald Publishing Limited [ISSN 1355-2546]
[DOI 10.1108/RPJ-04-2020-0076]

The authors acknowledge the financial support given by FCT – Portuguese Foundation for Science and Technology through the reference project UID/CTM/50025/2019 and the European Structural and Investment Funds in the FEDER component, through the Operational Competitiveness and Internationalization Programme (COMPETE 2020) [Project n^{0} 037902; Funding Reference: POCI-01-0247-FEDER-037902].

Received 17 April 2020
Revised 15 September 2020
Accepted 18 November 2020

solutions (Benz and Bonten, 2019; Wudy and Drummer, 2019). A series of experimental works has reported that SLS parts produced with processed powder present inferior overall quality with poor surface finishing and reduced mechanical performance as a result of critical modifications in powder consolidation, molecular weight and melting viscosity (Gibson *et al.*, 2010; Duddleston, 2015; Josupeit and Schmid, 2017; Paolucci *et al.*, 2019; Wudy and Drummer, 2019). Therefore, the reuse of processed powder is limited, and it must always be mixed with a certain amount of virgin material (Dotchev and Yusoff, 2009). The common mixture that is prescribed for the most of the SLS machine suppliers for standard applications is 50%–50% (DePalma *et al.*, 2020). However, economic and sustainable concerns require the optimization of SLS materials through the successful implementation of other mixture ratios with higher amounts of processed powder (Kumar and Czekanski, 2018; Fruggiero *et al.*, 2020). Nevertheless, the definition of an ideal ratio is not an easy assignment because it depends on the processed material, including its properties, level of reprocessing and location on the equipment (Dotchev and Yusoff, 2009; Gibson *et al.*, 2010; Josupeit and Schmid, 2016). Powder from locations exposed to lower building temperatures and/or to higher temperatures during reduced periods of time have tendency to be less damaged, and consequently, it requires less amount of virgin material in the mixture (Dotchev and Yusoff, 2009; Gibson *et al.*, 2010). Besides that, there is a large variety of interdependent SLS parameters related to the process itself (e.g. temperatures and laser setting), to the powder (e.g. size and shape) and to the part (e.g. position and orientation), which can be previously defined and optimized to influence the proper mixture ratio for each building job (Kumar, 2003; Bourell *et al.*, 2014; Hofland *et al.*, 2017). In addition to the powder management process, the position and orientation of the parts on the building platform are highly influential on the resulting properties, including on shrinkage, stair stepping effect and accuracy of details (Kumar, 2003; Caulfield *et al.*, 2007; Pacheco *et al.*, 2015; Delfs *et al.*, 2016). Most of the reported researches in the field are conducted with the Polyamide 12 (PA12) thermoplastic, that is the most used material in SLS, covering more than 90% of the market (Goodridge *et al.*, 2012; Schmid *et al.*, 2014; Sillani *et al.*, 2019). Because of its structure and morphological characteristics, the sintering behaviour of PA12 is well established, exhibiting a large processing window (i.e. the range between the crystallization and melting temperature), easy and quality processability and attractive costs (Zarringhalam *et al.*, 2006; Zarringhalam, 2007; Pham *et al.*, 2008; Bourell *et al.*, 2014; Paolucci *et al.*, 2019). However, the degradation phenomenon in SLS is dependent on the material, and therefore, specific powder management practices must be implemented for each building job (Gu *et al.*, 2019). For instance, sustainable methodologies are also particularly important for high performance materials due to their higher costs and temperatures required for the sintering. Thus, in recent years, similar researches focused on the powder reprocessing have been extended to non-conventional SLS materials, including polyetherketone (Ghita *et al.*, 2014) and polyethylene terephthalate (Gu *et al.*, 2019). However, regardless of the scientific progress, the recycling of SLS powder and its intrinsic dependence on material properties and process variables are still a critical concern for academic and industrial organizations of additive manufacturing. Therefore, this research focuses on the experimental evaluation of thermal, mechanical and morphological properties of PA12 parts in real conditions of sintering. To this aim, various mixtures of virgin and processed material with different thermal life-cycles are considered. As a final purpose, the work suggests an efficient practice for the SLS powder management process, through the validation of theoretical algorithms of reprocessing capable to predict the ideal mixture ratio to obtain quality final outputs.

2. Theoretical algorithms of reprocessing

Due to its known environmental impact, the recycling of polymeric materials is an old concern (Bernardo *et al.*, 1993). Since a few decades ago, plastic industries have been encouraged to establish sustainable and profitable solutions for the products by recovering processed material (Bernardo, 1998). Therefore, in the 1980's, the first theoretical models capable to predict the properties of mixtures of virgin and processed polymers were developed and published (Bernardo *et al.*, 1996). The main theory was based on standard operations of primary recycling and on different degradation effects revealed by polymeric materials during the reprocessing (Bernardo, 1998). Considering the flexibility and adaptability of the models to a variety of materials and properties, in the following years, some authors used experimental data to validate and optimize the algorithms, as performed by Bernardo *et al.* (1996). In *Frontiers in the Science and Technology of Polymer Recycling*, Bernardo, C. A. (1998) presents the derivation of the most relevant models based on two main methodologies. The first methodology is based on the determination of degradation curves and simple equations of mixture that can be extended to other processing technologies besides the conventional injection moulding (Bernardo, 1998). The second one considers a concept of the property loss in a single step and complex equations of mixture (Bernardo, 1998). Each theoretical model is composed by two final equations, one to be applied to properties than can be directly measured in the virgin material and other to properties that can only be measured after a building cycle to produce test specimens (below identified with a number and with a number and a letter, respectively). The final equations of the models that were considered in the scope of this research are presented as follows.

Linear law of mixtures: linear property loss [equations (1) and (*1a*)]:

$$\frac{\bar{P}_n}{P_0} = \frac{k - t\left[(1-k) - (1-k)^{n+1}\right]}{k} \tag{1}$$

$$\frac{P_n^*}{P_1} = \frac{k - t\left[(1-k) - (1-k)^{n}\right]}{k} \tag{1a}$$

Linear law of mixtures: exponential decay property loss [equations (2) and (2a)]:

$$\frac{\bar{P}_n}{P_0} = \frac{k + (1-k)^{n+1}\left(e^{-bn} - e^{-b(n+1)}\right)}{1 - (1-k)e^{-b}} \tag{2}$$

$$\frac{P_n^*}{P_1} = \frac{k + (1-k)^{n}\left(e^{-b(n-1)} - e^{-bn}\right)}{1 - (1-k)e^{-b}} \tag{2a}$$

Linear law of mixtures: exponential decay to an asymptotic value [equations (3) and (3a)]:

$$\frac{\bar{P}_n}{P_0} = \frac{P_a}{P_0} + \frac{a_0}{P_0}\,\frac{k + (1-k)^{n+1}\left(e^{-bn} - e^{-b(n+1)}\right)}{1-(1-k)e^{-b}} \tag{3}$$

$$\frac{P^*_n}{P_1} = \frac{P_a}{P_1} + \frac{a_1}{P_1}\,\frac{k + (1-k)^{n}\left(e^{-b(n-1)} - e^{-bn}\right)}{1-(1-k)e^{-b}} \tag{3a}$$

With [equations (4) and (4a)]:

$$a_0 = P_0 - P_a \iff \frac{P_a}{P_0} = 1 - \frac{a_0}{P_0} \tag{4}$$

$$a_1 = P_1 - P_a \iff \frac{P_a}{P_1} = 1 - \frac{a_1}{P_1} \tag{4a}$$

Logarithmic law of mixtures: property loss according to a power law [equations (5) and (5a)]:

$$\frac{\bar{P}_n}{P_0} = c_*^{(1-k)\,\frac{1-[(1-k)z]^n}{1-(1-k)z}} \tag{5}$$

$$\frac{P_n}{P_1} = c_*^{(1-k)\,\frac{1-[(1-k)z]^{n-1}}{1-(1-k)z}} \tag{5a}$$

Where k is the ratio of virgin material in the mixture, n the number of the building cycle, t the slope of the degradation curve, P_0 the value of the property of the virgin material, P_1 the value of the property after the first cycle, P_n the value of the property in the n cycle, P_a the asymptotic value, a_0 the difference between the original and the asymptotic value of the property, a_1 the difference between the value of the property after one building cycle and the asymptotic value and b, c_* and z specific law parameters (Bernardo, 1998).

3. Materials and methods

To completely evaluate the effect of the reprocessing characteristics of the powder on the resulting SLS part properties, an unfilled PA12 powder, i.e. the PA2200 from EOS GmbH, was successively processed through five consecutive building cycles without any mixture with new material and in a mixture of 70% of processed with 30% of virgin material. The first cycle of a standard mixture of 50%–50% was also considered as a matter of reference. The experiments were conducted in the EOS P 396 with the process parameters fixed in the EOS standard mode (Table 1).

In all building cycles, the properties of the powder and the resulting test specimens were evaluated. For the analyses, it was considered powder from different locations of the equipment to identify the corresponding thermal characteristics, level of degradation and appropriateness to be included in a mixture. Therefore, it was systematically collected a sample of virgin powder, powder from the supply bins (i.e. powder that was not sintered but that was inside the building chamber) and powder near and far the parts (Figure 1). Before characterization, all powder was sieved in an EOS Modular Unpacking and Sieving Station.

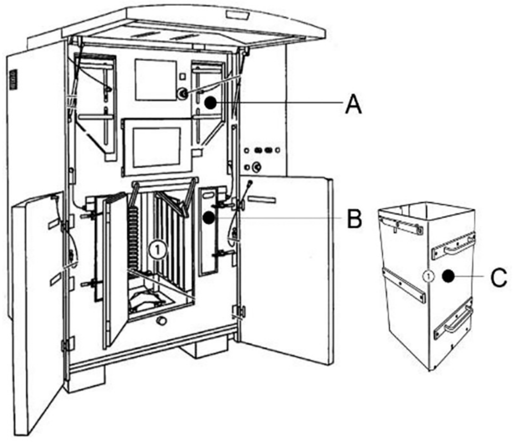
The test specimens were modelled according to 1BA type defined by ISO 527–2 (Figure 2) (ISO, 1996) and positioned at five different building orientations (i.e. 0°, 30°, 45°, 60° and 90°) in the centre of the EOS P 396 building platform, considering the coordinate system defined by ASTM 52921–13 (Figure 3) (ASTM International, 2013). All data files required for the building job were prepared using Magics Materialize, EOS PSW and EOS RP Tools software.

After production, a series of characterization tests was conducted. A *Mettler Toledo* balance was used to determine the mass of all specimens. Tensile tests were accomplished in an *Instron 5969 Universal Testing System* with video extensometer at a minimum of five specimens per orientation and condition at 10 mm/min with a load-cell of 50 kN at room temperature. A differential scanning calorimetry (DSC) analysis was carried out in a *Netzsch DSC 200 F3 Maia* in a first heating rate of 10°C/min, from 20°C to 230°C, under a nitrogen atmosphere, to identify the characteristic transition temperatures, the corresponding enthalpies and the degree of crystallinity of the powders and specimens. A *TA Q500* was used to perform a thermogravimetric analysis (TGA) to evaluate the variation of the mass of the samples during a heating program at 10°C/min, from 40°C to 700°C, under a nitrogen atmosphere. A *Nano SEM FEI Nova 200* was used to perform the morphological analysis of the powders and specimens through scanning electron microscopy (SEM). Both types of samples were coated with 15 nm of gold, and the analysis

Table 1 SLS process parameters

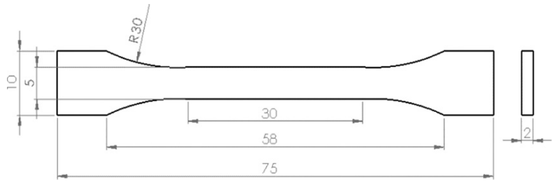
Building temperature	178°C
Warm up temperature	160°C
Removal chamber temperature	130°C
Layer thickness	0.12 mm
Laser operating mode	Sorted
Beam offset	0.390 mm
Recoater speed	120 mm/s
Laser power (*Hatching*)	40 W
Laser power (*Contour*)	34 W

Figure 1 SLS powder from the (*A*) feed containers, (*B*) supply bins and (*C*) removable frame of the EOS P 396 equipment



Source: *Adapted from* EOS GmbH (2016)

Figure 2 Test specimen 1BA ISO 527–2 (dimensions in mm)



was set at an accelerating voltage of 10 kV. The images of the projected area of the powder particles were obtained to determine their size, using *Image J*. The specimens were sectioned with liquid nitrogen to analyse the longitudinal and transversal sections.

4. Discussion of results

4.1 Qualitative parts appearance

After the sintering process and post-production operations, the overall appearance of the specimens produced was qualitatively recorded. For the same building cycle and type of powder, specimens oriented at 0° presented the greatest resolution and accuracy of fine details, comparing to the other orientations studied (Figure 4).

With the reprocessing of the material through the building cycles, these effects were more pronounced, and the surface finishing of the corresponding specimens was notoriously worst, in particular when less amount of virgin material was considered for the sintering. Specimens oriented at 30°, 45° and 60° exhibited reduced resolution, pronounced stair stepping effect and inferior quality on surfaces directed to the top (Figure 5). This qualitative result is in accordance with Bacchewar *et al.* (2007) and Delfs *et al.* (2016) that proved higher average roughness on upward-facing surfaces of SLS parts.

Other defects were undifferentiated observed along the surface of the specimens produced with reprocessed powder. Some of them presented both opaque and translucent areas with small depressions on their surface and higher thickness in the external contour than in the centre, revealing planar deformation (Figure 6). There were not observed significant modifications of colour and roughness.

4.2 Mass evaluation

Figure 7 describes the variation of mass of specimens produced with 0%, 30% and 50% of virgin powder with the number of cycles [Figure 7 (*left*)] and the corresponding normalized values through the curve of loss of property identified as P_n/P_1 [Figure 7 (*right*)].

The experiments showed that regardless of the ratio of virgin material and the building cycle, the mass was higher for specimens at 0° and decreased to specimens at 90°, evidencing a more effective powder consolidation in specimens horizontally produced. Comparing with the nominal value of 0.930 g, specimens produced with powder without mixtures exhibited lower values with a loss of mass around 20% after the second building cycle. In these conditions of sintering, specimens at 0° presented a mass of 0.900 g in the first cycle and 0.710 g in the fifth, whereas specimens at 90° presented a mass of 0.750 g in the first and 0.578 g in the fifth. With 30% of virgin material, the average mass of the specimens increased, reaching a maximum loss of 5%. For instance, in the fifth building cycle, specimens at 0° presented a mass of 0.909 g and specimens at 90° presented a mass of 0.777 g. These values are comparable to those obtained in the first cycle without mixtures. In the first cycle, specimens with 30% of virgin powder ensured similar values of mass comparing to the reference of 50%–50%, i.e. 0.943 g for specimens at 0° and 0.871 g for specimens at 90°.

4.3 Mechanical properties

The results of tensile tests showed that the mechanical properties are highly influenced by the amount of virgin material considered in the mixture. Based on the stress-strain curves obtained from the experiments, it was possible to verify that the elastic modulus of specimens produced with powder without mixtures decreased with the number of cycles (Figure 8). The elastic modulus of specimens at 0°, which presented the highest value in all building cycles, decreased from 1,600 MPa in the first to 740 MPa in the fifth. This reduction of more than 50% evidences inferior tensile strength

Figure 3 Orientation and position of SLS specimens in the EOS P 396 building platform

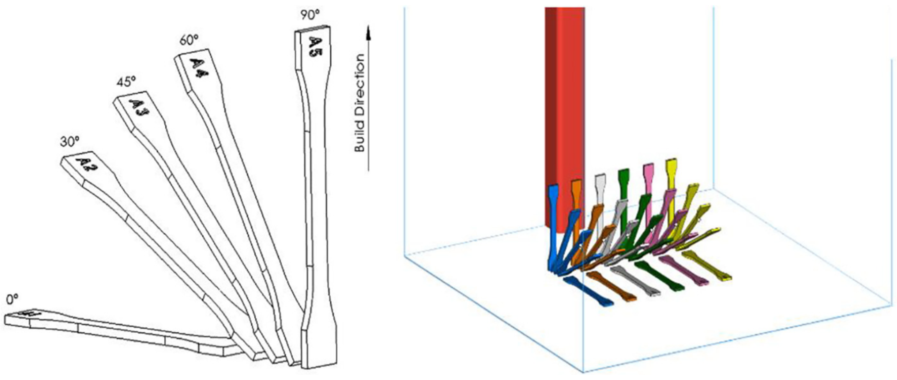


Figure 4 Resolution of fine details of SLS specimens at 0° and 30°

Figure 5 Surface of SLS specimen at 30° directed to (*A*) top and (*B*) bottom

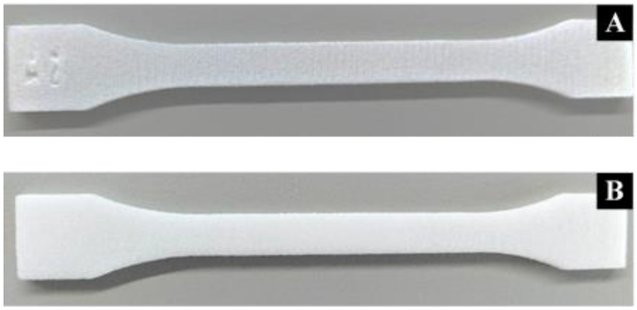
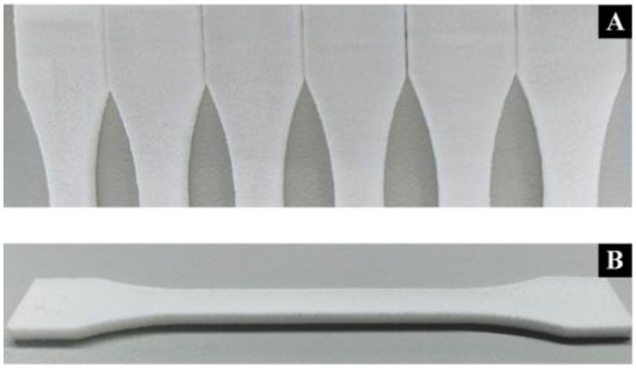


Figure 6 (*A*) Superficial defects and (*B*) planar deformation of SLS specimens



and stiffness of the parts with the reprocessing. On the other hand, the elastic modulus of parts produced with 30% of virgin material did not decrease so sharply with the number of cycles. This mixture ratio ensured a maximum loss of property of 10% with 1,535 MPa after five consecutive building jobs, just below the reference value of 1,660 MPa obtained for the standard mixture of 50%–50% in the initial cycle.

The tensile stress at yield and tensile stress at break presented a similar behaviour between each other and in accordance with the respective elastic modulus (Figure 9 and Figure 10, respectively). As expected, the tensile stress of specimens produced with powder without mixtures decreased for all building orientations with the number of cycles. Specimens at 0° exhibited the highest values in all cycles, presenting 46 MPa at yield and 45 MPa at break in the first one. These values decreased to 25 MPa at yield and 24 MPa at break in the fifth cycle, evidencing a loss of property around 50%. With 30% of virgin material, the tensile stress recorded values of 45 MPa at yield and 43 MPa at break for specimens at 0° in the first cycle, with a maximum loss of property of 10% in five consecutive building jobs. These values are comparable to those obtained in the first cycle of a mixture of 50%–50%, i.e. 46 MPa of tensile stress at yield and 45.7 MPa of tensile stress at break.

4.4 Thermal properties

The DSC analysis evidenced significant differences between the melting performance of the SLS powders and corresponding test specimens (Figure 11). The representative DSC thermograms showed that the characteristic thermal transitions exhibit peak points with different location and dimension, evidencing that the powders present more perfect and organized crystallites with a bigger dimension than the specimens. It suggests that the period of time established between the deposition of two consecutive layers of powder during the sintering process to produce the specimens was not enough to induce a crystalline structure with well-ordered spherulites as efficiently comparing to the previous process of production of SLS powders (i.e. solution precipitation in ethanol at high temperatures and pressures (Dadbakhsh *et al.*, 2017; Josupeit and Schmid, 2017)). It has a direct effect on the crystal perfection index of the samples, as proved before by Chen *et al.* (2018). In addition, it is possible to detect a single peak point for the powders and two for the specimens, proving the presence of two populations of crystallites with distinct morphological uniformity and different melting behaviour. It may be an effect of the characteristic crystal forms of the polymorphic PA12 material, α and γ.

Furthermore, the DSC analysis showed that the melting temperature (T_m) of the new virgin powder is 186.7°C. All other collected powders showed a T_m between 187°C and 189°C, proving the direct effect of the successive reprocessing on the thermal properties of the material. On the other hand, the T_m of the corresponding specimens is between 180°C and 184°C. Although the action of the laser beam during the sintering process affects the T_m in about 6°C from the powders to the specimens, these values did not significantly change with the building cycles and types of powder, leading to a loss of property of less than 10%. During the processing, the SLS operating parameters also influence the degree of crystallinity of the samples until 24%, from 50%–60% in powders to 36%–42% in specimens. However, the recorded values exhibited a maximum loss of property of 10% in five building jobs.

In accordance, the TGA analysis also revealed some thermal differences among the collected samples (Figure 12). All thermograms evidenced a single mass loss event without any final carbonized residue at 700°C. Regarding the characteristic temperatures of degradation, it was verified that the virgin powder began to degrade at 420°C, and all other powders degraded at 404°C in the first cycle and 395°C after the third. These results confirm the occurrence of degradation effects that increased with the level of reprocessing. The initial degradation of the specimens occurred between 385°C and 400°C, proving the different melting performance of the samples.

Figure 7 Experimental results of mass of specimens (*left*) and corresponding normalized values (*right*)

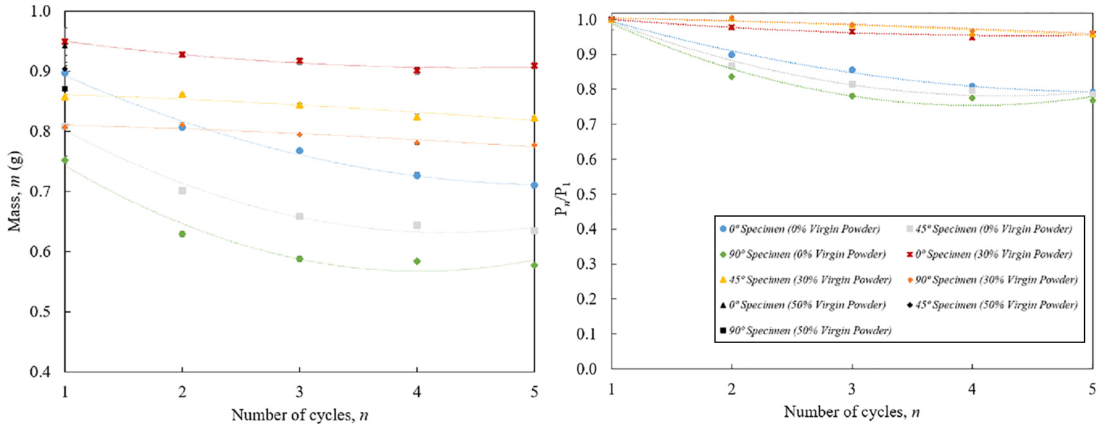


Figure 8 Experimental results of elastic modulus of specimens (*left*) and corresponding normalized values (*right*)

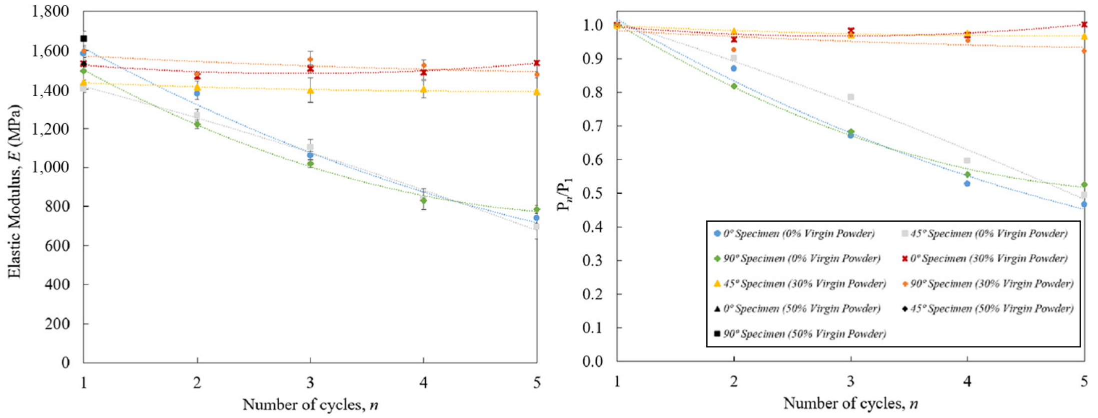
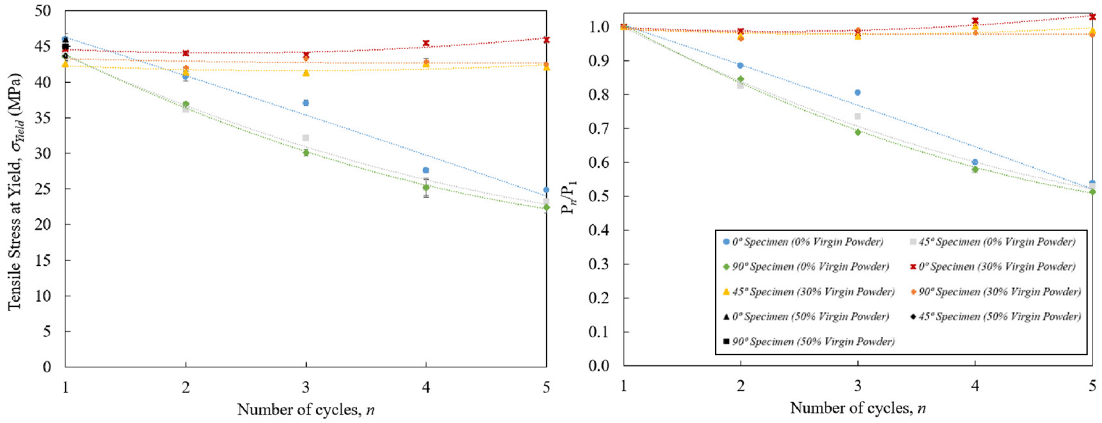


Figure 9 Experimental results of tensile stress at yield of specimens (*left*) and corresponding normalized values (*right*)



4.5 Morphological properties

The SEM analysis did not show significant morphological differences between the powders collected from different locations, mixture ratios and building cycles (Section 3). However, some common characteristics that may have influence in the flowability of the particles and their sintering behaviour were observed in all of them. There were observed both spherical and extended particles causing dispersions of shape and size [Figure 13 (*A*) and (*B*)], powders with irregular, unsmooth and cracked surfaces [Figure 13 (*C*)] and agglomerations of particles to form larger powders [Figure 13 (*D*)]. Regardless of these effects, the average size of the

Figure 10 Experimental results of tensile stress at break of specimens (*left*) and corresponding normalized values (*right*)

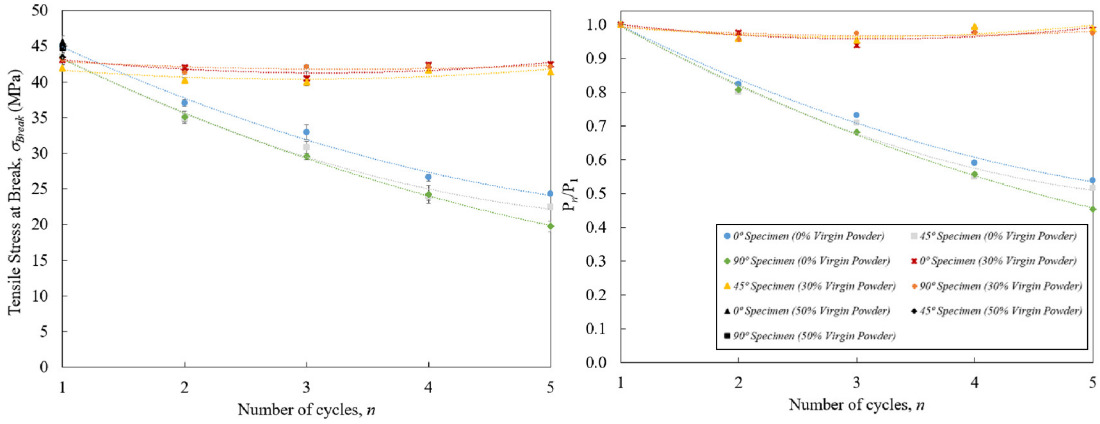


Figure 11 Representative DSC thermograms of SLS samples

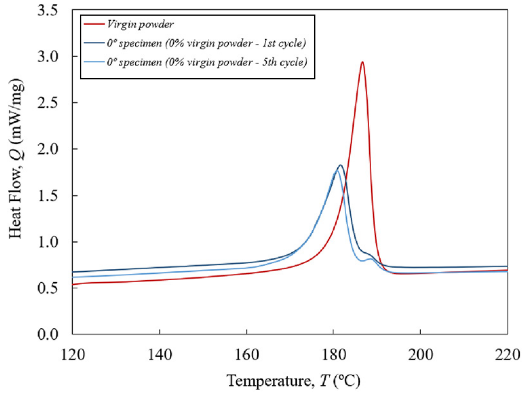
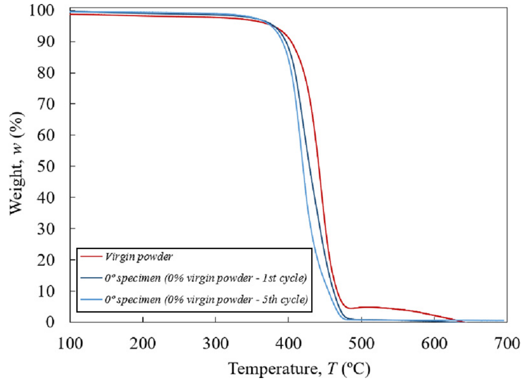


Figure 12 Representative TGA thermograms of SLS samples

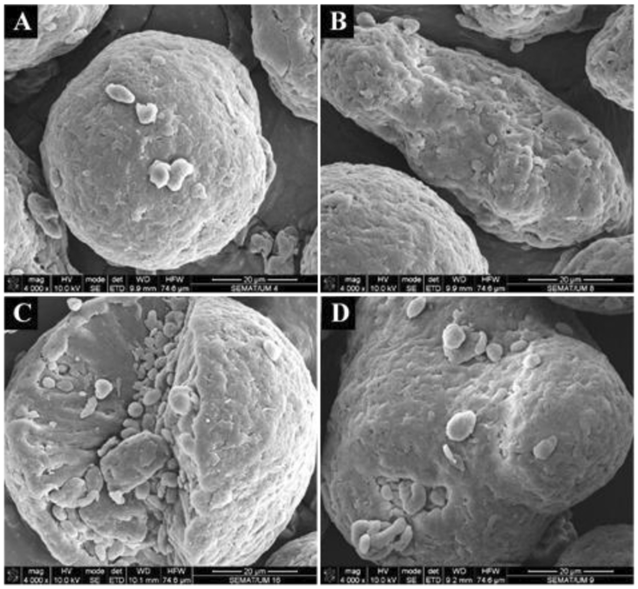


particles, between 60 μm and 70 μm, and the powder roundness, between 0.7 and 0.8, remained almost unchanged for all types of powder and number of cycles.

In addition, this morphological analysis revealed that the transversal section of specimens produced with a standard mixture ratio of 50%–50% does not exhibit significant differences depending on the building orientation [Figure 14 (*A*) and (*B*)]. Specimens oriented at 0° and 90° are both characterized by a porous cross-section with a well-defined crystalline structure [Figure 14 (*C*) and (*D*)].

However, it was observed that the content of porosity is tendency higher with the number of building cycles, especially in specimens produced with less amount of virgin material (Figure 15). This qualitative evaluation allows to understand and justify the mechanical behaviour reported in subsection 4.3. Although specimens produced without virgin powder presented a structure with increased content of porosity through the building cycles [Figure 15 (*A*) and (*B*)], specimens produced with 30% of virgin powder exhibited structures morphologically more similar between each other and with the standard reference [Figure 15 (*C*) and (*D*)]. It explains the reduction of the tensile stress at yield from 45 MPa with 30% of virgin powder to 25 MPa without mixtures in the fifth building cycle. As expected, these results prove that the overall

Figure 13 Morphological characteristics of SLS powder particles



Notes: (A) Spherical shape; (B) extended shape;(C) cracks; (D) agglomeration mechanical performance is strongly affected by the content of porosity and morphological structure of the corresponding SLS part.

4.6 Experimental validation of reprocessing algorithms

The experimental validation of the theoretical algorithms of reprocessing was performed using an optimization program to ensure the accuracy of the fitting of the experimental results to the models. The custom-made program used in the research uses the least square method and the Hooke–Jeeves algorithm to the models presented in Section 2. As the algorithms are more valuable to describe properties with remarkable variation with the number of cycles, the methodology is following detailed for the mechanical properties (see subsection 4.3).

Considering the experimental conditions and the evolution of the results with the number of cycles, the validation of the algorithms was only performed for linear laws of mixtures. Therefore, instead of an individual fitting of the curves, the results were adjusted to the models 1, 2 and 3, through a maximum of 10,000 iterations allowed by the program, in a combined effect of both k values, 0 and 0.3, to allow a more accurate extrapolation of the results. For the selection of the optimum solution to describe the data, it was considered the least square derivations (LSD) and the evolution of the models with the number of cycles. Table 2 summarizes the LSD and the specific law parameters of the corresponding models.

The results show that the LSD values are similar for all mechanical properties. Although the model 2 presents the smallest deviations and a great convergence, the models 1 and 3 also exhibit an acceptable approximation to describe the system in five building cycles. Of all valid solutions, preference was given to models with simple formulation and reduced number of law parameters, such as the models 1 and 2. Therefore, the model 3 was not elected as the first solution. In addition, considering a high number of building cycles, the evolution of the mechanical properties described in Figures 8, 9 and 10 better fit an exponential behaviour reproduced by the model 2 than a linear behaviour of the model 1. Therefore, according to the multiple criteria, the *linear law of mixtures: exponential decay property loss* [equations (2) and (2a)] was selected as the model that more accurately described the loss of all mechanical properties with the number of building cycles. As the *linear law of mixtures: exponential decay property loss* only depends on one parameter, b, and as it was similar for the elastic modulus, tensile stress at yield and tensile stress at break, it was possible to generalize a single theoretical curve which, on average, predicts the loss of mechanical properties with the number of building cycles, n, for different ratios of virgin PA12 material in the mixture, k, with $b = 0.1334$ (Figure 16). An arbitrary number of 20 building jobs was defined to illustrate the results for a theoretical high number of reprocessing cycles to identify the upper limits of the powder recycling.

Figure 14 Transversal section of specimens with 50% of virgin powder in the first cycle at (*A*) 0° (low magnification), (*B*) 90° (low magnification), (*C*) 0° (high magnification) and (*D*) 90° (high magnification)

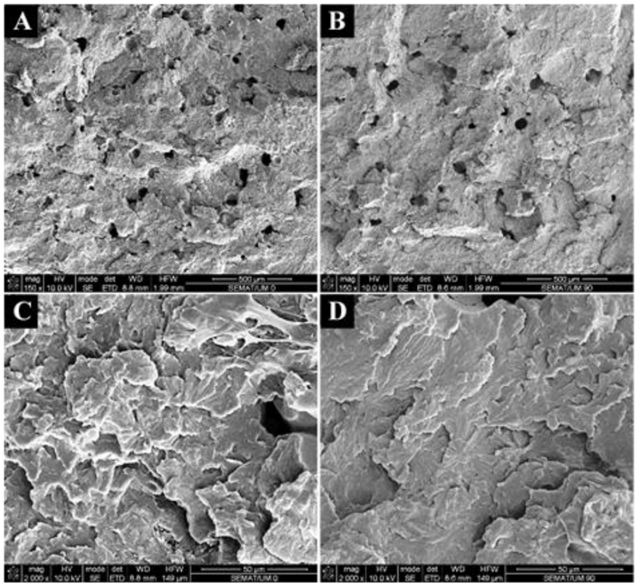


Figure 15 Transversal section of specimens at 0° in (*a*) first cycle without mixtures, (*B*) fifth cycle without mixtures, (*C*) first cycle with 30% of virgin powder and (*D*) fifth cycle with 30% of virgin powder

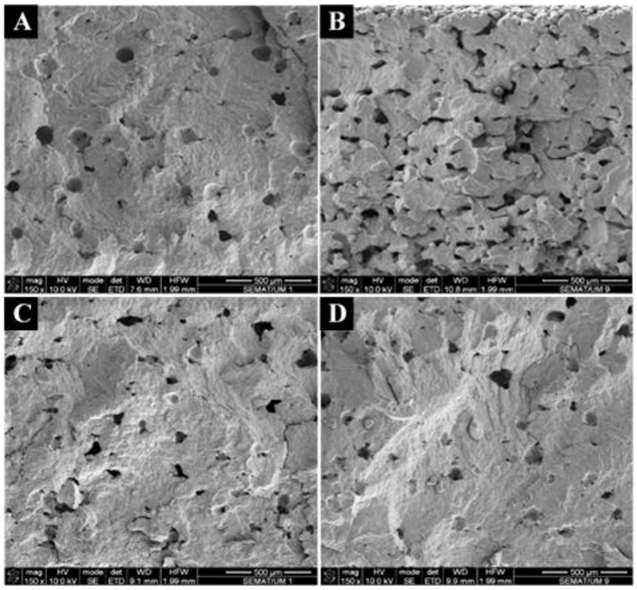
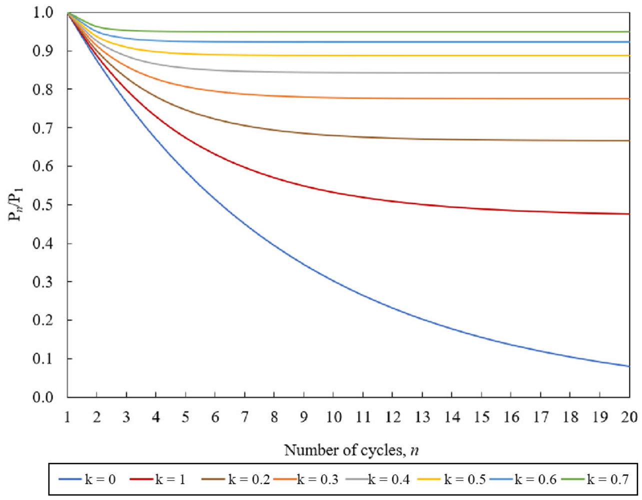


Figure 16 proves that there is a loss of mechanical properties as a function of the number of building cycles, in different increments depending on the ratio of virgin material. In the initial cycles, the loss of properties is similar for all k values; however, the difference of P_n/P_1 increases with the number of cycles until a critical and stable value at a high level of reprocessing. The maximum loss of properties reachable in each situation, when $n \rightarrow \infty$, can be assessed through the corresponding *steady state algorithm* presented by Bernardo, C. A. (1998). The steady state algorithm of the *linear law of mixtures: exponential decay property loss* showed that SLS parts produced without any amount of virgin material exhibit a loss of properties higher than 50%, on average, from the sixth cycle. In that condition, P_n/P_1 reaches critical values after a very high number of building jobs, proving that the process becomes unfeasible from a certain cycle if any amount of new material is considered for the sintering. However, regardless of the

Table 2 Fitting of the theoretical models 1, 2 and 3 to the mechanical results

	Model 1		Model 2		Model 3			
Mechanical properties	**LSD**	***t***	**LSD**	***b***	**LSD**	**a_1/P_1**	**P_a/P_1**	***b***
Elastic modulus (0°)	0.1190	0.1185	0.1184	0.1446	0.1197	6.6613	−5.6613	0.0183
Elastic modulus (90°)	0.0719	0.1161	0.0685	0.1432	0.0719	4.7985	−3.7985	0.0252
Tensile stress at yield (0°)	0.1043	0.0936	0.1037	0.1079	0.1051	7.1093	−6.1093	0.0134
Tensile stress at yield (90°)	0.0952	0.1092	0.0935	0.1314	0.0957	6.5862	−5.5862	0.0170
Tensile stress at break (0°)	0.0810	0.1051	0.0785	0.1259	0.0813	6.2478	−5.2478	0.0173
Tensile stress at break (90°)	0.1057	0.1198	0.1050	0.1471	0.1064	6.6242	−5.6242	0.0186

Figure 16 Dependence of the mechanical properties of SLS PA12 parts on *n* for different *k* values



building cycle, when 10% of virgin powder is added, the loss of property is not higher than 53%, and an incorporation of 20% reaches a maximum of 33% from the initial values. All other *k* values achieve a loss of properties of less than 20% regardless of the number of cycles. These assumptions demonstrate that the minimum amount of virgin material needed to produce SLS parts with desirable properties can be defined in advance using this methodology. For instance, if the maximum admissible loss of mechanical properties for a certain application is 30%, the SLS parts can be produced with powder that was processed a maximum of three times, a mixture with 10% of virgin material until the fourth cycle, a mixture with 20% until the seventh cycle or any other mixture with an higher amount of virgin material. This procedure can be applied to other SLS equipment and extended to evaluate different properties and materials, depending on the model that best fit the experimental results.

5. Conclusions

SLS requires fine management of a mixture ratio of virgin and processed material to obtain final parts with desired properties. However, the identification of the minimum amount of virgin material to be considered in the process is challenging for the additive manufacturing society. Focused on that concern, this research proved that the characteristics of the reprocessed powder and the building orientation of the parts have a critical influence on the resulting outputs. The experiments showed that if only processed material is considered for the sintering, the mass and mechanical properties of the SLS parts are compromised, exhibiting a property loss up to half of the initial value in five consecutive reprocessing cycles. These negative effects are reduced when the amount of virgin material in the mixture increases. Complementing the experimental data with the results of the theoretical algorithms of prediction, it was shown that a mixture ratio of 30% of virgin with 70% of processed material can effectively be used to produce SLS parts with a good compromise between costs and overall performance. In addition, it was observed that the theoretical algorithms of reprocessing used in this research well fitted the experimental results, proving their adequacy to describe the degradation effects experienced by the polymeric materials in SLS. In this regard, the proposed methodology can be used as an optimization tool to reduce the economic and environmental impact of the material, with real advantages for academic and industrial practitioners in the field.

In future work, the relationship between relevant SLS process parameters and the capability of powder recycling will be studied using the approach used in this research. The implementation of a design of experiments covering other mixture ratios and different parameterization setting could be helpful to improve the adjustment of the experimental results with the theoretical solutions with a minimum number of experiments, saving costs and time of analysis.

References

ASTM International (2013), ISO/ASTM 52921 Standard Terminology for Additive Manufacturing – Coordinate Systems and Test Methodologies, pp. 1-6.

Bacchewar, P.B., Singhal, S.K. and Pandey, P.M. (2007), “Statistical modelling and optimization of surface roughness in the selective laser sintering process”, *Proceedings of the Institution of Mechanical Engineers, Part B: Journal of Engineering Manufacture*, Vol. 221 No. 1, pp. 35-52.

Benz, J. and Bonten, C. (2019), “Temperature induced ageing of PA12 powder during selective laser sintering process”, *AIP Conference Proceedings*, Vol. 2055.

Bernardo, C.A. (1998), “Derivation and validation of models to predict the properties of mixtures of virgin and recycled polymers”, in Akovali, G., Bernardo, C.A., Leidner, J., Utracki, L.A. and Xanthos, M. (Eds), *Frontiers in the Science and Technology of Polymer Recycling*, Springer, pp. 215-247.

Bernardo, C.A., Cunha, A.M. and Oliveira, M.J. (1993), "The effect of recycling on the properties of thermoplastics composites", *The Interfacial Interactions in Polymeric Composites*, pp. 443-448.

Bernardo, C.A., Cunha, A.M. and Oliveira, M.J. (1996), "An algorithm for predicting the properties of products incorporating recycled polymers", *Advances in Polymer Technology*, Vol. 15 No. 3, pp. 215-221.

Bernardo, C.A. (1998), "Derivation and validation of models to predict the properties of mixtures of virgin and recycled polymers", in Akovali, G., Bernardo, C.A., Leidner, J., Utracki, L.A. and Xanthos, M. (Eds), *Frontiers in the Science and Technology of Polymer Recycling, Springer*, pp. 215-247.

Bourell, D.L., Watt, T.J., Leigh, D.K. and Fulcher, B. (2014), "Performance limitations in polymer laser sintering", *Physics Procedia*, Vol. 56, pp. 147-156.

Caulfield, B., McHugh, P.E. and Lohfeld, S. (2007), "Dependence of mechanical properties of polyamide components on build parameters in the SLS process", *Journal of Materials Processing Technology*, Vol. 182 Nos 1/3, pp. 477-488.

Chen, P., Wu, H., Zhu, W., Yang, L., Li, Z., Yan, C., Wen, S. and Shi, Y. (2018), "Investigation into the processability, recyclability and crystalline structure of selective laser sintered polyamide 6 in comparison with polyamide 12", *Polymer Testing*, Vol. 69, pp. 366-374.

Dadbakhsh, S., Verbelen, L., Verkinderen, O., Strobbe, D., Van Puyvelde, P. and Kruth, J.P. (2017), "Effect of PA12 powder reuse on coalescence behaviour and microstructure of SLS parts", *European Polymer Journal*, Vol. 92, pp. 250-262.

Dastjerdi, A.A., Movahhedy, M.R. and Akbari, J. (2017), "Optimization of process parameters for reducing warpage in selected laser sintering of polymer parts", *Additive Manufacturing*, Vol. 18, pp. 285-294.

Delfs, P., Töws, M. and Schmid, H.J. (2016), "Optimized build orientation of additive manufactured parts for improved surface quality and build time", *Additive Manufacturing*, Vol. 12, pp. 314-320.

DePalma, K., Walluk, M.R., Murtaugh, A., Hilton, J., McConky, S. and Hilton, B. (2020), "Assessment of 3D printing using fused deposition modeling and selective laser sintering for a circular economy", *Journal of Cleaner Production*, Vol. 264.

Dotchev, K. and Yusoff, W. (2009), "Recycling of polyamide 12 based powders in the laser sintering process", *Rapid Prototyping Journal*, Vol. 15 No. 3, pp. 192-203.

Duddleston, L.J. (2015), *Polyamide (Nylon) 12 Powder Degradation during the Selective Laser Sintering Process*, University of WI (Madison).

EOS GmbH (2016), Operations manual EOS P 396 - Functional description.

Fruggiero, F., Lambiase, A., Bonito, R. and Fera, M. (2020), "The load of sustainability for additive manufacturing processes", *Procedia Manufacturing*, Vol. 41, pp. 375-382.

Ghita, O.R., James, E., Trimble, R. and Evans, K.E. (2014), "Physico-chemical behaviour of poly (ether ketone) (PEK) in high temperature laser sintering (HT-LS)", *Journal of Materials Processing Technology*, Vol. 214 No. 4, pp. 969-978.

Gibson, I., Rosen, D. and Stucker, B. (2010), *Additive Manufacturing Technologies - Rapid Prototyping to Direct Digital Manufacturing*, Springer.

Goodridge, R.D., Tuck, C.J. and Hague, R.J.M. (2012), "Laser sintering of polyamides and other polymers", *Progress in Materials Science*, Vol. 57 No. 2, pp. 229-267.

Gu, H., Bashir, Z. and Yang, L. (2019), "The re-usability of heat-exposed poly (ethylene terephthalate) powder for laser sintering", *Additive Manufacturing*, Vol. 28, pp. 194-204.

Hofland, E.C., Baran, I. and Wismeijer, D.A. (2017), "Correlation of process parameters with mechanical properties of laser sintered PA12 parts", *Advances in Materials Science and Engineering*.

ISO (1996), ISO 527-2 Plastics – Determination of Tensile Properties, pp. 1-8.

Josupeit, S. and Schmid, H. (2016), "Temperature history within laser sintered part cakes and its influence on process quality", *Rapid Prototyping Journal*, Vol. 22 No. 5, pp. 788-793.

Josupeit, S. and Schmid, H.J. (2017), "Experimental analysis and modeling of local ageing effects during laser sintering of polyamide 12 in regard to individual thermal histories", *Journal of Applied Polymer Science*, Vol. 134 No. 42, pp. 1-10.

Kumar, S. (2003), "Selective laser sintering: a qualitative and objective approach", *JOM*, Vol. 55 No. 10, pp. 43-47.

Kumar, S. and Czekanski, A. (2018), "Roadmap to sustainable plastic additive manufacturing", *Materials Today Communications*, Vol. 15, pp. 109-113.

Pacheco, R.M., Torres, J.A. and Cardenas, T. (2015), *Fabrication, Mechanical Testing, and Thermal Analysis of Additively Manufactured Polymers Using the EOS*, Advanced Qualification of Additive Manufacturing Workshop, Santa Fe, NM.

>Paolucci, F., van Mook, M.J.H., Govaert, L.E. and Peters, G. W.M. (2019), "Influence of post-condensation on the crystallization kinetics of PA12: from virgin to reused powder", *Polymer*, Vol. 175, pp. 161-170.

Pham, D.T., Dotchev, K.D. and Yusoff, W.A.Y. (2008), "Deterioration of polyamide powder properties in the laser sintering process", *Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science*, Vol. 222 No. 11, pp. 2163-2176.

Schmid, M., Amado, A. and Wegener, K. (2014), "Materials perspective of polymers for additive manufacturing with selective laser sintering", *Journal of Materials Research*, Vol. 29 No. 17, pp. 1824-1832.

Sillani, F., Kleijnen, R.G., Vetterli, M., Schmid, M. and Wegener, K. (2019), "Selective laser sintering and multi jet fusion: process-induced modification of the raw materials and analyses of parts performance", *Additive Manufacturing*, Vol. 27, pp. 32-41.

Wudy, K. and Drummer, D. (2019), "Aging effects of polyamide 12 in selective laser sintering: molecular weight distribution and thermal properties", *Additive Manufacturing*, Vol. 25, pp. 1-9.

Zarringhalam, H. (2007), *Investigation into Crystallinity and Degree of Particle Melt in Selective Laser Sintering, Loughborough University Institutional Repository*, Loughborough University.

Zarringhalam, H., Hopkinson, N., Kamperman, N.F. and Vlieger, J.J. (2006), "Effects of processing on microstructure and properties of SLS nylon 12", *Materials Science and Engineering: A*, Vols 435/436, pp. 172-180.

Corresponding author

Ana C. Lopes can be contacted at: acarinalopes@dep.uminho.pt