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Ageing processes in laser sintered and injection moulded PA12 following hygienic reprocessing

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Abstract
Purpose – The purpose of this paper is to describe the ageing behaviour of polyamide 12 (PA12) after clinical use. The research is focused on the comparison of the processing methods injection moulding and laser sintering.
Design/methodology/approach – Test specimens are subjected to a cyclic stress of defined bending, cleaning, disinfection and sterilization. The focus of interest in this research is the degradation and reduction of mechanical properties.
Findings – Mechanical and optical changes of the materials after clinical use and hygienic reprocessing are evaluated and discussed.
Research limitations/implications – This article is focused on PA12 and, therefore, enables a very specific statement for the clinical use of PA12. The processing methods could have different impacts depending on the polymer.
Originality/value – With the increasing application of polymers in medical devices, the mechanical properties must be ensured even after long-term clinical use. A systematic research with a realistic and still-defined cyclic stress is shown in this paper. Especially the testing of laser sintered polymers compared to injection moulded material has an important message for future patient-specific products.

Keywords Ageing, Injection moulding, Hygienic reprocessing, Laser sintering, Polyamide 12, Sterilization

Paper type Research paper

Introduction
Plastics are more and more replacing traditional materials like stainless steel and glass in medical applications, not only for disposable products and packaging materials but also in reusable medical devices. The hygienic treatment of these products is an important prerequisite for reprocessing. During the use and the reprocessing, the materials are exposed to physical, chemical and thermal stresses affecting the ageing process (Tröger et al., 2008; Massey, 2005).

As part of a research project at the Institute of Medical and Polymer Engineering (Technische Universität München, Germany) in cooperation with SKZ (German Plastics Centre, Würzburg, Germany), several autoclavable thermoplastics are loaded with a cycle of use, cleaning, disinfection and sterilization corresponding to the clinical use. Afterwards their properties and modifications are analysed. The experimental use is realized by a static bending load with different outer fibre strains and an affecting medium, the simulated body fluid (SBF).

The quick and flexible way of manufacturing out of electronic data enables, for example, indentations and joints manufactured in only one step. Those advantages of laser sintering are unique compared to conventional manufacturing technologies, such as injection moulding of plastics. These two manufacturing methods are compared in relation to ageing caused by the sterilization processes. In particular, the mechanical properties in a tensile test, the fracture pattern, the surface topography and the liquid absorption before and after the stress cycles are analysed and discussed. To obtain significant results, the injection moulded specimens are made of polyamide 12 (PA12) pellets (VESTAMID® L1670, Evonik Degussa GmbH, Marl, Germany) and the laser sintered specimens are made of a powder (PA2200, EOS GmbH, Krailling, Germany), which is based on the same VESTAMID®.

Among engineering plastics, polyamide is an often used material for laser sintering. In medical engineering, polyamides are used, for example, for catheter tubes, syringes, artificial cardiac valves and components of dialysis equipment (Wintermantel and Ha, 2009; Jayabalanan, 1995).

This study was part of the research project 16577N of the FSKZ research association. The project was, on the basis of a resolution of the Lower House of the German Parliament, promoted by the German Ministry of Economic Affairs and Technology (BMWi) via the Federation of Industrial Research Associations “Otto von Guericke” (AiF) within the framework of the programme for the promotion of Joint Industrial Research projects (IGF). The authors would like to thank for the financial support.

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Materials and methods

To compare laser sintered specimens with injection moulded specimens, the geometry as shown in Figure 1 was designed specially adjusted to the dimensions of the experimental equipment. For the production of injection moulded specimens, the PA12 polymer VESTAMID® L1670 is processed with the injection moulding machine KM50 180 EX (Krauss Maffei Technologies GmbH, Munich, Germany). This material is characterized primarily by its low density (1.01 g/cm³), a good stress crack resistance and abrasion resistance. The including heat stabilizers for polyamides lead to a good heat resistance and, thus, can be steam sterilized at 134°C (N.N., 2011). The specimens have been produced with a four-cavity-mould with a melt temperature of 220°C and a mould temperature of 80°C. The injection velocity was chosen with 30 mm/s, the injection pressure with 166 MPa and the pressure at hold with 40 MPa.

The laser sintered specimens are produced on the laser sintering machine P700 (EOS GmbH, Krailling, Germany). With f-theta lenses, the specimens can be generated at a process temperature of about 176°C with layers of 0.1 mm thickness. The manufacturing of the layers takes place by alternating cross-strategy in the xy-plane. Therefore, the x or y direction was generated in z-direction, an isotropic component is formed in the xy plane. Therefore, the x or y direction was chosen to apply the mechanical load in the tensile tests. The thickness is generated by layers in z-direction, an isotropic component is formed in the xy plane. Therefore, the x or y direction was chosen to apply the mechanical load in the tensile tests. The laser sintered PA12 is biocompatible according to EN ISO 10993-1 and USP/level VI/121°C, thus enabling it for the use for medical devices. As PA12 in general, the PA2200 is characterized by particularly high strength and rigidity, good chemical resistance and long-term stability. The density of the material in the laser sintered state is 0.93 g/cm³ (N.N., 2010). To investigate the influence of clinical treatment cycles, a process is implemented that simulates the average clinical life of reusable medical devices (Figure 2). First, the specimens are loaded with a static bending under the influence of SBF.

![Figure 1](image_url)

**Figure 1** Dimensions of the specimens (all dimensions in mm)

Then the test specimens are prepared for reuse. This requires first a cleaning and disinfection process, followed by a sterilization process. To obtain information about the influence of the cycle number, three series of experiments with 5, 10 and 20 cycles have been tested.

The immersion in SBF under static bending load is carried out by the method described in DIN EN ISO 22088-3: 2006-11. Resistance to environmental stress cracking is considered in this standard and, therefore, the outer fibre strain is used for measuring the load. Mechanical load in combination with media impact can lead to a fautele ageing with environmental stress cracking (Schaumann et al., 2011). To define the mechanical load, a constant outer fibre strain is calculated as described below:

\[
es_x = \frac{h}{2r + h} \cdot 100\%
\]

where:
- \(e_x\) : outer fibre strain [%]
- \(h\) : thickness of the specimen [mm]
- \(r\) : radius of curvature of the bending template [mm].

Up to five test specimens can be clamped on the bending templates, as shown in [Figure 3(a)]. They consist of the main body, manufactured from polyoxymethylene, two white jaws and four thumbscrews. To obtain information about the impact of the load, different radii and unloaded specimens are used. Therefore, different outer fibre strains can be implemented. In this research, outer fibre strains of 0, 0.7, 1.0 and 1.3 per cent have been investigated. Special brackets made of glass are used to realize a circulation of the SBF around the unloaded specimens. The specimens are placed in the shoulder height on the glass plates and fixed by a second glass plate which is put onto the shoulders of the specimens. SBF solution is used as test fluid. Its ion concentration correlates to human blood plasma. It is produced by dissolving various salts in demineralized water and subsequently adjusting it to a pH of 7.4 (pH of blood). It is heated at 37°C (body temperature) for the load cycles (Ohtsuki, 2003, Kokubo et al., 1990).

As shown in [Figure 3(b)], two glass basins are placed into each other. In the inner basin, the clamped specimens are stored in the SBF. The outer basin which contains water, a circulation pump, a heater and a temperature sensor is used to keep the temperature constant at 37°C. Two stirrers in the inner basin ensure a continuous mixing of the SBF.

![Figure 2](image_url)

**Figure 2** Procedure for treatment of medical devices after use

![Figure 3](image_url)

**Figure 3** (a) Bending template for specimens; (b) Test-rig with bending templates. The outer basin is filled with water for stable temperature. The inner basin is filled with SBF and has two stirrers for a uniform mixing of the fluid.
Cleaning and disinfection are the first steps of treatment in clinical use. These steps are implemented by the washer-disinfector WD 150 (Belimed AG, Zug, Switzerland) that meets the requirements of EN ISO 15,883. The 65-minute standard programme for surgical instruments (A0 3,000) is used. This programme represents the first step of reprocessing for the investigated polyamides. It starts with a 3-minute pre-rinse of cold water. Afterwards, the cleaning process begins, and the device heats the water up to 62°C and keeps this temperature for 10 minutes. Meanwhile, a dosage of 5 ml per litre of a universal detergent (Beliclan M universal, Chemische Fabrik Dr Weigert GmbH & Co. KG, Hamburg, Germany) is used. At the end of the cleaning programme, a thermal disinfection follows while deionized water is heated three minutes to temperatures above 90°C. A following drying process (125°C, 3 minutes) completes the cleaning process.

For sterilization of the specimens, the steam sterilizer Steritop (Belimed AG, Zug, Switzerland) is used. It complies with DIN EN 13,060 for small steam sterilizers. The used programme “prion” comprises of the three phases of conditioning, sterilizing and drying phase, (see Figure 4).

During the period of conditioning, air inclusions are eliminated by a fractionated pre-vacuum air removal to prevent that bacteria that can survive the sterilization in air inclusions. During the sterilization phase, the chamber is heated to at least 134°C for a period of 18 minutes, resulting in condensation of the saturated steam on the cooler surface of the samples. This results in a swelling of the microorganisms that lowers their heat resistance. Afterwards, a vacuum with no steam injection realizes the drying phase (Reichert and Young, 1997; McDonnell andSheard, 2012).

Polyamide properties strongly depend on the moisture content (Eyerer et al., 2005). Therefore, it makes sense to compare the contaminated specimens in relation to a non-contaminated reference. The reference test is realized by drying the virgin polyamide samples in a desiccator with phosphorus pentoxide (P₂O₅).

Mechanical properties are measured by a universal testing machine Z050 (Zwick GmbH & Co.KG, Ulm, Germany). Tensile tests were conducted in accordance with ISO 527 with a constant testing speed of 50 mm/minute. The characteristic values for comparison are the elongation at break and the relative residual strength of the aged specimens related to the yield strength of the virgin material without clinical treatment cycles (reference).

It is assumed that the injection moulded and the laser sintered specimens show a different behaviour of swelling. The recording media can be reconstructed on the approximate percentage increase of the weight of the specimens.

To study the surface composition and roughness the instrument, μsurf® (Nano Focus AG, Oberhausen, Germany) is used. The non-contact measurement of surface topography is based on the white-light confocal measurement principle. When applying the roughness analysis function, properties are determined vertically and horizontally to the surface. The considered vertical parameters are the arithmetic mean roughness Sa and the root mean square Sq. The cut-off wavelength λc used for the injection moulded specimens is 800 μm and for the laser sintered specimens 8,000 μm (Nimz, 2002; Kreil, 2008).

The scanning electron microscope (SEM) JSM-5400 (JEOL Ltd., Eching, Germany) is used for analysis of selected fracture surfaces from the tensile tests. The samples are sputtered with a 15 nm thick gold layer.

Results

Increase in weight

The percentage increase in weight refers to a reference dried in a desiccator. A distinction is made between the following outer fibre strains 1.3, 1, 0.7 and 0 per cent. The measurements are performed after three, six and nine test cycles being stored at room temperature and room humidity for one day after the last contact to the media. The significant part of the weight increase takes place in the phase of the first three cycles (see Figure 5). Thereafter, the additional increase in weight is marginal. In general, it can be seen that specimens bonded by a greater outer fibre strain absorb more medium. A direct comparison shows that the laser sintered specimens gain less weight than the injection moulded.

Topography

It is crucial to examine what changes arise in the surface during the ageing of polymers. This is examined while different outer fibre strains are compared. Whereas the injection moulded specimens do not show differences in the roughness measurement, the laser sintered specimens show significant differences (see Figure 6). The highest roughness values arise at the reference specimens with an average Sa of 55 microns and 62 microns Sq. The other specimens, which have gone through 20 cycles, are much lower on average. Here, no explicit trend can be seen depending on the outer fibre strain.

As it can be seen in the 3D images of the profile meter μsurf® (Figure 7), the injection moulded specimens show a significant roping on the surface caused by manufacturing. The injection moulded specimens do not show any differences between the loaded specimens [Figure 7(b)] and the reference [Figure 7(a)]. On the contrary, the laser sintered specimens show pronounced differences in surface texture between the loaded specimens and the reference. This can be seen in the 3D images (Figure 7), as well as the SEM images (Figure 8). Agglomerates can be seen on the surface of partially fused PA12 material on the reference specimens [Figures 7(c) and

Figure 4 Temperature and pressure profile in the sterilization programme “prion” of the autoclave Steritop 23 L (Belimed AG, Zug, Switzerland)
8(a)]. The loaded specimens [Figures 7(d) and 8(b)] show largely fused powder particles with relatively small height differences in the topography.

Mechanical properties
In Figure 9(a), the typical viscoelastic behaviour of the injection moulded PA12 can be seen with pronounced necking before break. For the reference specimens as well as for the loaded specimens, the yield stress ranges from 40 to 45 MPa. The elongation at break decreases from 450 to 250 per cent.

The typical brittle behaviour of laser sintered PA12 is shown in [Figure 9(b)]. It can be seen that the yield stress after 20 cycles drops from about 55 MPa for the reference specimen to about 45 MPa for the loaded specimen. A significant difference in the curves can be recognized in the part of the necking of the specimen after the yield point. While this section can be seen for the reference specimens, the loaded specimens break before reaching the yield point. The elongation at break is in each case in the range of approximately 18 per cent.

In Figure 10, the elongation at break of injection moulded and laser sintered PA12 is shown for different stress cycles and outer fibre strains. The elongation at break of the injection moulded specimens [Figure 10(a)] has a value of 375 per cent for the reference and decreases with the number of cycles. The elongation at break after 20 cycles is between 110 and 250 per cent. A clear influence of the outer fibre strain cannot be seen. The laser sintered reference specimens [Figure 10(b)] show with 17 per cent the lowest value of elongation at break. The highest value of about 21 per cent is reached by the specimens which have undergone five cycles. With increasing cycle number, the average elongation at break decreases. Those which have undergone 10 cycles are about 20 per cent and those of 20 cycles about 19 per cent. Again, no clear influence of outer fibre strain can be seen. As it can be seen in Figure 11, the relative residual strength of the injection moulded specimens is constant over the number of cycles with values between 91 and 94 per cent. An influence of the outer fibre strain cannot be inferred. The relative residual strength of laser sintered specimens after 5 and after 10 cycles is about 93 per cent, as shown in Figure 11b. After 20 cycles, a significant reduction shows a decrease to about 89 per cent residual strength. An influence of the outer fibre strain cannot be recognized.

For simulating long-term use of reusable products, the laser sintered polyamide was also exposed to 75 reprocessing cycles [see Figures 10(b) and 11(b)]. A further decrease down to around 15 per cent of elongation at break and 80 per cent of residual strength could be detected.

To draw further conclusions about toughness or brittleness of the material, SEM images of selected fracture surfaces are examined. While the laser sintered specimens break almost without any necking, the injection moulded specimens show an explicit necking before break. The fracture surface of the laser sintered specimens [Figure 12(a)] is over the entire cross-section similar rough. The injection moulded test specimen [Figure 12(b)] shows at its edge a smooth fracture surface, which is changing to rough and fibrous towards the middle.

Discussion
Increase in weight
Most polar polymers absorb water because polar groups in the polymer chains are able to bind water, what may also cause a
change of mechanical properties (Baschek et al., 1999). During the sterilization of the test specimens, the main part of weight increase takes place during the first three cycles for injection moulded as well as for laser sintered specimens. For more than three cycles, the increase of weight is marginal for injection moulded specimens. The material seems to be saturated and no further increase of weight is expected. For laser sintered test specimen, an increase of weight is slower and up to nine cycles growing. Afterwards, there can be expected a saturation also for the laser sintered specimens. The laser sintered specimens gain less weight increase than the injection moulded, what may be explained by the degree of crystallization caused from the different manufacturing processes (Oberbach et al., 2004, Lasoski and Cobbs, 1959).

**Topography**

Because of the roughness of the laser sintered surfaces, these probes are more susceptible for abrasion and surface degradation than injection moulded parts. In Figures 7 and 8, the effects of sterilization can be seen. The combination of heat and humidity seems to have a significant impact on the surface. The top layer of molten polyamide powder seems to be removed by the cleaning and sterilization process, and the measured roughness values decrease after sterilization, but
molten powder agglomerations in their globular form still dominate the topography. The granular texture have the effect of micro notches and, therefore, may yield to a loss of mechanical properties (Blattmeier et al., 2012).

**Mechanical properties**

The two production processes lead to fundamentally different failure behaviours. Injection moulded specimens show a typical ductile failure, whereas laser sintered probes show brittle failure. This can be seen in the diagrams of Figure 9, as the laser sintered specimen cracks in the non-linear, viscoelastic part of the curve, while the injection moulded specimen of PA12 show pronounced necking. Elongation at break for laser sintered PA12 is significantly lower, whereas yield strength is similar for both production processes.

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**Figure 9** (a) Example of a stress-strain diagram for injection moulded specimens; (b) Example of a stress-strain diagram for laser sintered specimens

![Stress-strain diagrams](image)

**Figure 10** (a) Elongation at break of the injection moulded test specimens for different outer fibre strains, $n = 5$, error bars represent standard deviation; (b) Elongation at break of the laser sintered specimens for different outer fibre strains, $n = 5$

![Elongation at break](image)

**Figure 11** (a) Residual strength of injection moulded specimens for different outer fibre strains, $n = 5$; (b) Residual strength of the laser sintered specimens for different outer fibre strains, $n = 5$

![Residual strength](image)

**Note:** Error bars represent standard deviation
Because of the different initial failure behaviour, a degradation of mechanical properties affects directly the strength of the laser sintered PA12, while for injection moulded parts, elongation at break will be reduced first until the yield point is reached, before brittle failure and a reduction of strength will appear.

Being exposed to steam sterilization, injection moulded parts embrittle, whereas the values for elongation at break for laser sintered specimens increases after the first testing cycles. This increased elongation at break comparing the reference tensile specimen with specimens loaded with five cycles of sterilization can be explained by the softening effect of absorbed water. As the absorption of water has a major impact during the first cycles of load, the softening can just be seen after the first testing step of five cycles. Afterwards, the specimens are nearly saturated and the elongation at break slightly decreases because of the degradation (hydrolysis) or morphological changes of the polyamide.

The brittle behaviour of the laser sintered tensile specimens compared to the ductile behaviour of the injection moulded specimens can again be explained with the different manufacturing processes. On the one hand, the different topography and the porous structure of the laser sintered probes in comparison to the injection moulded PA12 causes micro notches that will prohibit homogeneous necking of the material and, therefore, yield to a reduced elongation at break. On the other hand, the (local) heat input as well as the cooling rates of the material during processing is very different. This may influence the degree of crystallization and, therefore, also yield strength and elongation at break (Blattmeier et al., 2012).

Conclusion

The impact of clinical use and hygienic reprocessing on the properties of laser sintered and injection moulded PA12 has been investigated. Laser sintered and injection moulded samples have been exposed to a cyclic stress of simulated use, cleaning, disinfection and sterilization.

The different initial state of the specimens has influence on the topography, water absorption and mechanical properties. The increase of weight during the first cycles due to water absorption is for both processes similar, whereas topography is just affected for the laser sintered specimens with their granular texture.

A decrease of mechanical properties caused by clinical use and hygienic reprocessing (sterilization) can be observed. But even after 20 cycles, relative residual strength remains above 85 per cent for both materials. For all discussions, the different initial states of laser sintered and injection moulded specimens must be kept in mind. Whereas injection moulded PA12 shows a ductile behaviour with pronounced necking before break, laser sintered PA12 shows a brittle behaviour but with a higher yield strength. Even after 75 cycles, no drastic decrease of mechanical properties (relative residual strength above 77 per cent) has been determined for laser sintered PA12. This indicates that laser sintered PA12 may be a suitable material for (at least some) reusable clinical products.

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Further reading


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