THE EFFECTS OF DRY HEAT STERILIZATION ON PARTS USING SELECTIVE LASER SINTERING

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Abstract

Selective Laser Sintering (SLS) is a manufacturing process that can build arbitrarily shaped parts without part specific tooling. Its advantages have been employed in many different fields, one of these being medical surgery. Currently, SLS is limited in medical applications as a pre-operative modeling tool. For SLS manufacturing to progress in areas like compliant surgical tooling and patient specific bone matrices, concurrent work is needed to investigate the effects of medical sterilization on SLS materials. This paper presents the results of sterilization experiments on SLS parts built from nylon 11. To simulate the process of introducing tools into a sterile environment, these specimens were subjected to multiple rounds of dry heat sterilization. Changes to the dimensions, tensile strength and flexibility were recorded and analyzed. It was found that the specimens' dimensions remained relatively constant. Both the tensile modulus and the flexural modulus decreased as the sterilization cycles progressed. The tensile modulus decreased by 25% and the flexure modulus decreased by 19% after ten rounds of sterilization.

Introduction

The nexus between medicine and engineering grows stronger as the relational benefit the two shares is realized. Both fields exist for the betterment of humanity so it is natural that they have concurrent and contributing applications. medical research. The goal of this research is to advance the applications of selective laser sintering (SLS) into manufacturing parts for sterile fields.

Selective laser sintering is one of a number of manufacturing techniques broadly classified as Solid Freeform Fabrication (SFF). This area of manufacturing includes different layer-based manufacturing processes that have significant advantages over traditional manufacturing methods. SLS uses powdered materials to build parts without the spatial constraints that limit typical machining processes. A computer model (usually built using computer-aided design or CAD) is sliced into thin cross sections that are selectively melted (also known as sintering) according to the cross-sectional geometry using a computer controlled laser. Because unsintered powder surrounds parts, there is no need for support structures for overhangs or complex geometries. A leveling roller spreads fresh powder over the powder bed, and the laser selectively melts, or sinters, an area of the powder based on the part's cross-section. With advances in materials and processing technologies, SLS has found application in many fields of engineering and manufacturing. In particular, in the field of surgery and surgical reconstruction, SLS has emerged as an appropriate tool for more than just physical modeling [1].

Since SLS selectively forms its parts by sintering powder using a laser, no tooling is required. Because of this, inventory is limited to providing sufficient powder quantity for builds. The machinist's skills are unnecessary; a computer directs the SLS machine to produce parts with dimensions as precise as ±.005" [2]. This direct data-to-part process has interesting implications, because parts could be potentially designed on one side of the world in CAD, emailed to a service bureau for manufacturing, and finally delivered to the end user. In fact, one

of the first investigative applications of SLS was to send a "three dimensional fax" in 1991 [3]. Also, since SLS parts are not limited spatially, a complex multiple part assembly can be manufactured with the parts in the assembled state.

Potential Applications

SLS has found applications in many industries, one in particular being medicine. This research explored the use of SLS to create parts such as medical instruments, implantable devices or bone matrices. Existing and potential applications of SLS within the field of medicine are discussed in this section.

Implantable devices used in reconstructive surgery, such as hip or knee replacements, are typically not patient specific. Building devices such as these orthopedic implants using SLS would allow unique geometries customized to the patient. Materials used in reconstructive surgery are limited by their biocompatibility. Hydroxyapatite is a biocompatible candidate appropriate for SLS that could be used for these kinds of applications [4]. Bone replacement therapy is practiced to combat traumatic injury or disease. One major problem with current therapies is rejection, since the human body is very particular with regard to bone microstructure. Since it is capable of producing small intricate geometries, SLS is a potential approach for constructing patient specific bone replacement. SLS has already been applied to the construction of patient specific prosthetic sockets [5]. Three-dimensional scans of a patient's residual limb provide a foundation for the design of these sockets in CAD. Also, prosthetic feet and ankle-foot orthotics have been prototyped [6, 7].

Research Objectives

It is hypothesized that dry heat sterilization will have no appreciable effect on the dimensional or material properties of nylon 11 parts manufactured with SLS. The SLS process requires temperatures up to 185° C, and the dry heat sterilization process used in this thesis only reaches a temperature of 121° C. Also, it is standard practice to use non-virgin powder (overflow or part cake powder) to build parts with minor loss of strength. For this reason, the nylon 11 material should not degrade due to dry heat sterilization. To prove this hypothesis, the following objectives were pursued:

1. Build test specimens suited for flexural and tensile testing.

2. Subject these specimens to multiple rounds of sterilization while removing random specimens in each round to create groups of appropriate sample size with varying sterilization exposures.

3. Monitor the dimensional changes of each specimen following each sterilization cycle.

4. Apply tensile and flexural tests to the specimen groups, paying close attention to the number of sterilization rounds associated with each group.

5. Observe and analyze any trends in the dimensional, flexural and tensile data.

Experimental Methods

The tests performed in this research were guided by pre-established standards. Efforts were made to reduce the variability of the testing procedures and increase consistency. All

tensile and flexure testing was performed on an Instron 3340 Series machine at The University of Texas at Austin. Similar tests were conducted on a United SSTM-20 kN tensile tester at Harvest Technologies (Belton, TX) to verify the data obtained UT Austin. Both platforms used external strain gauges to monitor elastic deformation in the tensile tests.

The test methods used in this research were guided by American Society for Testing of Materials (ASTM) standards. The flexure testing standard is ASTM D790. This method requires that the specimen being loaded to break or fail within the 5% strain limit of the test. Otherwise, accurate flexural strength cannot be determined. The tensile test standard is ASTM D638. This standard is designed to produce tensile property data for the specification of plastic materials.

Each flexure specimen was placed on a three point bending platform, centered on the two bottom supports. Only one specimen was tested at a time. The flexure test began with the upper member touching the flexure bar, but causing no deflection. The tension test began with the tensile bar gripped in both the upper and lower jaws. Figure 1 shows one of the specimens in tension.

Figure 1. Tensile test.

To accurately record cross head displacement during non-plastic deformation, an extensometer was placed on the specimen until the program prompted the user to remove it. The extensometer is seen in Figure 1 attached to the middle of the tensile specimen.

The test specimen types were chosen based on the material characteristic tests performed and the polyamide material used, nylon 11. The tensile specimens were specified by ISO 3167. Figure 2 shows a representative picture of the specimen and its dimensions. This type of specimen was chosen because it is commonly used for many different tests with plastics, specifically tensile testing.

Tensile Specimen Dimensions

Overall
Length: 150 mm
Thickness: 4 mm

Center Section
Width: 10 mm
Length: 80 mm

Figure 2. ISO 3167 with dimensions.

The flexure specimen specified by ASTM D790 is appropriate for the three point bend test. For thermoplastic or thermoset materials, D790 suggests that a rectangular specimen of dimensions 127x12.7x3.2 mm^3 be used.

The specimens used for testing in this research were built using a 3D Systems Vanguard HiQ Sinterstation. The build parameters for the test specimens are given in Table 1: The material used in the build was 100% virgin nylon 11 powder.

Table 1. Description of Build Parameters

Laser Power (Watts)	Scan Spacing (inches)	Part Bed Temp. (Celsius)	Feed Bin Temp. (Celsius)
36	0.008	186	186

A diagram describing the orientation of the test specimens during the build is shown in Figure 3. The layers in the figure provide a convenient means of describing how the build was set up, as discussed below.

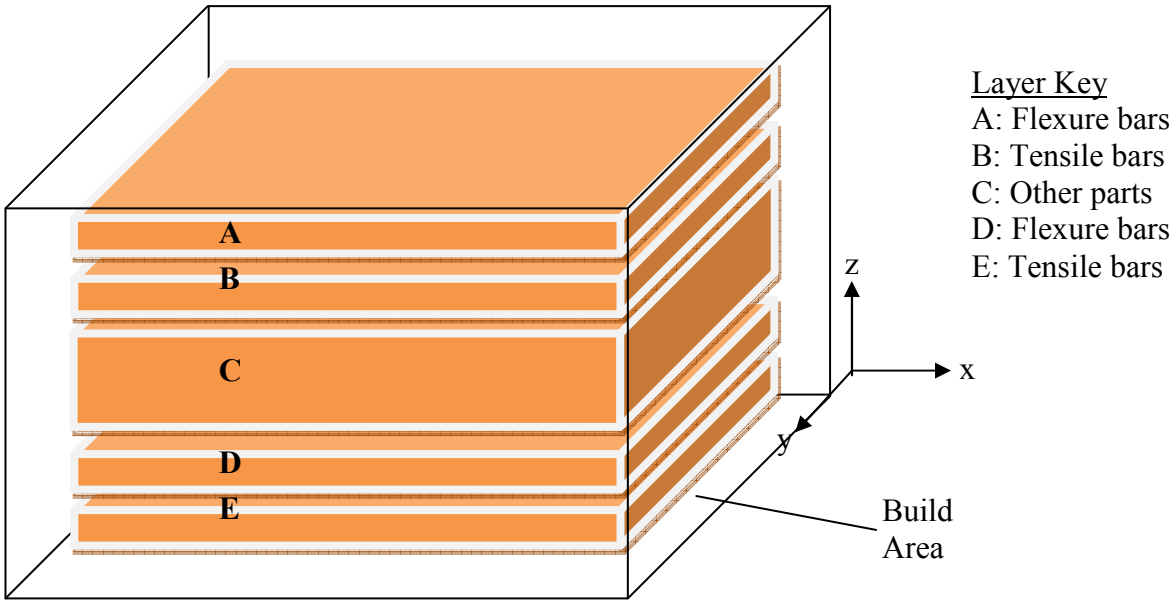


Figure 3. Diagram of Build Setup for Test Specimens.

The build area outlined in Figure 3 describes the walls in the build bin in the SLS machine. The front face of the layers corresponds to the front face of the SLS machine, with the *z* direction defining the direction of height increase through the build process. Layer C contained parts built for other research projects. The test specimens for this research were located in layers A, B, D and E. Each of these layers contained two layers of the same type of specimen, either flexure or tensile.

The entire build was removed from the machine 12 hours after the build was completed, and then cooled another 6 hours on a processing table. All parts were labeled as the break out progressed according to their height and location in the build. There were two parts discovered to have been built with deformities. Both parts were on the outer extreme of the build area. It is possible that these parts cooled too fast and curled, since layers from these parts were found in the overflow bins. The powder roller most likely lifted these parts as they curled and pushed them into the overflow bins. An initial check of one flexure specimen gave a density of .9349 g/cm^3. The published density of nylon 11 is 1.01 g/cm^3.

A Getinge (Rochester, NY) Castle 133 Vacuum Steam Sterilizer autoclave was used for this research. The temperature and pressure specifics are presented in Table 2. The specimens were not stored in any special manner between cycles, and cycles were run every 4-5 days. To observe trends in material properties due to the effects of sterilization, groups of test specimens were cycled through from one to ten rounds of sterilization. After all of the samples completed the first cycle, four tensile and four flexure samples were randomly chosen for removal. This process was repeated for ten rounds. After ten cycles, there were groups of specimens that had been sterilized once, twice and all the way up to ten times. A control group of ten flexure and ten tensile specimens was never put through the autoclave cycle.

Table 2. Sterilization thermal and pressure cycle.

Stage	Time (min:sec)	Temp. (°F)	Pressure (psig)
Purge	0:00	131	0.38
Condition	3:37	234	9.09
Heat Up	4:52	160	-19.83
Exposure	6:23	251	16.77
Exhaust	26:23	251	16.57
Vacuum	27:07	160	-19.85
Air In	42:08	120	-26.12
Complete	42:57	125	-3.85

After each sterilization cycle, the flexure samples were dimensioned using a set of digital calipers with an accuracy of ±.001". Each specimen's length, width and height were recorded after each cycle until the specimen was removed from the sample population. The dimensions of the flexure bars were taken from the same points of contact each round. Width was taken from what the user perceived as the middle, and height was taken at the edge of the part at this same location. The tensile specimens were not dimensioned because of their awkward dog bone shape. The control group of tensile specimens was also dimensioned after every cycle and recorded with the test samples. This allowed the observation of any trends in volume change. It also provided a good indication of the validity of this data. The percent change in length, width and height were recorded. From this data, the percent change in volume of the specimens versus sterilization cycle was produced.

Results

Figure 4 shows the percent change in volume versus the sterilization cycle. There are 40 data points for cycle 1 since there were 40 flex samples put through the first round of sterilization. The six controls do not contribute to this data since they were never sterilized. The average percent change was found for each cycle and graphed in a similar manner in Figure 5. A positive percent change means that, on average, the volume of the parts increases. A negative volume change, like in cycles 2, 5, 7, 9 and 10, indicates an average loss of volume in the specimens. The small variations in volume change are probably due to limited measuring resolution and not actual volume changes.

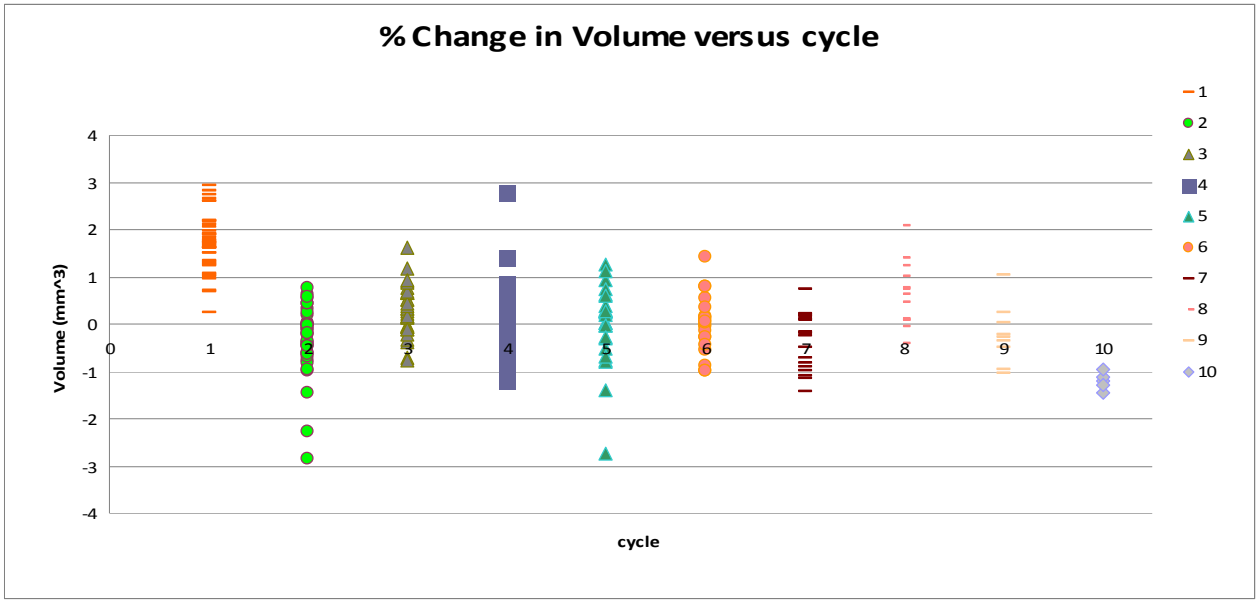


Figure 4. Percent change in volume of flexure specimens versus sterilization cycle.

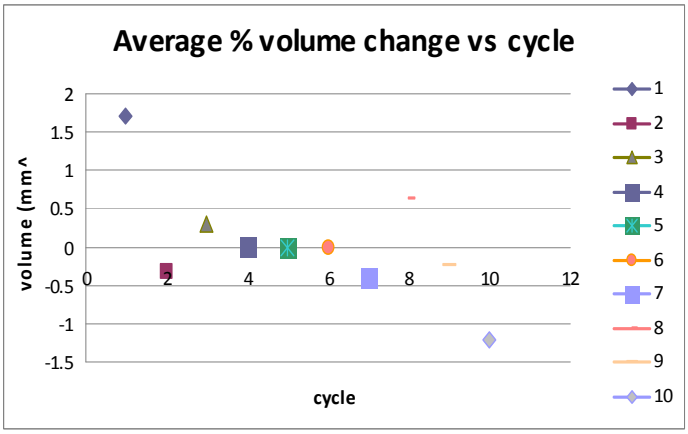
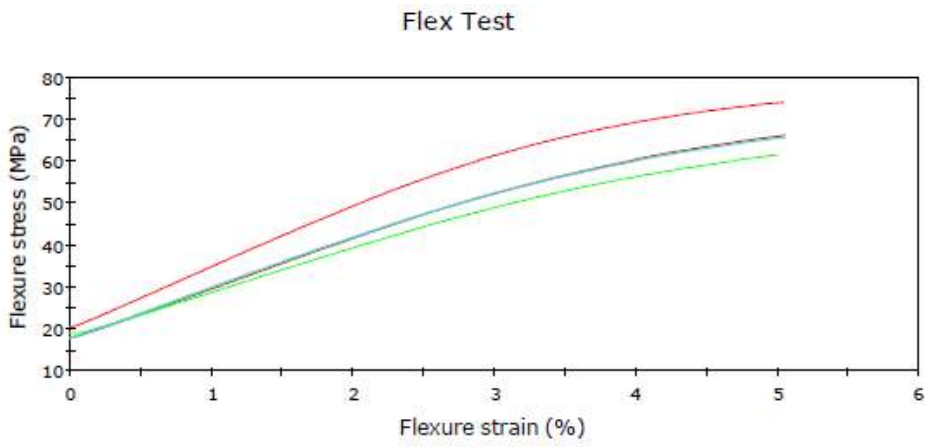


Figure 5. Average percent volume change.

A flexure stress versus strain graph corresponds to each group of flexure specimens. There are a total of 11 output files, one for the control group and one for each of the 10 sterilization cycles. The output data includes the maximum load (N), maximum stress (MPa), flex modulus (MPa) and the flexure extension at maximum flexure load. An example of test output for cycle 1 is shown in Figure 6.



	Specimen label	Maximum Load (N)	Maximum Stress (MPa)	Flex Modulus (MPa)	Flexure extension at Maximum Flexure load (cm)	Comment
1	A6	140.12	74.05	1,497.34	0.71449	
2	F9	143.97	66.16	1,229.92	0.58265	
3	B5	125.57	61.56	1,082.71	0.59456	
4		145.37	65.67	1,232.34	0.57929	
Mean		138.76	66.86	1,260.58	0.61775	
Standard Deviation		9.06733	5.21606	172.65664	0.06483	
Minimum		125.57	61.56	1,082.71	0.57929	
Maximum		145.37	74.05	1,497.34	0.71449	

Figure 6. Flexural test data for cycle 1.

The flexural characteristics of materials are an important index to their performance and easy to interpret. Data corresponding to maximum load, maximum stress and flexure extension at maximum flexure load will not be discussed. The mean and standard deviation of flexural modulus for each cycle was obtained from the data. These values were calculated by the testing program.

To investigate changes in test specimen flexibility, the flexural modulus of each group was graphed versus cycle number. This graph can be seen in Figure 7, along with error bars corresponding to the standard deviation of each cycle. It is clear that the flexural modulus decreases as the number of sterilization cycles progresses. This means that the average stress required to deflect the bars a constant amount decreases as the number of cycles progresses. In other words, the bars become more flexible and less resistant to bending as the number of cycles increases. The average flexural modulus of the control specimens was 1,266 MPa, while the flexural modulus of after ten sterilization cycles was 1,026 Mpa, a 19% difference.

It should be noted that the standard used for this test, ASTM D790, requires that the specimen either break or fail within the 5% strain limit of the test. None of the flexure specimens in this research broke when tested.

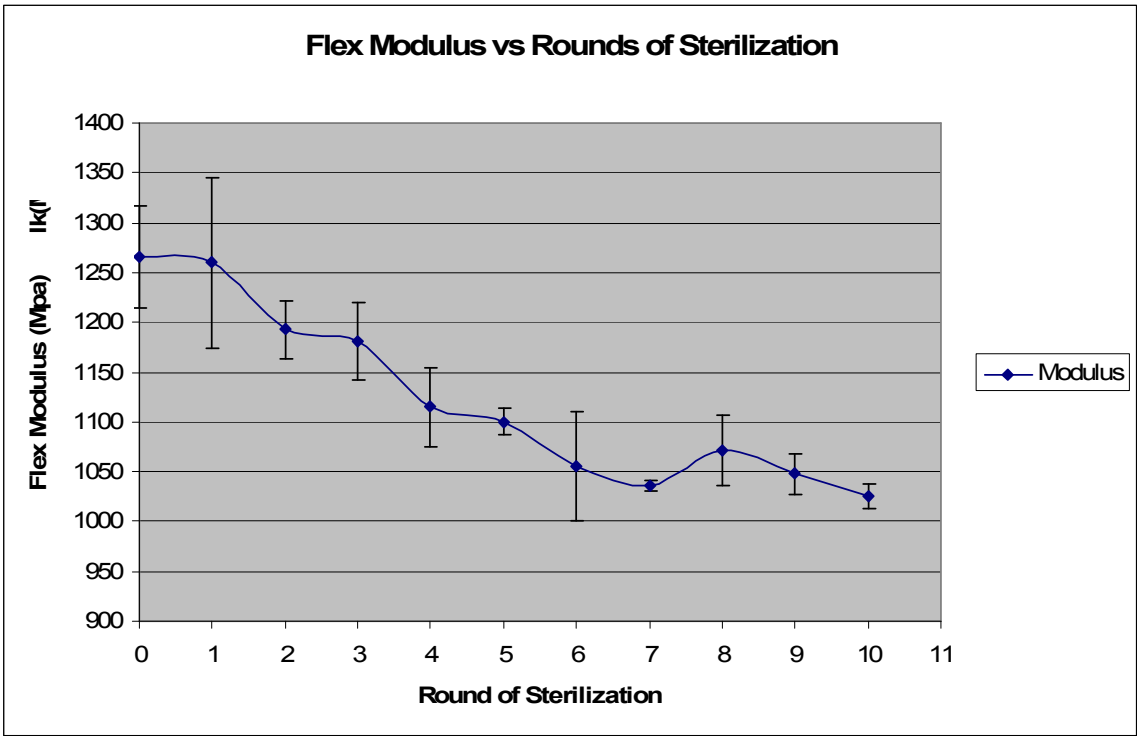
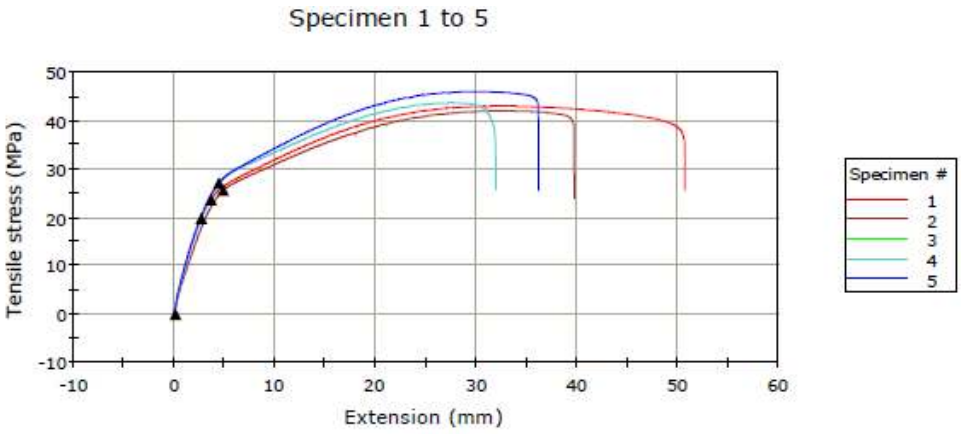


Figure 7. Flexural modulus versus sterilization cycle.

The output data for the tensile specimens of cycle 1 is seen in Figure 8. There are only four specimens in this cycle because the specimen clamps were not tightened during the tension test of specimen 3. The output graphs display tensile stress versus specimen extension. The pre-yield slope of these curves produces the modulus. The yield points, indicated by small black triangles, are all relatively close while the extensions at break vary greatly. The break pattern seen in this specimen group is representative of the other ten groups.

Similar to the data seen from the flexural specimens, the tensile modulus is presented versus sterilization cycle in Figure 9. The sudden dip in elastic modulus during cycle 7 is most likely due to user error. Since four specimens represent each cycle, an anomaly of this magnitude is unlikely. It must be noted that the modulus recorded for cycle 7 is the lower than all following cycles.

The data show that after 10 sterilization cycles, a modulus loss of 25% occurred. As the modulus decreases, less force is required to induce the same amount of specimen extension.



	Modulus (Automatic) (MPa)	Tensile stress at Break (Standard) (MPa)	Tensile extension at Break (Standard) (mm)
1	1,253.67409	35.09562	0.38275
2	1,220.97417	38.08018	0.38373
3	-----	0.04784	-0.40324
4	1,402.39572	32.59428	0.38236
5	1,268.38904	34.84898	0.38463
Mean	1,286.35826	28.13338	0.22605
Standard Deviation	79.85595	15.82094	0.35178

Figure 8. Tensile test data for cycle #1.

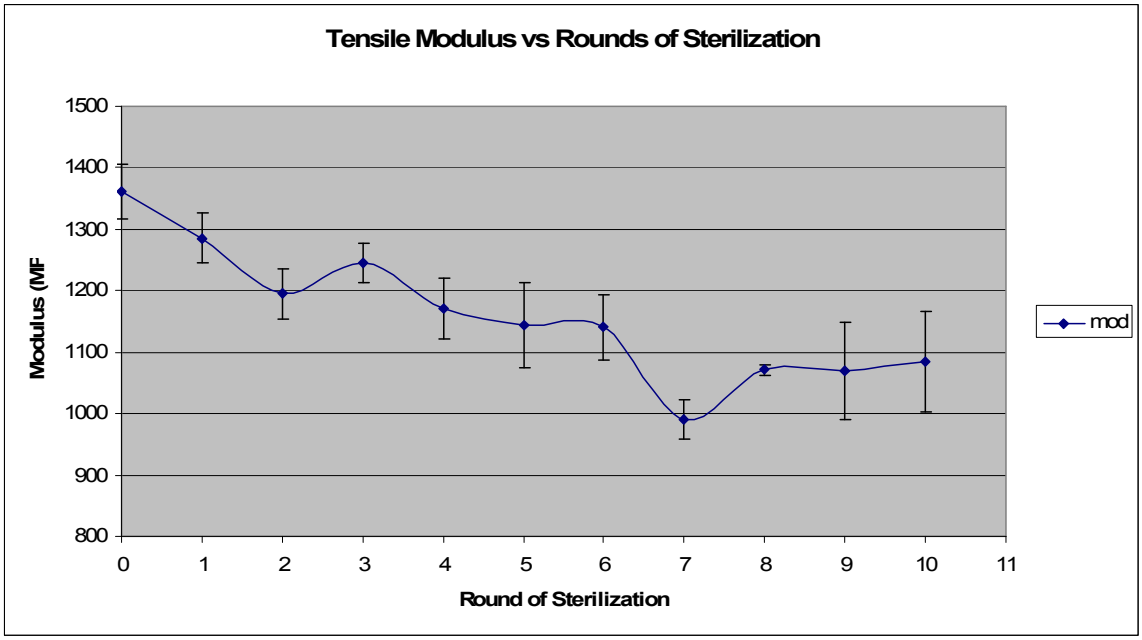


Figure 9. Tensile Modulus versus sterilization cycle.

The flexure modulus and tensile modulus of the specimens appear to degrade as sterilization cycles progress. To distinguish between actual material degradation and statistical variance, a Student's t-test was performed. The test performed investigates the probability that the trends seen in the flexure and tensile moduli were due to material degradation and not

statistical variance. Specifically, the t-test will indicate when the difference between the means of the control and test specimens is statistically significant. This test is influenced by the number of specimens in each sample and their standard deviations.

For each case, the sample sizes for the control and test specimens were both 4. Based on the moduli and their standard deviations, a t-statistic was computed for each cycle. This number was compared to the corresponding t-distribution value, which is based on the desired level of certainty (95% in this case) and the degrees of freedom (6 in this case, 8 total data points in the two groups minus 2) [8]. If the calculated t-statistic is greater than the distribution value, then the two means are significantly different. The critical value for 6 degrees of freedom and a 95% level of certainty is 2.447. This value is the same for both the tensile and flexural data.

The results of the t-test for the flexure modulus are presented in Table 3. As the table shows, the critical value is reached at cycle 5. At this point, the t-statistic exceeds the distribution value and the two means become statistically different.

Table 3. T values for flexure modulus.

Cycle	T Statistic
1	0.060009
2	1.24427801
3	1.3176711
4	2.32970326
5	3.15404731
6	2.81308329
7	4.48828551
8	3.15255105
9	3.97945406
10	4.57059951

The results of the t-test for the tensile modulus are presented in Table 4. Only cycles 1 and 3 exhibit means that are not significantly different from the control mean. The high t-statistic value from cycle 7 is due to the fact that its mean was significantly lower than the control mean. While the mean of cycle 8 was not as low as cycle 7, it had a very tight standard deviation and a high t-statistic was calculated. This t-test analysis confirms that the trends seen in the both flexure and tensile moduli indicate decreasing mechanical properties.

Table 4. T values for tensile modulus.

Cycle	T Statistic
1	1.247057299
2	2.749511866
3	2.108490685
4	2.833899243
5	2.628964314
6	3.148677132
7	6.711802395
8	6.306763569
9	3.18092205
10	2.962812139

Discussion

The changes in the flexure specimen dimensions were small relative to the precision of the dimensioning tool used. The caliper used to dimension all of the samples has a rated accuracy of 0.02 mm and a resolution of 0.01 mm. Because of this, differences of 0.02 mm between cycles are not significant and can be attributed to uncertainty. A standard flexure volume is 5556.25 mm^3. The maximum error equivalent would be 5597.02 mm^3. The difference between these volumes is 0.01%; therefore changes of volume of 0.01% are not significant. The actual changes of the specimen dimensions for width and height were on the order of 0.01 mm to 0.05 mm. For length, it was often on the order of 0.05 to 0.1 mm. Figures 4 and 5 include this error, and cycles 1-2 and 7-10 show volume changes above 0.01%. Also, there was no noticeable increase in standard deviation of the percent changes due to the decrease in the number of specimens as the cycles progressed.

It should be noted that the appearance (color, shape and texture) of the flexure specimens never changed throughout the sterilization cycle process. Interestingly, the ink from the permanent marker used to mark the parts bled through to nearby areas of the specimens. Referring to Figures 4 and 5, the volume of the flexure bars seems to be non-constant. An increase in volume of 1.71% was recorded after cycle 1, and a decrease in overall volume of -1.21% was recorded after cycle 10. It is difficult to prove the volumes of the specimens were actually ever changing, even after cycles 1 and 10, since there is no control comparison. It would have been beneficial, from an analysis standpoint, to measure a group of controls that were not being sterilized after the end of each cycle to compare. Also, the method of measuring the samples was assumed to be a constant process but in fact the points of contact made for measuring the specimens varied for each round. With the variability in dimensioning and the inherent error in the measurement method, the volumes of the flexure specimens are determined to be unchanged by the sterilization cycle used in this research.

Published values for the flexural modulus vary. Table 5 shows various modulus values published by different companies and research groups.

Table 5. Published values of the flexural modulus of Nylon 11.

Company/Group Name	Flex Modulus (psi)	(MPa)
Directed MFG	126,000	869
Indian Plastic Portal	145,000	999
Polymer Web	145,000	999
Granta CES Edupack	133,000	917
Arkema	162,000	1120
3D Systems	186,000	1285

The value published for Arkema's Nylon 11 is the relevant value in Table 5 since the material used in this research was purchased from Arkema. The original modulus of the parts was 1266 MPa, while Arkema's published value is 1120 MPa. The modulus of the flexural specimens did not drop to this value until cycle 4. The value of this modulus is less important to this research than its change over the course of the sterilization cycles. However, a possible explanation for this difference in modulus is that the flexure specimens did not break after the 5% strain required by ASTM D790. Also, differences in process parameters used to build the specimens could result in differences in the moduli.

From Figure 7, it is evident that the average flexural modulus for each cycle decreases as the rounds of sterilization progress. Since the sterilization cycles exposed the flexure specimens to elevated heat without water vapor, the degradation of the parts can be attributed strictly to thermal effects. Unfortunately, there is generally no accepted mechanism for thermal decomposition of nylons. There are many proposed chemical degradation mechanisms, but none of these occur until 300° C [9]. Since the exposure temperature during the sterilization cycles was 121° C, none of these established degradation mechanisms were can explain a loss in flexural modulus. Instead, degradation due to the complexities of the microstructure of SLS parts probably caused this drop in modulus. The microstructure of nylon parts built using SLS is atypical due to the layer-based manufacturing process and the inherent porosity. At this point, thermal degradation mechanisms in nylon parts built using SLS are unknown. One hypothesis for this mechanism is a decrease of molecular weight of the nylon particles, which causes shortening of the polymer chain lengths. This in turn could reduce the crystallinity of the material [10].

Similar to the flexural modulus, the tensile modulus of nylon 11 has many different published values. Several published values can be seen in Table 6. Again, these values are provided for reference to the tensile specimens' actual tensile strength, but the change in tensile strength is more important than the nominal value.

Table 6. Published values for tensile modulus of nylon 11.

Company/Group Name	Tensile Modulus (kpsi)	(Mpa)
Directed MFG	202-275	1,392-1,896
Granta CES Edupack	180-190	1,240-1,310
3D Systems	232	1600
Indian Plastic Portal	261-268	1,850-1,800

The tensile modulus decreased more than the flexural modulus after 10 cycles of sterilization (25% versus 19%). On the whole, the modulus decreased after every round. The increases in rounds 3 and 8 are exceptions but the focus of this research is the general trend of decrease in modulus as the number of cycles increases. Similar to the discussion concerning flexural modulus degradation, reasons for the degradation of these tensile specimens are difficult to find.

Conclusions

The losses in flexural and tensile modulus due to 10 rounds of dry heat sterilization are significant. Also, it is assumed that the trends observed in Figures 7 and 9 will continue as sterilization cycles continue. This research was a first attempt at quantifying this phenomenon, and with repeated experiments an average percent loss of material integrity per cycle can be established. This implies that for certain applications, if a required factor of safety is known and the material properties of a certain part are known, a maximum number of times a part can be safely sterilized can be determined. For example, a surgical tool built by SLS will be designed with a certain factor of safety to ensure the tool will not fail due to the strength demands of the surgical procedure. As the tool is sterilized and reused for different procedures, this factor of safety will decrease. Based the results of this research, the rate at which this safety factor decreases can be estimated and tool life for specific applications can be established. It should be noted that dry heat sterilization is not the accepted method for sterilization of critical items, which require steam sterilization. Additional effects from normal steam sterilization could further degrade sintered parts. This is a topic for future research.

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