Professorship for Polymer Engineering

Sustainable Laser Sintering with PA12

Applications for re-use of aged powder

hogeschool Windesheim

Colophon

Title: Sustainable Laser Sintering with PA12 – Applications for re-use of aged powder

Publicationnumber: LKT-3DPR-106641-1909

Publication date: August 2019

Authors: G.Heideman, Dr. Ir.
P.Dijkstra, B.eng.

Funded by: SiA KIEM-VANG

In collaboration with: Bender Techniek
Schaepman Lakfabrieken, Hempel

Photography: Windesheim Zwolle

Lines of research:

1. Circulaire economie
2. Industrial Additive Manufacturing *(3D printen)*
3. Hybride ontwerp
4. Duurzaam produceren

Deze publicatie wordt uitgebracht door het Lectoraat Kunststoftechnologie, een praktijkgerichte onderzoeksgroep op Hogeschool Windesheim die zijn basis heeft in Engineering & Design. Zoals passend bij lectoraten in combinatie met de gebruikte subsidieregeling, is het onderzoek uitgewerkt tot een TRL niveau van maximaal 7: demonstratie systeemprototype in operationele omgeving. Het werk is zo opgeschreven dat het na-werkbaar is, maar bedrijfsspecifieke data is soms weggelaten.

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Summary

Selective Laser Sintering, or SLS printing for short, is a method to produce parts with good mechanical properties, detail and high productivity. It has been in use for some years for functional and load-bearing prototypes; in recent years it is used increasingly for end-use components from one-off units up to batches of thousands of products.

The process works by fusing sections of a powder bed (usually PA12) layer after layer. The unfused powder serves as support material, which is subject to high temperatures for several hours in an inert (nitrogen-rich) environment. This has an effect on PA12 often called ageing, causing a waste stream of PA12 powder which cannot be re-used in the printing process.

The increasing use of SLS printing as well as the increasing importance of sustainability for industry and society underlines the necessity to find sustainable, practical and commercially viable solutions to the waste stream of aged PA12. In partnership with coating manufacturer Schaepman Lakfabrieken B.V. (part of the Hempel Group) and Dutch distributor for AM machines Bender Additive Manufacturing B.V, the Professorship for Polymer Engineering explored applications in which PA12 waste material from laser sintering may be re-used.

Various existing routes of re-use were found, some of which have already been commercialised. These methods include re-use as filament material for FDM printing, a re-use programme for moulding, and 'rejuvenated' PA12: aged SLS powder of which the properties are restored for SLS printing.

The latter method of re-use was investigated in more detail, where a comparison was made between powder, processing and product properties of rejuvenated versus standard EOS PA2200. Generally, the rejuvenated material is a suitable alternative to EOS PA2200, with both appearance and mechanical properties generally equivalent to one another. The rejuvenated material however does seem more sensitive to the temperature and laser settings (and possibly batch-to-batch differences), which can lead to lower strength and toughness in the Z-direction (between the layers). The process needs to be carefully dialled in as well as monitored to obtain best results with respect to processing and mechanical properties of the end product.

Besides re-use in laser sintering, a new application for re-use was identified: using the aged PA12 powder in texture coatings as a replacement to virgin Polyamide powder. Tests indicate that the powder achieves an equivalent aesthetic to one of Hempel's current commercial coatings, even when comparing aged powder from different batches. It is also free of (large) impurities that would disrupt the texture. The tests are an encouraging first validation of the powder's applicability in texture coatings, although more research is required to fully validate the aged material for this application.

The research shows that responsible, sustainable re-use of waste material from SLS printing is technically feasible in multiple applications. Some applications have in fact already been commercialised. Further research is recommended to further contribute to improving the re-use processes and connecting parties with waste material to parties that can re-use the material in a sustainable way.

1. Introduction

In recent years the Additive Manufacturing (AM) industry is growing rapidly and the technology is becoming more widely adopted; amongst them Selective Laser Sintering (SLS). The method has a high production capacity, accuracy and delivers part properties suitable for load-bearing components. The most commonly used material is Polyamide 12 (PA12). It is selected for its excellent processability, consistent product quality and good mechanical properties. SLS-printed PA12 is used for production of functional prototypes, one-off components and as an alternative to moulding for small to medium production series.

In an average build job, less than 20% of the build volume is sintered together, meaning that only 20% virgin powder has to be added after a printing job to fill the same build volume. However, the properties of the unsintered (support) powder change during the printing process; a process referred to as ageing. The aged powder cannot be fully re-used in the printing process. Generally, between 35% and 50% virgin powder has to be added to the aged powder to regain the right properties for processing. As a result, a waste stream of aged powder builds up over time, compromising the sustainability of the production process.

Although the aged powder is no longer suitable for the SLS process, there may still be ways to use the powder in other applications or processing methods. With this in mind, the Professorship for Polymer Engineering has collaborated with Bender Additive Manufacturing B.V. (Dutch distributor for EOS) and Schaepman Lakfabrieken B.V. (manufacturer of coatings and part of the Hempel Group) to explore applications for aged PA12 waste powder resulting from the Selective Laser Sintering process.

This report first describes the printing process, PA12 ageing in SLS and its implications to get an understanding of the reason why there is a waste stream and why re-use is a viable solution. Next, an evaluation is made of new and existing applications for re-use of the aged powder. Of these applications, two were selected and studied in more detail. The research focused on EOS PA2200, which is one of the most commonly used grades of (unreinforced) PA12 in laser sintering.

2. SLS-printing and material properties for processing

This chapter describes the printing process, the desired properties of the feedstock material for processing and the powder ageing process of PA12 in SLS printing and serves as background information and context to the research.

2.1. SLS printing process

In figure 1, the chamber of an SLS printer is displayed. The printing process works by depositing a polymer powder bed (I) inside a building chamber using a wiper (II). The printing surface area (III, highlighted in orange) is heated from above by a heater (IV). The temperature of the top powder layer approaches the melting temperature (Tm) for semi-crystalline polymers and glass-transition temperature (Tg) for amorphous polymers. The temperature is kept just low enough to prevent powder coalescence. The bed is heated to approximately 170°C for processing of PA12 (semi-crystalline).

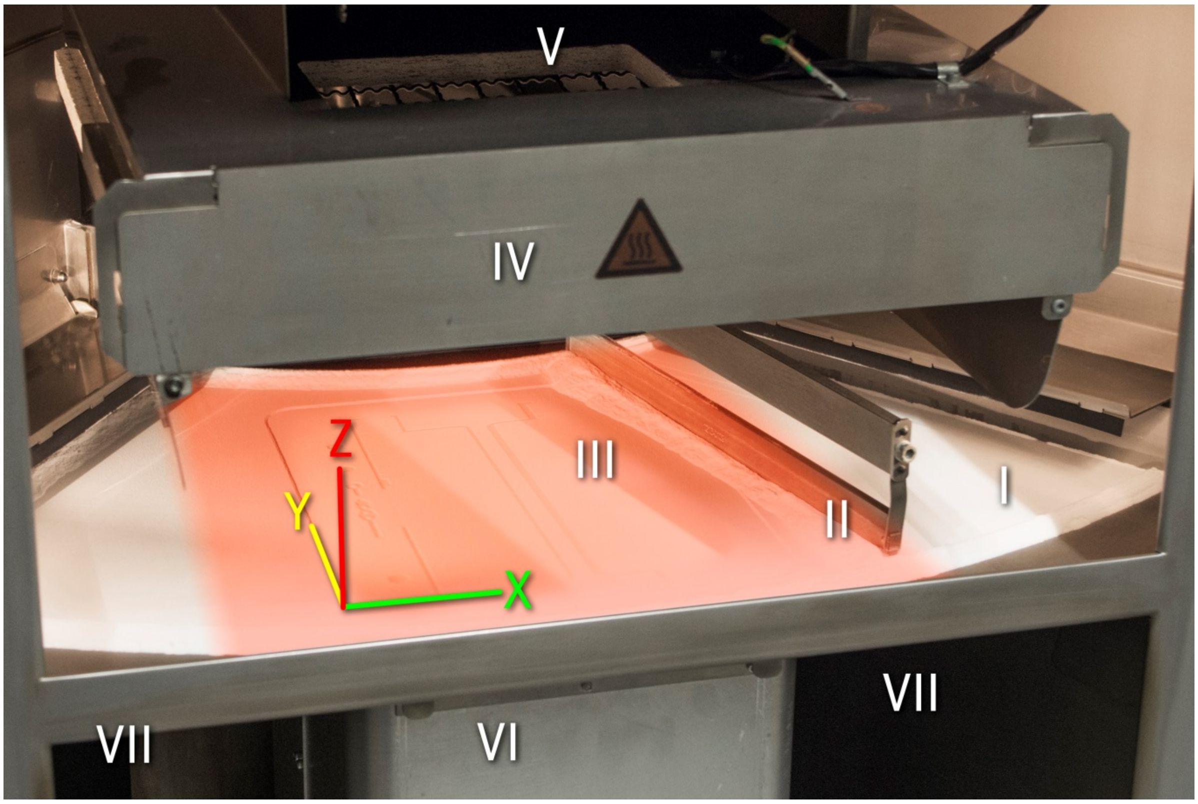

Figure 1: The building and removal chamber of the EOS Formiga P100 printer. The coordinate system and key components are marked for reference.

Next, a moving laser beam (V) heats the material further to form a layer of the desired parts or products. After the cross-section of one layer is sintered, the printing surface is lowered by one layer thickness (generally 0.1mm) into a building tray (VI), a new layer of powder is deposited, and the process is repeated. The removal chamber in which the building tray is situated is kept at an elevated temperature (ca. 150°C for PA12) by heaters (VII) on either side of the building tray. Doing so enables the building tray to cool down evenly after printing, maximizing accuracy and minimizing warpage effects. During the pre-heating, printing and cooling processes, the building and removal chamber are filled with nitrogen to prevent oxidation/degradation of the polymer.

2.2. Desired material properties for SLS

Selective Laser Sintering requires specific material properties for the benefit of processing and product quality. This paragraph briefly discusses what properties are required and/or desirable based on reports from various sources [1-3].

Particle/powder properties

The base material needs to be a powder. The powder is deposited but not compacted. The powder needs to flow freely in order to achieve consistent powder bed deposition and bulk density of the powder (which in turn affects process and product quality). This is best achieved with smooth, regularly shaped particles (spherical or potato-shaped). Particles thicker than the layer thickness (100 μm) are unwanted as they could disrupt the powder bed. At the same time, small particles become airborne too easily during deposition. As such, a typical average particle size is 40-70μm and has a size distribution sufficiently narrow to prevent problems with airborne particles or a disrupted powder bed.

Sintering properties

To successfully sinter the material, the laser radiation should be absorbed efficiently to melt the powder layer. When the powder melts, there is limited time for the powder to coalesce before it cools down again. Without the option to compact the material, a low zero-viscosity (η_0) is required to achieve good coalescence.

It is not only important to achieve strong bonding within the layer, but also between the layers. Therefore, some of the laser radiation should be transmitted so the top layer coalesces with the layer below it as well.

Thermal properties

Contrary to most Additive Manufacturing technologies, in SLS, the material that is sintered together is not directly connected or fixed to a build plate. Instead the unsintered powder acts as support material. Temperature gradients can cause layers to shrink unevenly after sintering and cause it to warp or curl up, causing inaccurate parts or even impair the deposition of subsequent layers.

Heating the powder bed near its Tm or Tg minimizes temperature gradients between powder bed and the molten cross-section. In addition, keeping semi-crystalline materials above their crystallization temperature (Tc) both at the printing surface and in the building tray prevents shrinkage and curling from crystallisation during the build process.

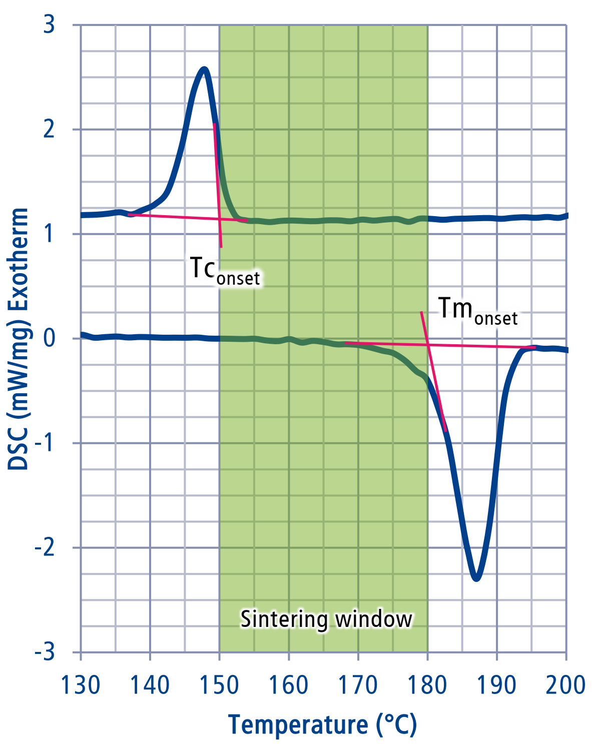

Figure 2: Schematic representation of a typical sintering window of SLS-PA12.

In addition to minimal temperature gradients, a narrow melting peak (Tm) is required to prevent coalescence of the powder bed. A wide temperature region between the onsets of Tm and Tc is also required, so there is neither coalescence nor crystallisation of the powder in that temperature region. This so-called sintering window is critical for stable processing and good mechanical properties. A typical sintering window for SLS-PA12 is displayed in Figure 2.

2.3. Ageing of PA12 powder in SLS

Contrary to conventional processing, in SLS-printing, the polymer is exposed to high temperatures for (tens of) hours during each build job. A nitrogen atmosphere is applied inside the printer to prevent oxidation/degradation of the polymer. Although oxidation is avoided, some grades of PA12 for SLS, such as EOS PA2200, undergo changes at processing temperatures and react chemically inside the printer. Aged powder is reported to possess a higher Molecular weight, zero-viscosity and polydispersity [2, 4]. Ageing effects tend to be worse nearby printed products because the powder is exposed to higher temperatures in those areas [5].

The aged PA12 material coalesces poorly compared to virgin material during sintering, leading to decreased bonding, increased porosity and inferior mechanical properties. Raising the bed and chamber temperatures or increasing energy provided by the laser adversely affects process stability and part properties, so process settings cannot properly compensate for ageing. This means that instead of adding only virgin material to compensate for material use for printed products in previous build jobs, a higher percentage of virgin material is added to the aged material to obtain properties suitable for processing.

It must be noted that different grades of PA12 for SLS-printing show different ageing characteristics. Whereas some grades show clear increases in zero viscosity (EOS PA2200), other grades (Arkema Orgasol PA12) are unaffected by exposure to high temperatures [2]. Grades that do not age may be processed again by adding little or no virgin material (in case of Arkema Orgasol, the supplier recommended refresh ratio is as low as 10%, a ratio which allows the process to be run without a resulting waste stream). The differences are not limited to processability (zero-viscosity) either: in a comparison between two grades it is reported that the ageing grade offers more isotropic mechanical properties than the non-ageing grade because it has the ability to undergo covalent bonding between the layers [6].

Although there are different materials and material grades available, it should be recognized that not all companies that own a SLS printer will be able to switch from one material (grade) to another. For one, not all SLS printers have freely adjustable processing settings. In addition, not every company has the required in-depth knowledge of the process to change the parameters and optimize the process.

3. Possible routes to re-use aged SLS-PA12 powder

Reducing the waste stream of PA12 from SLS printing is not as straight forward as switching material or changing the processing parameters, as described in paragraph 2.3. Instead, re-use in other applications may provide a responsible, sustainable and feasible solution. This chapter discusses a variety of processes in which the PA12 material may be re-used.

Fluidized Bed Powder Coating

In fluidized bed powder coating, a container with polymer powder is fluidized by an airflow coming from the bottom of the container. A product is heated to above the melting temperature of the polymer and briefly dipped into the fluidized bed, melting adjacent powder which sticks to the product. PA12 is one of the materials used for such coatings. Because the (aged) SLS-PA12 material is in powder form, it may be suitable for re-use in fluidized bed powder coating. However, the process may depend on a low viscosity and consistent powder properties for high quality coatings, making chances of success in this route uncertain.

Additive in texture coatings

Polyamide is not only used as a base material for coatings, but also used in some coatings as an additive to add a grainy texture. In this application, the material helps create a certain aesthetic. Powder form, particle size (distribution), particle shape and purity are important properties of the material in this application. These same properties have to meet strict requirements for laser sintering. If aged material still meets these requirements, it may be suitable as an additive in coatings. This route of re-use is studied in Chapter 4.

Moulding material (Extrusion, IM)

Like many thermoplastics, there are Polyamide 12 grades for extrusion and injection moulding. Although SLS-PA12 is not tailored to moulding, it is possible to process it by moulding. It is in fact already used as a route for re-use: EOS has a recycling programme within Germany for aged PA2200 material, in which the aged material is taken back free of charge and guarantees sustainable re-use in collaboration with a moulding partner [7, 8]. The size of the moulding industry means a large stream of material may potentially be re-used this way.

Filaments for FDM printing

Since it is possible to mould the material, it may also be feasible to extrude the material into a filament and re-use it as a material for FDM printing. Although it is not known if this route is commercialized yet, research has been conducted on this subject [9].

Selective Laser sintering (through powder rejuvenation)

Although the aged material is not reusable in laser sintering as is, there are a few companies who offer a service to rejuvenate aged powder. The ageing process of SLS-PA12 is effectively reverted to obtain properties that are suitable for the laser sintering process. Chapter 5 reports the study into rejuvenated PA2200 material, its processing and product properties in comparison with the standard mixture of 50% virgin and 50% aged EOS PA2200.

4. Re-use as an additive in texture coatings

One of the methods proposed for re-use is to use the powder as an additive in coatings. Schaepman Lakfabrieken B.V. offers a product line of coatings called Belticryl® that feature a grainy texture. The texture coating combines abrasion and wear resistance with a grainy, satin aesthetic that conceals scratches and scuff marks that may occur from hard and extended use.

Schaepman currently uses a virgin Polyamide powder as an additive to obtain the texture. From both circular and economical viewpoints, it is interesting to validate whether the waste stream of Polyamide-12 powder from SLS printing could be used as the additive instead of a virgin material.

4.1. Validation methods

Amongst other properties, Schaepman selects the powder according to its particle shape and size distribution. These properties need to be consistent from batch to batch. Impurities or agglomerates are not acceptable as they will show up as inconsistencies in the coating.

Whereas the virgin material currently in use by Schaepman complies with the specifications, the powder waste stream might contain impurities from handling & processing. Agglomerates might also be present as a result of (partial) melting of particles close to the sintering area or prolonged exposure to close to the material's melting temperature. In SLS printing it is common practice to sieve the residual powder from a print job, as agglomerates and impurities could affect process stability. The EOS unpacking system at the Windesheim University features a 245µm sieve. As such, agglomerates and impurities are expected to be smaller.

To test for agglomerates, it was opted to analyse the particle size distribution. Three PA2200 waste streams of different origin (material batch and thermal history) were gathered and compared with virgin PA2200 material. The analysis was performed by Schaepman using Laser diffraction (Mie scattering, wet dispersion, Malvern Instruments Mastersizer).

In addition to laser diffraction, sample coatings were produced and applied on test panels to assess their aesthetic effect. These were compared with a test panel coated one of Hempel's commercial products. All test panels were coated with a layer thickness of between 40 and 50µm. The same concentration of powder additive was used for all coatings, between 1 and 5%.

4.2. Particle size distribution

From the results of particle size analysis (Table 1, Figure 3 and Figure 4), it becomes clear that all aged powders have an average size (D [4;3]) around 62µm.

	Virgin	Aged #1	Aged #2	Aged #3	
Dv (10)	39,8	39,0	38,9	39,1	µm
Dv (50)	61,6	60,4	60,4	59,7	µm
Dv (90)	93,0	90,7	90,4	89,7	µm
D [4;3]	63,7	62,2	62,1	62,2	µm

Table 1: Statistical values of the particle size distribution of virgin and waste stream PA2200 powders.

In addition, the virgin and aged powders have a similar size and size distribution; as such the SLS printing process seems to have little effect on particle size distribution. The differences that are present are expected to have a negligible or acceptably small effect on the appearance of the coating.

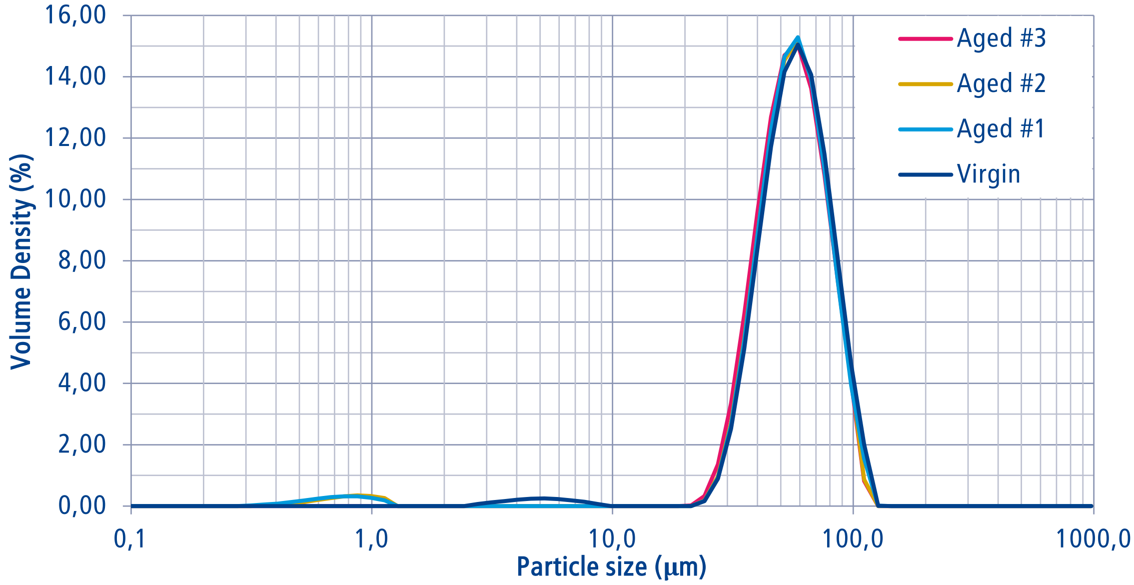

Figure 3: Particle size distribution on a logarithmic scale.

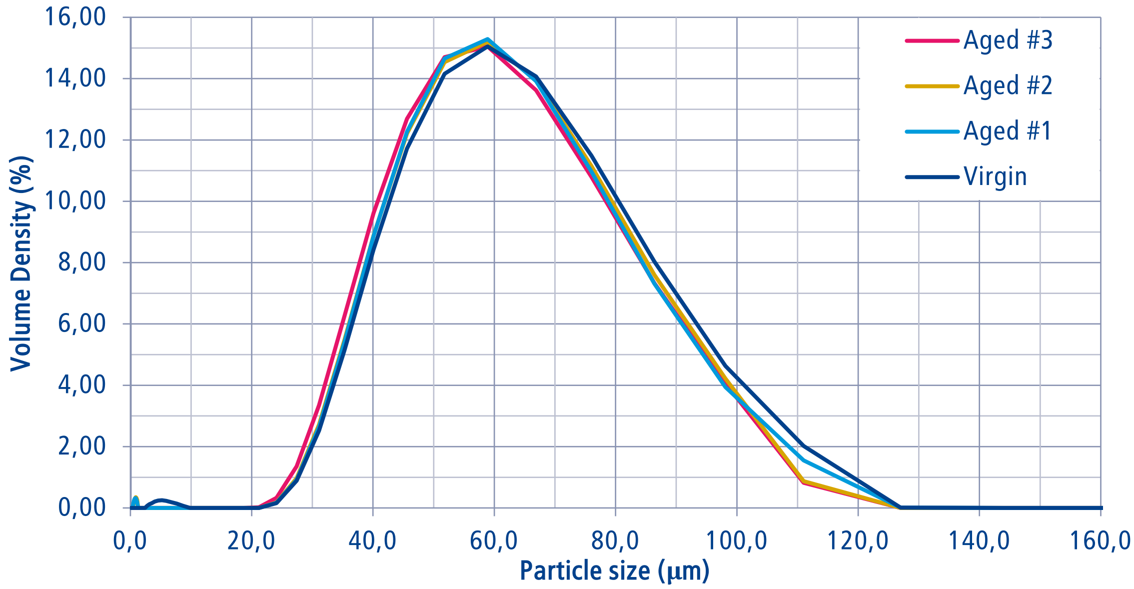

Figure 4: Particle size distribution on a linear scale.

Low concentrations of particles under 10µm are present, of which the size and concentration varies for each sample. However, since the coating is applied at 40-50µm, they should not have any effect on the coating's appearance. More importantly, no large particles or agglomerates were detected. This indicates the waste stream powders may indeed be suitable for producing a coating with a uniform and consistent finish.

4.3. Test coatings

The appearance of the coatings with the aged PA12 is similar to two of Hempel's commercial products, although both products use a slightly different grain size than the aged PA12 has. The closest matching commercial coating has a smaller grain/particle size and was chosen for comparison. In the sample coatings made with aged powder, no agglomerates or impurities were found. The samples with aged powder feel and appear slightly coarser than the commercial coating, as to be expected, but overall do achieve a very similar look and feel. The differences between the coatings from different aged powders are small. The coating made from aged powder #3 appears slightly coarser, even though layer thickness and particle size of the coatings of the three aged powders are highly similar.

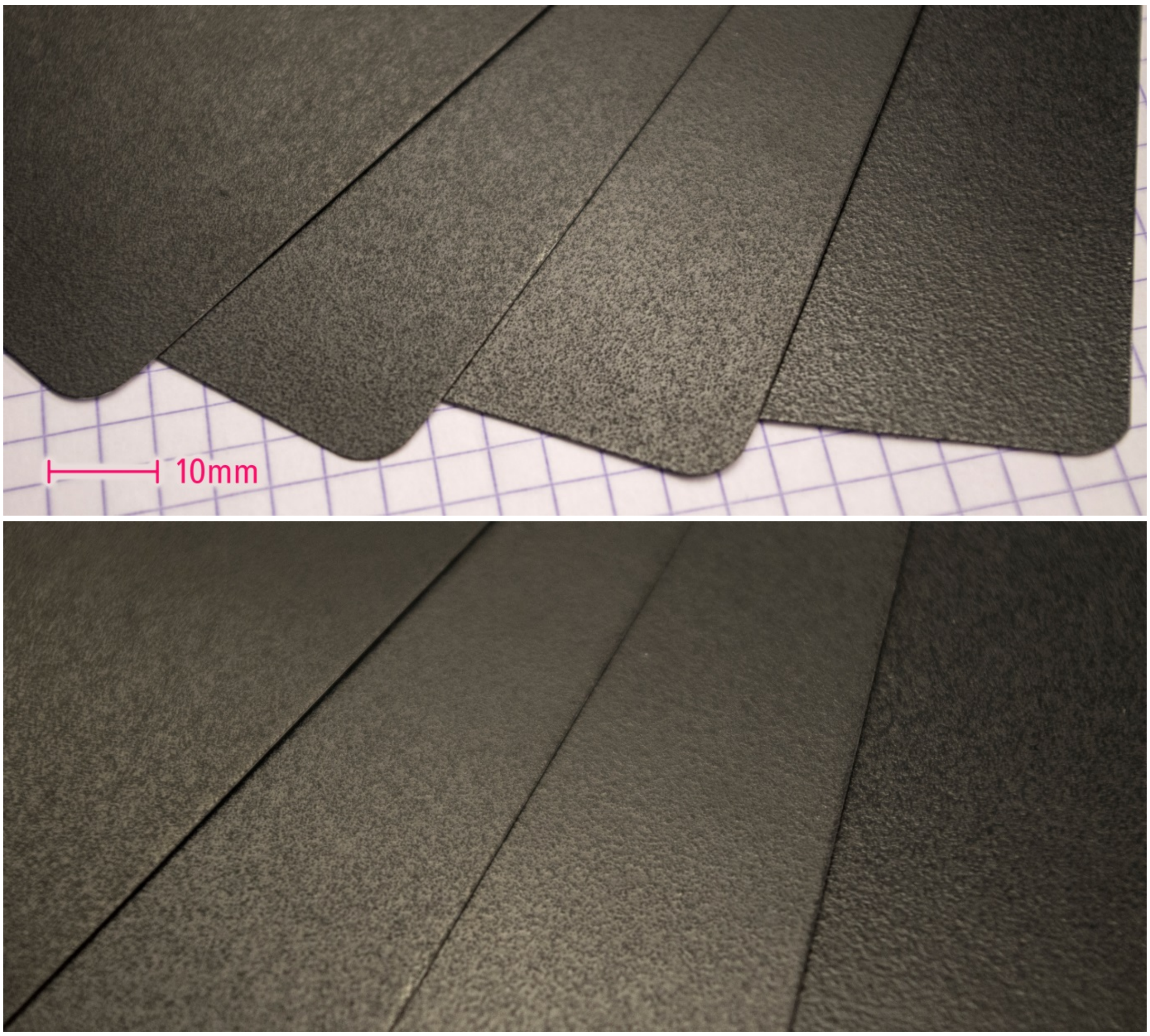

Figure 5: The coating samples using different types of powder. Top: overview picture. Bottom: detail picture. In order from left to right on each picture: Commercial Belticryl coating, coating with aged powder #1, coating with aged powder #2 and coating with aged powder #3. The coatings are 40-50µm thick and feature the same concentration of powder.

Overall, the coatings made with aged powder have a very similar appearance to the commercially available coating. The visual effect and finish of the coated test panels underlines the potential of this application for the powder. The result justifies further testing of the powder as an additive in a commercial product.

5. Re-use in Laser Sintering through powder rejuvenation

Another route for high-end re-use could be to revert the ageing process of the material, as so to make it suitable again for laser sintering. This method could improve sustainability of the laser sintering process whilst also retaining the economic value of the material. A company has already developed this technology, which is referred to as a powder rejuvenation process. The process is offered commercially as a service to rejuvenate existing waste streams of companies alternatively, the company also stocks rejuvenated material.

As a commercially available route for re-use, it was opted to compare rejuvenated PA2200 with the standard feedstock material, which is a mix of 50% virgin PA2200 mixed with 50% aged material. Testing took place at the Windesheim University on an EOS Formiga P100. The aged and virgin material originated from the same batch. However, due to the scale of the rejuvenation process, it was not possible to obtain rejuvenated material from this same batch. Instead, rejuvenated material was used from a random batch of PA2200.

5.1. Validation methods

Even if the rejuvenated material is suitable for laser sintering, its properties may differ from PA2200. Differences in the properties of the powder may lead to different requirements for processing and different product properties. As such, it was opted to study properties of material, process and the product properties. The rest of the chapter discusses various relevant properties.

5.2. Powder properties

As explained in chapter 2, the powder properties are crucial for a stable printing process and high quality product. Particle shape was studied under a microscope, Mie scattering laser diffraction was used to compare the particle size distributions and the thermal properties were compared using Differential Scanning Calorimetry (DSC).

Particle shape

Virgin and aged PA2200 originating from the same batch were compared (Figure 6). Both virgin and aged materials consist of similarly sized, potato-shaped particles with a somewhat irregular, rough surface. The similarity between the powders indicates that the ageing process has little effect on the particle shape.

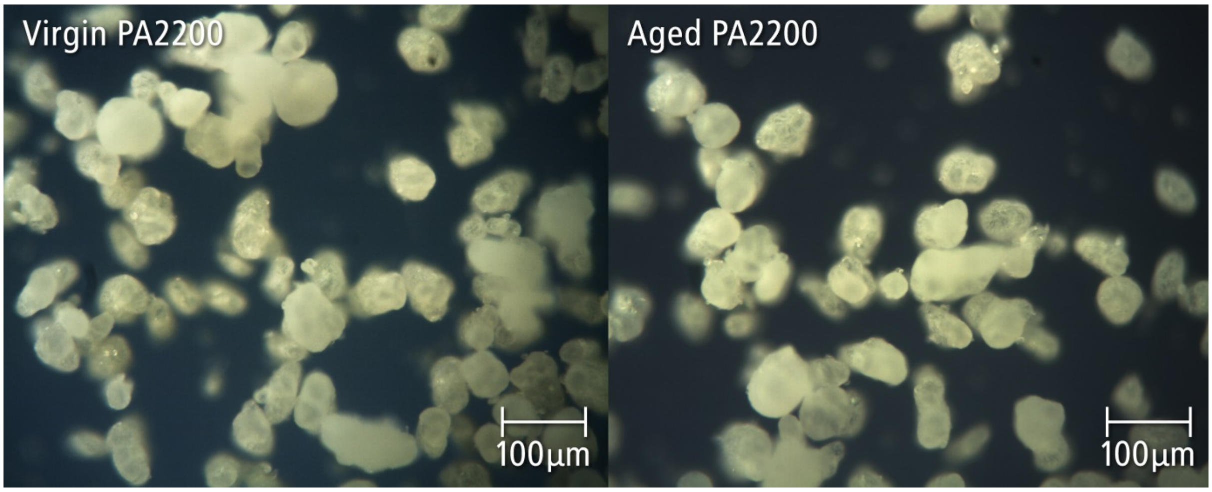

Figure 6: Particle shape of virgin and aged PA2200 from the Windesheim University, originating from the same batch.

Next, rejuvenated and mixed PA2200 were compared (Figure 7). Again, the powders have a similar shape to each other, as well as compared to the virgin and aged powders. As such, it was concluded that the rejuvenation process also has little effect on the shape of the powder particles and should not affect processing.

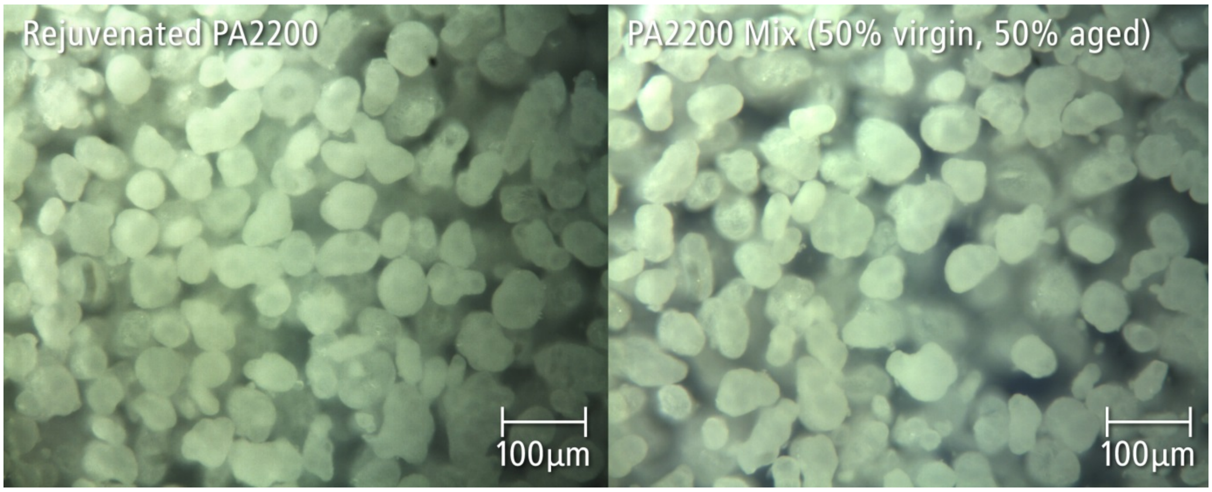

Figure 7: Particle shape of rejuvenated versus 50/50 mixed PA2200 powder.

Particle size distribution

The particle size distributions (Figure 8) of rejuvenated and mixed PA2200 are similar. The results for both materials are also comparable to those found for various aged powders that were studied for re-use in coatings (Figures 3 and 4, Chapter 3). It was concluded that the rejuvenation process has little effect on particle size distribution and should not lead to different processing characteristics.

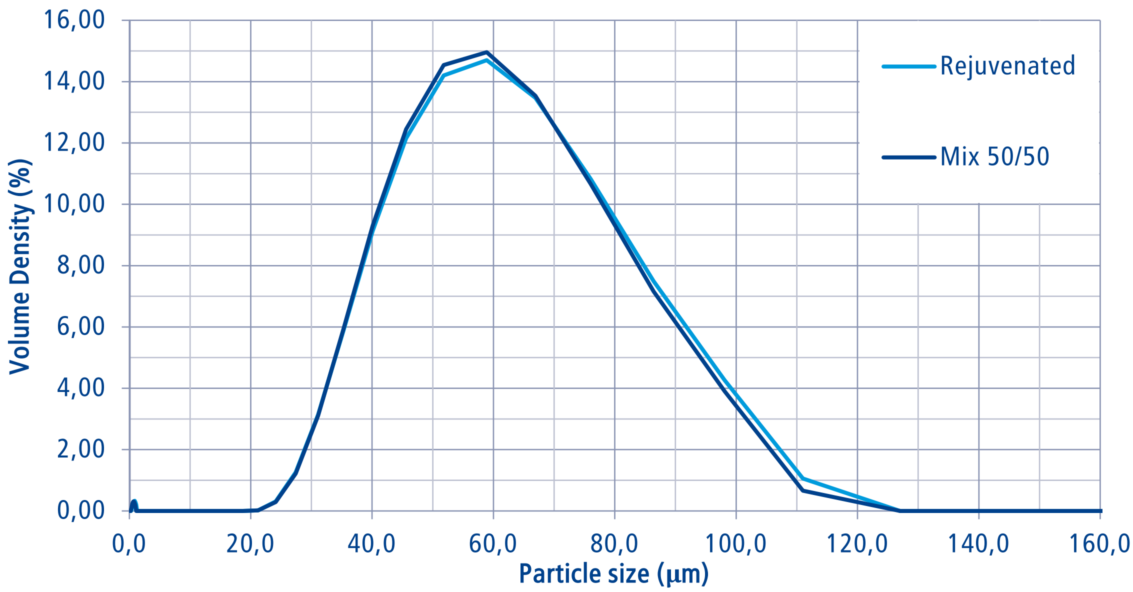

Figure 8: Particle size distribution plot of rejuvenated versus 50/50 mixed PA2200 powder.

Thermal properties

Using Differential Scanning Calorimetry (DSC), the thermal properties were compared for virgin, aged, mixed and rejuvenated powder. The samples were tested with a single heating scan from 20 to 210°C, held at 210°C for 5 minutes, ending with a cooling scan from 210 to 20°C. The scan rate was 10°C/minute for heating and cooling. The results (Figures 9, 10 and Table 2) show a close resemblance of the specimens. The peak in the heating curve of the rejuvenated is steeper and more pronounced than the mixed (standard) material.

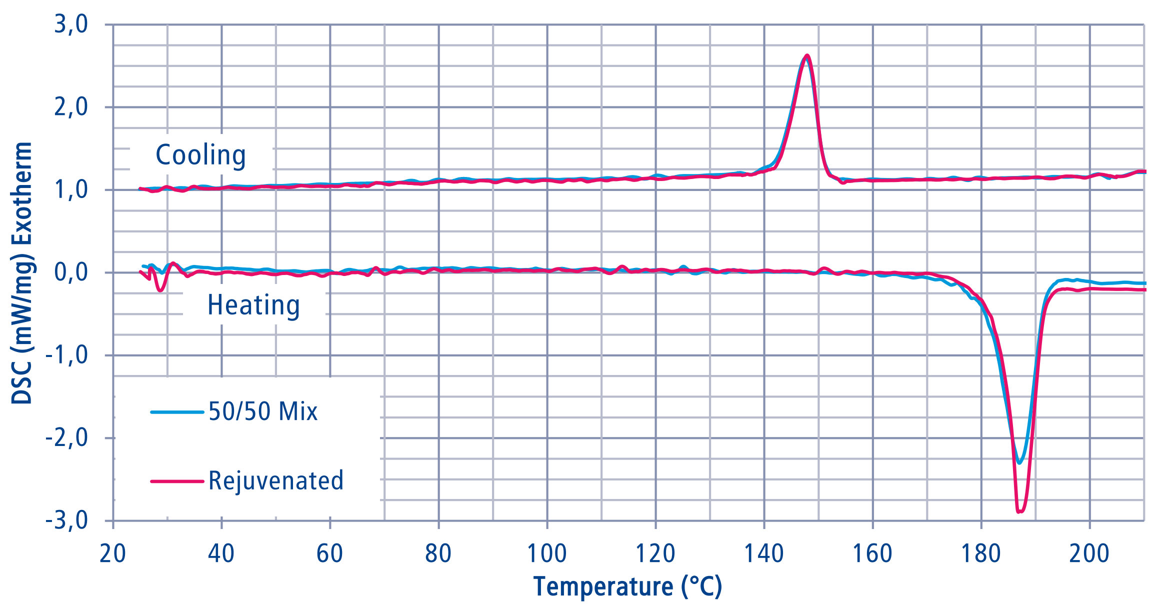

Figure 9: DSC plot with a heating and cooling curve of rejuvenated PA2200 and a 50/50 mix of virgin and aged PA2200.

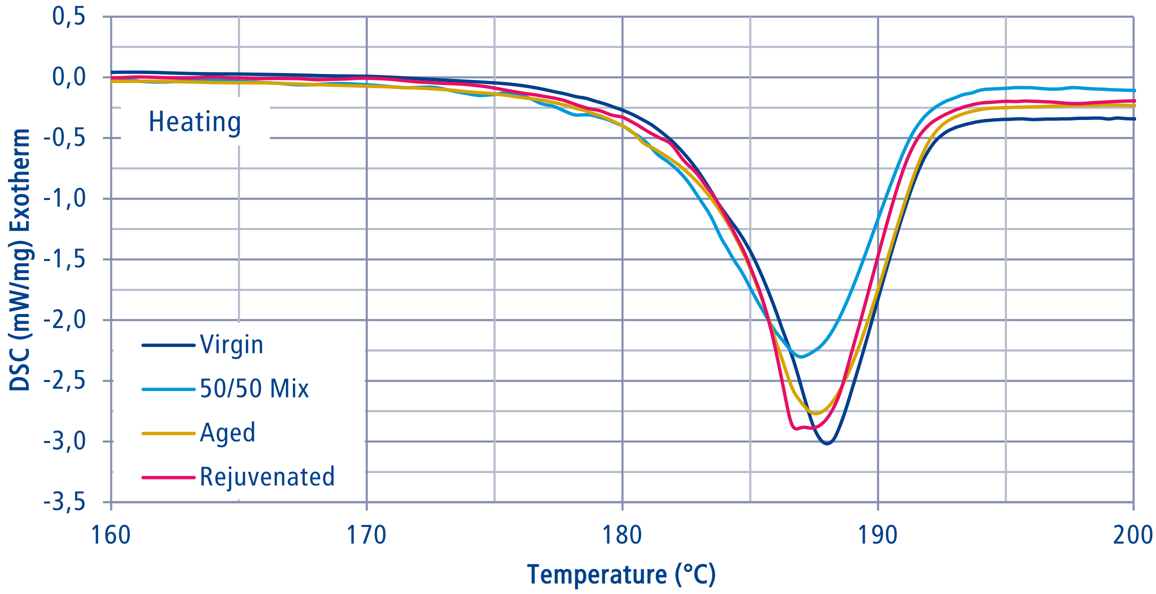

Figure 10: Melting peak from DSC measurements of PA2200 with various types of thermal history and treatment.

A closer inspection of the melting peaks including separate aged and virgin materials show that the melting trajectory of the rejuvenated, virgin and aged materials are similar. The mixed material has a slightly wider melting peak, but a similar crystallinity (Table 2). The wider melting peak could be the result of mixing two powders (with a different thermal history) together.

	Virgin	50/50 Mix	Aged	Rejuvenated
Crystallinity (%)*	41,02	42,69	44,82	44,61
Melt peak temperature, Tm (°C)	188,0	187,0	187,6	186,8

*Table 2: Crystallinity and melt peak temperature of the DSC specimens. *The crystallinity was calculated with a melting enthalpy of 245J/g for fully crystalline PA12 [10].*

The crystallinity and temperature at the peak (Table 2) of rejuvenated and aged material is similar. The crystallinity of the mixed and virgin material is slightly lower. The differences between mixed and rejuvenated powder may lead to small differences in the sintering process and product properties but should not affect processability.

5.3. Processing tests & specimen production

Processing tests were performed in preparation of specimen production on an EOS Formiga P100 machine. Based on the study of the rejuvenated powder and mixed PA2200 powder the materials were treated as highly similar. As such, the same settings were used to process both materials initially (a process chamber of 171°C and a removal chamber of 149°C). Whereas with the mixed material a smooth powder bed was deposited over the entire surface, with the rejuvenated material the wiper broke up the powder bed as it moved over the bed to deposit new material (Figure 11). The affected areas were consistently outside of the printing volume and occurred solely in the front area of build chamber.

The area of the printing volume appeared flat, smooth and homogeneous. Therefore, it was decided to produce a batch of test specimens using the same machine settings as with the 50/50 mix.

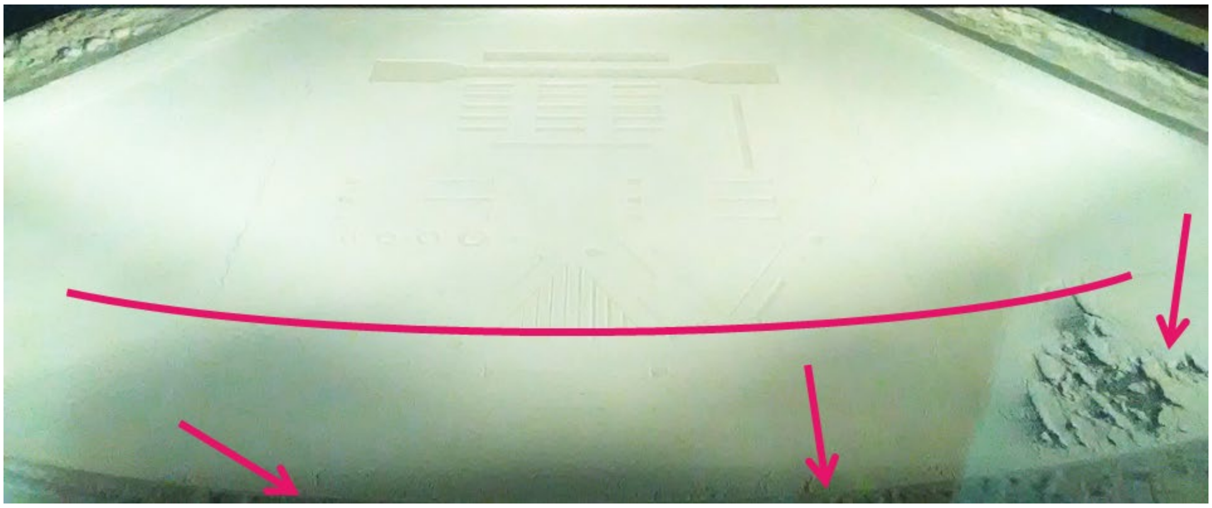

Figure 11: Powder bed during initial testing, where a breakup of the powder bed is visible near the arrows. The breakup only occurred in the front area of the printer, in front of the indicated line and outside the actual sintering area.

In addition, processability was further studied with a second run of tests and a second batch of material. Upon feedback to the supplier about the powder bed break-up, the supplier instructed to flush the material through the printer before use to allow electrostatic charges in the powder to dissipate before processing the material, and to lower the removal chamber temperature by 4°C.

With these changes, no more breakups of the powder bed were seen (Figure 12) and test productions showed a stable sintering process (no curling) and no warpage of the final product. The new settings and flushing process were used for production of a second batch of test specimens. In Table 3, the temperature settings are listed for both batches.

Figure 12: Powder bed during testing after flushing the powder through the machine and lowering the removal chamber temperature. No more breakups of the powder bed were detected.

Material	Process Chamber (°C)	Removal Chamber (°C)
50/50 Mix	171	149
Rejuvenated, batch 1	171	149
Rejuvenated, batch 2	171	145

Table 3: Machine temperature settings used for the various build jobs.

In the layout of the build job (Figure 13) the mechanical testing specimens were placed in the back of the building volume, where the powder bed appeared stable both in- and outside the printing area for all machine temperature settings. Specimens for roughness and visual properties were produced in the front half of the building area.

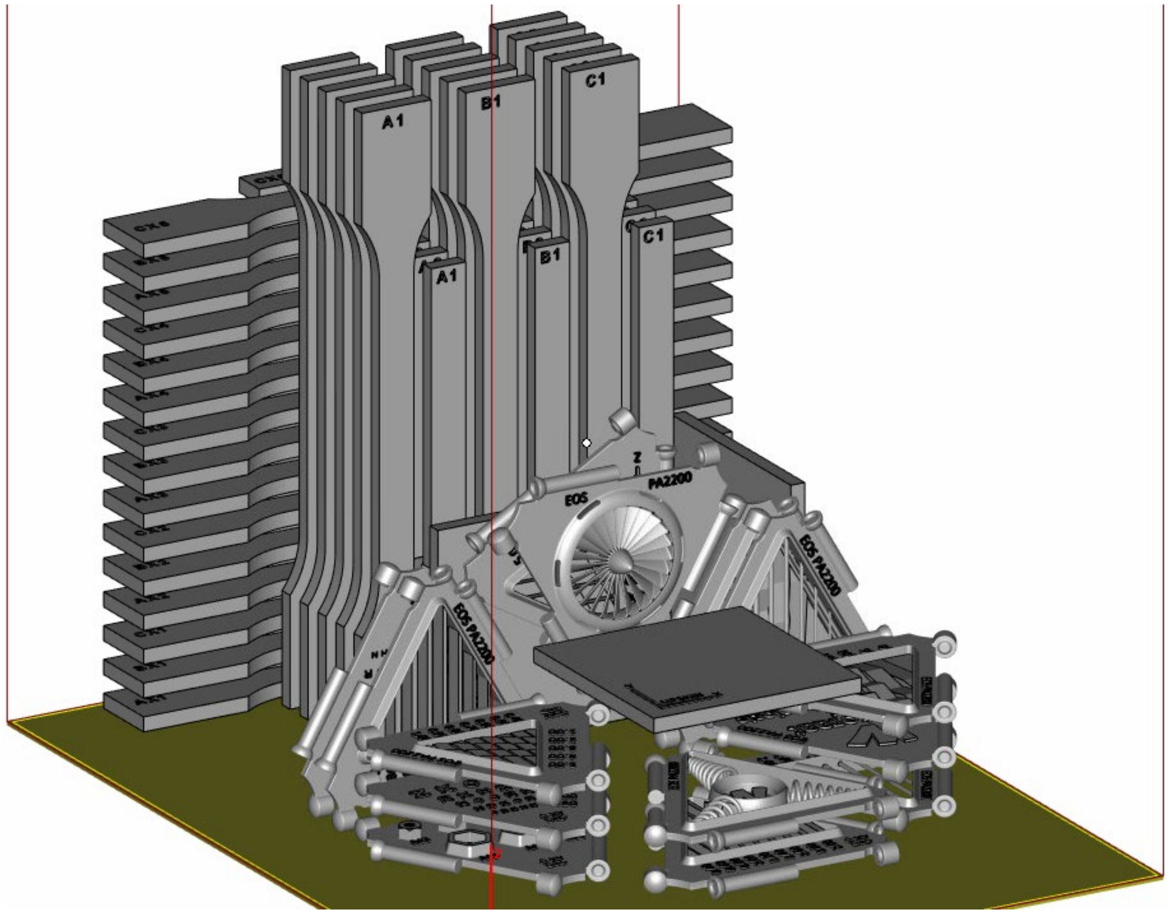

Figure 13: Layout for production of test specimens. The ochre plane in the lower part of the image represents the XY-plane / building area of the machine; the Z-direction is vertical.

Mechanical testing specimens were produced using three laser energy densities (listed in Table 4) with five specimens for each setting. For the other tests, single specimens were produced with the intermediate energy density. Tensile and impact specimens were conditioned at 23°C, 50%rH for five days before testing.

Laser intensity (W)	Energy Density E_D (J/mm^2)
18,5 (C)	0,0296
21,0 (A)	0,0336
23,5 (B)	0,0376

Table 4: Laser energy densities used for the mechanical test specimens. All jobs were printed with 0,1mm layer thickness.

5.4. Product properties

The appearance of the parts, tensile and (Charpy notched) impact properties, density and roughness of the rejuvenated versus the standard PA2200 were compared. Each of these properties is discussed below.

Visual properties

Specimens of rejuvenated and mixed material were compared (Figure 14) on aspects such as colour (yellowing), impurities, visibility of the layers/stepping and the laser exposure paths (hatching, outline, etc), sharpness and thickness of details, lettering and gaps. The sample parts of the rejuvenated and standard material showed no distinguishable differences.

Figure 14: Comparison of visual properties of rejuvenated and standard PA2200. In both pictures, the rejuvenated material is on the left, and the PA2200 on the right (on top of the rejuvenated sample). No differences were found that distinguish the materials/products from each other.

Tensile strength

The Ultimate Tensile Strength (UTS, also known as Maximum tensile strength or Maximum stress, Figure 15) in the X-direction is comparable for all three test series and laser energy densities, and in fact even exceed manufacturer specification (dotted line). This may be the result of differences in process settings between those used by the supplier and used in this research, or different conditioning circumstances between production and testing (different moisture uptake) than used by the supplier.

In the Z-direction, the tensile strength is lower for all test series than the X-direction and slightly lower than specified by the supplier. Since the properties in the Z-direction are more sensitive to processing conditions, this may explain the difference. The laser energy density has no significant effect on the UTS for the standard PA2200, whereas it does for the rejuvenated material. The cause of this difference could not be determined during the research, but it may be a result from the rejuvenation process. Job 1 of the rejuvenated material seems to be more strongly affected than Job 2, which may be attributed to a difference in processing temperatures or batch-to-batch differences.

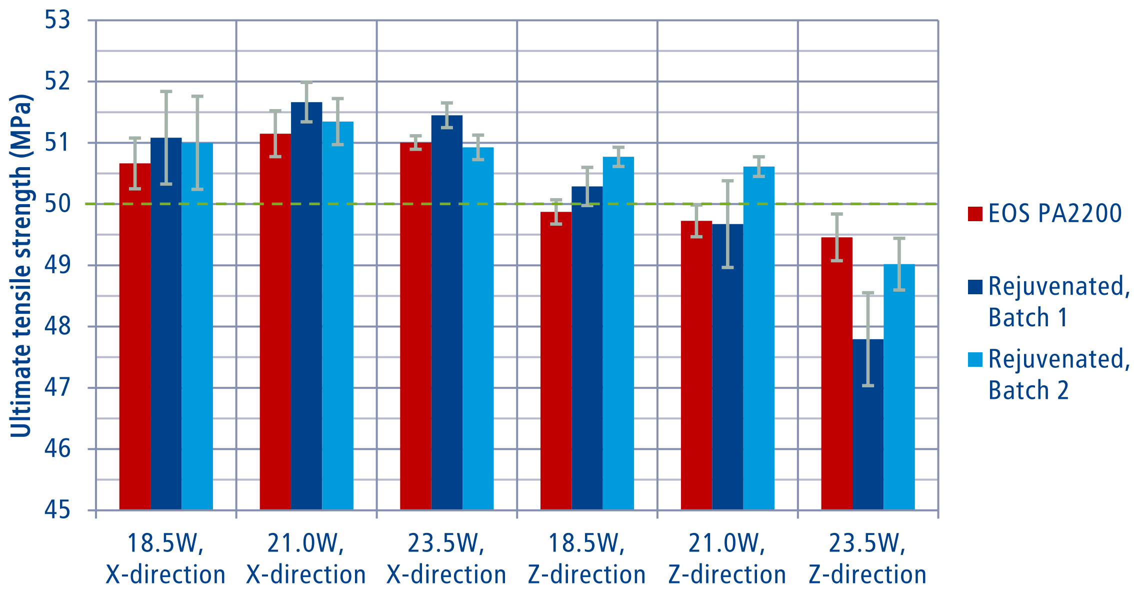

Figure 15: Comparison of Ultimate tensile strength (UTS) in the X- and Z-direction of rejuvenated versus standard PA2200 at various laser energies. The (green) dotted line is EOS' specification for PA2200 (Appendix A).

Young's Modulus

Although there are significant differences in Young's Modulus (Figure 16) between some series, the results appear scattered and no clear differences could be distinguished between the rejuvenated and standard material. What does stand out is that the Young's modulus is significantly higher than specified by the supplier. If different conditioning circumstances were used by the supplier than in this research, this may cause a different moisture uptake and therefore different Young's modulus. Since this property is measured at relatively low loads and displacements, the use of different testing equipment and protocols may also cause noticeable differences.

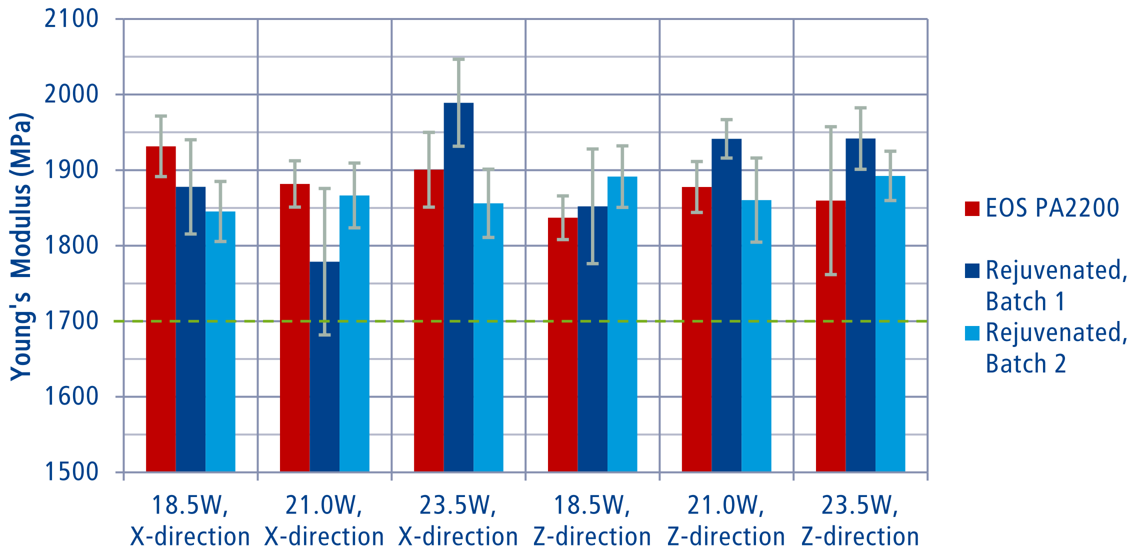

Figure 16: Comparison of Young's Modulus in the X- and Z-direction of rejuvenated versus standard PA2200 at various laser energies. The (green) dotted line is EOS' specification for PA2200 (Appendix A).

Strain at break

As depicted in Figure 17, in the X-direction the standard and rejuvenated materials possess comparable properties that slightly exceed the supplier specified value. Laser power has little effect on both rejuvenated and standard material in the X-direction.

In the Z-direction however, significant differences are observed between the standard and rejuvenated material. Whereas laser power has a limited effect on strain at break of the standard material, there is a pronounced effect on the strain at break of the rejuvenated material. This effect is stronger for batch 2 than batch 1. Also, whereas batch 2 considerably exceeds the strain at break of the standard material at the lowest laser power, batch 1 has a lower strain at break than the standard material at all tested laser power settings. The dependency on laser power could be the result of the rejuvenation process.

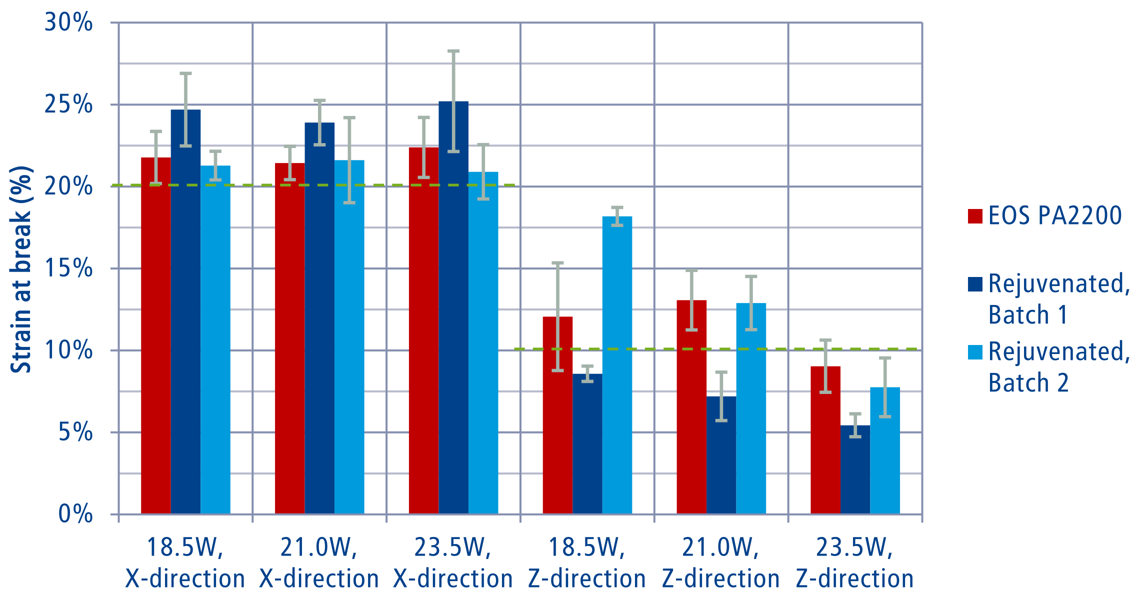

Figure 17: Comparison of Strain at break in the X- and Z-direction of rejuvenated versus standard PA2200 at various laser energies. The (green) dotted line is EOS' specification for PA2200 (Appendix A).

Impact strength

No clear differences were observed between the rejuvenated and standard material for the notched impact strength (Figure 18), nor a clear difference in impact strength between the two batches of rejuvenated material.

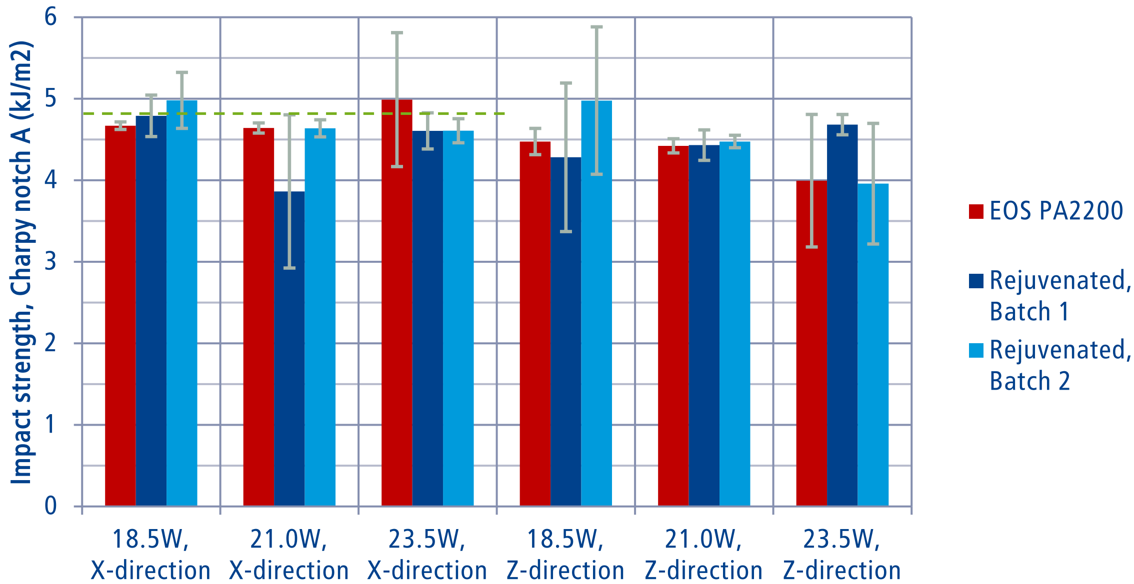

Figure 18: Comparison of Charpy notched (A) impact strength in the X- and Z-direction of rejuvenated versus standard PA2200 at various laser energies. The (green) dotted line is EOS' specification for PA2200 (Appendix A).

Density

The density (Figure 19) was determined using the impact test specimens before applying the notch. The density of the rejuvenated material varies more at different laser powers and printing directions than the standard PA2200 material. The density of the Z-direction is slightly lower than the X-direction for both materials, suggesting higher porosity. This may influence the mechanical properties, although density values correspond or exceed those found on the EOS PA2200 datasheet.

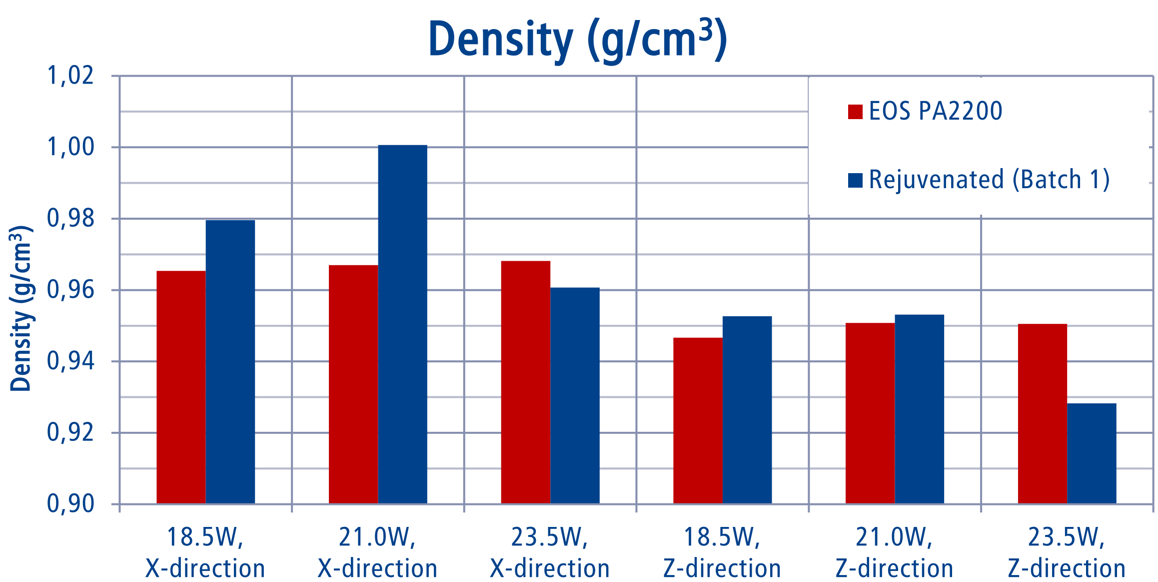

Figure 19: Density of standard material and batch 1 rejuvenated material, measured using the impact test specimens.

Roughness

The Ra roughness values (Figure 20) show minor differences and between the two materials for the same direction, the differences are even insignificant.

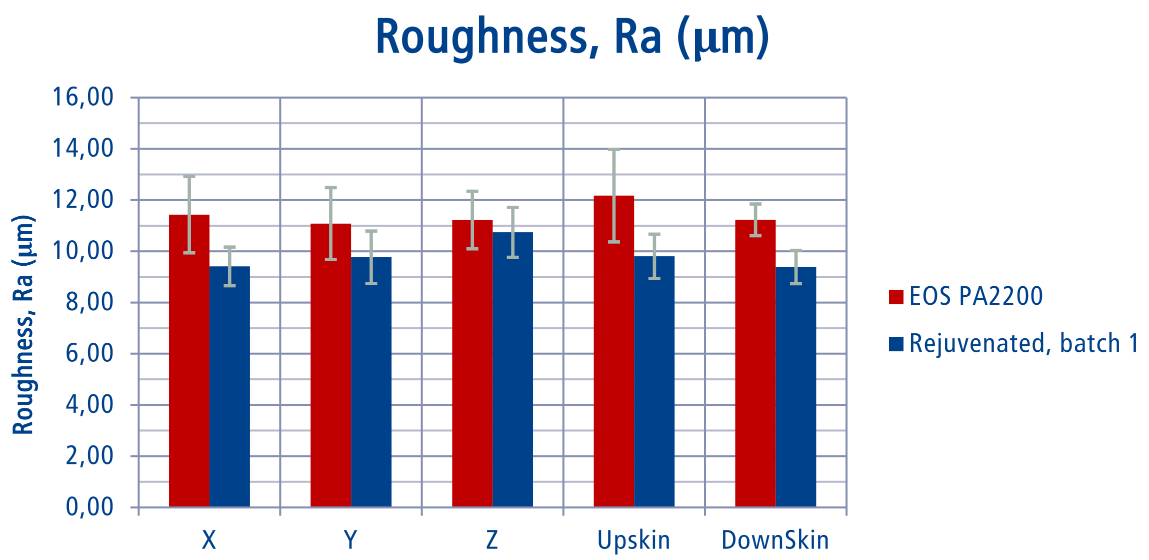

Figure 20: Roughness (Ra) measurement of standard material and batch 1 rejuvenated material.

The Rt roughness values (Figure 21) of the upskin and downskin are lower for the rejuvenated material than the standard PA2200 material; the differences of the X, Y and Z directions are insignificant.

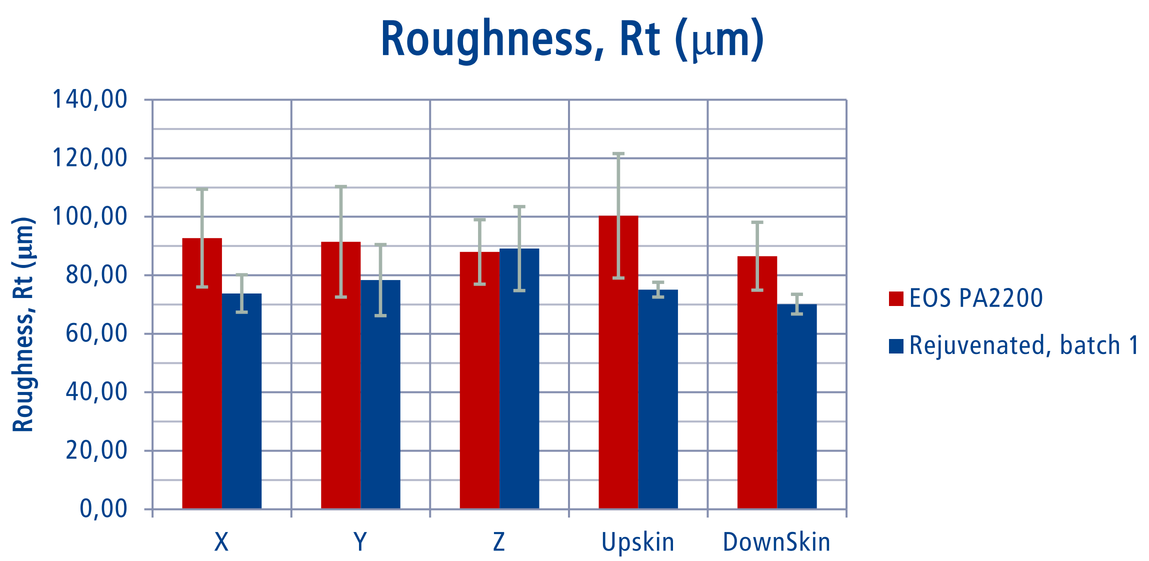

Figure 21: Roughness (Rt) measurement of standard material and batch 1 rejuvenated material.

The findings of the roughness measurement support the visual test, where no obvious differences, including the surface quality, were observed.

Overall, the rejuvenated PA2200 has largely similar product properties to mixed PA2200, although the rejuvenated material seems to be more sensitive to process settings. Possibly there are also batch to batch differences. The tests underline the potential of the rejuvenated material, however more research is necessary to obtain more insight in the cause of the variation in the results.

6. Conclusions & recommendations

In this research, two routes of re-use for the waste stream of aged PA12 powder were studied.

The study into re-use in texture coatings led to encouraging results: Aged powder from various batches was found to have a suitable particle size distribution and was free of impurities. The test coatings with the aged powders provided a similar aesthetic compared to a commercial coating. It is recommended that more aspects, such as processability, wear resistance and long-term properties, are tested to confirm the applicability of aged SLS-PA12 as a replacement for virgin Polyamide powder in texture coatings.

The study into rejuvenated PA12 within the Selective Laser Sintering shows that the rejuvenated PA12 powder is an equivalent and worthy alternative to the standard (50% aged, 50% virgin) PA12 powder. The rejuvenated material however appears to be more sensitive to the process settings (chamber temperatures, laser power), and batch-to-batch differences could play a role as well. The sensitivity to the process settings becomes apparent in the stability of the powder bed during printing and the tensile strength and strain at break between the layers (the Z-direction). Maximizing the results may require frequent testing and adjustment of settings and in-depth knowledge of the process.

It is recommended that the effects of process settings and batch-to-batch differences to the mechanical properties in the Z-direction of rejuvenated PA12 are studied in further detail. In addition, it is recommended to include testing of rheological properties of SLS powders as well as to include research into build-up of electrostatic charge in the feedstock material.

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Appendix A – Material datasheet EOS PA2200

e-Manufacturing Solutions

PA 2200 Performance 1.0
PA12 — EOS GmbH - Electro Optical Systems

Product Texts

Product Texts

This whitish fine powder PA 2200 on the basis of polyamide 12 serves with its very well-balanced property profile a wide variety of applications. Laser-sintered parts made from PA 2200 possess excellent material properties:

• high strength and stiffness
• good chemical resistance
• excellent long-term constant behaviour
• high selectivity and detail resolution
• various finishing possibilities (e.g. metallisation, stove enamelling, vibratory grinding, tub colouring, bonding, powder coating, flocking)
• bio compatible according to EN ISO 10993-1 and USP/level VI/121 °C
• approved for food contact in compliance with the EU Plastics Directive 2002/72/EC (exception: high alcoholic foodstuff)

Typical applications of the material are fully functional plastic parts of highest quality. Due to the excellent mechanical properties the material is often used to substitute typical injection moulding plastics. The biocompatibility allows its use e.g. for prostheses, the high abrasion resistance allows e.g. the realisation of movable part connections.

100 µm layer thickness
Performance is the parameter set of choice for parts with high demands on mechanical properties and fracture behaviour, especially when the part is going to be subjected to multiaxial loading in all three directions. Performance parts are characterized by the highest degree of isotropic strength and rigidity. The choice of 100 µm layer thickness results in fine resolution and also very high surface quality and detail resolution.

Mechanical properties	Value	Unit	Test Standard
Izod Impact notched (23°C)	4.4	kJ/m²	ISO 180/1A
Shore D hardness (15s)	75	-	ISO 7619-1

3D Data	Value	Unit	Test Standard
The properties of parts manufactured using additive manufacturing technology (e.g. laser sintering, stereolithography, Fused Deposition Modelling, 3D printing) are, due to their layer-by-layer production, to some extent direction dependent. This has to be considered when designing the part and defining the build orientation.			
Tensile Modulus			ISO 527-1/-2
X Direction	1700	MPa	
Y Direction	1700	MPa	
Z Direction	1700	MPa	
Tensile Strength			ISO 527-1/-2
X Direction	50	MPa	
Y Direction	50	MPa	
Z Direction	50	MPa	
Strain at break			ISO 527-1/-2
X Direction	20	%	
Y Direction	20	%	
Z Direction	10	%	
Charpy impact strength (+23°C, X Direction)	53	kJ/m²	ISO 179/1eU
Charpy notched impact strength (+23°C, X Direction)	4.8	kJ/m²	ISO 179/1eA
Flexural Modulus (23°C, X Direction)	1500	MPa	ISO 178

Thermal properties	Value	Unit	Test Standard
Melting temperature (20°C/min)	176	°C	ISO 11357-1/-3
Vicat softening temperature (50°C/h 50N)	163	°C	ISO 306

Other properties	Value	Unit	Test Standard
Density (lasersintered)	930	kg/m³	EOS Method
Powder colour (ac. to safety data sheet)	White	-	-

Last change: 2010-03-21 Source: www.materialdatacenter.com Page: 1/2

Contact information

Professorship for Polymer Engineering (Lectoraat Kunststoftechnologie)
Campus 2-6
8000 GB Zwolle
T: 088-4699700
E: kunststoftechnologie@windesheim.nl
I: www.windesheim.nl/kunststoftechnologie

Personal contact information

Margie Topp
Professor
T: 088 - 469 7203
E: m.topp@windesheim.nl

Geert Heideman
Associate Professor
T: 088 - 469 8919
E: g.heideman@windesheim.nl

Paul Dijkstra
Researcher
T: 088 - 469 8851
E: p.dijkstra@windesheim.nl

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Professorship for Polymer Engineering

Sustainable Laser Sintering with 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

Selective Laser Sintering (SLS) with Polyamide 12 is increasingly used for production of functional components for prototyping and end-use. Common grades of PA12 powders age and cause a stock of unsintered powder material that cannot be re-used within the SLS process. This research explores and validates processes and applications that could drive sustainable re-use of the material.

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