THE INFLUENCE OF POST-SLS-BUILD ANNEALING ON NYLON 11 MATERIAL PROPERTIES

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REVIEWED, Accepted August 22, 2012

Abstract

Functional energy storage and return prosthetic and orthotic devices have been manufactured out of Nylon 11 using selective laser sintering due to its high ductility and energy return properties. However, there is concern that material voids caused by incomplete sintering may compromise material properties and lead to premature fracture. Post-build annealing has the potential to eliminate voids caused by incomplete sintering and increase part ductility and strength. The purpose of this study was to post-build anneal Nylon 11 tensile specimens at 1) slightly below their melting temperature, 2) their recrystallization temperature, and 3) their glass transition temperature for two different time durations (12 and 24 hours) to assess the effectiveness of annealing in improving ductility and strength. Specimens annealed at their glass transition temperature had significantly greater percent elongations and lower Young's moduli than specimens annealed close to their melting or recrystallization temperatures. At each temperature, specimens annealed for shorter durations demonstrated a greater increase in percent elongations and a greater decrease in Young's moduli. Annealing at the glass transition temperature for 12 hours resulted in the highest percent elongation, although it was not significantly different from the control (unannealed) specimens. However, at these annealing conditions Young's modulus significantly decreased from the control specimens. Across all annealing conditions, Young's modulus and percent elongation were found to be negatively correlated. Future work should focus on annealing specimens for additional combinations of temperature and duration to further improve ductility while minimizing the negative effects on part strength.

Introduction

Energy storage and return (ESAR) prosthetic devices are commonly manufactured out of carbon fiber, which requires extensive production costs and time. In contrast, selective laser sintering (SLS), an additive manufacturing technique, has proved to be a powerful alternative involving less production time and cost while allowing for more complex, customizable designs. Nylon 11 has been used to manufacture ESAR prosthetic and orthotic devices due to the material's desirable properties, including high flexural strength and ductility and low energy dissipation [1-3]. However, there is concern that small voids caused by incomplete sintering may compromise material properties and lead to premature fracture.

Post-build annealing of SLS parts has the potential to decrease the number of voids and improve material properties through refining the material structure and making it more homogeneous. When the temperature of Nylon 11 is incrementally increased, it passes through three phases, with the transition points between these phases being the glass transition temperature, recrystallization temperature and melting temperature [4]. Annealing just below the melting temperature (~186°C for Nylon 11) may complete the sintering and eliminate remaining voids [5]. However, annealing at high temperatures has also been shown to decrease the ultimate elongation [6]. Alternatively, annealing in the recrystallization range may allow the material to form more perfect crystals, improve the regularity of polymer chains, and increase interlamellar ties [4]. The increase in interlamellar ties reduces brittleness and increases ductility [4]. Studies have shown that Nylon 11 crystallinity reaches a maximum when annealed at 165°C [7]. Annealing between the glass transition temperature ($T_g = 45°C$) and recrystallization temperature can reduce residual stresses and increases movability of chains [7]. Within this range, annealing at a temperature closer to the glass transition temperature has been shown to improve ductility [6]. However, improving ductility through annealing can adversely affect material strength [6].

The purpose of this study was to examine the influence of post-SLS-build annealing on Nylon 11 material properties to identify the combination of annealing temperature and duration that maximizes part ductility without adversely affecting part strength. Specifically, we analyzed Nylon 11 tensile specimens annealed at 1) slightly below their melting temperature, 2) their recrystallization temperature, and 3) their glass transition temperature for two different time durations (12 hours and 24 hours). Based on previous work [6, 7], we expected that annealing between the glass transition and recrystallization temperatures would yield the greatest improvement in ductility with only modest changes in strength.

Methods

Nylon 11 tensile specimens (n=154) were manufactured using SLS, annealed at 80°C, 165°C or 186°C for 12 or 24 hours, and mechanically tested to determine specimen ductility and strength quantified by percent elongation and Young’s modulus, respectively.

Nylon 11 Test Specimens

Specimens were manufactured using a blended 50/50 mix of virgin and single-use overflow Nylon 11 powder (PA D80-ST, Advanced Laser Materials, Temple, TX) in a Vanguard HiQ/HS Sinterstation (3D Systems Corporation, Rock Hill, SC) using the temperature parameters specified in Table 1. A 14 x 11 array of 154 tensile specimens designed using ASTM D638 was created. Specimens were placed in the build volume such that the longest dimension of the specimen was parallel to the movement of the roller, with each specimen 0.15” apart in both the horizontal and vertical directions (Fig. 1). A heat shield was added on the top and bottom of the build volume to facilitate more gradual cooling of the specimens. Once the build was complete and allowed to cool, the specimens were separated from the unsintered powder, bead blasted and air blown to remove excess powder.

	Time	Temperature [°C]				
		Part Bed	Left Feed Bin	Right Feed Bin	Cylinder	Piston
Warm-Up	0:00:00	34	33	33	27	27
	0:08:58	100	97	118	138	81
	2:00:02	188	141	142	138	150
	2:48:26	188	142	144	138	150
Build	2:48:26	188	142	144	138	150
	12:59:11	188	142	141	138	150
Cooldown	12:59:11	188	142	141	138	150
	14:01:44	185	90	92	85	115
	17:40:13	57	44	49	46	66
	43:18:28	35	33	34	28	27

Table 1: Temperature parameters of the SLS build for a blended 50/50 mix of virgin and single-use overflow Nylon 11 powder in a Vanguard HiQ/HS Sinterstation.

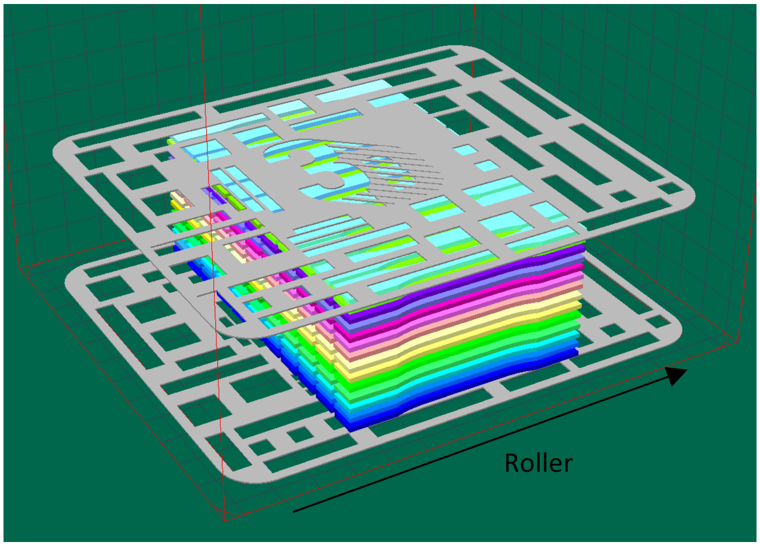


Figure 1: Schematic of the SLS build volume containing a 14x11 array of tensile specimens and a heat shield on both the top and bottom of the build.

Annealing

Specimens were then annealed at three different temperatures (80°C, 165°C or 186°C) for two different durations (12 or 24 hours) yielding six annealing temperature-duration combinations. In addition, a control set that received no annealing was used for comparison. To control for variations in material properties across the build, specimens in the four outermost columns, two on each side, of the 14x11 array were randomly assigned to condition sets and specimens in the central seven columns were systematically distributed to the seven condition sets. A temperature-controlled oven (Model 5851, National Appliance Company, Portland, OR) was used to anneal each group of test specimens. For each condition set, specimens were placed on a rack 1" above the oven's hot plate. The rack was used to render a more uniform temperature distribution throughout the test specimen than direct placement on the heating element. To prevent oxidation, the door was sealed and the oven chamber was evacuated and backfilled with nitrogen, which minimized the amount of oxygen remaining in the oven. At the end of the desired annealing duration, the heating element was turned off and the specimens were allowed to cool slowly until the oven reached room temperature.

Tensile Testing

The material properties of the tensile specimens were determined using ASTM D638 (Instron 3345, Norwood, MA). An extensometer was used to improve resolution until the strain reached a value of 0.055 mm/mm, which corresponded to a point after the end of the elastic region of the stress-strain curve. From these measurements, percent elongation and Young's modulus were determined and compared across annealing conditions (temperature, time).

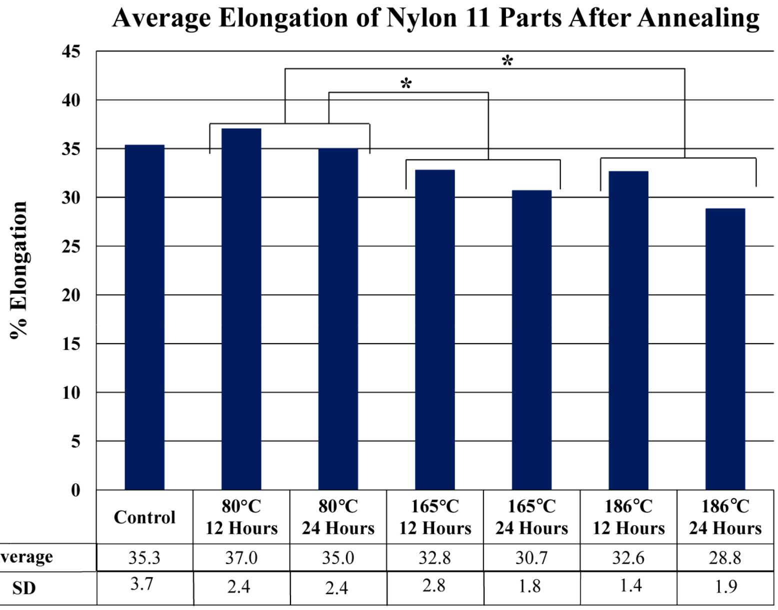
Statistical Analysis:

A two-way (temperature, time) MANOVA was used to compare the percent elongation and Young's modulus across conditions using SPSS 16.0 (SPSS, Inc. Chicago, IL). When significant differences were detected, Tukey pair-wise comparisons were performed to determine which condition sets were significantly different from the others and identify the condition set that most improved percent elongation. Independent sample t-tests were then used to compare the percent elongation and Young's modulus in this condition set to those in the control (unannealed) set. The equal variance assumption was tested by Levene's Test for Equality of Variances for both independent sample t-tests to ensure the appropriate t-test was performed. The Pearson's correlation coefficient was calculated to determine the relationship between percent elongation and Young's modulus.

Results

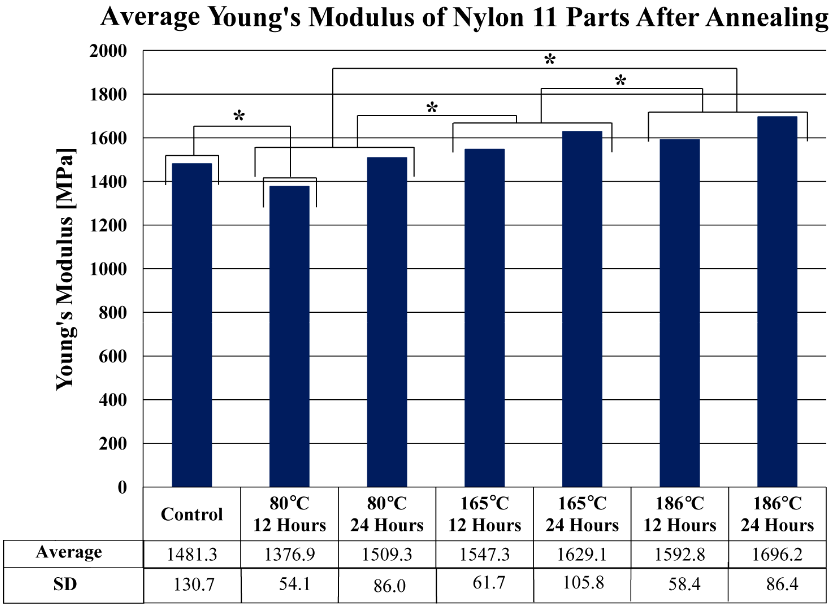
Within the annealing condition sets, percent elongation significantly increased and Young's modulus significantly decreased as annealing duration and temperature decreased (all $p \leq 0.000$), but the interaction between duration and temperature did not influence the percent elongation ($p=0.200$) or Young's modulus ($p=0.4100$). Annealing at 80°C increased the percent elongation compared to annealing at 186°C ($p=0.000$) and 165°C ($p=0.000$), but there was no difference between the percent elongation of specimens annealed at 186°C and 165°C ($p=0.138$) (Fig. 2). Annealing at 80°C decreased the Young's modulus compared to annealing at 186°C ($p=0.000$) and 165°C ($p=0.000$), while annealing at 165°C also significantly decreased the Young's modulus compared to the specimens annealed at 186°C ($p=0.029$) (Fig. 3). At each temperature, annealing for the shorter duration (12 hours) increased percent elongation ($p=0.000$) and decreased Young's modulus ($p=0.000$).

The specimens annealed at 80°C for 12 hours produced the highest average percent elongation of all conditions, but they had the lowest average Young's modulus. Although the highest average percent elongation occurred in this annealing condition set, the increase in percent elongation was not significant when compared to the control set ($p=0.082$) while the decrease in Young's modulus was significant compared to the control set (p=0.001). A negative correlation (p=0.000, R=-0.701) was identified between the Young's moduli and percent elongations, indicating that post-build annealing of SLS tensile specimens had opposite effects on material ductility and strength.



	Control	80°C 12 Hours	80°C 24 Hours	165°C 12 Hours	165°C 24 Hours	186°C 12 Hours	186°C 24 Hours
Average	35.3	37.0	35.0	32.8	30.7	32.6	28.8
SD	3.7	2.4	2.4	2.8	1.8	1.4	1.9

Figure 2: Average percent elongation and standard deviation (SD) of annealed Nylon 11 specimens. Annealing duration had a significant effect on percent elongation at each temperature. Significant differences between annealing temperatures are indicated with an asterisk (*).

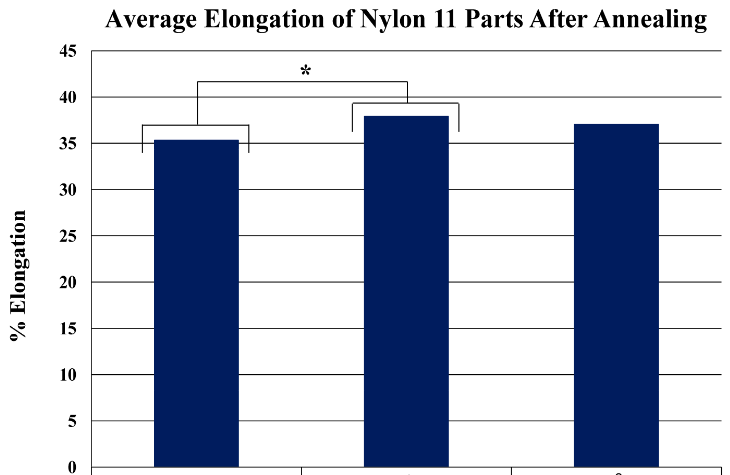


	Control	80°C 12 Hours	80°C 24 Hours	165°C 12 Hours	165°C 24 Hours	186°C 12 Hours	186°C 24 Hours
Average	1481.3	1376.9	1509.3	1547.3	1629.1	1592.8	1696.2
SD	130.7	54.1	86.0	61.7	105.8	58.4	86.4

Figure 3: Average Young's modulus and standard deviation (SD) of annealed Nylon 11 specimens. Annealing duration had a significant effect on Young's modulus at each temperature. Significant differences between annealing temperatures are indicated with an asterisk (*).

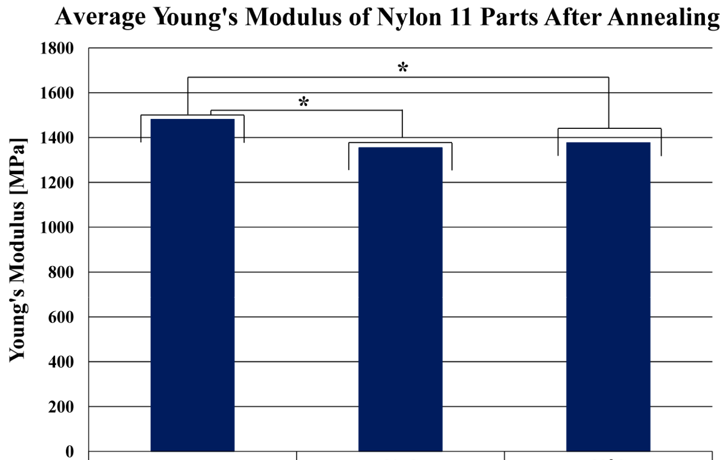
Discussion

As specimens were annealed for shorter durations at lower temperatures, percent elongation increased while Young's modulus decreased. This trend, in addition to the negative correlation identified between the two variables, indicated that annealing for a shorter duration might further improve ductility but at the expense of decreased strength. Since percent elongation increased at the shorter time duration, a post-hoc test was performed to assess whether even shorter time durations would further improve the ductility. In this post-hoc test specimens were annealed at 80°C for 6 hours. There was no significant difference in percent elongation (Fig. 4) or Young's modulus (Fig. 5) when annealed for 6 hours versus 12 hours (p=0.225 and p=0.257, respectively). However, there was an increase in percent elongation (Fig. 4) and decrease in Young's modulus (Fig. 5) relative to the control (unannealed) specimens (p=0.009 and p=0.000, respectively).



	Control	80°C 6 Hours	80°C 12 Hours
Average	35.3	37.9	37.0
SD	3.7	2.2	2.4

Figure 4: Average percent elongation and standard deviation (SD) of annealed Nylon 11 specimens from the post-hoc trials and previous condition sets. Significant differences between annealing conditions are indicated with an asterisk (*).



	Control	80°C 6 Hours	80°C 12 Hours
Average	1481.3	1354.4	1376.9
SD	130.7	74.3	54.1

Figure 5: Average Young's modulus and standard deviation (SD) of annealed Nylon 11 specimens from the post-hoc trials and previous condition sets. Significant differences between annealing conditions are indicated with an asterisk (*).

These results suggest that the annealing parameters that significantly improve percent elongation compromise material strength, which is consistent with previous work with nylon rod stock [6]. The Young's moduli from the specimens annealed at 80°C for 12 and 6 hours (Fig. 5) fall outside the range of acceptable values (1400-1800 MPa). Thus, although ductility was improved, material strength was compromised. Future work should include exploration of additional annealing temperature and duration combinations to improve ductility while minimizing the negative effects on strength.

One potential limitation of this study is that during the annealing process, the specimens were placed on a rack one inch above the oven hot plate, potentially resulting in uneven heating of the specimens. However, since the annealed specimens were less than 4 mm thick, the temperature distribution within each specimen was likely uniform. However, this annealing configuration may not be ideal for thicker parts. Thus, future work should include development of a three-dimensional thermal model of parts during annealing to analyze the temperature distributions across parts with various thicknesses. Such a model could be used to optimize the annealing configuration to achieve a uniform temperature distribution across specimens.

Conclusions

This study explored the influence of post-SLS-build annealing on Nylon 11 material properties. The results indicate that annealing at 80°C for 12 hours produces higher percent elongations and lower Young's moduli than annealing at 165°C or 186°C. However, no significant difference in percent elongation was found between specimens annealed at 80°C for 12 hours and the control (unannealed) specimens. In addition, Young's modulus was significantly decreased in those specimens annealed at 80°C for 12 hours compared to the control specimens. Young's modulus and percent elongation were found to be negatively correlated and post-hoc trials indicated that annealing at 80°C for a shorter duration further improved percent elongation, although it lead to further decreases in the Young's modulus. Future work should focus on annealing specimens for additional combinations of temperature and duration to further improve ductility while minimizing the negative effects on material strength.

Acknowledgments

This work was supported by VA grant 1 I01 RX000311 and the NSF Graduate Research Fellowship Program. The contents are solely the responsibility of the authors and do not necessarily represent the official views of the VA or NSF.

References

1. Faustini M.C., Neptune R.R., Crawford R.H., Stanhope S.J. (2008), "Manufacture of Passive Dynamic Ankle-Foot Orthoses Using Selective Laser Sintering", *IEEE Transactions on Biomedical Engineering*, Vol. 55, pp. 784-790.
2. South B.J., Fey N.P., Bosker G., Neptune R.R. (2011), "Manufacture of Energy Storage and Return Prosthetic Feet Using Selective Laser Sintering", *Journal of Biomechanical Engineering*, Vol. 132, pp.15001-1-15001-6.
3. Fey N.P., Klute G.K., Neptune R.R. (2011), "The Influence of Energy Storage and Return Foot Stiffness on Walking Mechanics and Muscle Activity in Below-Knee Amputees", *Clinical Biomechanics*, Vol. 26, pp. 1025-1032.
4. Ghosh, P. (1997), "Thermal Transitions in Polymers", in *Fundamentals of Polymer Science*.
5. Roder T.M., Colbert G.P., Glenn W.B. Jr., Bongers J., Mooij H. (1995), "Techniques of Melt Processing", in Kohan, M.I. (Ed.), *Nylon Plastics Handbook*, Hanser/Gardner, Cincinnati, OH, pp. 191-248.
6. Scheetz H.A., Kenney W.E., Heinze M. (1995), "Secondary Treatment", in Kohan, M.I. (Ed.), *Nylon Plastics Handbook*, Hanser/Gardner, Cincinnati, OH, pp. 450-486.
7. Zhang Q., Mo Z., Liu S., Zhang H. (2000), "Influence of Annealing on Structure of Nylon 11", *Macromolecules*, Vol. 33, pp. 5999-6005.
8. Williams J.C.L., Watson S.J., Boydell P. (1995), "Properties", in Kohan, M.I. (Ed.), *Nylon Plastics Handbook*, Hanser/Gardner, Cincinnati, OH, pp. 291-358.