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Original article

Effects of Aging and Refreshment Ratio on the Strength Properties of Selectively Laser Sintered Polyamide 12

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ABSTRACT

This study investigated how the tensile properties of selectively laser-sintered polyamide 12 (PA12) specimens are affected by aging and refresh ratio. Starting with a new powder, printing cycles of approximately ten hours were performed, during which tensile and density specimens were printed. After each cycle, the powder was tested for melt flow index (MFI). In the first part, the best processing direction was determined. It was found that tensile strength, modulus of elasticity, elongation at break and MFI showed a linear trend, with the independent variable being the number of hours at elevated temperature. This was analyzed by linear regression. MFI increased with the number of hours at elevated aging, while all other properties mentioned decreased.

Key words: *polyamide 12, aging, refresh ratio, density, tensile strength, selective laser sintering*

1. INTRODUCTION

Selective laser sintering (SLS) produces a large amount of excess powder. To reuse it, it must be mixed in the correct ratio with the new, unused powder. After several passes of selective laser sintering, the excess powder begins to accumulate, which is associated with a significant cost. The objective of this study is to economically evaluate the SLS process based on powder utilization efficiency. Optimal utilization of this technology can only be achieved with good powder control.

On the market, SLS is very promising and competitive because it offers great freedom in design and high consistency of mechanical properties. After each layer is sintered, another layer of powder is applied with a recoater. This new layer is sintered again, leaving the unsintered powder of the previous layers as a support powder [2]. This makes the process a quasi-isothermal process [3]. The surrounding unsintered powder also serves as an insulating layer to ensure uniform cooling and homogeneous crystallization. In this way, the process allows undercuts, holes, and more complex shapes in the products. An important feature of this process is that the unsintered powder can be reused for the next process cycle after sieving. The limitations of this process are the relatively small variety of polymer powders that can be used [4].

Polyamide 12 (PA12) is by far the most commonly used and makes up the bulk of the available literature on SLS printing [5]. This in pure form of PA12 or PA12 compounds, which are almost always used for commercial purposes. In addition, progress and results have been made with other polyamides, elastomeric polymers, and more "exotic" polymers, but these are inherently more limited. Compared to injection molding, the required granulation is much higher, which increases the initial cost of the process [6].

The mechanical properties of SLS products depend on a variety of parameters such as granulation, ageing, degree of refreshment, power density, etc [7]. In this study, the influence of ageing and refreshment ratio is investigated by measuring the melt flow index (MFI) of PA12 powder, tensile strength, elastic modulus, density and to a limited extent dimensional deviation. The focus of this study is more on the ageing process of the powder.

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2. EXPERIMENTAL RESEARCH

2.1 Materials

PA12 smooth V2 powder with excellent surface resolution and navy grey in colour has been used to prepare the samples in this study. The powder particle size was 18-90 µm (Mean particle size 38 µm and ISO 13320) which was provided by Sinterit S.P.

2.2 Methods

The cubes and tensile samples were fabricated using Sinterit Lisa PRO SLS machine. The machine is fitted with an infrared laser diode with a power of 5W, the wavelength of the emitted light is 808 nm. The laser scanner type is of the form XY. The important processing parameters are depicted in Table 1. Three cubes having a dimension of 1000 mm3 were fabricated for each testing condition. Three tensile specimens were fabricated for each testing condition and dimensions of a tensile specimen is provided in Fig. 1 which is ISO slandered with number ISO-527-2-5A. The fresh powder undergone multiple print cycles until the mechanical properties are relatively poor.

Table 1 *List of variables and levels used in the experiment*

Layer Height	0.125 mm
Refresh ratio	25%
Print bed temperature	177.5 °C
Print chamber temperature	140°C
Laser power ratio	1.00
Energy scale laser power	1.30
Max energy / cm³, infill	250.0
Cooldown time	5400 s

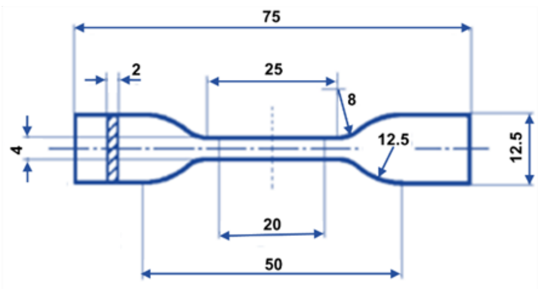

Fig. 1 *Dimensions of the tensile specimen.*

Three different orientations were chosen: 0 ° (horizontal), 45 ° (oblique) and 90 ° (vertical), keeping the main axis of the tensile specimens horizontal (see Fig. 2). However, after each printing cycle, the parts are manually cleaned and glass bead blasted to remove loosely bound, unsintered PA12 particles adhering to the surfaces of the specimens. The remaining powder from the overflow container, the conveyor bed and the support powder around the specimens is sieved for eighteen minutes with a sinterite powder sieve.
A test apparatus according to the standard SIST EN ISO 1133-2012 was used to measure the mass flow rate. The temperature was set at 210°C and a weight of 5 kilograms was used. MFR could be calculated by measuring the elapsed time of extrusion of 0.711 cm³ of compressed PA12, which was in the barrel for five minutes to ensure homogeneous melt.

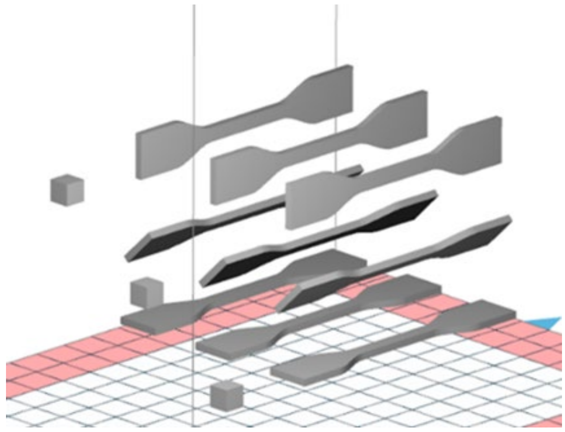

Fig. 2 *Tensile specimen orientation*

The MFI was calculated by using equation (1) expressed in cm³ per ten minutes. Where A is the volume of that is extruded by the piston, a correction factor of 600 to transform the equation to cm³ per ten minutes, l is the length of the cylinder and t the elapsed time.

$$MVRT\left(T, m_{nom}\right) = \frac{A \cdot 600 \cdot l}{t} \qquad (1)$$

After each completion of fabrication, all the above measurements were taken and recorded. Once the exhaustion point was determined, a nominal operating point was defined with a specific MFI. The data from the MFI was then used to apply a refresh ratio to the aged and exhausted powder to achieve the nominal operating point. A tumbler was used to homogeneously mix virgin and aged powder for up to two hours and retest which was done incrementally. After the nominal MFI was reached, a new print cycle of ten hours was performed to determine if the mechanical properties are back to the same values. To reach this nominal point with the MFI, incremental steps of the refresh ratio were applied, with tumbling mixing between each step. After fabricating with the refreshed powder, another final production cycle was processed by applying a refresh ratio of 30 % to the last mixed powder and hence, another ten more hours of aging was applied-

3. RESULTS AND DISCUSSION

3.1 Fabricating orientation

Table 2 listed the values of ultimate tensile strength (UTS) and elongation at break (EaB) of the tensile specimens which were fabricated in the first step of the study where their stress-strain curves are given in Fig. 3.
The absolute deviation of the dimensions in thickness was on average 5.1 % from the desired dimension, which was similar for the other orientations. The absolute deviation of

the dimensions in thickness was on average 5.1 % from the desired dimension, which was similar for the other orientations. With an average deviation of 4.1 % for the horizontal print and 8.6 % for the vertical samples (rotated 90 °). The absolute deviation of the 45 ° rotated samples for width was on average only 0.3 %, while for the horizontal and vertical samples it was on average 6.1 % and 1 % respectively. Eventually, in the first step, the best orientation with the best mechanical properties was found to be an angular orientation of 45 ° rotation.

Table 2. *Ultimate tensile strength (UTS) and elongation at break (EaB) of the tensile specimens in the first step of the study*

Samples	UTS (in MPa)	EaB (in %)
1. Horizontal	46.9	11.1
2. Horizontal	51.4	7.6
3. Horizontal	41.3	6.8
4. Vertical	50.3	8.7
5. Vertical	45.9	8.6
6. Vertical	45.5	9.6
7. 45° angled	50.5	10.5
8. 45° angled	54.6	8.4
9. 45° angled	57.1	9.7

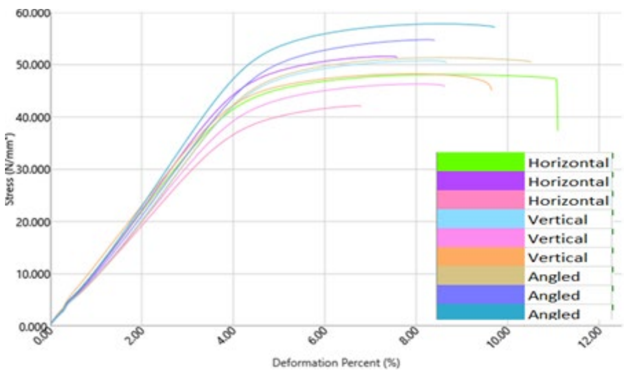

Fig. 3 *Stress-strain curves of the tensile specimens fabricated in the first step of the study*

3.2. Aging effect

Table 3 provids an overview of aging exposed hours and their effects on the metallurgical properties. A total of ten fabricating runs were made with a fabricating time of about nine to ten hours each. It is important to note that each cycle includes a warm-up time and a cool-down time, so the exposure time reported here is not at an elevated temperature of a constant 177.5°C, the printing temperature, and that each column represents the average of several measurements. Density, tensile strength, and Young's modulus show a clear downward trend. The MFI measurements show a clear upward trend.

Fig. 4 shows the linear regression model from the hours exposed-density data set, the graph shows a significant deviation from a horizontal line. The model is defined as $Y = -0.0005758 \times X + 1.012$, with an r^2 value of 0.5113, indicating that the fit is neither good nor bad, which could be explained by the small deviations in the data. A p-value of 0.0201 indicates a statistically significant relationship.

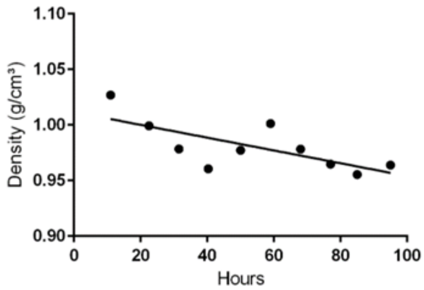

Fig. 4 *Linear regression hours exposed vs. density*

Fig. 5 shows the linear regression model of the ultimate tensile strength defined as $Y = -0.1915 \times X + 46.80$ with an r^2 coefficient of 0.7126 which implies a reasonably good fit. A significant deviation from the horizontal can also be seen. A p-value of 0.0021 strongly suggests a statistically significant relationship.

Table 3 - *Aging exposed hours and their effects on the metallurgical properties*

Exposed (hours)	Density (g/cm³)	MFI	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Absolute deviation thickness (%)	Absolute deviation width (%)
0	-	13.11	-	-	-	-	-
11	1.026	13.73	50.13	1656.38	9	5.17	0.34
22.5	0.999	13.91	40.16	1391.43	7.56	2.33	1.08
31.5	0.978	16.56	38.96	1192.18	8.26	2.33	1.08
40.333	0.960	18.88	34.1	1116.19	8.2	2.17	0.83
50	0.977	18.49	35.26	1142.98	7.4	3.5	1
59	1.001	18.9	40.93	1258.65	7.96	3.5	2.33
68	0.978	21.15	34.6	1016.55	8.3	5.5	2,17
77	0.964	21.37	31.06	1016.8	7.45	4.5	1.08
85	0.955	21.95	29.2	962.73	7.26	3.33	2.58
95	0.963	22.89	30.3	947.55	7.4	2.67	1.92

The linear regression model for the Young's modulus is shown in Fig. 6 and is defined as Y = -6.960×X + 1546 with an r^2 value of 0.7695. The deviation from horizontal is significant. A p- value of 0.009 strongly suggests a statistically significant relationship.
For the melt flow index the model is shown in Fig. 7 and defined by Y = 0.1104×X + 12.85. The deviation from the horizontal is significant and the r^2 value is 0.9520. A p-value of less than 0.0001 strongly suggests a statistically significant relationship.

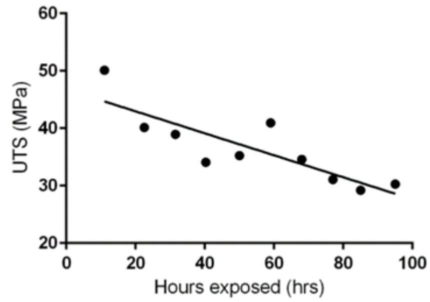

Fig. 5 *Linear regression hours exposed vs. UTS*

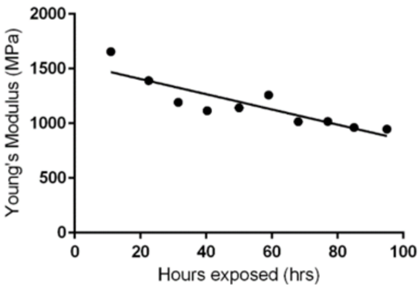

Fig.6 *Linear regression hours exposed vs. Young's modulus*

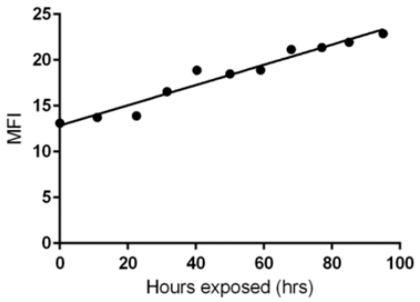

Fig 7 *Linear regression hours exposed vs. MFI*

3.3. Refresh ratio

These values imply that these models acceptably correlate the exposed hours and the MFI value, UTS, Young's modulus, and density as linear dependent variables. The elongation at break and absolute deviations for thickness as well as for width do not initially give the impression of a downward or upward trend, but seem to be rather constant in general, but the linear regression suggests otherwise. For EaB and absolute deviation for width, the models are defined as Y = -0.01353×X + 8.671, r^2 = 0.4979, p=0.0338 and Y = 0.01887×X + 0.3718, r^2=0.5405, p=0.02450, respectively, indicating that there is a correlation. However, the absolute deviations of the thickness show a non-significant curve with an r^2 value of 0.0049, which is too low to speak of a correlation. In addition, the MFI was measured of the Sinterit PA12 Smooth starter powder as a reference. This powder is supplied by Sinterit for mixing with virgin material for the first print after which the normal refreshing ratios can be applied. The MFI was measured at 20.25, which, if the other data is consulted, suggests an aging time or exposure time of about 60 hours at elevated temperatures. This is not stated in the Sinterit data sheet. Here, a nominal operating point of UTS of 35 MPa is chosen. This gives an EaB of 7.5 to 8 percent and an MFI between 18.5 and 19. By gradually refreshing the aged powder, as mentioned earlier, this MFI value is approximated and then tested. It resulted in a stop of adding virgin powder when this point was reached and Table 4 is provided after recalculating the refreshing ratio.

Table 4. *Refreshing ratio*

Applied refreshing ratio (in%)	MFI
9.09	22.97
16.65	21.61
23.07	20.50
28.58	20.15
33.33	19.13

3. CONCLUSION

In this study, the influence of aging and refreshing ratio on the mechanical properties of PA12 was investigated. An angled orientation of 45° degrees rotated by keeping the major axis horizontal of the tensile specimens was obtained as the best orientation.
Linear regression analyzes of the results yielded models that can relate the number of hours the powder is exposed to elevated temperatures to a number of properties. Since ultimate tensile strength and melt flow index show a credible linear dependence on the number of hours the powder has been aged, it can be said that these two values can be indicative of each other.
The melt flow index, ultimate tensile strength and the Young's modulus show a clear trend with acceptable probability. Density, elongation at break and absolute dimensional deviation in width show a plausible linear dependence on the hours the powder was exposed to elevated temperatures.
By applying a refresh ratio to the aged powder, the melt flow index of this working point was approximated by intermediate measurements of the melt flow index of the powder. The linear regression model suggests a linear dependence with high plausibility, with the refreshing ratio as the independent variable and the melt flow index as the dependent variable.
When the melt flow index of the working point was reached, a new print cycle was performed and the same

measurements as before were recorded. This showed that it is possible to obtain good mechanical properties if a sufficient refreshing ratio is applied.
In a final test, another refresh ratio was applied to this refreshed powder, which now had an additional aging time. The mechanical properties of this last printout showed that by applying a refreshing ratio after each cycle, the properties slightly decrease. It can be said that the powder has changed from virgin to reused polyamide 12 powder.

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NOTE

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