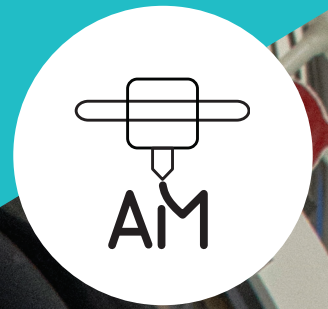


Lectoraat Kunststoftechnologie

Investigating the influence of heat treatment in a pressurised atmosphere on the ductility of SLS-printed PA12

Professorship for Polymer Engineering



Colophon

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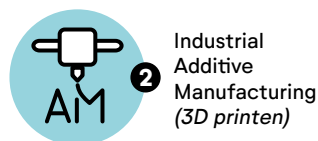
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Lines of research:



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economie



Industrial
Additive
Manufacturing
(3D printen)



Hybride
ontwerp



Duurzaam
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Investigating the influence of heat treatment in a pressurised atmosphere on the ductility of SLS-printed PA12

A thesis submitted in partial fulfilment of the requirements for the degree

Master of Science

in Polymer Engineering

Presented to the Department of Engineering & Design

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September 30th 2020

by Paul Dijkstra

University of
Applied Sciences

Windesheim



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Table of Contents

Nomenclature & abbreviations	3
Abstract	4
1. Introduction	5
2. Review of SLS- printed PA12 ductility	6
2.1. Introduction to SLS printing	6
2.2. Ductility assessment of SLS- printed PA12.....	7
2.3. Causes for low ductility of SLS- printed materials	8
2.4. Heat treatment in a pressurised atmosphere	11
3. Outlook on Hot Isostatic Pressing of SLS- printed PA12.....	13
3.1. Requirements for post- processing of semi- finished components.....	13
3.2. Boundary & processing conditions for densification using HIP.....	13
3.2.1. Temperature	14
3.2.2. Pressure	14
3.2.3. Time	15
3.3. Preliminary experiments	15
3.4. Hypotheses.....	16
4. Materials & methods	17
4.1. Material & printing parameters.....	17
4.2. Test specimens	18
4.3. Heat treatment in isostatically pressurised atmosphere	19
4.4. Characterisation	20
4.4.1. Part density	20
4.4.2. Tensile properties	21
4.4.3. Impact strength	21
5. Results	22
5.1. Visual observations.....	22
5.1.1. Autoclave- treated specimens	22
5.1.2. HIP- treated specimens	24
5.2. Density of powder- filled cylinders	25
5.3. Density of solid impact specimens	26
5.4. Mechanical properties of solid samples	28
6. Discussion	32
6.1. The influence of melting and particle fusion on ductility	32
6.2. Reduction in ductility of SLS- printed PA12 after pressurised heat treatment	34
7. Conclusions	35
8. Recommendations	36

References.....	37
Appendix A: Material, printing parameters & procedure.....	40
Appendix B – Theory complementary to the discussion (H6)	44



Nomenclature & abbreviations

Term (Unit)	Description
AM	Additive Manufacturing, a collective name for production methods wherein parts are built by the addition of material, often layer-by-layer.
Autoclave (treatment)	A method wherein parts are subjected to heat treatment at a high, isostatic pressure.
E (MPa)	Young's Modulus, the relationship between stress and strain measured in tensile testing, measured between 0.05 to 0.25% of elongation.
EaB (%)	Elongation at Break, the percentage of elongation in tensile testing as determined by the extensometer at the moment of fracture.
ED (J/mm ² , J/mm ³)	Energy Density, a unit of measure that expresses the energy input per surface area by the laser in the SLS- printing process.
FDM	Fused Deposit Modelling, an extrusion-based AM- method for polymers.
HIP (treatment)	A method wherein parts are subjected to heat treatment at a high, isostatic pressure.
IM	Injection Moulding, a forming method wherein polymer is melted and subsequently injected into a cold cavity where the material resolidifies.
M (g)	Mass.
PA12	Polyamide 12, a type of thermoplastic.
P _{hold} (bar)	Hold pressure, a pressure in the Hot Isostatic Pressing process that is sustained for a period of time.
Powder- filled cylinder	A type of specimen used in the pressurised heat treatments experiments
Pressurised heat treatment	Other (more generic) term for HIP and autoclave treatments.
Pycnometry	A method wherein object volume is measured using Archimedes' principle.
SLS	Selective Laser Sintering, an AM- method that uses polymer powder.
Solid	Short term for parts of which the entire cross- section was sintered during SLS- printing. It is <u>not</u> meant that parts are non- porous.
T _g (°C)	Glass- transition temperature.
T _{hold} (°C)	Hold temperature, a temperature in the Hot Isostatic Pressing process that is sustained for a period of time.
t _{hold} (hours)	Hold time, the duration in the Hot Isostatic Pressing process for which the hold temperature and hold pressure are sustained.
T _m (°C)	Melting temperature.
Treated (parts)	Short term for parts subjected to autoclave or HIP treatment.
UTS (MPa)	Ultimate Tensile Strength, the highest stress measured in tensile testing before necking and fracture.
V (cm ³)	Volume.
X	Coordinate axis parallel to the layers deposited in SLS- printing.
Y	Coordinate axis parallel to the layers deposited in SLS- printing.
Z	Coordinate axis in the build direction, perpendicular to the layers deposited in SLS- printing.
ρ (g/cm ³)	Part density.

Abstract

In the last decade, Selective Laser Sintering (SLS) of Polyamide 12 (PA12) has evolved into a production method for end-use components in non-demanding applications. There is increasing interest from the industry to apply SLS for demanding applications such as machine parts and orthopaedics, where safety is vital and high ductility is required. SLS-printed PA12 is strong but like other SLS-printed polymers, relatively brittle as a result of pores in the material. The state-of-the-art SLS-printing process cannot produce fully dense parts, so attention turned to post-processing and in particular a process called Hot Isostatic Pressing (HIP), a process that applies elevated temperature and isostatic pressure. HIP is used for moulding of dense materials from metal, ceramic and polymer powders and also for pressurised heat treatment to increase density and ductility of Additively Manufactured metal components. Experiments were performed to gain insight into the influence of heat treatment in a pressurised atmosphere on the part density and mechanical properties of SLS-printed PA12. Parts were treated for 4 hours at a temperature of 175°C and pressures of 18 and 1500 bar in separate experiments. Parts mostly retained their shape and under specific conditions a small increase in part density was observed, however the ductility and other mechanical properties decreased under the tested circumstances. It seems that changes to the SLS-printed PA12 parts dominate over the influence of HIP to part density.



1. Introduction

In recent years, the Additive Manufacturing (AM) industry has grown significantly and production of end-use components has become an important and fast-growing application of AM [1]. Particularly Selective Laser Sintering (SLS) is of interest, as it combines the design freedom and the flexible production planning of Additive Manufacturing with high productivity. In combination with some materials, such as PA12, good mechanical properties are achieved and it is used to produce parts for functional and load-bearing applications [1, 2].

As the mechanical properties of SLS-printed PA12 are used for load-bearing applications, it could be a suitable technology to adopt for demanding applications such as machine parts, spare parts and orthopaedics. In such applications, part integrity can have a pivotal role in safe product operation and therefore require that materials possess high ductility, meaning the material must be able to absorb considerable amounts of energy through plastic deformation prior to fracture.

This study starts with a literature review on SLS-printed PA12 and how its ductility is influenced in the printing process as well as by post processing. The rest of the study focuses on one particular post processing technique, heat treatment under isostatic pressure, including an experimental phase to gain insight into the influence of this post processing method on the ductility of SLS-printed PA12.

2. Review of SLS-printed PA12 ductility

This chapter introduces the Selective Laser Sintering (SLS) printing process and summarizes the findings of the author's literature review on improving the ductility of SLS-printed PA12 [3]. For an in-depth understanding of the subject matter it is recommended that the literature review is read in its entirety.

2.1. Introduction to SLS printing

In SLS printing, parts are built up layer by layer from a thermoplastic polymer powder. The building process is performed inside a pre-heated chamber filled with inert gas. The printing cycle of each layer starts with lowering the build plate by one layer thickness (Figure 1- a), after which a layer of powder is deposited (Figure 1- b). This layer is heated further to just below the melting temperature (T_m) for semi-crystalline polymers or the glass-transition temperature (T_g) for amorphous polymers (Figure 1- c). Next, a (galvanometer) scanner moves a laser beam over the powder bed in a pattern that represents the object's cross-section in that layer (Figure 1- d). Areas exposed to the laser beam briefly become fluid and fuse together to form a layer of the object. The build plate is then lowered by one layer thickness, powder is deposited once more and the process is repeated, fusing successive together to form three-dimensional objects.

Once building is completed, the build tray is removed from the printer and allowed to cool down. When cooled down, parts are taken out of the build volume and most of the powder is removed from the objects, after which any remaining powder on the part surface is removed from the surface by glass bead blasting. Unsintered powder support material is commonly 'refreshed' (mixed) with virgin powder and re-used in the printing process.

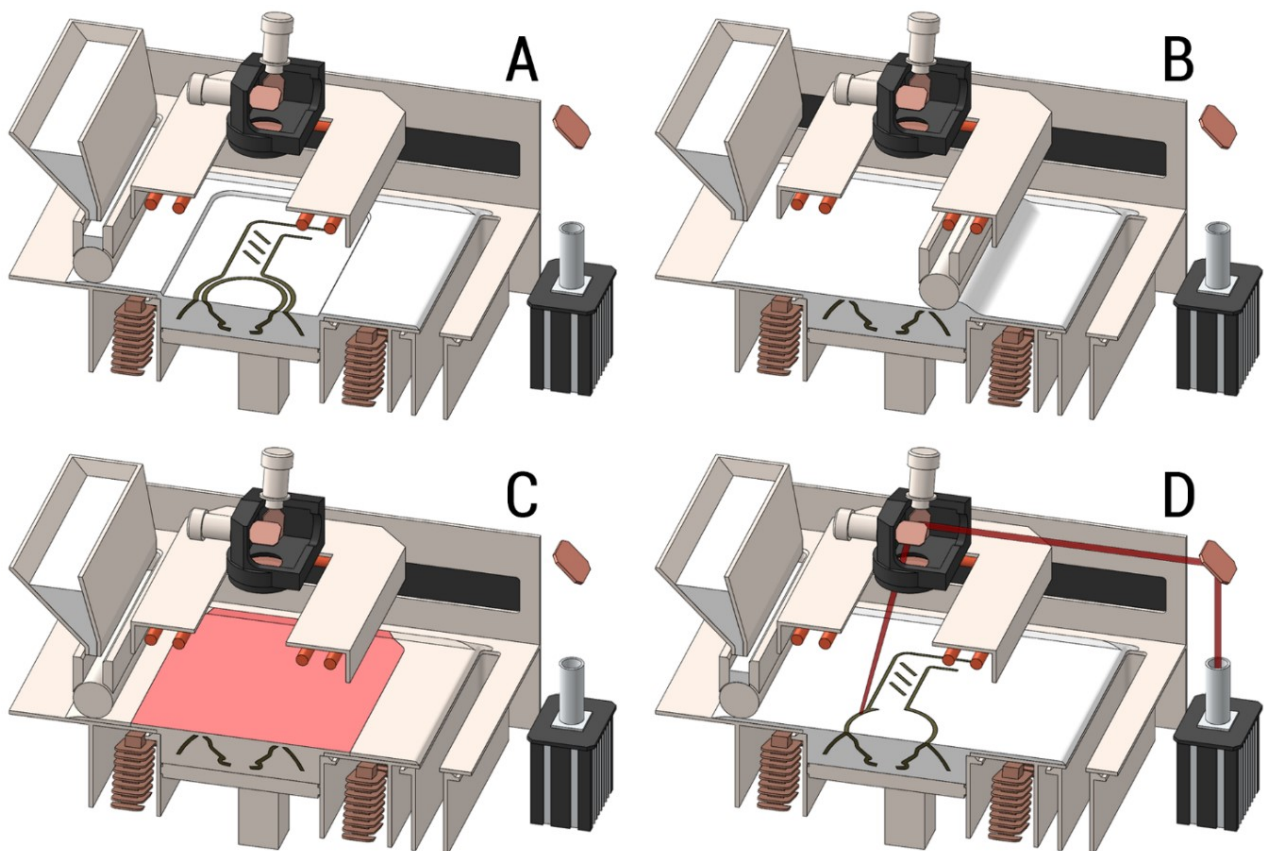


Figure 1: The basic steps in SLS: A: Lowering of build plate, B: Powder deposition, C: Powder bed heating, D: Sintering by laser.

Contrary to Additive Manufacturing (AM) techniques that use filament or resin, there is no need for a printed fixture to the build plate or printed support material thanks to the powder bed. In addition, the powder bed allows objects to be nested above, around and inside each other without printed support material, which increases production capacity compared to filament and resin AM techniques. Parts built with SLS can be distinguished by a slightly rough surface finish, the absence of marks from printed support structures and geometries may include complex shapes, hinging and/or interlocking features.

The most commonly used material in SLS-printing is PA12 thanks to its easy processability, widely applicable mechanical and chemical properties and the favourable balance between production cost and performance [3]. SLS-printed PA12 possesses a level of strength that enables applications beyond prototyping and is therefore also commonly used for end-use components in static and low-stress applications, such as brackets and housings.

2.2. Ductility assessment of SLS-printed PA12

For demanding applications where high strength and safety are required, it is important that materials are not only strong, but also highly ductile, meaning that the material is able to absorb considerable amounts of energy through plastic deformation prior to fracture. A comparison between SLS-printed and injection moulded PA12 was made. From the stress-strain diagrams (Figure 2) and fractured specimens (Figure 3) it can be seen that little to no neck formation occurs before fracture of SLS-printed PA12, whereas injection moulded PA12 exhibits considerably higher ductility, displaying necking followed by drawing before fracture.

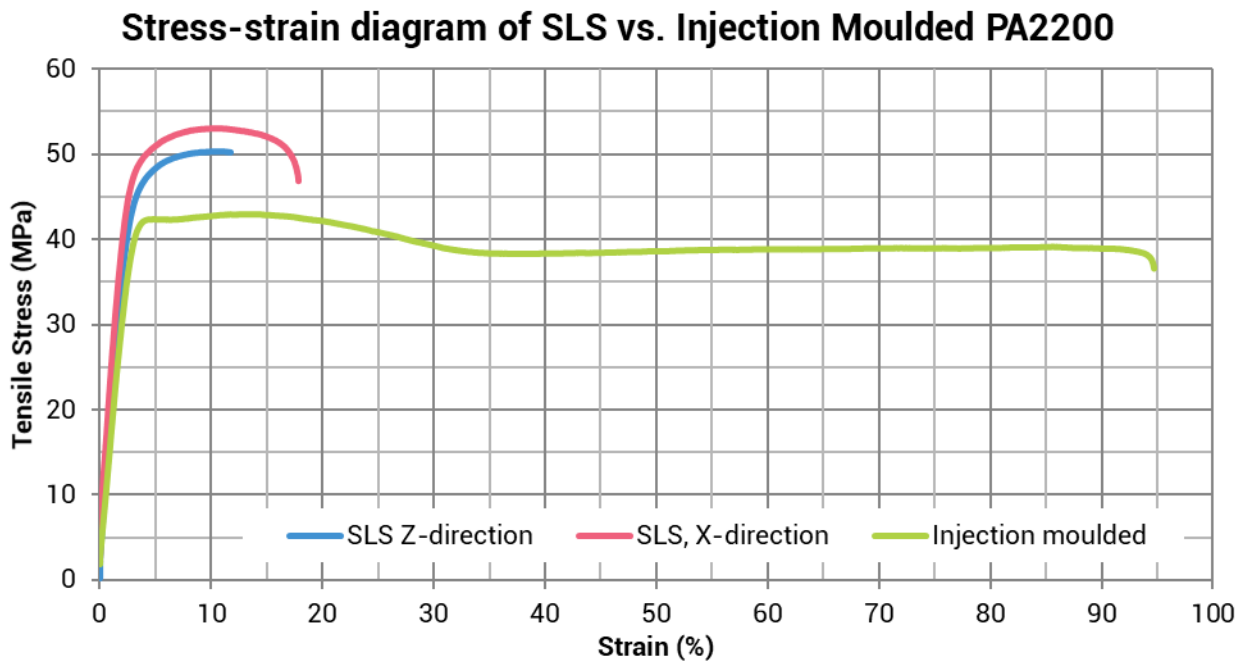


Figure 2: Stress-strain diagram comparing properties of ISO 527-2/1A tensile specimens, tested at 50mm/minute, using SLS printed EOS PA2200 specimens printed in the X- and Z-directions, printed with an energy density (ED) of 0.0336J/mm² and 0.1mm layer thickness, and injection moulded EOS PA2200 specimens. All specimens were conditioned at 23°C and 50%rH for five days before tensile testing [4].

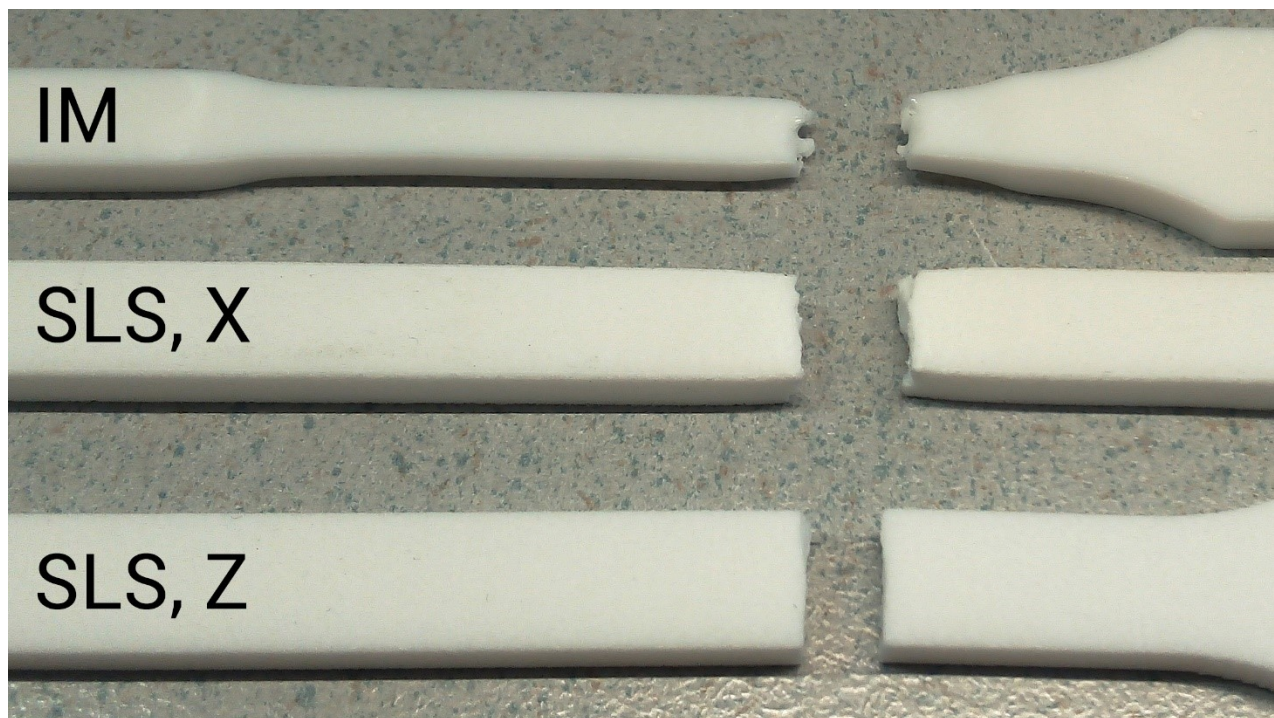
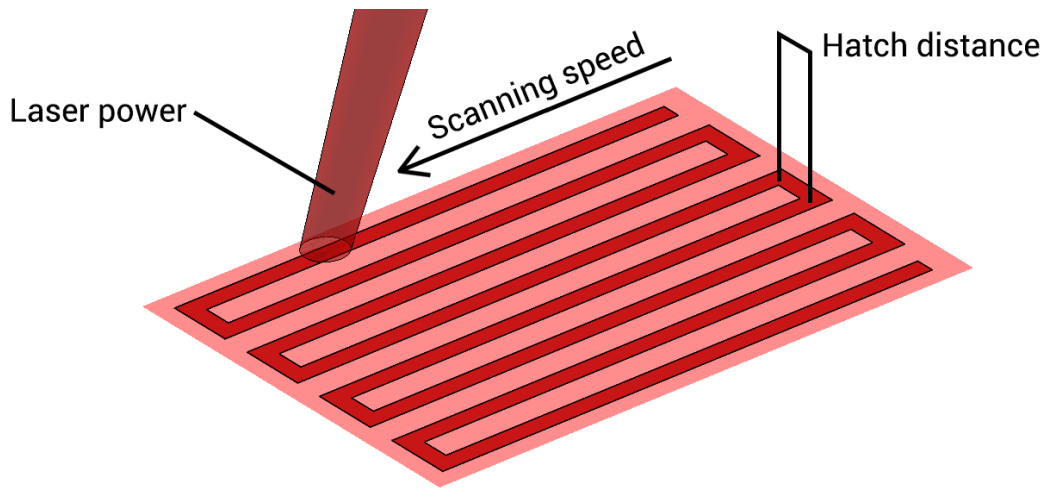


Figure 3: Comparison of tensile specimens made from EOS PA2200 [4], where the top specimen is injection moulded and displays neck formation and growth before fracture, the middle specimen is SLS-printed with the loading direction printed in the X-direction and displays fracture upon formation of a neck, and the bottom specimen is SLS-printed with the loading direction printed in the Z-direction and there is no visible neck formation before fracture.

Not only for SLS-printed PA12 but also for other SLS-printed polymers it is reported that these are either considerably less ductile compared to the (injection) moulded polymer or not ductile altogether [5- 11]. This indicates that the low ductility is not a material property but caused by processing conditions. SLS-printed materials are currently not suitable for applications where high ductility is required. However if the causes behind the low ductility of SLS-printed materials can be understood, it may be possible to overcome them.

2.3. Causes for low ductility of SLS-printed materials

In the author's literature study [3], the processing conditions and resulting material properties of SLS-printed and injection moulded PA12 were compared. For sintering, semi-crystalline polymers like PA12 must be heated to above their melting temperature. It is evident that the sintering process is strongly influenced by the zero-shear viscosity, which reduces with increasing temperature of the polymer and is favourable for the fusion of the polymer particles. Temperatures in the sintering process are controlled by the temperature of the powder bed prior to sintering and the laser energy input per surface area. The latter is commonly expressed as the energy density (ED), which consists of the parameters laser power, scanning speed and hatch distance, as depicted in Figure 4.



$$\text{Energy density, } E_d \text{ (J/mm}^2\text{)} = \frac{\text{Laser Power (J/s)}}{\text{Scanning speed (mm/s)} * \text{Hatch distance (mm)}}$$

Figure 4: Schematic of laser exposure of a surface area and the equation of energy density (ED) that describes the amount of energy per surface area that is applied by the laser during the sintering process. The energy density is sometimes also expressed as an energy per volume, wherein the energy density also accounts for layer thickness.

For SLS-printed materials including PA12 and as depicted in Figure 5, it is observed that part density increases with energy density [4, 12]. However even at higher energy densities the part density for SLS-printed PA12 is lower than 1.01g/cm³, the reported density of injection moulded PA12 [13]. The lower part density is widely attributed to porosity and is reported to be in the order of 3-8% for SLS-PA12 [14- 16].

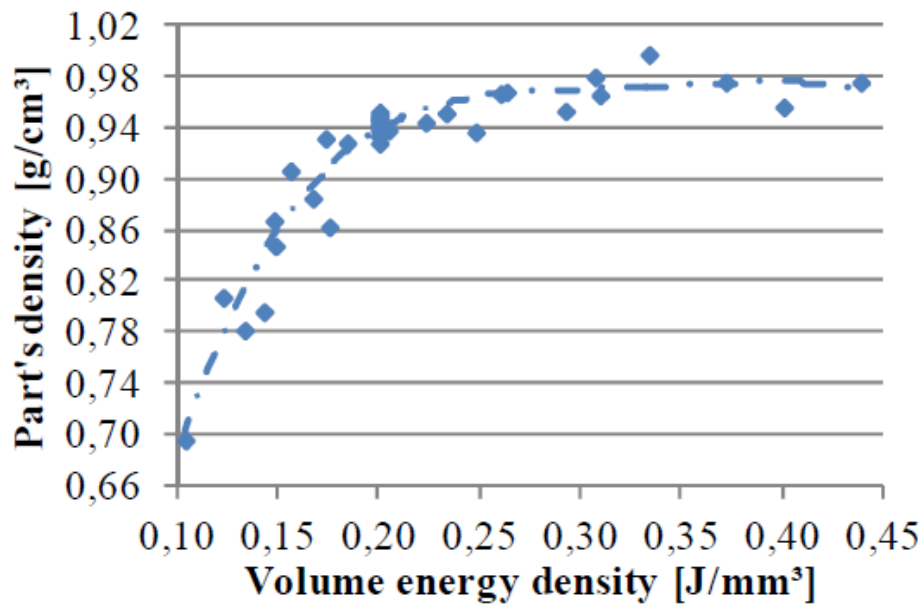


Figure 5: The effect of laser energy density on part density (left) and elongation at break (right) of SLS-printed PA12 [12].

It is also reported that pore morphology depends on energy density, with a predominantly open structure of interconnected pores at low energy densities, which changes to a structure of predominantly closed, isolated pores as the energy density increases beyond 0.020J/mm² [16]. The distribution of pores through the parts is also uneven, with reports that a higher concentration of pores occurs at the interface between layers, as may be seen in Figure 6 [16, 17].

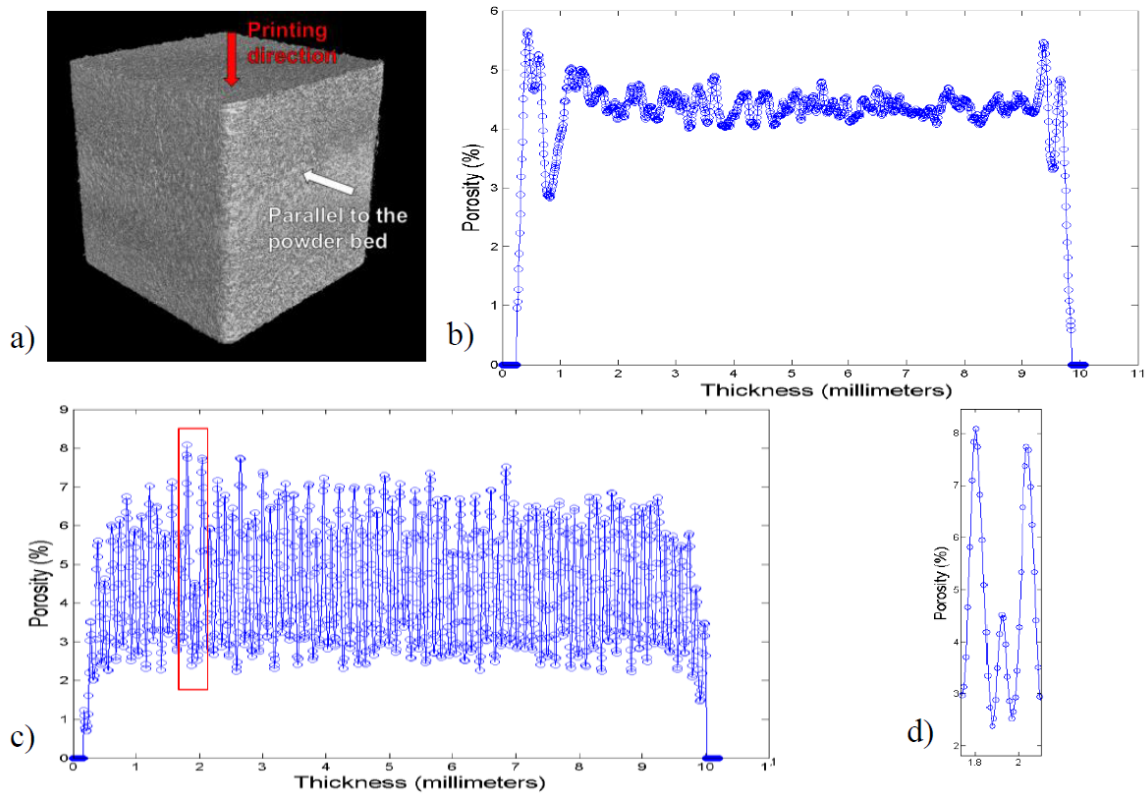


Figure 6: X-ray computer tomography of SLS-printed PA12 [17], showing a) View of the sample with reference to the different directions; b) Porosity distribution along the direction parallel to the powder bed platform and c) along the printing direction d) Detail of the porosity distribution along the printing direction (red rectangle in c).

Pores cause stress concentrations under load due to which local stresses exceed nominal stresses. This can severely affect the mechanical properties observed on a macroscopic scale. In fact as displayed in Figure 7, the elongation at break, like part density, is strongly dependent on the energy density [4, 12, 18].

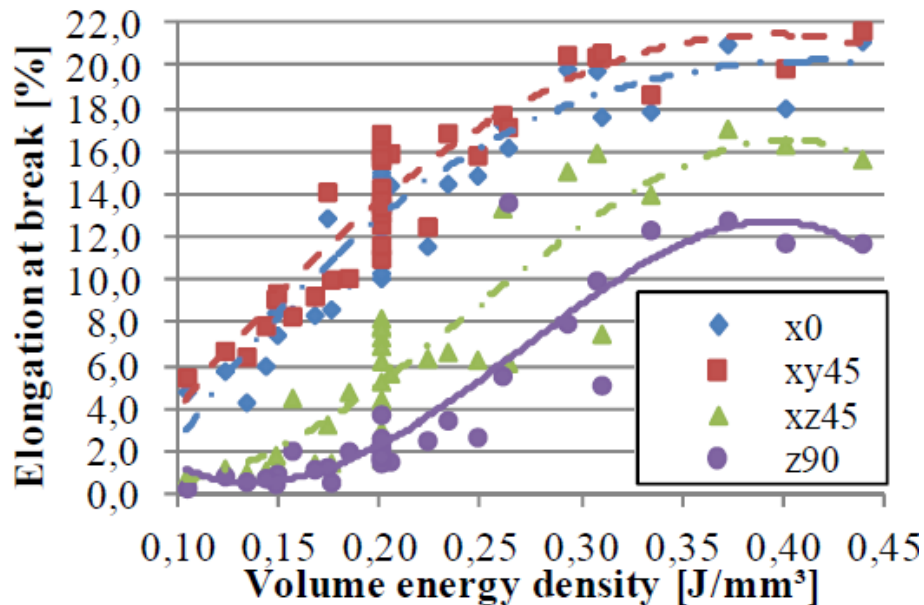


Figure 7: The effect of laser energy density on elongation at break of SLS-printed PA12 for specimens printed with the tensile direction in different orientations. The x0 specimens have the tensile direction parallel to the layers, the z90 specimens have the tensile direction perpendicular to the layers, i.e. in the build direction [12].

Although part density and ductility increase with energy density, this is only applicable within a limited range of energy density. In fact, at energy densities over 0.035J/mm^2 thermal degradation and negative effects to ductility of SLS-printed PA12 are reported [19]. Moreover energy densities significantly over 0.035J/mm^2 have a negative effect on part definition and accuracy [3], as displayed in figure 8. This means that increasing the energy density would not a viable solution even if thermal degradation could be avoided. As such, alternative solutions are needed to reduce porosity and increase ductility.

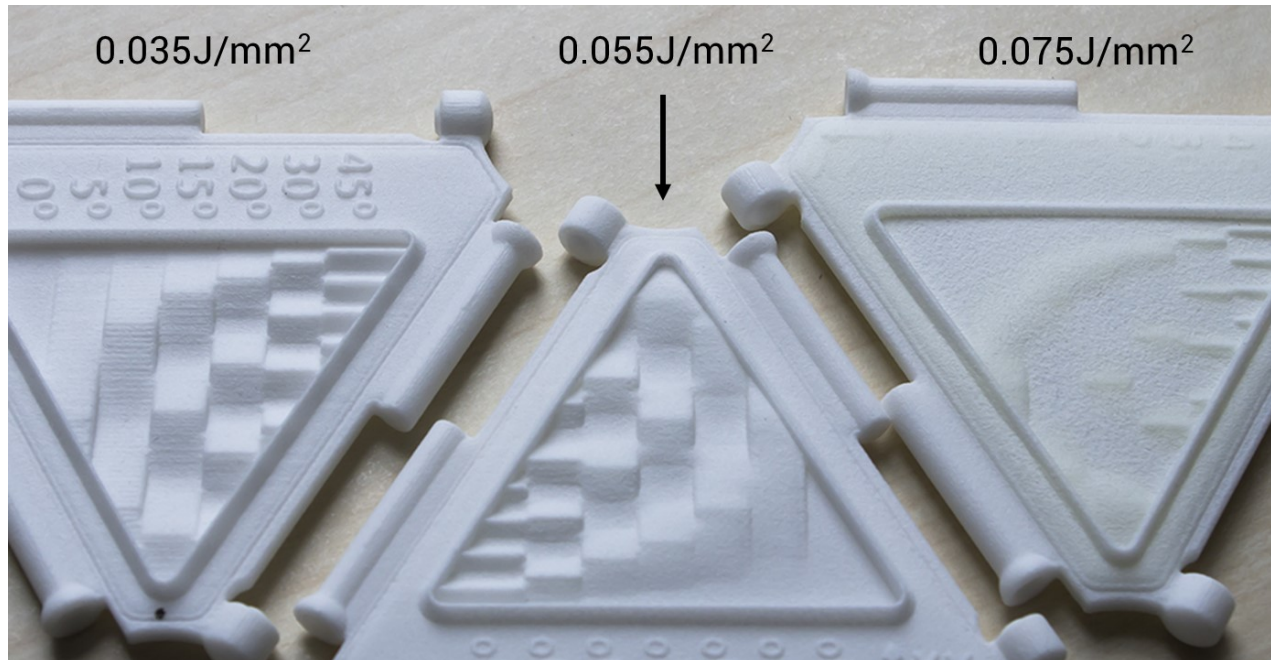
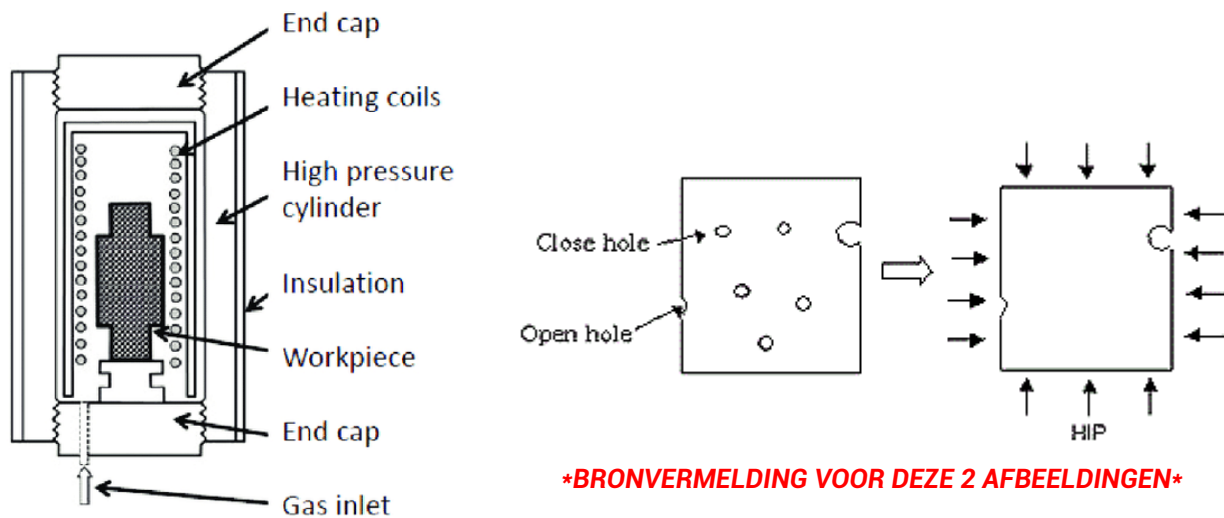


Figure 8: The effect of energy density on part detail and accuracy. It is visible that applying energy densities above 0.035J/mm^2 in SLS-printing of PA12 causes material outside the exposed cross-section to sinter, causing a negative and detrimental effect to part accuracy [4].

2.4. Heat treatment in a pressurised atmosphere

The author's literature study discusses several processes post-sintering that show an effect on ductility. Amongst these processes is the heat treatment of parts in a pressurised atmosphere, such as may be performed with Hot Isostatic Pressing (HIP) and autoclave processing.

A schematic representation of HIP is shown in Figure 9- left and the phases in the process in table 1. Before the process, the porous products are placed in a chamber which is subsequently closed. A vacuum may be applied to remove oxygen. Next, the chamber is heated to the desired temperature and the internal pressure of the chamber is increased using an inert gas, most often argon or nitrogen. Gas cannot flow from the chamber into any of the closed pores within the products, which results in a pressure differential between chamber and pores and causes stress inside the material. As the temperature increases, the material's yield stress reduces whilst the applied pressure continues to increase. The hold pressure and temperature, called P_{hold} and T_{hold} respectively, are selected such that the pressure differential causes stresses higher than the yield stress of the material. This leads to plastic deformation of the material and compression of the gas inside the closed pores. If the pressure were immediately relieved, the gas inside the closed pores would expand again. Instead by maintaining the pressure and temperature for a chosen period of time, an irreversible size reduction of closed pores occurs (Figure 9- right). This period is referred to as the hold time, t_{hold} . A mechanism is reported where the gas molecules inside the closed pores dissolve into the matrix material, diffuse through it and release into the HIP chamber [20]. After the hold time, temperature and pressure are simultaneously reduced.



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Figure 9, Left: Layout and components of HIP machine. Right: Schematic representation wherein closed pores are compressed and eliminated, where open pores in contact with the product surface remain.

Description	Pressure	Temperature
Before start	$P = 1 \text{ bar}$	$T < T_g$
Chamber evacuation	$0 < P < 1 \text{ bar}$	$T < T_g$
Heating + pressurisation	$1 \text{ bar} < P < P_{\text{hold}}$	$T_g < T < T_{\text{hold}}$
Hold phase	$P = P_{\text{hold}}$	$T = T_{\text{hold}}$
Cooling + depressurisation	$1 \text{ bar} < P < P_{\text{hold}}$	$T_g < T < T_{\text{hold}}$

Table 1: phases of HIP process

Typical applications of HIP are processing of metals and ceramics from powder feedstock and densification of semi-finished metal products. In recent years, various studies reported that HIP reduced and under the right circumstances entirely eliminated porosity of metal components produced with powder-based Additive Manufacturing technologies similar to SLS, which in all cases resulted in increased ductility [21-23].

For polymers, applications include reduction of void content in thermoplastic composites (autoclave) and moulding of products from PTFE and UHMWPE powders (HIP) [24-26]. In the field of polymer Additive Manufacturing, a study reports an increase in the density of amorphous polymer parts made by Fused Deposit Modelling (FDM) after post-treatment in a hot press using pressures in excess of 500 bar in a temperature below up to around glass-transition temperature (T_g) [27]. The effect on ductility was unfortunately not reported.

From reports in literature it appears that Hot Isostatic Pressing is capable of reducing porosity and may increase ductility too. However, no studies or reports were found on heat treatment in a pressurised environment or its effect on part properties of SLS-printed polymers, neither does there seem to be a commercialised product, process or service wherein SLS-printed polymer parts are post-processed at high temperature and pressure. As such it is considered all the more interesting to further investigate whether Hot Isostatic Pressing may be used as a method to reduce the porosity and increase the ductility of SLS-printed PA12 parts.

3. Outlook on Hot Isostatic Pressing of SLS-printed PA12

In the literature study, it was established that heat treatment in a pressurised atmosphere, also called Hot Isostatic Pressing (HIP), reduces porosity and increases ductility of numerous materials. No reports were found on this subject for Selective Laser Sintering (SLS) of polymers and it was suggested as a subject for further investigation and experiments. With the goal of increasing the ductility of SLS-printed PA12, this chapter elaborates what requirements and boundary conditions must be met in a HIP process for SLS-printed PA12 parts and what process conditions may be suitable.

3.1. Requirements for post-processing of semi-finished components

The motivation for experiments with HIP stems from the need for an industrially viable Additive Manufacturing (AM) process chain for the production of highly ductile polymer parts. Of course HIP is only industrially viable if it improves part properties. However, it is also important that the core strengths and advantages of SLS are maintained:

- Tooling-free manufacture;
- Cost competitive manufacture for single products and small series;
- Manufacture of complex part geometries, including interlocking and hinging features;
- Short lead times of typically up to several days.

HIP of SLS-printed PA12 parts is only successful when the shape of the parts is maintained. In other words, sagging and distortion must be avoided, and if shrinkage occurs due to densification, it may need to be compensated for with scaling factors. Moreover, HIP must be performed without the use of moulds or dies to support the products in part to keep the method tooling-free, but also because supporting tools would introduce limitations with regard to freedom of shape of the parts. Last but not least, the duration of treatment affects cost and lead time. Although for a broadly applicable process, the effect of HIP treatment on part cost and lead time are important, these aspects are ignored in the rest of this study as the focus lies on the influence of HIP on the part properties of SLS-printed PA12.

3.2. Boundary & processing conditions for densification using HIP

Based on the description of the HIP process in paragraph 2.4 it is apparent that the material and process must meet several boundary conditions in order for densification to occur:

- A direct connection between the chamber and pores should not exist, so that flow of gases from the chamber into the pores is impeded;
- Gas molecules in the pores must be able to dissolve into and permeate through the material so that pore size can be irreversibly reduced;
- The material must be plastically deformable, which may be aided by raising the temperature;
- The yield stress of the material must be considerably lower than the pressure applied;

A direct connection between the chamber and pores must be avoided. Materials with an open pore structure may be placed in a vacuum bag or have the part's exterior surfaces coated to close direct connections between the chamber and pores. Materials with a closed pore structure do not require bags or coatings before HIP. As described in paragraph 2.3, the pore structure of SLS-printed PA12 depends on energy density applied during sintering and a predominantly closed pore structure is obtained for energy densities above 0.020J/mm^2 [16]. As such it is expected that SLS-printed PA12 possesses a pore structure suitable for HIP when printed with sufficient energy density.

For irreversible reduction of pore size using HIP, the gas in the pores must be able to permeate through the polymer. It is reported that permeation of gases through polymers occurs when difference in pressure exists on opposite sides of the polymer [28]. Permeation can be described by the 'solution-diffusion' mechanism, wherein gas molecules at the high concentration interface are absorbed into the polymer. This causes a concentration gradient of the gas molecules in the polymer which drives gas molecules to diffuse within the polymer. At the low concentration interface of the polymer, desorption of gas molecules occurs. Because increasing pressure in the chamber and subsequent compression of the pores during HIP increases concentration of gas molecules on both sides of the polymer, it may be expected that permeation occurs into the polymer both from the pores and the chamber. The pore size continues to decrease under maintained pressure in the chamber so long as gases from the pore are absorbed into the polymer.

It is reported that in general, polymers in rubbery state have a higher permeability than in glassy state [28]. Although no information was found specifically on the permeability of inert gases through PA12, a study on the permeability of helium, argon and nitrogen through PE, PA11 and PVDF reports that above the glass-transition temperature, permeability increases considerably with temperature [29]. For nitrogen – the primary inert gas used for SLS printing – the permeability through PA11 increased by over 13x between 69°C and 129°C [29]. Based on this information it seems that increasing the temperature reduces the time required to reduce pore size by a given amount or to eliminate pores altogether.

3.2.1. Temperature

The influence of temperature is not just limited to permeability. For semi-crystalline polymers such as PA12, the modulus and strength of the material drop particularly as the temperature increases to above the glass-transition temperature (T_g) and melting temperature (T_m). Below the T_g of SLS-printed PA12 at approximately 45°C [30], the material is strong, stiff and relatively brittle, so it is not a practical temperature range to compress the pores. Above the melting temperature of SLS-printed PA12 at 184°C [31], the polymer is a fluid and whilst pores may be compressed easily, the polymer will not be able to retain its shape.

In between the glass-transition temperature and melting temperature, semi-crystalline polymers are in a rubbery state and it may be expected that there is a temperature in this range where the polymer can be easily deformed to compress the gas inside the pores whilst the material is sufficiently strong and rigid that parts maintain their shape. It is desirable to increase the temperature as high as possible without losing part shape, as the required pressures and time are minimised that way. Multiple reports state that heat treatment of SLS-printed PA12 parts at atmospheric pressure up to 180°C for up to 16 hours did not result in significant distortion of specimens which were laid flat on a wire rack [32, 33]. Several studies report that the melting temperature of thermoplastics increases with applied pressure [34-36], the rate of which was determined at 20°C / 1000 bar for PA12 [34]. As such, it might be possible to apply a hold temperature that exceeds the melting temperature at atmospheric pressure (184°C) if a hold pressure in excess 500 bar is applied and if the hold pressure is reached before the hold temperature and is maintained in the first stages of cooling.

3.2.2. Pressure

Besides applying a high temperature to facilitate permeability and pliability, pressure is needed to reduce porosity. No literature was found on heat treatment in a pressurised atmosphere for SLS-printed PA12 or other printed polymers, as such it is argued that the effect of pressure should be tested over a broad range of pressures. Information from other processes was taken to gauge the range of pressures within experiments should take place. For HIP processes of various metals, hold pressures of between 1000 to 2000 bar are reported with the pressure depending strongly on the type of metal [20-23, 37]. For HIP processing of UHMWPE, hold pressures of around 700 to 1400 bar are reported [38, 39]. For injection



moulding, the typical range of packing pressures for PA12 lies in the range of 500 to 1500 bar [40, 41]. Whilst numerous high-pressure processes are reported, the void content of thermoplastic composites is reduced by heat treatment in an autoclave using pressures in the order of 10 bar or even by placing the material in a vacuum bag and keeping the chamber at atmospheric pressure [42-44].

3.2.3. Time

Lastly, it should be expected that the consolidation of the polymer, compression of pores and the permeation of gas molecules through the polymer takes time. For HIP processing of UHMWPE and numerous metals, hold times in between 1 to 4 hours are reported [20-23, 37-39]. For autoclave processing of thermoplastic composites, hold times as short as 20 minutes and less are reported [42-44]. It is considered that a hold time of 1 to 4 hours provides a practical and suitable starting point to study the effects of HIP on SLS-printed PA12.

3.3. Preliminary experiments

As described in paragraph 3.2, compression of pores and permeation of gas molecules through the polymer are aided by a hold temperature that is as high as possible. At the same time, melting must be avoided as parts may distort, or in worse cases, the melted polymer may contaminate or damage the equipment. Preliminary experiments with SLS-printed PA12 specimens were carried out to establish a safe maximum temperature and to test whether the pressure-dependent melting temperature reported in literature (see paragraph 3.2.1) may allow temperatures to be increased above the PA12's atmospheric melting temperature.

For the preliminary experiments, cubes with a size of 20x20x20mm were printed from EOS PA2200 (PA12) using an energy density of 0.0336J/mm². As depicted in Figure 10, three different types of cubes were printed: A wireframe cube with a 1mm beam thickness, 'solid' cubes with a spherical cavity inside filled with unsintered PA12 powder, and cubes that are printed 'solid' throughout.

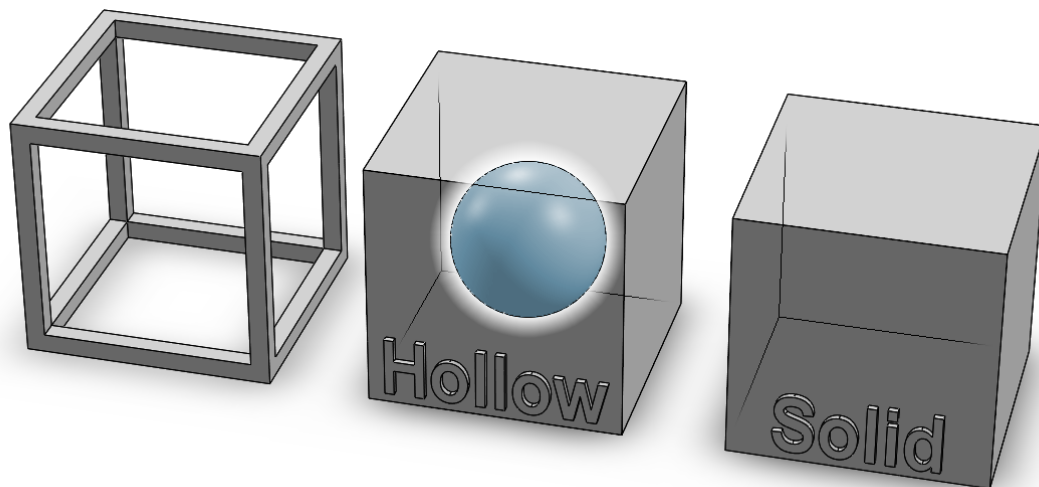


Figure 10: 3D models of the specimens for the preliminary HIP experiments. Left: A wireframe cube with a beam thickness of 1mm. Centre: A 'solid' cube with a spherical volume of unsintered powder inside it, marked as 'Hollow'. Right: A solid cube of which the material exposed by the laser and sintered throughout, marked as 'Solid.'

One experiment was performed with a hold phase of 45 minutes at 175°C and 1100 bar, which is below the melting temperature of PA2200 at atmospheric pressure of 184°C [31]. The other experiment was performed with a hold phase of 1 hour at 190°C and 1000 bar, which is above the melting temperature at atmospheric pressure and is to test whether the reported 20°C increase in melting temperature for each 1000 bar of pressure [34] may be exploited in the HIP process.

The specimens processed at 175°C (Figure 11, top) appear the same as the 3D model and no part deformation or other changes are visible compared to untreated specimens. However, the specimens processed at 190°C (Figure 11, bottom) show significant changes in appearance: the wireframe cube has collapsed, the surface has become smooth and glossy and the shape of the cubes has become rounded. In addition, for the cubes containing the powder-filled cavity, the walls of the cube became slightly concave.

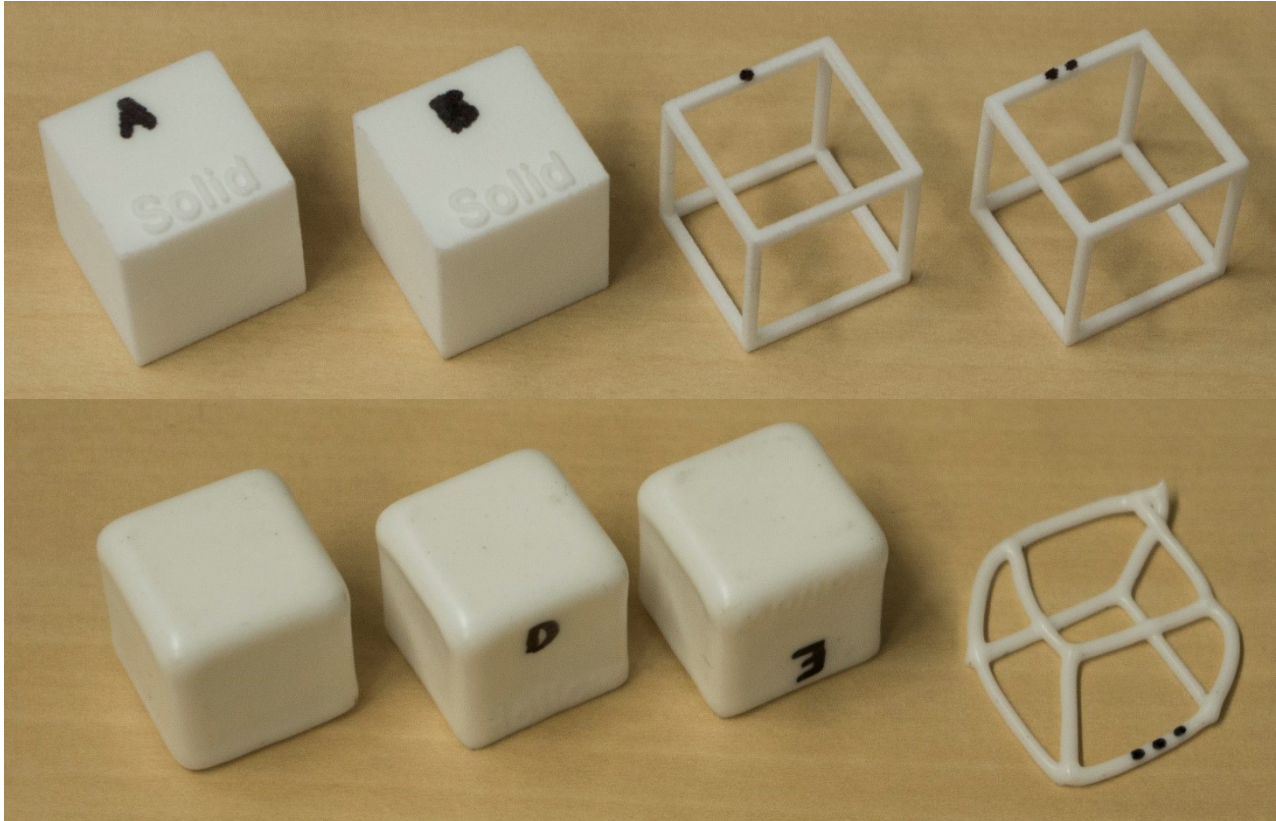


Figure 11, Top: Solid and wireframe specimens after treatment at 175°C and 1100 bar for 45 minutes. Bottom: Solid (left), Hollow (centre cubes marked D and E) and wireframe specimens after treatment at 190°C and 1000 bar for 1 hour.

The difference between the two experiments can be attributed to the difference in temperature and means that the reported pressure- dependent melting temperature of PA12 [34] could not be successfully exploited using the conditions in the experiment. For the remainder of this study, 175°C was chosen as the maximum safe processing temperature for HIP. In addition it was opted to apply a longer hold time of 4 hours for all remaining experiments as so to maximise the potential for densification to occur.

3.4. Hypotheses

Based on the study into Hot Isostatic Pressure in this chapter, it is expected that heat treatment of SLS-PA12 at 175°C for 4 hours at isostatic pressure will:

1. Reduce porosity as pressure increases;
2. Improve ductility by reduced porosity.

The two hypotheses will be tested with further experiments, the applied materials and methods of which are described in the next chapter.

4. Materials & methods

4.1. Material & printing parameters

The specimens were produced from EOS PA2200, a grade of PA12 with an average particle size of 57 μ m [45] that is specifically developed for processing by SLS and commonly used within the industry but also for research purposes. Specimens were printed using a mixture of 50% virgin powder and 50% unsintered powder recycled from prior build processes, as recommended by the material supplier [46]. Both virgin and recycled material originate from batch 919036. The recycled material has a controlled and traceable thermal history and the recycled material itself was homogenised inside a closed drum using a mixing station (EOS) for 20 minutes before it was mixed with virgin material. The mixed virgin and recycled powder was homogenised for 20 minutes and stored for at least 24 hours before processing, as recommended by the material supplier [46].

Production was performed on an EOS P100 machine under nitrogen using a layer thickness of 0.1mm and a process chamber temperature of 171°C. Since the part density, pore morphology and mechanical properties are reported to depend on energy density [4, 12, 16, 18, 19], specimens for mechanical testing were printed at two energy densities, 0.024J/mm² and 0.036J/mm². Both energy densities fall within a range in which a predominantly closed pore structure is reported for two other grades of unfilled PA12 [16]. The 0.036J/mm² energy density falls within the range in which optimal strength and elongation at break are reported [12]. The underlying thought is that specimens of both energy densities possess the closed pore structure required for HIP but exhibit significantly different mechanical properties prior to pressurised heat treatment. The complete list of printing parameters is documented in Appendix A.

Since reports found in the literature study point towards lower ductility in the build direction (Z-direction) and higher porosity at the interface between layers [16, 17], mechanical specimens were built with their load direction during testing oriented along the Z-direction. Specimens were positioned alongside each other in the build tray by spacing them over the X- and Y-axes allowing specimens of the same type and same energy density to be built simultaneously and from the same layers of powder. The layout of the build tray is shown in Appendix A.

After processing, the build tray was left inside the printer under inert gas until parts had cooled to below 60°C. Parts were then unpacked and bead blasted using glass impact beads (Potters Ballotini, 70-110 μ m diameter) propelled by compressed air at a pressure of 4 bar. The specimen sets were stored dry prior to treatment. More information on cooling, unpacking and storage procedures are documented in Appendix A.

4.2. Test specimens

Whilst heat treatments at pressures at 18 bar were carried out in an autoclave with ample space, heat treatments at 1500 bar were carried out in a Hot Isostatic Press with an available volume of Ø82mm x 160mm with the cylindrical space oriented vertically. It was opted to combine individual specimens into specimen sets by connecting them with the 3D- printed equivalent of sprues as commonly used in injection moulding. Printing specimens as a set maximises the use of available space in the chamber, facilitates with correct placement and orientation of specimens and ensures that specimens are evenly spaced and supported during processing. A code is 3D- printed onto the specimen set for identification.

The specimen set consists of a number of specimens of several types. As the mechanical properties of SLS- printed PA12 are reported to be dependent of wall thickness [4, 47, 48], specimens for mechanical testing were printed in multiple thicknesses. The mechanical specimens, depicted in Figure 12, were 2mm and 4mm thick for tensile testing whereas impact specimens were 4mm and 8mm thick.

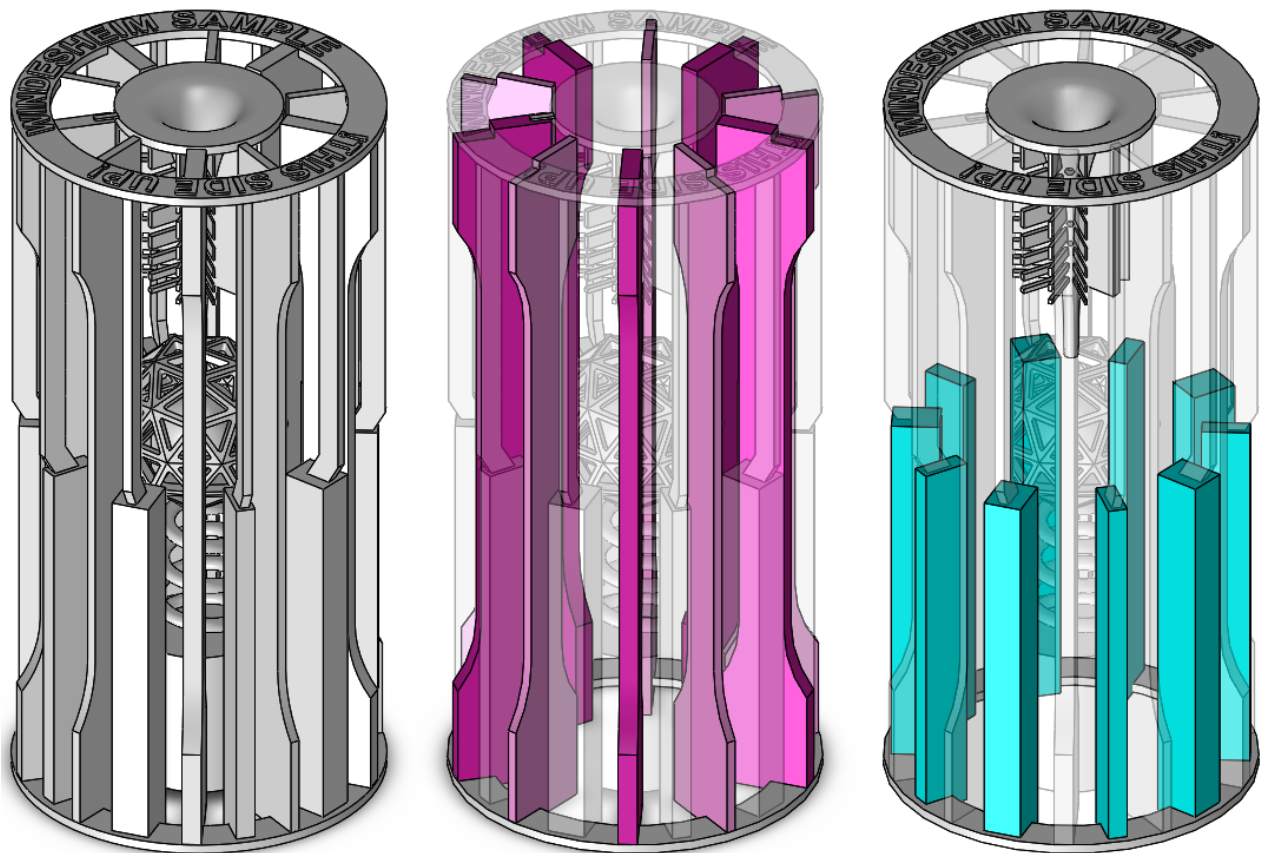


Figure 12: Specimen set shown on the left, with the tensile specimens highlighted in the middle magenta and the impact specimens highlighted on the right in cyan.

As depicted in Figure 13, an array featuring overhanging pins and walls of various thicknesses was included to obtain qualitative information about the influence of different treatments on the shape of complex geometries, as well as a coil spring and a geodesic dome with a ball nested inside it. Lastly, as also depicted in Figure 13, each specimen set contains a hollow cylinder with a wall thickness of 3mm. A volume of the powder bed is enclosed by the walls of the cylinder in the build process, creating a component with an outer shell with closed pores but a high internal porosity. This part is referred to in the remainder of the report as a 'powder-filled cylinder.'

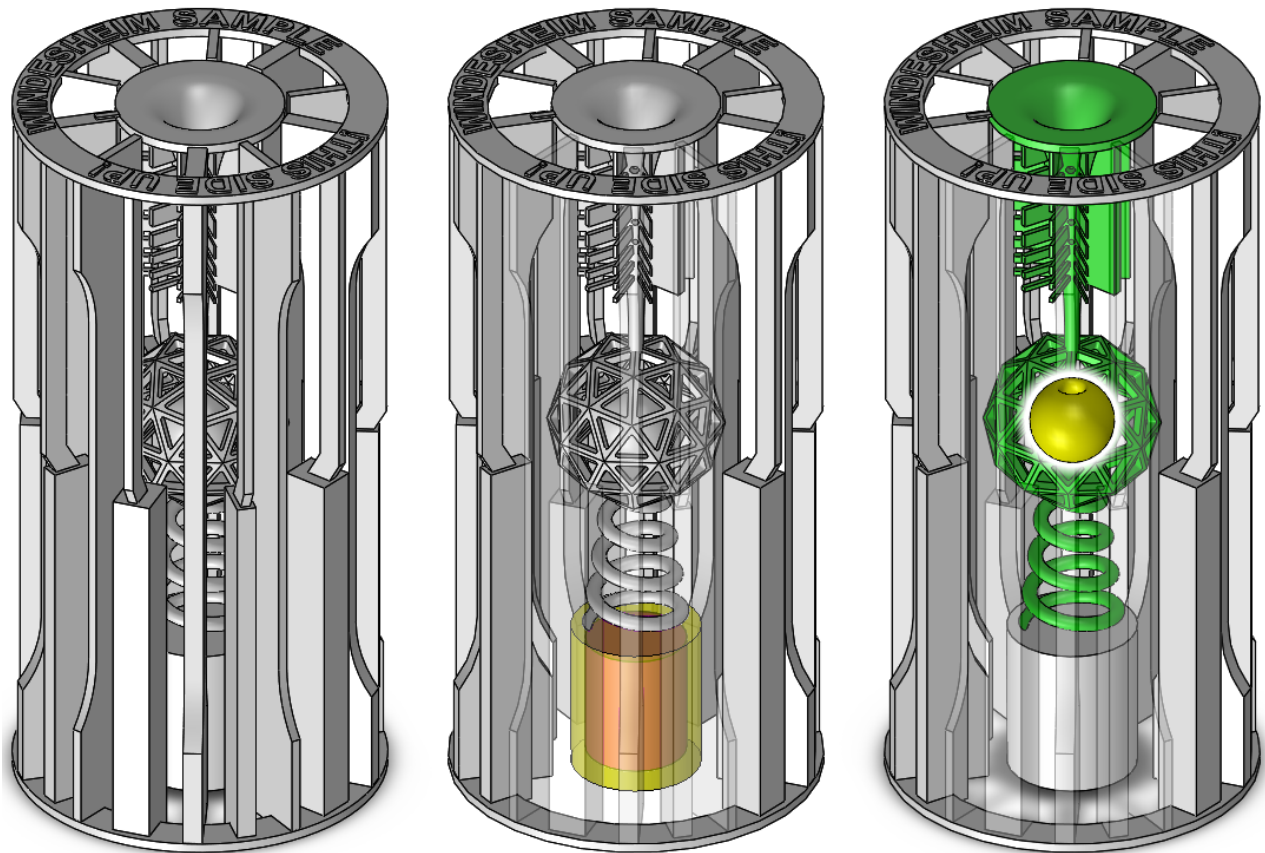


Figure 13: Specimen set shown on the left. In the middle, the powder-filled cylinder is highlighted in yellow & orange with yellow for the sintered wall and orange for the powder core. On the right, the product samples are highlighted in green and yellow on the right. The product samples consist of a coil spring, a geodesic dome with a ball printed as a separate part inside it, and a cone with attached to it a range of thin-walled overhanging features of different wall thicknesses.

4.3. Heat treatment in isostatically pressurised atmosphere

A hold temperature of 175°C and hold time of 4 hours was chosen for all heat treatments and two values were used for the hold pressure: 18 bar and 1500 bar. The treatment at 18 bar was performed in an Autoclave (Scholz). Specimen sets of both energy densities were processed simultaneously in the autoclave. After closing the chamber, heating was applied with a rate of 2.6°C/minute and pressurisation with nitrogen at a rate of 1.2 bar/minute. After the hold phase, the temperature was decreased at 2.6°C/minute whilst pressure was held until the last 15 minutes of cooling, upon which the pressure was released. The treatment at 1500 bar was performed in a Hot Isostatic Press (Quintus) for a specimen set printed at an energy density of 0.036J/mm². The chamber was put under vacuum, after which pressurisation was carried out at room temperature to 700 bar. Next, a heating rate of 10°C/minute was applied and pressure increased to the hold pressure. After the hold phase, the heating was turned off and the pressure released. An overview of the experiments is displayed in Table 2.

Treatment	Energy density	Pressure	Temperature	Time
	ED (J/mm ²)	P _{hold} (bar)	T _{hold} (°C)	t _{hold} (hours)
Reference	0.024	As-printed, no treatment		
	0.036			
Autoclave	0.024	18	175	4
	0.036			
HIP	0.036	1500		

Table 2: The applied combinations of energy density and heat treatment conditions.

4.4. Characterisation

4.4.1. Part density

HIP is expected to reduce porosity and as a result increase part density. Part density was determined using the pycnometry method. A pycnometer consists of a container and a conical lid that features a small hole in the top, which together enclose a specified internal volume.

The pycnometer method is carried out in several steps. In Figure 14, the steps are shown in order from left to right. First, the part is placed into the container which is then filled with fluid up to near the edge of the container. Next, the lid is placed onto the container, displacing air and excess fluid through the hole in the lid. Excess fluid on the exterior of the pycnometer is removed. The pycnometer now encloses a specified volume consisting of the object surrounded by the fluid. The mass of the pycnometer containing the object and fluid is then measured.

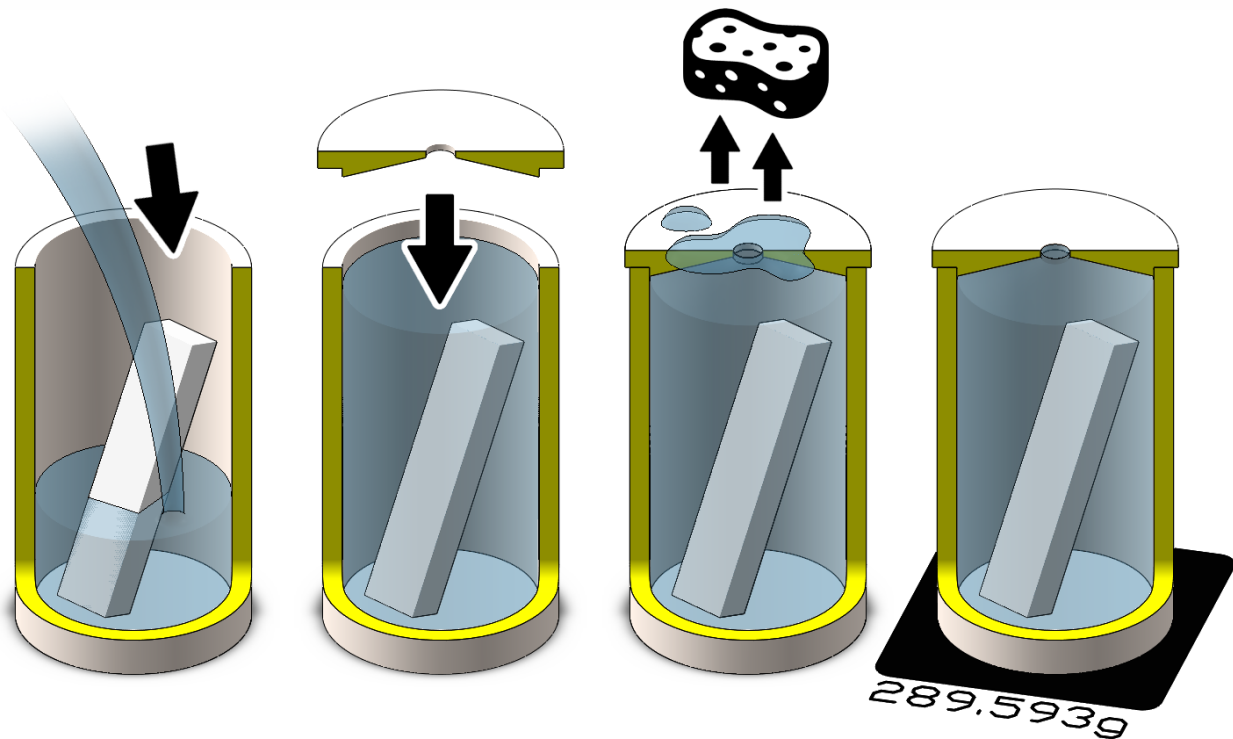


Figure 14: Schematic of pycnometry method. An object is placed in the pycnometer and the pycnometer is filled with fluid. The conical lid is placed on top, forcing air and excess fluid to exit through a small hole in this lid. Excess fluid on the exterior is removed after which the mass of the filled pycnometer is measured.

The object's density is calculated by Equation 1 and requires the mass of the empty pycnometer as well as the fluid density. The latter is calculated with the same steps as shown in Figure 14 with the exception that no object is placed inside the pycnometer so the volume inside it consists of only the fluid. With the pycnometry method, the volume of the part is determined including its closed pores into which the fluid cannot flow, therefore differences in porosity cause differences in part density.

$$\rho_{\text{part}} = \frac{M_{\text{part}}}{V_{\text{pycnometer}} - (M_{\text{pycnometer with part \& fluid}} - M_{\text{pycnometer}} - M_{\text{part}}) * \rho_{\text{fluid}}}$$

$$\text{with: } \rho_{\text{fluid}} = \frac{M_{\text{pycnometer with fluid}} - M_{\text{pycnometer}}}{V_{\text{pycnometer}}}$$

$$\text{and: } \rho = \text{density (g/cm}^3\text{)} \quad M = \text{mass (g)} \quad V = \text{volume (cm}^3\text{)}$$

Equation 1: Calculation of part density with the pycnometry method.



Part density was determined on impact test specimens prior to mechanical testing (80x10x4mm and 80x10x8mm) as a representation of solid printed components, as well as powder-filled cylinders (Ø27x32mm) as a representation of highly porous components. Weight was determined using scales with a 0.001g resolution (KERN PLJ 720), a pycnometer with a 100cm³ internal volume and demineralised water as a fluid.

4.4.2. Tensile properties

To evaluate mechanical properties of the samples, the Elongation at Break (EaB), Ultimate Tensile Strength (UTS) and the Young's Modulus (E) were determined on a tensile testing machine (Zwick Z050, testXpert II software) featuring a 50kN load cell (HBM) and a contact-type extensometer (Zwick MultiXtens).

Prior to testing, the tensile specimens were conditioned at 23°C and 50% relative humidity for 1 week. An automatic test sequence was specified. Specimens were manually placed followed by pre-loading at 10N, after which the extensometer attached itself to the specimen with a distance of 75mm between the upper and lower arms of the extensometer. A crosshead speed of 1mm/minute was then applied to determine the Young's modulus. After 0.25% elongation as measured by the extensometer, the speed of the crosshead automatically increased to a speed of 50mm/minute to elongate the specimen up until fracture. All reported values are an average of 5 tests with accompanying standard deviation unless stated otherwise.

4.4.3. Impact strength

The impact strength of SLS-printed PA12 was determined using impact testing. Similarly to the tensile tests, impact strength was tested for multiple specimen thicknesses, 4mm and 8mm, with 5 specimens per thickness. Tests were performed using the Charpy method with specimens in the edgewise position. The notch (Type A as specified in ISO 179-1) was machined into the specimens after printing and post-treatment using a dedicated machining device (Zwick). The impact tests were performed on an electronic impact testing machine (Zwick, testXpert II software) using a 2J hammer.

5. Results

SLS-printed PA12 was heat treated at 175°C in an Autoclave at 18 bar and in a Hot Isostatic Press (HIP) at 1500 bar. Based on the information in paragraph 2.4 and chapter 3, it was expected that both treatments reduce porosity and that HIP treatment reduces porosity further than the autoclave treatment. Moreover, it was expected that ductility increases as a result of reduced porosity. This chapter discusses the results of the experiments as described in chapter 4.

5.1. Visual observations

The specimen sets were inspected and compared visually after treatment, starting with the autoclave-treated specimens.

5.1.1. Autoclave-treated specimens

The specimens after the Autoclave treatment (18 bar) are displayed in Figures 15- 17. It can be clearly seen in Figure 15 that compared to the untreated powder-filled cylinder (shown on the left), the treated cylinders were compressed during their post treatment, with slightly more compression for the cylinder printed at 0.024J/mm² energy density (shown in the centre) compared to 0.036J/mm² energy density (shown on the right).

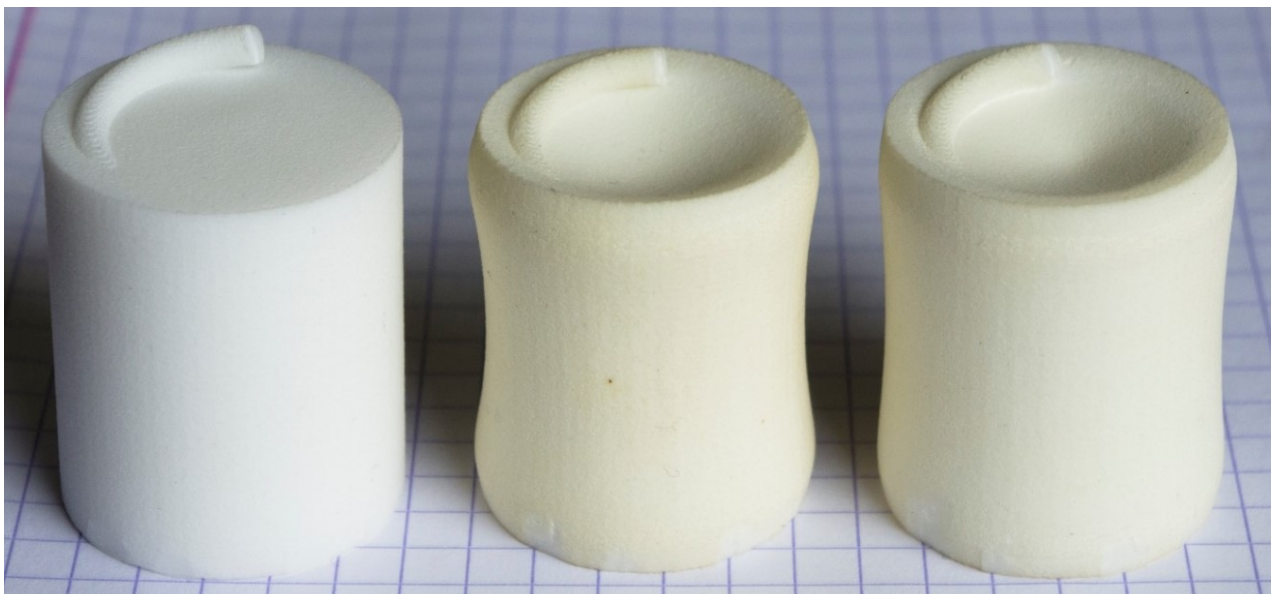


Figure 15: Comparison of powder-filled cylinders, in order from left to right: 0.036J/mm² without post treatment (reference), 0.024J/mm² autoclave treated and 0.036J/mm² autoclave treated.

The rest of the specimens, which were printed solid (sintered throughout), showed no visual signs of compression. As can be seen in figure 16, the 2mm thick tensile specimens were slightly warped for the treated specimen set printed at 0.024J/mm² but not for the treated specimen set printed at 0.036J/mm².

In figure 17 it can be seen that the thinnest (0.4mm thick) overhanging features on the treated 0.024J/mm² energy density sample also warped, but not on the treated 0.036J/mm² energy density sample. The rest of the mechanical specimens (figure 16), overhanging features with a thickness of 0.8mm and thicker (figure 17), the coil spring and geodesic dome (figure 17) have retained their original shape. Moreover, the ball inside the geodesic dome could move around inside the dome both before and after treatment, showing that components that touch each other did not stick together during post treatment.

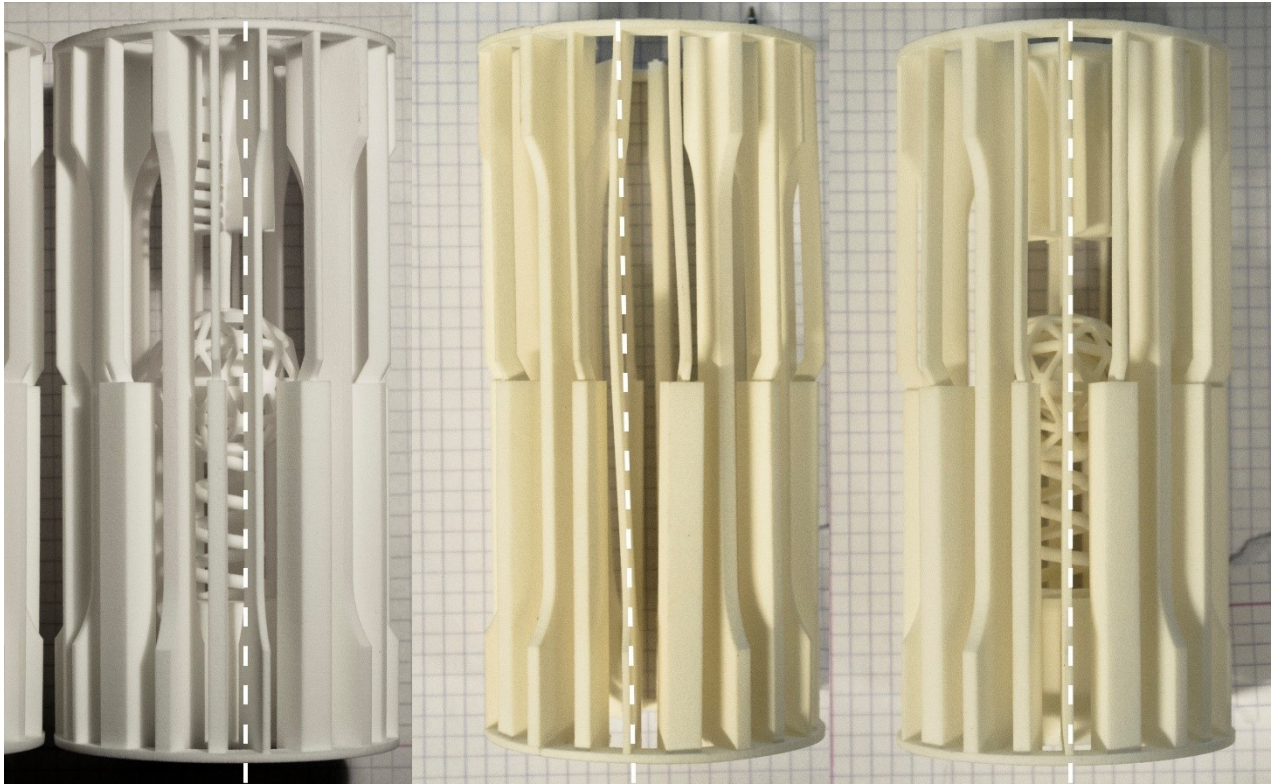


Figure 16: Comparison of specimen sets, in order from left to right: 0.024J/mm² without post treatment (reference), 0.024J/mm² autoclave treated and 0.036J/mm² autoclave treated. As may be observed with help of the dashed line, the 2mm thick tensile specimens have warped on the autoclave-treated 0.024J/mm² printed set but not the others.



Figure 17: Comparison of 3D part geometries, in order from left to right: 0.036J/mm² without post treatment (reference), 0.024J/mm² autoclave treated and 0.036J/mm² autoclave treated. The 0.4mm thick overhanging features near the arrow have warped, all other part features have retained their shape.

In Figures 15- 17 it is visible that surface yellowing occurred for both treated specimen sets. The material below the surface was unaffected, which can be seen in Figure 15 near the base of the cylinders where they were cut off from the rest of the specimens. The surface yellowing of the autoclave treated specimens could indicate oxidation and may affect the mechanical properties.

In summary, the autoclave treatment has visibly compressed the powder-filled cylinders whereas on the whole, solid printed parts retain their original shape well. Although surface yellowing occurred as well as some warpage for thin-walled features printed 0.024J/mm^2 , the specimen sets are suitable for further testing.

5.1.2. HIP-treated specimens

In Figure 18- left, the HIP treated specimen set is displayed. The sample set, printed at an energy density of 0.036J/mm^2 and treated at a pressure of 1500 bar, showed no yellowing. No warpage was observed to the solid, fully sintered specimens, and similar to the autoclave treated specimens, the ball and geodesic dome have not stuck together during treatment.

In Figure 18- Right, a comparison of untreated, autoclave treated and HIP- treated powder- filled cylinders is shown. The HIP- treated (A5, right, 1500 bar) powder- filled cylinder is compressed noticeably more than the autoclave- treated (A1, centre, 18 bar) cylinder. Similar to the autoclave treatment however, no visible cues of densification (such as compression or a difference in size) were observed for the other components of the specimen set.



Figure 18, Left: Specimen set after HIP-treatment. Right: Comparison between the powder-filled cylinders printed with 0.036J/mm^2 viewed from two angles, with from left to right: Untreated/Reference (A4), Autoclave (A1) and HIP (A5).

In summary, the HIP-treated solid specimens have retained their shape and are suitable for testing. Whereas there are no visible signs of densification for the tensile and impact specimens, the compression on the powder- filled cylinder is clearly visible. To better understand the effect of heat treatment at isostatic pressure on SLS-printed PA12, part density was measured.

5.2. Density of powder-filled cylinders

Part density was determined using the pycnometry method and used to gauge porosity. As displayed in Figure 19, the part density of the treated cylinders has increased in comparison to the untreated cylinders. Moreover, it seems that part density increases with the applied pressure in the treatment, confirming the observations made in paragraph 5.1 and proving that the performed treatments at high temperature and isostatic pressure have successfully increased part density of components with a highly porous interior.

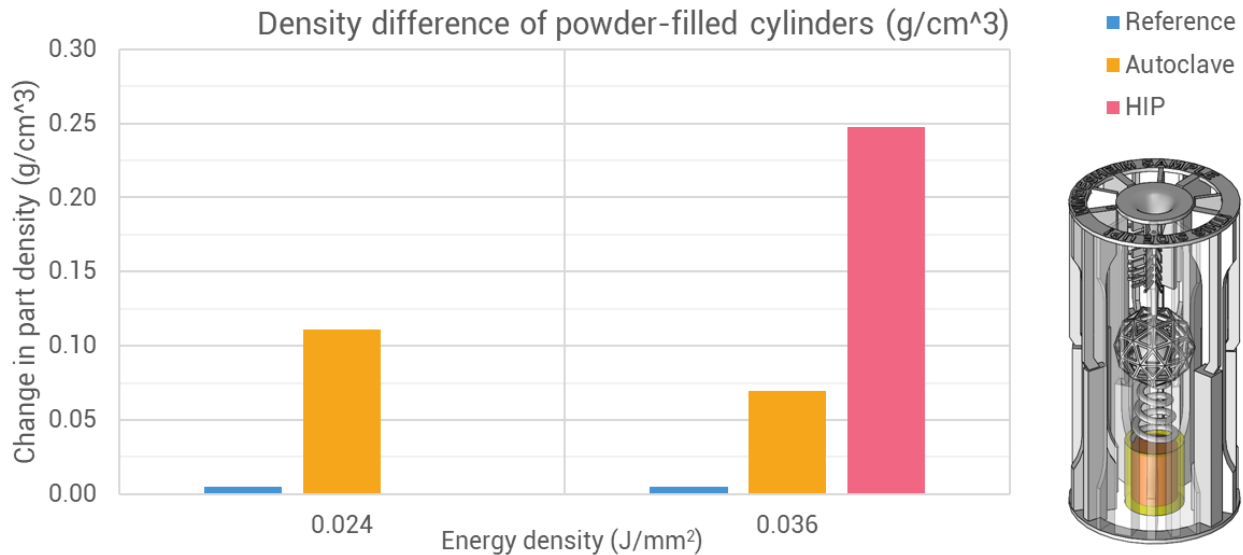


Figure 19: Density of powder-filled containers after pressurised heat treatment. The datapoints are $n=1$.

To gain qualitative insight into the mechanism of densification, the treated cylinders were annealed at 175°C in air at atmospheric pressure for 2 hours and left to cool down inside the closed oven. The underlying thought of the annealing treatment is that if gases are trapped in pores under high pressure, the cylinders will re-expand if the material is made pliable in an environment at atmospheric pressure.

The diameter and the narrowest point of the treated cylinders before and after annealing was measured, as displayed in Table 3. It is clear that the diameter of the autoclave-treated material does not increase and only a minor re-expansion occurs for the HIP treated material.

Cylinder #	Diameter at narrowest section (mm)			
	Before annealing	After annealing	Diameter increase	
			mm	%
REF 036	26.90	N/A		
ACL1 036	25.76	25.79	0.03	0.12%
HIP1 036	22.67	23.72	1.05	4.63%

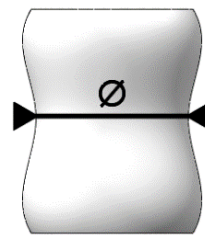


Table 3: Diameter at the narrowest section of the treated powder-filled cylinders before and after annealing, as indicated on the image to the right of the table. The datapoints are an average of 3 measurements on 1 powder-filled cylinder per treatment.

After annealing, the autoclave treated (18 bar) cylinder was intact but the HIP treated (1500 bar) cylinder had cracked, as depicted in Figure 20. The cracking could be indication of internal stresses inside the HIP treated material. As both the autoclave treated and HIP treated cylinders show little re-expansion, it is considered that after treatment but prior to annealing, the container did not contain a high internal pressure.

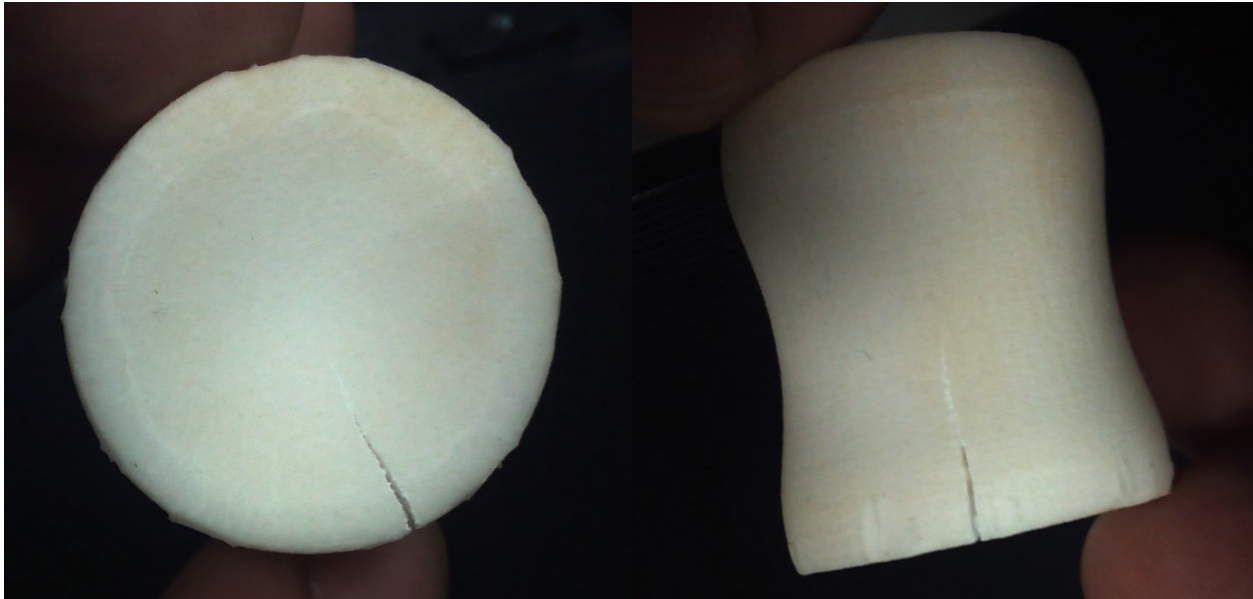


Figure 20: The HIP-treated cylinder after the annealing process depicted from two angles. A crack is clearly visible in the specimen.

In summary, SLS-printed PA12 can be irreversibly compressed at a temperature of 175°C using pressure, although the cracking of the HIP-treated (1500 bar) specimen during annealing also indicates that internal stresses may be present in the HIP-treated material.

5.3. Density of solid impact specimens

Using the pycnometry method, part density of the impact specimens was determined. In Figure 21, the part density of the 4mm thick impact specimens is plotted relative to the reference of the same thickness and energy density.

For the specimens printed with an energy density of 0.024J/mm² the part density of the autoclave-treated specimens (18 bar) is lower than the reference. For the specimens printed with a 0.036J/mm² energy density, the part density after both autoclave and HIP (1500 bar) treatments also seems to be lower than the untreated reference. This is an unexpected result and indicates that specimens have not densified but may have expanded.

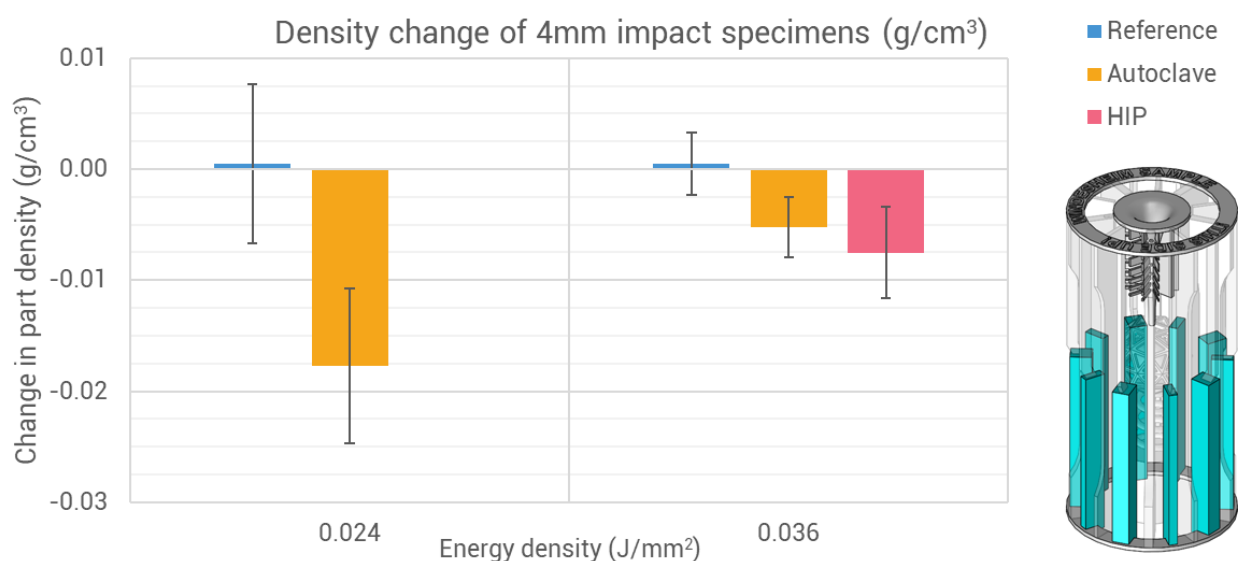


Figure 21: Density of Autoclave and HIP-treated 4mm thick impact specimens relative to the density of the untreated reference impact specimens of the same energy density and thickness. The datapoints are n=5, the error bars display 1x standard deviation above and 1x below the average.

In Figure 22, the part density of the 8mm thick impact specimens is plotted as a difference compared to the reference of the same thickness and energy density. At an energy density of 0.024J/mm^2 the autoclave treatment makes no statistical difference to part density. At an energy density of 0.036J/mm^2 it seems that a pressure treatment does increase part density. Although the standard deviations between the reference and autoclave-treated specimens overlap, the standard deviations of the reference and HIP-treated specimens do not, indicating a significantly higher part density after HIP treatment.

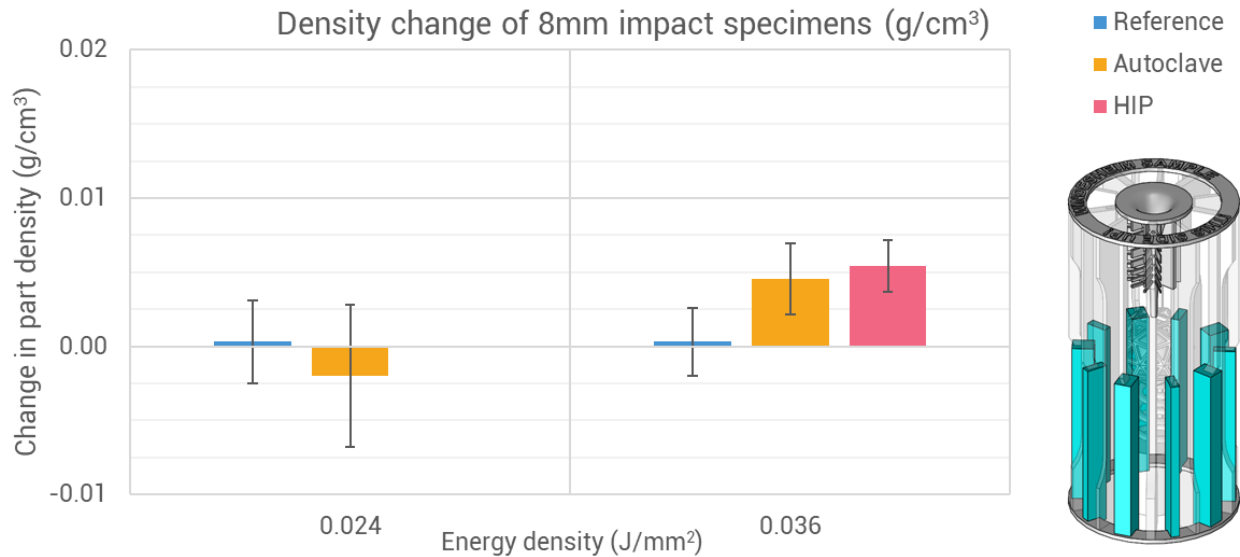


Figure 22: Density of Autoclave and HIP-treated 8mm thick impact specimens relative to the density of the untreated reference impact specimens of the same energy density and thickness. The datapoints are $n=5$, the error bars display 1x standard deviation above and 1x below the average.

The measured absolute density of the 8mm thick specimens printed at 0.036J/mm^2 were around 1.00g/cm^3 . To determine whether the measured increase in density is indeed significant, the 8mm thick specimens printed at 0.036J/mm^2 were placed in demineralised water to determine whether they sink or float. As displayed in Figure 23, the 8mm reference specimens (left) floated whereas the HIP-treated specimens (right) sank in demineralised water.

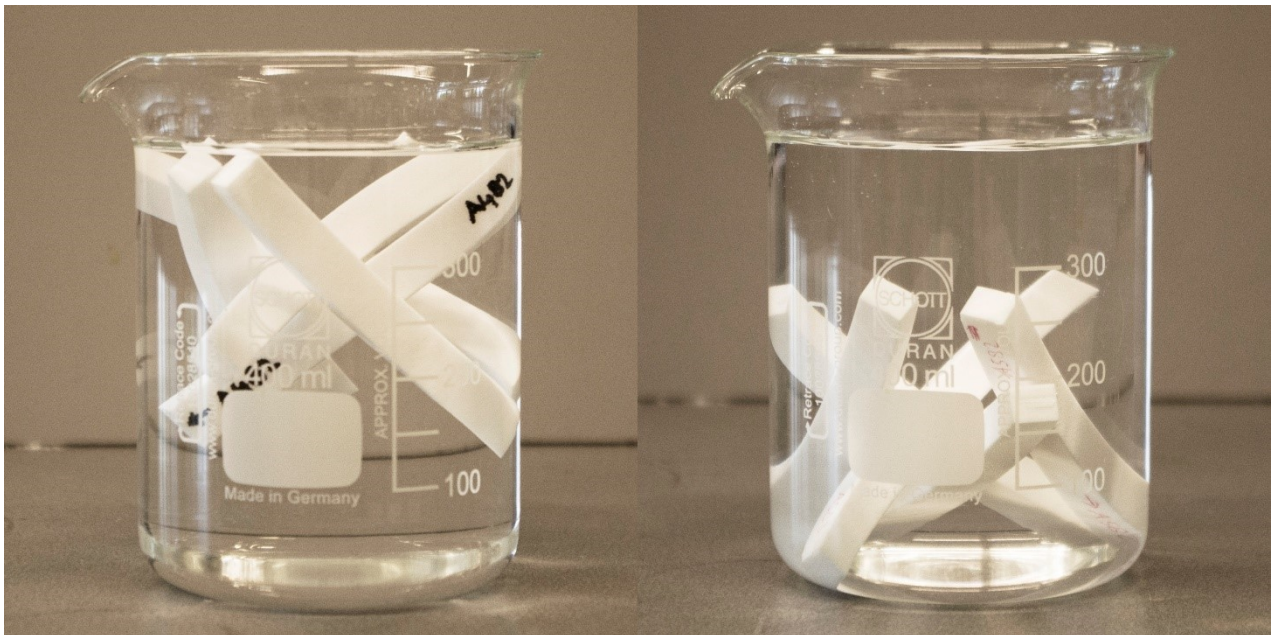


Figure 23: The 8mm thick untreated (reference) impact specimens printed with an energy density of 0.036J/mm^2 (Left) float whereas the HIP-treated specimens of the same thickness and energy density (Right) sink.

The 'float or sink' test proves that a significant increase in density is created by the HIP post treatment. From the findings in the current and last paragraph it seems that whilst heat treatment at high isostatic pressures can increase part density, the effect of the treatment depends on the energy density applied during the sintering process as well as specimen thickness.

5.4. Mechanical properties of solid samples

First, the impact strength is compared, displayed in Figures 24 and 25 of specimens printed at an energy density of 0.036J/mm² and 0.024J/mm² respectively. At both energy densities and specimen thicknesses a trend is visible where impact strength reduces with increased applied pressure during the treatment.

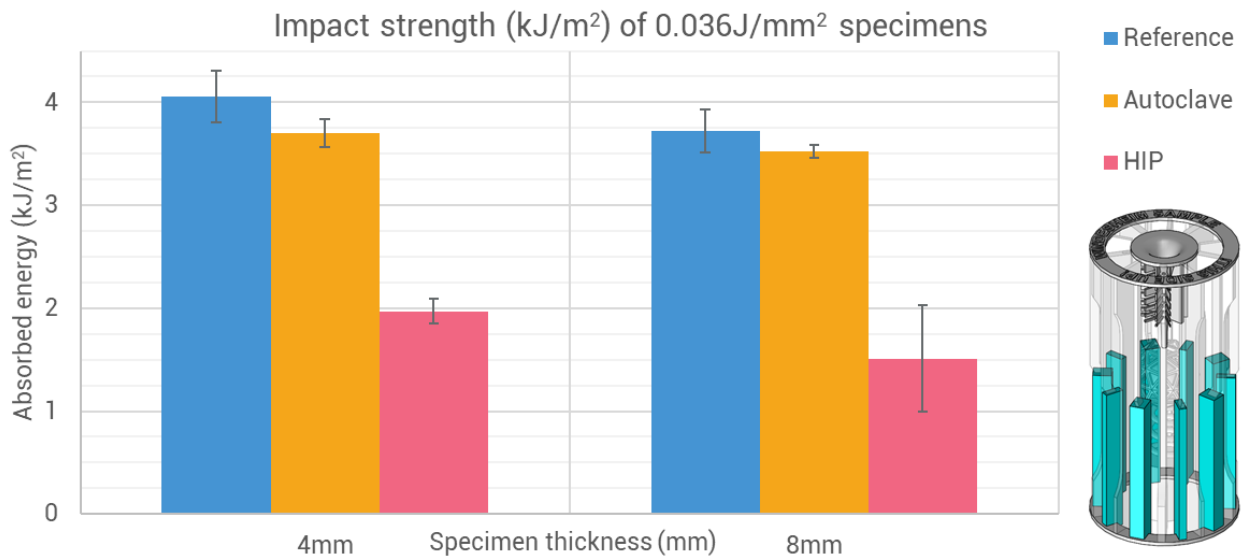


Figure 24: Charpy notch A edgewise impact strength (kJ/m²) for untreated (reference), autoclave and HIP-treated specimens printed in thicknesses of 4mm and 8mm at an energy density of 0.036J/mm². The tests were performed using a 2J hammer. The datapoints are n=5, the error bars display 1x standard deviation above and 1x below the average.

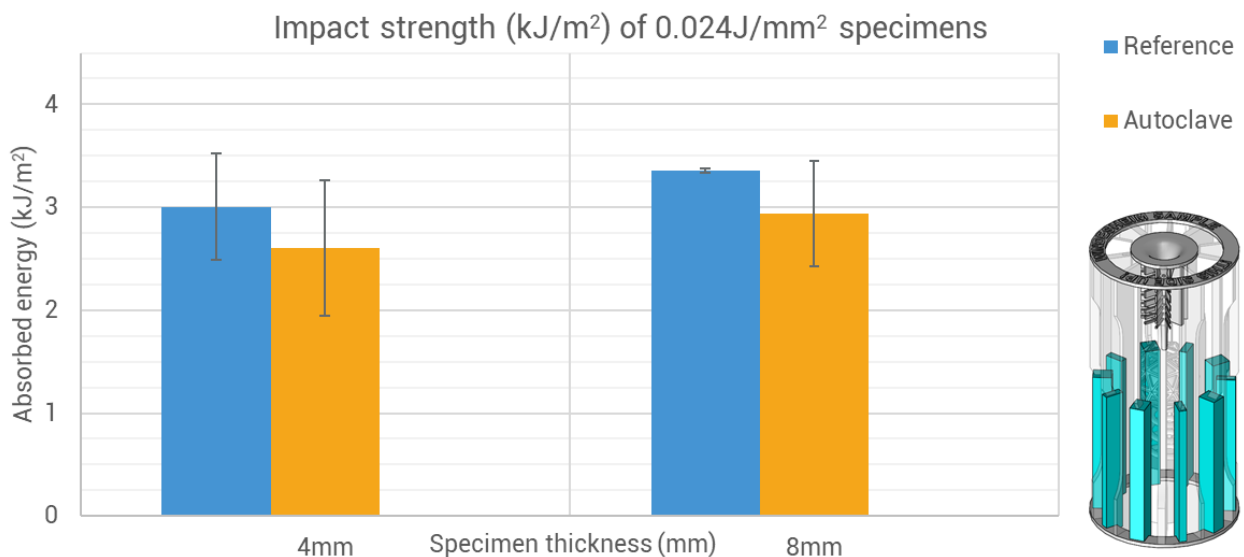


Figure 25: Charpy notch A edgewise impact strength (kJ/m²) for untreated (reference), autoclave and HIP-treated specimens printed in thicknesses of 4mm and 8mm at an energy density of 0.024J/mm². The tests were performed using a 2J hammer. The datapoints are n=5, the error bars display 1x standard deviation above and 1x below the average.

The ultimate tensile strength is plotted in Figure 26 and 27 for specimens printed at an energy density of 0.036J/mm² and 0.024J/mm² respectively. In line with reports in literature [4, 47- 49], the tensile strength of untreated SLS- PA12 is higher for thicker specimens. For the effect of pressurised heat treatment a similar trend to the impact strength is visible: at both thicknesses and energy densities, specimens show a reduced ultimate tensile strength compared to the reference material. The tensile strength seems more strongly affected by the treatments at 0.024J/mm² energy density than at 0.036J/mm².

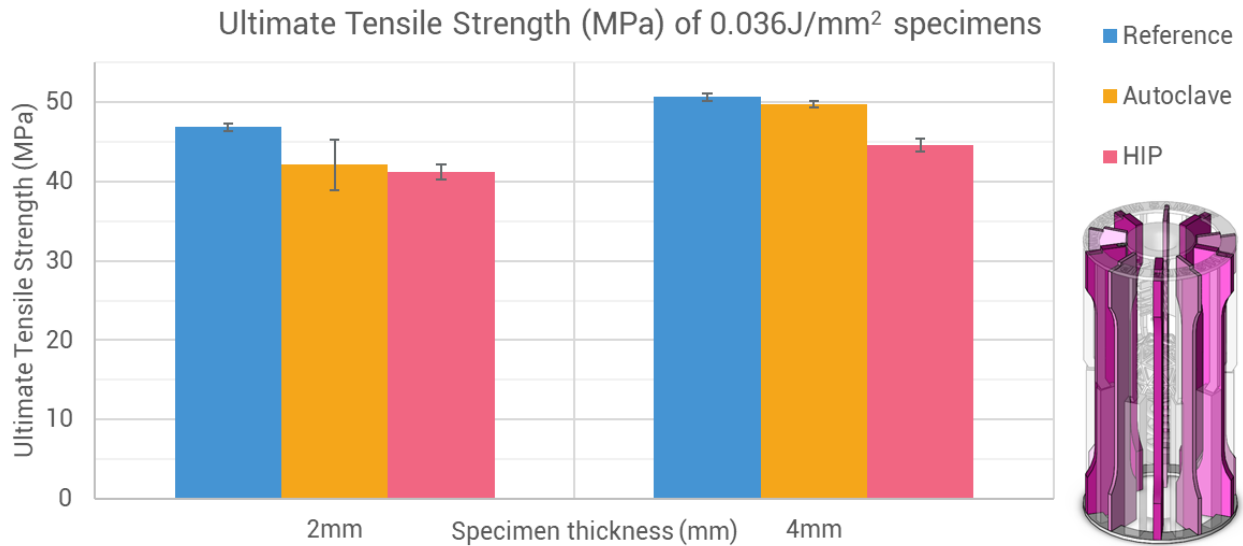


Figure 26: Ultimate tensile strength (MPa) for untreated (reference), autoclave and HIP-treated specimens printed in thicknesses of 2mm and 4mm at an energy density of 0.036J/mm². Tests were performed using a crosshead speed of 50mm/minute after measurement of the Young's modulus at 1mm/minute. The datapoints are n=5, the error bars display 1x standard deviation above and 1x below the average.

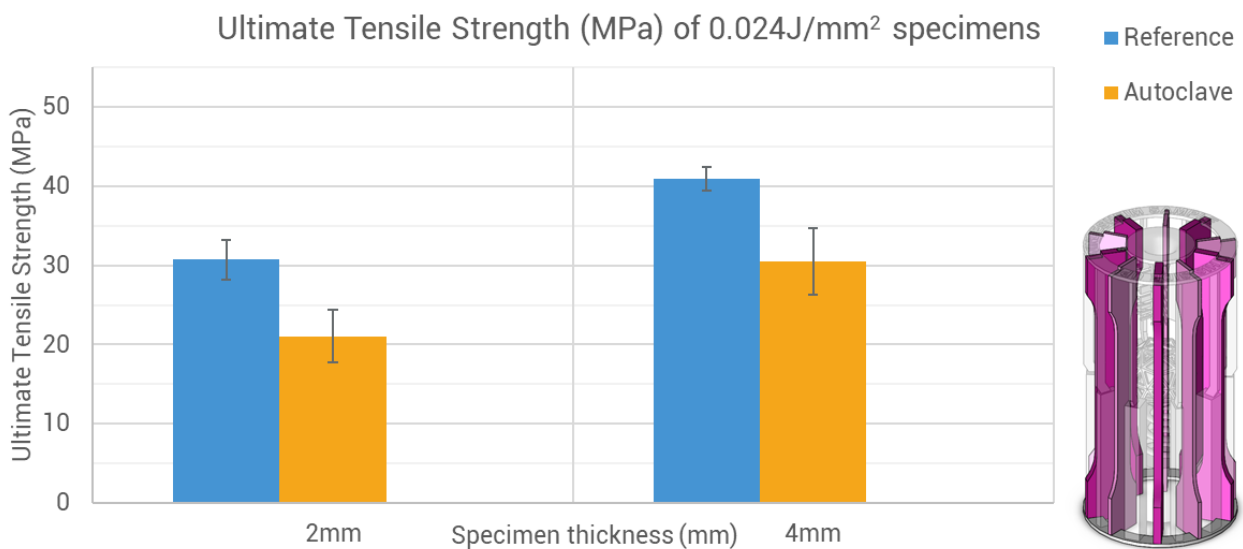


Figure 27: Ultimate tensile strength (MPa) for untreated (reference), autoclave and HIP-treated specimens printed in thicknesses of 2mm and 4mm at an energy density of 0.024J/mm². Tests were performed using a crosshead speed of 50mm/minute after measurement of the Young's modulus at 1mm/minute. The datapoints are n=5, the error bars display 1x standard deviation above and 1x below the average.

A comparison of the elongation at break is shown in Figure 28 and 29 for specimens printed at an energy density of 0.036J/mm² and 0.024J/mm² respectively. Similarly to reports in literature [4, 12, 18, 50], the elongation at break is higher at the higher energy density. For the effect of pressurised heat treatment a similar trend is visible to the impact strength and ultimate tensile strength, where the treated specimens have a reduced strain at break compared to the untreated specimens of the same thickness and energy density.

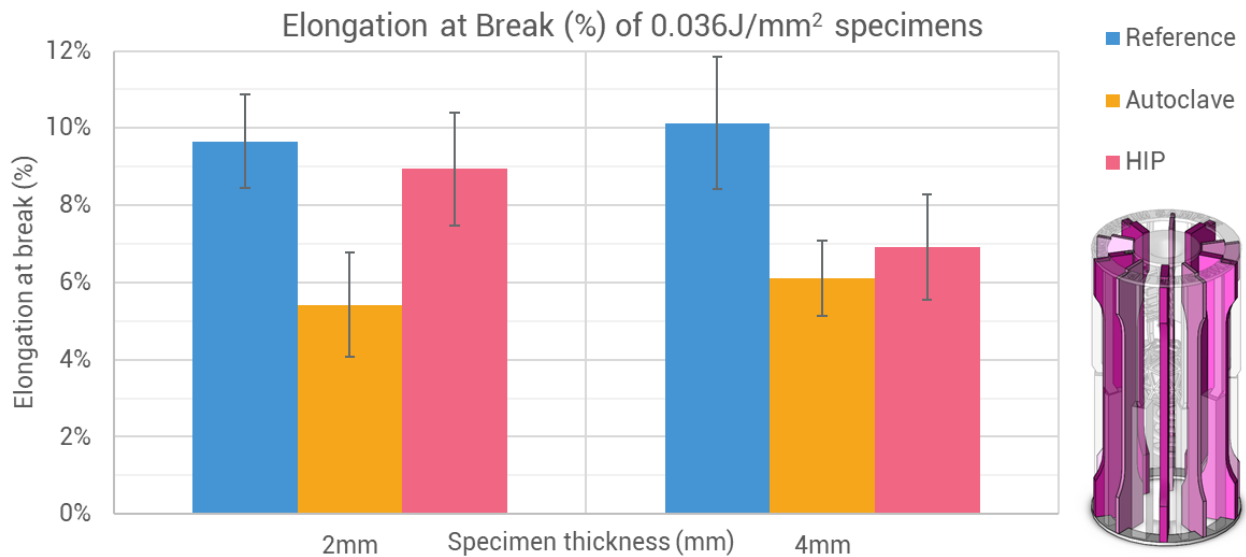


Figure 28: Elongation at break (%) for untreated (reference), autoclave and HIP-treated specimens printed in thicknesses of 2mm and 4mm at an energy density of 0.036J/mm². Tests were performed using a crosshead speed of 50mm/minute after measurement of the Young's modulus at 1mm/minute. The datapoints are n=5, the error bars display 1x standard deviation above and 1x below the average.

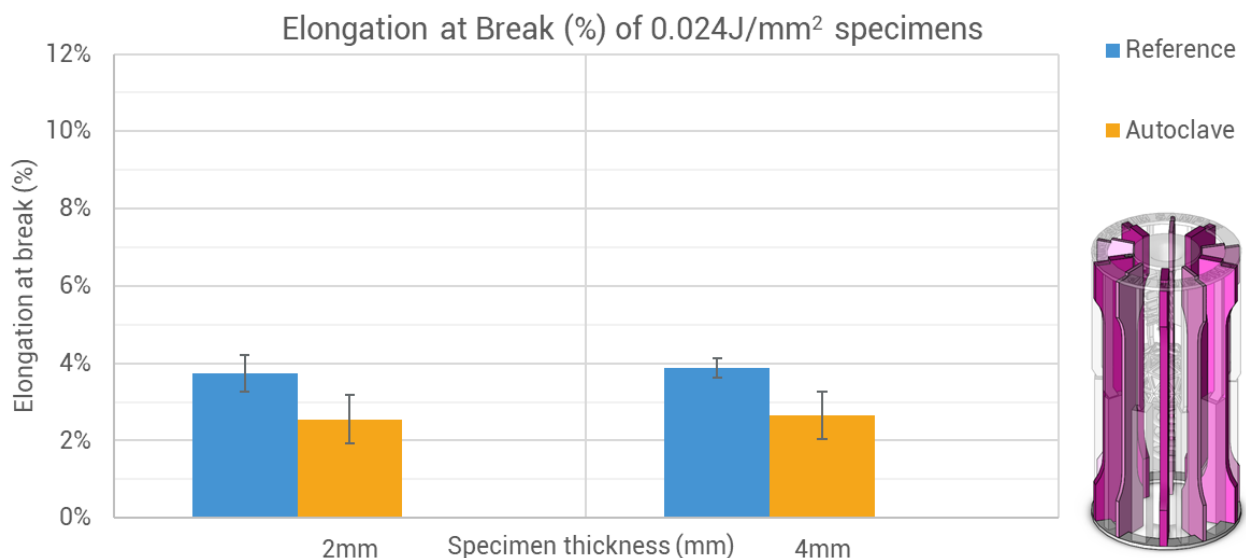


Figure 29: Elongation at break (%) for untreated (reference), autoclave and HIP-treated specimens printed in thicknesses of 2mm and 4mm at an energy density of 0.024J/mm². Tests were performed using a crosshead speed of 50mm/minute after measurement of the Young's modulus at 1mm/minute. The datapoints are n=5, the error bars display 1x standard deviation above and 1x below the average.

Lastly, the Young's modulus of the specimens is plotted in Figure 30 and 31 for specimens printed at an energy density of 0.036J/mm^2 and 0.024J/mm^2 respectively. As can be observed, the Young's modulus of the HIP-treated specimens is noticeably lower than the reference of the same energy density at both specimen thicknesses, and the same applies for the autoclave-treated specimens printed with an energy density of 0.024J/mm^2 .

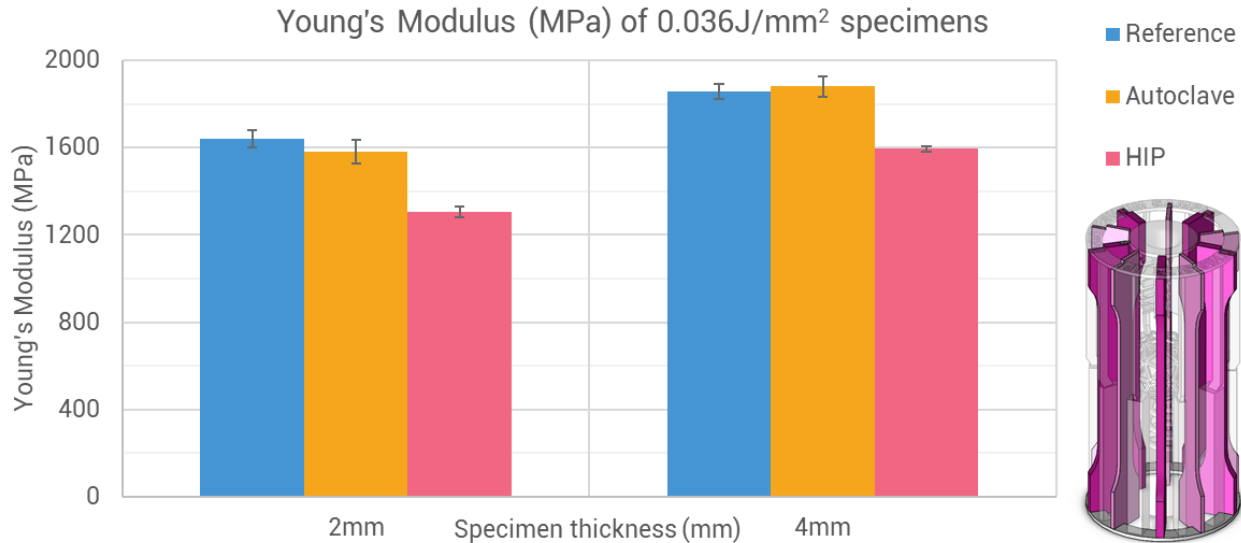


Figure 30: Young's Modulus (MPa) for untreated (reference), autoclave and HIP-treated specimens printed in thicknesses of 2mm and 4mm at an energy density of 0.036J/mm^2 . Tests were performed using a crosshead speed of 1mm/minute and a pre-load of 10N. The datapoints are $n=5$, the error bars display 1x standard deviation above and 1x below the average

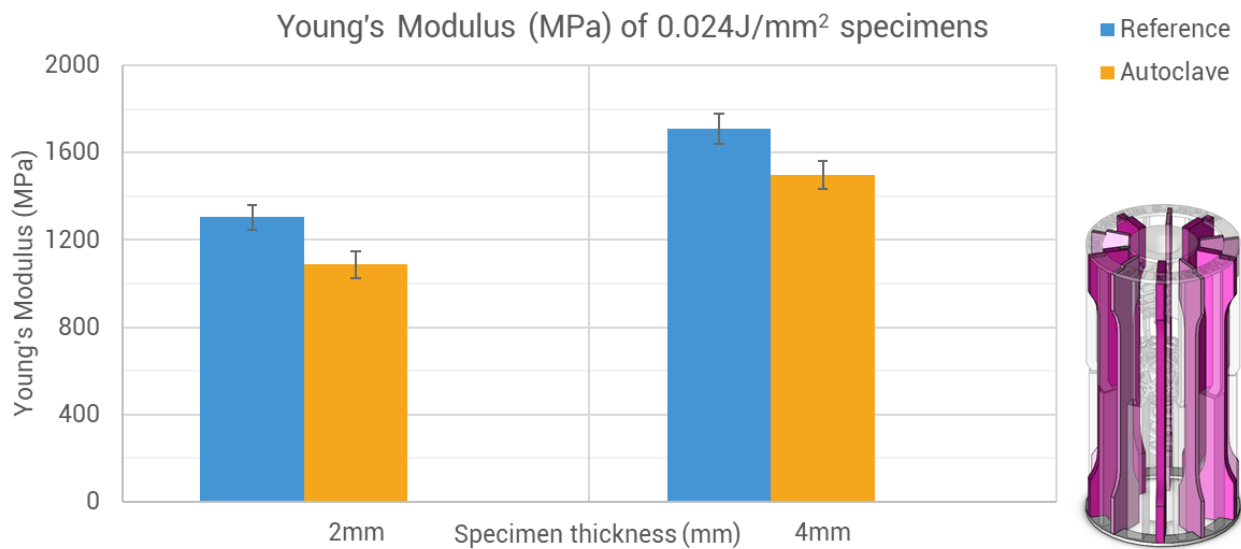


Figure 31: Young's Modulus (MPa) for untreated (reference), autoclave and HIP-treated specimens printed in thicknesses of 2mm and 4mm at an energy density of 0.024J/mm^2 . Tests were performed using a crosshead speed of 1mm/minute and a pre-load of 10N. The datapoints are $n=5$, the error bars display 1x standard deviation above and 1x below the average

The results show that heat treatment at isostatic pressure up to 1500 bar can influence the density of SLS-printed PA12 parts, but does not result in increased modulus, strength or ductility. In the next chapter, a possible explanation is discussed.

6. Discussion

In this study, the hypothesis that heat treatment of SLS-printed PA12 in a pressurised atmosphere increases part density and ductility was tested. Based on the results in chapter 5, the hypothesis is rejected. The discussion on the results is further elaborated below.

6.1. The influence of melting and particle fusion on ductility

From the results in the last chapter it is clear that neither untreated, autoclave treated or HIP- treated SLS-printed PA12 possesses a comparable ductility to the injection moulded PA12 as described in chapter 2. Moreover, the influence of pressurised heat treatment on the mechanical properties were not consistent with the influence in part density, which raises questions as to whether porosity is the main cause for the lower ductility of SLS- printed PA12 compared to injection moulded PA12.

For this reason, differences between injection moulding and SLS- printing were considered. For injection moulding of PA12 the recommended melt temperatures are 230-290°C [40] to which the polymer is typically subjected to for the order of a minute or longer prior to cooling. In contrast, as described in the literature study [3], laser exposure during the sintering process on a particle level occurs in a fraction of a second.

As shown in Figure 32- Left [19], laser exposure results in a temperature spike where the temperatures above 230°C last only for less than half a second. As shown in Figure 32- Right [19], the temperature of the sintering surface 10 seconds after exposure is less than 10°C above its melting temperature (T_m) of 184°C [31] even under optimal conditions. Combined with the reports of unmolten particle cores in SLS- printed PA12 parts [51, 52], clearly there is a considerably difference in the melting and particle fusion of SLS- printed PA12 compared to injection moulding. Perhaps the melting temperature and duration of the melting sequence is more influential to ductility of SLS- printed PA12 than anticipated based on the literature study.

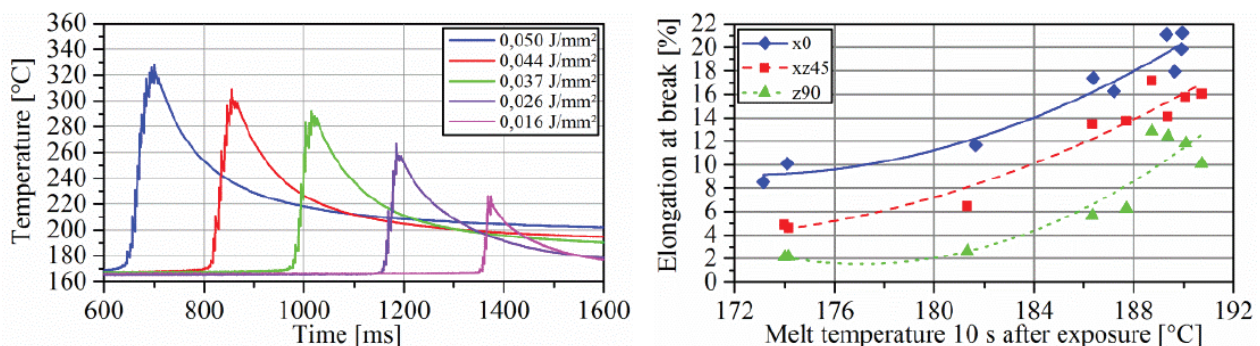


Figure 32, Left: Temperature change over time during laser exposure at different energy densities [19]. Right: The effect of the melt temperature 10 seconds after laser exposure on the elongation at break [19].

A small experiment was set up with post-treatment above the melting temperature, using tensile specimens printed in the same orientation (Z- direction) using the same type of PA12 (EOS PA2200) as for the specimen sets specified in paragraph 4.2. The tensile specimens were post-processed in an oven in air at atmospheric pressure and 190°C for 2 hours, ca. 6°C above the reported melting temperature of PA2200 [31]. Parts were supported in the experiment to prevent sagging and distortion, and after treatment, parts were left in the oven to cool down gradually. The specimens were subsequently tested on a tensile testing machine with extensometer (Testometric) at 50mm/minute.

In figure 33, the stress-strain diagrams of the tensile specimens after treatment at 190°C are compared to those of the injection moulded and SLS-printed PA12 presented in paragraph 2.2. It is observed that up to 10% elongation, the untreated SLS-printed PA12 and the SLS-printed PA12 post-processed at 190°C have a comparable progression of stress and strain. Just above 10% elongation however, the untreated SLS-printed PA12 fractures without a prior reduction in strength (neck formation), whereas the SLS-printed PA12 post-processed at 190°C reduces in strength (neck formation) and continues to elongate (neck growth) considerably prior to fracture.

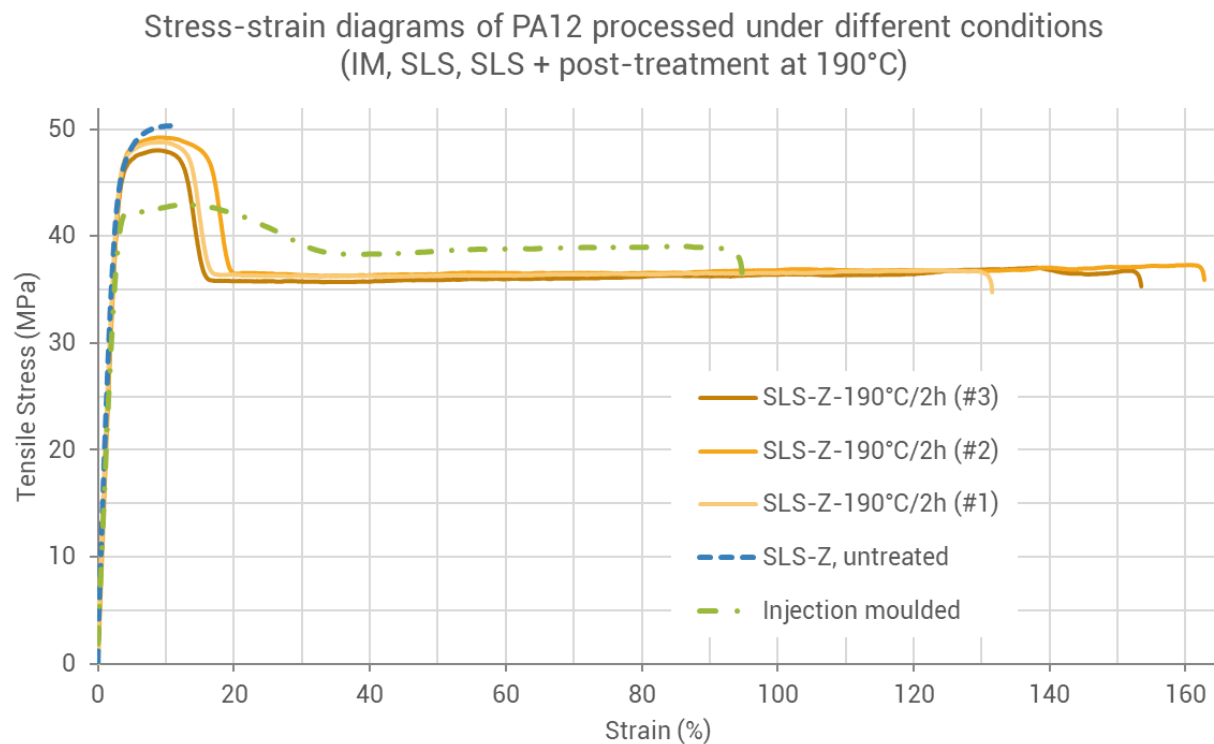


Figure 33: Stress-strain diagram comparison of injection moulded PA12, SLS-printed PA12 without post-treatment and SLS-printed PA12 post-treated in air at atmospheric pressure and 190°C for 2 hours. All SLS-printed specimens were printed from EOS PA2200 with a layer thickness of 0.1mm, oriented in the Z-orientation and printed at an energy density of 0.0336J/mm². All tests were performed at a speed of 50/mm minute.

Based on the considerable increase in ductility after post-treatment at 190°C observed in this experiment, it appears as if ductility is influenced more strongly by the temperature and duration of the melting process than by porosity. Assuming this is true, it may be that processing above T_m results in more mobility of polymers chains and coupled with the longer residence time above T_m results in more entanglements between the polymer chains, increasing ductility.

6.2. Reduction in ductility of SLS-printed PA12 after pressurised heat treatment

The ductility of the SLS-printed PA12 post-treated at 175°C and high pressure was not only lower than injection moulded PA12: It was lower than untreated SLS-printed PA12 as well. Possible explanations for this unexpected result are discussed below.

In the visual observations (paragraph 5.1) it was noted that the surface of the autoclave-treated parts had yellowed whilst the HIP-treated parts had not. As pointed out in paragraph 4.4, the chamber was put under vacuum prior to pressurisation and heating during the HIP experiment, whereas during the autoclave experiment the air inside the chamber was not removed prior to pressurisation and heating. The observed surface yellowing of the autoclave treated specimens is therefore attributed to oxidation. Although oxidation could have affected the mechanical properties, the autoclave-treated specimens generally have higher strength than the HIP-treated specimens, which had not yellowed. As such, it is considered that yellowing did not have a substantial influence on the mechanical properties.

Instead, it is considered more likely that the reduction in ductility is related to the applied pressure. In paragraph 5.2 it was observed that annealing of the HIP-treated (1500 bar) powder-filled cylinder resulted in the formation of a crack in the component. The crack formation could indicate that substantial internal stresses may have been present in the material after treatment for at least the HIP-treated material.

The reasons for cracking or the presence of internal stresses are uncertain. It is worthwhile noting that in the HIP-treatment, heating was not applied until a pressure of 700 bar was reached, and pressure continued to increase during the heating phase that followed. As PA12's glass-transition temperature is above room temperature, the material was still rigid, strong and relatively brittle when it was exposed to pressures of 700 bar. The applied pressures might have caused damage to the material.

In Appendix B, a theory describes a sequence of effects that might have occurred during HIP and might explain how it caused internal stresses as well as the thickness-dependent influence to part density. Since there are many uncertainties with regard to the mechanisms that occurred during treatment, the theory in appendix B is only regarded as an idea.



7. Conclusions

In this thesis, insight was gained into the ductility of SLS-printed PA12, the relationship of processing conditions during printing to ductility as well as the influence of heat treatment in an isostatically pressurised atmosphere on part density and mechanical properties of SLS- printed PA12.

In the literature it was established that SLS- printed PA12 contains residual pores, which have a negative effect on its ductility. It has also become clear that the ductility of SLS- printed PA12 is considerably lower than that of injection moulded PA12. It was proposed continue study into post- processing of printed components to improve ductility. Experiments were performed wherein SLS- printed PA12 parts were printed at energy densities of 0.024 and 0.036 J/mm² and heat treatments were subsequently applied at pressures of 18 and 1500 bar at 175°C for a hold time of 4 hours.

It is shown that on the whole, the post- treated parts have retained their shape and components that touched each other have not stuck together. Warpage did occur for some thin- walled (2mm and thinner) specimens and part features printed at 0.024J/mm². For powder- filled cylinders (components with a sintered outer shell and a powder- filled core), it is clear that part density increases with applied pressure. Subsequent annealing treatment resulted in little to no re- expansion of and shows that gas has permeated out of the pores. Part density of solid (sintered throughout) components were ambiguous, with an increase in part density for 8mm thick specimens but a reduction at 4mm thickness.

The Ultimate Tensile Strength, Elongation at Break, Young's Modulus and Impact strength did not increase for any of the specimens subjected to pressurised heat treatment. For the specimens treated at 1500 bar a particular reduction in mechanical properties was measured, and it must be concluded that the applied treatments if anything reduce the mechanical properties.

It was hypothesized that part density and ductility would increase with increasing pressure of the treatment. The influence of the applied pressure to part density and mechanical properties are not consistent with each other. As such it must be concluded that not changes in part density but changes within the material dominate the influence to the mechanical properties in the performed experiments. With the observation of cracks in the 1500 bar post- treated material that was subsequently annealed, it is thought that the treatment caused internal stresses in the parts.

Lastly, neither treated or untreated SLS- printed PA12 possesses a comparable ductility to injection moulded PA12. It seems that although porosity influences ductility, it alone does not cause the considerable difference in ductility between injection moulded and SLS- printed PA12. The fusion process in sintering features only a short spike at temperatures far above the melting temperature and it otherwise lower in temperature than the melting process applied in injection moulding. It is believed that processing above the melting temperature for a longer period of time resulted in more entanglements between polymer chains for the moulded material and contributes to its higher ductility. In a small post- processing test of SLS- printed PA12 above the melting temperature (190°C for 2 hours), ductility seems to increase considerably, indicating that duration of the melting and particle fusion process is very influential to ductility.

8. Recommendations

Although insights were gained into the influence of pressurised heat treatment of SLS-printed PA12 components on its part density and mechanical properties, the influences of pressurised heat treatment are yet to be fully understood. It is recommended that the subject is studied further, particularly the order in which pressure and temperature are increased and decreased as well as the rate at which they are increased and decreased. It is also recommended specifically to try experiments with heating to the hold temperature prior to pressurisation, as well as lower cooling and depressurisation rates.

For future measurements of porosity, it is recommended that porosity is measured directly instead of or complementary to pycnometry. Preferably, X-ray Computer Tomography is applied, a method that is capable of not only measuring volume porosity inside a complete object, but also local changes in porosity and even pore size and shape of individual pores. It is expected that the additional information on the influence to pores are necessary to better understand the mechanisms in pressurised heat treatment.

Whilst ongoing study into the subject of pressurised heat treatment below the melting temperature will increase the understanding of its mechanisms and the effects on part properties, it is uncertain whether this will ultimately lead to a method to increase the ductility of SLS- printed polymers. Based on the findings in paragraph 6.1, the importance the melting and particle fusion process seems to have been underestimated.

The literature study pointed out limitations in the ability of additional energy input for increased particle fusion within the printing process itself. Instead, heat treatment of printed parts could provide a solution by increasing temperatures above the melting temperature (T_m). In the discussion (chapter 6), initial tests revealed that post-processing above the melting temperature at atmospheric pressure may noticeably increase ductility. It cannot be expected that printed objects can support themselves above the melting temperature, as such it is suggested that treatment of SLS- printed PA12 components above the melting temperature are carried out whilst parts are supported. This could be done in a bed of powder, similarly to the printing process but with a powder that does not melt, such as glass beads. Alternatively, parts could be placed inside a liquid bath with a high boiling temperature, low reactivity and a similar density to PA12, such as silicone oil.



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Appendix A: Material, printing parameters & procedure

This appendix contains additional information on material, machine, parameters and procedures applied for the production of specimens for the experimental phase of this study.

The material used in this study is PA2200 (product no. 9012-0014), a grade of unfilled PA12 supplied by the company EOS and specifically developed for use in Selective Laser Sintering. All powder feedstock was used from a single batch (no. 919036) which has a specified melting peak temperature of 187.3°C on its inspection report.

Specimens were printed using a refresh ratio of 50% virgin powder and 50% unsintered powder recycled from prior build processes. For PA2200, post-condensation is reported of the unsintered powder in literature, which is a primary reason for the refresh ratio. The thermal history of the recycled powder was controlled to obtain a consistent and reproducible state of powder. The thermal history of the recycled powder is one printing cycle of 300mm height.

Since the material deposited in the first layers is exposed to high temperatures for a longer time, the unsintered powder was homogenised inside a closed drum using a mixing station (EOS) for 20 minutes. The unsintered powder was stored for at least 24 hours before it was mixed with virgin powder in order to reduce static charge of the powder. The virgin and recycled powder were mixed with the previously mentioned 1:1 ratio. The mixed powder was homogenised once more inside a closed drum for 20 minutes using the mixing station and stored for at least another 24 hours before it was used in the printing process.

The build tray was prepared for an EOS P100 machine with the layout displayed in Figure A1. As depicted, the specimen sets, described in detail in paragraph 4.2, were oriented with the load direction of the mechanical specimens in the Z-direction of the printing process. The specimen sets were built in two jobs: the first containing sets printed at an energy density of 0.036J/mm², the second containing sets printed at 0.024J/mm². All specimen sets were placed at the same position in the Z-direction - 10mm above the build platform – so they were built simultaneously. For specimen sets printed at the same energy density, only the X- and Y-coordinates differ. All specimen sets were placed at least 27mm away from the edge of the build plate and at least 8mm away from each other.



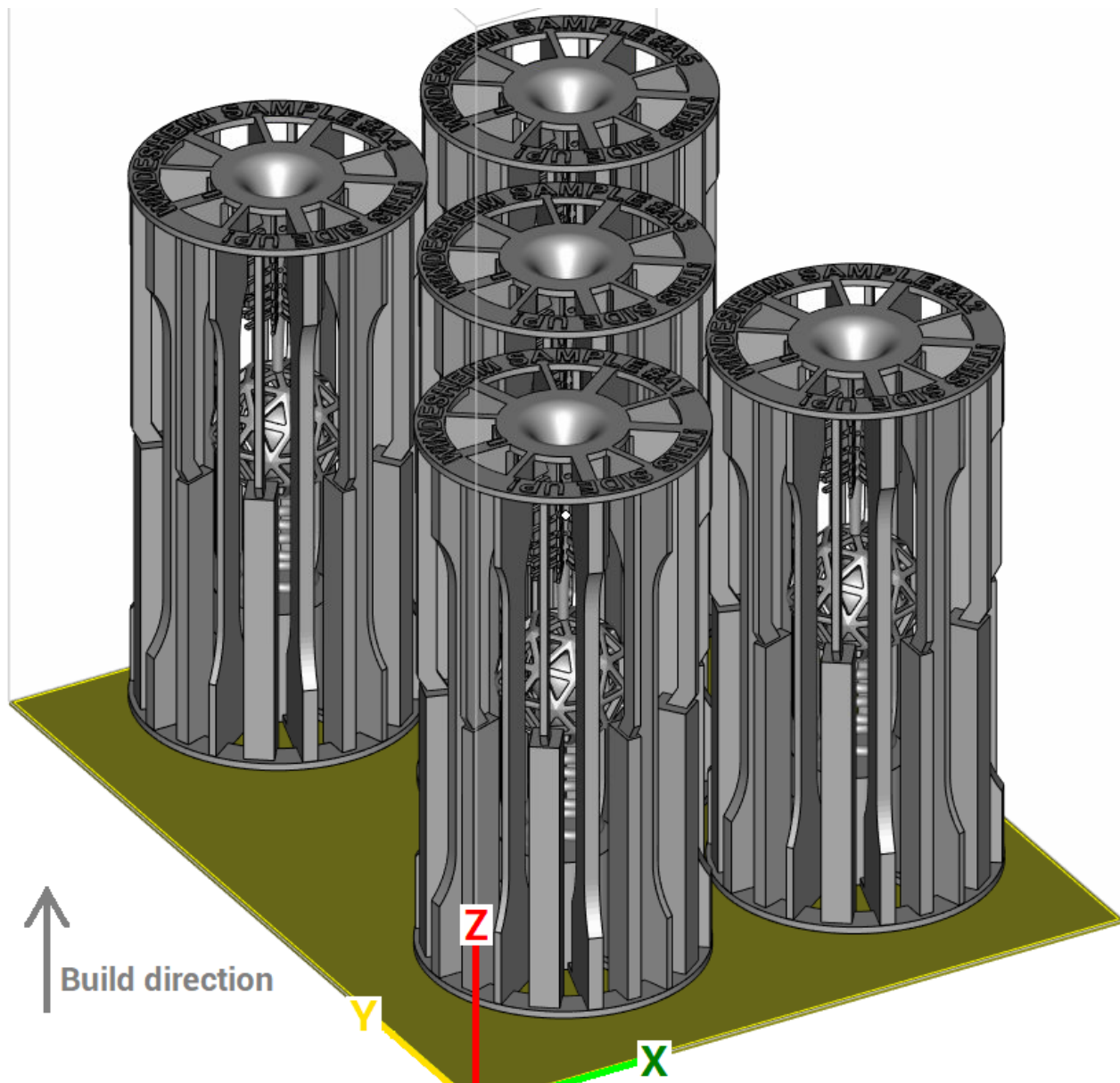


Figure 1A: Layout of one of the build processes, wherein specimens of the same type and energy density are placed on different positions over the X- and Y-axes but the same position in the Z-axis, resulting in simultaneous printing of the specimens.

The printing process was performed on an EOS P100 machine (Serial number SI1248) using a layer thickness of 0.1mm using a curved wiper (product no. 1213-0109) as per manufacturer recommendation. Powder dosing was set to -0.3. The beam offset was set to 0.30mm, the shrinkage compensation was set to 3.38% in the X-direction, 3.41% in the Y-direction, Z(0) to 2.20% and Z(300) to 1.60%. The optics were cleaned per manufacturer specification prior to processing. The temperature of the process chamber was set to 171°C, the temperature of the removal chamber to 149°C. The process and removal chambers were flushed with nitrogen prior to pre-heating and supplied with nitrogen by the machine's integrated nitrogen generator throughout the pre-heating, building and cooling stages to prevent oxidation. Samples were printed in two different energy densities: 0.024J/mm² and 0.036J/mm². The full list of exposure parameters is displayed in Figures A2 and A3.

Laser setting A, ED = 0.036J/mm²

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Figure A2: Laser parameters of the 0.036J/mm² energy density specimens.

Laser setting B, ED = 0.024J/mm²

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Figure A3: Laser parameters of the 0.024J/mm² energy density specimens.



After printing, the heating was turned off but the nitrogen flushing stayed active. The parts were left to cool inside the build tray and inside the machine. Once the chamber was below 80°C, the temperature in the core of the build tray was measured using a pin thermometer. The build tray was removed from the machine and parts were unpacked only after temperatures in the core of the build tray were measured below 60°C as so to minimise the risk of part distortion. After unpacking, parts were bead blasted using Potter's Ballotini 70-110µm impact glass beads propelled by compressed air at a pressure of 4 bar.

After bead blasting, the specimen sets were visually inspected, several basic measurements were taken after which parts were stored in closed Polyethylene bags with Silica gel bags (2x 10g) before and during shipment to the service providers for post-processing.

Appendix B – Theory complementary to the discussion (H6)

In chapter 5 it is observed that the influence of pressurised heat treatment on part density seems to be dependent of thickness and that ductility of all specimens subjected to pressurised heat treatment reduced. In the discussion (chapter 6) it becomes clear that there is too little evidence to pinpoint the cause(s) of these effects.

A theory was written down as to what mechanisms might have occurred during HIP that could explain the observed effects. Since there are many uncertainties with regard to the mechanisms that actually occurred during treatment, this theory B is only regarded as an idea.

A reduction in mechanical properties under for all specimens subjected to pressurised heat treatment, whereas part density increases only in some conditions whilst it reduces in others. A theory is presented about the mechanisms that occurred in the pressurised heat treatment.

First of all, some basic mechanisms are noted. In heat treatment at isostatic pressure, a pressure differential is created between chamber (higher pressure) and pores (lower pressure) which result in stresses in the polymer. Heating is applied to put the polymer in a rubbery, pliable state and reduce the yield strength so that the applied pressure compresses the pores and reduce in size.

Pore size is irreversibly reduced by a permeation mechanism. Permeation is described in literature [28, 41] as the transport of gas from a higher to a lower concentration environment by dissolution (absorption) into, diffusion within and release (desorption) from the polymer. The increased pressure in the pore forces transport of gas molecules into the polymer.

In both the Autoclave and HIP treatments, chamber pressure was built up before the material was heated beyond the glass-transition temperature. It is likely that the material was exposed to considerable pressure for an extended period before the combined increase in pressure and reduction in yield strength compressed the pores. With pores in an uncompressed state, gas molecules may have permeated from the chamber into the polymer and even into pores. Since it is reported that diffusion within the polymer is the slowest of the three mechanisms (absorption, diffusion and release) [28], this may create circumstances where permeation of gas molecules from chamber to pores has only affected pores nearer to the product surface but did not permeate into pores deeper in the product.

Assuming permeation of gas molecules occurs into pores near the product surface, this could increase the internal pressure in these pores, reducing the pressure differential between those pores and the chamber and ultimately the compression of these pores. Since the latter drives permeation of gas molecules from pores into the polymer, it might have occurred that pores near the product surface did not permeate gas into the polymer whereas pores deep in the product did.

If permeation of gas molecules from the chamber into pores occurred, those pores could expand beyond their original size during depressurisation and cooling and result in increased porosity and decreased part density. If some residual, elevated pressure also remained in these pores, this could create internal stresses in the polymer.

The theory presents a sequence of mechanisms wherein gas molecules permeated into pores nearby the product surface, which could cause a pore size increase and internal stresses near the part surface



whereas pores deeper in the product could still decrease in size. It provides a possible explanation to the observed reduction in part density at 4mm thickness and an increase of part density at 8mm thickness for the same treatments, as well the reduction in mechanical properties for all treated specimens.

The present work provides no data that proves or disproves the theory. Since the theory is based on assumption on top of assumption, it should be considered as merely an idea of what might have happened during the HIP process.

An indication as to whether the theory holds true could be provided by additional heat treatments under different conditions, aimed to test specific mechanisms that are part of this theory. A way to indicate whether the theory holds true would be to measure porosity with X-ray Computed Tomography (X-ray CT). With this method, the number of pores, their location, size and shape are characterised in detail [14, 15, 17] so that it could be identified whether pore size has increased near the surface and decreased in the core of thicker parts.

In collaboration with



Green_PAC

Polymer Application Centre



Investigating the influence of heat treatment in a pressurised atmosphere on the ductility of SLS-printed PA12

About the professorship

The Professorship for Polymer Engineering of University of Applied Sciences Windesheim was founded in 2009; the group's objective is to improve the knowledge base on sustainable processing of plastics and composites within and through the higher education system. Its primary function is as a research group in Polymer Engineering, delivering output in the field of applied science. The team operates within market based projects and comprises lectures from Civil Engineering, Industrial Product Design and Mechanical Engineering. The output of the projects is integrated into the curriculum of these study programmes.

Summary

In the last decade, Selective Laser Sintering (SLS) of Polyamide 12 (PA12) has evolved into a production method for end-use components in non-demanding applications. There is increasing interest from the industry to expand production for demanding applications such as machine parts and orthopaedics, where safety is vital and materials must be highly ductile. SLS-printed PA12 has high strength, but is porous and relatively brittle compared to injection moulded PA12. A study was done into post-processing of SLS-printed PA12 and in particular heat treatment in an isostatically pressurised atmosphere. Experiments were performed to gain insight into the influence of heat treatment in a pressurised atmosphere on the part density and mechanical properties of SLS-printed PA12.