

Examination of the Physical and Chemical Properties of Duraform Polyamide Powder Used in Selective Laser Sintering

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Abstract

The atomic force microscope (AFM) is capable of examining material properties on the micro- and nanoscale that can affect performance, durability, and reliability of materials used in the process. The Duraform polyamide (PA) nylon powder used in the selective laser sintering (SLS) machine is exposed to temperatures as high as 143°C during a build. SLS is a form of rapid prototyping, building an object a layer at a time, which uses lasers to sinter each layer out of powder and fuse it to the previous layer. A glaze point, the point when the powder just begins to melt, is established prior to each build and is used to set the temperature of the entire machine. Exposure to these high temperatures for extended periods can cause the powder to be physically altered and affect the quality of the finish on a build. Expensive new powder must be added eventually to ensure the quality of a build. Use of the AFM in tapping mode can provide a detailed image of surface characteristics of the powder without damaging the sample. Analysis of the powder used in SLS will provide the machine operator with information on how the high temperatures of the process affect the physical features of the powder. This information could allow the powder life to be extended by careful control of the laser power and glaze point determination.

Keywords: Atomic Force Microscope (AFM), Selective Laser Sintering (SLS), nanoscale, tapping mode, polyamide (PA) nylon powder, rapid prototyping

1. Introduction

Selective Laser Sintering (SLS) is one of the processes used in rapid prototyping to design or build prototype parts that can be tested for aesthetic value, ergonomics, and other relevant characteristics depending on the application. The SLS process can be ineffective when weak or poor quality parts are generated and have a negative impact on the production process. These defects are often caused by the powder used in the SLS machine being altered after reuse. Only a portion of the powder present in the SLS machine is used to build the object but the entire supply is exposed to the machine's environment. After each build the excess powder is sifted through a fine mesh and used in future builds. Over time, the constant exposure to this environment causes the powder to produce lower quality parts both in appearance and strength. The defects include rough or rippled finishes and weaker mechanical properties. This research examines what material properties are altered during the powder's life as well as to what degree using primarily an atomic force microscope. The information will provide an explanation of why part quality degrades over time from a physical perspective.

1.1. selective laser sintering

SLS is a process that builds a 3-dimensional object one layer at a time. For each layer a platform brings powder to the build area and a small amount is deposited over the powder bed by a roller. A scanning system and a CO₂ laser trace over the powder surface and fuse the powder particles together to make another layer of the object. After each

layer is sintered the powder piston moves up to deliver more powder and the build piston moves down to drop the object the thickness of one layer (Figure 1). Every layer is a uniform depth but the cross section of it can vary greatly. The powder bed is maintained at two different temperatures during the building process. The build area, where the sintering occurs, is kept at a higher temperature than where the powder is brought to the powder bed. These two areas are separated by a thin piece of metal to help maintain the temperature gradient.

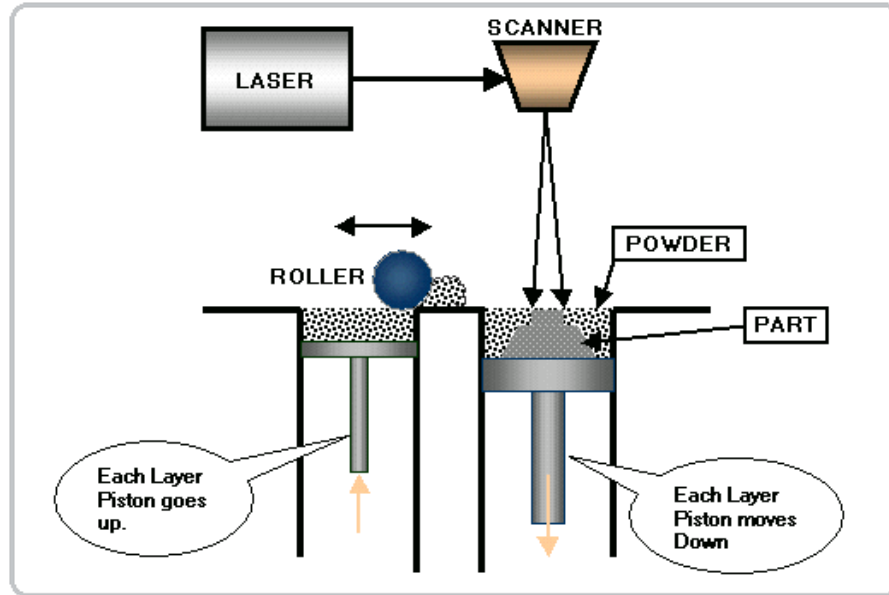


Figure 1 Diagram of SLS process³

When the object is complete it is located at the bottom of the build chamber. The surrounding powder provides support for the entire structure so complex parts can be made without the need for support structures. SLS parts are made from a variety of materials. In addition to the Duraform Polyamide (PA) nylon powder small amounts of glass or metal can be added to this powder to yield different material characteristics. The powder focused on for this research is the PA because it is the most commonly used and therefore experiences the most problems with poor surface finishes and weaker mechanical properties.

1.2. problems associated with SLS

A primary cause of powder alteration is the high temperature of the SLS machine. Prior to each build a glaze point, when the powder just begins to melt or look moist, is established for the powder. The build area is then set to 12° C below the glaze point and the powder trays are set to 25° C below the glaze point. The SLS machine at the Milwaukee School of Engineering, where research was conducted, was run at 142° C in the build area and 126° C in the powder trays. During a build only a small portion of the powder is used in the build but the rest of the powder is still subjected to these conditions.

Excess sintering is also a problem in the SLS. The laser is guided by a scanning system that has the computer design loaded into it. However, even with this precise method powder near the object being built can be partially or completely sintered since it is so close to its melting point. This accidental sintering causes larger particles to form. After each build the powder is sifted through a fine filter but sometimes particles cannot be broken apart. Even if the particles are broken apart it is not clear what effect this sintering has on the overall physical properties of the powder and what effects if any these have on object finishes and mechanical properties.

1.3. atomic force microscopes

The atomic force microscope (AFM) is a type of scanned-proximity microscope. Unlike traditional microscopes the AFM does not use light and lenses but rather it is more like a blind person reading Braille because a cantilever and tip raster scan across the sample's surface. The tip experiences attractive and repulsive forces with the sample

surface and causes the cantilever to deflect from its original position. Deflection of the cantilever is measured by a position sensitive detection system (Figure 3). Differences in the signals determine the vertical and lateral deflection. The image produced is a topographical map and can be used to generate a 3D surface plot. Two modes are used in AFM: contact and tapping. Contact mode drags a stationary tip directly over the sample where as tapping mode has the tip oscillating at a high frequency and only briefly comes in contact with the sample surface during a scan. Tapping mode has the advantage of not damaging softer samples and will not disturb particular samples such as the ones examined in this research. Tips used in tapping are made of silicon, have a higher spring constant than those used in mode ($60\text{-}80\text{ N/m} \gg 0.06\text{ N/m}$), and a high resonant frequency ($\sim 282\text{ kHz}$). The microscope located at the Milwaukee School of Engineering is a Multimode Scanning Probe Microscope (SPM) made by Veeco (Figure 2). It performs a full range of both atomic force microscopy and scanning tunneling microscopy.

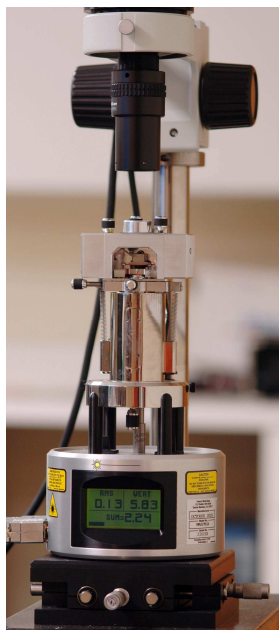


Figure 2 Veeco Multimode SPM

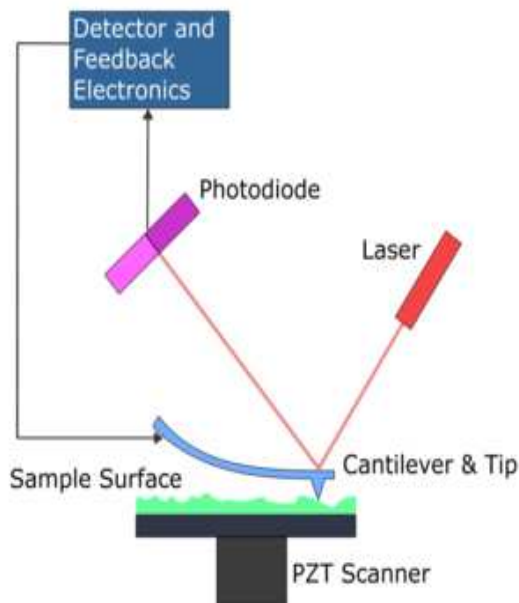


Figure 3 AFM diagram²

1.4. material properties

The AFM has software, Nanoscope Version 5.30r3.sr3, that is able to determine many material properties based on captured data and images. Histograms, roughness, surface area, and particles size are all determined in this software. Other parameters are obtained by selecting a section of a captured image and running the desired calculation. Results are displayed in the viewing area.

1.5. chemical properties

Using infrared (IR) spectroscopy the chemical composition of a material can be determined and differences between samples can be seen. The covalent bonds in organic molecules vibrate upon absorption of infrared radiation at the frequencies specific to the types of atoms involved in the bond. In IR spectroscopy a sample is hit with light waves in the infra red spectrum and reading is obtained by what energy levels are absorbed and which are allowed to pass through. Readings are composed of peaks and valleys that correspond to different functional groups and covalent bonds which can be identified using predetermined charts.

Melting range is determined experimentally in a lab using a capillary tube filled with the material which is then placed on a heating source and the temperatures when the material first starts to melt and when it is finished are recorded. A melting range is obtained instead of a melting point which is common in polymer samples since multiple elements are involved. Melting range tests were run several times to ensure accurate and reproducible results.

2. Objective

The aim of this project is to determine what material and chemical properties of the PA powder are affected during the SLS process and to what degree. The extent of these alterations related to time is also important to better understand what factors of the powder are causing poor finishes and weak mechanical properties. This requires taking images of powders that have been in the SLS machine for varying amounts of time and comparing the readings.

3. Method

To accurately measure how the physical and chemical properties of PA powder change over time samples must be taken that have been exposed to build type condition for different amounts of time. Physical characteristics were determined with the AFM and chemical bonding characteristics were examined via IR spectroscopy. Melting range determination will provide insight into contamination or chemical changes. For each of these tests, initial experiments compared virgin (or unused) powder to powder used for 20 hours. If a difference was observed in a physical or chemical property, then samples at various build times were collected and analyzed.

3.1. sample collection

In order to replicate the build environment of the SLS machine powder samples were placed in a drying oven that was maintained at a nearly constant 142° C, the build temperature in the SLS machine. The samples were taken out of the oven at 25 hour increments up to 150 hours. The cutoff point was set at 150 because this is the point where powder that has been in the machine must be replaced or mixed with virgin powder. Samples were contained in heat resistant containers but not covered to allow for convection and radiation and more accurately model the SLS environment. Samples from the SLS machine were also obtained that had gone through several build cycles and had build times of 20 and 35 hrs.

3.2. sample preparation

For both the AFM and IR spectrometer the sample must be compacted into a flat disc. This procedure is beneficial to the AFM because it ensures the sample stays in a specific location which is especially important when using landmarks to take multiple images of a single surface. However, when compacting samples it is important to not exert too much pressure as to avoid crystallization for AFM samples. Polymer samples for the AFM were prepared in two ways. In one case the samples were pressed into a pellet between two stainless steel cylinders under 1000 pounds of pressure from a hydraulic press. The other case placed loose powder directly on to the viewing disc similar to the process of applying glitter to glue. A small amount of adhesive was placed on the viewing disc and powder was placed directly on top of this. The adhesive was allowed to cure and the excess powder was removed.

For IR spectroscopy the disc must be nearly transparent. To do this 25 mg of powder was mixed with about 75 mg of KBr and compressed at high pressures. For this examination the material properties are not important so the pressure can go as high as is necessary to produce a quality sample. The polymer powder is expected to have peaks in the regions of 1720-1640 wave numbers (cm^{-1}) for the amide¹. The structural formula for the primary compound of Duraform PA powder is related to nylon and contains an amide group that is highlighted in Figure 3. The R in the structure refers to the structure that for proprietary reasons is unknown to users.

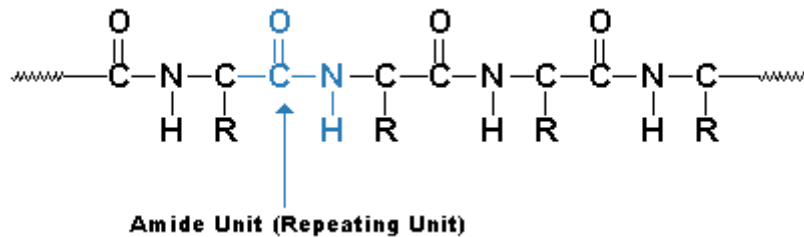


Figure 4 Nylon Structural Formula⁴

As shown in Figure 4 the amine group is a carbon atom double bonded to an oxygen atom and also single bonded to a nitrogen atom. Since this functional group repeats through the molecule it is sometimes referred to as a polyamide. Multiple strands of nylon are connected by hydrogen bonding between the oxygen of one amide group and the hydrogen attached to the nitrogen of another. These hydrogen bonds are where nylon gets its strength and durability. These bonds will also be indicated by the IR machine with strong and wide peaks in the region of 3200-3550 wave numbers (cm^{-1}). A comparison of peak location and size will show chemical changes in the powder.

3.3 microscope calibration

Ensuring the microscope was scanning accurately was of vital importance in this research. When taking images of samples that range in size from 50-90 microns an imaging error of one micron represents a ten percent error in data. Calibration of the microscope is performed in contact mode rather than tapping. A contact mode probe has four tips, only one used while imaging, and is made of silicon nitride as opposed to a single silicon tip used in tapping mode. The tip used for the calibration had the highest spring constant of the four tips, 0.58 N/m. During calibration silicon grating of known dimensions (Figure 5) is imaged in contact mode using specific scan parameters given in the manual. Using a captured image the distance between two points is measured by the computer.

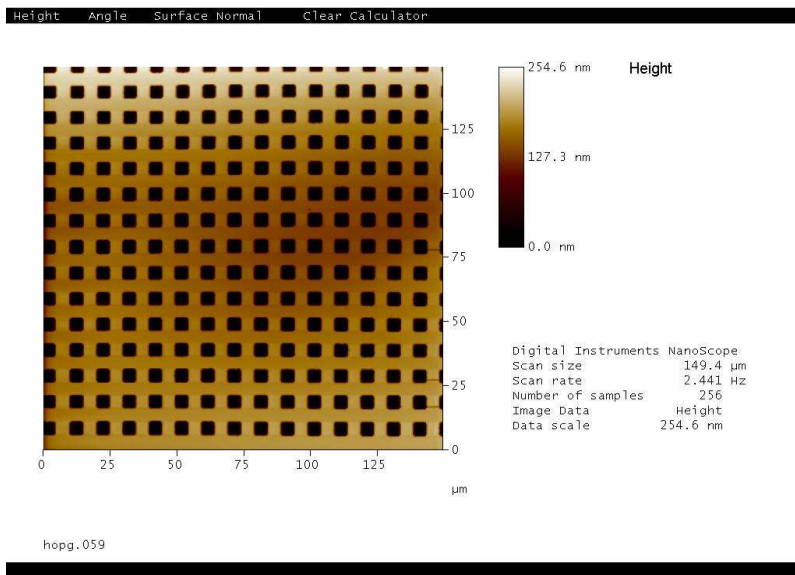


Figure 5: Silicon grating calibration image

If the measured distance is wrong the correct value must be entered into the calibration menu. This process must be repeated for all viewing axes until the microscope is reading proper dimensions at all times. After the calibration process is complete a final image is taken and all known dimensions are checked for accuracy.

4. Results

The first image taken by the AFM was of virgin powder compressed into a thin disc using the method above (Figure 6). A surface plot was generated from the scan and the scan parameters are shown in the upper right hand corner. The image of the powder was different than expected after optical examination of the powder. Compacted powder samples did not provide accurate and reproducible images. The pressure required to adequately compact the powder sample to avoid loose particles also pushed the powder above its melting point and caused it to change its physical properties. In the figure below this can be seen by no visible particles only a flat surface with ridges throughout. Compacting powders for imaging would usually be a valuable method but with this particular sample prove ineffective.

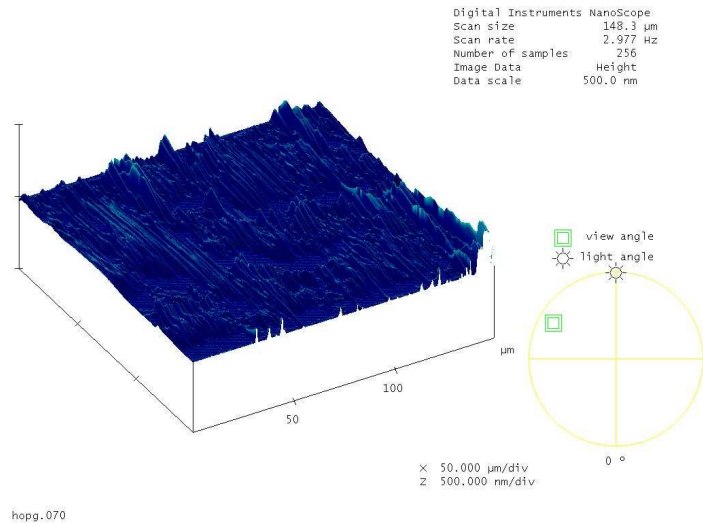


Figure 6 Image of PA powder (148.3 micro meter scan size)

Images, after the original, were taken using loose powder mounted directly on viewing discs. Images that were of high quality and reproducible took a number of scans. The type of adhesive used on the viewing disc did not always hold the particles in their exact location and when working on such a small scale movement of a particle that is not even visible with the naked eye can dramatically affect results. Additionally, placement of the tip was important. The AFM has a height factor that is entered prior to the scan with a maximum value of 5601 nm (5.601 micrometers). Therefore, it was necessary to find locations on the sample surface that displayed particles within this range otherwise the tip would strike the particles causing the cantilever to deflect greatly which result in large interferences on the image.

Scan frequency was set at 0.25 or 0.5 hertz. Lower frequencies were necessary to get quality images and avoid disturbing particles of powder. A scan frequency of 0.5 hertz produced quality images with half the scan time of the 0.25 frequency. However, the 0.25 frequency allowed for greater details in the images and required less movement of the tip to find good sample surfaces. The scan size was kept at 150 micrometers for most scans to ensure entire particles were present in a scan so calculations could be run effectively.

Only the three different samples from the SLS machine were used in the imaging. Placing samples in a drying oven at 143 °C resulted in the powder oxidizing. In the SLS machine nitrogen is pumped into the build area to prevent this and this was not done in the drying oven. The oxidation made comparisons between powder samples unreliable due to the added layer on the sample surface.

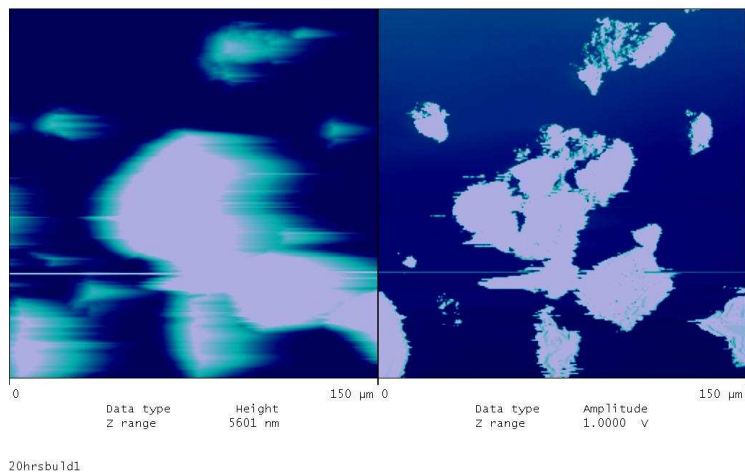


Figure 7 Image of PA powder with 20 hrs build time (150 micro meter scan size)

4.1. physical properties

Images that were captured, like Figure 6, were analyzed using the nanoscope software. Particle size and shape varied greatly during scans and between different powder samples. The volume distribution already present in the powder made quantification of the particle size change difficult to characterize. Overall the shape of particles became less uniform with powder being exposed to SLS environment.

The roughness of particles decreased overall as powder was exposed to the SLS environment. This held true for individual particles and scans containing several particles. A specific reduction was not noticed but the roughness calculations did decrease.

4.2. melting range

Table 1 Melting Range

<u>Trial</u>	0 hrs build		20 hrs build		35 hrs build	
	<u>Start*</u>	<u>Finish*</u>	<u>Start*</u>	<u>Finish*</u>	<u>Start*</u>	<u>Finish*</u>
1	181	184	185	188	185	189
2	180	185	185	189	184	189
3	182	185	184	188	185	190
4	180	184	185	189	184	190
Avg:	180.7	184.5	184.7	188.5	184.5	189.5

* - in degrees Celsius

Table 1 shows the melting ranges of the different powder samples examined in this research. The most drastic change is seen between 0 hours build time and 20 hours build time. The starting point for the 20 hours build powder is higher than the finishing point of the 0 hrs build powder. The temperatures for the 35 hrs build powder does not make a major change but the finishing point is a degree higher than the 20 hrs build powder. These differences in melting point help suggest changes in physical properties that may explain the uneven sintering that occurs with the powder despite the thermodynamic testing differences of melting point determination and the sintering process. Changes in melting point occur at different rates throughout the powder. Therefore, some powder will sinter completely while other powder has not even begun to sinter. Additionally, if the glaze point was not determined again prior to the build the laser would not have enough power to push the powder over its melting point and incomplete sintering would occur.

4.3. infrared spectrum

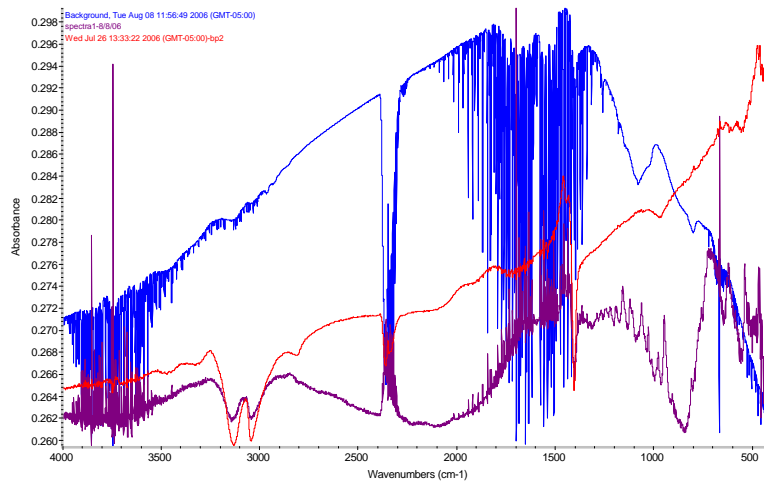


Figure 8 IR spectrum

The spectrum above represents a virgin powder sample. The blue band is a background sample while the purple and red bands are two different samples. Absorbance for the two different samples is different but the bands do parallel each other. A peak occurred around 3200 cm^{-1} as was expected for the hydrogen bond to join two strands of nylon. However, the peak at $1720\text{-}1640\text{ cm}^{-1}$ was not present to indicate the amide.

5. Conclusions

This research has determined a method for measuring the physical properties of PA powder using AFM and the IR. The information gained will allow operators to better understand how the powder is being affected throughout the build process and hopefully allow them to extend the life of the powder through careful adjustments of build area temperature and laser power. The difference in melting ranges shows that the powder is being altered at a microscopic level, not just at the macroscopic level.

6. Further Work

A great deal of research is still needed in this area. The cost of the different forms of powder does not look to decrease anytime soon so an understanding of how the powder is altered during builds and what affect this has on surface finish and mechanical properties is critical. In order for accurate comparisons to be drawn between different powder samples a standardized mounting procedure must be developed. The most logical approach would be to use a high powered optical microscope to place the powder particles and then use the AFM to image different samples.

Other work should include extending this set of procedures to other powders used in the SLS machine. Powder samples should also be directly exposed to the SLS environment for different periods of time to more accurately model how the powder is affected and to avoid the layer of oxidation that develops without the presence of nitrogen.

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