POST PROCESSING TREATMENTS ON LASER SINTERED NYLON 12

B.A. King*, A.E.W. Rennie*, J.P. Taylor*, G.R. Bennett†

*Lancaster University, Engineering Department, Lancaster, UK

†Euriscus Ltd, Chesham, UK

Abstract

The laser sintering of polymers is an established process producing components with well-documented material properties. Whilst these properties are inferior to those of injection moulded nylon 12, they are suitable for prototyping and several specialist production applications. Broadening the applicability of the process to a wider range of manufacturing applications, can be accomplished by rendering the material properties of sintered nylon closer to those of injection moulded nylon. This paper reports on a series of post-processing treatments which have been carried out to enhance the mechanical properties of sintered nylon. The work has examined the effects of heat, pressure, infiltration with methyl methacrolate and combinations of these treatments. Results are reported on the impact of the treatments on the elongation and Ultimate Tensile Strength (UTS) of the test samples, with heated pressured samples improving UTS by 2MPa, and infiltrated parts increasing elongation by 5.2%.

Introduction

Since the late 1980s, the Laser Sintering (LS) of polymers has widespread use as a rapid prototyping technology [1]. The basic process of using a scanned, focussed laser beam to selectively melt polymer powder has remained unchanged. Improvements in laser power and the speed and accuracy of the scanning galvanometers have resulted in a small improvement in part accuracy, and a reduction in build times. The most common material which is used in the LS process is nylon 12 (Polyamide 12) as its thermal and mechanical properties are highly suited to the LS process [2]. The material properties of PA12 LS components has not changed since the early days of production [3][4]. Sintered nylon 12 has a lower ultimate tensile strength and a significantly lower elongation than components manufactured by other processes such as injection moulding[5][6][7]. The authors sought to investigate low cost post-processing techniques to determine if they have the capability of extending the material properties of sintered PA12 components.

Materials and Method

Several different post processing combinations were considered, namely:

1. Vacuum infiltration of PA 12 components with Poly Methyl Methacrylate(PMMA);
2. Application of heat;
3. Application of heat and pressure;
4. Combinations of these approaches.

The goal in each case was to determine the effect of the post-processing on the part quality, ultimate tensile strength, and elongation. To test the effects of these various post-processing techniques, a standard test coupon geometry was selected, as defined by BS EN

ISO 527-5:2009. These were manufactured using a Vanguard HiQ™ LS machine. Additionally, a simple injection moulding tool was manufactured to produce the same geometry from PA 12 beads. This was done so that there could be a comparison with an alternative manufacturing process.

The vacuum infiltration process is readily available as it is used to seal the surface porosity found in investment castings and other metal and plastic parts. Measurements on the parts before and after the infiltration process found that there were no discernible changes to the exterior dimensions of the coupons.

In order to apply heat and pressure to the coupons, a dedicated rig was manufactured (Figure 1). The cylindrical pressure chamber was manufactured from 304 stainless steel.

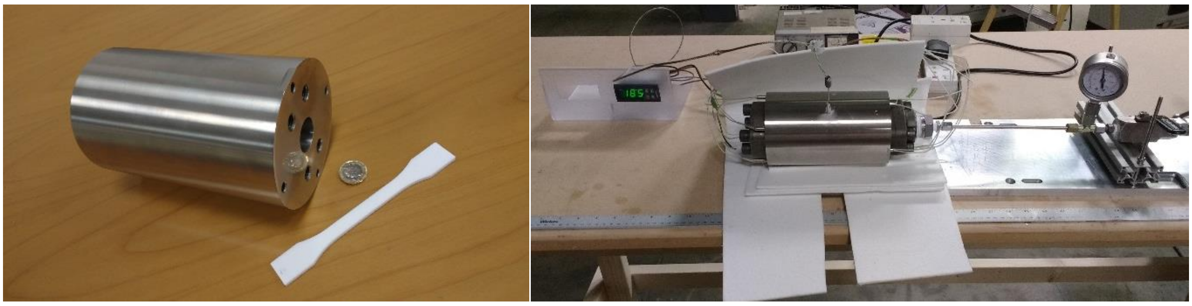

Figure 1a. Manufactured cylinder, **1b**. Pressurisation oven

The cylinder was heated by means of eight 110W 4" long cartridge heaters, four inserted at each end. Control was effected by means of a Carel IR32V2L000 temperature control unit. The oven temperature was monitored via a Type K thermocouple which could be inserted into the body of the oven. The rate at which the oven was heated was limited, so that 45 minutes was required to come to full temperature. The oven's gas feed was through a high temperature isolation valve. Between the valve and the oven was a high temperature gas pressure gauge, capable of displaying pressures up to 6000 psi (40MPa). Gas could be introduced to the oven at any time, but in these experiments, the parts were heated for at least one hour before the high pressure nitrogen was introduced.

The oven was provided with a loose blanket of insulation material to provide some insulation during heating periods. This blanket could be easily removed to facilitate cooling after the heating period was completed. After each heated pressurisation phase, the electrical power to the cartridge heaters was removed, and the oven was allowed to cool. Once below 30 ºC, the pressure was relieved, and the chamber could then be opened. After each heated pressurisation phase, the electrical power to the cartridge heaters was removed, to allow the oven to cool. Once below 30 ºC, the pressure was relieved, and the chamber could then be opened.

Post Processing Trials

The component parts were treated with a variety of post processing techniques. One requirement of these techniques was that they should be low cost and the relatively easy to apply so that if successful they could be considered for inclusion into a production process for LS parts. The processes used are

i) Vacuum Infiltration

A set of eight parts were vacuum infiltrated using PMMA this process is widely used for sealing castings and other porous items. Following the application of the process, external dimensions of the test coupons were found to have changed by less than 20µm. A UK company, ‘Ultraseal’ performed this task. In bulk, this treatment costs less than US$ 1 per part, and part turnaround is typically less than 48 hours.

ii) Application of heat – (secondary sintering)

The melting point of Duraform™ is listed as 184°C, but this is for the unprocessed powder. An experiment was undertaken to find the maximum temperature at which Duraform™ parts would sag under their own weight. To this end a test coupon was simply supported in two aluminium blocks in an oven. The oven temperature was increased at 5°C intervals, and the part left to temperature stabilise for 30 minutes. A non-contact infra-red thermometer was used to measure the temperature at the end of each 30 minute period. Whilst the part softened with temperature, no appreciable distortion was observed up to and including a temperature value of 185°C. However, as shown in Figure 2, significant distortion occurred at 190°C.

Figure 2. Photograph showing the sag which has occurred to a test coupon held at a temperature of 190°C

It was decided that the maximum permitted temperature at which pats could be tested was, therefore 185°C [8]. Coupons were placed in the cylindrical test chamber, with no pressure applied, and heated to 185°C for a period of two hours. They were then allowed to cool down naturally and submitted for tensile testing

Application of heat and pressure

To investigate the effect of pressure and temperature on the LS test coupons, the pressurised test chamber was used. Due to the size of the interior of the test chamber, only four coupons could be tested simultaneously. To prevent part-to-part adhesion, each part was wrapped in an aluminium foil jacket, which had been treated with dry PTFE spray, to prevent adhesion.

The parts were loaded into the pressure oven, and the chamber, and the chamber was heated to 185°C. The parts were left to temperature stabilise for one hour. Nitrogen gas was introduced to the chamber, directly from a standard industrial gas bottle. The pressure on the bottle, and thus in the chamber was 23 MPa (3335 psi). It should be noted that the injection pressure range recommended for nylon 12 which is injection moulded lies in the range 20 – 100 MPa. [9]

The parts were then left in this state for a period of two hours, and the heating then removed. The chamber and parts were allowed to cool over a period of six hours. The pressure was released, and the chamber opened. Parts were submitted for tensile testing.

It was a matter of concern that the connected porosity of the LS component could be sufficiently extensive as to allow the nitrogen gas complete access to the interior of the part, during the pressurisation phase of the process, effectively nulling its application. To test this possibility, several hollow test coupons were produced. The skin thickness was 0.8mm. There was no method of allowing powder escape from the interior. These parts were also treated with the heat/pressurisation process, and it was found that the parts collapsed, as would be expected if the surface skin were impervious to the gas seepage. This result provided some confidence that the nitrogen gas would not seep into the part sufficiently to prevent overall exterior pressure. Table 1 summarises the methods of treating parts.

Table 1. Combination of post processing treatments which were tested.

No post-processing	Part vacuum infiltrated	185^{o}C only applied	185oC and 23MPa applied
x			
	x		
		x	
			x
	x		**x**

Results

A minimum of three samples were made for each of the combinations shown in Table 2. Each coupon was tested to destruction on a Zwick tensile test machine.

Two test samples were sufficiently similar (results within 5% of each other), the first sample data was used for the results. If the two were dissimilar by more than this amount, the third sample was taken, and the average of the two closest results was used here. If no two results agreed to better than 5%, the intention was to build additional samples, however, this situation did not arise.

The ultimate tensile strength of the parts, along with the elongation is tabulated in Table 2

Table 2. UTS and Elongation results for samples

Sample		UTS (MPa)	Elongation (%)
PA12 Injection moulded part		47.9	379.0
ABS Injection moulded part		44.0	9.5
LS Part	plain	45.7	12.5
	heated only	15.8	9.1
	heated and pressurised	47.5	7.3
	infiltrated	29.9	19.8
	Infiltrated, heated, pressurised	39.0	4.8

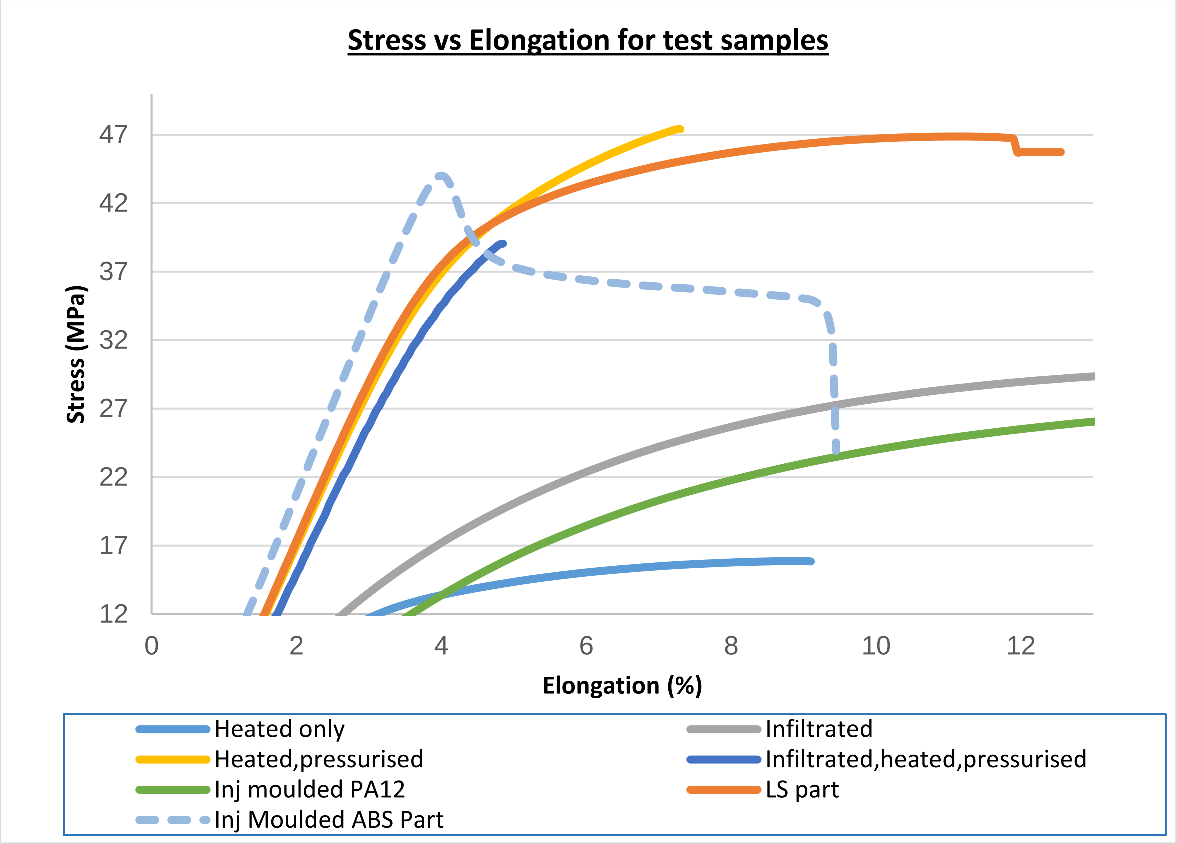

Figure 3. Stress-elongation graph for all samples

The results of the tensile testing are shown in Figure 3. It should be noted that whilst Figure 3 shows the extent of elongation of all LS components, it does not show the full elongation of the injection moulded part. This is shown in Figure 4, along with the plain 'as built' LS part.

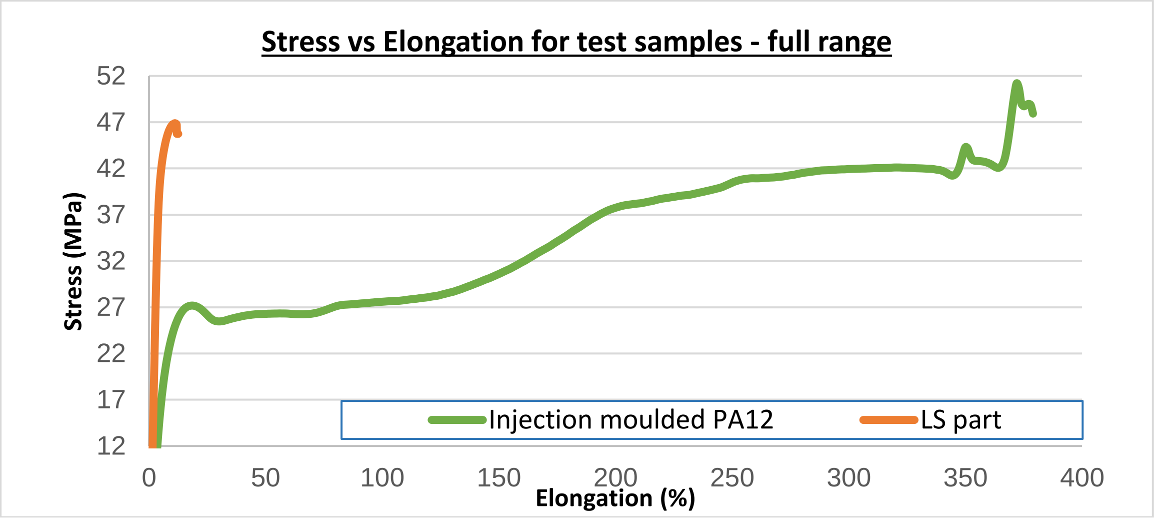

Figure 4. To scale stress-elongation graph for non-treated samples and injection moulded PA12

Discussion

As can be seen, the UTS and elongation values of injection moulded PA12 are larger than any of the LS or processed LS components. The elongation, in particular is some 30X larger, clearly demonstrating the difference in processing conditions between the two processes. Indeed in this respect LS PA12 behaves more like the mechanical test results for ABS would indicate that an LS has tensile properties which are more similar to injection moulded ABS rather than injection moulded PA12.

The post processing techniques which have been applied to the LS components have altered the mechanical performance of the LS components.

i) Infiltration

The infiltration with PMMA has improved the elongation performance of the LS coupons, and has almost doubled the elongation to break, but at the cost of a lower UTS. It is assumed that the infiltrant has reduced the possibility of crack formation and propagation, particularly on the surface of the part, which has improved the resistance to surface fracture mechanisms. PMMA has a UTS of 60 – 80 MPa, and an elongation to fracture of 5%.The test performance of our samples would indicate that there can be little or no connected porosity within the parts, as the resulting matrix of the PMMA and LS part has a reduced UTS. The mechanism for this requires further study.

ii) Application of Heat and Pressure

The application of heat alone has not improved the performance of the LS parts, and heat damage appears to have occurred to the part. The part was heated in air, rather than in an inert atmosphere and the presence of oxygen appear to have damaged the PA12. Both the UTS and elongation have fallen.

The application of heat under pressurised nitrogen has resulted in some improvement. The UTS has been increased by around 5%, and the elongation has reduced slightly. No warping or distortion was observed on the part. The improvement to UTS is probably due to a reduction to the internal, non-connected porosity of the part, and further work to test this hypothesis is required. However, the limited nature of the elongation is indicative that the internal porosity is still an important factor in the formation and propagation of cracks which lead to the fracture of the coupons instead of continued elongation.

Conclusions

LS PA12 does not have the same mechanical characteristics as injection moulded PA12. The UTS value of LS parts are some 5 % lower, whereas the elongation is 30 times lower. To the extent of UTS and elongation values, the most similar injection moulded material is probably ABS. Infiltration with PMMA improves the elongation of LS parts, but at the cost of reduced UTS. Heating LS components under pressure improves the UTS of the material, making it very similar to injection moulded material, but the UTS is not significantly changed. Further improvement may be achieved by increasing the temperature at which the pressure is applied, and indeed by increasing the pressure applied to the part. If the temperature of processing is to be increased, some type of support for the component will be required to prevent ‘sag’.

Some improvements to mechanical properties have been found, however further work is necessary to determine if LS components can indeed, be processed so that they have the same properties as injection moulded PA12.

Whilst LS PA12 does not perform in the same manner as its injection moulded counterpart, it does behave in a similar manner to injection moulded ABS, which has material properties which find great acceptance as a material used for production applications. LS PA12 may find greater acceptance for production applications which presently use ABS.

Further Work

This investigatory work indicates that there may be a possibility of improving the mechanical properties of LS nylon 12. Further work will include:

i) Microscopic examination of the structure of LS components before and after the heat/pressure post processing activity.
ii) Increasing the temperature of processing, but supporting the coupon, either by embedding the part in conductive beads (e.g. stainless steel ball bearings) or by supporting the part in a suitable liquid.
iii) Increasing the pressure applied to the part from the present 20 MPa to 100 MPa. This will require the use of a high pressure compressor.
iv) It would be interesting to melt LS PA12 powder in the unit, contained in a suitable shape, at high pressure, to determine the properties of the resulting part. If a significant improvement is found, it would then be interesting to consider running the laser sintering process in a high-pressure atmosphere.

Acknowledgment

The authors wish to acknowledge the *Engineering & Physical Sciences Research Council* (grant reference EP/K50421X/1), Euriscus Ltd and the *European Regional Development Fund* part-funded Low Carbon Lancashire Innovation Hub (grant reference 19R16P01012) for the financial support contributing to the research presented in this paper.

References

[1] Wohler Report 2015 ISBN 978-09913332-1-9 p17-20

[2] Y. Way et al., "Investigation of the Thermal Properties of Different Grades Polyamide 12 (PA12) in Improving Laser Sintering Process (SLS)", Applied Mechanics and Materials, Vols. 548-549, pp. 294-296, 2014

[3] L. Duddleston “Polyamide (Nylon) 12 Powder Degradation During The Selective Laser Sintering Process”, MSc, University of Wisconsin, 2015

[4] J.P. Kruth et al, “Polystyrene-Coated Alumina Powder Via Dispersion Polymerization For Indirect Selective Laser Sintering Applications”, Journal of Applied Polymer Science, Vol.128, pp.2121-2128, May 2013

[5] J.A.Nelson et al “Effects of Scan Direction and Orientation on Mechanical Properties of Laser Sintered Polyamide-12”, Advanced Design and Manufacturing Technology, Vol 7, No 2, September 2014

[6] J.A. Nelson et al, “Effect of Process Conditions on Temperature Distribution in the Powder Bed During Laser Sintering Of Polyamide-12”, Journal of Thermal Engineering, Vol 1, No 3, pp 159-164, July 2015

[7] J.P. Kruth, S.Kumar “Statistical Analysis of Experimental Parameters in Selective Laser Sintering”, Advanced Engineering Materials, August 2005, Vol.7, pp.750-75

[8] Processing of Vestamid™ L, D, E and Terra, Evonik Industries Vestamid Processing document, Evonik, August 2011

[9] 3D Systems ‘Duraform’ datasheet March 2012